

**TUESDAY 06/Sep/2011**

09h00	<b>Plenary 4: Mathias Wessling</b> (Aachen University of Technology, Germany) <b>Product and Process Development for Postcombustion CO2 capture</b> (Location: Auditorium)		
10h00	<b>Coffee break</b> (Location: Edificio VII)		
	<b>Session 4: Methods and tools for managing the complexity</b> (Location: Anfiteatro 1D)	<b>Session 5: Bioresources and bioenergy</b> (Location: Anfiteatro 1A)	<b>Session 6: Chemical and biological process-product engineering</b> (Location: Anfiteatro 1B)
10h20	<b>Envirome-guided metabolic reconstruction by projection to latent pathways (PLP)</b> Teixeira, Ana; Ferreira, Ana; Portela, Rui; <a href="#">Dias, Joao</a> ; Oliveira, Rui	<b>Integrating photosynthesis with microbial fuel cell. Study of the acclimatisation stage</b> <a href="#">Fernandez Morales, Francisco</a> <a href="#">Jesus</a> ; Lobato Bajo, Justo; Rodrigo Rodrigo, Manuel; Serrano Algarra, Lorena; Gonzalez del Campo García Villarubia, Araceli	<b>Study of catalytic activity and stability of peroxidase in ionic liquids as alternative co-solvents</b> <a href="#">Tavares, Ana Paula</a> ; Rodriguez, Oscar; Macedo, Eugénia
10h50	<b>Optimal Scheduling in Semiconductor Manufacturing</b> <a href="#">Castro, Pedro M.</a> ; Aguirre, Adrián M.; Zeballos, Luis J.; Méndez, Carlos A.	<b>Development of a model for the thermal control of photobioreactors based on first-principles</b> <a href="#">Rosa, Jorge</a> ; Costa, Luís; Reis, Marco S.; Saraiva, Pedro A.	<b>Bioactivity of Merlot grape (Vitis vinifera) pomace extracts</b> Oliveira, Daniela A.; Smânia Jr., Artur; Smânia, Elza F.A.; <a href="#">Ferreira, Sandra R. S.</a>
11h10	<b>Prediction of Escherichia coli single gene deletion mutants by hybrid in silico models</b> <a href="#">Portela, Rui Miquel Correia</a> ; Dias, João; Oliveira, Rui	<b>Microalgae for brewery wastewater treatment and biodiesel production</b> Caetano, Nídia de Sá; <a href="#">Melo, Ana</a> <a href="#">Carolina</a> ; Mata, Teresa Margarida; Simões, Manuel José Vieira	<b>Study and development of decorative paints for photoinactivation of microorganisms</b> <a href="#">Magalhães, Pedro</a> ; Meireles, António; Oliveira, Fernanda; Mendes, Adélio; Nunes, Olga C.
11h30	<b>Modelling biochemical networks with intrinsic time delays</b> <a href="#">von Stosch, Moritz</a> ; Oliveira, Rui; Peres, Joana; Feyo de Azevedo, Sebastião	<b>Lipase production from olive mill wastewaters by Aspergillus ibericus</b> Oliveira, Felisbela; Abrunhosa, Luís; Dantas, Danielle; Gonçalves, Cristiana; Venâncio, Armando; <a href="#">Belo, Isabel</a>	<b>Catalytic Cracking of High Density Polyethylene Using USY zeolites – a TG/DSC Study</b> Cañadas, Paloma; Jaśkiewicz, Maja; Coelho, Anabela; <a href="#">Lemos, Francisco</a> ; Lemos, Maria Amélia
11h50	<b>Modeling the formation of complex recombinant products through hybrid metabolic flux analysis</b> <a href="#">Carinhas, Nuno</a> ; Bernal, Vicente; Teixeira, Ana Palma; Carrondo, Manuel José Teixeira; Alves, Paulo	<b>Comparison of membrane performance of PDMS-based membranes during ethanol/water pervaporation and fermentation broth pervaporation</b> Cheou, Simon; Coukour	<b>Synthesis of vesiculated polyester particles</b> <a href="#">Dias, Ângela Maria</a> ; Mendes, Adélio; Machado, João; Moniz, Jorge; D. Magalhães, Fernão

	Manuel Jose Teixeira, Alves, Paula Marques; Oliveira, Rui	<u>Chivaud, Simon</u> , Gaykawau, Sushil; Straathof, Adrie J.J.; Van der Bruggen, Bart	
12h10	<b>Multiple Modelling of CHO cell cultures through the computation of minimal sets of EFM</b> <u>Zamorano, Francisca</u> ; Jungers, Raphaël; Vande Wouwer, Alain; Bastin, Georges	<b>Efficient Biopolymer (PHA) production from biobase surplus feedstocks using mixed microbial cultures</b> <u>Albuquerque, Maria da Graça</u> ; Pinto, Fatima; Adiutori, Rocco; Reis, Maria	<b>Resolution of a chiral racemate by batch chromatography, batch chromatography with recycle, and two-column semi-continuous simulated moving bed</b> <u>Silva, Ricardo Jorge Sousa da</u> ; Rodrigues, Rui Cláudio dos Reis; Mota, José Paulo Barbosa
12h30	<b>Lunch</b> (Location: Edifício VII)		
14h00	<b>Plenary 5: Massimo Morbidelli</b> (Institute of Chemical and Bioengineering, Switzerland) <b>Aggregation and Gelation of Polymer Colloids under Shear</b> (Location: Auditorium)		
	<b>Session 7: Materials development for process and product innovation</b> (Location: Anfiteatro 1D)	<b>Session 8: Process development: intensification and sustainability</b> (Location: Anfiteatro 1A)	<b>Session 9: Chemical and biological process-product engineering</b> (Location: Anfiteatro 1B)
15h00	<b>Development and characterization of Pd-based membranes for hydrogen purification</b>  Alves Gomes, Vânia Maria; Vasconcelos Miguel, Carlos; Tosti, Silvano; Pacheco Tanaka, David Alfredo; Tavares, Carlos José; Magalhães Mendes, Adélio Miguel; <u>Palma Madeira, Luis Miguel</u>	<b>Magnetic Ionic Liquids in combination with a membrane device for carbon dioxide recovery</b>  Albo, Jonathan; Afonso, Carlos; <u>Crespo, João</u> ; Irabien, Angel	<b>Crude Oil Microbial Desulfurization: a viable green technology for sulfur elimination in refineries.</b>  <u>Ferreira, I. Filipa</u> ; de Carvalho, Carla C.C.R.; Wang, Daniel; Aires-Barros, M. Raquel
15h30	<b>Valorization of Coffee grounds by oxypropylation</b> Soares, Belinda; Aniceto, José; Freire, Carmen; Brandão, Inês; <u>Silva, Carlos</u> ; Portugal, Inês; Neto, Carlos	<b>The Ion-Exchange Membrane Bioreactor: Effect of Membrane Module Configuration on the Process Performance</b> Ricardo, Ana Rita; Reis, Maria A.; Crespo, João G.; <u>Velizarov, Svetlozar</u>	<b>Application of a straightforward methodology to estimate a national inventory of PCDD/PCDF release</b> <u>Quina, Margarida Maria João</u> ; <u>Pedro</u> , Rui; Gando-Ferreira, Licínio; Quinta-Ferreira, Rosa
15h50	<b>Influence of the iron precursor in the preparation of Fenton-like catalysts with activated carbon as support for the degradation of the dye Orange II</b> <u>Duarte, Filipa Mesquita</u> ; Maldonado Hódar, Francisco José; Madeira, Luis Miguel	<b>Modeling of the Water-Gas Shift Reaction – Packed-Bed vs. Membrane Reactors</b> Alves M., Yaidelin; Mendes, Diogo; Mendes, Adélio; <u>Madeira, Luis M.</u>	<b>Simultaneous nitrification/denitrification (SND) coupled to sulfide oxidation in a sequencing fed-batch biofilm reactor treating domestic effluent from UASB reactor: preliminary results</b> <u>Moraes, Bruna</u> ; Foresti, Eugenio
16h10	<b>Tuning the shape-selectivity of a bifunctional catalyst used for the ring opening of aromatics</b> Gutiérrez, Alazne; <u>Arandes, José M.</u> ; Castaño, Pedro; Bilbao, Javier	<b>Process Intensification for the ethyl lactate synthesis: Integrated pervaporation reactor</b> <u>Pereira, Carla Sofia</u> ; Silva, Viviana Manuela; <u>Pinho, Simão Pedro</u> ; Rodrigues, Alírio Egídio	<b>Excess sludge reduction by its enzymatic solubilisation</b> Aragón, Carlos; <u>Coello, Dolores</u> ; Quiroga, José M <sup>a</sup>
16h30	<b>New sealing method for dye-</b>	<b>Arsenic Removal without</b>	<b>Comparison of CO2 removal</b>

## PROCESS INTENSIFICATION FOR THE ETHYL LACTATE SYNTHESIS: INTEGRATED PERVAPORATION REACTOR

C.S.M. Pereira<sup>a</sup>, V.M.T.M. Silva<sup>a,\*</sup>, S.P. Pinho<sup>b</sup>, A.E. Rodrigues<sup>a</sup>

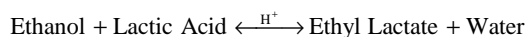
<sup>a</sup>LSRE/LCM – Laboratory of Separation and Reaction Engineering, Faculdade de Engenharia da Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

<sup>b</sup>LSRE – Departamento de Tecnologia Química e Biológica, Instituto Politécnico de Bragança, Campus de Santa Apolónia, 5301-857 Bragança

\*viviana.silva@fe.up.pt

### Introduction

Ethyl lactate is an important organic ester, which is biodegradable, produced by renewable resources and can be used as food additive, perfumery, flavor chemicals, solvent and pharmaceutical preparations<sup>[1]</sup>. It is a green solvent and could replace a range of environment-damaging halogenated and toxic solvents (for example: Nmethylpyrrolidone, toluene)<sup>[2]</sup>. The conventional way to produce ethyl lactate is the esterification of lactic acid with ethanol in the presence of an acid catalyst, according to the reaction:



The conversion of this reaction is limited by the chemical equilibrium and in order to obtain higher ethyl lactate yields it is necessary to shift the reaction towards products formation.

Multifunctional reactors, where reaction and separation take place into a single unit, such as Reactive Distillation, Chromatographic Reactors and Pervaporation Membrane Reactors allow, in addition to obvious savings in equipment costs, significant improvements in process performance for this kind of reactions. By removing one of the products from the reaction zone (usually water), the equilibrium limitation can be overcome and 100 % conversion can be achieved. The Pervaporation Membrane Reactor (PVMR) has been receiving a lot of attention, being its efficiency demonstrated<sup>[3-5]</sup> for several reversible reactions. However, to implement the synthesis of ethyl lactate in a PVMR unit as well as to improve the performance of the overall PVMR process it is needed a clear and quantitative understanding of the kinetic reaction and permeation performance. In a previous work<sup>[6]</sup> a detailed kinetic study was carried out for the synthesis of ethyl lactate using a heterogeneous ion exchange resin, Amberlyst 15-wet, as catalyst.

In this work, the effect of feed temperature, feed composition and flow rate on the pervaporation performance of a commercial hydrophilic silica membrane (from Pervatech BV) is evaluated by batch experiments (BP), testing different binary mixtures involved in the synthesis of ethyl lactate. An integrated pervaporation adsorptive membrane reactor is being developed by packing the tubular membrane with the catalyst, the ion exchange resin Amberlyst-15wet that acts, also, as selective adsorbent to water.

Although the number of works dealing with PVMR in the last years is significant, most of them use simplified mathematical models to predict the behaviour and to optimize the PVMR units. Usually, effects as concentration and temperature polarization, or temperature drop on the pervaporation process are neglected. However, these effects can be very significant on the performance of the PVMR under certain working conditions, and therefore will be accounted in a detailed mathematical model for both BP and PVMR units. The experimental data will be compared with simulation results, which are both fundamental for the PVMR optimization in the production of the ethyl lactate green solvent.

### Results

Binary aqueous mixtures of ethanol, ethyl lactate and lactic acid were dehydrated using a commercial silica membrane supplied by Pervatech BV (The Netherlands), in the temperature range 48 °C to 71 °C, at feed pressure of 2.2 bar. The effect of feed temperature and composition on the pervaporation performance was evaluated by batch experiments in absence of mass transfer limitations (see Figure 1). The microporous silica membranes have high flux and high selectivity for water, for ethanol and ethyl lactate permeation is small while lactic acid does not permeate at all. In summary, the permeances for all species through the microporous silica membranes, as a function of temperature and feed water content, are described by:

$$Q_{\text{memb},\text{Eth}} = 2.36 \times 10^{-12} \exp\left(\frac{22.60 \times 10^3}{RT}\right) (\text{mol} / (\text{s.m}^2.\text{Pa}))$$

$$Q_{\text{memb},\text{EL}} = 1.99 \times 10^{-9} \exp\left(\frac{10.42 \times 10^3}{RT}\right) (\text{mol} / (\text{s.m}^2.\text{Pa}))$$

$$Q_{memb,W} = 3.278 \times 10^{-11} \exp(18.64x_w) \exp\left(-\frac{50377x_w - 32326}{RT}\right) \text{ (mol / (s.m}^2\text{.Pa))}$$

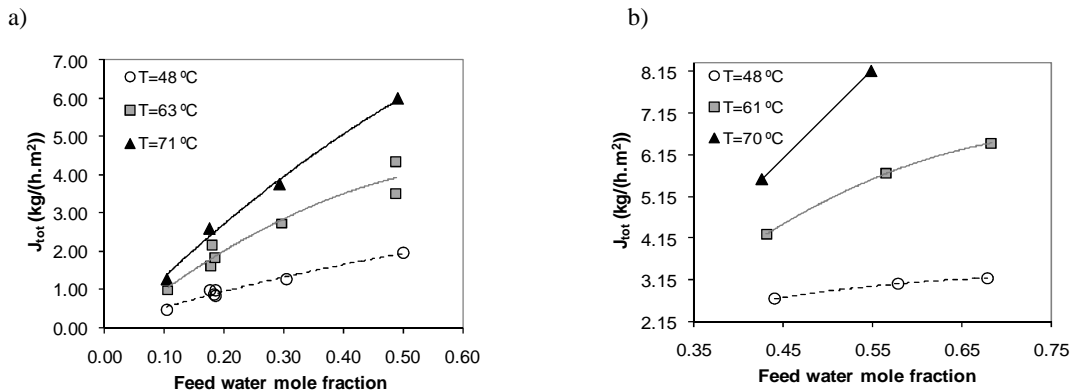


Figure 1- Influence of feed water mole fraction on total permeation flux at different operating temperatures: a) Water/Ethanol mixtures; b) Water/Ethyl lactate mixtures.

A mathematical model was developed for the batch pervaporation membrane, considering (i) plug flow for the bulk fluid phase; (ii) total feed volume inside the tank and retentate velocity inside the membrane variations due to permeation of components; (iii) concentration polarization, where the resistance due to the diffusive transport in the boundary layer is combined with the membrane resistance in a global membrane resistance; (iv) non-isothermal operation due to heat consumption for species vaporization; and (v) temperature polarization. The batch pervaporation membrane model was validated experimentally and, therefore, it was extended to the integrated pervaporation membrane reactor packed with the catalyst Amberlyst-15wet. This model was used to evaluate the performance of the PVMR in both isothermal and non-isothermal conditions (Figure 2). It was concluded that non-isothermal operation worsens the performance of the PVMR, being even worse than that obtained in the fixed bed reactor. In isothermal conditions, the PVMR is a very attractive solution leading to near lactic acid depletion (98 % conversion) and ethyl lactate purity of 96 %, when operating at 70°C.

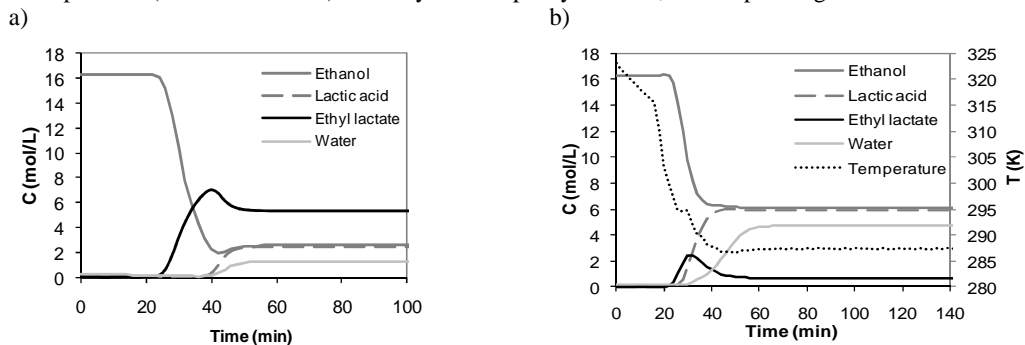


Figure 2- Concentration histories at the PVMR outlet: a) isothermal operation (50°C); b) non-isothermal operation.

## References

- [1] J. Muse and H.A. Colvin. Use of ethyl lactate as an excipient for pharmaceutical compositions. Patent 20050287179 A12005.
- [2] R. Datta and T. Shih-Perng. Esterification of fermentation-derived acids via pervaporation. US Patent No. 5723639,1998.
- [3] Y. Zhu, R.G. Minet and T.T. Tsotsis, A continuous pervaporation membrane reactor for the study of esterification reactions using a composite polymeric/ceramic membrane, Chem. Eng. Sci. 51 (1996) 4103-4113.
- [4] B.G. Park and T.T. Tsotsis, Models and experiments with pervaporation membrane reactors integrated with an adsorbent system, Chem. Eng. Process. 43 (2004) 1171-1180.
- [5] K. Tanaka, R. Yoshikawa, C. Ying, H. Kita and K.I. Okamoto, Application of zeolite membranes to esterification reactions, Catal. Today 67 (2001) 121-125.
- [6] C.S.M. Pereira, S.P. Pinho, V.M.T.M. Silva and A.E. Rodrigues, Thermodynamic equilibrium and reaction kinetics for the esterification of lactic acid with ethanol catalyzed by acid ion exchange resin, Ind Eng Chem Res. 47 (2008) 1453-1463.