



Experimental and theoretical investigation of supercritical drying of silica alcogels



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ABSTRACT

Extraction of ethanol from pores of cylindrical silica alcogel samples using supercritical CO₂ (scCO₂) in a tubular extraction vessel was investigated both by experiments and simulations. Partial differential equations representing mass transfer within the cylindrical silica alcogel phase and in the external scCO₂ phase were developed and solved using finite difference method. The percent removal data as a function of time were found to be in good agreement with model results using mass transfer coefficients regressed from the experimental data. The mass transfer coefficients were found to be higher by about a factor of three from two of the correlations tested which were developed for supercritical extraction. Effect of scCO₂ flow rate on the drying was investigated through experiments and simulations. Increasing flow rate led to a decrease in effluent concentration at a specific time but did not significantly affect rate of extraction of ethanol. Effects of the magnitude of the effective diffusion coefficient and alcogel thickness on drying were investigated through simulations. Drying time of the alcogel decreased with decreasing gel thickness and increasing effective diffusion coefficient.

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1. Introduction

Silica aerogel, a continuous network of connected microscopic beads is a nanoporous solid material with several unique properties such as interconnected open pore structure, large internal surface area, large pore volume, high porosity, low density, low thermal conductivity and low dielectric constant [1,2]. The properties of these materials make them outstanding for a wide variety of applications: (1) transparent thermal and acoustic insulators; (2) inter-metal dielectric materials; (3) fillers for paints, varnishes, etc.; (4) catalytic supports and adsorbents; (5) host materials for drug delivery [1–3].

Silica aerogels are produced by a set of chemical reactions resulting first in a sol and subsequently in a gel. Subsequently, the liquid solvent is then removed from the alcogel, which is called the drying of the alcogel [3,4]. Removal of the liquid solvent in such a way to avoid as much as possible its textural modifications preserving its original nanoporous network is the most difficult stage in aerogel production [3–6]. If the gels are air dried, the liquid–vapor phase boundaries which develop with time in its pores during evaporation results in very high capillary pressures which cause collapse of the pores [4,5,10]. Differential strain arising from capillary pressure

can be eliminated by using the supercritical drying process. Supercritical drying of the alcogel is extraction of the primary solvent in the pores of the gel with supercritical fluids, commonly supercritical carbon dioxide (scCO₂). During supercritical drying, formation of two phases (a liquid and a vapor one) in the pores of the gels are prevented thereby collapse of the porous gel network can be avoided. As a consequence of supercritical drying of the alcogel, highly porous aerogel structure can be obtained [3,5–8,13].

An understanding of the kinetics of supercritical drying of silica alcogel and modeling of the process is necessary to provide insight into material development, scale-up and optimization of the aerogel manufacturing process.

There are a few studies in the literature on supercritical drying of alcogels with scCO₂. Novak and Knez [9] investigated drying of a 1.4 cm thick and 4 cm tall silica alcogel sample, the pores of which were filled with methanol using a 100 ml autoclave with both liquid and scCO₂. The alcogel sample was placed in the middle of the vessel which was then filled with methanol. Subsequently, the vessel was charged with CO₂ up to 70 bar. The outlet valve was then opened and liquid methanol initially surrounding the gel was removed by CO₂ flowing at a particular flow rate. Then, the flow rate of CO₂ was reduced and methanol was extracted from the pores of the alcogel at this flow rate for a certain period of time. The outlet valve was subsequently closed and the vessel was heated to 40 °C causing the pressure to increase to 90 bar. Then, the outlet valve was opened and the vessel was slowly depressurized to ambient pressure. It

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was observed that duration of extraction had an important effect on the transparency and on the formation of cracks in aerogel samples. Insufficient time of extraction resulted in a non-transparent area inside of the alcogel or caused the unextracted methanol to transform to a vapor phase during depressurization leading to the subsequent evaporation of the liquid into the gas phase and damaged the aerogel sample. Width of the damaged, non-transparent area could be calculated using an equation as a function of Fourier number which is related to diffusion time, diffusion coefficient and gel radius. Since the diffusion time and dimensions of the samples were known in each experiment, diffusion coefficient of methanol in CO₂ in the silica alcogel could be determined by fitting the experimental data to the theoretical model for the cylindrical sample using least-squares method.

Drying of silica alcogels with scCO₂ was also investigated by Van Bommel and de Haan [10]. A 1.5 cm thick alcogel submerged initially in ethanol in an extractor with a volume of 600 ml was dried pumping scCO₂ through the extractor with a flow rate in the range of 1.0–1.3 kg/h. Monolithic silica aerogels were obtained at 35 °C and above 85 bar. The drying time was found to increase with thickness of the sample. As the operating temperature and pressure increased from 85 bar and 35 °C to 140 bar and 70 °C, the drying time slightly decreased from 3 h to about 2 h and 45 min.

A two-way mass transfer model for the supercritical drying of silica alcogel was developed by Mukhopadhyay and Rao [11]. It was assumed that the alcogel had a parallel-pore configuration where each pore had one end closed and the other end open to the scCO₂ stream. The radius of each pore was assumed to be constant during the extraction. It was suggested that diffusion of CO₂ into ethanol in the pores and its dissolution in ethanol leads to increase in liquid volume and thus the excess pore liquid spills from the pores. The spilled amount was computed by calculating the volume increase over a time step and subtracting the ethanol volume therein in the previous time step. Variation of CO₂ concentration with time and distance in the alcogel was determined utilizing Fick's second law. The effective diffusion coefficient was taken as a function of both molecular and Knudsen diffusion coefficients and the molecular diffusion coefficient was a function of ethanol mole fraction. Effect of gel thickness, temperature, pressure and CO₂ velocity on drying at 313 K and 100 bar was examined by simulations. It was found that gel thickness and flow rate of scCO₂ substantially affected the drying time; lower flow rate noticeably increased the drying time which increased with decreasing temperature and slightly increased with increasing pressure. The authors did not compare the results with experimental data.

Orlović et al. [12] investigated supercritical drying of alumina/silica alcogel with carbon dioxide in a 70 cm³ tubular extractor (Autoclave Engineers Supercritical Extraction Screening System) at 313 K and 80 bar. The pores of the gel were entirely filled with of 1-butanol (solvent). The change in the alcogel weight as a function of drying time was measured and modeled by assuming unsteady state, one-dimensional and unidirectional diffusion of the solvent through the pores. Four different methods were used to calculate the effective diffusivity. In the shrinking core models, a single value of the effective diffusivity was used for the whole aerogel sample; however these models did not agree with experimental data. The parallel pore model and the pores in series model utilized different effective diffusivity values for each pore size with a local tortuosity value for each pore size and they showed a far better agreement with experimental data. Furthermore, effect of drying temperature and drying body dimensions on the drying time were investigated by simulations. It was concluded that the drying time of the alcogel diminished with decreasing alcogel thickness and increasing temperature.

García-González et al. [13] investigated drying of alcogels prepared from different precursors with different densities and

morphologies. 1.2 cm diameter × 3 cm long alcogel rods were dried with a flow rate of 0.234 kg/h in a 25 ml tubular vessel at 318 K and 110 bar. The outlet stream from the autoclave was expanded to atmospheric pressure and was passed through vials which were immersed in a dry ice bath. The gaseous stream exiting the vials was passed through an alcoholmeter to determine its ethanol content. Thus, the amount of ethanol extracted could be determined as a function of time. Ethanol removal from the rods was assumed to be controlled by diffusion. The analytical solution of a model based on Fick's second law in cylindrical coordinates was used to calculate amount of ethanol removed as a function of time. Diffusion coefficient was regressed from experimental data. The assumption of Fickian diffusion as the only mass transfer mechanism for the extraction of solvent from the alcogel network in supercritical drying failed for the initial stage of the extraction, whereas the model revealed good agreement after this initial stage.

In this study, understanding of the kinetics of supercritical drying of silica alcogel and modeling of the process was aimed. Partial differential equations representing mass transfer within a cylindrical silica alcogel phase and in the flowing scCO₂ phase in a tubular extraction vessel were developed and solved using finite difference method. Mass transfer occurred by diffusion inside the alcogel and by convection from the surface of the alcogel to the flowing scCO₂ stream. A convective mass transfer term was also used to describe mass transfer along the tubular vessel. The ethanol concentration in the flowing scCO₂ phase and within the alcogel was determined as a function of time and position. Experiments with continuous flow of scCO₂ stream around a cylindrical alcogel in a tubular vessel were also carried out and mass of ethanol removed was measured as a function of time. The experimental data were compared to model results. The extraction vessel and sample geometry was such that the derived differential equations were sufficiently well representative of the drying process inside the vessel and the boundary conditions were well-defined. The effect of CO₂ flow rate on the alcogel drying was investigated both by experiments and simulations.

2. Materials and methods

2.1. Chemicals

Tetraethylorthosilicate (TEOS) (98% purity; AlfaAesar), ethanol (99.9% purity; Merck), hydrochloric acid (HCl) (37% purity; Riedel-de Haen), ammonia (NH₃) (2.0 M in ethanol; Aldrich) were used as received. CO₂ was obtained from Messer Aligaz and had a stated purity of 99.9%.

2.2. Preparation of cylindrical silica alcogel samples

Three cylindrical silica alcogel rods with 0.85 cm diameter × 10 cm height, 0.85 cm diameter × 12 cm height and 1.19 cm diameter × 15 cm height were prepared using a conventional two step sol-gel process [3–7]. TEOS was used as the silica precursor, HCl as the acid catalyst, and NH₃ as the base catalyst. As the first step, a solution was prepared by mixing TEOS, ethanol and water with the mass ratio 1:1:0.34. Subsequently, the acid catalyst was added (2.0 M in ethanol) to accelerate the hydrolysis reactions. The mixture was stirred at room temperature for 60 min. Then, the base catalyst was added to the solution to increase the rates of condensation reactions. Before gelation, the solution was poured into plastic cylindrical molds (1.2 cm diameter × 17 cm height and 0.88 cm diameter × 15 cm height) and sealed. After gelation, the resulting alcogel was soaked in an aging solution of equi-volume mixture of water and ethanol at 50 °C for 24 h in an oven. During the aging process, further condensation reactions take place

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