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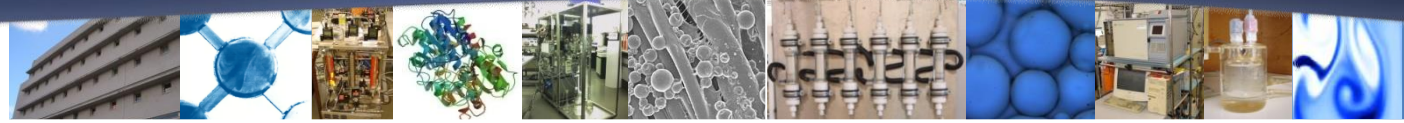

SIMULATED MOVING BED REACTOR

Process Intensification

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LABORATÓRIO ASSOCIADO
LSRE
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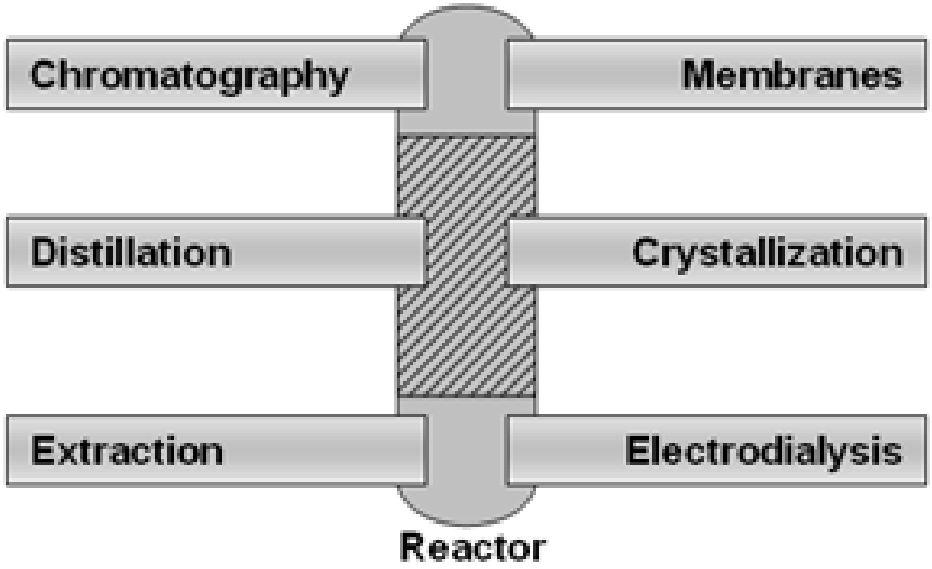
Outline

- Introduction
  - Process Intensification
  - The Simulated Moving Bed Reactor Concept
- Design Methodology
  - Mathematical Model
  - Reactive/Separation Regions
- Process Development
  - CASE STUDY: Ethyl Lactate
    - Ethyl Lactate Green Solvent
    - Thermodynamic equilibrium & reaction kinetics
    - Fixed Bed Adsorptive Reactor
    - SMBR Experimental Validation
    - Separation Region vs Reactive Separation Region
    - Effect of different operating parameters
- Other Applications: Acetals Production
  - Acetals as Green Fuel Additives
  - SMBR experimental validation for acetals production
  - SMBR Process Integration for 1,1-diethoxyethane (DEE) Production
- Conclusions

Process Intensification

Multifunctional Reactors

Specially suited for equilibrium limited reactions



The use of Multifunctional Reactors leads to:

Better energy efficiency

Conversion beyond the equilibrium value

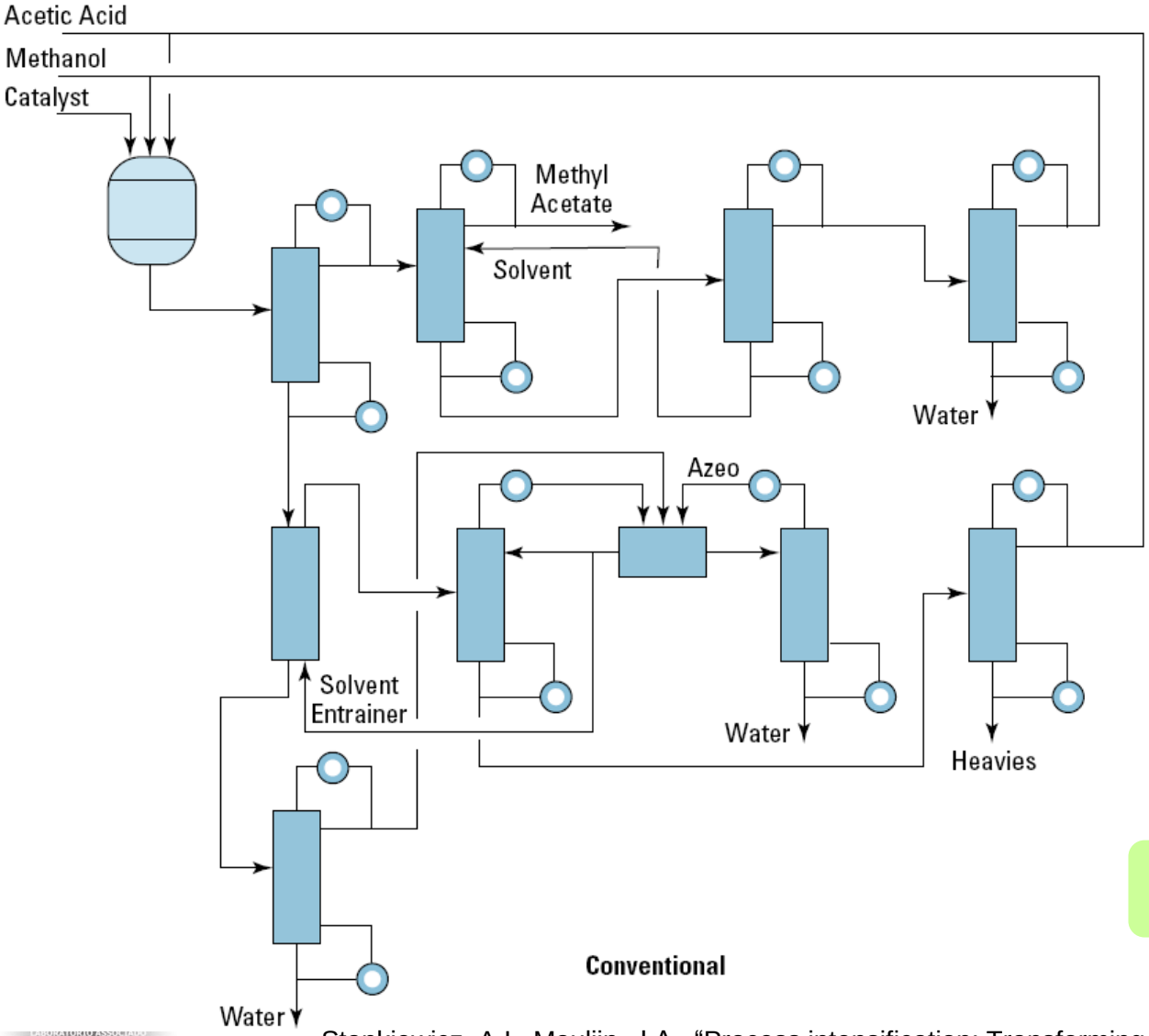
Productivity improvement

Lower solvent consumption

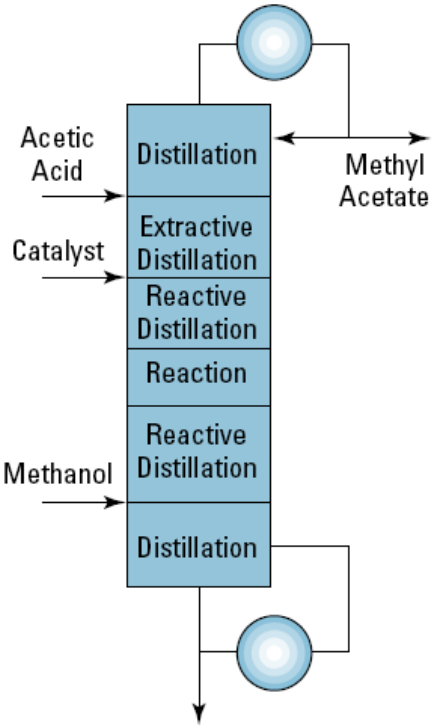
Smaller production plants

Process Intensification

Process Intensification - Methyl acetate plant of Eastman Chemical



Conventional



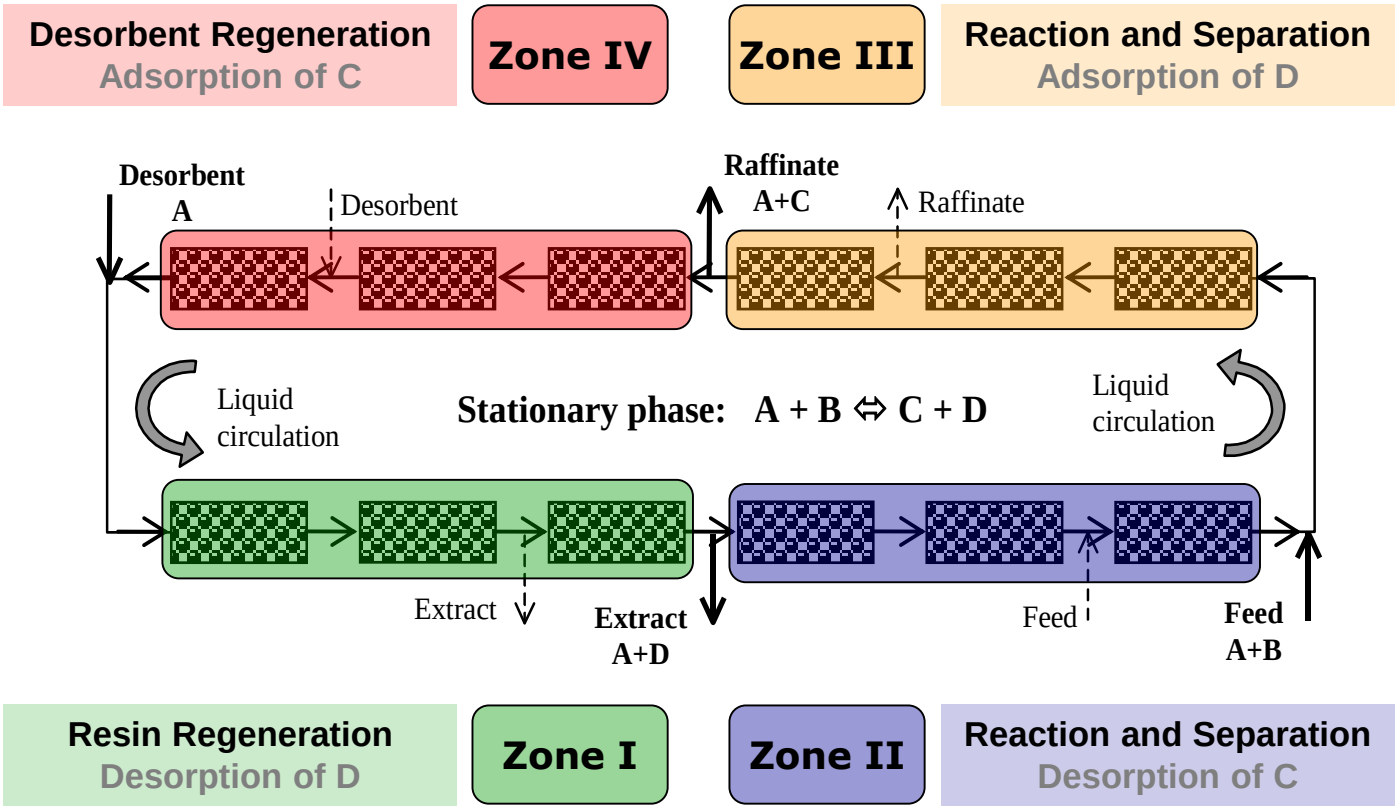
Task-Integrated

1/5 of the capital cost
1/5 of the energy

Stankiewicz, A.I., Moulijn, J.A., "Process intensification: Transforming chemical engineering", (2000) Chemical Engineering Progress, 96 (1), pp. 22-33.

Simulated Moving Bed Reactor (SMBR)

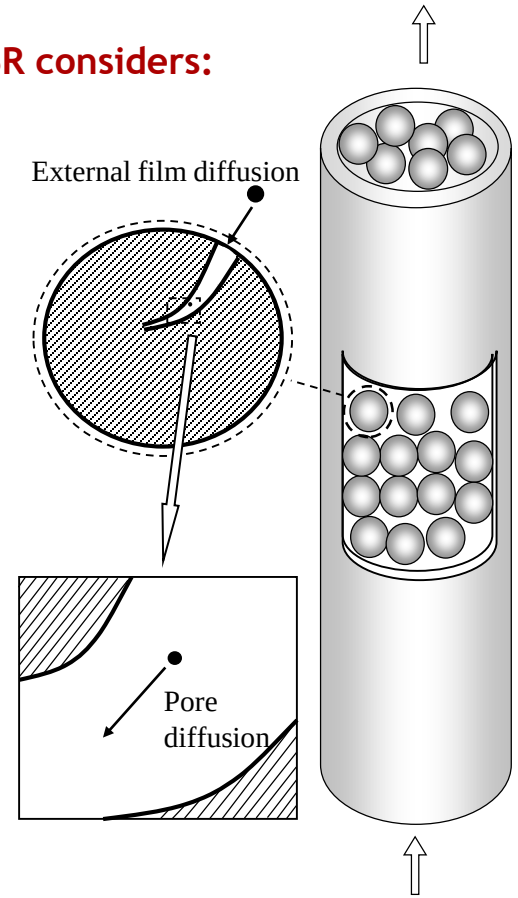
equilibrium-limited reversible reaction
reactions in series or in parallel
reactions with inhibiting or poisoning product
reactions involving temperature-sensitive compounds



SMBR Mathematical Model

The mathematical model used to describe the performance of the SMBR considers:

- axial dispersion flow for the bulk fluid phase;
- linear driving force (LDF) approximation for the inter and intra-particle mass transfer rates;
- multi-component adsorption equilibrium at the adsorbent phase;
- liquid velocity variations due to reaction and adsorption/desorption;
- constant porosity and length of the packed bed;
-isothermal operation.



Schematic representation of mass transfer mechanisms in a SMB column.

SMBR Model Equations

Bulk fluid mass balance to component i, in column k

$$\frac{\partial C_{ik}}{\partial t}+\frac{\partial (C_{ik}u_k)}{\partial z}+\frac{(1-\varepsilon)}{\varepsilon}\frac{3}{r_p}K_{L,ik}\left(C_{ik}-\overline{C}_{p,ik}\right)=D_{ax,k}\frac{\partial}{\partial z}\left(C_T\frac{\partial x_{ik}}{\partial z}\right)$$

Pellet mass balance to component i, in column k

$$\varepsilon_p\frac{\partial \overline{C}_{p,ik}}{\partial t}+(1-\varepsilon_p)\frac{\partial q_{ik}}{\partial t}=\frac{3}{r_p}K_{L,ik}\left(C_{ik}-\overline{C}_{p,ik}\right)+\upsilon_i\rho_p\eta r(\overline{C}_{p,ik})$$

Interstitial fluid velocity variation

$$\frac{du_k}{dz}=-\frac{(1-\varepsilon)}{\varepsilon}\frac{3}{r_p}\sum_{i=1}^{n}K_{L,ik}V_{mol,i}\left(C_{ik}-\overline{C}_{p,ik}\right)$$

Initial and Danckwerts boundary conditions

$$t=0:\quad C_{ik}=\overline{C}_{p,ik}=C_{ik,0}\qquad q_{ik}=q_{ik,0}$$

$$z=0:\quad u_kC_{ik}-D_{ax,k}\left.\frac{\partial C_{ik}}{\partial z}\right|_{z=0}=u_kC_{ik,F}\qquad u_k=u_{k,0}$$

$$z=L_C:\quad \left.\frac{\partial C_{ik}}{\partial z}\right|_{z=L_c}=0$$

Mass transfer parameters

Axial dispersion coefficient

$$Pe=\frac{u\,L}{\varepsilon\,D_{ax}}$$

Global mass transfer coefficient

$$\frac{1}{K_L}=\frac{1}{k_e}+\frac{1}{\varepsilon_p\,k_i}$$

Glueckauf (1955)

$$k_i=\frac{5\,D_m/\tau}{r_p}$$

Wilson and Geankoplis correlation

$$Sh_p=\frac{1.09}{\varepsilon}\left(Re_p\,Sc\right)^{0.33}$$

Reynolds number

$$Re_p=\frac{\rho\,d_p\,u}{\eta}$$

Sherwood number

$$Sh_p=\frac{k_e\,d_p}{D_m}$$

Schmidt number

$$Sc=\frac{\eta}{\rho\,D_m}$$

SMBR Model Equations

Nodes Mass balances

Desorbent node

$$C_{i(j=4,z=Lc)} = \frac{u_1}{u_4} C_{i(j=1,z=0)} - \frac{u_D}{u_4} C_i^D$$

$$u_1 = u_4 + u_{Ds}$$

Feed node

$$C_{i(2,z=Lc)} = \frac{u_3}{u_2} C_{i(3,z=0)} - \frac{u_F}{u_2} C_i^F$$

$$u_3 = u_2 + u_F$$

Extract node

$$C_{i(j=1,z=Lc)} = C_{i(j=2,z=0)}$$

$$u_2 = u_1 - u_X$$

Raffinate node

$$C_{i(j=3,z=Lc)} = C_{i(j=4,z=0)}$$

$$u_4 = u_3 - u_R$$

SMBR Performance Parameters

Performance Parameters

Raffinate Purity (%)

$$PUR = 100 \int_{t}^{t+N_c t^*} C_{R,C}\,dt \Big/ \left(\int_{t}^{t+N_c t^*} \left(C_{R,B} + C_{R,C} + C_{R,D} \right) dt \right)$$

Extract Purity (%)

$$PUX = 100 \int_{t}^{t+N_c t^*} C_{X,D}\,dt \Big/ \left(\int_{t}^{t+N_c t^*} \left(C_{X,B} + C_{X,C} + C_{X,D} \right) dt \right)$$

Conversion (%)

$$X = 1 - \left(Q_X \int_{t}^{t+N_c t^*} C_{X,B}\,dt + Q_R \int_{t}^{t+N_c t^*} C_{R,B}\,dt \right) \Big/ \left(Q_F C_{F,B} N_c t^* \right)$$

Productivity ($Kg_C/(L_{ads}.day)$)

$$PR = Q_R \int_{t}^{t+N_c t^*} C_{R,C}\,dt \Big/ \left((1-\varepsilon) V_{unit} N_c t^* \right)$$

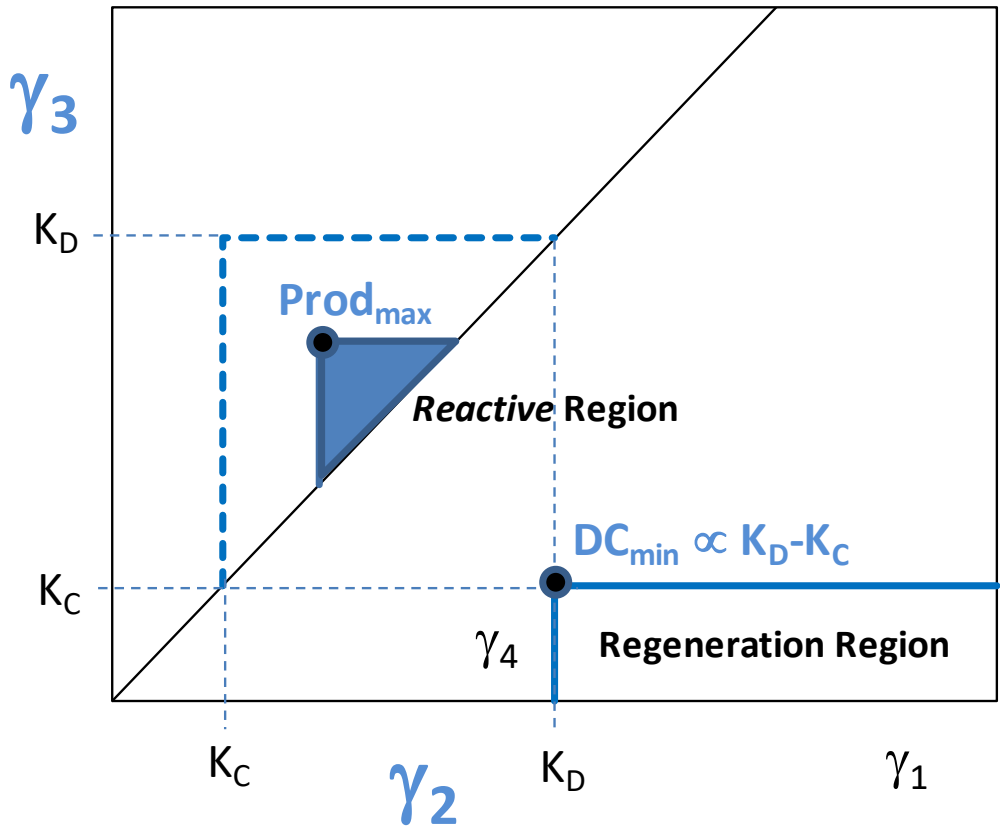
Desorbent Consumption (L_A/Kg_C)

$$DC = N_c t^* \left(Q_D C_{D,A} + Q_F \left(C_{F,A} - \upsilon_A X C_{F,B} \right) \right) \Big/ \left(Q_R \int_{t}^{t+N_c t^*} C_{R,C}\,dt \right)$$

SMBR Design Methodology

In the case of linear isotherms and irreversible reaction

The size of the region depends on Damköhler number $\left(Da = \frac{\rho_b k_c \varepsilon L}{(1-\varepsilon) u} \right)$



SMBR performance

Extract purity

Raffinate Purity

Conversion

Productivity

Desorbent Consumption

Design parameter

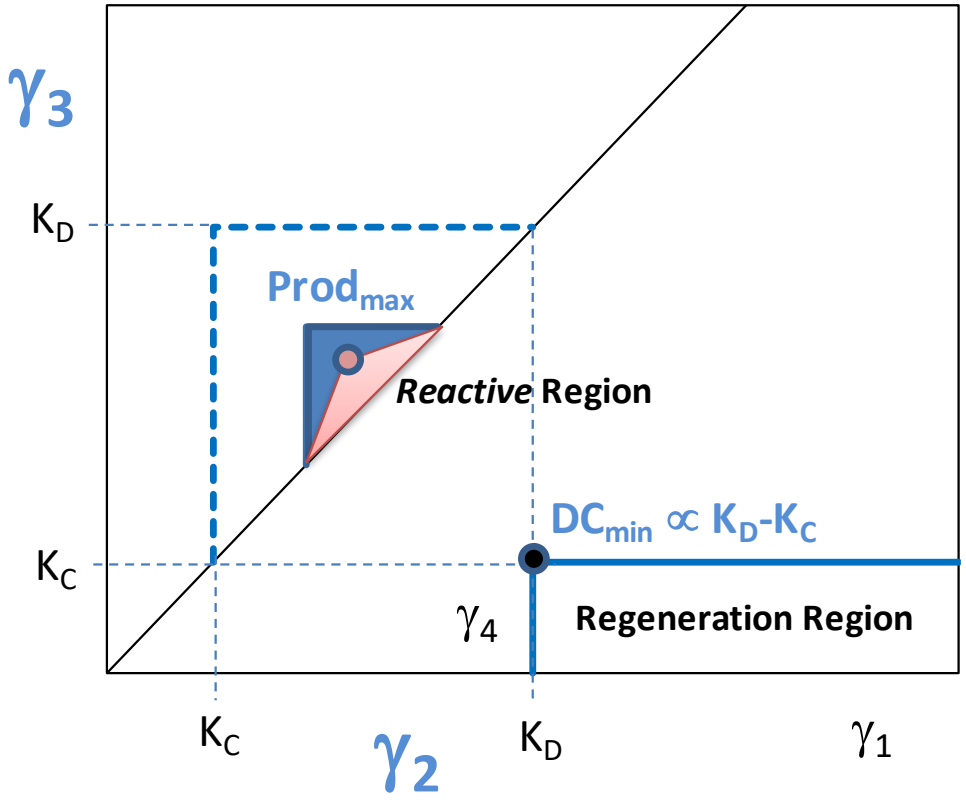
$$\gamma_i = \frac{1-\varepsilon_b}{\varepsilon_b}\left(\frac{Q_j}{Q_s}\right)$$

Fricke, J., Schmidt-Traub, H., "A new method supporting the design of simulated moving bed chromatographic reactors ", Chemical Engineering and Processing 42, pp. 237-248, 2003.

SMBR Design Methodology

In the case of linear isotherms and reversible reaction

The size of the region depends on Damköhler number, and on reaction equilibrium constant



SMBR performance

Extract purity

Raffinate Purity

Conversion

Productivity

Desorbent Consumption

Design parameter

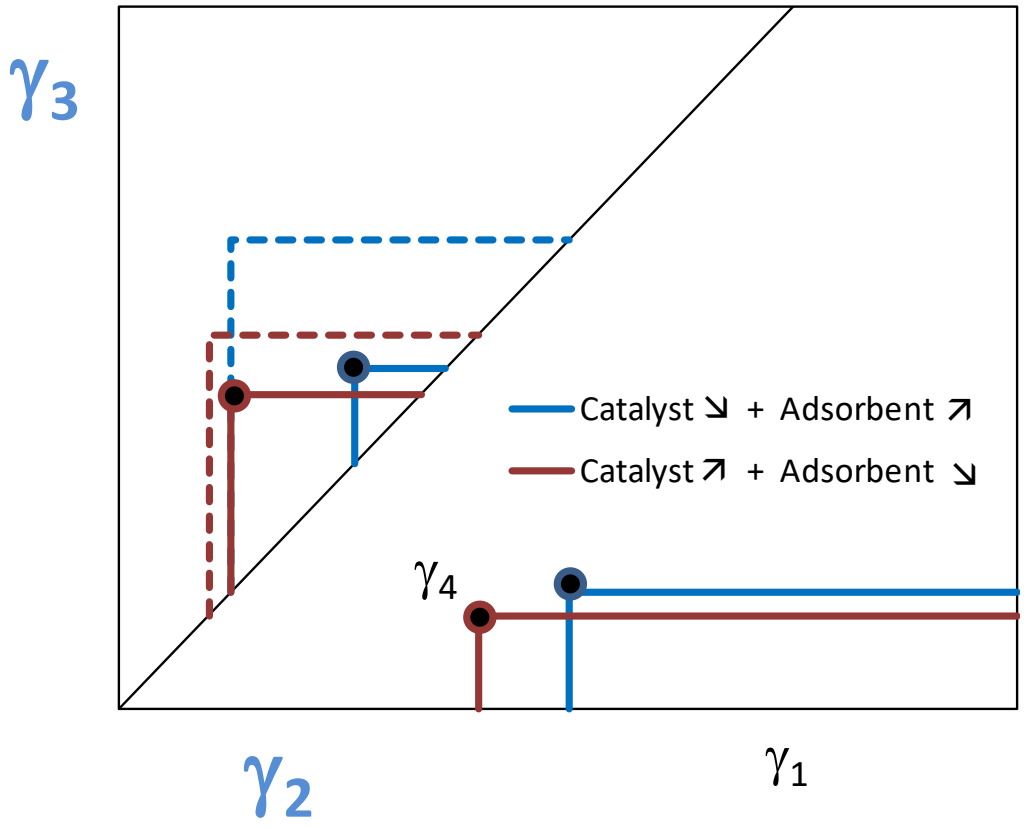
$$\gamma_i = \frac{1-\varepsilon_b}{\varepsilon_b}\left(\frac{Q_j}{Q_s}\right)$$

Fricke, J., Schmidt-Traub, H., "A new method supporting the design of simulated moving bed chromatographic reactors ", Chemical Engineering and Processing 42, pp. 237-248, 2003.

SMBR Design Methodology

Competition between adsorption and reaction

For systems **controlled by reaction kinetics**, it is advantageous to decrease adsorption capacity and increase catalytic activity of the solid.



SMBR performance

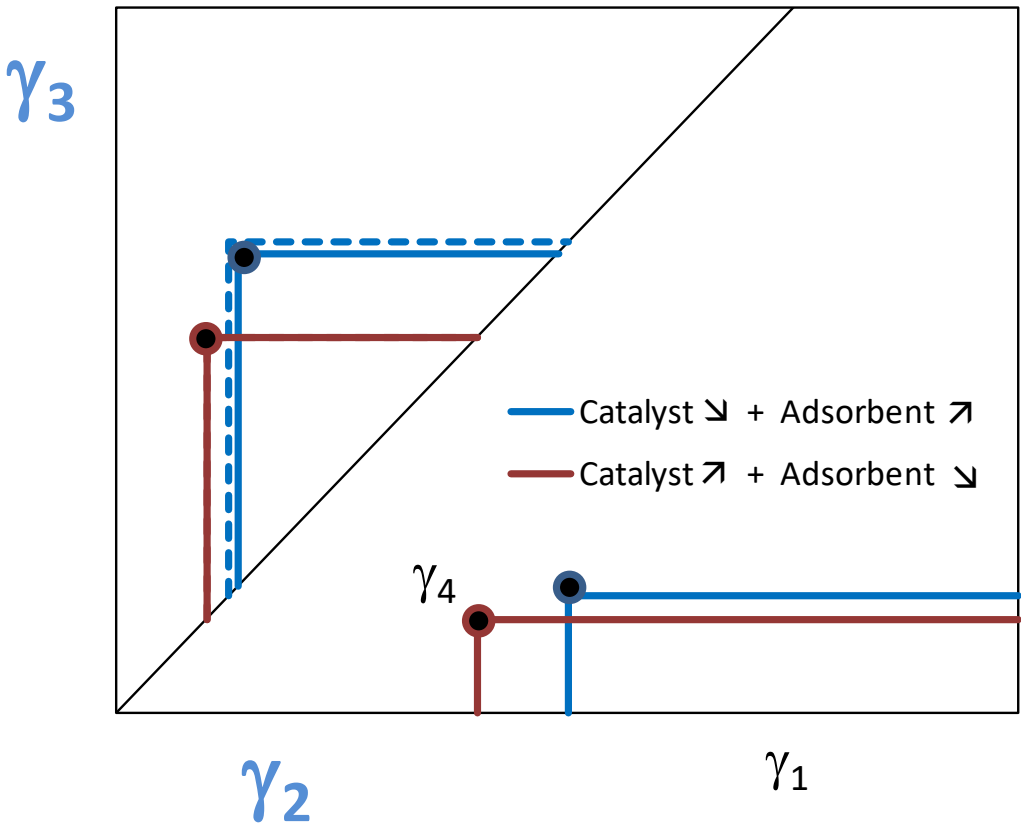
Productivity

Desorbent Consumption

SMBR Design Methodology

Competition between adorption and reaction

For systems **controlled by separation**, it would be acceptable to decrease adsorption capacity of the solid if the desorbent recovery duty is high.

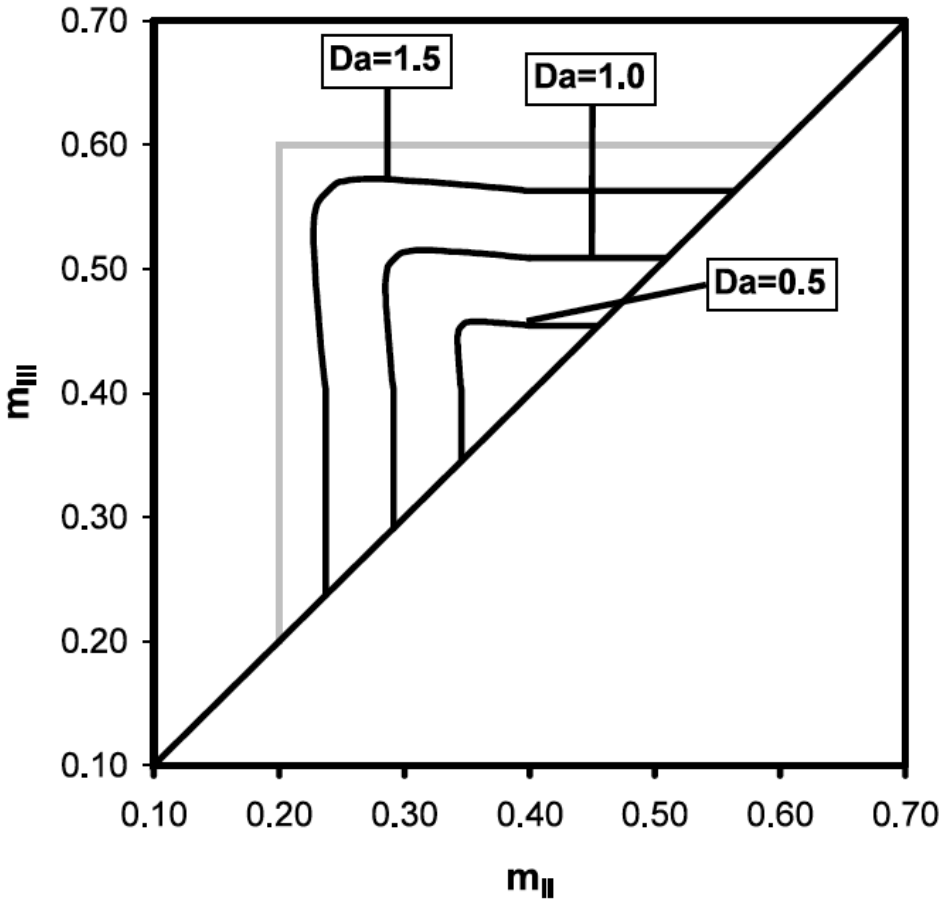


SMBR performance

Productivity

Desorbent Consumption

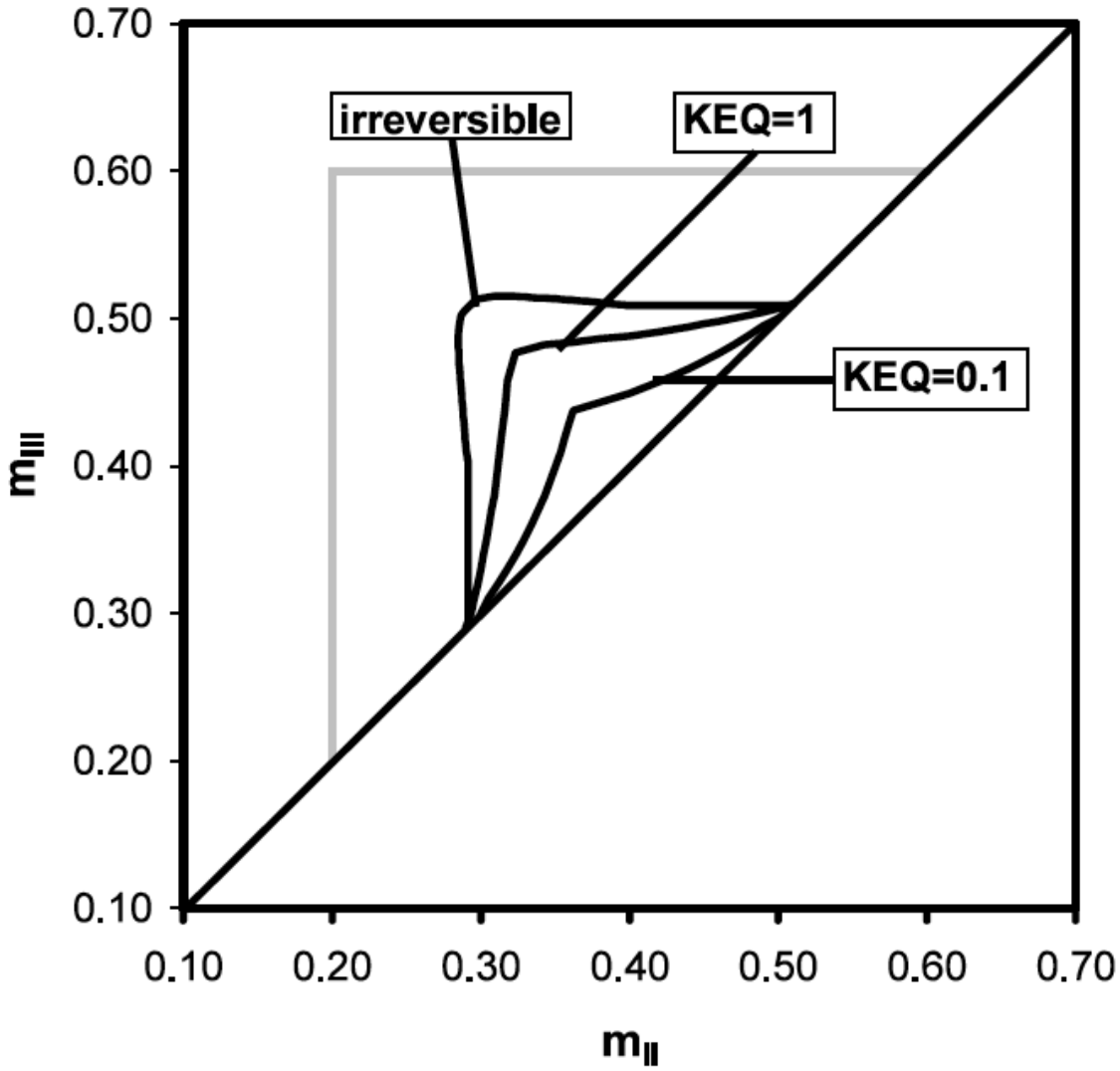
Effect of the reaction kinetics



A_----- B+C
Irreversible reaction
Linear isotherms:
Henry constants
0.4 for A
0.2 for B and 0.6 for C

Fricke and Schmidt-Traub
CEP 42(2003)237-248

Effect of the equilibrium constant



Fricke and Schmidt-Traub
CEP 42(2003)237-248

SMBR Process Development

1. Batch reactor

1.1 Equilibrium experiments

- Equilibrium constant
- Standard properties of reaction
- Standard formation properties of species

1.2 Kinetic experiments

- Mass transfer: pore diffusion limitations
- Reaction rate law
- Mathematical model of the batch reactor

2. Fixed bed

2.1 Tracer experiments

- Bed porosity
- Axial dispersion

2.2 Binary adsorption experiments

- Equilibrium multi-component adsorption isotherms
- Mass transfer limitations in absence of reaction
- Mathematical model of the fixed bed column

2.3 Reaction experiments

- Mass transfer limitations
- Fixed bed reactor model validation

3. SMBR

3.1 Equilibrium Theory: SMB

- Regeneration region: sections I and IV
- Separation region: sections II and III

3.2 Modeling and Simulation

- Reactive-separation region: sections II and III
- Internal concentration profiles at pseudo steady state
- Extract and Raffinate concentration histories

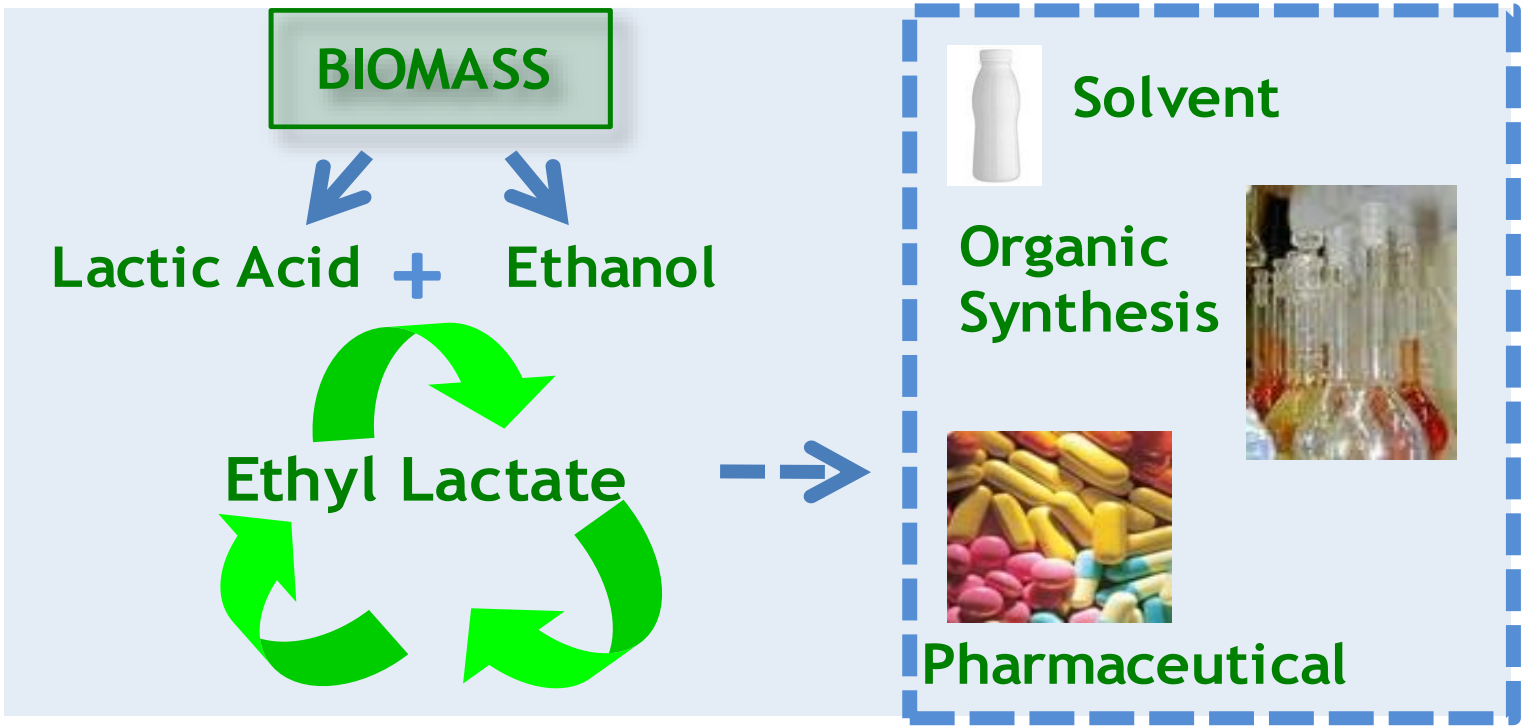
3.3 Operation

- SMBR experiments
- Model validation and SMBR optimization

SMBR Process Development

Ethyl Lactate Green Solvent

Bio-based products: one opportunity

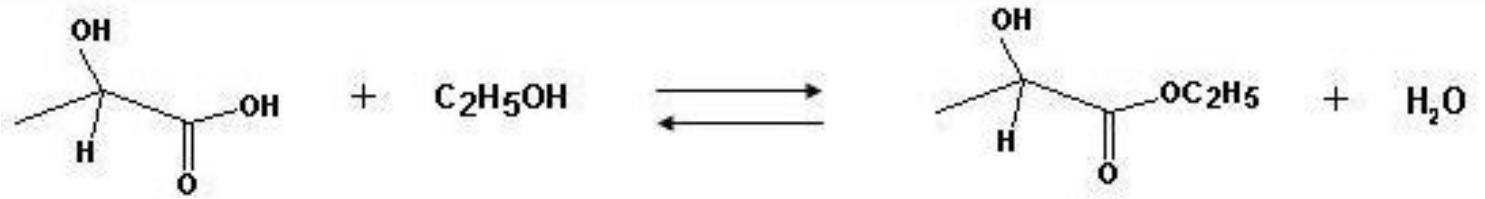


The worldwide solvent market is about 30 million pounds per year, where ethyl lactate can have an important share.

Pereira CSM, Silva VMTM, and Rodrigues AE, Green Solvent Ethyl Lactate: Properties, Applications and Production Processes - a Review, Green Chem. 2011, DOI:10.1039/C1GC15523G.

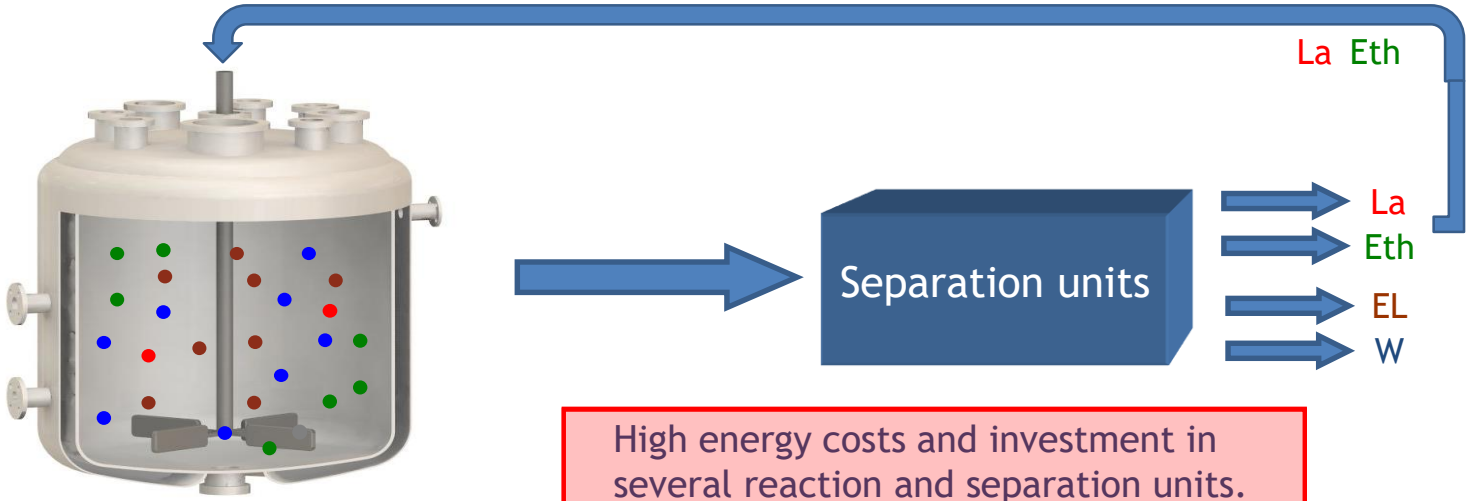
SMBR Process Development

Case Study: Ethyl Lactate



Lactic Acid (La) + Ethanol (Eth) ⇌ Ethyl Lactate (EL) + Water (W)

Equilibrium conversion ≈ 54% (70ºC, $r_{A/B}$=1.1)



High energy costs and investment in several reaction and separation units.

Development of a new efficient process for the sustainable ethyl lactate synthesis by using intensified processes.

Thermodynamic equilibrium & reaction kinetics

Non-Ideal Mixture Model

- Equilibrium Constant Determination
  - Non-ideal system liquid phase reaction

$$K_{eq} = \prod_i a_i^{v_i}$$

  - Esterification of lactic acid with ethanol

Ethanol (Eth) + Lactic Acid (La) ⇔ Ethyl Lactate (EL) + Water (W)

$$K_{eq} = \frac{a_{EL_e}\ a_{W_e}}{a_{Eth_e}\ a_{La_e}} = \frac{x_{EL_e}\ x_{W_e}}{x_{Eth_e}\ x_{La_e}} \frac{\gamma_{EL}\ \gamma_{W}}{\gamma_{Eth}\ \gamma_{La}} = K_X\ K_\gamma$$

Equilibrium composition measured experimentally

Activity coefficients computed by UNIQUAC

SMBR Process Development

Thermodynamic Equilibrium

Operating Conditions

Temperature Range: 50-90ºC

Initial Molar Ratio of Reactants: 1.1-2.8

T (*K*)	x_{Eth}	x_{La}	x_{EL}	x_{W}	γ_{Eth}	γ_{La}	γ_{EL}	γ_{W}	K_{eq}
323.15	0.360	0.178	0.373	0.089	1.056	1.239	1.356	1.693	3.929
323.15	0.334	0.177	0.384	0.105	1.056	1.263	1.394	1.663	3.929
323.15	0.181	0.185	0.453	0.181	1.026	1.324	1.701	1.529	3.929
333.15	0.356	0.181	0.377	0.086	1.065	1.240	1.339	1.685	4.122
333.15	0.331	0.180	0.387	0.102	1.066	1.264	1.375	1.655	4.122
333.15	0.179	0.187	0.454	0.179	1.040	1.329	1.664	1.520	4.122
343.15	0.353	0.185	0.380	0.082	1.074	1.240	1.322	1.677	4.312
343.15	0.330	0.181	0.388	0.101	1.076	1.265	1.356	1.647	4.312
343.15	0.180	0.187	0.454	0.180	1.053	1.333	1.630	1.512	4.312
343.41	0.451	0.168	0.330	0.051	1.061	1.154	1.234	1.783	4.317
343.41	0.450	0.170	0.331	0.050	1.061	1.154	1.234	1.783	4.317
353.4	0.198	0.198	0.453	0.152	1.075	1.335	1.530	1.527	4.504
362.87	0.447	0.172	0.333	0.048	1.071	1.151	1.213	1.772	4.678
362.87	0.446	0.173	0.335	0.046	1.071	1.151	1.213	1.772	4.678

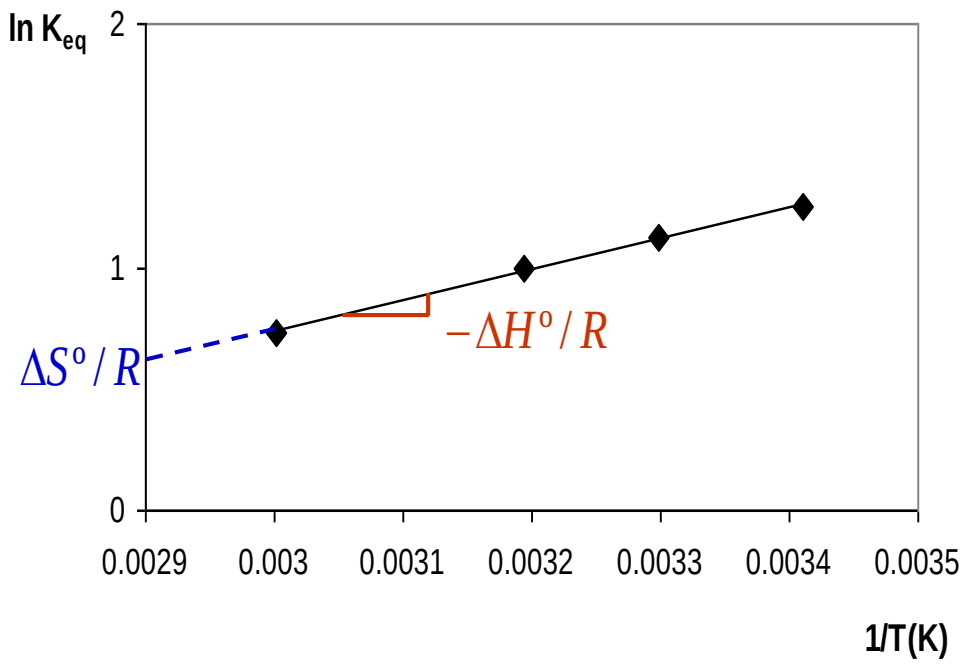
Pereira CSM, Pinho SP, Silva VMTM, Rodrigues AE. Ind Eng Chem Res. 2008; 47:1453-1463.

SMBR Process Development

Thermodynamic Equilibrium

The dependence of the equilibrium constant on temperature was described by the **Van't Hoff Equation:**

$$ln(K_{eq}) = \frac{\Delta S^0}{T} - \frac{\Delta H^0}{RT}$$



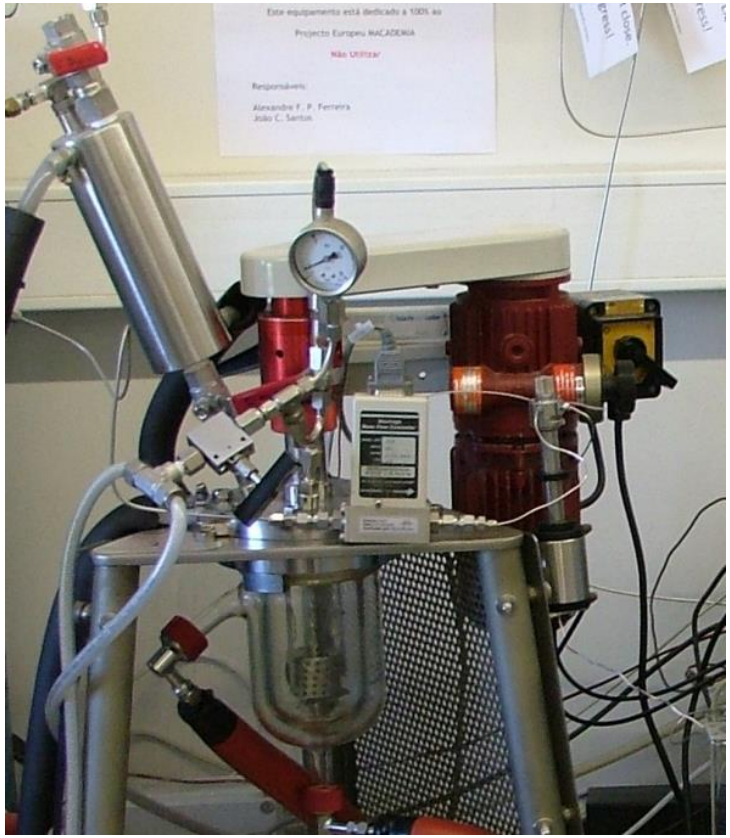
$$\ln K_{eq} = 2.9625 - \frac{515.13}{T(K)}$$

ΔH = 4.28 *kJ/mol*

Endothermic reaction

SMBR Process Development

Batch Reactor



Catalyst basket

Amberlyst-15 wet Resin

Operating Conditions

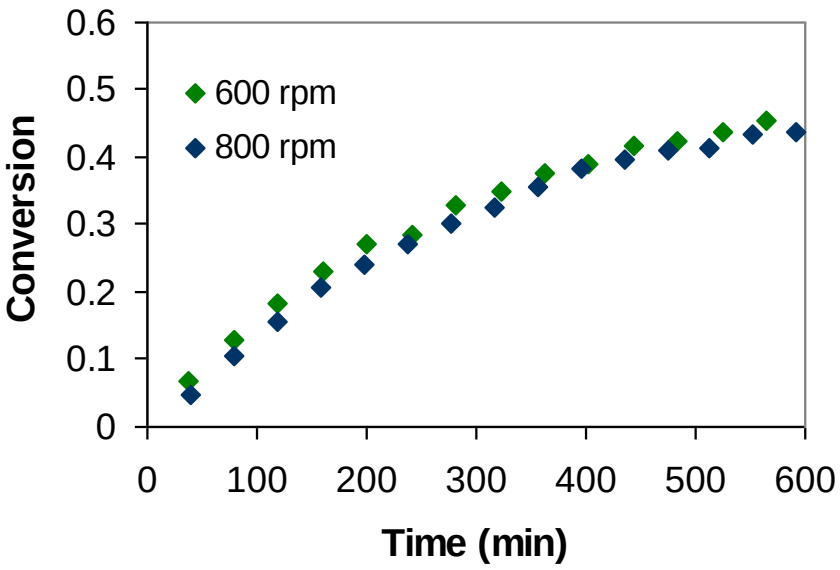
- **Initial Molar ratio of reactants**
  - 1.1 to 1.8
- **Temperature**
  - 323-353K
- **Pressure**
  - 6.0 bar
- **Reaction volume**
  - 550mL
- **Mass of dry catalyst**
  - 6-20g

Pereira CSM, Pinho SP, Silva VMTM, Rodrigues AE. "Thermodynamic equilibrium and reaction kinetics for the esterification of lactic acid with ethanol catalyzed by acid ion-exchange resin", Ind Eng Chem Res. 2008; 47:1453-1463.

SMBR Process Development

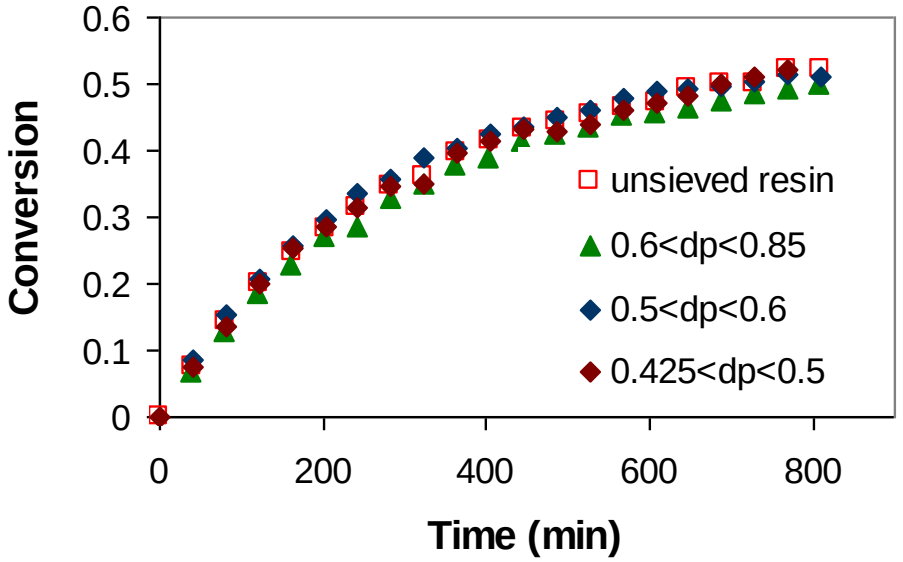
Kinetic Preliminary Studies

Effect of the stirrer speed



n_{Eth}/n_{La}=1.82; T=324.18 K; 2.4 wt.% of A15; dp=0.5 < dp < 0.6 mm.

Effect of the particle size



n_{Eth}/n_{La}=1.82; T=324.18K; 2.4 wt.% of A15.

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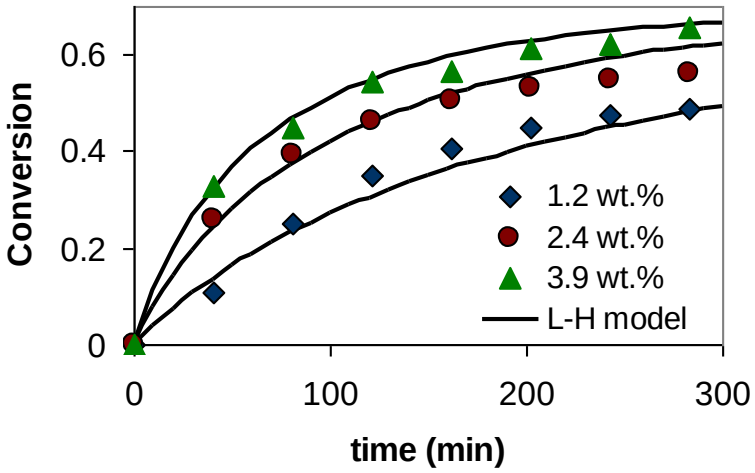
SMBR Process Development

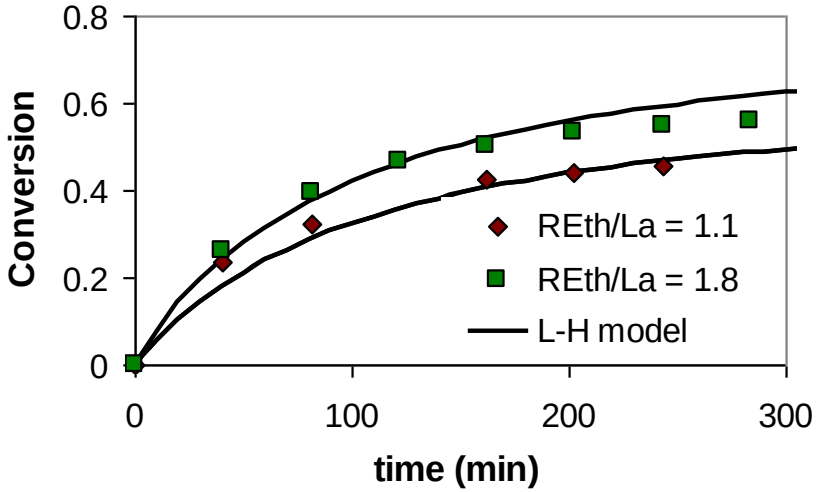
Kinetic Results

Effect of catalyst loading



n_{Eth}/n_{La}=1.82; T=353.49 K; dp≈0.685.

Effect of initial molar ratio of reactants



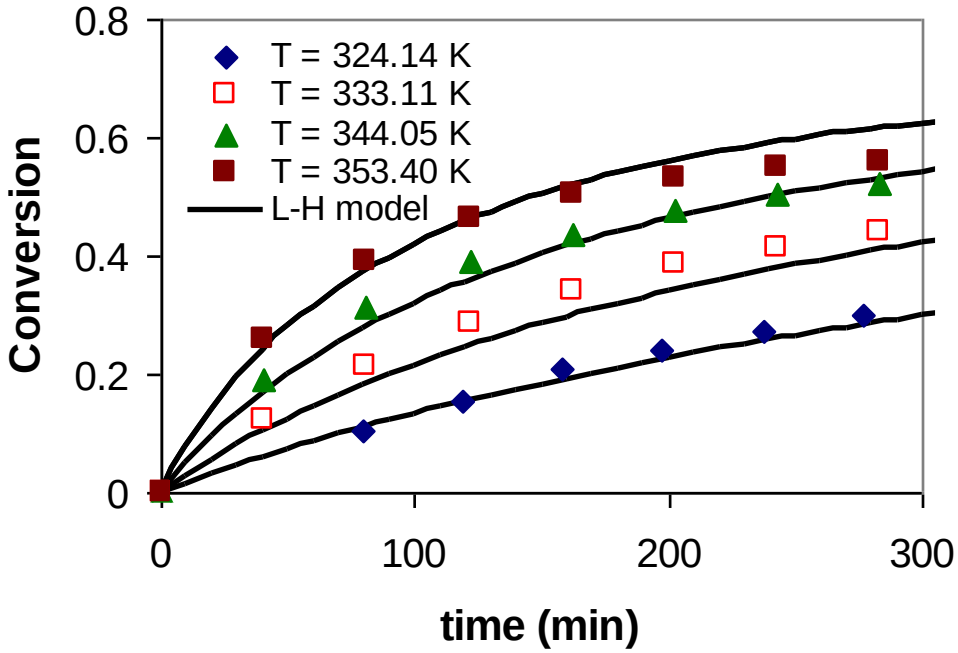
T=344.05 K; 2.4 wt.% of A15; dp≈0.685 mm.

Pereira CSM, Pinho SP, Silva VMTM, Rodrigues AE. Ind Eng Chem Res. 2008; 47:1453-1463.

SMBR Process Development

Kinetic Results

Effect of reaction temperature



n_{Eth}/n_{La}=1.82; 2.4 wt.% of A15; dp≈0.685.

Pereira CSM, Pinho SP, Silva VMTM, Rodrigues AE. Ind Eng Chem Res. 2008; 47:1453-1463.

SMBR Process Development

Langmuir-Hinshelwood mechanism

1. Adsorption of reactants

Adsorption of ethanol

$$Eth + S \xleftrightarrow{K_{s,\,Eth}} Eth.S$$

Adsorption of lactic acid

$$La + S \xleftrightarrow{K_{s,\,La}} La.S$$

2. Surface reaction between the adsorbed species

Controlling Step

$$Eth.S + La.S \overset{K_1}{\Longleftrightarrow} EL.S + W.S$$

3. Desorption of products

Desorption of ethyl lactate

$$EL.S \xleftrightarrow{K^*_{s,\,EL}} EL + S$$

Desorption of Water

$$W.S \xleftrightarrow{K^*_{s,\,W}} W + S$$

Multi-component Langmuir adsorption Isotherm

$$\theta_i = \frac{K_{s,i}\, a_i}{1 + \sum_{j=1}^{N} K_{s,\,j}\, a_j}$$

Reaction Rate

$$r = k_c \frac{a_{Eth}a_{La} - \frac{a_{EL}a_W}{K}}{(1 + K_{s,Eth}a_{Eth} + K_{s,La}a_{La} + K_{s,EL}a_{EL} + K_{s,W}a_W)^2}$$

5 parameters:

1 kinetic constant

4 adsorption constants

Simplified Reaction Rate

$$r = k_c \frac{a_{Eth}a_{La} - \frac{a_{EL}a_W}{K}}{(1 + K_{s,Eth}a_{Eth} + K_{s,W}a_W)^2}$$

3 parameters:

1 kinetic constant

2 adsorption constants

Kinetic Modeling

- Model without internal diffusion
  - Batch Reactor Mass Balance to Ethyl Lactate

$$\frac{1}{w_{cat}}\frac{d\,n_{EL}}{d\,t} = r = k_c \frac{a_{Eth}a_{La} - a_{EL}a_W / K_{eq}}{(1 + K_{s,Eth}a_{Eth} + K_{s,W}a_W)^2}$$

r_{exp} r_{theo}

Langmuir Hinshelwood model

- Initial Condition

$t = 0, \quad n_{EL} = 0$

- Objective Function

$$SRS = \sum \left(r_{\exp} - r_{theo}\right)^2$$

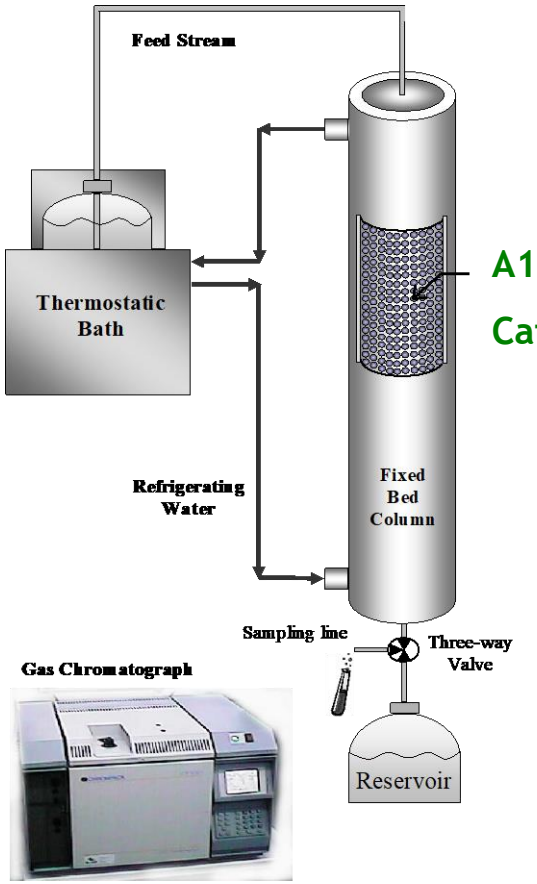
Kinetic and adsorption constants.

T (ºC)	k_C (mol/g.min)	$K_{s,W}$	$K_{s,Eth}$
20	0.0335	15.825	4.160
50	0.2250	15.765	3.713

Fixed Bed Adsorptive Reactor

SMBR Process Development

Fixed Bed Adsorptive Reactor



A15 resin

Catalyst and Adsorbent

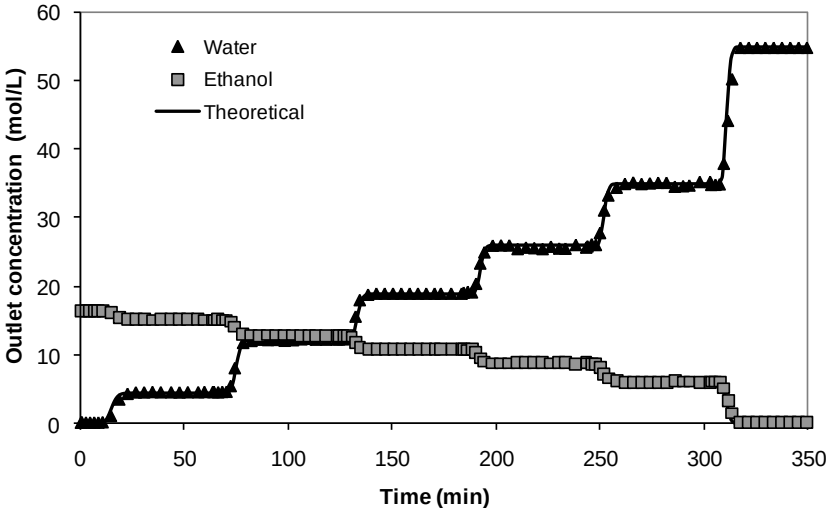
FBR experimental set-up.

Characteristics of the fixed bed column.

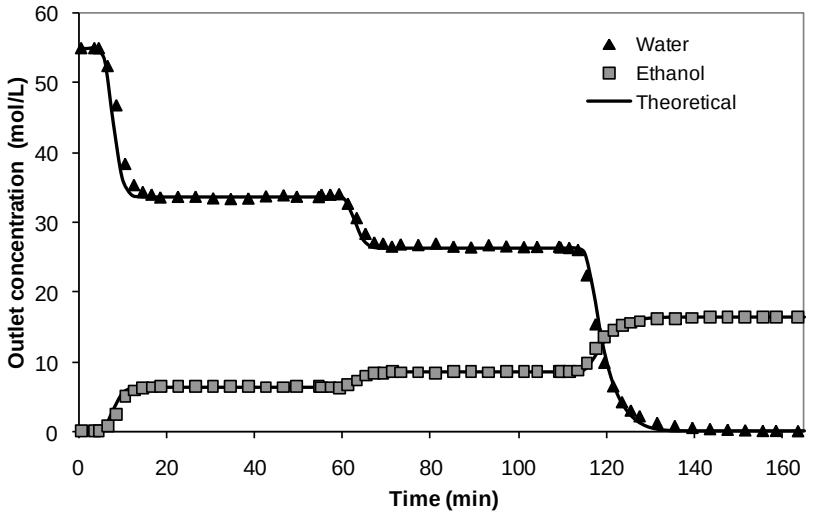
Solid weight (A15)	25 g
Length of the bed (L)	12 cm
Internal diameter (D_i)	2.6 cm
Average radius of resin beads (r_p)	372.5 μm
Bulk density (ε_b)	390 Kg/m^3
Bed porosity (ε)	0.36
Resin particle porosity (ε_p)	0.36 *
Peclet number	75

*Lode F., M. Houmard, C. Migliorini, M. Mazzotti and M. Morbidelli, Chem Eng Sci. 56(2): 269-291, 2001.

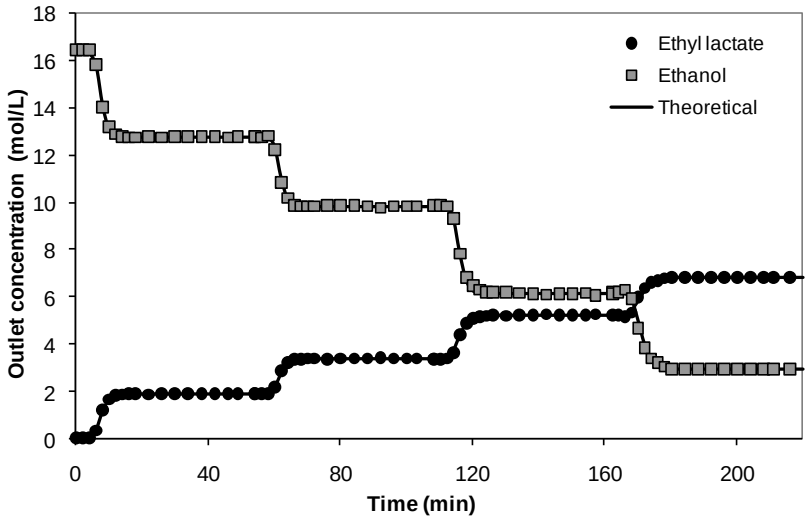
Experimental and Simulated Breakthrough Curves



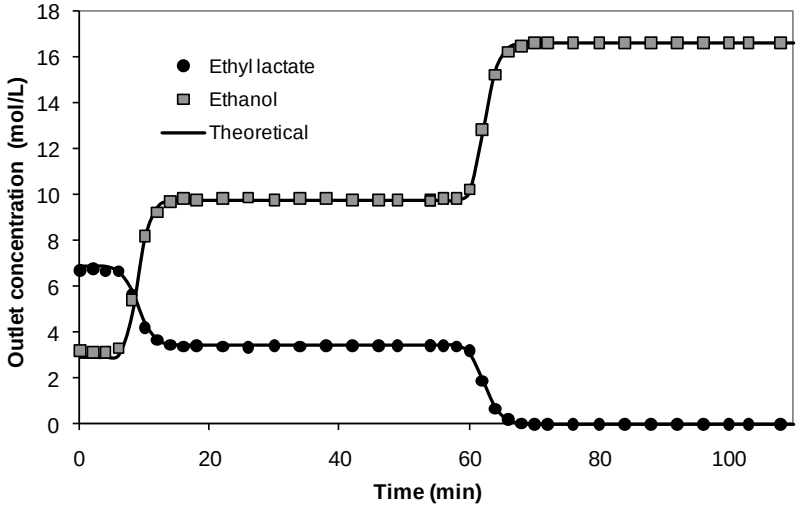
Water displacing ethanol, T=50ºC.



Ethanol displacing water, T=50ºC.



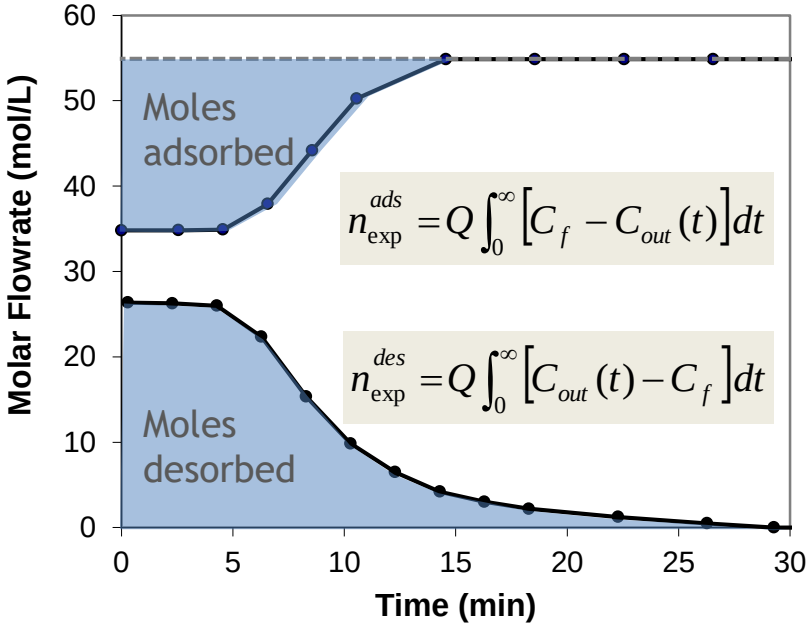
Ethyl lactate displacing ethanol, T=50ºC.



Ethanol displacing ethyl lactate, T=50ºC.

SMBR Process Development

Binary adsorption experiments



Langmuir Isotherm model

$$\bar{q}_i = \frac{Q_i K_i \bar{C}_{p,i}}{1 + \sum_{j=1}^{NC} K_j \bar{C}_{p,j}}$$

molar adsorption capacity

equilibrium constant

Parameters at 50 °C

Component	Q (mol/$L_{wet\ solid}$)	K (L/mol)
Ethanol	6.30	3.068
Lactic acid	4.94	4.085
Ethyl lactate	3.23	1.815
Water	20.58	7.055

Amount adsorbed:

$$n_{theo}^{ads} = \left[\varepsilon + (1-\varepsilon)\varepsilon_p\right]\left(C_f - C_0\right) + (1-\varepsilon)(1-\varepsilon_p)\left[q(C_f) - q(C_0)\right]$$

Amount desorbed:

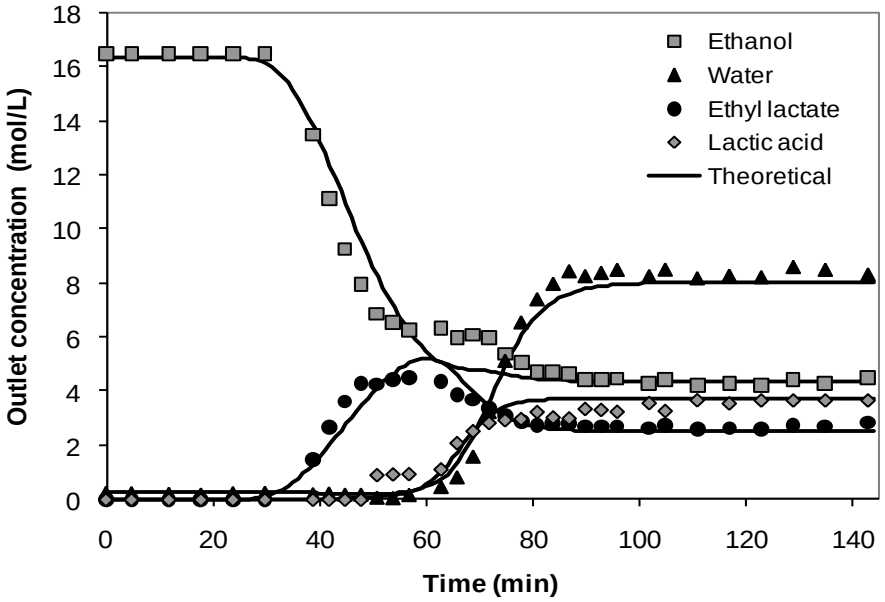
$$n_{theo}^{des} = \left[\varepsilon + (1-\varepsilon)\varepsilon_p\right]\left(C_0 - C_f\right) + (1-\varepsilon)(1-\varepsilon_p)\left[q(C_0) - q(C_f)\right]$$

$$fob = \sum_{k=1}^{nt}\left[\left(n_{\exp}^{ads} - n_{theo}^{ads}\right)^2 + \left(n_{\exp}^{des} - n_{theo}^{des}\right)^2\right]$$

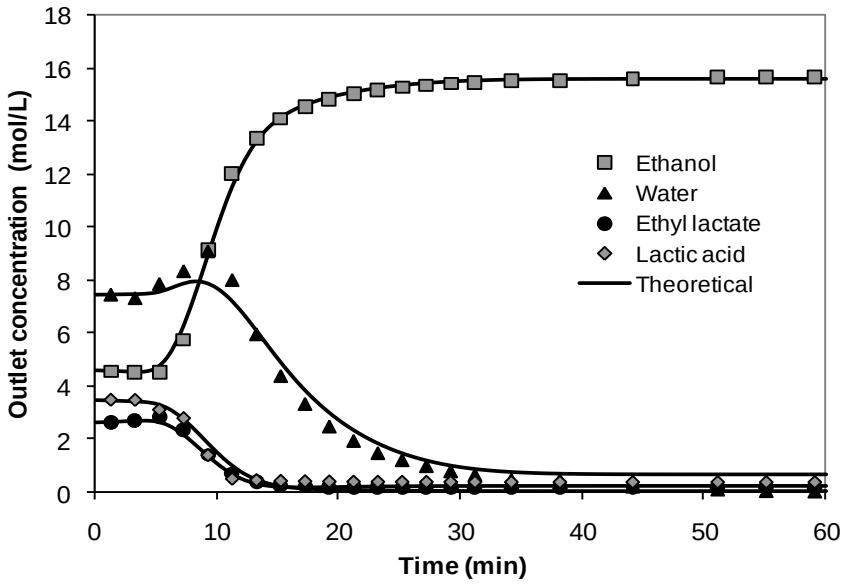
SMBR Process Development

Kinetic Experiments

Production Step



Regeneration Step

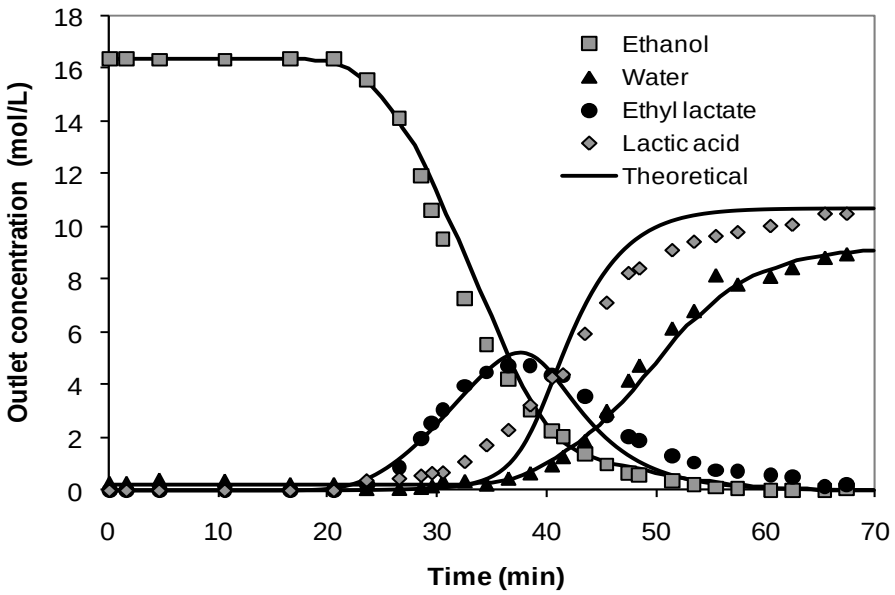


Concentration histories at the outlet of the fixed bed adsorptive reactor:
Production step - column initially saturated with ethanol and then fed with a mixture of ethanol and lactic acid solution (Q = 1 *mL/min*, $C_{La,F}$ = *5.88 mol/L*, $C_{Eth,F}$ = *6.60 mol/L*, $C_{W,F}$ = *5.87 mol/L*);
Regeneration step - column fed with ethanol (Q = 4.3 *mL/min*).
T=50ºC

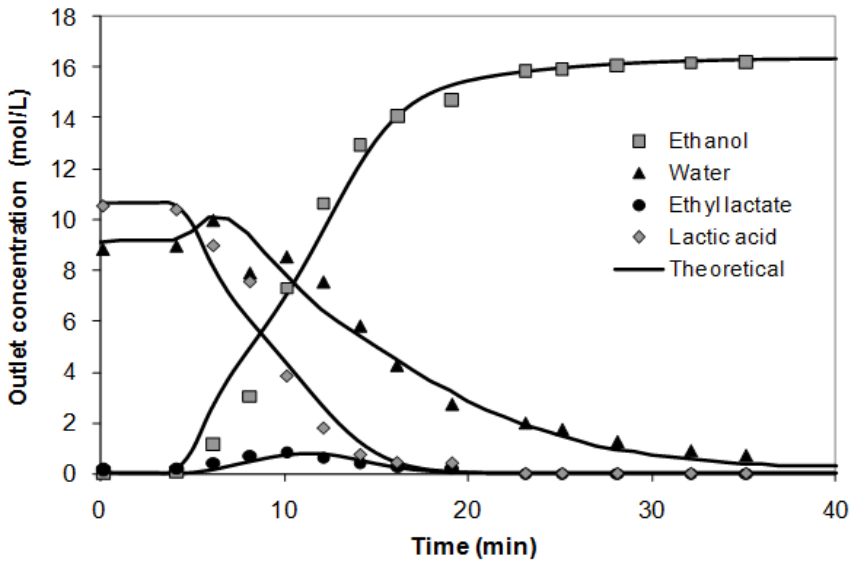
SMBR Process Development

Kinetic Experiments

Production Step



Regeneration Step

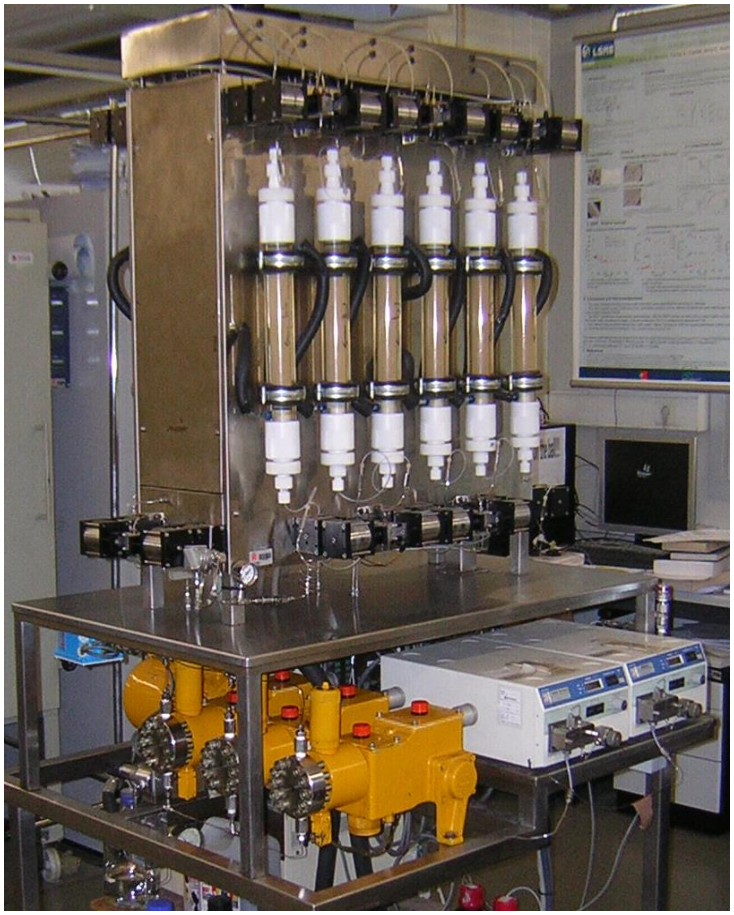


Concentration histories at the outlet of the fixed bed adsorptive reactor:
Production step - column initially saturated with ethanol and then fed with lactic acid solution (86 wt.% in water), Q = 1.3 *mL/min*;
Regeneration step - column fed with ethanol (Q = 4.3 *mL/min*).
T=50ºC

Simulated Moving Bed Reactor

SMBR Process Development

SMBR Experimental set-up



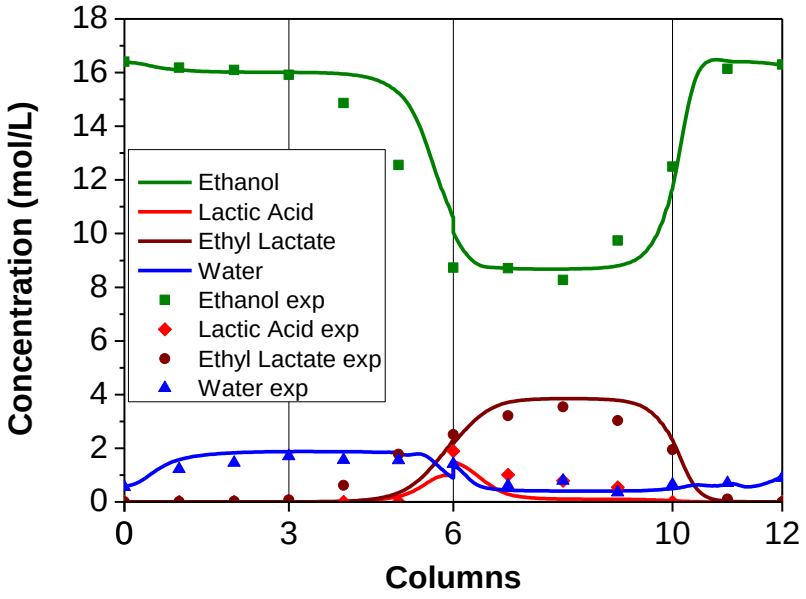
The Licosep 12-26 SMB Pilot Unit
(Novasep, France)

- SMB pilot scale unit LICOSEP 12-26;
- 12 columns (23 cm long and 2.6 cm internal diameter) were used;
- Packing: Amberlyst 15-wet;
- Inlet and outlet flowrates delivered by HPLC pumps;
- Feed and raffinate pumps maximum flowrate of 10 ml/min;
- Desorbent and extract pumps maximum flowrate of 30 ml/min;
- Recycling flowrate delivered by a diaphragm pump (20-120 ml/min).

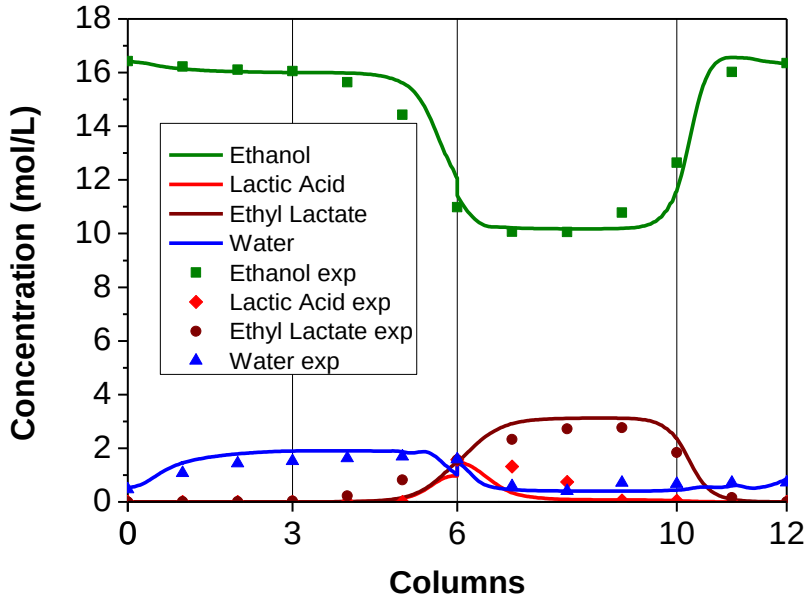
SMBR Process Development

SMBR Experimental Validation

Run 1



Run 2



Desorbent: Ethanol

Feed: Lactic acid solution (85 wt.% in water)

Catalyst/Adsorbent: Amberlyst-15 wet Resin

T= 50°C, configuration: 3-3-4-2, Q_D=27.4 mL/min,

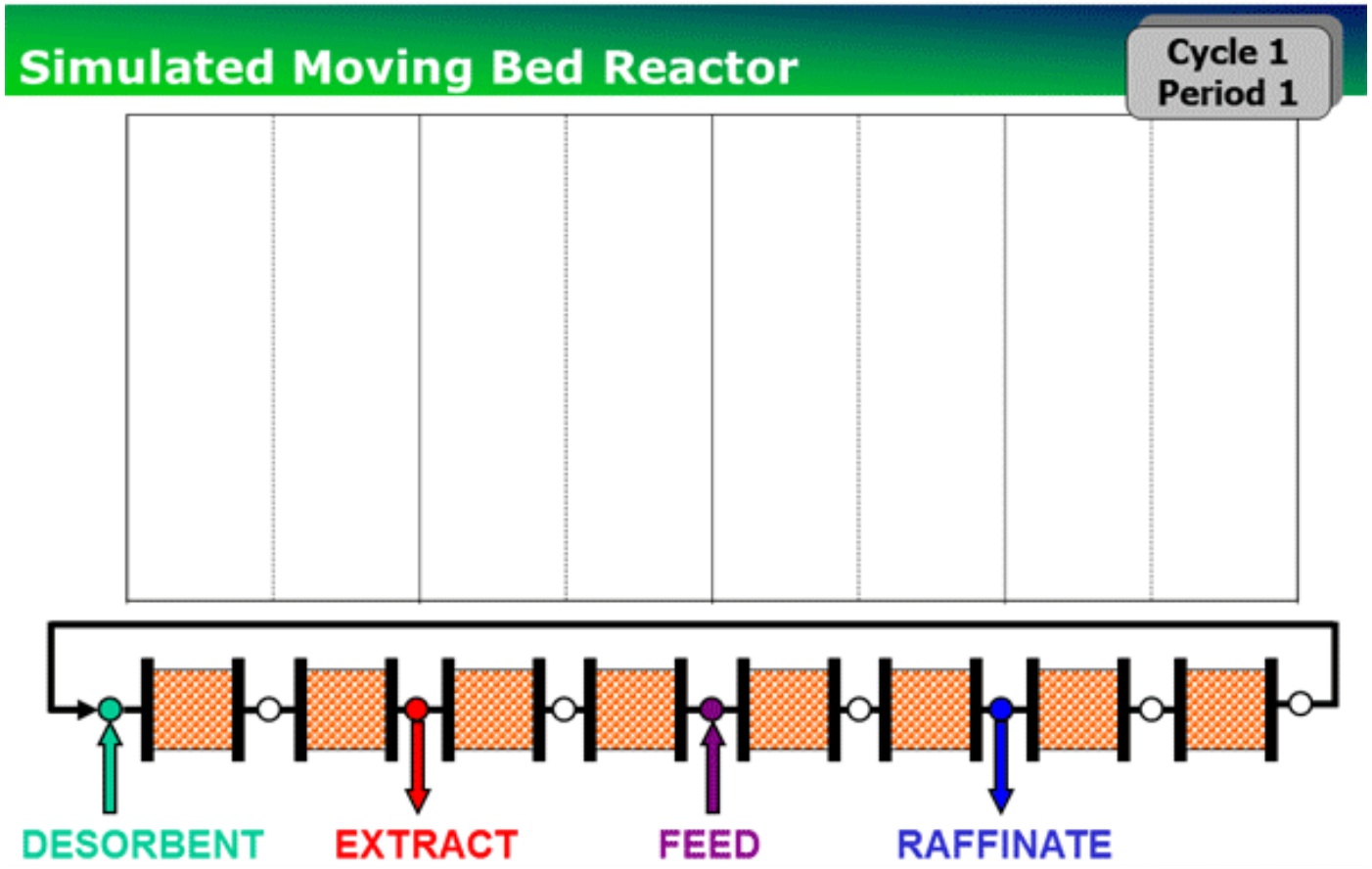
Q_F=1.80 mL/min, Q_R=8.8mL/min and Q_{rec}=24.7mL/min.

Run 1: t*=2.9 min; Run 2: t*=3 min.

Experimental and simulated concentration profiles in SMBR at the middle of the switching time at cyclic steady-state (13th cycle).

SMBR Process Development

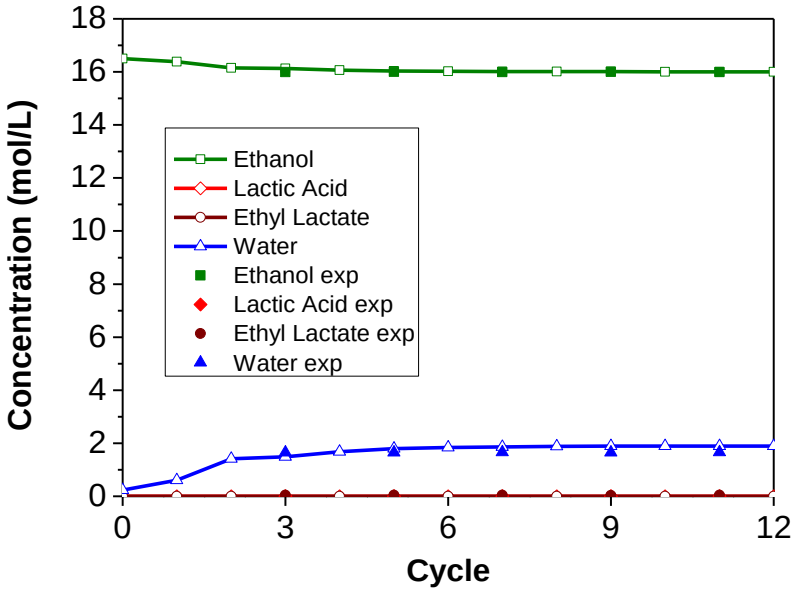
Concentration Profiles



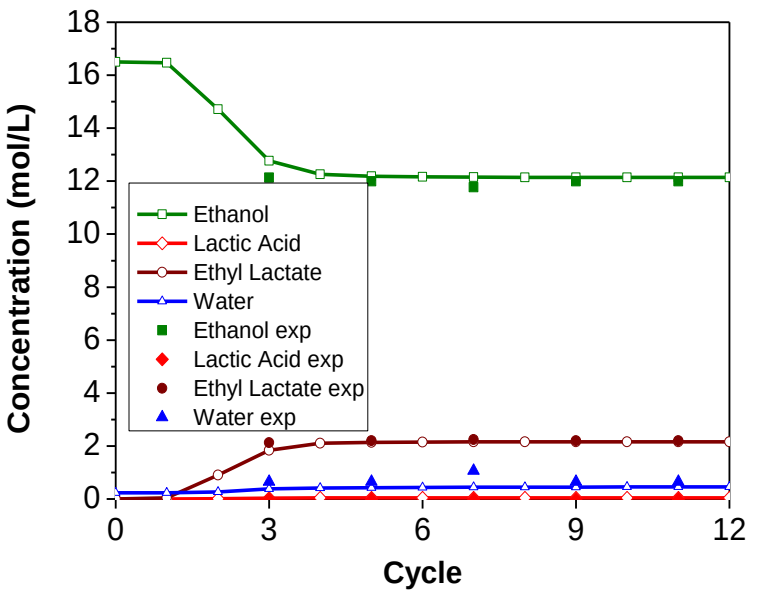
SMBR Process Development

SMBR Experimental Validation

Extract



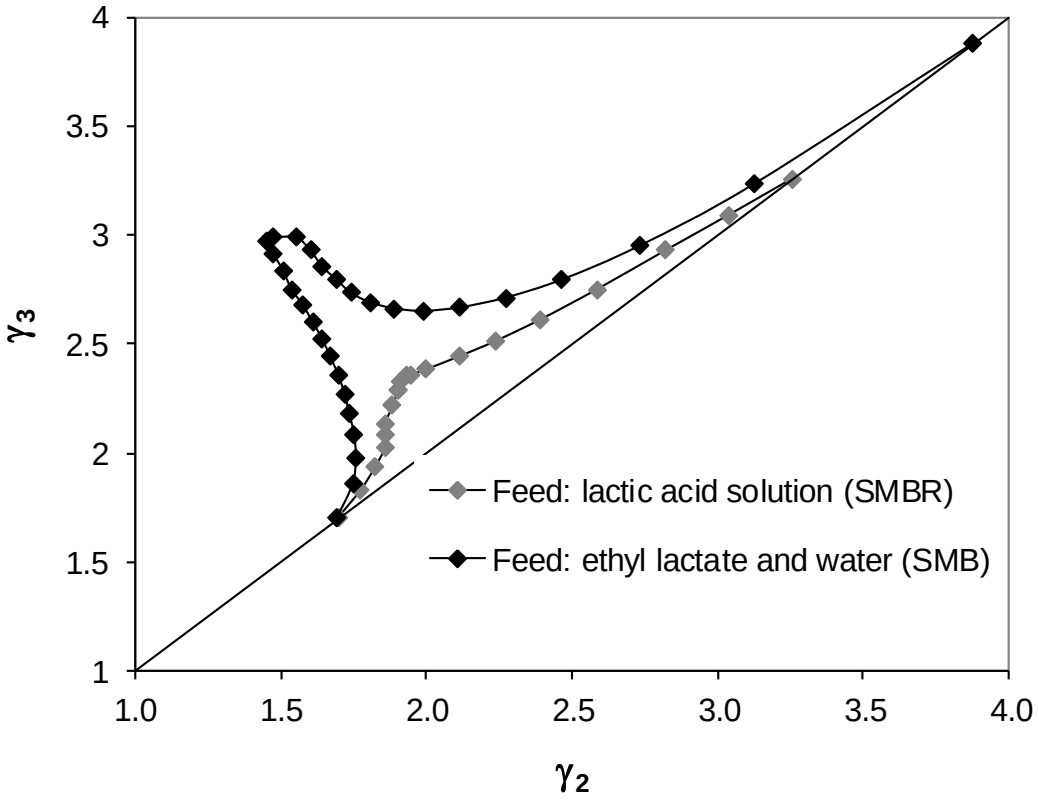
Raffinate



Experimental and theoretical average concentration for the conditions of Run 2 in the extract and raffinate streams.

SMBR Process Development

Separation Region vs Reactive Separation Region

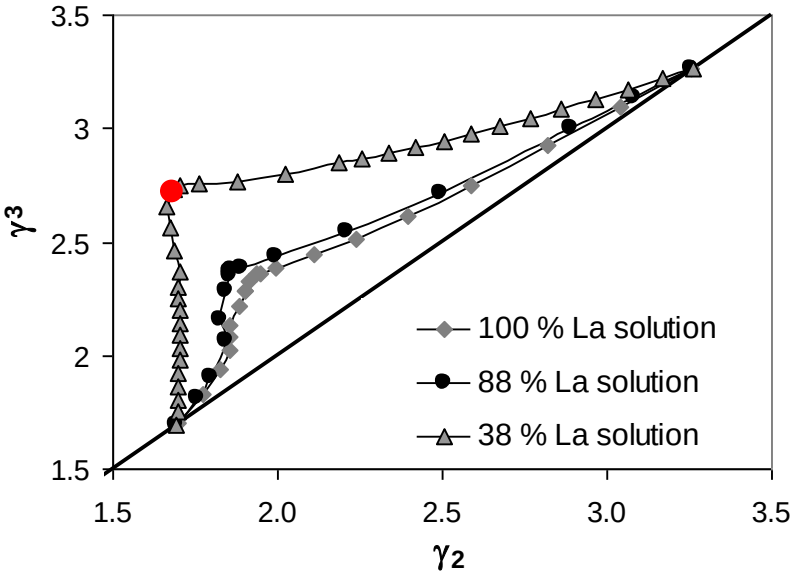


Reactive/separation region for the case where lactic acid solution is fed to the SMBR ($C_{LA,F}$ = 10.75 mol/L; $C_{W,F}$ = 9.48 mol/L) and separation region for ethyl lactate and water fed to the SMB ($C_{EL,F}$ = 6.47 mol/L; $C_{W,F}$ = 12.17 mol/L). (γ_1 = 4.698; γ_4 =1.492; T=50ºC; 95 % purity).

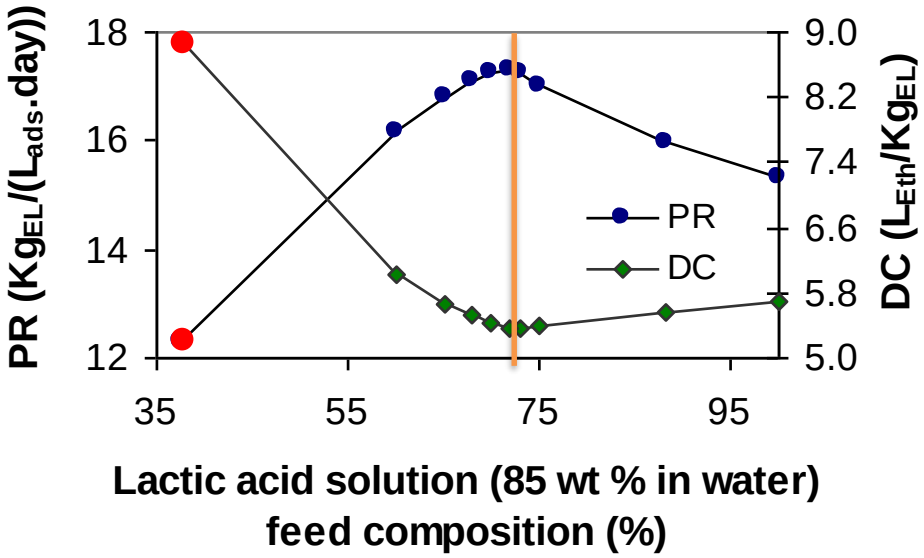
SMBR Process Development

Effect of Feed Composition

Reactive/Separation region (95 % Purity)



Influence of the feed composition in the PR and DC for the optimal operating points (95% Purity)



Operating conditions: Configuration 3-3-4-2; t*=2.7 min; Q_D = 58 mL/min; $Q_{recycle}$=27 mL/min.

72 % mole fraction of Lactic acid ⇒

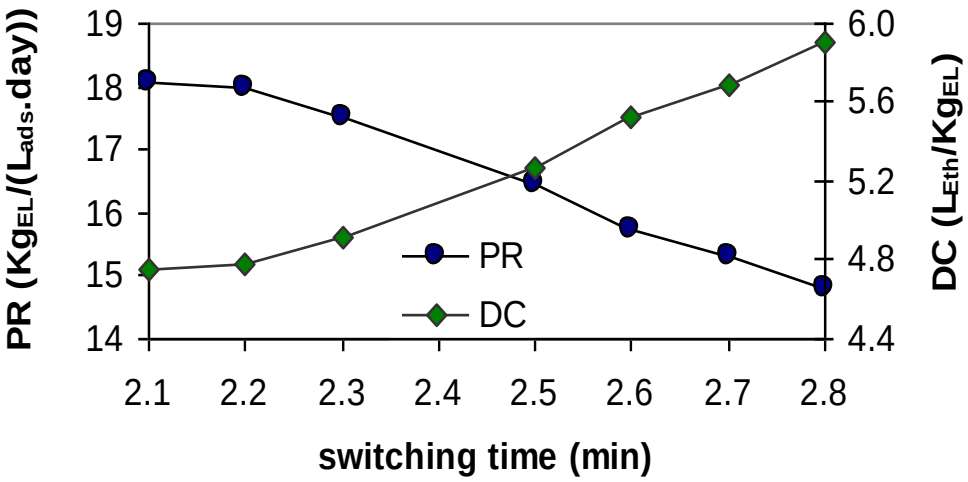
$$PR = 17.33\ kg_{EL} L_{resin}^{-1}.day^{-1}$$

$$DC = 5.36\ L_{Eth}.kg_{EL}^{-1}$$

SMBR Process Development

Effect of Switching Time

Influence of the t* in the PR and DC for the optimal operating points (95% Purity)



2.1 min

The solid is not being completely regenerated in section 1

solid flow rate increases (*Us=Lc/t**)

Operating conditions:

Q_D = 58 mL/min; $Q_{recycle}$ = 27 mL/min;

Configuration: 3-3-4-2;

Feed: La solution (85 wt % in water).

From 2.8 min to 2.1 min

+ 22 % PR

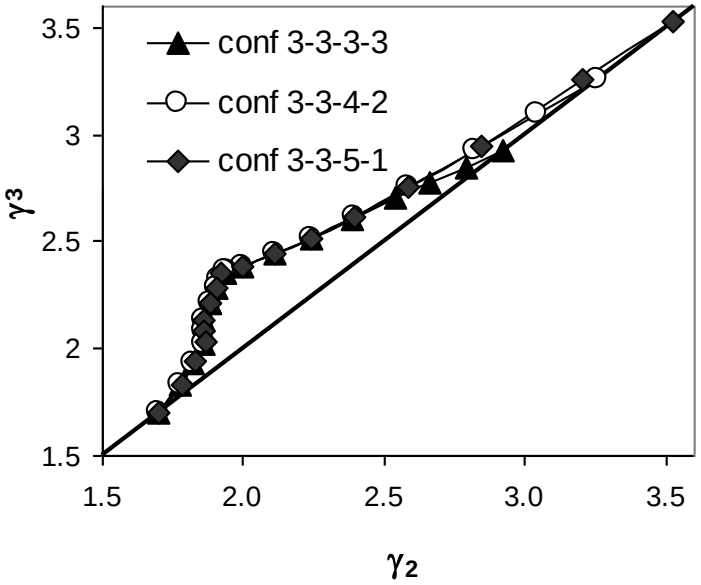
- 19.6 % DC

Reduce downstream costs

SMBR Process Development

Effect of SMBR Columns Arrangement

Reactive/Separation region (95 % Purity)



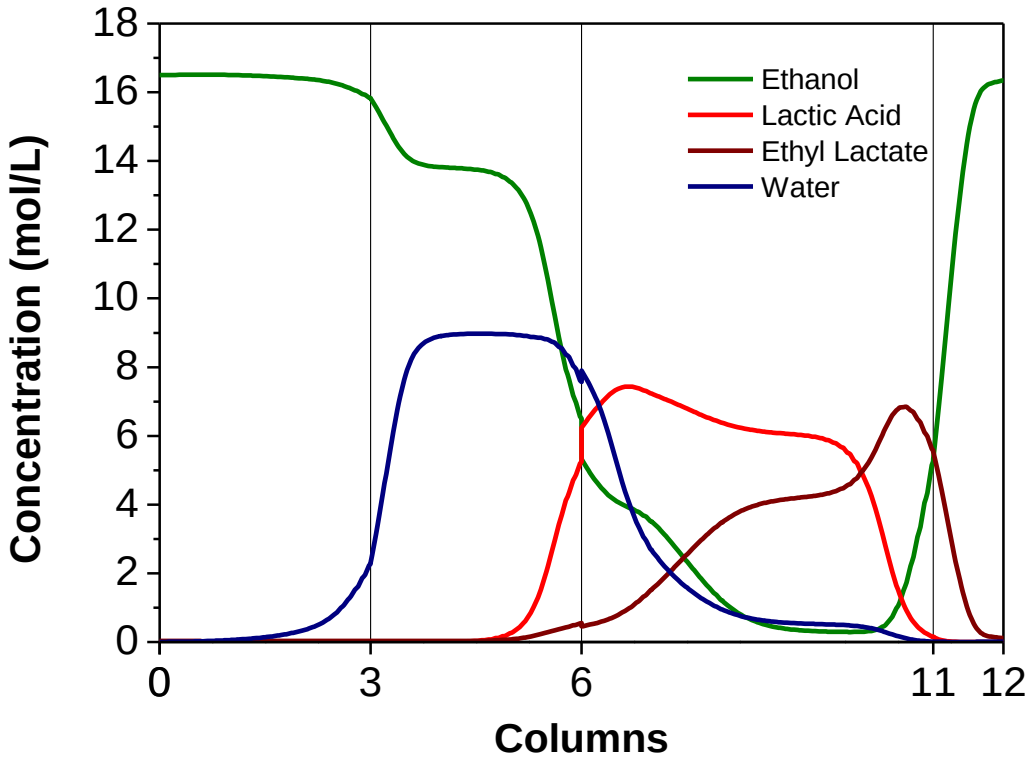
Operating conditions:
Q_D = 58 mL/min; $Q_{recycle}$ = 27 mL/min;
Configuration: 3-3-4-2;
t*=2.7 min
Feed: La solution (85 wt. % in water).

Performance parameters for the optimal operation points for the different SMBR configurations.

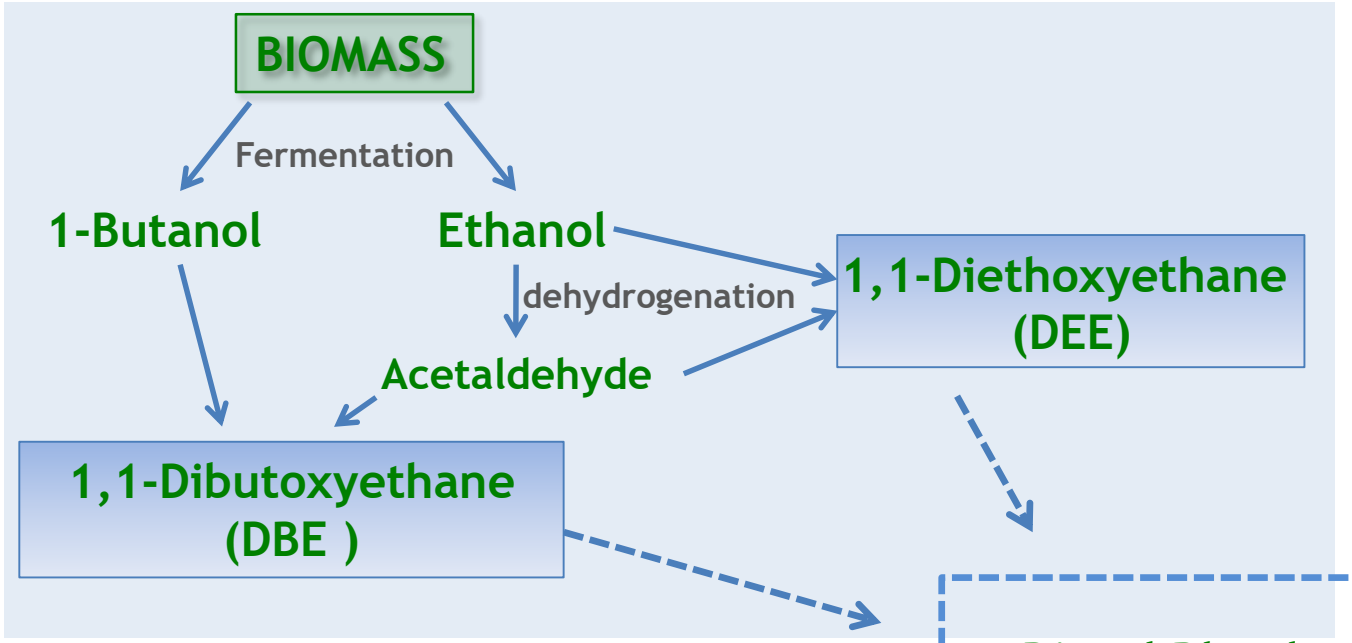
Columns arrangement	3-3-3-3	3-3-4-2	3-3-5-1
Raffinate Productivity (kg_{EL}/L_{A15}/day)	14.97	15.33	15.36
Desorbent Consumption (L_{Eth}/kg_{EL})	5.83	5.68	5.67

Effect of SMBR Columns Arrangement

Concentration profiles at the middle of the switching time at cyclic steady state for the optimal operating point of the SMBR configuration 3-3-5-1.



Other Applications: Acetals Production



Diesel blends with 10% of DEE leads:

- 13% reduction in CO
- 8% reduction in CO_2
- 21% reduction in PM

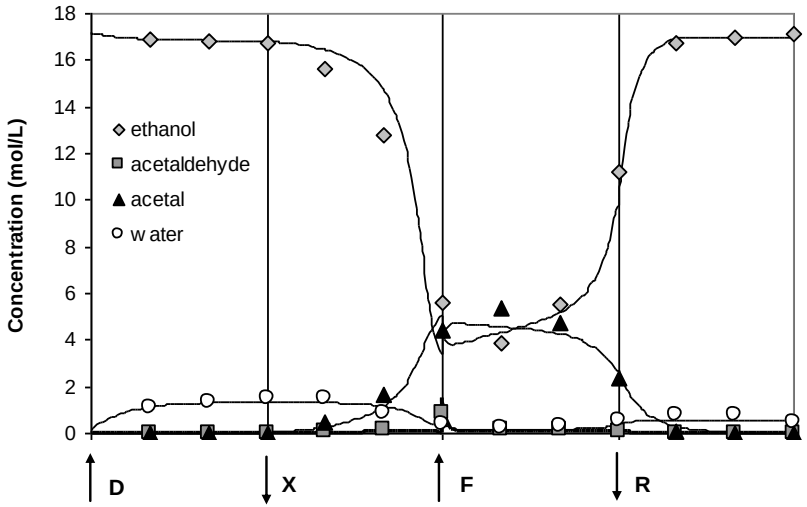
Enhance the renewable fraction in diesel and reduce emissions of CO_2, CO and, mainly, Particulate Matter.

F. Frusteri, L. Spadaro, C. Beatrice, C. Guido, "Oxygenated additives production for diesel engine emission improvement", Chem. Eng. J. 134 (2007), 239-245.
K. Nord, D. Haupt, "Reducing the Emission of Particles from a Diesel Engine by Adding an Oxygenate to the Fuel", Environ. Sci. Technol. 2005, 39, p. 6260-6265.

Other Applications: Acetals Production

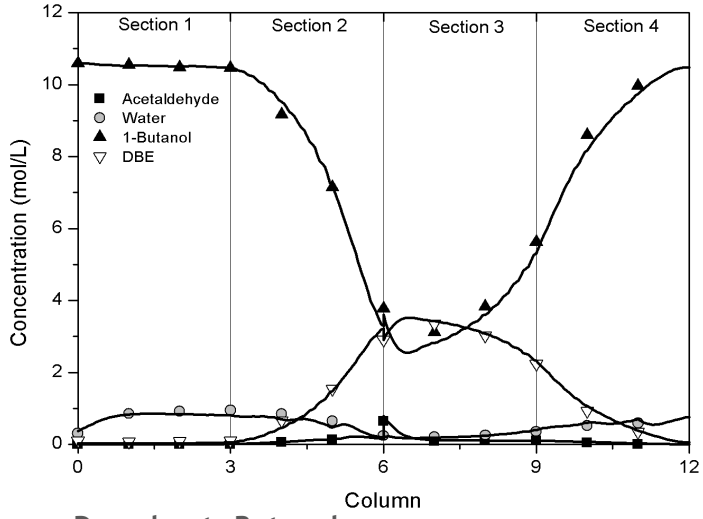
SMBR Experimental Validation

DEE Production



Desorbent: Ethanol
Feed: Ethanol + Acetaldehyde
Catalyst/Adsorbent: Amberlyst-15 wet Resin
T=10ºC.

DBE Production



Desorbent: Butanol
Feed: Butanol + Acetaldehyde
Catalyst/Adsorbent: Amberlyst-15 wet Resin
T=25ºC.

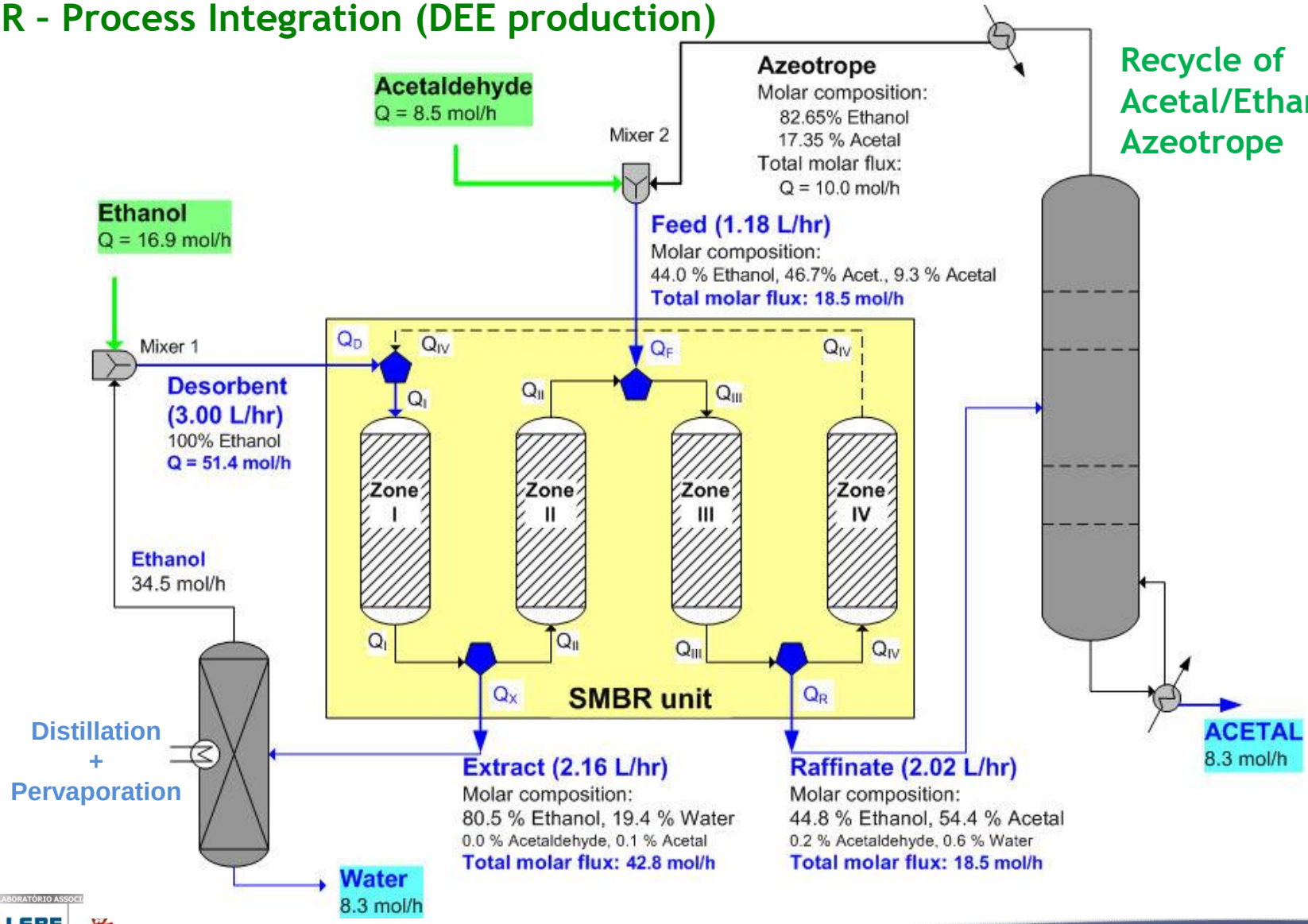
Experimental and simulated concentration profiles in SMBR at the middle of the switching time at cyclic steady-state .

V.M.T.M. Silva and A.E. Rodrigues, Novel process for diethylacetal synthesis, AlChE J. 51 (2005) 2752-2768.

N.S. Graça, L.S. Pais, V.M.T.M. Silva and A.E. Rodrigues, Analysis of the Synthesis of 1,1- Dibutoxyethane in a Simulated Moving-Bed Adsorptive Reactor, submited to Chem. Eng. and Processing: Process Intensification.

Other Applications: Acetals Production

SMBR – Process Integration (DEE production)



Conclusions

- *The combination of reaction and separation in a single unit (multifunctional reactors) is one of the process intensification methods, which may avoid constraints arising from thermodynamic equilibrium and may lead to more efficient as well as more economical processes.*

- *SMBR technology is one of the most interesting multifunctional reactors. It exhibits high conversion (far beyond equilibrium value), high productivity and operates at moderate temperatures. However, it requires further separation units for desorbent recovery from both extract and raffinate streams. Different methodologies to minimize the desorbent consumption should be evaluated.*

LSRE
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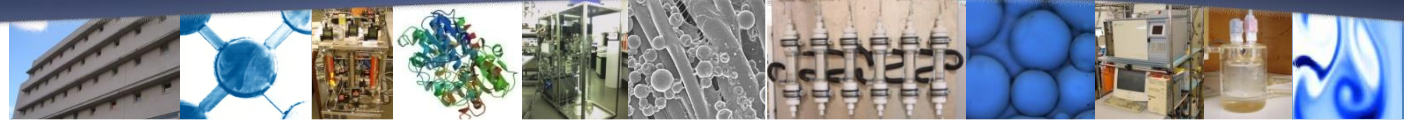


SIMULATED MOVING BED MEMBRANE REACTOR - PERMSMBR

Process Intensification

Alírio E. Rodrigues

LABORATÓRIO ASSOCIADO
LSRE
icm

Outline

- Simulated Moving Bed Membrane Reactor (PermSMBR)
  - Concept
  - Configurations
  - Mathematical Model

- PermSMBR Process Development
  - Ethyl Lactate Case Study
    - Pervaporation Membrane Reactor Concept
    - Pervaporation Performance
    - Pervaporation Membrane Reactor Performance
    - PermSMBR Vs SMBR

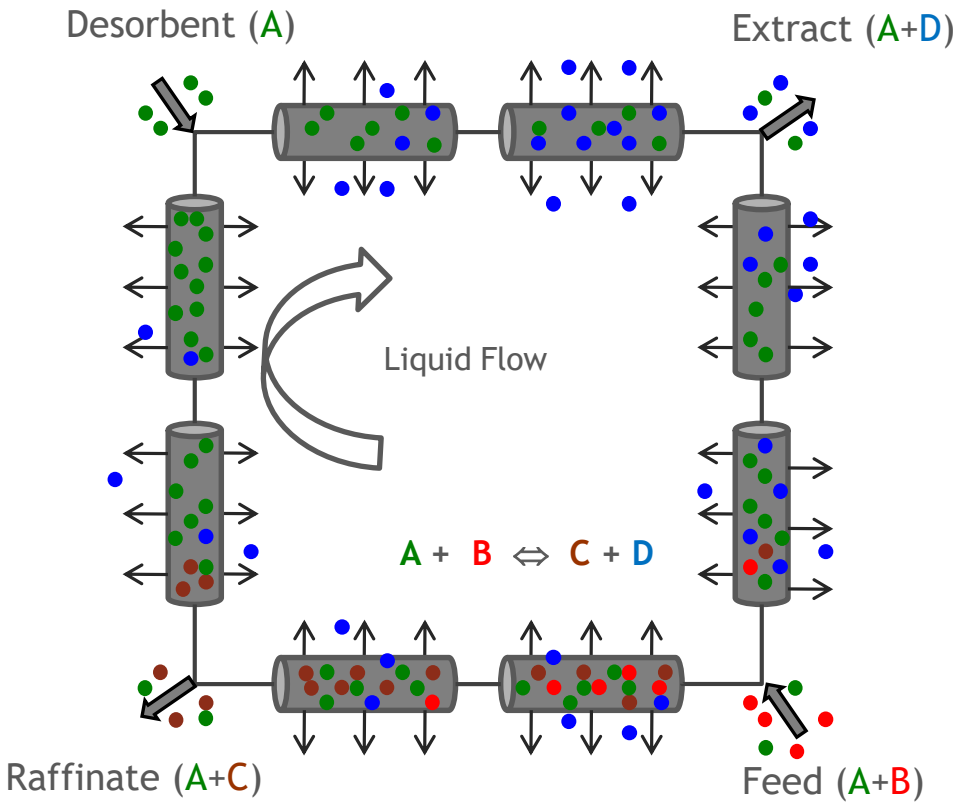
- PermSMBR Process Evaluation for Acetals Production
  - 1,1-Diethoxyethane Production
  - 1,1-Dibuthoxyethane Production (*EuroBioref Project*)

- Conclusions

Simulated Moving Bed Membrane Reactor (PermSMBR)

New Hybrid Technology – Developed & Patented by FEUP (LSRE)

SMBR integrated with selective permeable membranes.



PermSMBR process scheme.

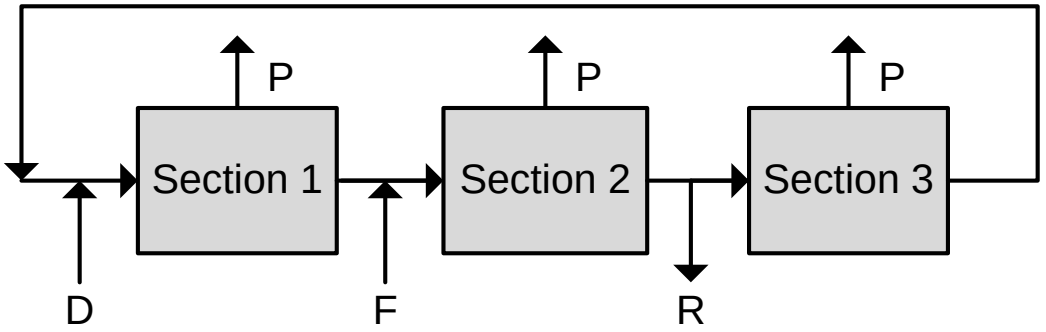
Schematic representation of a membrane packed with catalyst/adsorbent.

Silva VMTM, Pereira CSM, Rodrigues AE. Simulated Moving Bed Membrane Reactor, new hybrid separation process and its applications. PT Patent 104496 (2009); WO Patent 2010/116335, 2010.

Simulated Moving Bed Membrane Reactor (PermSMBR)

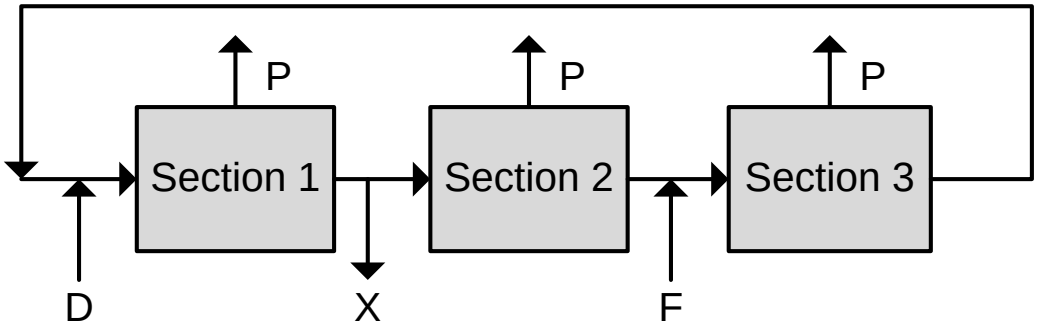
PermSMBR Configurations: 3 Sections

Membranes selective to the most adsorbed product



2 inlet ports: feed (F) and desorbent (D) streams; 1 outlet port: raffinate (R) stream.

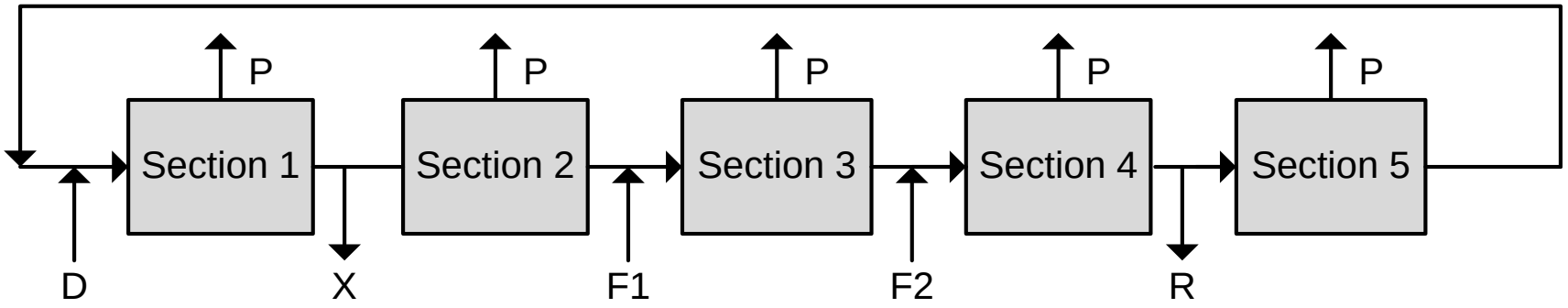
Membranes selective to the less adsorbed product



2 inlet ports: feed (F) and desorbent (D) streams; 1 outlet port: Extract (X) stream.

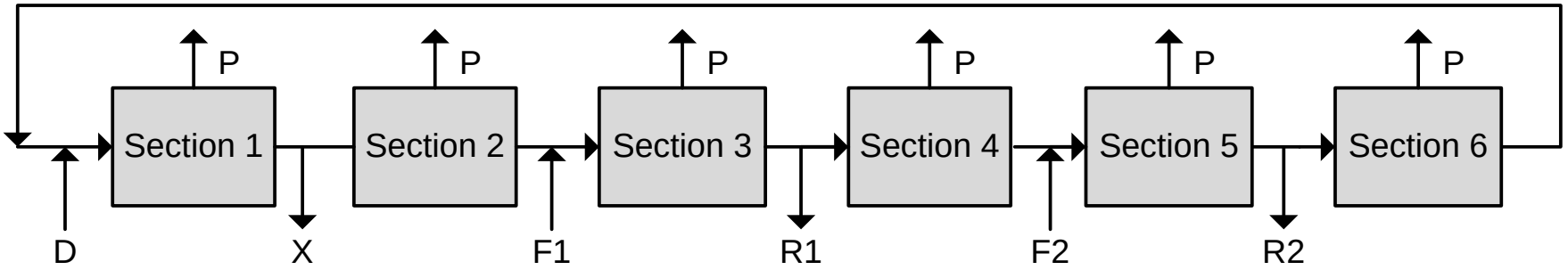
Simulated Moving Bed Membrane Reactor (PermSMBR)

PermSMBR Configurations: 5 Sections



3 inlet ports: 2 feed streams (F1 and F2) and a desorbent stream (D); 2 outlet ports: extract (X) and raffinate (R) streams.

PermSMBR Configurations: 6 Sections



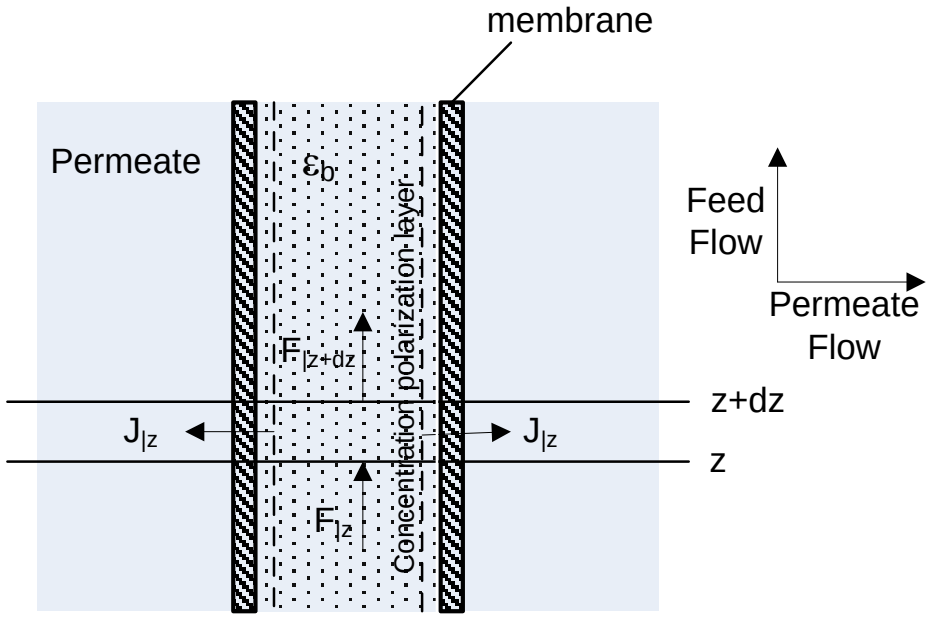
3 inlet ports: 2 feed streams (F1 and F2) and a desorbent stream (D); 3 outlet ports: extract (X) and raffinate (R1 and R2) streams.

PermSMBR Mathematical Model

The mathematical model used to describe the performance of the PermSMBR considers:

- axial dispersion flow for the bulk fluid phase;
- linear driving force (LDF) approximation for the inter and intra-particle mass transfer rates;
- multi-component adsorption equilibrium at the adsorbent phase;
- liquid velocity variations due to reaction, adsorption/desorption and species permeation;
- constant porosity and length of the packed bed;
- membrane concentration polarization;
- isothermal operation.

PermSMBR column with 20 membranes



Fluxes inside one membrane of the PermSMBR, where F is the molar flux in the feed side (retentate) and J is the permeate molar flux through the membrane.

PermSMBR Model Equations

Bulk fluid mass balance to component i, in column k

$$\frac{\partial C_{ik}}{\partial t}+\frac{\partial (C_{ik}u_k)}{\partial z}+\frac{(1-\varepsilon)}{\varepsilon}\frac{3}{r_p}K_{L,ik}\left(C_{ik}-\overline{C}_{p,ik}\right)=D_{ax,k}\frac{\partial}{\partial z}\left(C_T\frac{\partial x_{ik}}{\partial z}\right)-\frac{A_m}{\varepsilon}J_{ik}$$

Where $J_{ik}=\mathrm{k}_{\mathrm{ov},ik}(a_{ik}p_i^{\,0}-y_{ik}P_{perm})$

Pellet mass balance to component i, in column k

$$\varepsilon_p\frac{\partial \overline{C}_{p,ik}}{\partial t}+(1-\varepsilon_p)\frac{\partial q_{ik}}{\partial t}=\frac{3}{r_p}K_{L,ik}\left(C_{ik}-\overline{C}_{p,ik}\right)+\upsilon_i\rho_p\eta r(\overline{C}_{p,ik})$$

Interstitial fluid velocity variation

$$\frac{du_k}{dz}=-\frac{(1-\varepsilon)}{\varepsilon}\frac{3}{r_p}\sum_{i=1}^{n}K_{L,ik}V_{mol,i}\left(C_{ik}-\overline{C}_{p,ik}\right)-\frac{A_m}{\varepsilon}\sum_{i=1}^{n}J_{iK}$$

Initial and Danckwerts boundary conditions

$$t=0:\ C_{ik}=\overline{C}_{p,ik}=C_{ik,0}\quad q_{ik}=q_{ik,0}$$

$$z=0:\ u_kC_{ik}-D_{ax,k}\left.\frac{\partial C_{ik}}{\partial z}\right|_{z=0}=u_kC_{ik,F}\quad u_k=u_{k,0}$$

$$z=L_C:\ \left.\frac{\partial C_{ik}}{\partial z}\right|_{z=L_c}=0$$

PermSMBR Model Equations

Node Mass Balances

Desorbent node

$$C_{i(j=4,z=Lc)} = \frac{u_1}{u_4} C_{i(j=1,z=0)} - \frac{u_D}{u_4} C_i^D$$

Feed node

$$C_{i(2,z=Lc)} = \frac{u_3}{u_2} C_{i(3,z=0)} - \frac{u_F}{u_2} C_i^F$$

Extract node

$$C_{i(j=1,z=Lc)} = C_{i(j=2,z=0)}$$

Raffinate node

$$C_{i(j=3,z=Lc)} = C_{i(j=4,z=0)}$$

Mass transfer parameters in the resin bed

Axial dispersion coefficient[1]

$$\varepsilon Pe_p = 0.2 + 0.011 \mathrm{Re}_p^{0.48}$$

$$Pe_p = d_p u / D_{ax} \quad \mathrm{Re}_p = \rho\, d_p u / \eta$$

Global mass transfer coefficient[2]

$$\frac{1}{K_L} = \frac{1}{k_e} + \frac{1}{\varepsilon_p k_i}$$

Mass transfer in the polarization layer

Global membrane mass transfer coefficient[3]

$$\frac{1}{k_{ov,i}} = \frac{1}{Q_{memb,i}} + \frac{\gamma_i^* p_i^0 V_{mol,i}}{K_{bl}}$$

Boundary layer coefficient (Lévêque correlation[4])

$$Sh = 1.62\, \mathrm{Re}^{0.33}\, Sc^{0.33} \left(\frac{d_{\mathrm{int}}}{L} \right)^{0.33} \qquad (\mathrm{Re} < 2300)$$

$$Sh = \frac{k_{bl}\, d_{\mathrm{int}}}{D_m} \qquad Sc = \frac{\mu}{\rho D_m} \qquad Re = \frac{\rho\, d_{\mathrm{int}}\, u}{\mu}$$

PermSMBR Performance Parameters

Performance Parameters

Raffinate Purity (%)

$$PUR = 100 \int_{t}^{t+N_c t^*} C_{R,C}\,dt \Big/ \left(\int_{t}^{t+N_c t^*} \left(C_{R,B} + C_{R,C} + C_{R,D} \right) dt \right)$$

Extract Purity (%)

$$PUX = 100 \int_{t}^{t+N_c t^*} C_{X,D}\,dt \Big/ \left(\int_{t}^{t+N_c t^*} \left(C_{X,B} + C_{X,C} + C_{X,D} \right) dt \right)$$

Conversion (%)

$$X = 1 - \left(Q_X \int_{t}^{t+N_c t^*} C_{X,B}\,dt + Q_R \int_{t}^{t+N_c t^*} C_{R,B}\,dt \right) \Big/ \left(Q_F C_{F,B} N_c t^* \right)$$

Productivity ($Kg_C/(L_{ads}.day)$)

$$PR = Q_R \int_{t}^{t+N_c t^*} C_{R,C}\,dt \Big/ \left((1-\varepsilon) V_{unit} N_c t^* \right)$$

Desorbent Consumption (L_A/Kg_C)

$$DC = N_c t^* \left(Q_D C_{D,A} + Q_F \left(C_{F,A} - \upsilon_A X C_{F,B} \right) \right) \Big/ \left(Q_R \int_{t}^{t+N_c t^*} C_{R,C}\,dt \right)$$

(1) Butt JB. Reaction kinetics and Reactor Design. NJ: Prentice-Hall: Englewood Cliffs; 1980.
(2) Silva VMTM, Rodrigues AE. Dynamics of a fixed-bed adsorptive reactor for synthesis of diethylacetal. AIChE J. 2002;48(3):625-634.
(3) Wijmans JG, Athayde AL, Daniels R, Ly JH, Kamaruddin HD, Pinnau I. The role of boundary layers in the removal of volatile organic compounds from water by pervaporation. J. Membr. Sci. 1996;109(1):135-146.
(4) Lévêque MA. Les lois de transmission de chaleur par convection. Annal. Mines 13. 1928:201.

PermSMBR Process Development

1. Batch reactor

1.1 Equilibrium experiments

- Equilibrium constant
- Standard properties of reaction
- Standard formation properties of species

1.2 Kinetic experiments

- Mass transfer: pore diffusion limitations
- Reaction rate law
- Mathematical model of the batch reactor

2. Fixed bed

2.1 Tracer experiments

- Bed porosity
- Axial dispersion

2.2 Binary adsorption experiments

- Equilibrium multi-component adsorption isotherms
- Mass transfer limitations in absence of reaction
- Mathematical model of the fixed bed column

2.3 Reaction experiments

- Mass transfer limitations
- Fixed bed reactor model validation

3. Pervaporation Membrane Reactor

3.1 Pervaporation experiments

- Permeance
- Mass transfer limitations

3.2 Pervaporation Membrane Reactor

- Pervaporation membrane reactor model

4. PermSMBR

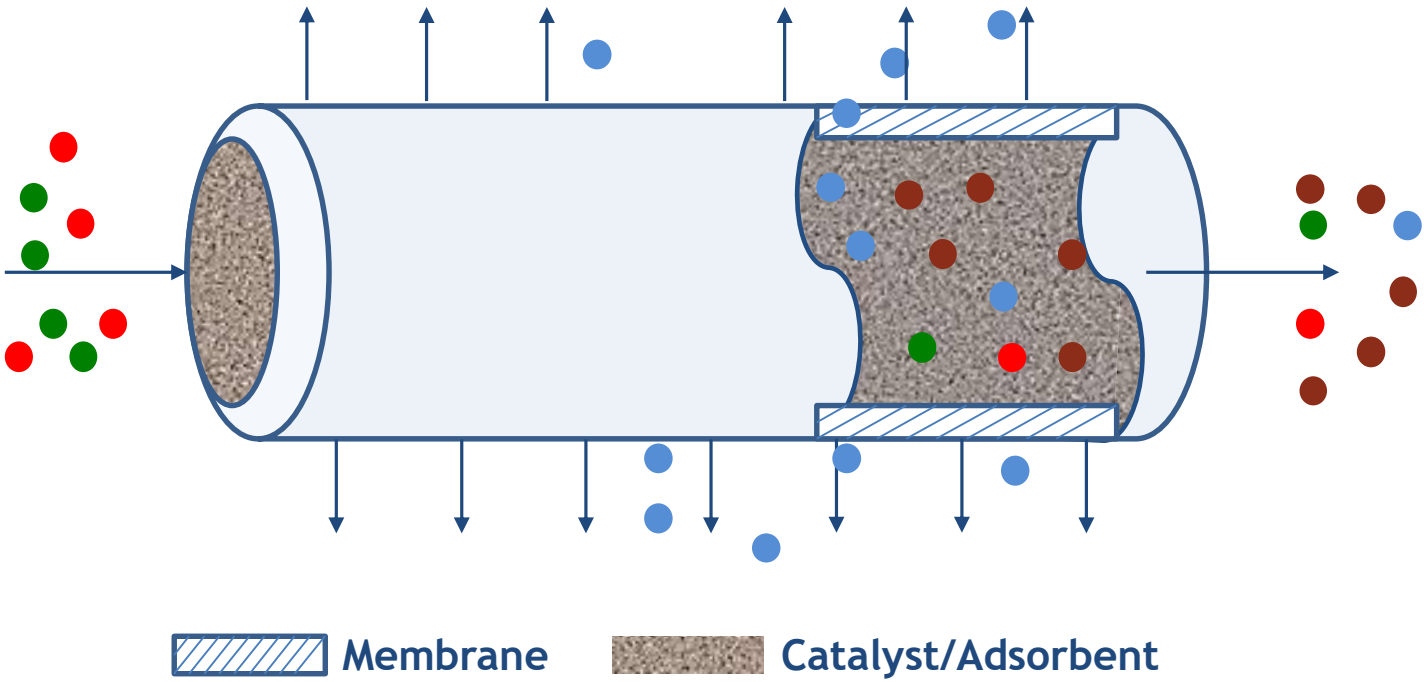
- Modelling and simulation
- Reactive-Separation regions

LSRE
LABORATORY OF SEPARATION AND REACTION ENGINEERING

LABORATÓRIO ASSOCIADO
LSRE

Pervaporation Membrane Reactor

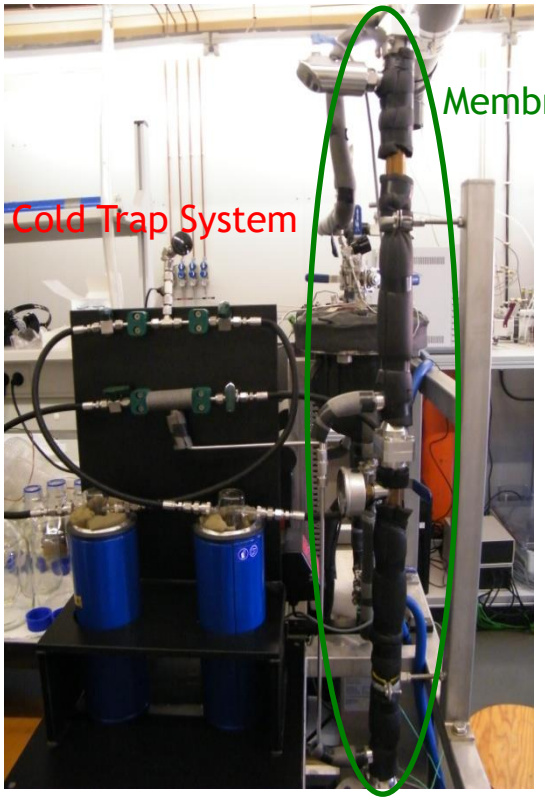
Ethanol + Lactic Acid ⇔ Ethyl Lactate + Water



Schematic representation of a continuous pervaporation membrane reactor.

Pervaporation Membrane Reactor

PVMR Unit



Side view

Stack of silica membranes from Pervatech.

- 2 tubular commercial water selective membranes (Pervatech BV, The Netherland).

Modified silica (methyl silica) selective layer coated onto gamma alumina applied inside of an asymmetric ceramic tube (10mm outer diameter, 7 mm inner diameter, 50 cm long).

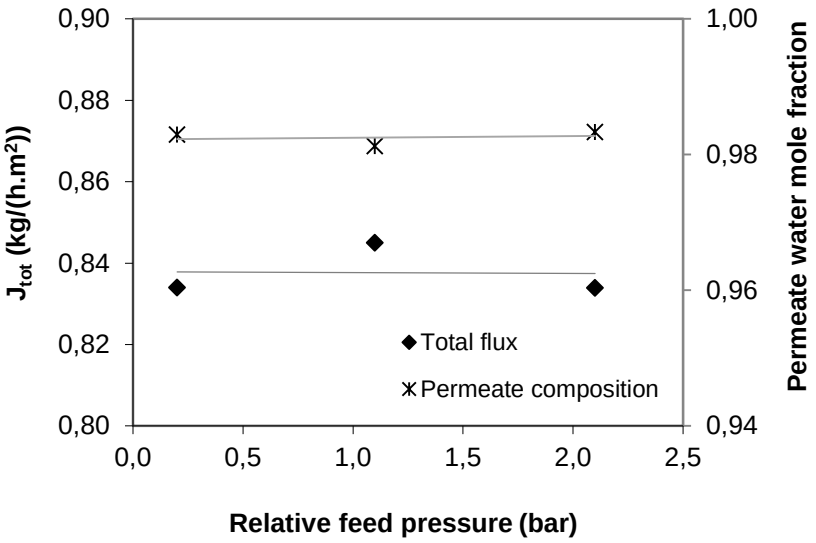
Effective area per tube of about 110 cm^2.

Pervaporation Membrane Reactor

Pervaporation Performance: Preliminary Studies

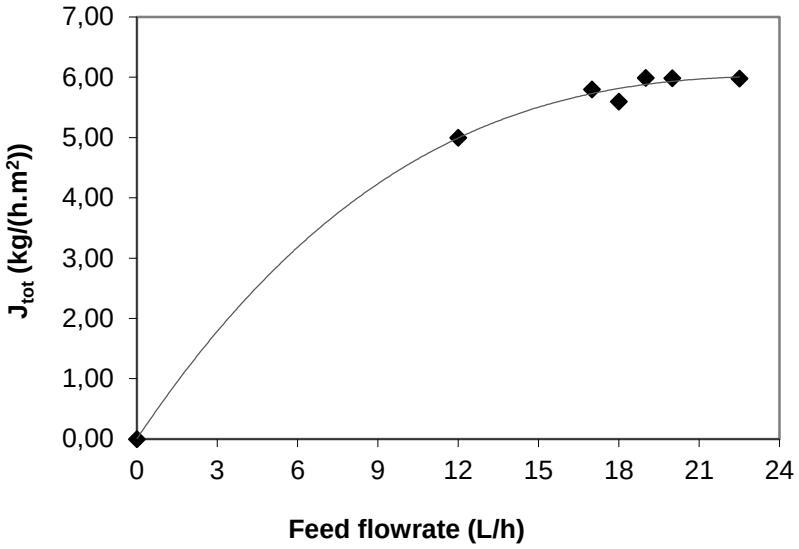
Pressure Effect

Evaluation of membrane quality



Feed: Ethanol solution (81.7 molar % in water), T = 321.15 K and P_{perm} = 20 mbar.

Feed Flowrate Effect



Feed: Ethanol solution (50 molar % in water), T = 343.15 K and P_{perm} = 25 mbar.

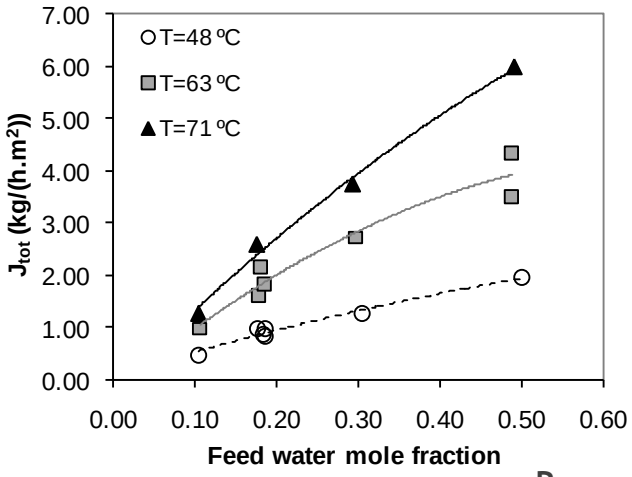
Remaining experiments performed at a feed flowrate of 20L/h!

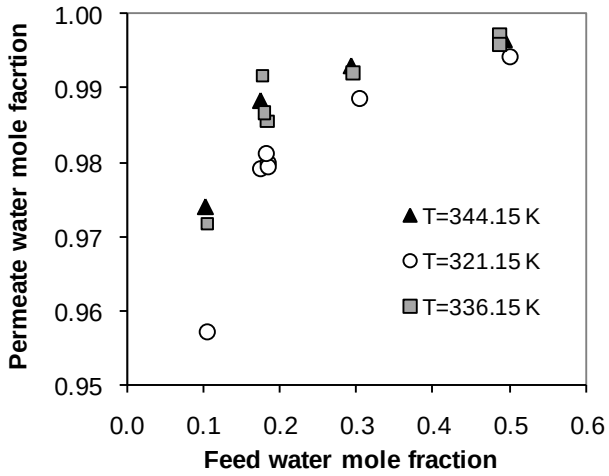
Pereira CSM, Silva VMTM, Pinho SP, Rodrigues AE. J. Membr. Sci. 2010;361(1-2):43-55.

Pervaporation Membrane Reactor

Pervaporation Performance

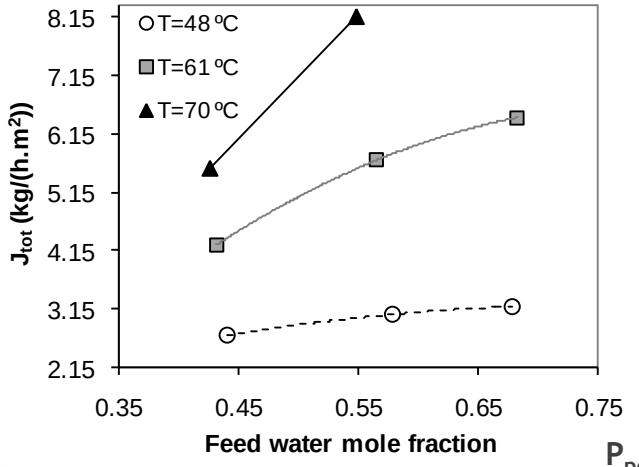
Water/Ethanol Mixtures

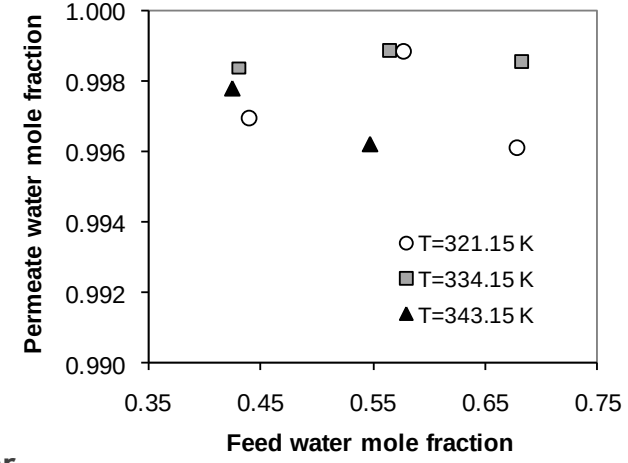




P_{perm} ~25 mbar.

Water/Ethyl lactate Mixtures



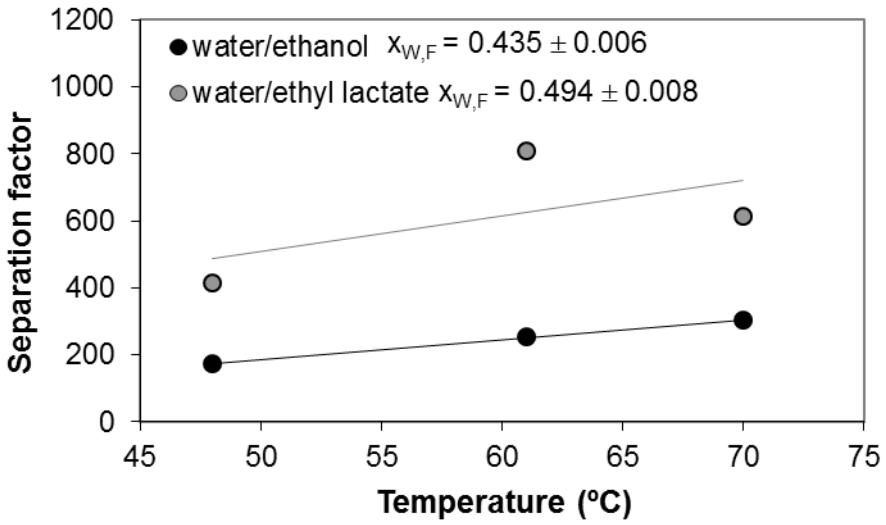


P_{perm} ~ 20 mbar.

Pervaporation Membrane Reactor

Pervaporation Performance

Temperature effect on the separation factor



Separation Factor

$$\alpha = \frac{y_i x_j}{x_i y_j}$$

x = mole fraction in the feed side

y = mole fraction in the permeate side

Physical Properties.

Component	*Radius of gyration (Aº)* [1]	*Dipole moment (Debyes)* [1]	Vapour Pressure (bar) at 323.15 K
Water	0.615	1.8497	1.24×10^{-1}
Ethanol	2.259	1.6908	2.94×10^{-1}
Ethyl Lactate	3.622	2.4000	1.92×10^{-2}
Lactic Acid	3.298	1.1392	1.08×10^{-3}

1) X. Feng, R.Y. Huang, Liquid separation by membrane pervaporation: a review, Ind. Eng. Chem. Res. 36 (1997).

Pervaporation Membrane Reactor

Pervaporation Performance

The solution diffusion model[1] was applied to describe the species permeation:

$$J_i = Q_{memb,i}(x_i \gamma_i p_i^{\,0} - y_i P_{perm})$$

permeance

$$J_i = w_{perm,i} J_{tot}$$

The species permeance dependence on temperature was found by an Arrhenius-type equation:

$$Q_{memb,i} = Q_{memb,0} \exp\left(\frac{-E_{perm,i}}{RT}\right)$$

pre-exponential factor

activation energy of permeation

$$E_{perm,i} = E_{D,i} + \Delta H_s$$

ΔH_s → heat of the adsorption

$E_{D,i}$ ↓ activation energy of diffusion

Pervaporation Parameters.

Component	$Q_{memb,0}$ (mol/(s.m^2.Pa))	E_{perm} (kJ/mol)	MRD (%)
Ethanol	2.36×10^{-12}	-22.60	14.51
Ethyl lactate	1.99×10^{-9}	-10.42	24.13
Water	$3.278 \times 10^{-11} \exp(18.64 x_W)$	$50.377 x_W$-32.326	13.94

1) J.G. Wijmans, R.W. Baker, The solution-diffusion model: A review, J. Membr. Sci. 107 (1995) 1-21.

Pervaporation Membrane Reactor

Batch Pervaporation Model

- non-isothermal operation;
- flow pattern described by axial dispersed plug flow model;
- solution-diffusion model for species permeation;
- 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;
- temperature polarization;
- velocity variations due to species permeation.

Pervaporation Membrane Reactor Model

additionally includes

- velocity variations due to adsorption/desorption rates;
- the column length and packing porosity are assumed constant;
- external and internal mass transfer for adsorbable species combined in a global particle resistance.

Pereira CSM, Silva VMTM, Pinho SP, Rodrigues AE. J. Membr. Sci. 2010;361(1-2):43-55.

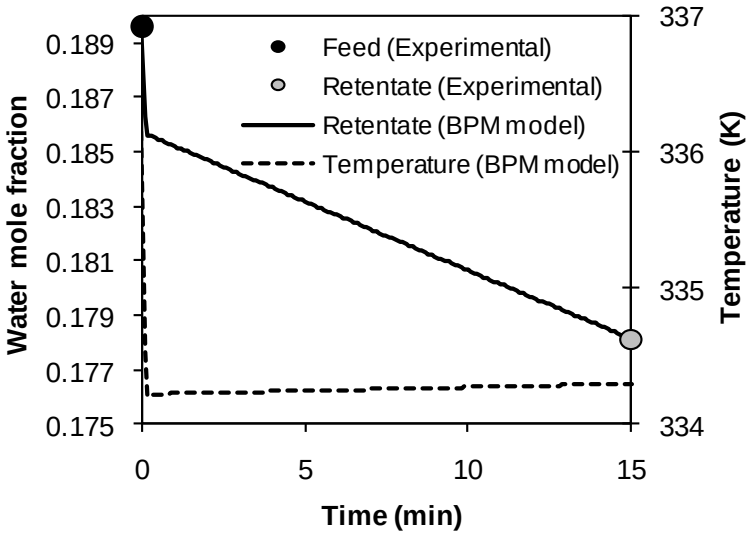
Pervaporation Membrane Reactor

Batch Pervaporation: Experimental and Simulation

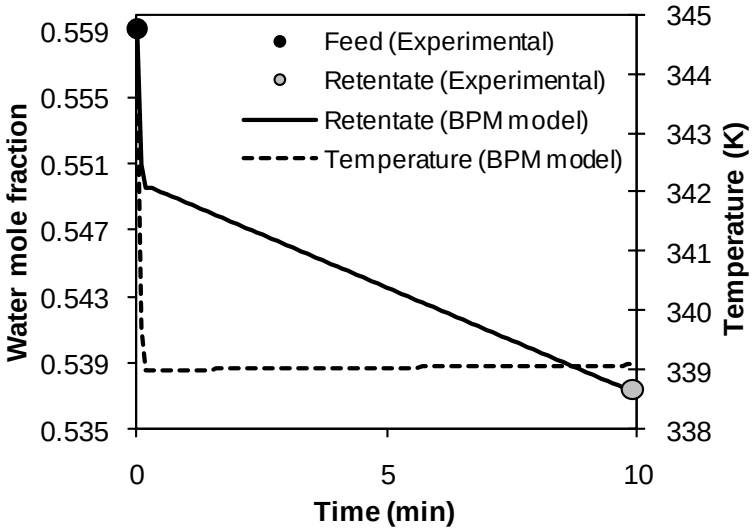
Dehydration of Ethanol

Dehydration of Ethyl Lactate

Evolution of water composition on retentate and temperature predicted by the non-isothermal BPM model.



Feed: Ethanol solution (81 molar % in water), T=336 K, P_{perm} = 17 mbar.



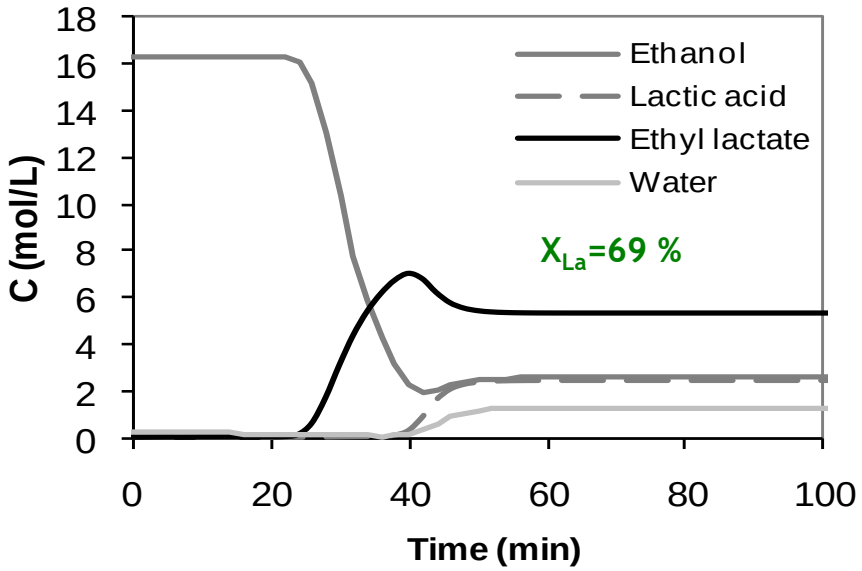
Feed: Ethyl lactate solution (44 molar % in water), T=344 K, P_{perm} = 42 mbar.

Pervaporation Membrane Reactor

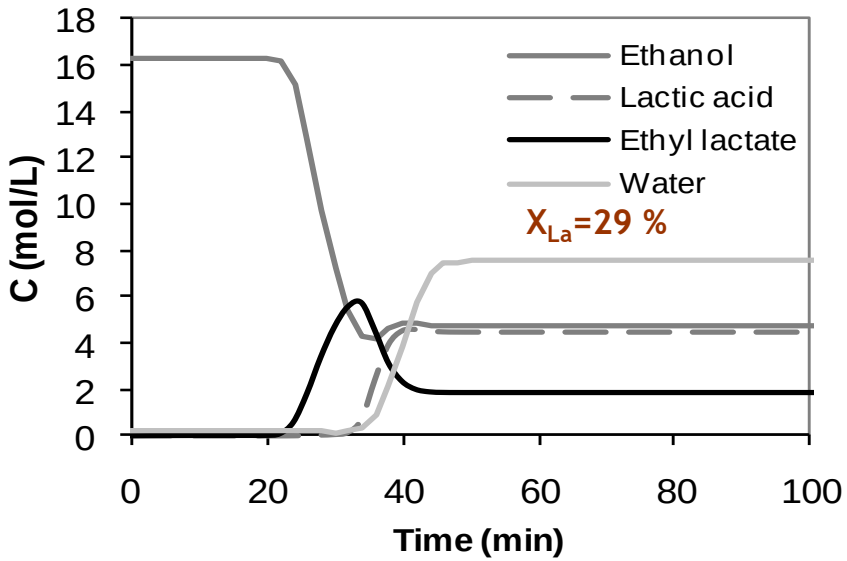
Performance Evaluation

Isothermal Operation

Pervaporation Membrane Reactor



Fixed Bed



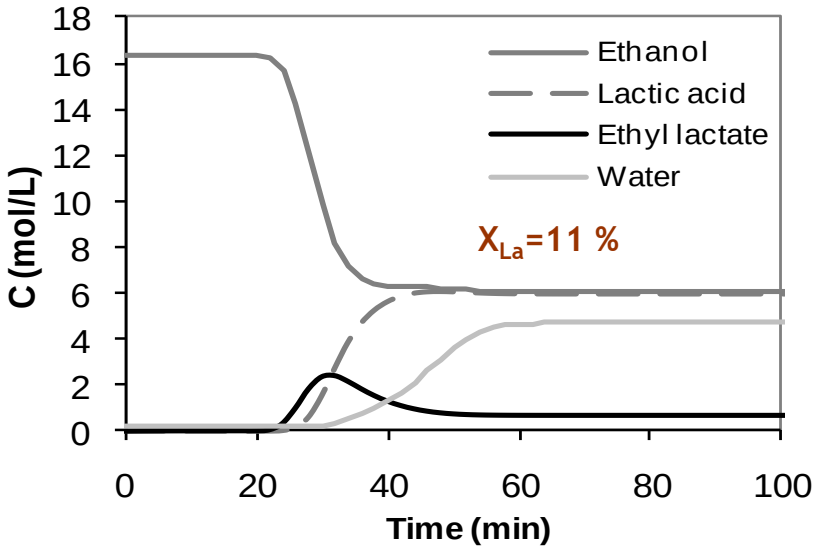
Simulated concentration histories at the reactor outlet.
Feed: $x_{Eth,Feed}$= 0.355, $x_{La,Feed}$=0.343, $x_{W,Feed}$=0.303; Flowrate=1.0 mL/min; P_{perm}=10 mbar; T_{Feed}=50°C.

Pervaporation Membrane Reactor

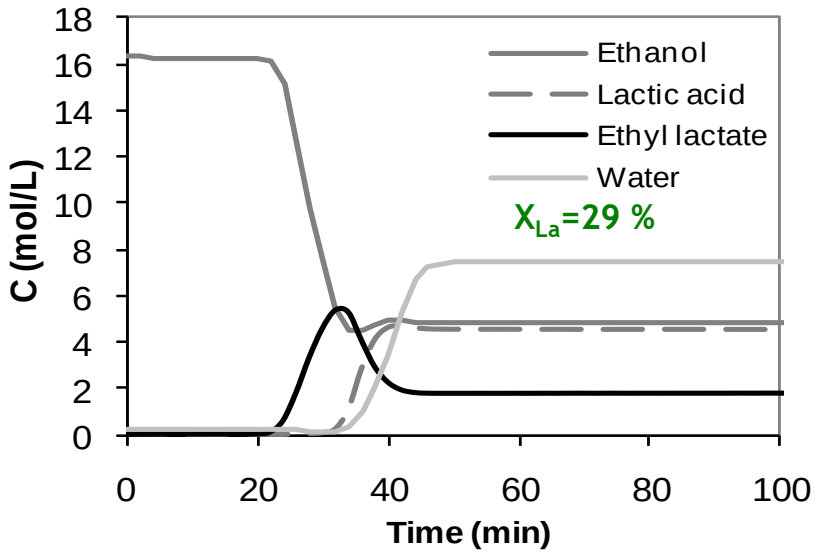
Performance Evaluation

Non-isothermal Operation

Pervaporation Membrane Reactor



Fixed Bed Reactor



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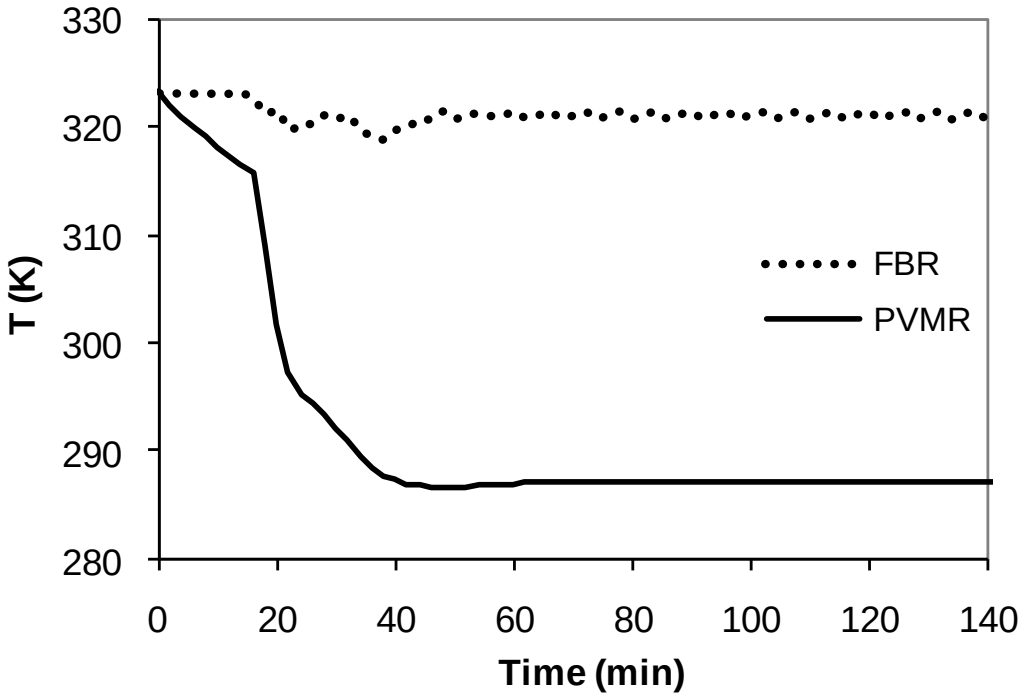
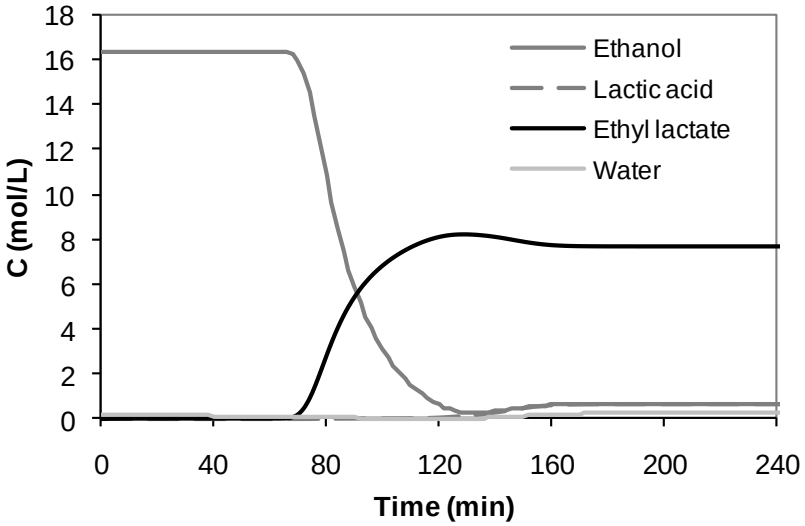
Pervaporation Membrane Reactor

Non-isothermal Operation



Temperature histories at the outlet of the FBR and of the PVMR.

Pervaporation Membrane Reactor

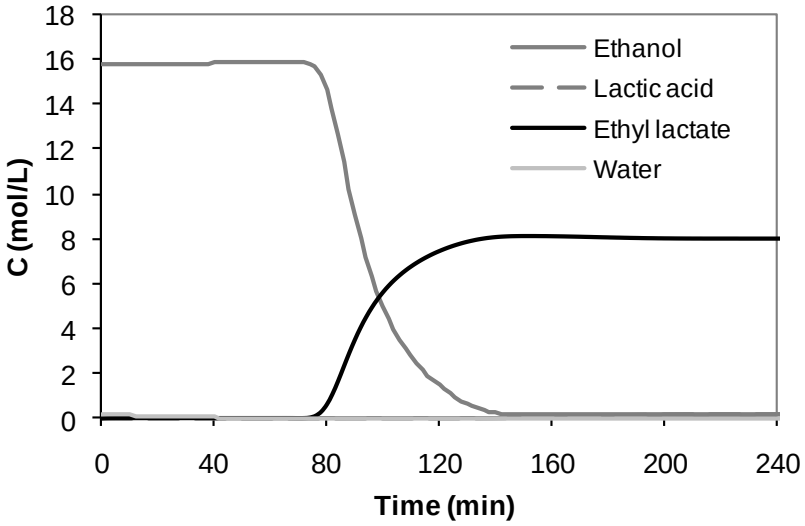


T=50 ºC

5 tubular membranes (250 cm long)

Lactic acid conversion: 93 %

Ethyl lactate purity: 84 %



T=70 ºC

Lactic acid conversion: 98 %

Ethyl lactate purity: 96 %

Simulated concentration histories at the reactor outlet.
Feed: $x_{Eth,Feed}$= 0.355, $x_{La,Feed=}$0.343, $x_{W,Feed}$=0.303;
Flowrate=1.0 mL/min; P_{perm}=10 mbar.

PermSMBR VS SMBR

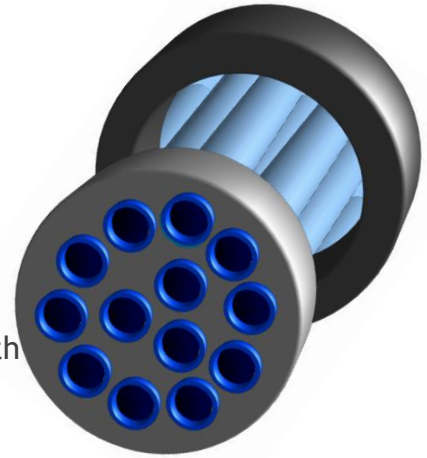
Geometrical Specifications

12 columns, each column with 13 commercial hydrophilic tubular membranes (Pervatech BV)

	SMBR	PermSMBR
Solid weight (A15)	47.6 g	47.6 g
Length of the bed (*L*)	23 cm	25.45 cm
Internal diameter (D_i)	2.6 cm	0.7 cm
Bed porosity (ε)	0.4	0.424*
Bulk density (ρ_b)	390 kg/m^3	374 kg/m^3

* Theuerkauf J, Witt P, Schwesig D. *Powder Technol*. 2006;165(2):92-99.

Stack of silica membranes from Pervatech.



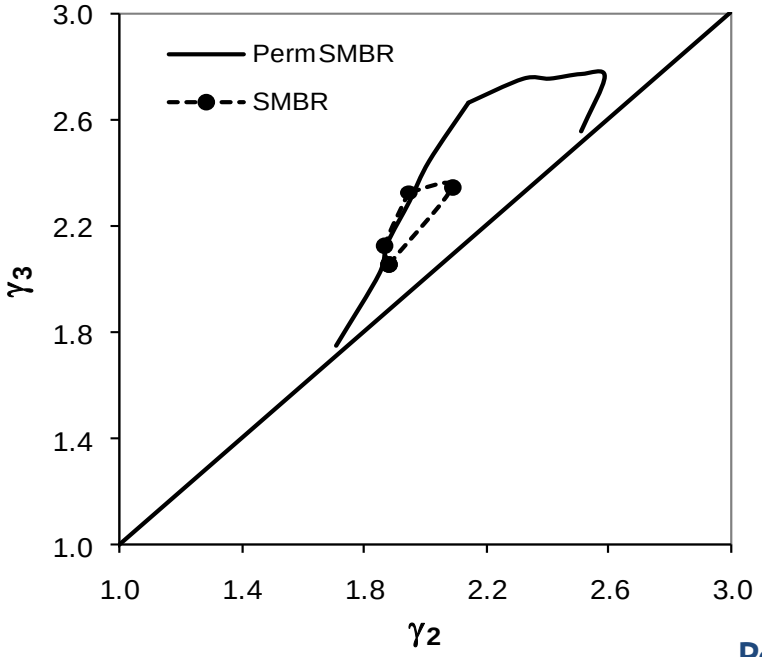
PermSMBR column with 13 membranes.

Catalyst & Selective Adsorbent to Water

Amberlyst-15 wet Resin.

PermSMBR Vs SMBR

Reactive Separation Region (criteria: 95 % extract, raffinate purity and lactic acid conversion).



Operating conditions:

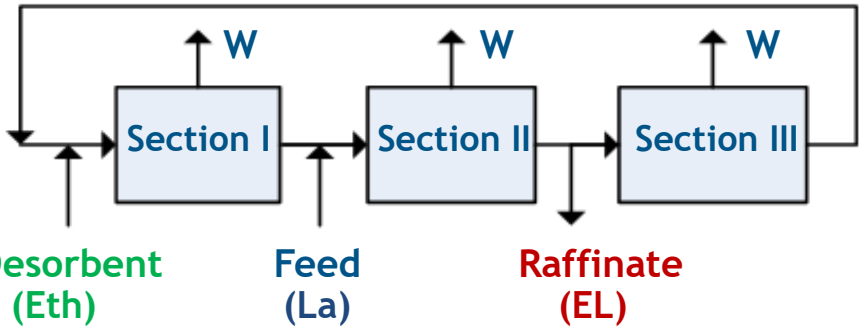
Q_D = 58 mL/min; $Q_{recycle}$=27 mL/min; $t^*_{PermSMBR}$=2.323 min; t^*_{SMBR}=2.1 min; Configuration: 3-3-4-2; T=50°C.

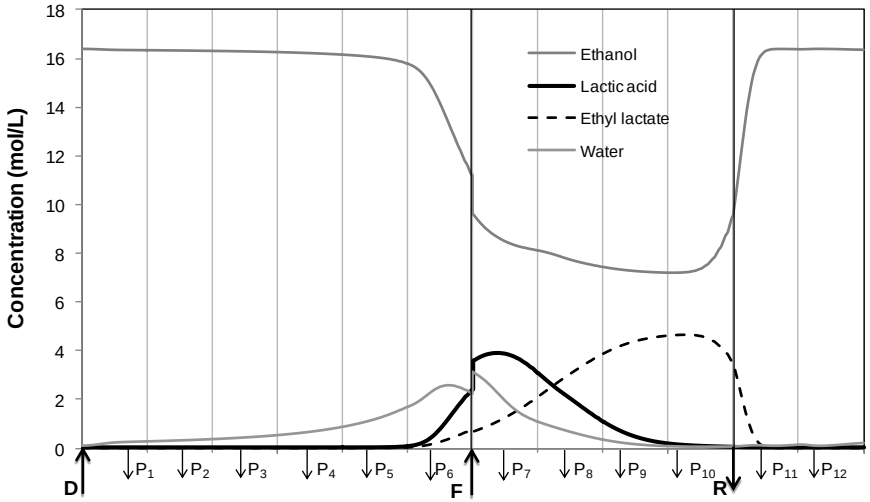
Performance parameters at the optimal operating points.

	SMBR	PermSMBR	Improvement
PR ($Kg_{EL}.L_{resin}^{-1}.day^{-1}$)	18.06	24.19	33.94 %
DC (L_{Eth}/Kg_{EL})	4.75	3.41	28.21 %

PermSMBR Vs SMBR

PermSMBR 3 sections (PermSMBR-3s)
elimination of extract stream





Operating conditions: Q_D = 58 mL/min; $Q_{recycle}$=27 mL/min; $t^*_{PermSMBR}$=2.323 min; Configuration: 6-4-2; T=50°C.

Conversion: 99,18 %

PUR: 96.15 %

PR: 16.51 $kg_{EL}.L_{resin}^{-1}.day^{-1}$

DC : 1.96 L_{Eth}/kg_{EL}

SMBR (4 zones)

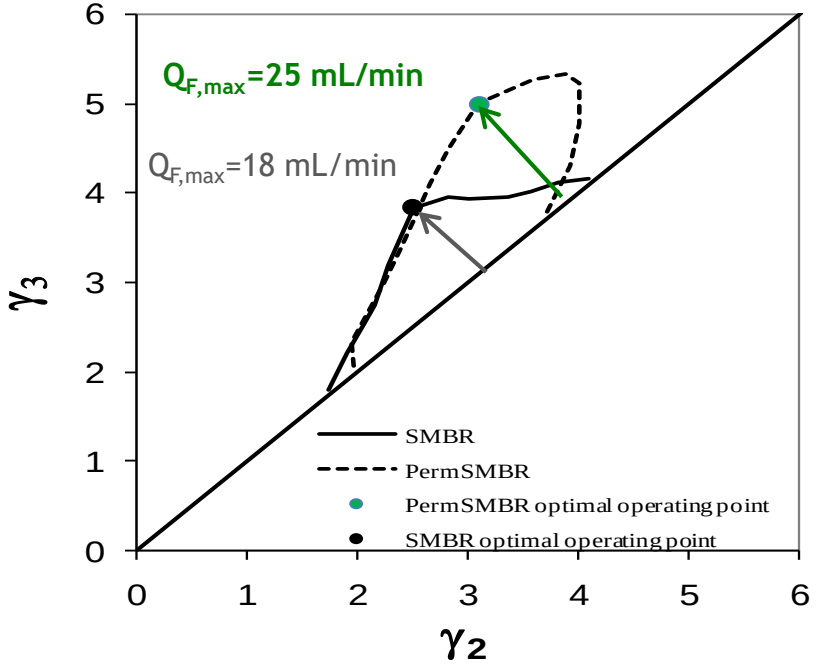
DC : 5.20 L_{Eth}/kg_{EL}

62 % higher DC

PermSMBR: DEE Production

Reactive Separation Regions

(criteria: 95 % extract, raffinate purity and acetaldehyde conversion).



Operating conditions: Q_D =50mL/min; $Q_{recycle}$=20 mL/min; $t^*_{PermSMBR}$=4.1 min; t^*_{SMBR}=3.7 min; Configuration: 3-3-3-3; Feed: 51% acetaldehyde in ethanol; T=50ºC.

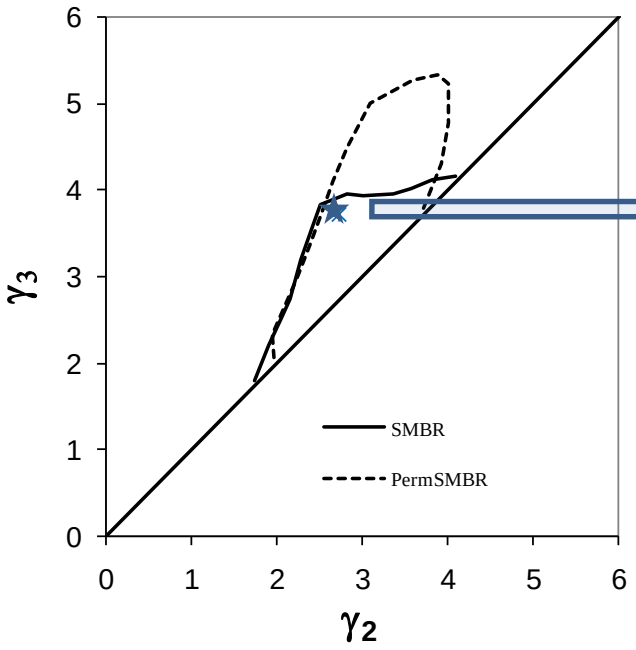
Performance parameters at the optimal operating points.

	PR ($Kg_{DEE}.L_{resin}^{-1}.day^{-1}$)	DC ($L_{Ethanol}/Kg_{DEE}$)
SMBR	27.40	2.47
PermSMBR	41.95	1.47
Improvement	**53.12 %**	**40.50 %**

Same Purity and Conversion Requirement
=> Higher Productivity
=>Lower Desorbent Consumption

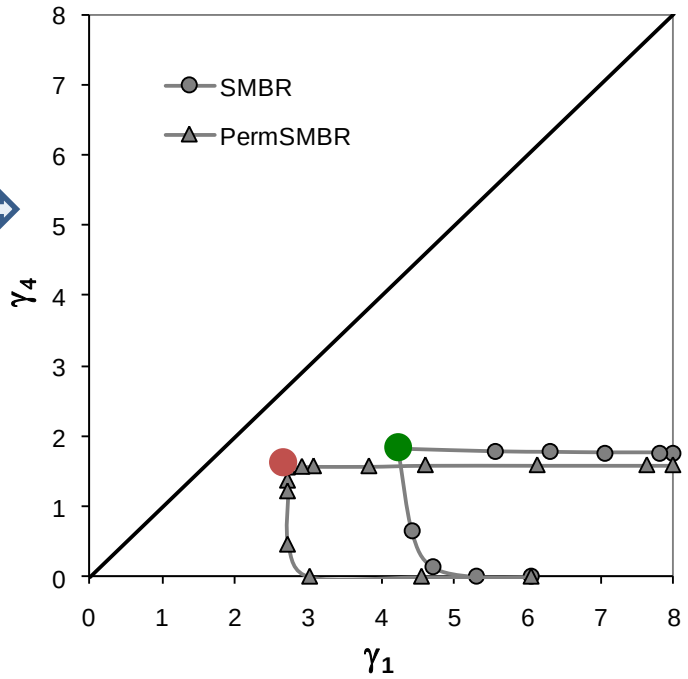
PermSMBR: DEE Production

Reactive Separation Regions



Q_F=13 mL/min

Regeneration Regions



	DC ($L_{Ethanol}/Kg_{DEE}$)
SMBR	2.06
PermSMBR	0.64
Improvement	**69 %**

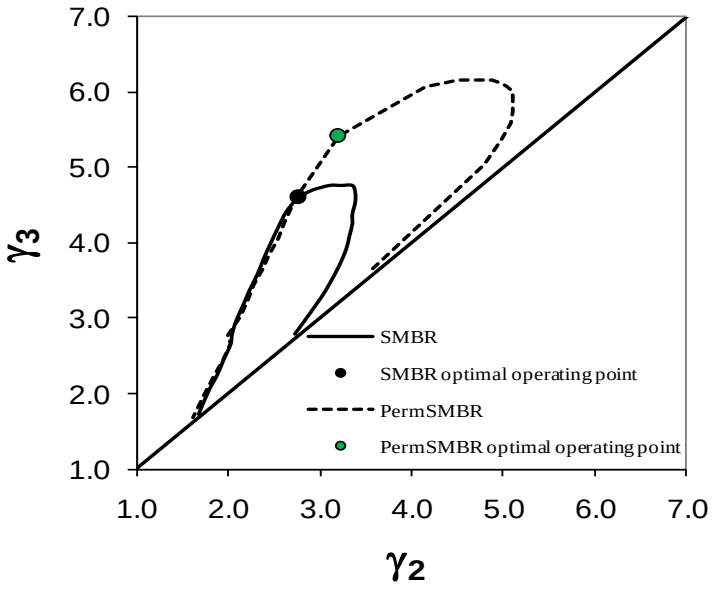
Operating conditions: γ_2=2.727 and γ_3=3.712 , $t^*_{PermSMBR}$=4.1 min; t^*_{SMBR}=3.7 min; Configuration: 3-3-3-3; Feed: 51% acetaldehyde in ethanol; T=50°C. Criteria: 95 % extract, raffinate purity and acetaldehyde conversion.

Same Productivity => Less Desorbent Consumption

PermSMBR: DBE Production

Reactive Separation Regions

(criteria: 95 % extract, raffinate purity and acetaldehyde conversion).



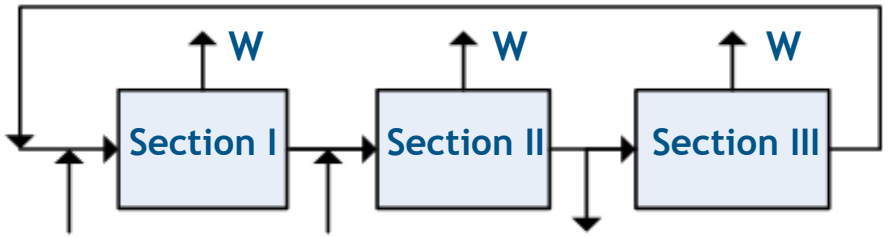
Operating conditions: Q_D =105mL/min; $Q_{recycle}$=21 mL/min; $t^*_{PermSMBR}$=3.4 min; t^*_{SMBR}=3.1 min; Configuration: 3-3-3-3; Feed: 51% acetaldehyde in n-butanol; T=50°C.

Performance parameters at the optimal operating points.

	SMBR	PermSMBR	Improvement
PR ($Kg_{DBE}.L_{resin}^{-1}.day^{-1}$)	53.15	64.15	**20.70 %**
DC ($L_{Butanol}/Kg_{DBE}$)	2.69	2.15	**20.07 %**

PermSMBR: DBE Production

PermSMBR 3 sections (PermSMBR-3s)
elimination of extract stream



PermSMBR-3s (T=50°C) → Low Productivity (8.04 $kg_{DBE}.L_{resin}^{-1}.day^{-1}$)
Permeation through the membranes overloaded
95 % purity criterion not achieved

Performance parameters at the optimal operating points (T=70°C)

	SMBR	PermSMBR	PermSMBR-3s
PR ($kg_{DBE}.L_{resin}^{-1}.day^{-1}$)	53.95	72.06	70.97
DC ($L_{Butanol}/kg_{DBE}$)	2.64	1.84	0.42

Less Desorbent Consumption
Less one separation unit
(no extract stream to be treated)

Conclusions

- *Throughout a methodic procedure, considering the detailed study of the reaction kinetics, adsorption equilibrium and permeation, it is possible to model, design and simulate the viability of the new hybrid technology, PermSMBR, for synthesis of different compounds;*

- *The PermSMBR proved to be more efficient than the SMBR in all the cases studied, having higher productivities and lower desorbent consumptions, for the same purity and conversion criteria. Moreover, the PermSMBR operated with just 3 sections (PermSMBR-3s) allows the elimination of a subsequent separation unit for desorbent recovery:*