Experimental and Theoretical Investigation of Supercritical Drying of Composites of Silica Aerogels with Polymers

Can Erkey [a*], Yaprak Özbakır[a]

[a*] *Department of Chemical and Biological Engineering, Koc University, 34450 Sarıyer, Istanbul, Turkey*

cerkey@ku.edu.tr

ABSTRACT

Nanostructured composites of silica aerogels with polymers are promising for use as core materials in transparent vacuum insulation panels. An important factor which governs the economics of production of such panels is the capital and operating costs associated with the supercritical drying process and the effects of the polymer content on drying times. Therefore, an understanding of the kinetics of supercritical CO_2 (sc-CO_2) drying of silica aerogel composites and modeling of the process is necessary to provide insight into material development, scale-up and optimization of the composite aerogel manufacturing process.

In this study, partial differential equations representing mass transfer within a cylindrical silica alcogel phase and in the bulk sc-CO_2 phase were developed and solved using finite difference method. The effects of CO_2 flow rate, gel thickness and gel porosity which changed with polymer content on drying times were investigated. The model results were also compared to experimental data obtained in an extraction vessel designed such that sc-CO_2 flowed around a cylindrical alcogel synthesized with diameters around 1 cm and heights ranging from 10 cm to 16 cm. Solvent in the outlet stream of extractor was collected in glass vials sealed and submerged in a dry ice bath to minimize evaporation and condense all of the ethanol. Experiments were carried out at 313 K and 100 bar and drying times ranged from 3 to 8 hours. Increasing flow rate resulted in a decrease in trying times.

The mass transfer coefficients were regressed from experimental data and ranged from 3.08×10^{-4} ms^{-1} to 6.59×10^{-4} ms^{-1} and were found to be in good agreement with values calculated from the correlations in the literature developed for supercritical extraction from porous matrices. Mass transfer coefficients increased with increasing flow rate. The effect of the polymer content on drying could be estimated by taking into account of the change of porosity with polymer incorporation. This is the first study that shows the importance of convective mass transfer on the kinetics of drying.

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, high thermal insulation value and low dielectric constant [1, 2], making them outstanding for a wide variety of applications. 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. Removal of the liquid solvent in such a way to avoid as much as possible its textural modifications preserving its original intact, nanoporous network is the most difficult stage in aerogel production [3-7]. Differential strain arising from capillary pressure can be eliminated by using the supercritical drying process [7-10]. However, the fragility issue of the aerogel materials imposes limitations on transportation, application, handling and operational lifetime of the aerogel materials. It is possible to make it much stronger by increasing their tensile strength by compounding with polymers.

There are few studies in the literature in modeling of supercritical drying of alcogel with sc-CO_2. Mukhopadhyay and Rao [7] modeled two-way mass transfer of ethanol and sc-CO_2 to and from the alcogel in a vessel which was initially filled with pure ethanol at a temperature of 313 K and at a pressure of 40 bar. Concentration variation of CO_2 with time and distance from the open end was calculated utilizing Fick's second law combining both molecular and Knudsen diffusion with composition dependences of the binary liquid phase diffusivity of ethanol-CO_2. The convective mass transfer of ethanol from the open-end of the pore assisted by the flow of CO_2 was calculated using correlations for the Sherwood number. They concluded that ethanol is removed mostly by spillage because of the volume expansion in the pore liquid by dissolution of sc-CO_2 and slightly by convective evaporation towards the end of the drying period. Moreover, it was concluded that gel thickness and flow velocity of sc-CO_2 strongly affects the drying time. As flow velocity decreases, it significantly increases and it increases with reducing temperature and increasing pressure. García-González et al. [9] investigated drying of alcogels prepared from different precursors with different densities and morphologies. 1.2 cm diameter x 3 cm long alcogel rods were dried with a flow rate of 0.234 kg/h in a 25 ml-tubular at a temperature of 318 K and pressure of 110 bar. Ethanol-rich liquid 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 device to determine its ethanol content. Furthermore, they modeled alcogel drying by using Fick's second law in cylindrical coordinates. 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 for the removal of the very tiny amount of remnants of ethanol.

In this present work, the kinetics of supercritical CO_2 drying of silica aerogel composites and modeling of the process is investigated by comparing model results and experimental studies of drying. Partial differential equations representing mass transfer within a cylindrical silica alcogel phase and in the bulk sc-CO_2 phase in the tubular extraction vessel were developed and solved using finite difference method. The extraction vessel and sample geometry was designed such that the differential model equations derived were sufficiently well representative the drying process and the boundary conditions were well-defined. The primary difference of this study from the other works is that the model equations incorporated both diffusion and convective mass transfer; thus, the change in concentration of ethanol in

CO_2 as a function of time and position in two dimensions within the alcogel phase as a function of time and position in the free volume of the vessel. Moreover, experimental studies with continuous flow of a sc-CO_2 stream through the concentric annulus in which cylinder shaped alcogels occupy almost half of the free volume of the extraction vessel have been carried out and the model results were compared to the experimental data and reported.

MATERIALS AND METHODS

Preparation of cylindrical silica alcogel samples

Silica alcogel samples were prepared using the conventional two step sol-gel process [2]. Tetraethylorthosilicate (TEOS, 98% purity; AlfaAesar) was used as the silica precursor, hydrochloric acid (HCl, 37% purity; Riedel-de Haen) as the acid catalyst, and ammonia (NH_3) (2.0 M in ethanol; Aldrich) as the base catalyst. As the first step, a solution was prepared by mixing TEOS, ethanol (99.9% purity; Merck) and water with the mass ratio 1:1:0.34. Next, the acid catalyst was added (0.048 M in ethanol) to accelerate the hydrolysis reactions. The mixture was stirred at room temperature for 60 min. Then, the base catalyst (2.0 M in ethanol) was added to the solution to increase the rates of condensation reactions. Before gelation, the solution was poured into a plastic syringe-based mold 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. Finally, the aging solution was replaced with pure ethanol in which the resulting alcogels were soaked for 4 days; solvent exchange with fresh ethanol was repeated several times leading to remove any impurities and water remaining in the pores of the alcogel.

Drying: Supercritical Drying of Silica Alcogel with Sc-CO_2

Subsequent to the alcogel preparation, supercritical extraction of the alcohol fully occupying in the pores of the alcogel was performed. A schematic diagram of the extraction unit used in this study is shown in Figure 1. It basically consists of a high pressure extraction vessel with a volume of 26 ml, a pump, a separator, a carbon dioxide cylinder, a gas flow meter and a control unit controlling the temperature of the extractor.

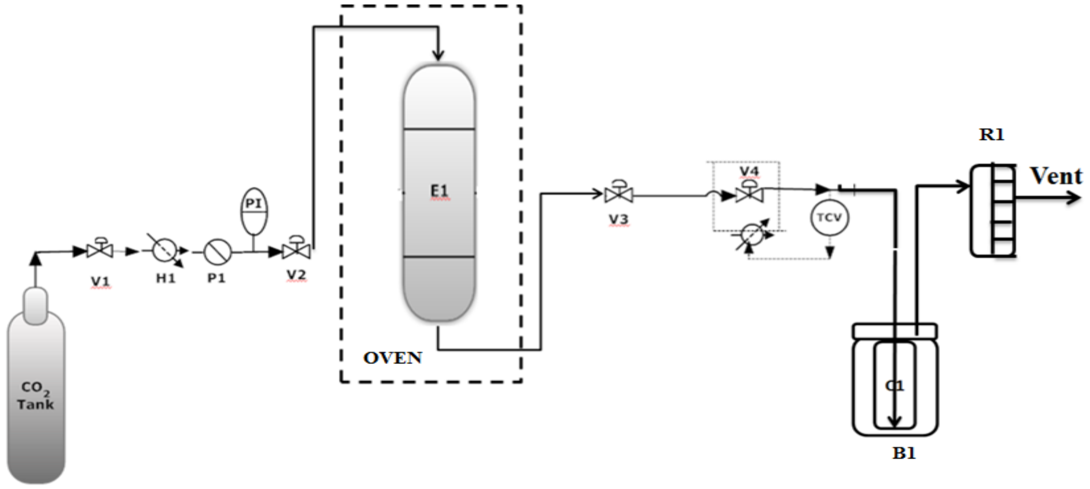
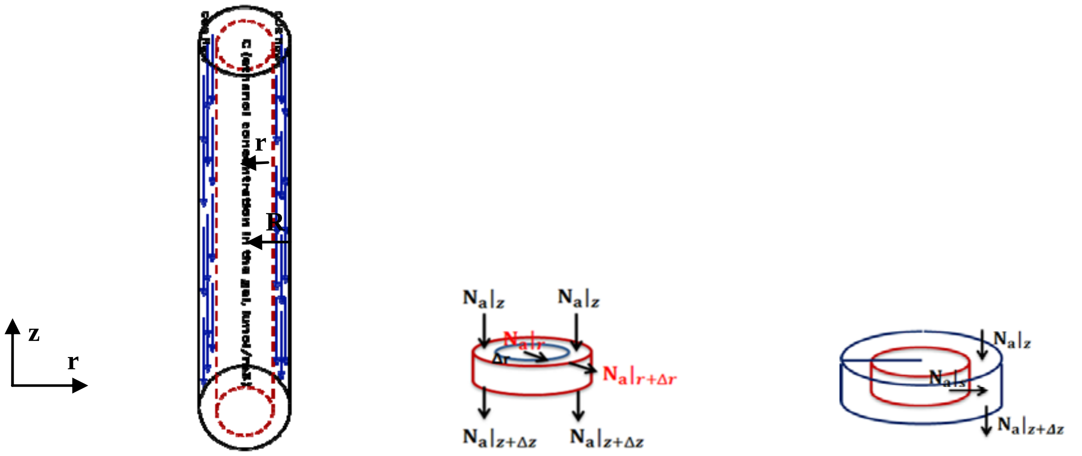


Figure 1: Schematic representation of process flow diagram of the supercritical drying with sc-CO_2 in Continuous Flow (V1-V4: valves; P1: Pump; H1: Cooler; E1: Extraction vessel; PI: Pressure transducer; TCV: Thermocouple; C1: Ethanol Collection Vial; B1: Ethanol-Dry ice bath; R1: Rotameter.

The extraction vessel (E1 in Figure 1) was initially filled with ethanol to prevent contact of the sample with air and evaporation of the solvent from the gel leading to the shrinkage of the solid and the occurrence of cracks. Then, the alcogel rod was weighed and immediately submerged in ethanol in the vessel. Temperature of the vessel and of the micro-metering valve (V4 in Figure 1) controlling the CO_2 flow rate, were set to 313.15 K and the vessel was preheated to the extraction temperature. After temperature stabilization, the system was pressurized with carbon dioxide until the desired operating pressure of 100 bar was reached (P1 in Figure 1). The outlet micro-metering (V6 in Figure 1.) valve was adjusted to give the desired flow rate of CO_2 (1.5 L/min or 3 L/min). The outlet flow of CO_2 from the extractor was expanded through a restrictor valve (V4 in Figure 1.). The gaseous CO_2 stream was then separated in two streams: a gaseous stream enriched in CO_2 and a liquid stream which is enriched in ethanol. The gaseous stream vented through a fume hood and the liquid stream was collected in glass vials sealed and immersed in a dry ice bath at ambient pressure and at -78 °C to minimize evaporation of ethanol in the stream and to condense almost all fraction of ethanol. Excess amount of ethanol added to the vessel was first totally removed from the vessel in about 5 min. Mass of ethanol extracted from its porous nature was subsequently started to be collected in the vials as a function of time and was weighed. After a certain period of time of the extraction, the vessel was gradually depressurized to the ambient pressure at 313.15 K and at a constant flow rate of CO_2 previously adjusted and the dried sample was subsequently collected from the vessel.

Modeling of Mass Transfer in Cylindrical Silica Alcogel

Supercritical extraction of the cylindrical alcogel in flowing stream of sc-CO_2 is shown in Figure 2. In development of model equations, ethanol concentration is assumed to be initially uniform throughout the alcogel volume.



Shell over the alcogel

(a)

Shell over the space between vessel wall and the alcogel surface

(b)

Figure 2 : Schematic representation of shell mass balance in the continuous system
(a) Representation of the shell over the cylindrical alcogel with thickness of Δr
(b) Representation of the shell over annulus of vessel and alcogel with thickness of Δz

Partial differential equations governing mass transfer in the pores of the alcogels were derived performing mass balances for one component in the system over a differential volume and segment of each alcogels (Figure 2 a). Molar mass balance of ethanol over the differential segments inside of the porous gel network and in the bulk flow in the vessel was separately done (Figure 2 b) The contribution of mass transfer through diffusion phenomenon to the ethanol removal from the cylindrical alcogel was evaluated by using Fick's second law in cylindrical coordinates.

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\,D_e\frac{\partial C_a}{\partial r}\right)+\frac{1}{r}\left(D_e\frac{\partial C_a}{\partial r}\right)+\frac{\partial}{\partial z}\left(D_e\frac{\partial C_a}{\partial z}\right)=\frac{\partial C_a}{\partial t} \qquad (2)$$

where C_a is concentration of ethanol in the wet gel, (kmol/m^3), D_e is effective diffusion coefficient, (m^2/s) and t is time (s), z and r is the direction that diffusion occurs in aerogel.

The removal of ethanol away from the alcogel surface to the bulk flow in the vessel assisted by the flow of sc-CO_2 and variation of ethanol concentration in the surrounding flow as a function of time and position is also depicted in the following equation developed.

$$\frac{2rK_x(C_s-C_v)}{(R^2-r^2)}-v_z\frac{\partial C_v}{\partial z}=\frac{\partial C_v}{\partial t} \qquad (3)$$

where C_v represents ethanol concentration in the bulk flow, (kmol/m^3), R is inner radius of the vessel (m), r is radius of the alcogel, K_x is mass transfer coefficient (m/s), v_z is velocity of the bulk flow of sc-CO_2 in the vessel.
The initial and boundary conditions are given by:

Initial Conditions : t=0 $C_a(r,z,0) = C_i$ (2.1a)
t=0 $C_v(z,0) = 0$ (2.2a)

Boundary Conditions: t>0 $\frac{\partial C_a}{\partial r} = 0$ at r=0 (2.1b)
t>0 $\frac{\partial C_a}{\partial r} = 0$ at z=0 (2.1c)
t>0 $\frac{\partial C_a}{\partial r} = 0$ at z=L (2.1d)
t>0 $N_{a,s} = K_x(C_s - C_v)$ at r=r (2.2b)
t>0 $N_{a,s} = N_{a,r}$ at r=r (2.2c)

where $N_{a,r}$ is diffusion flux kmol ethanol/s m^2.

Effective diffusivity in this porous material was calculated using the binary diffusion coefficient, material overall porosity and tortuousity, as shown in Eq. 3. The binary diffusivity of ethanol and sc-CO_2 at supercritical drying temperature and pressure was calculated using

Eq. 5 given below; the porosity was taken as the overall porosity and tortuosity values of 1.5 and 3 were used (commonly used values for porous materials [6]).

$$D_e = \frac{(D_{12}\varepsilon)}{\tau} \qquad (3)$$

Mukhopadhyay and Rao calculated the diffusivity at a particular composition, by Vignes Correlation below [7]:

$$D_{12}^{l} = (D^{og})^{x1}(D^{ol})^{1-x1} \qquad (4)$$

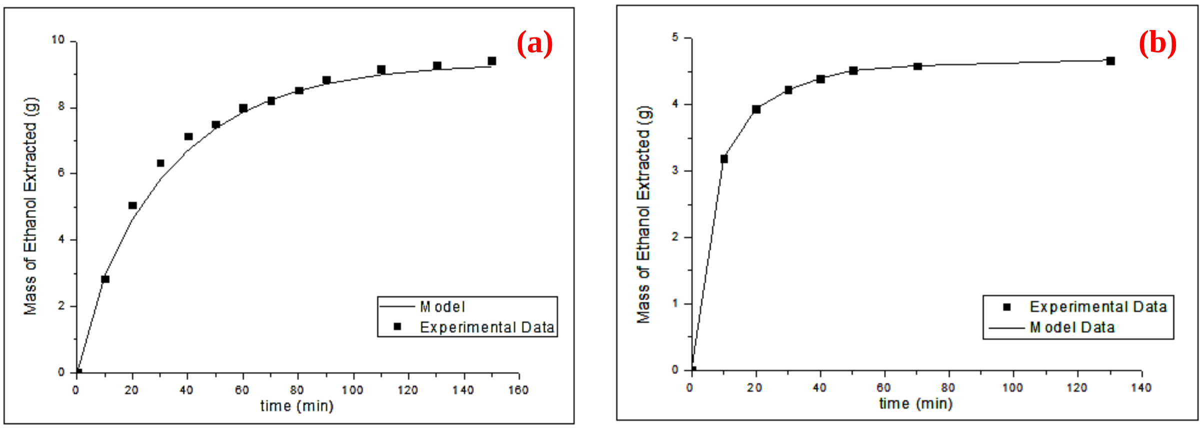
where (D^{og}) is binary diffusion coefficient of ethanol in sc-CO_2 in the ideally diluted state and (D^{ol}) is binary diffusion coefficient of sc-CO_2 in ethanol in the ideally diluted state. In this study, the average of the values of D^{og} and D^{ol} was used to calculate D_{12}^{l}.

For the prediction of the diffusivity of sc-CO_2 in ethanol (D^{ol}) at supercritical drying conditions and diffusivity of ethanol in sc-CO_2, the method of Wilke and Chang [21] shown by Eq. 3.3.2.4.3 was used.

$$D_{12} = 1.1728 * 10^{-16} \frac{T(\dot{x}_2 M_2)^{1/2}}{\mu_2 {V_1}^{0.6}} \qquad (5)$$

RESULTS

Figure 3 (a), Figure 3 (b) and Figure 3 (c) show mass of ethanol collected in the collection vial immersed in the dry ice bath as a function of time and the data obtained by the solution of the model equations. It can be seen that the present model proposed for the alcogel drying with sc-CO_2 for replacement of ethanol from the porous structure of the alcogel fits satisfactorily well with the experimental data. During the initial period of the drying, large amount of ethanol was removed from the porous structure of the samples due to a large difference in concentration of ethanol between the liquid phase in the alcogel pores and in the flowing stream of sc-CO_2 in the vessel leading to readily diffusion of ethanol out of the pores into sc-CO_2. The ethanol diffused in the vicinity of the gel surface is removed by convective mass transfer assisted by the continuous flow of sc-CO_2 in the vessel. Then, amount of ethanol extracted per unit time slowed down and diffusion controlled mass transfer mechanism predominated by the end of the process; however convective mass transfer of ethanol is still present in the process.



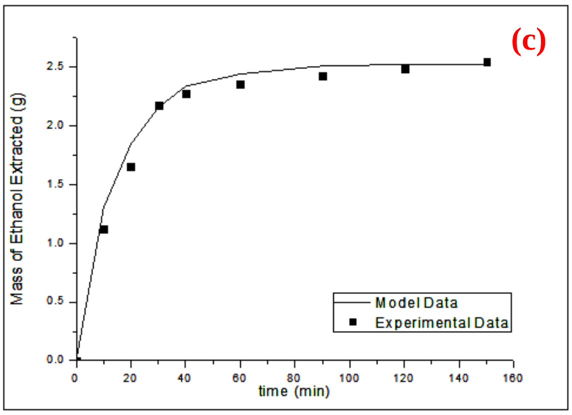


Figure 3: (a) Comparison of ethanol extraction with experimental data and mathematical model at 100 bar 40 ºC, v_z= 0.001065 ms^{-1}, K_x=3.08×10^{-4} ms^{-1}, sample thickness= 0.595 cm, sample length=15.9 cm **(b)** Comparison of ethanol extraction with experimental data and mathematical model at 100 bar 40 ºC, v_z= 0.00213 ms^{-1}, K_x=4.12×10^{-4} ms^{-1}, sample thickness= 0.475 cm, sample length=11.2 cm **(c)** Comparison of ethanol extraction with experimental data and mathematical model at 100 bar 40 ºC, v_z= 0.0128 m s^{-1}, K_x=6.59×10^{-4} ms^{-1}, sample thickness= 0.475 cm, sample length=9.18 cm

Mass transfer coefficients for the solutions of governing model equations of each sample in Matlab were compared with the calculated mass transfer coefficient values using proposed correlations in the literature. However, a mass transfer coefficient value, which is exactly fit with such a system of liquid- supercritical CO_2 extraction with continuous flow, has not already been included in the literature. Therefore, a couple of Sherwood number correlations which is analogous with our system were used. The calculated and estimated data of the mass transfer coefficient are tabulated in Table 4. Since the values are comparable and of the same order of magnitude, this agreement justifies the validity of the present model in view of the approximate nature of the mass transfer coefficient.

Table 4: Validation of estimated values of mass transfer coefficient values with

Sherwood Number Correlations	**K_x (ms^{-1}) (1)**	**K_x (ms^{-1}) (2)**	**K_x (ms^{-1}) (3)**
$Sh = 2 + 1.1 Re^{0.6} Sc^{1/3}$ [8]	2.49×10^{-4}	3.51×10^{-4}	5.21×10^{-4}
$Sh = 0.206 Re^{0.8} Sc^{1/3}$ [7]	1.86×10^{-4}	2.92×10^{-4}	6.58×10^{-4}
Estimated Value :	3.08×10^{-4}	4.12×10^{-4}	6.59×10^{-4}

Effects of Gel Porosity on Extraction

Effect of the polymer content on alcogel drying can be estimated by the change of porosity with polymer incorporation. As polymer content increases in the aerogel structure, its porosity decreases. The extraction time of ethanol alcogel phase with porosities of 98 %, 95% and 92 %, respectively, was examined by simulations. Figure 5 shows that extraction time barely decreases with increasing porosity. Ethanol is extracted slightly faster in the alcogel with the highest porosity because effective diffusivity shows a small increase with increasing porosity. This result is also important in estimating the drying time of polymer-silica aerogel composites such as PDMS-Silica aerogel and PVP- Silica aerogel composite since composite aerogels are less porous than silica aerogels. Thus, ethanol extraction time from the pores of the alcogel is expected to be a bit longer than that for the extraction of silica aerogels.

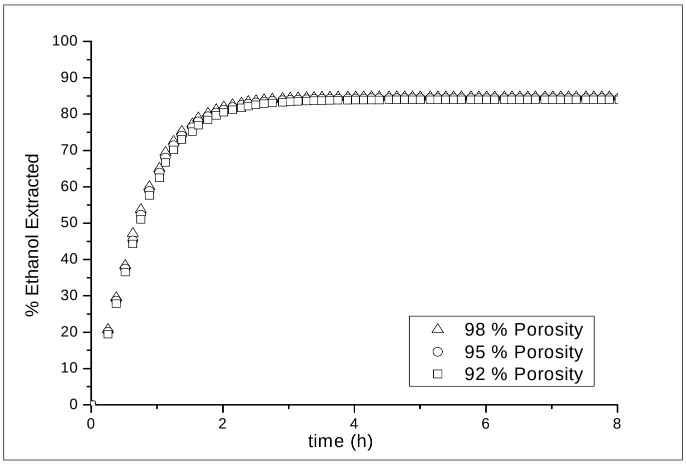


Figure 5: Effect of porosity on ethanol removal over time in spherical aerogels (T= 313 K, P=100 bar, gel thickness =2 cm, Kx=$1.3*10^{-5}$ m/s)

CONCLUSION

Coupled two dimensional and unsteady state mathematical model equations governing mass transfer within the alcogel phase and in the bulk phase were developed. The effect of the polymer incorporation into the silica aerogel structure on its drying time could be examined by the change of porosity with polymer incorporation through simulations. As porosity decreases, the extraction time of ethanol from the alcogel network slightly increased.

Supercritical drying of alcogel was described by a mass transfer mechanism based on convection and diffusion. Variation of ethanol concentration as a function of time and positions in the r and z directions within the aerogels and in the continuous flowing stream of sc-CO_2 were investigated. Mass of ethanol extracted from the pores of the alcogel was collected as a function of time in the vials submerged in the dry ice bath. The present model results and the experimental data of the ethanol extraction were found in satisfactorily good agreement. Mass transfer coefficient estimated from the experimental data was attained comparable and of the same order of magnitude with the correlations proposed in the literature for the supercritical extraction. This analogy justified the validity of the present model in the view of the approximate nature of the mass transfer coefficient. It is concluded that higher velocity of continuous sc-CO_2 flow and mass transfer coefficient accelerates the removal of primary solvent due to faster convective mass transfer and convective mass transfer of solvent mostly contributes to the process in the beginning of the extraction, whereas mass transfer through diffusion relatively predominates as extraction time progressed and less solvent remained in the alcogels, which is sluggish and takes long time for drying.

REFERENCES

[1] Soleimani Dorcheh, A. and M.H. Abbasi, Silica aerogel; synthesis, properties and characterization. Journal of Materials Processing Technology, 199(1-3) **2008**.: p. 10-26.

[2] Pajonk, G.M., ChemInform Abstract: Aerogel Catalysts. ChemInform, **1991**. 22(33): p. no-no.

[3] Hench, L.L. and J.K. West, *The sol-gel process.* Chemical Reviews, 90(1). **1990** p. 33-72.

[4] Rakesh P. Patel., N.S.P., Ajay M Suthar, *An Overview of Silica Aerogels.* International Journal, 1(4) **2009**. p. 1052-1057.

[5] Huijun Wu, Yantao Chen, Qiliang Chen, Yunfei Ding, Xiaoqing Zhou, and Haitao Gao, Synthesis of Flexible Aerogel Composites Reinforced with Electrospun Nanofibers and Microparticles for Thermal Insulation, Journal of Nanomaterials, 2013, **2013.**

[6] Aleksander Orlovic, Stojan Petrovic and Dejan Skala, Mathematical Modeling and Simulation of gel drring with supercritical caron dioxide, J. Serb. Chem. Soc.70 (1) **(2005)** 125-136.

[7] Mamata Mukhopadhyay and Bhatta Sankara Rao, Modeling of supercritical drying of ethanol-soaked silica aerogels with carbon dioxide, Journal of Chemical Technology and Biotechnology, 83 **(2008).** 1101-1109.

[8] Dana E. Knox, Solubilities in supercritical fluids, Pure Appl. Chem, 77(3) **2005**. 513-530.

[9] C. A. Garcia-Gonzalez, M.C. Camino-Rey, M. Alnaief, C. Zetzl, I. Smirnova, Supercritical drying of aerogels using CO_2: Effect of extraction time on the end material textural properties, Journal of Supercritical Fluids, 66 **2012** 297-306.