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Mathematical simulation of heat and mass transfer during controlled depressurization of supercritical CO_2 in extraction vessels

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ABSTRACT

Even after almost forty years of industrial application, companies are still reluctant to use supercritical (sc) CO_2 as a solvent for extractions due to the perceived high production costs. Literature on the matter suggests that, because extraction at high pressure needs to be done in batches, using multiple extraction vessels with simulated-countercurrent flow could reduce operational costs. However, the more extraction vessels used, the less time there is to recondition them in order to have a semi-continuous operation; and if the reconditioning, and particularly the depressurization, is done too fast, the vessel could become brittle and permanently damaged. With the goal of optimizing the depressurization process in mind, numerical simulation of temperature and mass was carried considering a 1-dm^3 vessel filled with a packed bed made with model materials using a mass flow function that depends on the chocked mass flux and a valve opening area. The correlation $Nu = 0.0777Da^{-0.0373}Ra^{0.397}$ was obtained for convective heat transfer at the vessel wall, and temperature, pressure, and vented mass flow were simulated with about 20% improvement in predictions in comparison to our previous correlation. To explore the use of the model for practical purposes, it was used to simulate depressurization processes with volumes up to 1 m^3 and with different initial conditions and vessel geometries so as to have a first approach on the effect of these parameters on the depressurization time. Simulated depressurization times reached a maximum value of 54.5 min for depressurizations of a 1-m^3 extraction vessel starting at 60 °C and 70 MPa, which are very plausible extraction conditions. This model can be used to determine optimal reconditioning time in industrial plants for cost minimization.

1. Introduction

Solvent extraction using supercritical (sc) CO_2 is currently a well stablished operation in the food industry, in processes such as decaffeination of coffee, removal of bitter flavors from hops, and extraction of high-value compounds [1]. Even though $scCO_2$ has many advantages over other organic solvents, and has been used as an extraction solvent for almost four decades, companies still hesitate when it comes to investing in this technology [1]. A reason for these doubts may be the perceived high costs associated with operating an extraction plant. However, cost optimization could prove to be the tool needed in order to refute such beliefs.

Núñez and del Valle [2] optimized production costs in a $scCO_2$ extraction plant. Some of the relevant variables for optimization were mass flow rate (inversely proportional to production costs; production costs decreased when increasing mass flow rate), aspect ratio of the extraction vessel (directly proportional to production costs for a constant superficial velocity of CO_2), and number of extraction vessels with simulated-countercurrent flow (inversely proportional to production costs). One limiting aspect of increasing the number of extraction vessels is the reconditioning time. For semi-continuous operation, an exhausted batch must be replaced for a fresh one in less time than required another vessel to become exhausted [3]. This means that as the number of extraction vessels of the plant, the time available for reconditioning decreases if a semi-continuous operation is desired.

The reconditioning process consists of four steps: (i) depressurization of the vessel, (ii) unloading of the exhausted material, (iii) loading of fresh material, and (iv) pressurization of the vessel. Of these stages, the least studied and the one with largest opportunities for optimization is the initial depressurization of the vessel. The focus of previous research has been mostly on safety aspects [4–6]

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Nomenclature

Latin letters

A	Valve opening area (m^2)
Da	Darcy number, $d_p^2\varepsilon^3 150^{-1}(1-\varepsilon)^{-2}L^{-2}$ (−)
d_p	Particle diameter (m)
F	Mass flow rate ($kg\,s^{-1}$)-
h	Heat transfer coefficient ($W\,m^{-2}\,K^{-1}$)
k	Thermal conductivity ($W\,m^{-1}\,K^{-1}$)
l	Packed bed material height (m)
L	Vessel height (m)
m	System fluid mass (kg)
Nu	Nusselt number, hLk^{-1} (−)
Pr	Prandtl number, $\nu\alpha^{-1}$ (−)
r	Radial position (m)
R	Vessel internal radius (m)
Ra	Rayleigh number, $g\beta\left(T_w-\bar{T}\right)L^3(\nu\alpha)^{-1}$ (−)
Re	Reynold number, $ud_p\nu^{-1}$ (−)
t	Time (s)
T	Temperature (°C or K)
u	Superficial velocity ($m\,s^{-1}$)
x	Vessel steel wall thickness (m)
z	Axial position (m)

Greek letters

α	Thermal diffusivity ($m^2\,s^{-1}$)
ρ	Density ($kg\,m^{-3}$)
ε	Porosity
ν	Speed of sound ($m\,s^{-1}$)

Subscripts

eff	Effective
f	Fluid
J	Jacket
l	Lid
s Solid	t
t	Time
w	Wall

and not on the mechanics of the depressurization or how they affect industrial operation. The one practical limitation that this process has is that, when done at high speeds, it results in low temperatures that turn the vessel become brittle [7] and damage it permanently.

Richter et al. [8] studied the controlled depressurization of an extraction vessel filled with pressed or pelletized organic material at pilot scale in order to identify the principles that rule this process. Their findings show that total packed bed porosity was fundamental in determining temperature and pressure changes within the vessel during depressurization, and that all the components of the extraction vessel (substrate, walls, and lids of the extraction vessel, CO_2) were relevant for the heat transfer in the system. In a follow-up work, Richter et al. [9] studied this same problem using an extraction vessel with a well-defined geometry and model materials made from glass or sintered steel. The results of this work were the validation of previous results [8] and a new correlation to estimate the convective heat transfer coefficient at the vessel wall (Eq. (1)). This correlation was better than the one proposed before because it included the Darcy (Da) dimensionless number as a parameter, which represents the relative effect of permeability of the substrate. This allowed for one equation for different materials instead of one for each.

$$Nu = 0.086Da^{-0.037}Ra^{0.357} \quad (1)$$

Table 1
Operation conditions used for simulation.

Temperature of heating water (°C)	60
Initial temperature (°C)	60
Initial pressure (MPa)	26
Radium of extraction vessel (mm)	38
Thickness of extraction vessel wall (mm)	18.5
Height of extraction vessel (mm)	230
Volume of extraction vessel (m^3)	0.001

Although an improvement from previous work, the experimental design proposed by Richter et al. [9] had some deficiencies. We believe the number of thermocouples placed in the vessel to be insufficient to stablish the existence of axial or radial temperature profiles throughout the depressurization. Also, it is difficult to measure the temperature of the fluid near the vessel wall; mass flow could have caused vibrations or movement in the thermocouple placed in there that could have in turn affected measurements. Because of this, we believe Eq. (1) should be reevaluated through simulation and optimization.

We believe it is possible to generate a mathematical model that can simulate the changes in temperature and pressure throughout the depressurization process. This model can be used to optimize the parameters of the correlation for convective heat transfer at the vessel wall, and to simulate the previous experimental results [9]. The model can be later used to obtain an optimal mass flow that will allow safe and fast depressurizations. Its ability to simulate depressurization processes at industrial scale will need to be assessed once experimental results are available at those conditions. By providing tools for optimizing the extraction process, our aim is to reduce uncertainties that prevent improving the productivity of industrial $scCO_2$ extraction processes, which in turn precludes this technology from being a widespread choice for the food industry.

2. Model development

This section is divided in three parts. The first one shows the assumptions and considerations made in order to simplify the model. The second part shows the equations used to model heat and mass transfer in the extraction vessel. Finally, we describe the numerical method used, how error and confidence intervals were calculated, and how we tested the effect of some operational parameters on depressurization processes.

2.1. Model assumptions

In order to produce a model for controlled CO_2 depressurization, several assumptions had to be made. First, differences in pressure within the extraction vessel were considered negligible. Physical properties of the packed bed (bulk density and porosity) and of the AISI 316 steel wall (thermal conductivity and heat capacity) were assumed to be constant during depressurization because of the small changes in them in the temperature interval between 250 and 350 K. The thermal diffusivity of steel was obtained from Bergman et al. [10].

Experimental results obtained by Richter et al. [9] were used to validate the results obtained through simulation. These experiments were carried out in a 1 dm^3 extraction vessel with a heating jacket and with experimental conditions shown in Table 1. The vessel was loaded with a packed bed made from three possible model materials: sintered stainless steel cylinders, glass beads, and glass Raschig rings. Experimental depressurizations with packed beds were carried out in two stages depending on the valve opening. Initially, the valve opening was small (flow coefficient $f_c = 0.0005$ provided by the needle valve manufacturer; flow coefficient is a measure of the efficiency of the valve in letting fluid flow) to avoid