Supporting Information

Pervaporation and Sorption Enhanced Reactive Cyclic Processes: the Butyl Acrylate Case Study

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Table S.1. Fundamental kinetic data obtained under batch conditions for the synthesis of butyl acrylate over Amberlyst-15 ion-exchange resin[1].

Parameter; Conditions	Result
Reaction rate, r	$r(mol.(g_{A15}^{-1}.min^{-1})) = k_c \dfrac{a_A a_B - \dfrac{a_C a_D}{K_{eq}}}{\left(1 + K_{S,D} a_D\right)^2}$
Kinetic constant, k_c	$k_c(mol.(g_{A15}^{-1}.\min^{-1})) = 1.52 \times 10^7 \exp\left(-\dfrac{66988}{RT}\right)$
Equilibrium constant, K_{eq}; (323-363) K	$K_{eq} = \exp\left(\dfrac{-1490}{T} + 7.21\right)$
Adsorption constant, $K_{s,D}$; (323-363) K	$k_{s,water}(mol.(g_{A15}^{-1}.\min^{-1})) = 1.589$

Table S.2. Multicomponent adsorption equilibrium parameters measured over Amberlyst-15 ion-exchange resin for Langmuir isotherms of butyl acrylate system[2].

Compound	Q_i (mol.L_{A15}^{-1}); 323 K; 363 K	K_i (L.mol^{-1}) 323 K; 363 K
n-Butanol (A)	4.88; 4.55	6.90; 7.07
Acrylic Acid (B)	6.52; 6.09	3.51; 1.90
Butyl Acrylate (C)	3.13; 2.91	2.67; 1.94
Water (D)	25.3; 24.2	48.7; 22.7

Table S.3. Multicomponent pervaporation data for butyl acrylate system measured with commercial hybrid silica membranes[3].

Compound	$Q_{m0,\,i}$ (mol.s^{-1}.m^{-2}.Pa^{-1})	$E_{perm,\,i}$ (kJ.mol^{-1})
n-Butanol (A)	5.66×10^{-13}	-26.62
Acrylic Acid (B)	5.17×10^{-10}	-9.37
Butyl Acrylate (C)	1.72×10^{-12}	-20.85
Water (D)	3.90×10^{-11}	-30.53

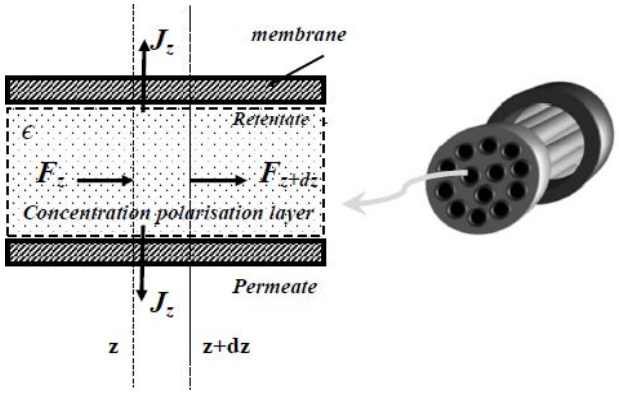

Figure S.1. Schematic representation of the fluxes through the membranes of the PermSMBR process. F corresponds to the flux and ε represents the bed porosity in the integrated configuration case where each membrane is packed with Amberlyst-15.

Table S.4. Experimental conditions and performance parameters of the different runs performed in SMBR LICOSEP pilot scale unit at 323 K with configuration 2-4-4-2 and a switching time of 3.1 min.

Parameter/Experiment	SMBR01	SMBR02
$C_{n\text{-butanol, F}}$ (mol.L^{-1})	6.04	0.60
$C_{AAc, F}$ (mol.L^{-1})	6.04	4.78
$C_{BAc, F}$ (mol.L^{-1})	-	3.64
$C_{water, F}$ (mol.L^{-1})	-	3.64
Q_F (mL.min^{-1})	0.86	2.10
Q_{Ext} (mL.min^{-1})	24.3	25.0
Q_{El} (mL.min^{-1})	29.7	29.2
Q_{Rec} (mL.min^{-1})	29.0	23.0
P_{Ext} (%)	57.1	54.4
P_{Raff} (%)	26.1	65.0
Conv (%)	29.1	32.8
Prod ($kg_{BAc}.(L_{ads}^{-1}.day^{-1})$)	0.223	1.67
DesC ($L_{n\text{-butanol}}.kg_{BAc}^{-1}$)	213	29.3

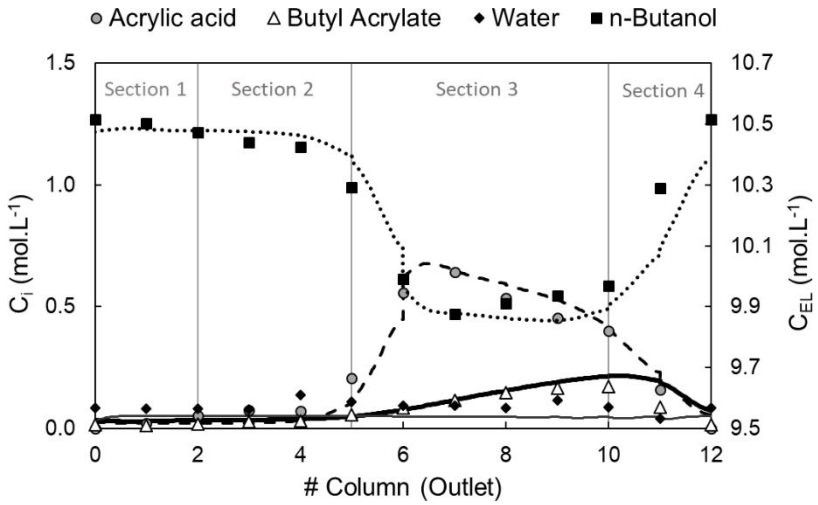

Figure S.2. Experimental and simulated concentration profiles in the SMBR LICOSEP unit at the middle of the switching time (3.1 min) and at cyclic steady state (13th cycle) at 323 K: run SMBR01.

References

(1) Ostaniewicz-Cydzik, A. M.; Pereira, C. S. M.; Molga, E.; Rodrigues, A. E., Reaction Kinetics and Thermodynamic Equilibrium for Butyl Acrylate Synthesis from n-Butanol and Acrylic Acid. *Ind. Eng. Chem. Res.* **2014,** *53*, 6647.

(2) Constantino, D. S. M.; Pereira, C. S. M.; Faria, R. P. V.; Ferreira, A. F. P.; Loureiro, J. M.; Rodrigues, A. E., Synthesis of butyl acrylate in a fixed-bed adsorptive reactor over Amberlyst 15. *AlChE J.* **2015,** *61*, 1263.

(3) Constantino, D. S. M.; Faria, R. P. V.; Ribeiro, A. M.; Loureiro, J. M.; Rodrigues, A. E., Performance Evaluation of Pervaporation Technology for Process Intensification of Butyl Acrylate Synthesis. *Ind. Eng. Chem. Res.* **2017**, *56*, 13064.