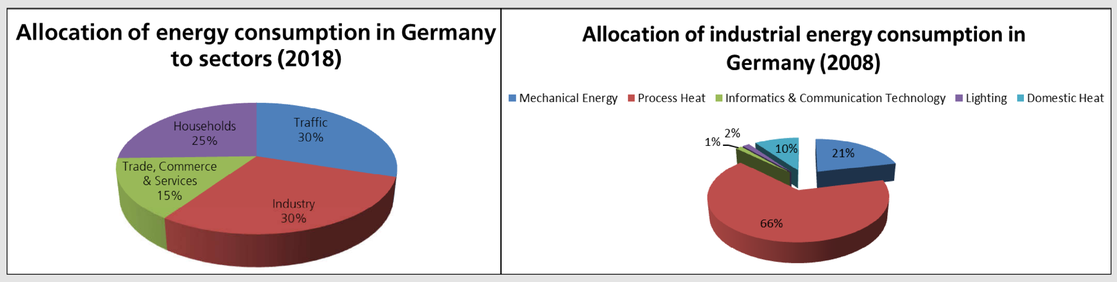
Analytical Setup for Kinetic investigations of Gel Ageing and Ambient Drying Processes

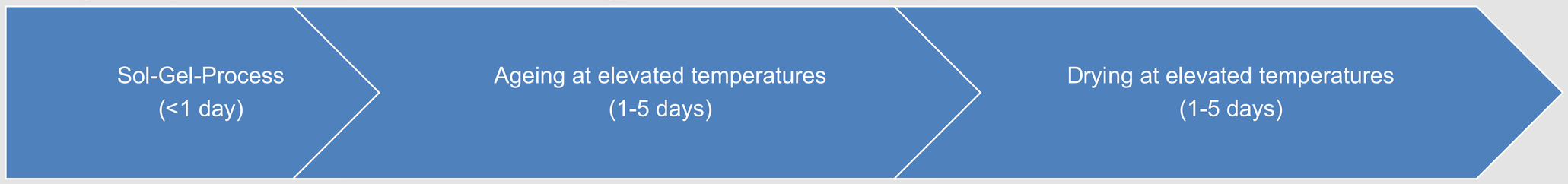
Introduction

Global challenges such as Climate Change require a set of actions to be implemented on a societal level including means to save energy and carbon dioxide. In Germany, industrial processes are responsible for about 20% of the total energy consumption emphasizing the need for saving energy in that area (scheme 1).[1] As aerogels have the potential to replace conventional materials in manifold markets, a high demand for their production is predicted urging industry to come up with an energy-efficient production.



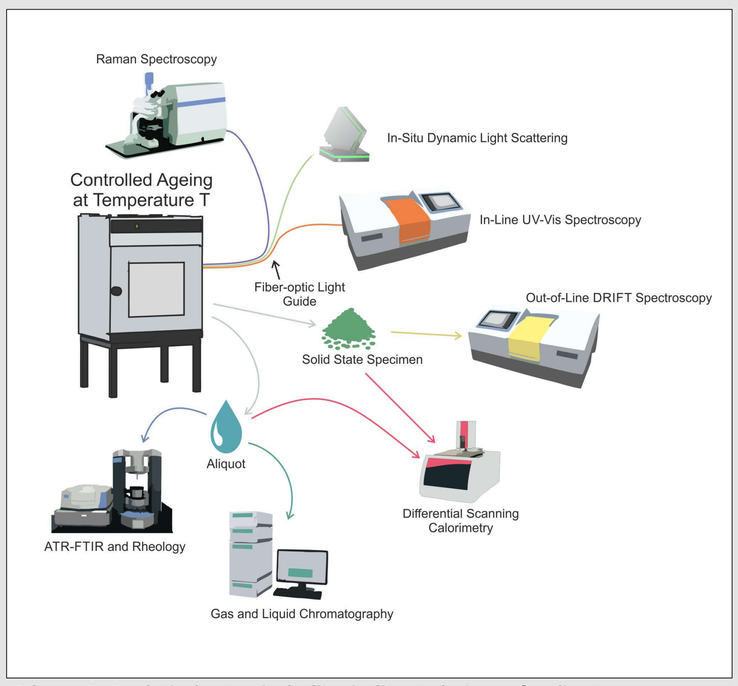
Scheme 1: energy consumption by the different sectors (left); final recipients of industrial energy (right)

Aerogels and xerogels are typically prepared by a sol-gel process followed by an ageing step in order to react remaining functional groups (e.g. condensation reaction), and a final drying step for the removal of the pore liquids (scheme 2).
This work focusses on setting up an analytical platform for *in situ* kinetic investigations of ageing and (ambient) drying steps with the aim of making these processes shorter and, thus, more energy-efficient.



Scheme 2: Production of aerogels/ xerogels by sol-gel process, ageing and drying

Experimental



Scheme 3: Analytical setup including in-line techniques for direct measurements

In-line analytical setup for real-time analysis of gel formation and gel ageing using:

- Dynamic light scattering (DLS) for determination of particle size and growth
- Ultraviolet/visible light absorption (UV-VIS) and
- Raman spectroscopy for monitoring polymerization in real-time (scheme 3)

Analytical setup for time-dependent analysis of aliquot samples during gelation and ageing:

- Analysis of volatiles (resorcinol) using gas chromatography coupled to mass spectroscopy (GC-MS)
- Analysis of reactive ingredients and non-volatiles using (derivatization followed by) High Pressure Liquid Chromatography (HPLC)

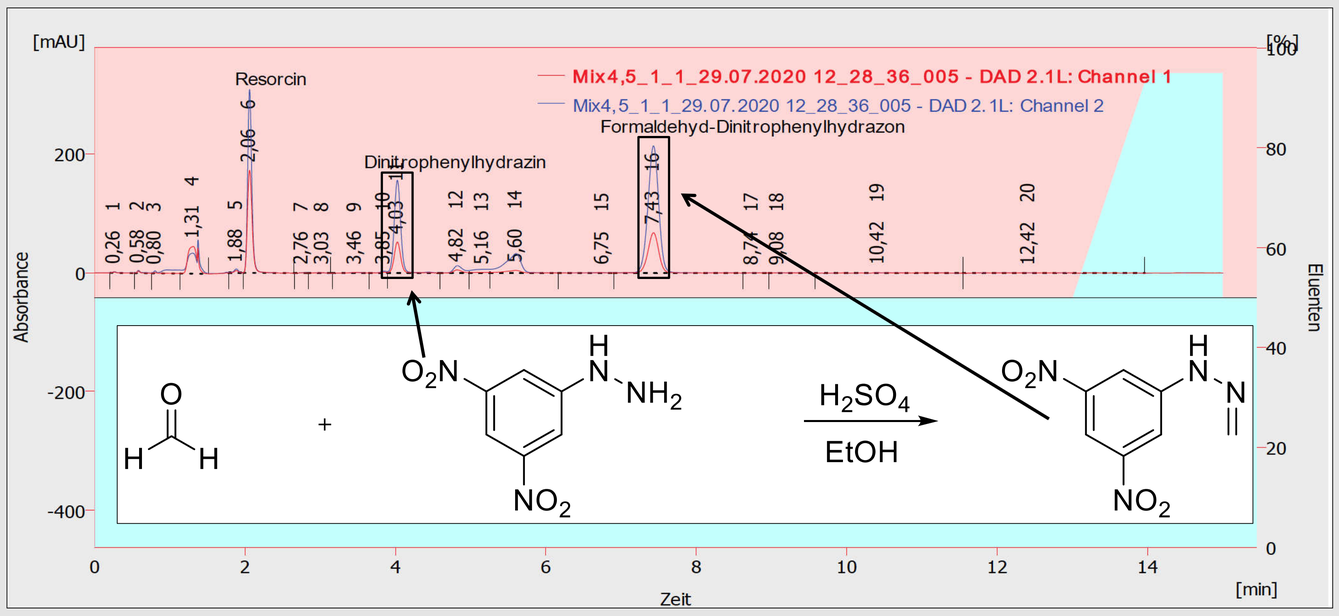
Analytical setup for time-dependent analysis of aliquot samples during ageing and drying:

- Various Infrared (IR) spectroscopy variants : Attenuated Total Reflection (ATR) and DRIFTS for solid samples and films
- Rheometer coupled to IR for determination of gel-point and curing behaviour
- Microwave-enhanced drying balance for determination of residual solvents

Results

Case Study: gelation and ageing of resorcinol-formaldehyde polymers: Analysis of time-dependent formaldehyde consumption using chemical derivatization and HPLC

- Analytical setup for time-dependent analysis of aliquot samples during gelation and ageing of resorcinol-formaldehyde:
- Formaldehyde reacts with 2,4-dinitrophenyl hydrazine to form the corresponding hydrazone (scheme 4)[2]
- HPLC methods for elution of the hydrazone in presence of resorcinol have been found
- The time-dependent analysis of aliquots from a RF sol-gel process is ongoing



Scheme 4: HPLC analysis of formaldehyde 2,4-dinitrophenyl hydrazone formed by conversion of formaldehyde and 2,4-dinitrophenyl hydrazine

Conclusions

- An analytical setup for kinetic investigations of aerogel production was designed.
- The setup including various in–line measurement techniques can provide kinetic data for gel formation, ageing, and drying as exemplified by HPLC analysis of the hydrazone of formaldehyde; this analysis is useful for monitoring the formaldehyde consumption during resorcinol-formaldehyde gel synthesis.
- In the coming months, the full-fletched analytical platform will used to monitor various aerogel production processes.

→ Aerogel production processes will be optimized with respect to time- and energy-efficiency.
→ To some extent, studies of scaling effects are envisioned in order to facilitate a possible industrial scale-up.

Acknowledgements
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References
[1] a) T. Klaus, C. Vollmer, K. Werner, H. Lehmann, K. Müschen, (Ed.: Umweltbundesamt), Dessau-Roßlau, **2010**; b) Umweltbundesamt auf Basis AG Energiebilanzen, **2019**.
[2] M. K. L. Bicking *et al*., *J. Chromatography A* **1988**, *455*, 310-315.

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