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Model development for sc-drying kinetics of aerogels: Part 1. Monoliths and single particles

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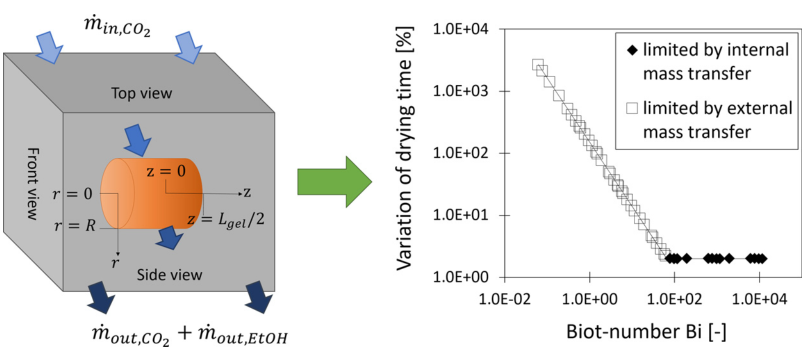
GRAPHICAL ABSTRACT



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ABSTRACT

A mass transport model for the supercritical drying of gels to aerogels in different sizes (monoliths or particles) and shapes (cylinder, sphere) was developed and evaluated. Physico-chemical data for the system CO_2/ethanol from literature at relevant process conditions were analyzed for a precise description of relevant physical properties. *In situ* measurements of the supercritical drying kinetics of gel monoliths using Raman spectroscopy were used to fit the tortuosity factor of the gel network. Apart from the fitted tortuosity factor the presented model is predictive. The model was analyzed in detail for the case of spherical gel particles. Theoretical minimal drying times were found to range in seconds for microparticles. The mass transfer step limiting the overall drying kinetics was analyzed using the dimensionless Biot number. The transition Biot number can be used for rational selection of the drying conditions (pressure, temperature, mass flow) to achieve a fast drying with low CO_2 consumption.

1. Introduction

Aerogels possess open mesoporous structures and due to their extraordinary properties (very low thermal conductivity, high BET-surface area, low density) have been suggested for numerous applications [1–7]. Nowadays, first industrial applications are already on the

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Nomenclature

a	Cohesion parameter of ethanol or CO_2 or of the ethanol − CO_2 mixture $\left[\frac{kg\cdot m^5}{s^2\cdot mol^2}\right]$
A	Dimensionless factor to solve the Peng-Robinson Equation of State [−]
A_{ac}	Cross-sectional area of the cylindrical autoclave $[m^2]$
A_p	Surface area of the spherical particle $[m^2]$
A_r	Surface area of the gel cylinder in radial direction $[m^2]$
A_z	Surface area of the gel cylinder in axial direction $[m^2]$
a_{CO_2}	$a_{CO_2} = 0.45724\cdot\frac{R_{uni}^2\cdot T_{c,CO_2}^2\cdot\alpha_{CO_2}}{P_{c,CO_2}}\left[\frac{kg\cdot m^5}{s^2\cdot mol_{CO_2}^2}\right]$
a_{EtOH}	$a_{EtOH} = 0.45724\cdot\frac{R_{uni}^2\cdot T_{c,EtOH}^2\cdot\alpha_{EtOH}}{P_{c,EtOH}}\left[\frac{kg\cdot m^5}{s^2\cdot mol_{EtOH}^2}\right]$
atm	Atmospheric pressure $[atm]$
b	Covolume parameter of the pure ethanol or CO_2 or of the ethanol − CO_2 mixture $\left[\frac{m^3}{mol}\right]$
$B_1 - B_7$	Constants [−]
Bi_m	Dimensionless Biot number [−]
$Bi_{m,transition}$	Dimensionless number [−]
b_{CO_2}	$b_{CO_2} = 0.07780\cdot\frac{R_{uni}\cdot T_{c,CO_2}}{P_{c,CO_2}}\left[\frac{m^3}{mol_{CO_2}}\right]$
b_{EtOH}	$b_{EtOH} = 0.07780\cdot\frac{R_{uni}\cdot T_{c,EtOH}}{P_{c,EtOH}}\left[\frac{m^3}{mol_{EtOH}}\right]$
c	Concentration $\left[\frac{mol}{m^3}\right]$
$c_{EtOH,f}$	Ethanol concentration in the bulk fluid $\left[\frac{mol_{EtOH}}{m^3}\right]$
$c_{EtOH,g}$	Ethanol concentration within the porous gel body $\left[\frac{mol_{EtOH}}{m^3}\right]$
c_{corr}	Correction factor for the molar volume of the ethanol − CO_2 mixture $\left[\frac{m^3}{mol_{EtOH}+mol_{CO_2}}\right]$
c_{corr,CO_2}	Correction factor for the molar volume of CO_2 $\left[\frac{m^3}{mol_{CO_2}}\right]$
$c_{corr,EtOH}$	Correction factor for the molar volume of ethanol $\left[\frac{m^3}{mol_{EtOH}}\right]$
$c_{corr,EtOH,atm}$	Correction factor for the molar volume of ethanol at atmospheric pressure $\left[\frac{m^3}{mol_{EtOH}}\right]$
$c_{mix,f}$	Mixture concentration in the bulk fluid $\left[\frac{mol_{EtOH}+mol_{CO_2}}{m^3}\right]$
$c_{mix,g}$	Mixture concentration within the porous gel body $\left[\frac{mol_{EtOH}+mol_{CO_2}}{m^3}\right]$
c_{p,CO_2}	Specific isobaric heat capacity of CO_2 $\left[\frac{J}{kg\cdot K}\right]$
c_{v,CO_2}	Specific isochoric heat capacity of CO_2 $\left[\frac{J}{kg\cdot K}\right]$
d_{ac}	Inner autoclave diameter $[m]$
D_{EtOH,CO_2}	Diffusion coefficient $\left[\frac{m^2}{s}\right]$
D^0_{EtOH,CO_2}	Diffusion coefficient of ethanol in supercritical CO_2 at infinite dilution $\left[\frac{m^2}{s}\right]$
$D^0_{CO_2,EtOH}$	Diffusion coefficient of supercritical CO_2 in ethanol at infinite dilution $\left[\frac{m^2}{s}\right]$
D_L	Axial dispersion coefficient $\left[\frac{m^2}{s}\right]$
f	Function [−]
i	Index [−]
j	Index [−]
J_i	Diffusive flux of component i $\left[\frac{mol}{m^2\cdot s}\right]$
J_v	Convective volumetric flow $\left[\frac{m^3}{m^2\cdot s}\right]$
K_{eff}	Factor $\left[\frac{m^2}{s}\right]$
$k_{CO_2,EtOH}$	Fitting parameter [−]
k_{EtOH,CO_2}	Fitting parameter [−]
L	Length of the packed bed, cylinder length $[m]$
$l_{ij},\ l_{ji}$	Fitting parameter [−]
$\dot{m}_{EtOH,CO_2}$	Mass flowrate of the ethanol − CO_2 mixture $\left[\frac{kg}{s}\right]$
max	Maximum [−]
M_{CO_2}	Molecular weight of CO_2 $\left[\frac{kg}{mol}\right]$
M_{EtOH}	Molecular weight of ethanol $\left[\frac{kg}{mol}\right]$
$m_{ij},\ m_{ji}$	Fitting parameter [−]
N_{comp}	Number of components [−]
N_p	Number of particles [−]
N_d	Number of data points [−]
$\dot{N}_{EtOH,b}$	Molar flow of ethanol crossing the boundary layer from the particle surface to the bulk fluid $\left[\frac{mol_{EtOH}}{s}\right]$
OF	Objective function [−]
P	Pressure $[Pa]$
$p_{ij},\ p_{ji}$	Fitting parameter [−]
$P_r = \frac{P}{P_c}$	Reduced pressure [−]
r	Radial coordinate of the spherical particle $[m]$
R	Particle radius, cylinder radius $[m]$
R_{uni}	Universal gas constant $\left[\frac{kg\cdot m^2}{s^2\cdot mol\cdot K}\right]$
$Re_l = \frac{\pi\cdot R\cdot U}{\nu_f}$	Reynolds number for the gel cylinder [−]
$Re_\psi = \frac{2\cdot R\cdot U}{\psi\cdot\nu_f}$	Reynolds number for the packed bed [−]
S	Number of discretization points in z-axis [−]
$Sc = \frac{\nu_f}{D_{EtOH,CO_2}}$	Schmidt number [−]
Sh	Sherwood number [−]
t	Time $[s]$
T	Temperature $[K]$
$T_r = \frac{T}{T_c}$	Reduced temperature [−]
$u = \frac{U}{\psi}$	Interstitial fluid velocity $\left[\frac{m}{s}\right]$
U	Superficial fluid velocity $\left[\frac{m}{s}\right]$
$\dot{V}$	Volume flow $\left[\frac{m^3}{s}\right]$
V	Volume $[m^3]$
v_{bp,CO_2}	Molar volume of CO_2 at the normal boiling point $\left[\frac{m^3}{mol}\right]$
v_{c,CO_2}	Molar volume of CO_2 at the critical point $\left[\frac{m^3}{mol}\right]$
$\bar{v}_i$	Partial molar volume of component i $\left[\frac{m^3}{mol}\right]$
v_{mix}	Mixture molar volume $\left[\frac{m^3}{mol}\right]$
V_p	Particle volume $[m^3]$
v^{PR}	Molar volume calculated using the Peng-Robinson equation of state $\left[\frac{m^3}{mol}\right]$
v^{VTPR}	Molar volume calculated using the volume translated Peng-Robinson equation of state $\left[\frac{m^3}{mol}\right]$
w	Fitting parameter [−]
wt	Mass fraction [−]
x_i	Molar fraction of component i $\left[\frac{mol_i}{mol_{EtOH}+mol_{CO_2}}\right]$
$x_{EtOH,f}$	Ethanol molar fraction in the bulk fluid $\left[\frac{mol_{EtOH}}{mol_{EtOH}+mol_{CO_2}}\right]$
$x_{EtOH,g}$	Ethanol molar fraction within the porous gel body $\left[\frac{mol_{EtOH}}{mol_{EtOH}+mol_{CO_2}}\right]$
z	Axial coordinate of the autoclave, axial coordinate within the cylindrical gel monolith $[m]$
Z	Compressibility factor to solve the Peng-Robinson Equation of State [−]

Greek letters

α	Cohesion or alpha function for a pure substance [−]
α_{CO_2}	

$$\alpha_{CO_2} = B_1 + \ln(P_{(r,CO_2)})\cdot(B_2 + B_3\cdot\ln(T_{(r,CO_2)}) - B_4\cdot\ln^2(T_{(r,CO_2)}) - B_5\cdot\sin(B_6\cdot\ln^2(P_{(r,CO_2)}))) - B_7\cdot\sin(\ln(T_{(r,CO_2)}))\ [-]$$