

# Investigation of Kinetics of Supercritical Drying of Calcium Alginate Algogel Particles

**İbrahim Şahin\*, Erdal Uzunlar, Can Erkey**

Department of Chemical and Biological Engineering, Koç University, 34450 Sarıyer, Istanbul, Turkey

[\\*isahin@ku.edu.tr](mailto:isahin@ku.edu.tr)

## ABSTRACT

Aerogels are nanoporous materials with unique properties such as high porosities, high surface areas and high pore volumes that are tunable by manipulation of synthesis conditions. Recently, aerogels in the form of particles are attracting increased attention for development of a wide variety of products for drug delivery, sensing, adsorption and catalysis. Supercritical drying is the most important step in production of aerogel particles. Therefore, kinetics of supercritical drying of gel particles is important for design, scale-up and optimization of industrial scale aerogel production facilities. In this study, we investigated supercritical drying of alginate gel particles in a packed bed. Spherical calcium alginate hydrogel particles with an average diameter of 0.4 cm were prepared by dripping a 1.5 wt% aqueous alginate solution into a 0.2 M aqueous CaCl<sub>2</sub> solution. The hydrogel particles were subjected to a stepwise solvent exchange procedure with ethanol before supercritical drying. The effects of temperature, pressure and CO<sub>2</sub> flow rate on the drying kinetics were investigated. A large fraction of the ethanol inside the pores was extracted in a very short time. Results indicate that although temperature affected the exit ethanol concentration profiles, drying time was not affected considerably. The CO<sub>2</sub> flow rate had a significant effect on drying times. A drying model which takes into account diffusion inside the pores, external mass transfer from the surface of the gel particles into the flowing CO<sub>2</sub> stream and convection and axial dispersion in the fluid phase was developed.

## INTRODUCTION

Unique material properties of aerogels, such as high porosity, high surfaces area and very low density, make them attractive for use in a variety of applications [1]. Current aerogel market is largely dominated by silica-aerogels due to their thermal insulation performance. However, emerging markets for aerogels, such as catalysis [2], sensing [1], adsorption [3] and drug delivery [4], demand aerogels with different materials properties. This demand can be met by introducing other types of aerogels than those based on silica. Thus, organic and hybrid aerogels are gaining increased attention over the last decade. For example, unlike silica aerogels, polysaccharide-based organic aerogels are biodegradable and well-suited for several pharmaceutical applications [4–6]. Similarly aerogels were synthesized not only in the form of monoliths but also as particles, like beads and granules, in order to increase their usability in various applications [4,7].

Synthesis of organic aerogels is similar to their inorganic counterparts involving gelation and drying steps. Removing the pore filling liquid from the gel during the drying step is a key process in order to maintain an open nanoporous structure and desired textural properties. Supercritical drying process is commonly used for this purpose. In this process, generally

supercritical carbon dioxide (scCO<sub>2</sub>) is passed over the entire body of wet-gel and extracts the pore filling liquid without formation of a vapor-liquid interface and subsequent collapse of the gel network due to capillary stresses. An understanding of the kinetics of supercritical drying is crucial for material development, scale-up and optimization of the aerogel manufacturing process.

Literature on kinetics of supercritical drying is mostly dominated by the studies involving the drying of monolithic silica based aerogels coupled with several modeling efforts [8]. Early studies treated the drying as a purely diffusion based process [9–11]. Garcia-Gonzalez et al. studied the drying of silica alcogels as cylindrical rods with 1.2 cm diameter and 3 cm length in a 25 ml tubular vessel at 318 K and 110 bar by measuring the ethanol amount in the exit CO<sub>2</sub> stream with respect to time [12]. A model based on Fick's second law with a constant effective diffusivity was proposed to describe the experimental data. The proposed model failed to predict the initial stage of drying whereas there was a good fit for the later stages using the same model. Therefore, they concluded that mass transfer at the gel- scCO<sub>2</sub> should also be considered. Griffin et al. investigated the drying of 2.5 mm, 5 mm and 7.5 mm cylindrical silica alcogels at 323 K and 12.4 MPa with different flow rates [13]. A two-dimensional mass transfer model based on pure diffusion with composition dependent effective diffusivity led to a good agreement with the experimental data. A more realistic model for drying of cylindrical silica alcogels was developed by Özbakir et al. [14]. The model treated the alcogel phase and flowing scCO<sub>2</sub> phase separately with a two dimensional diffusive model based on Fick's second law including the mass transfer of ethanol from alcogel surface to flowing scCO<sub>2</sub> stream. A good agreement with the proposed model results and experimental percent removal data as a function of time was obtained. Several experimental investigations concluded that increasing gel thickness or diameter resulted in increasing drying time due elongated diffusion paths [9,13–15]. Moreover, studies of Özbakir et al. and Griffin et al. showed that flow rate of scCO<sub>2</sub> was found to affect the initial phase of drying whereas the drying time was not affected considerably [13,14].

Previous studies on kinetics supercritical drying of wet-gels to prepare aerogels shows that current understanding of kinetics of supercritical drying for drying of organic and hybrid gels in the form of particles is limited. Therefore, in this study we aimed to investigate the drying of calcium alginate alcogel particles in a packed bed by varying operating conditions and proposed a physically realistic model by considering diffusion inside the pores, external mass transfer from the surface of the gel particles into the flowing scCO<sub>2</sub> stream and convection and axial dispersion in the fluid phase.

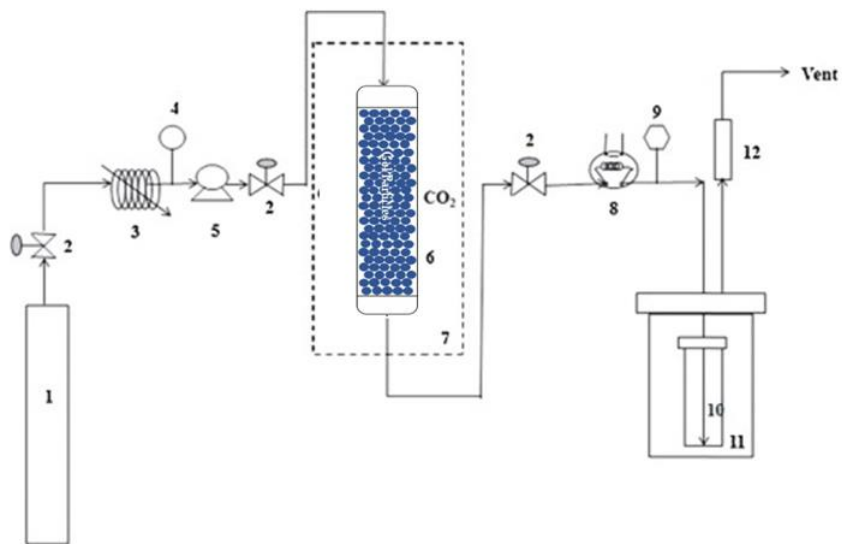
## **MATERIALS & METHODS**

Alginic acid sodium salt from brown algae (medium viscosity) and calcium chloride (anhydrous granular, >93%) were obtained from Sigma-Aldrich®. Calcium alginate beads were synthesized by the dripping method. Spherical calcium alginate hydrogel particles with an average diameter of 0.4 cm were prepared by dripping a 1.5 wt% aqueous alginate solution into a 0.2 M aqueous CaCl<sub>2</sub> solution with constant stirring. The hydrogel particles were subjected to a stepwise solvent exchange procedure with mixtures of ethanol with water (10%, 30%, 50%, 70%, 90% and 100% ethanol by vol., respectively) before supercritical drying.

Supercritical drying of prepared calcium alginate alcogels was performed in an Applied Separations Speed SFE unit (tubular vessels, volumes = 26 ml and 100ml). A schematic diagram of the drying unit used in this study is shown in Fig. 1. The vessel (6 in Fig. 1) was initially filled alcogel beads and excess ethanol to cover the whole packed bed of particles in order to prevent

possible evaporation of the solvent from the alcogel surface leading to shrinkage of the gel beads. The vessel was heated and pressurized to the drying temperature and pressure. Then, excess amount of ethanol initially added to the vessel was rapidly removed from the vessel in about 2-3 min. The desired flow rate of CO<sub>2</sub> (2-4 L/min at standard conditions) was adjusted using the micro-metering valve. The CO<sub>2</sub> stream from the extractor was expanded to ambient pressure and subsequently cooled by passing it through a vial immersed in a cooling bath composed of dry ice-acetone mixture at -75 °C. In doing so, ethanol rich liquid phase was collected into the vial whereas CO<sub>2</sub> rich gas phase was vented out. Ethanol extracted from the alcogel was collected in the separate vials within certain time intervals and was weighed. Drying was continued after there was no ethanol observed in the vial and then the vessel was slowly depressurized to ambient pressure at the set drying temperature. The dried sample was finally collected from the vessel.

The mass balance in the drying experiments was checked by weighing the alcogel particles and excess ethanol initially placed to the vessel before drying and comparing the summation of the two by the summation of the amount of ethanol collected in the vials and the weight of the aerogel particles.



**Figure 1.** Schematic representation of process flow diagram of drying unit used in our studies (1. CO<sub>2</sub> tank, 2. Valve, 3. Cooler, 4. Pressure transducer, 5. Pump, 6. Tubular extraction vessel, 7. Oven, 8. Micro-metering Valve, 9. Thermocouple, 10. Sample collection vial, 11. Dry ice cooling bath, 12. Rotameter [14].

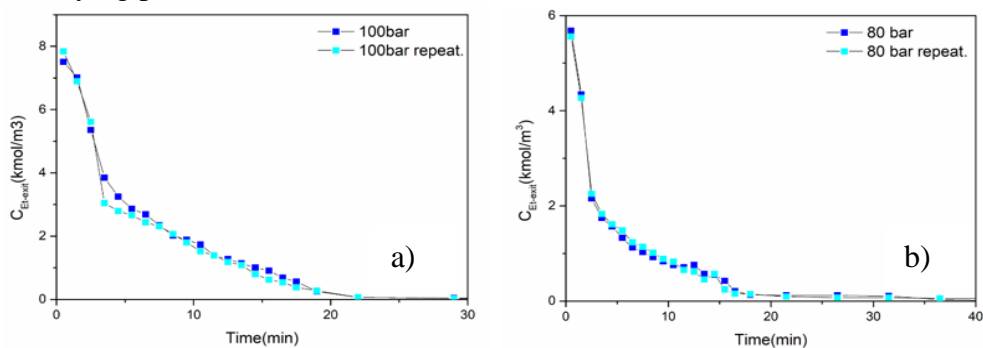
## RESULTS

In order to accurately evaluate the evolution of ethanol concentration during the course of supercritical drying, the mass balance for ethanol during a particular run should be closed with a reasonable percent deviation. Drying experiments at 313 K and 100-80 bars with CO<sub>2</sub> flow rate of 2 L/min using half-filled 100ml tubular vessel were initially performed to study mass balance closure and reproducibility. Entering and exit masses were compared as described in previous section and the percent difference between the two was found to be less than %1 in both of the experiments as shown in Table 1.

**Table 1.** Comparison of entering and exit masses for experiments at 100 bar and 80 bar.

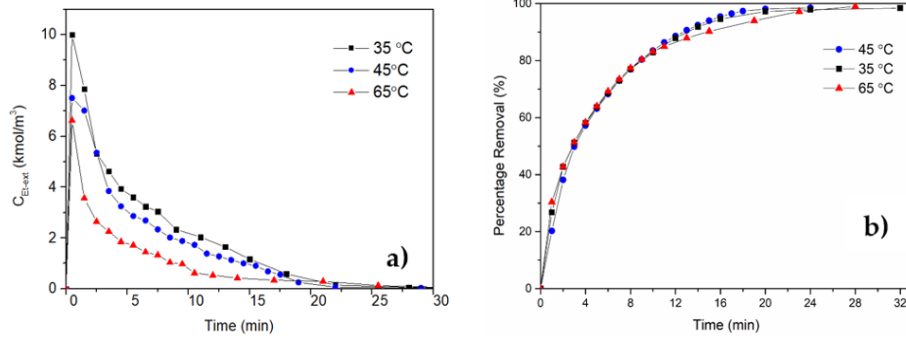
	Entering mass (g)			Exit mass (g)			Difference (%)
	Alcogel Mass	Excess Ethanol	Total	Aerogel Mass	Ethanol Exit	Total	
<b>100 bar</b>	24.0	19.2	43.2	1.110	41.72	42.8	0.93
<b>80 bar</b>	24.5	19.2	43.7	1.122	42.43	43.6	0.23

Moreover, plots of ethanol exit concentration, calculated using the collected ethanol amounts in the vial, versus time were plotted as in Fig. 2 for repeated experiments for each case. Added excess ethanol to cover the beads was not considered in development of the concentration versus time curves. A good reproducibility was obtained in both cases indicating the adequacy of the proposed drying procedures.



**Figure 2.** Concentration ethanol in the exit stream from the vessel as a function time for a) 100 bar, 313 K and 2 L/min CO<sub>2</sub> flow rate, b) 80 bar, 313 K and 2 L/min CO<sub>2</sub> flow rate.

Fig. 2 shows that there was a rapid decrease in ethanol concentration indicating a fast drying mechanism for first 4 minutes of drying. Calculations shows that almost 65% of the ethanol in the alcogel were extracted in this period. Then, the rate of concentration drop was decreased until the completion of drying. Subsequently, effects of operating conditions were investigated. Experiments were carried out in three different temperatures as 35 °C, 45 °C and 65 °C at 100 bar with an exit CO<sub>2</sub> gas flow rate of 2 L/min to investigate the effect of temperature on concentration profiles. Results were plotted in Fig. 3.



**Figure 3.** Ethanol exit concentration change (a) and percent removal (b) with time for different temperatures for supercritical drying of calcium alginate beads [8].

Temperature was found to affect the concentration profiles due to the change in the density of scCO<sub>2</sub> whereas the drying time was not changed considerably. In contrast, changing the flow rate influenced the drying time significantly since shorter drying times were found for faster CO<sub>2</sub> flow rates. A very small percent shrinkage was observed in all of the experiments.

A physical model taking diffusion of ethanol from the pores of gel, mass transfer of ethanol from gel surface to flowing CO<sub>2</sub> stream and convection and axial dispersion of ethanol in the CO<sub>2</sub> into account was proposed. Partial differential equation governing mass transfer of the solvent inside a spherical gel is given by;

$$\frac{\partial C_s}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 D_e \frac{\partial C_s}{\partial r} \right) \quad (1)$$

where  $C_s$  is concentration of ethanol in the gel;  $D_e$  is effective diffusion coefficient;  $t$  is time (s);  $z$  and  $r$  is the direction that diffusion occurs in the gel. The initial condition and the boundary conditions were selected as;

$$t = 0 \quad C_s = C_{s0} \quad (2)$$

$$r = 0 \quad \frac{\partial C_s}{\partial r} = 0 \quad (3)$$

$$r = R \quad D_e \frac{\partial C_s}{\partial r} = k_f (C_f - C_{fR}) \quad (4)$$

where  $C_f$  is concentration of the ethanol in the fluid phase (scCO<sub>2</sub>) ;  $R$  is the radius of the gel where  $C_{fR} = C_{sR}$ ,  $C_{sR} = C_s$  at  $r = R$ .

The partial differential equation obtained from a mass balance in a differential volume element outside of the gel in the fluid phase is given by;

$$\frac{\partial C_f}{\partial t} = D_L \frac{\partial^2 C_f}{\partial z^2} - u_0 \frac{\partial C_f}{\partial z} - \frac{3(1-\varepsilon)}{\varepsilon} \frac{1}{R} k_f (C_f - C_{fR}) \quad (5)$$

where  $D_L$  is axial dispersion coefficient;  $\varepsilon$  is the porosity of the gel;  $k_f$  external mass transfer coefficient;  $u_0$  is the velocity of scCO<sub>2</sub>. The initial condition and the boundary conditions were selected as;

$$t = 0 \quad C_f = 0 \quad (6)$$

$$z = 0 \quad u_0 C_f - D_L \frac{\partial C_f}{\partial z} = 0 \quad (7)$$

$$z = L \quad \frac{\partial C_f}{\partial z} = 0 \quad (8)$$

Eq. 1- 4 indicate that mass transfer mechanism inside the gel particles is diffusion whereas at the surface of the gel, where  $r=R$ , there is an external mass transfer from surface into the fluid phase. Symmetry and continuity boundary conditions were considered. Moreover, the right hand side of Eq. 5 accounts for mass transfer of ethanol in the fluid phase, the first term denotes the axial dispersion of ethanol, the second term denotes the mass transfer of ethanol by convection in the  $z$  direction in the vessel, the last term represents the mass transfer taking place between the gel surface and the flowing stream of  $scCO_2$ . Initially pores of the gel were assumed to be filled with pure ethanol as in Eq. 2. However, ethanol concentration in the flowing stream of  $scCO_2$  was assumed to be zero at the start of the drying according to Eq. 6. There was good agreement between experimental concentration profiles and the model results.

## CONCLUSION

In this study, kinetics of supercritical drying of calcium alginate algogel particles in a packed bed was investigated. Spherical calcium alginate particles with a diameter of 0.4cm were prepared and subsequently supercritical drying was performed to obtain aerogels. Kinetics were studied by monitoring exit ethanol amount during the course of drying. Temperature and pressure did not affect the drying time considerably whereas the influence of flow rate on drying time and exit ethanol concentration was significant. Moreover, a physical model considering diffusion of ethanol from the pores of gel, mass transfer of ethanol from gel surface to flowing  $CO_2$  stream and convection and axial dispersion of ethanol in the  $CO_2$  was proposed first time in the literature for the supercritical drying of gel to produce aerogels.

## ACKNOWLEDGEMENTS

We acknowledge European Union's Horizon 2020 research and innovation programme under grant agreement No 685648 for their funding and support.

## REFERENCES

- [1] J.L. Gurav, I.-K. Jung, H.-H. Park, E.S. Kang, D.Y. Nadargi, Silica Aerogel: Synthesis and Applications, *J. Nanomater.* 2010 (2010) 1–11. doi:10.1155/2010/409310.
- [2] C. Moreno-Castilla, F.J. Maldonado-Hódar, Carbon aerogels for catalysis applications: An overview, *Carbon N. Y.* 43 (2005) 455–465. doi:https://doi.org/10.1016/j.carbon.2004.10.022.
- [3] J. Stergar, U. Maver, Review of aerogel-based materials in biomedical applications, *J. Sol-Gel Sci. Technol.* 77 (2016) 738–752. doi:10.1007/s10971-016-3968-5.
- [4] Z. Ulker, C. Erkey, An emerging platform for drug delivery: Aerogel based systems, *J. Control. Release.* 177 (2014) 51–63. doi:10.1016/j.jconrel.2013.12.033.
- [5] T. Mehling, I. Smirnova, U. Guenther, R.H.H. Neubert, Polysaccharide-based aerogels as drug carriers, *J. Non. Cryst. Solids.* 355 (2009) 2472–2479. doi:10.1016/j.jnoncrysol.2009.08.038.
- [6] C.A. García-González, M. Alnaief, I. Smirnova, Polysaccharide-based aerogels - Promising biodegradable carriers for drug delivery systems, *Carbohydr. Polym.* 86 (2011)

- 1425–1438. doi:10.1016/j.carbpol.2011.06.066.
- [7] C.A. García-González, I. Smirnova, Use of supercritical fluid technology for the production of tailor-made aerogel particles for delivery systems, *J. Supercrit. Fluids.* 79 (2013) 152–158. doi:10.1016/j.supflu.2013.03.001.
- [8] İ. Şahin, Y. Özbakır, Z. İnönü, Z. Ulker, C. Erkey, Kinetics of Supercritical Drying of Gels, *Gels* . 4 (2018). doi:10.3390/gels4010003.
- [9] A.M. Orlović, S. Petrović, D.U. Skala, Mathematical modeling and simulation of gel drying with supercritical carbon dioxide, *J. Serbian ....* 70 (2005) 125–136. <http://scindeks.ceon.rs/article.aspx?artid=0352-51390501125O%5Cnpapers3://publication/uuid/C1E76FEF-7998-4759-B1BB-7353CE25B68B>.
- [10] P. Wawrzyniak, G. Rogacki, J. Pruba, Z. Bartczak, Effective diffusion coefficient in the low temperature process of silica aerogel production, *J. Non-Cryst. Solids.* 285 (2001) 50–56. doi:[https://doi.org/10.1016/S0022-3093\(01\)00431-8](https://doi.org/10.1016/S0022-3093(01)00431-8).
- [11] Y. Masmoudi, A. Rigacci, P. Ilbizian, F. Cauneau, P. Achard, Diffusion during the supercritical drying of silica gels, *Dry. Technol.* 24 (2006) 1121–1125. doi:10.1080/07373930600778270.
- [12] C.A. García-González, M.C. Camino-Rey, M. Alnaief, C. Zetzl, I. Smirnova, Supercritical drying of aerogels using CO<sub>2</sub>: Effect of extraction time on the end material textural properties, *J. Supercrit. Fluids.* 66 (2012) 297–306. doi:10.1016/j.supflu.2012.02.026.
- [13] J.S. Griffin, D.H. Mills, M. Cleary, R. Nelson, V.P. Manno, M. Hodes, Continuous extraction rate measurements during supercritical CO<sub>2</sub> drying of silica alcogel, *J. Supercrit. Fluids.* 94 (2014) 38–47. doi:10.1016/j.supflu.2014.05.020.
- [14] Y. Özbakır, C. Erkey, Experimental and theoretical investigation of supercritical drying of silica alcogels, *J. Supercrit. Fluids.* 98 (2015) 153–166. doi:10.1016/j.supflu.2014.12.001.
- [15] M. Mukhopadhyay, B.S. Rao, Modeling of supercritical drying of ethanol-soaked silica aerogels with carbon dioxide, *J. Chem. Technol. Biotechnol.* 83 (2008) 1101–1109. doi:10.1002/jctb.1996.