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SCIENTIFIC PAPER

519.87:54–148+541.18.045:628.937

MATHEMATICAL MODELING OF GEL DRYING WITH SUPERCRITICAL CARBON DIOXIDE

The most complex step in the production of aerogels is the supercritical drying step, and it is therefore important to study its dynamics using mathematical models. Alumina/silica aerogel was obtained using a one step sol–gel synthesis and subsequent drying with supercritical carbon dioxide. The wet gel weight change with time was monitored. The dry aerogel sample porous structure was determined using the BET method and nitrogen adsorption/desorption. Supercritical drying of the wet gel sample was represented as the unsteady and one dimensional diffusion of 1–butanol through aerogel pores filled with supercritical carbon dioxide. Different mathematical models describing supercritical drying of the wet gel cylindrical sample were developed. Shrinking core models used one value of the effective diffusivity for the whole material, and they failed to describe the drying experiment correctly. Parallel pore models used different effective diffusivity values for each pore size. The best simulation results were obtained using the parallel pore model with local porosity or tortuosity values for each pore size.

After dissolution of the reactants in an appropriate solvent and subsequent gelation of the sol, the formed wet gel can be dried by several methods. When elevated temperature and atmospheric pressure or vacuum are applied, the presence of two phases (a liquid and a vapour one) leads to the evolution of capillary pressure in the gel pores and, consequently, cracks occur in the gel network changing its original structure. The obtained material is known as a xerogel. Another available drying method is evacuation of the solvent using supercritical drying, which produces an aerogel [1,2]. Solvent and sol–gel reaction byproducts present in the gel pores are evacuated at a temperature and pressure higher than the critical temperature and pressure of the solvent or mixture, or by another supercritical extracting fluid with moderate values of critical parameters (commonly carbon dioxide). By the supercritical drying method, evolution of the capillary pressure is avoided and the original gel structure remains largely preserved [3,4]. Aerogels are usually described as open structure materials, typically highly porous, with low particle sizes and large surface areas. Some of the fields of potential aerogels applications are: optoelectronics, special technical ceramics and heterogeneous catalysis.

Since the supercritical drying procedure represents the most complex step in the production of aerogels, mathematical modeling of the supercritical drying procedure could provide important information about scale–up and process optimization. Mathematical modeling of the extraction of etheric oils and other herbal material with supercritial carbon dioxide [5–10], and of the extraction of heavy organic compounds from the soil (polluted soil remediation) with supercritical carbon dioxide [11–13], are widely represented in the literature. To the author's best knowledge, mathematical models desribing wet gel drying with supercritical carbon dioxide are, beside being oversimplified, rarely represented in the literature [14–16].

In this paper we present a mathematical model describing wet gel drying with supercritical carbon dioxide. Alumina/silica gel with zinc chloride was obtained using a one step sol–gel synthesis with 1–butanol as solvent. The obtained wet gel was dried with supercritical carbon dioxide, and the change of mass of the drying gel was monitored in time. The aerogel porous structure was analysed using BET method with nitrogen adsorbent. The model equation was solved using the finite element method and a FORTRAN program.

EXPERIMENTAL

Sol–gel synthesis was performed according to Miller et al. [17]. Aluminium tri–sec–butoxide (9.84 g, 0.04 mol) was mixed with 1–butanol (100 cm^3) and then TEOS (8.32 g, 0.04 mol) was added. The mixture was stirred vigorously and heated to 343 K for 5 min until a clear solution was obtained. The solution was cooled to room temperature. Then, it was hydrolised with water (18.75 cm^3, 1.04 mol) in which zinc chloride (3.75 g, 0.025 mol) had already been dissolved. The solution was stirred for 15 min and left to stand overnight (gelation). The obtained gel was a viscous liquid (particulate gel), and it contained, 1–butanol (solvent), ethanol (product of TEOS hydrolysis) and water. In order to obtain an active aerogel catalyst, it was necessesary to remove water, ethanol and part of the 1–butanol, prior to supercritical drying with carbon dioxide. Water, ethanol and a certain amount of 1–butanol were then removed by heating to 423 K, and a "densed" wet gel was obtained. A glass cylinder (open at one end) was then filled with "densed" wet gel (the gel cylinder dimensions were: 11 mm height and 11 mm diameter). The wet gel sample was then placed in a 70 cm^3 tubular extractor (Autoclave Engineers Supercritical Extraction Screening System), and filled with liquid carbon dioxide

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Paper received: May 20, 2001.
Paper accepted: June 8, 2001.

from a storage cylinder. The pressure was then raised above the critical one (74 bar) at room temperature. After reaching a pressure of 80 bar, the temperature was increased to 313 K. When the desired drying conditions were reached (100 bar and 313 K), supercritical carbon dioxide flow was started through the extractor. After 30 min, the flow was stopped, the pressure was released from the system (at 313 K in order to avoid two phases of carbon dioxide), and the sample was removed from the extractor. The sample weight was recorded, and the above described procedure was repeated at regular time intervals. The total consumption of carbon dioxide was recorded for each drying time interval. The experimental drying plot obtained using the described procedure, is shown in Figure 1.

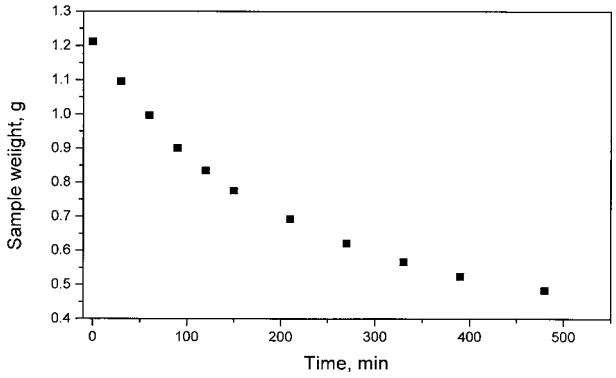

Figure 1. Experimental aerogel drying plot.

The experimental drying plot represents the wet aerogel weight change with drying time, as the result of unsteady, one dimensional and one directional diffusion of 1–butanol (solvent), through aerogel pores filled with supercritical carbon dioxide. Since the aerogel porous structure represents one of the key parameters determining the supercritical drying dynamics, a BET method using nitrogen adsorption/desorption at 77 K was used to obtain the pore size distribution of the dry

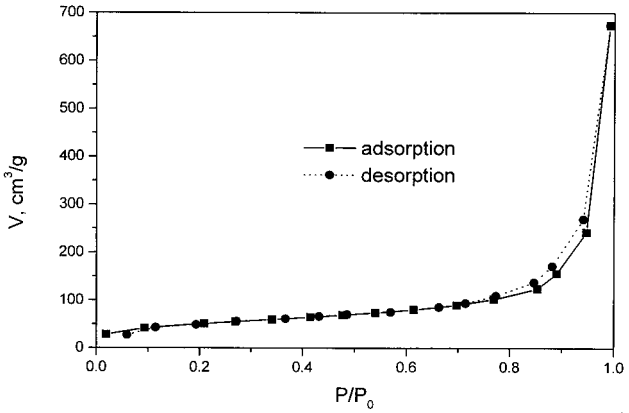

Figure 2. Adsorption/desorption isotherms of the aerogel..

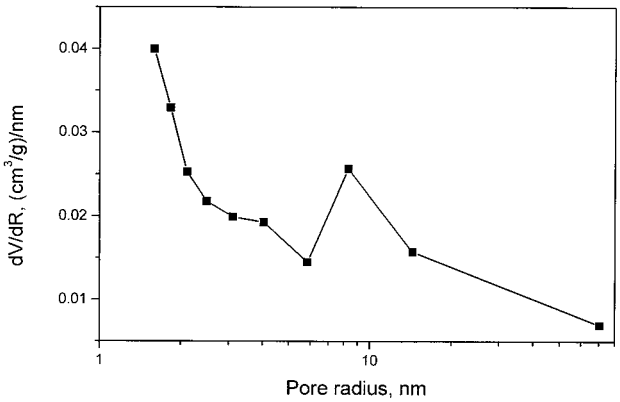

Figure 3. Pore size distribution of the aerogel.

aerogel. The adsoption and desorption isotherms are shown in Figure 2, and the pore size distribution plot (calculated using the BJH method) is shown in Figure 3. The specific surface area and total pore volume determined from BET measurements are: 175 m^2/g and 1.04 cm^3/g, respectively. When the supercritical drying experiment was finished, cracks were observed in the dry aerogel cylinder. This was expected since the wet aerogel was constrained in a glass cylinder. The volume of macropores (cracks) was calculated from the difference between the volume of lost 1–butanol (calculated from the total aerogel weight change after drying and the 1–butanol density at 298 K) and the total pore volume measured using the BET method (micro and mesopores). The distribution of pore volumes according to pore sizes is shown in Table 1.

Table 1. Pore radius, pore volume distribution, solvent weight distribution, local porosity and tortuosity of the aerogel.

Pore radius, 10^{-10}m	Pore volume, cm^3/g	1–butanol weight, g	Local porosity PPM1	Local tortuosity PPM2
>705	0.8210	0.3214	0.3630	1.00
705.08	0.7105	0.2870	0.3140	1.95
144.06	0.1550	0.0607	0.0685	2.40
83.05	0.0595	0.0233	0.0263	2.85
58.59	0.0359	0.0140	0.0159	3.30
40.45	0.0202	0.0079	0.0089	3.75
31.15	0.0150	0.0059	0.0066	4.20
24.95	0.0097	0.0038	0.0043	4.65
21.11	0.0075	0.0029	0.0033	5.10
18.38	0.0076	0.0030	0.0034	5.55
15.98	0.0039	0.0036	0.0041	6.00

MATHEMATICAL MODEL

Equation 1 represents the mathematical model of unsteady and one dimensional diffusion through a porous solid.

$$\frac{\partial C}{\partial t} = D_{eff} \frac{\partial^2 C}{\partial x^2} \quad (1)$$

The initial and boundary conditions are given as follows:

– initial condition

t = 0 (x=0) = C* and C (x>0) = Co

– boundary condition t > 0 C(x=0) = Ci.

The diffusional resistance of the supercritical carbon dioxide film above the wet/partially wet aerogel cylinder was neglected, and the 1–butanol concentration at the interface was taken to be equal to the 1–butanol concentration in the bulk supercritical carbon dioxide. The validity of this assumption was confirmed by the two orders of magnitude difference between the solubility of 1–butanol in supercritical carbon dioxide at 100 bar and 313 K, and the calculated average concentration of 1–butanol in supercritical carbon dioxide during our experiment. The solubility of 1–butanol in supercritical carbon dioxide (y_{Bu-OH} = 0.0135) was obtained using a CHEMSHARE DESIGN II computer software and the literature data [18].

The above partial differential equation with initial and boundary conditions, was solved numerically using the finite element method [19]. The partial derivatives in finite form are shown in Equations 2 and 3.

$$\frac{\partial C}{\partial t} = \frac{C_{i+1,j} - C_{i,j}}{\Delta t} + O(\Delta t) \quad (2)$$

$$\frac{\partial^2 C}{\partial x^2} = \frac{C_{i-1,j} - 2C_{i,j} + C_{i+1,j}}{(\Delta x)^2}) + 0\,[(\Delta x)^2] \quad (3)$$

The most important parameter of the mathematical model is the effective diffusivity of 1–butanol through aerogel pores filled with supercritical carbon dioxide. The effective diffusivity was calculated using the binary diffusivity coefficient, material overall porosity, constriction factor and tortuosity, as shown in Equation 4.

$$D_{eff} = \frac{D_{AB} \cdot \varepsilon_p \cdot \sigma}{\tau} \quad (4)$$

For micropores containing solids, Knudsen diffusivity can play an important role, and in that case the overall effective diffusivity can be calculated using Equation 5.

$$\frac{1}{D_{eff}} = \frac{\tau}{D_{AB} \cdot \varepsilon_p \cdot \sigma} + \frac{1}{D_K} \quad (5)$$

The binary diffusivity (1–butanol – carbon dioxide) at normal pressure and drying temperature was calculated using the Fuller, Schettler and Giddings empirical correlation [20] (Equation 6). The value of binary diffusivity at normal pressure was used to calculate the binary diffusivity at the supercritical drying pressure, using the Takahashi correlation [20] (Equation 7).

$$D_{AB} = \frac{10^{-3}\, T^{1.75}\, [(M_A + M_B)/M_A M_B]^{1/2}}{P[(\Sigma v)_A^{1/3} + (\Sigma v)_B^{1/3}]^2} \quad (6)$$

$$\frac{D_{AB}P}{(D_{AB}P)^+} = f(T_r, P_r) \quad (7)$$

The Knudsen diffusivity [21] was calculated using Equation 8.

$$D_K = \Psi \frac{2}{3} r_p \sqrt{\frac{8\,RT}{(\pi \cdot M_i)}} \quad (8)$$

Based on the method of calculation of effective diffusivity, four different mathematical models were developed. In the shrinking core model (SCM1) we used the effective diffusivity calculated from Equation 4. The binary diffusivity at the supercritical drying pressure and temperature was calculated using Equations 6 and 7, the constriction factor was assumed to be 1, the porosity was taken as overall porosity including macropores, and tortuosity values of 1.5 and 3 were used. The simulations obtained using SCM1 are shown in Figure 4. Another shrinking core model (SCM2) was based on the effective diffusivity calculated from Equation 5. In this model the binary diffusivity at the supercritical drying pressure and temperature was calculated using Equations 6 and 7, the constriction factor was assumed to be 1, the porosity was taken as overall porosity including macropores, the tortuosity value of 3 was used and the Knudsen diffusivity was obtained from Equation 8 with an average pore radius of $29.6 \cdot 10^{-10}$ m and ψ = 1. The simulation curve obtained using SCM2 is shown in Figure 5. The parallel pore model (PPM) was developed with the use of the pore size distribution data. In this model it was assumed that all pore sizes are present and in contact with supercritical carbon dioxide at each x value. For each pore radius a different effective diffusivity was calculated. In PPM1 the effective diffusivity of the macropores was calculated as the binary diffusivity, the effective diffusivities of the mesopores were calculated from Equation 4 with the use of the local values of the porosity for each pore size (Table 1) and the effective diffusivity of the micropores was calculated as the Knudsen diffusivity with a micropore average pore radius of $4.16 \cdot 10^{-10}$ m and ψ = 1. The local porosity values of the mesopores were calculated from the pore volume distribution and the overall pore volume of the aerogel. In PPM2 the effective diffusivity of the macropores was calculated as the binary diffusivity, the effective diffusivities of the mesopores were calculated from Equation 4 with the use of different values of tortuosity for each pore size (Table 1) and the effective diffusivity of the micropores was calculated as the Knudsen diffusivity with a micropore average pore radius of $4.16 \cdot 10^{-10}$ m and ψ = 1.

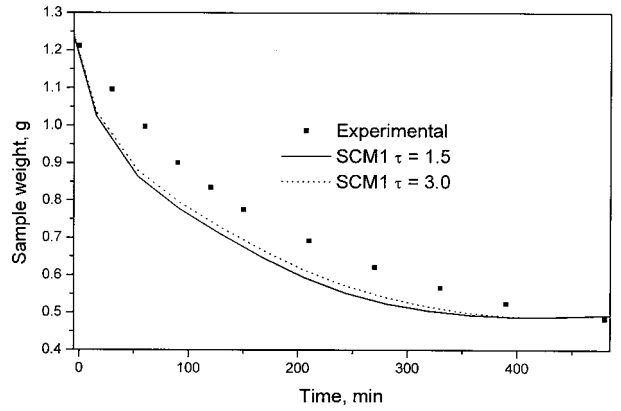

Figure 4. Simulations using SCM1 with different tortuosity values.

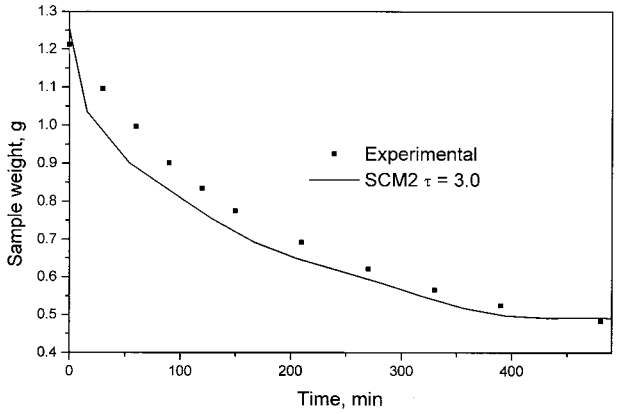

Figure 5. Simulation using SCM2.

The simulations obtained using PPM1 and PPM2 are shown in Figure 6.

The shrinking core model SCM1 which uses one value of the effective diffusivity for the whole material, fails to predict the experimental data well. This is expected, since the aerogel has a very broad pore size distribution. The accuracy of other shrinking core model SCM2, which also uses one value of the effective diffusivity for the whole material, is improved in comparison with SCM1. The main reason for the improved accuracy lies in the reduced effective diffusivity, due to the incorporation of the Knudsen diffusivity in the overall effective diffusivity. This is, however, physically unrealistic, since the average pore radius used to calculate the Knudsen diffusivity is too large for Knudsen diffusivity to occur. The best fits of the experimental data are achieved using PPM1 and PPM2. These models are based on local effective difusivity values. These local effective diffusivity values were obtained from the pore size distribution, with local porosity values (PPM1) or local tortuosity values (PPM2). Even parallel pore models fail to predict correctly the upper part of the experimental drying curve. The main reason for this are too large values of the effective diffusivity for the macropores and large mesopores. The correct fit of the lower part of the experimental drying curve with PPM1 and PPM2, confirms that the use of the local effective diffusivity values is needed in order to describe the supercritical drying process.

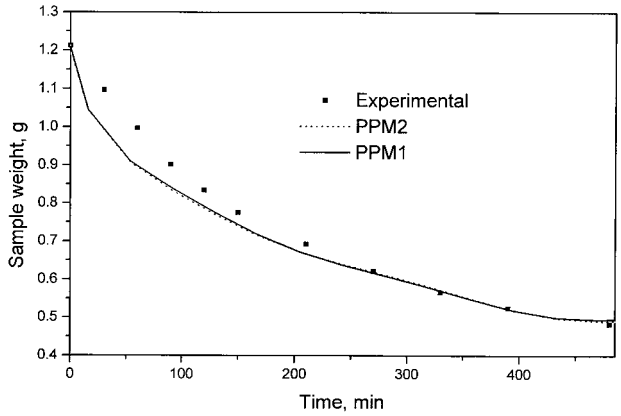

Figure 6. Simulations using PPM1 and PPM2.

CONCLUSION

Alumina/silica aerogel was obtained using a one step sol–gel synthesis and subsequent drying with supercritical carbon dioxide. The wet gel weight change was monitored during a supercritical drying procedure. The dry aerogel sample porous structure was determined using the BET method and nitrogen adsorption/desorption. Supercritical drying of the wet gel sample was represented as unsteady and one dimensional diffusion of 1–butanol through aerogel pores filled with supercritical carbon dioxide. Four different mathematical models describing supercritical drying of the wet gel cylindrical sample were developed. The shrinking core models used one value of the effective diffusivity for the whole material, and they failed to describe the drying experiment correctly. Parallel pore models used different effective diffusivity values for each pore size. Both parallel pore models (with local porosity values or local tortuosity values) simulated well the supercritical drying process.

LIST OF SYMBOLS

C – 1–butanol concentration in supercritical carbon dioxide, kmol/kmol

C* – solubility of 1–butanol in supercritical carbon dioxide, kmol/kmol

C_i – concentration at the solid/fluid interface, kmol/kmol

D_{AB} – diffusivity of 1–butanol in supercritical carbon dioxide, m^2/s

D_K – Knudsen diffusivity, m^2/s

D_{eff} – effective diffusivity, m^2/s

M – molecular weight, kg/kmol

P – pressure, bar

T – temperature, K

r_p – pore radius, m

R – gas constant, kJ/kmolK
t – time, min
x – axial distance, m

Greek letters

ε_p – porosity
Σv_i – molecular diffusion volumes in the Fuller, Schettler and Giddings correlation
σ – constriction factor
τ – tortuosity
ψ – geometric constant of the solid

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IZVOD

MATEMATIČKO MODELOVANJE SUŠENJA GELA NATKRITIČNIM UGLJEN DIOKSIDOM

(Naučni rad)

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Najsloženiji postupak u procesu dobijanja aerogelova predstavlja natkritično sušenje. U cilju ispitivanja dinamike i optimizacije procesa natkritičnog sušenja neophodno je proces opisati odgovarajućim matematičkim modelom i izvršiti njegovu simulaciju. Sintetizovan je alumosilikatni gel sa cink hloridom (katalizator za reakcije alkilacije) jednostepenim sol–gel postupkom. Eksperimentalna kriva sušenja mokrog gela sa natkritičnim ugljen dioksidom je dobijena merenjem promene mase gela sa vremenom u toku sušenja. Porozna struktura gela je karakterisana BET metodom i adsorpcijom/desorpcijom azota na 77 K. Razvijen je matematički model koji opisuje nestacionarnu jednodimenzionu difuziju rastvarača (1–butanola) kroz pore aerogela napunjene nadkritičnim ugljen dioksidom. Najvažniji parametar modela predstavlja efektivna difuzivnost. Na osnovu načina izračunavanja efektivne difuzivnosti dobijeno je nekoliko varijanti matematičkog modela. Prva dva modela su modeli sa neosušenim jezgrom, a koriste jednu vrednost efektivne difuzivnosti. Ovi modeli nisu dali dobro slaganje sa eksperimentalnim podacima. Zbog ove činjenice, kod modela sa paralelnim porama iskorišćeni su podaci o poroznoj strukturi aerogela tj. o raspodeli zapremine pora po veličini pora. Modeli sa paralelnim porama podrazumevaju da poroznu strukturu aerogela čine paralelne pore različitih dimenzija koje se istovremeno suše, ali imaju različite vrednosti za efektivne difuzivnosti u zavisnosti od dimenzija pora. Najbolje slaganje rezultata simulacije sa eksperimentalnim podacima nadkritičnog sušenja, dobijeno je sa modelom paralelnih pora kod koga su različite vrednosti efektivne difuzivnosti dobijene na osnovu različitih vrednosti za lokalne poroznosti ili lokalne izuvijanosti za pore različitih veličina.

Ključne reči: Matematičko modelovanje • Natkritično sušenje • aerogel • Efektivna difuzivnost •
Key words: Mathematical modeling • Supercritical drying • Aerogel • Effective diffusivity •