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Separation of ethanol–water liquid mixtures by adsorption on silicalite

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ABSTRACT

The separation of ethanol–water mixtures with ethanol-selective adsorbents by cyclic multi-column adsorption processes, such as concentration swing adsorption (CSA) or concentration thermal swing adsorption (CTSA), is attractive because practically pure ethanol can be obtained with high recovery and low energy requirement. In this work, the adsorption of ethanol–water liquid mixtures on a column packed with silicalite pellets has been studied. A theoretical model for predicting the column dynamics in this system has been developed, taking into account the effect of the mass transfer resistance in the whole concentration range (between 1 and 100% ethanol). The model, based on conservation equations, has been validated with experimental data obtained in a laboratory column. Experimental data on the column dynamics of the displacement of water by pure ethanol (the so-called ethanol rinse step in CSA or CTSA) are presented, which are not available in the literature. This displacement is required to recover fuel grade ethanol when the column is regenerated. An important mass transfer resistance has been found in the ethanol rinse step, resulting in low separation efficiency when CSA or CTSA cycles are applied to the studied system. The inclusion of a new step is proposed to overcome this problem. The developed model has been employed to estimate the performance of the modified cycle for separating an 8% ethanol–water mixture, and the results show that it can produce practically pure ethanol (>99.5% in weight) with high recovery (above 95%).

1. Introduction

Production of alcohol by fermentation of renewable resources like plant biomass is becoming an attractive method for increasing liquid clean fuel production. The conventional technology for producing ethanol by fermentation based on distillation to separate the ethanol from the fermentation mixture (4–10% w/w, [1]) is very energy-intensive, because the ethanol–water azeotrope (95.6% w/w ethanol) must be broken. Among the alternative techniques to separate this mixture, adsorption processes appear very interesting, since ethanol and water molecules differ in size and have different dipole moment [2]. Water-selective or ethanol-selective adsorbents can be used for this purpose. Hydrophilic zeolites, such as zeolite 3A, are currently employed for separating the ethanol–water mixture at high ethanol concentrations (from 92 to >99.5% w/w ethanol) [3,4]. Other water-selective adsorbents, including starch and cellulosic materials [5–7] and natural zeolitic materials [2] have also been proposed for ethanol dehydration. A previous distillation step is required to remove most of the water in the mixture (reaching about 92% w/w ethanol) for producing fuel grade ethanol (>99.5% w/w) with water-selective adsorbents. As ethanol is the minor component in the fermentation mixture, ethanol-selective adsorbents are interesting for this separation. In spite of this, less attention has been paid to them in the literature. Recently, Hashi et al. [8,9] have proposed the ethanol recovery from the fermentation broth via carbon dioxide stripping and adsorption with ethanol-selective adsorbents. Pitt et al. [1] proposed an adsorption process to recover ethanol from fermentation broths based on the adsorption of ethanol on hydrophobic sorbents. The column was regenerated by purging with hot air, recovering the desorbed ethanol by condensation. Later, two cyclic multi-column adsorption processes were proposed for the separation of bulk liquid mixtures (concentration swing adsorption, CSA [10], and concentration thermal swing adsorption, CTSA [11]) which can be used in the ethanol–water separation with ethanol-selective adsorbents. These processes are particularly attractive because they can theoretically produce 100% ethanol starting from a diluted ethanol–water mixture with 100% recovery (if the mass transfer resistances can be neglected) with a low energy of separation. The key steps in the CSA and CTSA processes are the adsorption and ethanol rinse steps. In the adsorption step the column previously filled with water is saturated with the feed ethanol–water mixture, and afterwards, in the ethanol rinse step, the column is rinsed with pure ethanol to displace water.

The objective of this work is to measure the column dynamics in the separation of liquid ethanol–water mixtures by adsorption with

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Nomenclature

q_c^*	adsorbed concentration in the crystal in equilibrium with the liquid in macropores, kg $\mathrm{kg}_{\mathrm{pellet}}^{-1}$
$\bar{q}_c$	average adsorbed concentration in the crystal, kg $\mathrm{kg}_{\mathrm{pellet}}^{-1}$
$\bar{c}_{\mathrm{macro}}$	average concentration in the macropores, kg $\mathrm{m}_{\mathrm{macropore}}^{-3}$
a	parameter defined in Eq. (2)
d_c	crystal diameter, m
D_c	intracrystalline diffusivity, $\mathrm{m^2\,s^{-1}}$
D_L	axial dispersion coefficient, $\mathrm{m^2\,s^{-1}}$
D_m	molecular diffusivity, $\mathrm{m^2\,s^{-1}}$
d_p	particle diameter, m
f	parameter defined in Eq. (22)
F	mass flow rate, $\mathrm{kg\,s^{-1}}$
k_c	mass transfer coefficient defined in Eq. (10), $\mathrm{s^{-1}}$
k_f	external mass transfer coefficient, $\mathrm{m\,s^{-1}}$
k_{macro}	mass transfer coefficient defined in Eq. (5), $\mathrm{m\,s^{-1}}$
L	column length, m
MTZ	mass transfer zone
N	adsorption rate, kg $\mathrm{m}_{\mathrm{bed}}^{-3}\,\mathrm{s}^{-1}$
n	number of components
P	pressure, bar
Q	flow rate, $\mathrm{m^3\,s^{-1}}$
Re	Reynolds number ($\rho\, u\, d_p/\mu$)
S_{bed}	column cross-section, $\mathrm{m^2}$
Sc	Schmidt number ($\mu/(\rho\, D_m)$)
t	time, s
t_D	parameter defined in Eq. (17), s
u	superficial velocity, $\mathrm{m\,s^{-1}}$
u_{cp}	velocity of the concentration wave in the constant pattern conditions, $\mathrm{m\,s^{-1}}$
V_D	parameter defined in Eq. (16), $\mathrm{m^3}$
W	mass of adsorbent in the column, kg
W_{column}	total weight of the column, kg
y	mass fraction

Greek symbols

ε	column voidage fraction, $\mathrm{m}_{\mathrm{void}}^{3}\,\mathrm{m}_{\mathrm{bed}}^{-3}$
$\varepsilon_{\mathrm{macro}}$	macropore porosity, $\mathrm{m}_{\mathrm{macropore}}^{3}\,\mathrm{m}_{\mathrm{particle}}^{-3}$
μ	liquid viscosity, Pa s
ρ	iquid density, $\mathrm{kg\,m^{-3}}$
ρ_p	particle density, $\mathrm{kg}_{\mathrm{particle}}\,\mathrm{m}_{\mathrm{particle}}^{-3}$
τ	macropore tortuosity

Subscripts

0	initial condition
1	ethanol
2	water
atm	at atmospheric pressure
F	feed condition
i	ith component
cp	constant pattern

Table 1
Adsorbent and bed properties (Silicalite T-4722).

Particle density	1186 $\mathrm{kg\,m^{-3}}$
Average particle size	375 μm
Crystal size	8 μm
Pore volume (from Hg porosimetry)	0.349 $\mathrm{cm^3\,g^{-1}}$
Bed length	0.1 m
Porosity between particles	0.38

silicalite pellets, with feed ethanol concentrations ranging between 1 and 100% (w/w). This adsorbent has been chosen because it is a hydrophobic molecular sieve with high selectivity to ethanol [12,13]. A theoretical model has been developed for predicting the column dynamics in this system. The model has been validated with experimental data obtained in a laboratory column, and it has been employed to simulate the separation of an 8% (w/w) ethanol–water mixture in a multi-column process including the adsorption and ethanol rinse steps. An additional step is proposed to avoid the ethanol loss in the ethanol rinse step.

2. Experimental

Absolute ethanol (>99.5% v/v) was purchased from Panreac (Spain). Water was obtained from a Milli-Q purifier (Millipore). Silicalite, in the form of spherical pellets of 3 mm, was supplied by Süd-Chemie (Product T-4722). The pellets were crushed and sieved, and the fraction with sizes between 250 and 500 μm was used in the experiments. The properties of this adsorbent are given in Table 1. The average size of the silicalite crystals was estimated roughly by SEM (from a SEM photograph with about 50 crystals). Previously, an adsorbent sample was immersed in water under agitation with a magnetic stirrer, until the crystals separated from the binder. The sample was dried afterwards.

The experimental setup is shown in Fig. 1. It consists of an aluminum column (15 cm long, 1.05 cm of internal diameter, 1.5 mm thick) loaded with the adsorbent (10 cm of bed, Fig. 3), resting on an analytical balance (1 mg to 310 g weighing range) connected online to a computer. The bed temperature is registered in a temperature logger. The column is connected to the liquid supply with a 1/16″ Teflon tube. The total weight resting on the balance was about 250 g, which was high enough to make the interference of the connecting tube unnoticeable. In each adsorption experiment, an ethanol/water mixture with a pre-established ethanol concentration was fed to the column with constant temperature at a fixed flow rate (1 ml/min) with a HPLC pump, taking liquid samples of the effluent, measuring the ethanol concentration with a RI detector. The concentration of sodium chloride in the tracer experiment was measured with a conductivity detector. The evolution of the

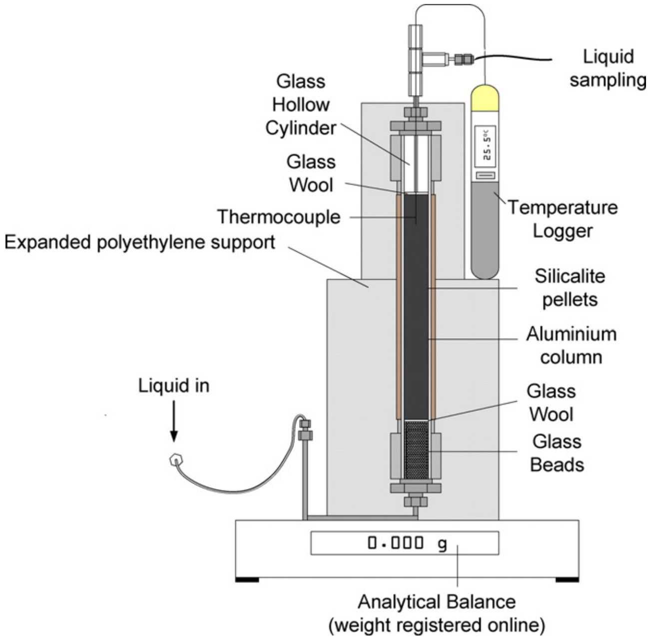

Fig. 1. Scheme of the experimental set-up.