

Detailed study of mass transfer kinetics during supercritical drying of biopolymer-based aerogels using spatially resolved Raman spectroscopy

M. P. Dirauf,^a A.S. Braeuer,^{a*}

^a TU Bergakademie Freiberg, Freiberg, 09599, Germany

*Andreas.Braeuer@tu-freiberg.de

1. Introduction

Drying (or extraction) of alcogels with compressed CO₂ is usually the final step of aerogel production and one of the most crucial steps that determines material properties as well as costs of the final aerogel product. Mass transfer kinetics inside the gels during drying are a complex interplay of the gel's matrix properties and diffusion and convection. Convection results from a change of the molar volume of the liquid mixture inside the pores.

In this work, we investigate into the drying kinetics of agar and whey protein isolate (WPI) alcogels with compressed CO₂ using one dimensional Raman spectroscopy. This *in situ* technique delivers temporally and spatially resolved composition profiles of the liquid mixture within the porous gels during drying. The composition profiles give very detailed insights into the mechanisms governing drying kinetics and allow to model the drying process. Studied parameters that might influence the drying kinetics include the gel matrix material and density, the CO₂ flowrate and pressure and temperature during supercritical drying.

2. Materials and Methods

Cylindrical hydrogel monoliths (d=12 mm, h=25 mm) of agar and WPI gels were synthesized according to common protocols^{1,2} and then converted to alcogels by stepwise solvent exchange with ethanol (EtOH) water mixtures. For supercritical drying with compressed CO₂, the gels were placed in a high-pressure autoclave with optical access on three sides so that the excitation laser can pass through the autoclave and the gel. Raman signals are then collected in a 90° angle to the excitation laser beam path. The optical setup is similar to the one already described elsewhere² albeit with a different excitation laser (P=500 mW, λ=730 nm). Spectra were recorded every minute.

3. Results and discussion

Here as an example, the gel matrix density, which influences the internal mass transfer inside the gel, and the CO₂ flowrate, which influences the external mass transfer outside the gel, are presented. Figure 1 shows the composition profiles during the drying of agar alcogels in compressed CO₂ at 10 MPa and 313 K. In the middle, composition profiles for agar gels with different agar fractions (1-3 wt%) are shown for three instances of time. Although the density of the gels increases by a factor of three from the 1 wt% to the 3 wt% gel, the gel matrix does not seem to have any significant influence on mass transfer kinetics during drying. Only the least dense 1 wt% gel shows slightly faster drying kinetics at t = 30 min and t = 60 min. This finding can be explained by the influence of gel matrix density on the porosity of the gels: For small matrix densities, matrix density only has a small influence on gel porosity and consequently the effective diffusion coefficient that determines mass transfer kinetics. However, with significant denser gels like 20 wt% WPI gels (not shown in this abstract), gel matrix density has measurable impact on drying kinetics.

Figure 1 (right) shows the influence of CO₂ flowrates from 0.31 g min⁻¹ to 2.5 g min⁻¹ of CO₂ as an important factor of external mass transfer. An increase of the flow regime from 0.31 g min⁻¹ to 0.63 g min⁻¹ does not show a significant change in drying kinetics. Only when the flowrate of CO₂ is increased to 2.5 g min⁻¹ changes in the composition profiles can be observed, with the highest flowrate leading to fastest mass transfer. The rather small influence of external mass transfer on the overall drying kinetics can be explained by the rather big monoliths, which have a small outer-surface to volume ratio, thereby diminishing any influence of external mass transfer.

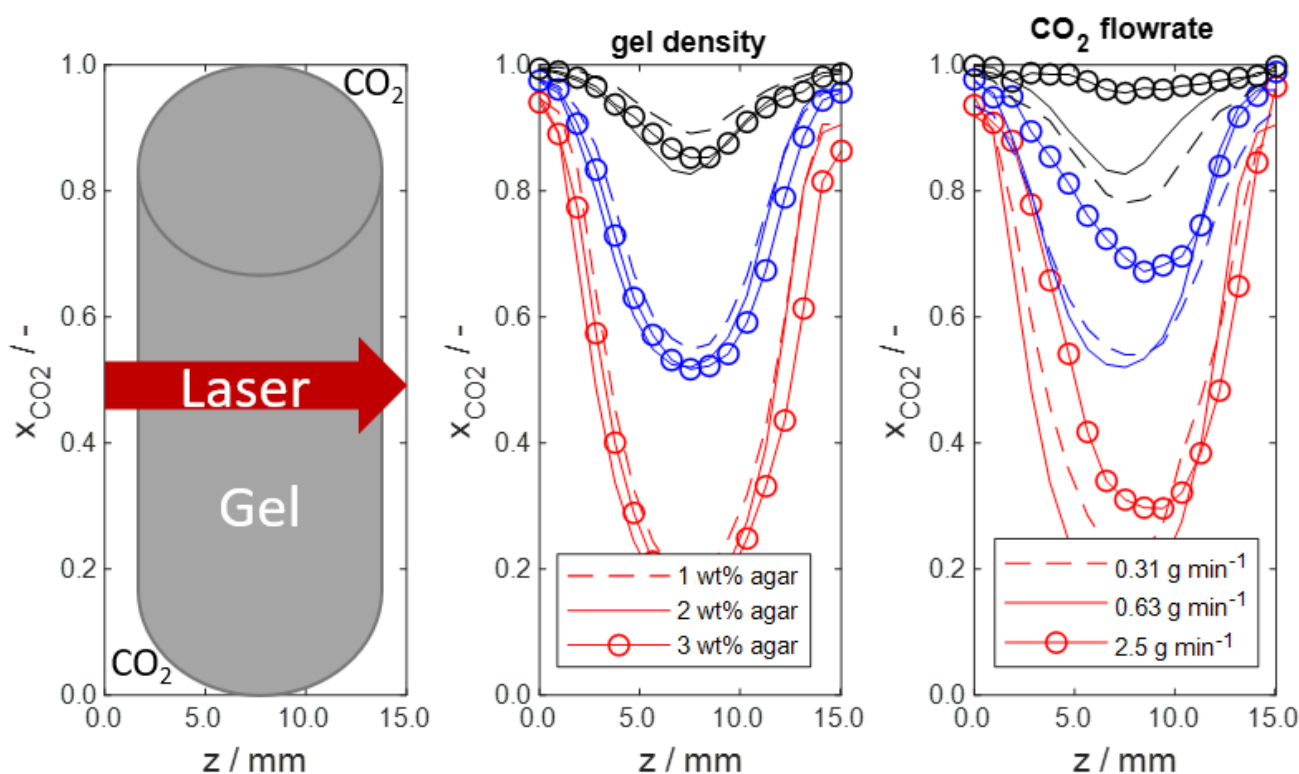


Figure 1. Influence of gel matrix density and CO₂ flowrate on composition profiles during supercritical drying of agar alcogels with CO₂ at 313 K and 10 MPa at $t=10$ min (red), $t=30$ min (blue), $t=60$ min (black). Reference condition is 2 wt% agar gels and CO₂ flowrate of 0.63 g min⁻¹. Left diagram shows the orientation of the gel and the laser beam during measurements.

Next to the influence of gel density and CO₂ flowrate on drying kinetics the influence of temperature, pressure and CO₂ density were measured as well but are not shown in this abstract.

4. Conclusions

Raman spectroscopy has been employed to gather spatially and temporally resolved composition profiles during the drying of biopolymer alcogels to aerogels. Influence of gel matrix material and matrix density, CO₂ flowrate, pressure and temperature on drying kinetics could be determined. While the insights on the internal mass transfer are of universal character, the influence of the CO₂ flowrate depends on both, the geometry of the gel and the drying vessel, and thus cannot be easily transferred to other experimental setups. The results of this study will be valuable to set up and particularly validate detailed models of mass transfer during supercritical drying of biopolymer-based aerogels.

Acknowledgement

The authors gratefully acknowledge financial support for parts of this work through the project BR 3766/19-1 by the German Research Foundation (Deutsche Forschungsgemeinschaft – DFG).

References

1. Z. K. Brown, P. J. Fryer, I. T. Norton, and R. H. Bridson, *J. of Supercrit. Fluids* **2020**, 54 (1), 89–95.
2. M. P. Dirauf, A. Hajnal, P. Gurikov, and A. S. Braeuer, *Food Hydrocolloids* **2021**, 120, 106916.