The Journal of Supercritical Fluids 136 (2018) 1–11

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu

Porous membrane cleaning using supercritical carbon dioxide. Part 2: Development of mathematical model and CFD simulations

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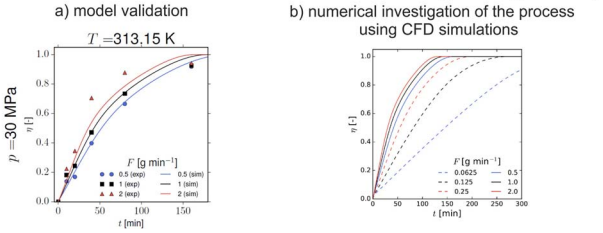
GRAPHICAL ABSTRACT

Mathematical model of membrane cleaning using $scCO_2$



ARTICLE INFO

Keywords:
Microfiltration membrane
Supercritical carbon dioxide
Cleaning
Mathematical model
CFD
OpenFOAM

ABSTRACT

The process of cleaning microfiltration membranes contaminated with soybean oil, using pure supercritical carbon dioxide as cleaning fluid, was considered. A mathematical model of the process was developed, implemented into CFD software and validated using experimental results. The mathematical model is based on the Volume of Fluid approach and includes porous zone treatment, variable fluid phase composition due to mutual solubility of the contaminant and the solvent, as well as phase transition. The developed model was implemented into the OpenFOAM toolbox and validated using experimental results. The results of CFD simulations using the mathematical model show a good agreement with experimental results. CFD simulations were performed in order to analyze the effect of solvent flow rate and the effect of oil phase swelling on the course of the process. The mass transfer mechanisms were identified. The developed model is an efficient tool for process optimization, scale-up, and high-pressure equipment design.

1. Introduction

Supercritical fluids (SCFs), especially supercritical carbon dioxide ($scCO_2$), have a great potential for replacing liquid organic solvents in numerous technologies for production and processing porous materials [1–9]. The application of $scCO_2$ instead of liquid organic solvents enhances the process safety and can potentially reduce the process cost and the environmental load due to the reduction of generated waste material. Investigation of process mechanisms, process optimization and scale-up remain the major challenges for industrial implementation of these novel technologies.

In this work, the process of microfiltration membrane cleaning using $scCO_2$ is considered as model process. In the standard implementation of the Temperature Induced Phase Separation (TIPS) method for manufacturing microfiltration membranes [10], large amounts of organic solvents are used as cleaning fluids in the final step of the manufacturing method, resulting in high process costs and process safety issues (fire hazard). It was shown that the use of $scCO_2$ has the potential for replacement of the organic solvents used in the standard variant of TIPS [11,12]. For prediction of the course of the process in various

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https://doi.org/10.1016/j.supflu.2018.01.028
Received 20 September 2017; Received in revised form 29 January 2018; Accepted 29 January 2018
Available online 03 February 2018

process conditions, e.g. for optimization purposes, a mathematical model of the investigated process is needed. Simplified mathematical modelling was employed for studying the process numerically [13]. However, no holistic mathematical model of the process, suitable for CFD simulations of the course of the process and including all significant transport phenomena, has been presented so far.

In the literature, several mathematical models of processes involving supercritical fluids are presented, including those suitable for performing CFD simulations. CFD simulations appear to be a promising tool for numerical investigation, optimization, and scale-up of this class of processes. The modelled processes include multiphase flows trough packed beds, including structured packing, in SFE systems [14–16], supercritical wood impregnation [17], near critical extraction through a porous membrane [18], fluid flow and heat transfer in micro-porous materials [19], and $scCO_2$ injections into geological structures for potential CO_2 storage [20]. Another example relates to CFD modelling for the process of supercritical fluid of alcogels and was investigated by Özbakır and Erkey [21]. In this process, ethanol is present in the pores of the alcogel and it has to be removed. The drying process resembles the membrane cleaning process studied in this work. However, in the case of alcogel drying, ethanol and $scCO_2$ have no miscibility gap. Moreover, the convection inside the pores of the alcogel is neglected and the convection in the bulk of the solvent is not explicitly modelled in the CFD code. Nonetheless, the simulation results were in a good agreement with experimental data. To sum up, no mathematical model for cleaning porous media using supercritical fluids in a system containing two separate fluid phases has been described in the literature so far.

The aim of the work is to investigate the course of the process of porous membrane cleaning using supercritical fluids, including its mechanisms, and to compare it with the standard process, in which liquid organic solvents are used as cleaning fluids, in order to assess whether supercritical carbon dioxide can replace them in the cleaning process. Cleaning capillary polypropylene microfiltration membranes contaminated with soybean oil (an oil used in the TIPS method) using pure supercritical carbon dioxide ($scCO_2$) is considered as investigated process. The research on porous membrane cleaning using supercritical carbon dioxide is presented in two parts:

- Part 1: Experimental investigation and analysis of transport properties [22], and
- Part 2: Development of mathematical model and CFD simulations (this article).

In Part 1, the process was investigated in a lab-scale experimental system, and the influence of process parameters on the course of the process was assessed. Moreover, the investigated process was compared with the reference process utilizing liquid propan-2-ol as cleaning fluid, and the role of transport properties of the fluids involved in the process was discussed. The main mass transfer mechanisms were identified and the influence of various process parameters on the course of the process was assessed. The aim of this article is to develop the mathematical model of the membrane cleaning process using $scCO_2$, to implement it into CFD software, to validate it using experimental results obtained in Part 1, and to investigate the process numerically using CFD simulations.

2. Mathematical model

2.1. Assumptions

The mathematical model of the investigated process was developed with the following assumptions:

- The membrane is treated as a quasi-continuous porous zone.
- Two fluid phases exist: the oil phase (1), containing mainly soybean oil, and the solvent phase (2), containing mainly carbon dioxide.
- Mutual solubility of soybean oil and $scCO_2$ is limited [23,24].
- The process is isothermal.
- The fluid flow is laminar and incompressible (local pressure changes in the domain are assumed to be small enough for the net effect of density variations of $scCO_2$, related to its compressibility, as well as the resulting changes in transport properties to be neglected).
- Phase transition occurs at the phase boundary of the two fluid phases, and the rate of mutual dissolution of soybean oil in the solvent phase, as well as $scCO_2$ in the oil phase is controlled by diffusive mass transfer at the phase boundary.

2.2. Model formulation

The mathematical model developed for the investigated process is an extension of the standard VOF model, in which the momentum transport equation is solved for a velocity field U, which is shared by both phases, while the fluid phase distribution is modelled by a scalar transport equation for the volume fraction α_1 of phase 1 [25]. The extension of the model includes the mathematical representation of the porous zone in the domain, compositions of both phases varying in space and time, as well as the phase transition occurring at the phase boundary. Inside the porous material, the superficial velocity formulation for the velocity field U was used.

For modelling the compositions in the fluid phases, the dimensionless concentration C_1 of soybean oil in the solvent phase and the dimensionless concentration C_2 of CO_2 in the oil phase was introduced:

$$C_1 = \frac{c_1}{S_1} \tag{1}$$

$$C_2 = \frac{c_2}{S_2} \tag{2}$$

where c_1 is the mass/volume concentration of the soybean oil in the solvent phase, c_2 the mass/volume concentration of CO_2 in the oil phase, S_1 the solubility of the soybean oil in the solvent phase, and S_2 the solubility of CO_2 in the oil phase. The values of both C_1 and C_2 are in the range from 0 to 1.

For modelling phase transition at the phase boundary, appropriate source terms for the U, α_1, C_1, and C_2 transport equations were added to the respective transport equations.

The divergence of velocity field U is given by equation:

$$\nabla\cdot\mathbf{U} = q_{\mathrm{U}} \tag{3}$$

The source term q_{U} can be nonzero only in the region of the domain, where the phase transition occurs, provided that both fluids are of different density.

The momentum transport equation is defined as follows:

$$\frac{\partial(\rho\mathbf{U})}{\partial t} + \nabla\cdot(\rho\mathbf{U}\mathbf{U}) - \nabla\cdot(\mu\nabla\mathbf{U}) - \frac{1}{3}\nabla(\mu(\nabla\cdot\mathbf{U})) = -\nabla p + \mathbf{f} \tag{4}$$

where ρ is the fluid density, U – the velocity vector, μ – the dynamic viscosity of the fluid, p – the pressure and f – the body forces, including the gravity force, the surface tension force and the flow resistance force in the porous material according to Darcy's law:

$$\mathbf{f} = \rho\mathbf{g} - \sigma K\mathbf{n} - \frac{\mu}{\kappa}\mathbf{U} \tag{5}$$

where ρ is the fluid density, g – the standard gravity, σ – the surface tension, n – a unit vector normal to the phase boundary, K – the curvature of the phase boundary, μ – the dynamic viscosity of the fluid, κ – the permeability of the porous material, and U – the velocity of the fluid.

The transport of the phase volume fraction α_1 is modelled according to the following equation: