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Prozessoptimierung auf Pilotskala zur Kosten und Energie-effizienten Produktion von Silikat-Aerogel mittels eines disruptiven chemischen Verfahrens

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Zusammenfassung

Auf Heizung, Lüftung und Klimatisierung von Gebäuden entfallen schwindelerregende 40 % des Energieverbrauchs in der Schweiz. Die Wärmedämmung von Gebäuden ist der kostengünstigste Weg, um die Treibhausgasemissionen zu senken und die verheerenden Auswirkungen des Klimawandels, die durch ineffizientes Heizen und Kühlen von Gebäuden entstehen, zu bekämpfen.

Die wichtigsten wissenschaftlichen und technischen Ziele dieses Projekts bestehen darin, den Weg für eine kosten- und energieeffiziente Produktion von Hochleistungsdämmstoff aus Silica-Aerogel zu ebnen, die auf der patentierten "Ein-Topf"- und "Strukturiertes Gel"-Produktionstechnologie basiert. Dies soll durch den Bau eines neuen Reaktors im Pilotmaßstab mit verbessertem Wärmeübergang im Inneren des Gelpakets (dem Schwachpunkt des 40-Liter-Pilotreaktors aus dem Vorprojekt) erreicht werden, gefolgt von der Inbetriebnahme, dem Betrieb, der Charakterisierung und der Optimierung im technischen Pilotmaßstab. Durch eine optimierte Rückgewinnung und Energieeffizienz können die Rohstoffkosten minimiert werden. Aufgrund der laufenden Arbeiten in unserem Labor wurde das Produktionskonzept von dem ursprünglich vorgeschlagenen kontinuierlichen, großen Produktionstunnel zu einem modulareren Ansatz geändert. Das neue Produktionskonzept basiert auf einer stangenförmigen Geometrie der Gelkörper, die eine sehr schnelle Wärmeübertragung auf das Gel ermöglicht, was für die Verbesserung wesentlich ist. Die Beweggründe für diese Änderungen waren:

- Kürzere Produktionszeiten als kritischer Parameter für eine kosteneffiziente Produktion wurden höher gewichtet, daher wurde ein modularer Ansatz entwickelt, der für die Wärmeübertragung optimiert ist.
- Ein modulares Konzept ist risikoärmer und flexibler als ein einzelner großer Produktionstunnel, bei dem die Investitionskosten für eine erste Produktionslinie sehr hoch wären, da nur ein großer Produktionstunnel in Frage käme. Außerdem würde jede Stilllegung aufgrund von Defekten, Wartungsarbeiten oder Änderungen die gesamte Produktion lahmlegen.
- Die Pilotanlage ist im Vergleich zum ursprünglichen Projekt viel näher an einer Produktionsanlage. Daher wird der Übergang von der Pilotanlage zur Produktion einfacher sein, da ein Großteil der technischen Herausforderungen bereits gelöst ist.

Das neue Produktionskonzept wurde zunächst in kleinem Maßstab validiert, was den Bau der großen Pilotanlage verzögerte, aber ein notwendiger Schritt war, um das Risiko zu verringern und eine Wissensbasis für den Bau der großen Pilotanlagen zu schaffen. Nachdem sich die Machbarkeit des neuen Konzepts im kleinen Maßstab bestätigt hatte (Produkt innerhalb der Spezifikationen, kurze Zykluszeiten, In-situ-Trocknung möglich), wurde die Großanlage geplant, gebaut und in Betrieb genommen.

Leider war die In-situ-Trocknung im großen Maßstab nicht machbar, aber es wurde ein alternativer Ansatz mit externer Trocknung gefunden, um Materialien innerhalb der Spezifikationen zu produzieren. Es wurde eine industrietaugliche, skalierbare Trocknungstechnologie ermittelt, deren Einsatz zur Trocknung von Silica-Aerogel innerhalb der Zielvorgaben mit Hilfe einer angemieteten Pilottrocknungsanlage validiert wurde. Die externe Trocknung verursacht zusätzliche Kosten (Trocknungsanlage), verkürzt aber die Zykluszeit erheblich und erwies sich als die wirtschaftlich bevorzugte Lösung, da die Trocknung nicht mehr im Reaktor erfolgt, also die Temperaturbedingungen im Reaktor zwischen den Chargen nicht mehr verändert werden müssen.

Am Ende des Projekts haben wir ein neues Produktionskonzept für die Herstellung von Silica-Aerogel-Granulat im Pilotmaßstab (80 l) demonstriert, Materialien für die Bemusterung von Partnern und potenziellen Kunden hergestellt, Konzepte für das Recycling von Lösemitteln demonstriert, bei denen nur ein Bruchteil des Lösemittels gereinigt werden muss, und, was am wichtigsten ist, das Know-how für die Auslegung und Kostenschätzung der Silica-Aerogel-Produktion geschaffen.

Résumé

Le chauffage, la ventilation et la climatisation des bâtiments représentent à eux seuls 40% de la consommation d'énergie de la Suisse. L'isolation thermique dans les bâtiments est le moyen le plus rentable de réduire les émissions de gaz à effet de serre et de négocier les effets dévastateurs du changement climatique associés au chauffage et au refroidissement inefficaces des bâtiments.

Les principaux objectifs scientifiques et techniques de ce projet sont d'ouvrir la voie à une production rentable et économe en énergie de super-isolant thermique en aérogel de silice, basée sur la technologie de production brevetée "one-pot" et "gel structuré" grâce à la construction d'un nouveau réacteur à l'échelle pilote avec transfert de chaleur amélioré à l'intérieur de la chambre de gel (point faible du réacteur pilote de 40 l du projet précédent), suivi de sa mise en service, de son exploitation, de sa caractérisation et de son optimisation au niveau de l'ingénierie à l'échelle pilote. Le recyclage optimal et l'efficacité énergétique minimisent le coût des matières premières.

A partir des activités en cours dans notre laboratoire, le concept de production a été modifié en une approche plus modulaire, par opposition au procédé de production continu en géométrie de tunnel initialement proposée. Le nouveau concept de production est basé sur une géométrie en forme de tube des corps de gel qui permet un transfert de chaleur très rapide vers le gel, ce qui est essentiel pour accélérer le procédé sol-gel et l'hydrophobisation. Les principales motivations derrière ces changements étaient:

- Une pondération accrue des temps de production plus courts en tant que paramètre critique pour une production rentable, d'où le développement d'une approche modulaire optimisée pour le transfert de chaleur.
- Des risques réduits et une flexibilité accrue pour un concept modulaire par rapport à un seul grand tunnel de production, pour lequel les CAPEX pour une première ligne de production seraient très élevés, car seul un grand tunnel de production serait faisable. De plus, tout temps d'arrêt dû à des défauts, à des opérations de maintenance ou à des modifications entraînerait l'arrêt de toute la production.
- L'installation pilote est beaucoup plus proche d'une installation de production par rapport au projet initial. En conséquence, la transition du pilote à la production sera plus facile, car davantage de défis d'ingénierie ont été résolus.

Le nouveau concept de production a d'abord été validé à petite échelle, ce qui a retardé la construction de la grande installation pilote, mais était une étape nécessaire pour réduire les risques et fournir une base de connaissances pour la construction des grandes installations pilotes. Une fois la faisabilité du nouveau concept validée à plus petite échelle (produit conforme aux spécifications, temps de cycle courts, séchage in situ possible), la grande installation a été conçue, construite et mise en service. Malheureusement, le séchage in situ n'était pas réalisable à grande échelle, mais une approche alternative, utilisant le séchage externe, a été trouvée pour produire des matériaux conformes aux spécifications. Une technologie de séchage évolutive et viable sur le plan industriel a été identifiée et son utilisation pour sécher l'aérogel de silice conformément aux spécifications choisies a été validée à l'aide d'une installation de séchage pilote de location. L'exigence d'un séchage externe augmente le coût (installation de séchage) mais réduit considérablement le temps de cycle (plus de séchage dans le réacteur, pas besoin de changer les conditions de température dans le réacteur entre les lots) et s'est avérée être la solution économiquement préférée.

À la fin du projet, nous avons démontré un nouveau concept de production pour la production de granulés d'aérogel de silice à l'échelle pilote (80L), produit des matériaux pour l'échantillonnage aux partenaires et clients potentiels, démontré des concepts de recyclage de solvants qui ne nécessitent la purification que d'une fraction du solvant, et surtout, a créé le savoir-faire pour informer sur la conception et les estimations de coûts pour la production d'aérogel de silice.

Summary

Heating, ventilation and air conditioning of buildings account for a staggering 40 % of Switzerland's energy consumption. The use of thermal insulation in buildings is the most cost effective way to decrease greenhouse gas emissions and negotiate the devastating effects of climate change associated with inefficient heating and cooling of buildings.
The main scientific and technical objectives of this project are to pave the way for a cost- and energy efficient production of silica aerogel thermal superinsulation based on the patented "one-pot" and "structured gel" production technology through the construction of a new pilot scale reactor with improved heat transfer inside the gel pack (the weak point of the pre-project 40 L pilot reactor), followed by its commissioning, operation, characterization and optimization at the engineering pilot scale level. Optimum recycling and energy efficiency minimize the raw materials cost.

Based on ongoing activities in our laboratory, the production concept has been modified away from the originally proposed continuous, large production tunnel to a more modular approach. The new production concept is based on a tube-like geometry of the gel bodies that enables for a very fast heat transfer to the gel, which is critical to speed up the sol-gel and hydrophobization process. The main motivations behind these changes were:

- Increased weighting of shorter production times as a critical parameter for cost-effective production, hence a modular approach that is optimized for heat transfer was developed.
- Lower risk and higher flexibility for a modular concept, compared to a single large production tunnel, for which CAPEX for a first production line would be very high, as only a large production tunnel would be feasible. In addition, any downtime due to defects, for maintenance, or for modifications would shut down the entire production.
- The pilot installation is much closer to a production facility compared to the original project. As a result, the transition from pilot to production will be easier, as more of the engineering challenges have been solved.

The new production concept was validated at small scale first, which delayed the construction of the large pilot facility, but was a necessary step to reduce risk and provide a knowledge basis for the construction of the large pilot facilities. Once the feasibility of the new concept was validated at the smaller scale (product within specifications, short cycle times, in situ drying possible), the large facility was designed, constructed and commissioned. Unfortunately, in situ drying was not feasible at the large scale, but an alternative approach, using external drying was found to produce materials within specifications. A scalable, industrially viable drying technology was identified and its use to dry silica aerogel to within target specifications validated using a rental pilot drying installation. The requirement for external drying does add cost (drying installation) but reduces the cycle time substantially (drying no longer in reactor, no need to change temperature conditions in reactor between batches) and was found to be the economically preferred solution.
At the end of the project, we have demonstrated a new production concept for silica aerogel granulate production at the pilot scale (80 L), produced materials for sampling to partners and potential customers, demonstrated solvent recycling concepts that only require purification of a fraction of the solvent, and most importantly, created the knowhow to inform on the design and cost estimates for silica aerogel production.

Main findings

- One-pot synthesis process implemented at the pilot scale
- Potential problems with continuous production tunnel identified (engineering difficulties; only possible at large scale, not at intermediate scale)
- New, modular all-in-one production concept validated at small scale (single cell reactor 1ZR)
- Modular concept implemented at large pilot scale (80L gel volume), material within specifications possible, but only with external drying
- Cycle time in reactor in 3 hours (including gelation, aging and hydrophobization), external drying of 30-45 minutes for an overall production time of 4 hours
- Solvent recycling without purification validated: 100% of syneresis and catalyst solutions and 46% of condensate can be re-used without purification. Purification required for other 54% of the condensate
- Separation of HMDSO through phase separation validated
- Scalable external drying technology tested and validated
- Materials for testing and sampling to partners/customers produced and aerogel granulate specifications determined with a packed bed thermal conductivity below 20 mW/(m.K) at 20°C.

Contents

Abbreviations

TEOS	Tetraethoxysilane
HMDSO	Hexamethyldisiloxane
P750	Polyethoxydisiloxane silica precursor
NMR	Nuclear Magnetic Resonance
LCA	Life Cycle Assessment
CAPEX	Capital expenditure
OPEX	Operation expenditure
4D75	Polyethoxydisiloxane silica precursor made from Dynasilan 40
EtOH	Ethanol
D40	Dynasilan ® 40
ATEX	European Directive 2014/34/EC concerning the placing on the market of explosion-proof electrical and mechanical equipment
CO_2e	CO_2 equivalent greenhouse gas emissions

1 Introduction

1.1 Background information and current situation

1.1.1 Motivation

Heating, ventilation and air conditioning of buildings account for a staggering 40 % of Switzerland's energy consumption. The use of thermal insulation in buildings is the most cost effective way to decrease greenhouse gas emissions and negotiate the devastating effects of climate change associated with inefficient heating and cooling of buildings [2-5].

Today's insulation markets are in dire need of change. Many conventional products such as glass wool or polystyrene foam are at the peak of their product lifecycle or have already passed it. At the same time, policy in the building and construction sector is imposing stricter insulation standards which result in thicker insulation layers [2,4]. Compared to Switzerland, few countries dedicate as many resources to the reduction of energy consumption and carbon emissions related to its building stock. Labelled building standards such as Minergie and subsidies for energy efficient buildings and retrofit are embedded into policy (Energy Strategy 2035 & 2050) and further supported by recently created competence centers (SCCERs). Up until now, stricter building codes have resulted in ever-increasing insulation layer thicknesses, because classical insulation materials have reached their technical performance limits and cannot keep up with envelope regulations. The same holds for industrial insulation applications (e.g. automotive, pipe insulation, distributed heating networks). In many cases, existing products are no longer able to keep up with increasing performance requirements.

Offering the same performance at half the thickness of a conventional insulation solution, the broad commercialization of silica aerogel could represent a new era for the insulation industry [2,4]. However, given its high production cost, the use of silica aerogel has been limited primarily to niche applications, where there are either no suitable alternative solutions, or where space savings combined with reduced maintenance efforts compensate the added materials cost (e.g. deep-sea pipelines, reduced corrosion in the oil-and-gas industry / refineries). Despite today's high market price, silica aerogel products worldwide are a 250M CHF per annum market with a CAGR growth rate of approximately 20% [6,7]. Aerogel based insulation solutions in Switzerland constitute a ~5 M CHF market. Building applications are still small volume compared to other aerogel markets (pipeline, oil/gas >100M CHF worldwide).

1.1.2 Efficient production of silica aerogel: innovation beyond the state-of-the art

The heart of our technology is the so-called "one-pot" simplified synthesis procedure (see patent WO 2015014813 A1) which leads to a significant reduction in raw material and solvent consumption as well as process complexity and process time 1,8. Traditionally in the synthesis of silica aerogels, a concentrated silica sol is diluted with a solvent, typically alcohol, to tailor the density of the final product and gelation is induced by a base catalyst 9,10. After aging, the gel is immersed in a solution containing a hydrophobization agent 11-16, e.g. hexamethyldisiloxane (HMDSO), activated by an acid catalyst. The additional alcohol serves only to define the silica concentration and gel density, and its addition increases the amount of hydrophobization solution that is required to displace it during the hydrophobization step. In the one-pot process, we dilute the concentrated sol with a mixture of ethanol and the hydrophobization agent, where the latter is inactive under the basic gelation conditions and does not disturb the gelation and aging processes. After aging 17-20, the hydrophobization agent is activated by the addition of the acid catalyst to initiate the silylation. A unique feature of the one-pot process is that the recovered process solvent composition is very close to that of the initial starting solution mixture and as a result, most of the solvent can be recycled without additional purification. This translates into a massive reduction in embodied energy and global warming potential compared to today's state of the art: life cycle analysis (LCA) indicates that the adoption of the one pot process reduces greenhouse gas emissions from 880 to 630 kg CO_2e per m^3 of aerogel (*Figure 16*).

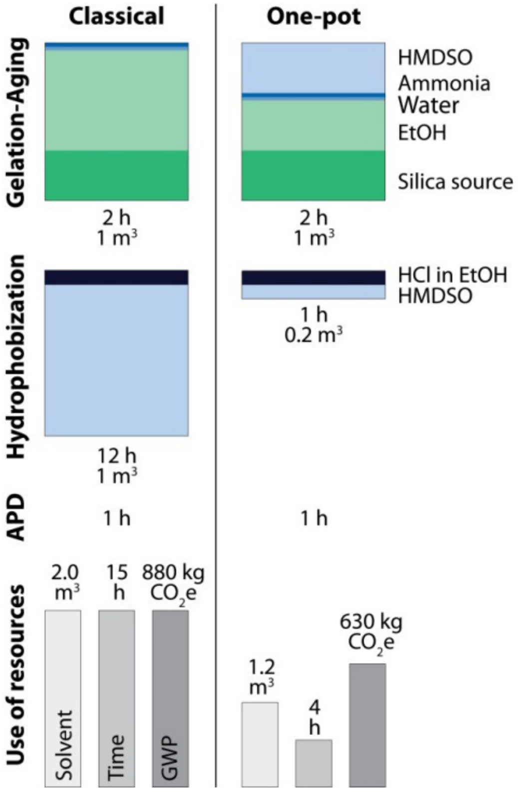


Figure 1: Comparison of the classical with the one-pot production process from an LCA perspective 1

At laboratory scale, aerogels with properties identical to commercial materials (Cabot, Enersens) were produced in a total of only four hours including gelation, aging, hydrophobization and ambient pressure drying of the gels. Such a short production cycle is critical to reduce the production cost, as the capacity of a production facility scales strongly with the residence time. Conversely, the required size of the production facility, and thus the capital expenses, to reach a target capacity scales linearly with the residence / process time. At the 40 L pilot scale in the stationary setup currently installed at Empa, these times were as long as 32 h due to the nature of the reactor design (a vessel at room temperature being placed inside a convective drying oven) which in turn limited heat transport and caused very slow heating of the vessel's contents. Decreasing heating time at pilot scale is one of the main aims of this project.

A second major innovation is the structuring of the gel body into one-dimensional rods of limited diameter (~10 mm), which obviates the need for crushing a previously assembled larger gel body. Gel crushing leads to high shear loads on the gel, which results in a high fraction of aerogels in fine powder (typically 30% by volume), a less desired and less valuable product. The structured nature of the gel bodies minimizes inward diffusion times of the hydrophobization catalyst and maximize yield of granulate product (WO 2016124680 A1).

Particularly, the combination of the two patents represents a clever and highly synergistic approach, which allows the one-pot process to be carried out at pilot and industrial scale effectively with minimal time and raw material / CAPEX efforts. More importantly, since the unit cell of a structured gel remains the same over all scales (lab – pilot – industrial), the entire process is fully scalable – provided that heat transport into larger gel rod packs is not rate limiting.

1.2 Purpose of the project

The main scientific and technical objectives of this project are to pave the way for a cost- and energy efficient production of silica aerogel based on the patented “one-pot” and “structured gel” production technology through the construction of a new pilot scale reactor with improved heat transfer inside the gel pack (the weak point of the pre-project 40 L pilot reactor), followed by its commissioning, operation, characterization and optimization at the engineering pilot scale level. Optimum recycling and energy efficiency minimizes the raw materials cost, and this is the key benefit of the existing, patented Empa one-pot technology.

The current BFE P&D project aims to minimize also the capital and operational expenses and paving the way for industrial production by developing and demonstrating the production technology. Key targets for a cost-effective production technology that minimizes both capital and operational expenses are: 1) a simple production technology (less complex installations minimize CAPEX, less downtime minimizes OPEX); 2) fast throughput times (smaller installation for same production capacity minimized CAPEX, faster throughput maximizes worker’s efficiency and minimized OPEX).

1.3 Objectives

The main objective of this project was the design, construction, commissioning, operation and optimization of a pilot facility for the production of silica aerogel granulate, characterization of the process in terms of mass and energy balance and the production of sample materials to distribute to potential partners and customers.

The project has been structured in four workpackages:

- WP1. Simulating continuous production at semi-industrial pilot scale
- WP2. Process optimization: reducing capital and operating expenses (CAPEX and OPEX) through reduced production times and maximum solvent reuse
- WP3. Process monitoring, LCA analysis
- WP4. Produce sample materials for partners, customers and product development

The following milestones were set at the start of the project:

- M1: Pilot commissioning completed (15.05.2018)
- M2: Process time and solvent reuse optimized (15.12.2018)
- M3: Design criteria production plant, costs validated (15.06.2019)
- M4: Mass-energy flow diagram completed. Full LCA (15.09.2019)
- M5: First 20 m^3 of aerogel distributed, samples distributed to selected partners (15.06.2019)

2 Description of facility

The first concept of a large scale pilot plant that should enable the continuous production of aerogel on a conveyor belt like construction was rejected, after findings in the laboratory proved the manufacturing in a semi batch like process will be more successful. Therefore, the activities on the large engineering pilot have been delayed compared to the original schedule and Milestone 1 (“Pilot commissioning completed”) has not been completed on time. This delay is the price to implement and validate the new production concept and, in our evaluation, the benefits of these outweigh the delay.

Based on the findings in smaller scale reactors, the pilot reactor was designed, constructed and commissioned. After initial modifications to the pilot hall (installation of sufficient electrical power, construction of steel platforms, etc.). The pilot was constructed on the Empa campus during December 2018- February-2019.

The manufacturing concept for the production of silica aerogels includes minimized solvent consumption. This is partly due to the process itself, but also due to ability of the recycling. Although the reuse of solvents is proven, the installation of the downstream process to reuse them in a daily batch is not yet implemented. The unit includes a condenser in order that the wet gel can be dried directly in the sol-gel reactor. However, various runs in the reactor showed that the same quality could not be reached as in smaller scale. Therefore it was decided to remove the in situ drying to an external concept towards the end of the project.

2.1 Change in concept

Based on activities in our laboratory, the production concept has been modified away from the originally proposed continuous, large production tunnel to a more modular approach. The new production concept is based on a tube-like geometry of the gel bodies that enables for a very fast heat transfer to the gel, which is critical to speed up the sol-gel and hydrophobization process.

The main motivations behind these changes were:

- Increased weighting of shorter production times as a critical parameter for cost-effective production, hence a modular approach that is optimized for heat transfer was developed.
- Lower risk and higher flexibility for a modular concept, compared to a single large production tunnel, for which any downtime due to defects, for maintenance, or for modifications would shut down the entire production.
- Identification of difficulties associated with transfer of the organogels from the synthesis reactor/tunnel to the drying installations, particularly with respect to minimizing VOC emissions and maximizing solvent recovery (these difficulties were partly identified during the BFE Gelsec project). The new modular production concept, in theory, enables an all-in-one production, including drying and is carried out in a closed system. The all-in-one drying concept was validated at the smaller scale (see 3.2), but implementation at the larger scale has proven difficult, and is no longer pursued (see 3.3).

The new production concept also has an additional advantage:

- The pilot installation is much closer to a production facility compared to the original project. As a result, the transition from pilot to production will be easier, as more of the engineering challenges have been solved.

2.2 Demonstration of new production concept at smaller scale

Because of the afore-mentioned changes to the production concept, it was decided to test the feasibility of this new production concept first on a smaller scale with two intermediate, smaller-sized reactors. As part of the overall aerogel piloting activities (*Figure 3 left*), we have thus taken a temporary step backwards in terms of batch volume to enable us to 1) optimize the processing time (by optimizing heat transport and pressure-temperature conditions); 2) achieve an all-in-one production concept; and 3) solve basic engineering questions at the smaller scale before constructing the large scale engineering pilot.

A first reactor, 4LR (*Figure 2*), demonstrated that the new, all-in-one process was possible and the flexible design enabled us to identify the best operating parameters in terms of geometry and shorten the production time substantially down to 7 h. In the same time the recipe was optimized, a smaller load of base and acid catalysts could be used. The 4LR reactor design however is not directly scalable.

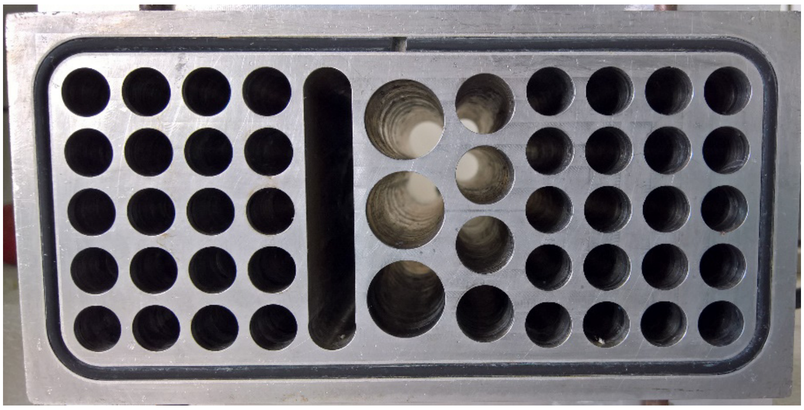


Figure 2: Top view of the 4LR reactor. The different shapes enabled experiments to find the best operating parameters in terms of geometry

A second reactor, 1ZR (*Figure 3 right*) was designed, commissioned and used to further reduce the processing time to below 5 h, with a good quality of the produced materials, and provided critical data for the best operating conditions of the large, pilot scale reactor. Because the 1ZR reactor represents a single cell of the targeted, large pilot reactor, the materials, the sol-gel and hydrophobization processes undergo the same pressure-temperature path in the 1ZR reactor as they will in the large pilot reactor. As a result, the production process optimization (time, pressure, temperature, chemistry) can be carried out to a large extent in the 1ZR reactor and this is also how we have proceeded. In this way, the intermediate stage 1ZR reactor has enabled us to achieve part of Milestone 2 ("Process time and solvent reuse optimization") ahead of schedule, albeit at a smaller scale. Particularly the demonstration of a total cycle time within 5 h, and the demonstration of in situ drying through the use of a closed process design, is a strong achievement. The aerogel granulate produced by the fast, all-in-one process in the 1ZR reactor have been characterized extensively to ensure that they meet target specifications in terms of thermal conductivity, density, granulometry and mechanical properties.

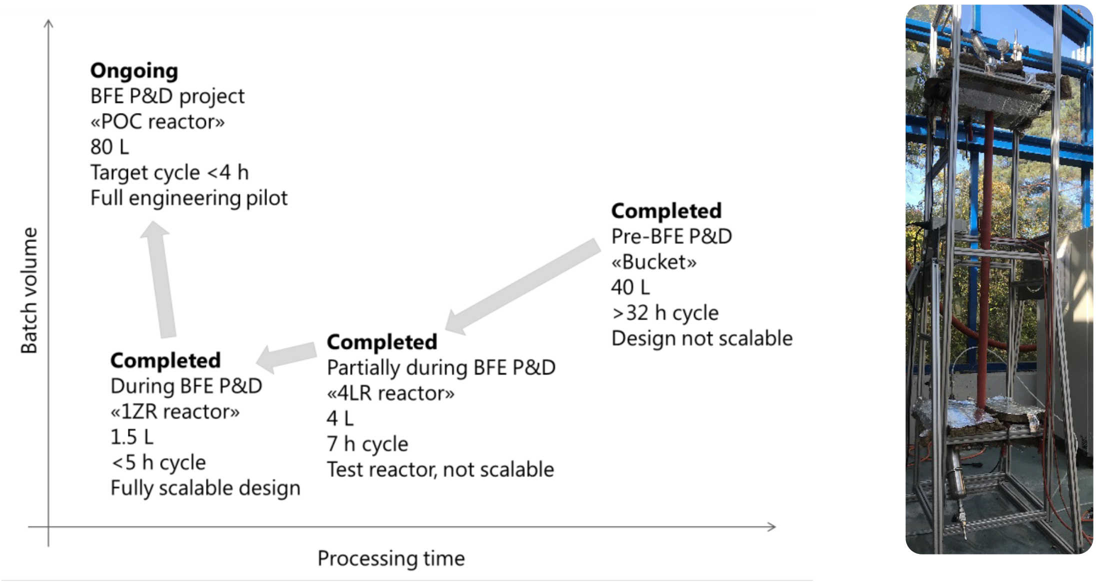


Figure 3: (left) Schematic overview of the evolution of the various Empa silica aerogel pilot reactors in terms of processing time and production volume; (right) 1ZR reactor.

2.3 Large pilot facility with the new production concept

2.3.1 Pilot installation design

Based on the success with the 1ZR reactor, we have proceeded with the design (*Figure 8*, *Figure 9*) of the 80 L engineering pilot with its entire periphery (solvent and gas handling, piping, waste and storage system). The reactor combines the already known principle of a tube bundle heat exchanger with 155 tubes, in combination with the mass flow of chemicals that is needed for the production of aerogels.

- The pilot installation consists of three main reactor vessels:
    - R-1000: sol-gel reactor vessel, 80 L (Figure 7)
    - B1010: sol mixing vessel, 150 L (Figure 6)
    - B1013: catalyst purge feed vessel, 40 L
- Solvent management system
    - B1058: IBC (1000 L) for recyclate
    - B1054 and B1056 (200 L), B1052 (1000 L) for main solvents
    - B1060, B1070, B1080: Mixture reservoirs (140 L) for condensate, syneresis, sol concentrate (Figure 5)
    - B1012, B1014, B1016, B1018: Minor components vessel (25 L) for acid and base catalysts, water (Figure 4)

- Auxiliary
    - W1020: Condenser with cooling loop
    - F1091: VOC active carbon filter
    - Lauda heating system (50 kW) and cooling system (15 KW for condenser)

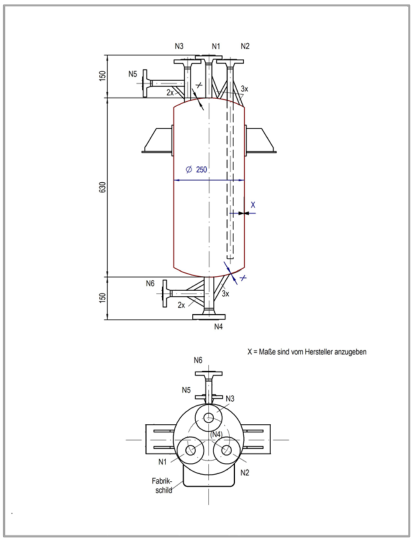


Figure 4: Container (B1012; B1014; B1016; B1018) for base and acid catalyst, and water.

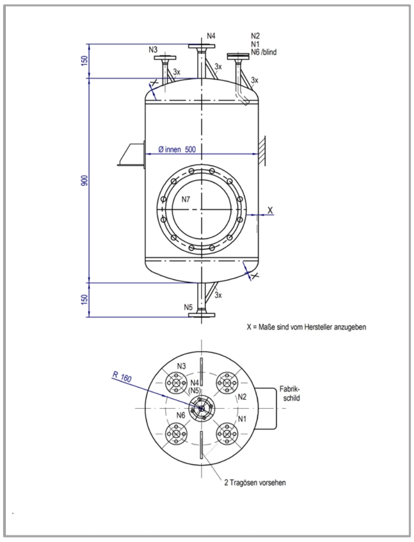


Figure 5 Reservoir tank (B1060; B1070; B1080) for sol precursor, modification solution, syneresis

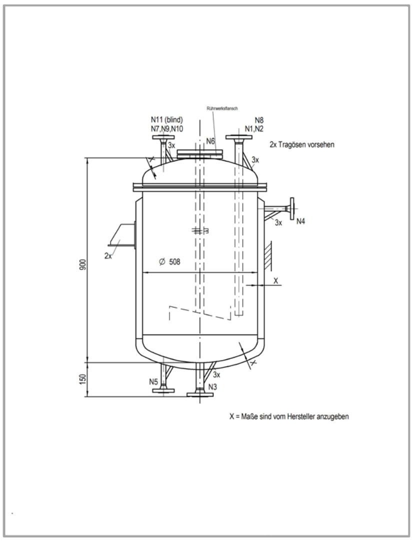


Figure 6: Batching tank (B1010), the mixing vessel above the tube bundle reactor.

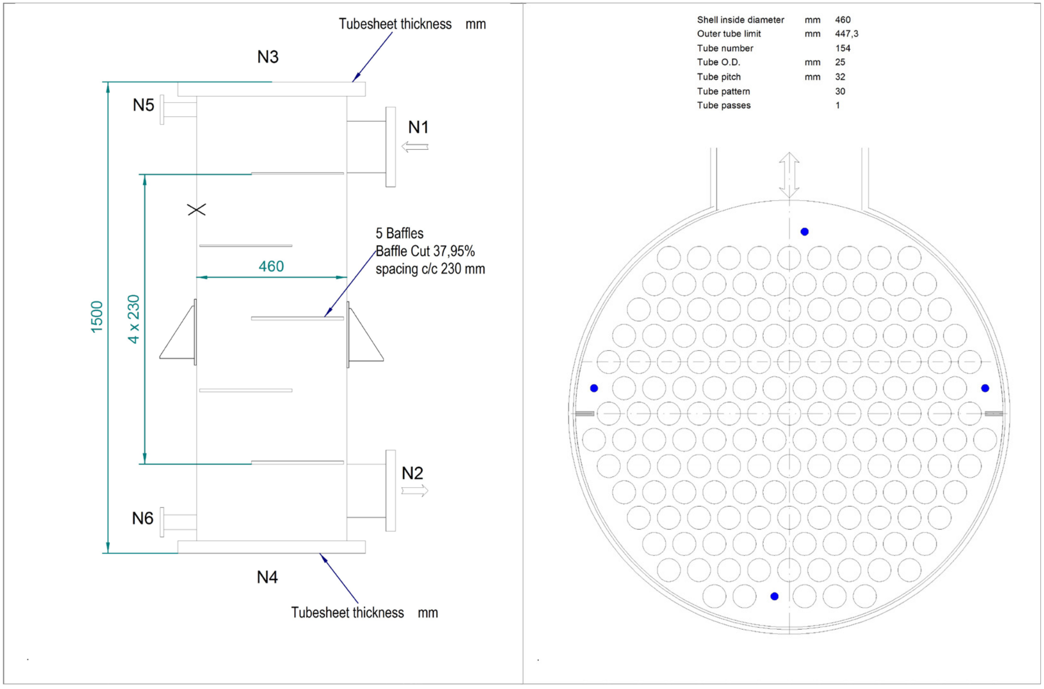


Figure 7: Tube bundle reactor (R1000), the side view (left) without the closing head and feet part. The cross section (right) shows the 155 tubes for the sol gel reaction and alignment notches in blue for head and feet part.

The pilot installation is computer controlled and closely resembles how a future production facility would be engineered. The mixing vessel is equipped with a balance; the chemicals can be controlled over their mass, directly at the pilot. This makes it possible to adjust the chemicals to achieve tailorable surface chemistry and desired density of the product, i.e. degree of hydrophobization and content of SiO2. The process itself does not need any external handling of chemicals when running, but since organic solvents are used, Ex Zones must be considered (Ex-Zone 2). The valves are controlled with compressed air or, where necessary for safety reasons, with nitrogen. The components of the pilot plant are designed to withstand the chemicals used during the synthesis (strong bases and acids, stainless steel of appropriate quality). The unit is constantly flooded with nitrogen to avoid the presence of critical gas mixtures (ethanol-air). All components of the pilot, including the raw materials and waste storage vessels, the reactor and the periphery, are also thoroughly grounded.

The plant is operated by two people for safety reasons, but could also be operated by one person (with a greater time investment). Because of practical considerations with staffing availability, one workday (approx. 8 h) is needed to produce one batch of aerogel, but up to 3 batches could be produced per day in a 24 hour operation cycle, or even more if the wet gel is removed and externally.

2.3.2 Overview of flow charts

Mass flow

In *Figure 8* all the various tanks, the condenser and exhaust are highlighted, in *Figure 9* the tube bundle reactor (R1000), the mixing vessel (B1010) and the catalyst purge feed vessel (B1013). The containers for catalysts and water (B1012, B1014, B1016, B1018); the containers from the reservoir tank (B1060, B1070, B1080) and the main solvents (B1052, B1054, B1056) are directly connected to the mixing vessel (B1010) above the bundle reactor. The mixing vessel is used for the preparation of the chemicals, by weighing, stirring and tempering them and is adjusted by a doser. The mixing vessel itself is connected directly to the tube bundle reactor (R1000) to fill it and to the catalyst purge feed vessel (B1013) for providing chemicals, or discharge excess material. It has also a direct link to the reservoir tank for the sol precursor (B1060), for a fast transfer after preparation. The catalyst purge feed vessel (B1013) in turn is connected to the reservoir tanks (B1060, B1070, B1080) to pump back the chemicals either for storage or reuse. Only the reservoir tanks are directly connected to the IBC tank for recyclate (B1058). The tube bundle reactor (R1000) has only direct connection to the mixing vessel (B1010) above and to the catalyst purge feed vessel (B1013) below.

Mass transfer

The catalysts and the water (B1012, B1014, B1016, B1018) are transferred to the mixing vessel (B1010) using nitrogen overpressure in the vessel. To fill the catalysts and water, the solutions are prepared in canisters and filled separately through valves (VH1012.02, VH1014.02, VH1016.02, VH1018.02) using an external diaphragm pump while there is no overpressure inside the tanks. The chemicals from the reservoir tanks (B1060, B1070, B1080) and the main solvents (B1052, B1054, B1056) use diaphragm pumps (P1052, P1054, P1056, P1065, P1075, P1085) for transferring. The purge feed vessel is also equipped with a diaphragm pump (P1090) for controlling the mass flow of the chemicals in the heart of the pilot installation. The transfer from the mixing vessel (B1010) to the tube bundle reactor (R1000) is controlled by gravity. As soon as the reactor is filled, a liquid level switch (Liquiphant) changes the valves so excess is transferred to the catalyst purge feed vessel (B1012). All the automatic valves are controlled by nitrogen gas where necessary, or compressed air where it's not crucial. There are several valves available, that make it possible to take samples from various tanks (VH1052.03, VH1054.03, VH1056.03, VH1065.02, VH1075.02, VH1085.02, VH1012.01, VH1014.01, VH1016.01, VH1018.01, VH1010.25, VH1000.26, VH1013.10, VH1090.02).

Pressure

The whole pilot installation has constantly 0.2 bar overpressure using nitrogen gas to prevent the formation of explosive gases in default state. The tanks for water and catalyst (B1012, B1014, B1016, B1018) are flooded with 2 bar nitrogen gas during operation. The mixing vessel (B1010) is always pressure adjusting, that the corresponding medium can flow into it. The same applies to the catalyst purge feed vessel (B1013). The tube bundle reactor (R1000) has in the head and in the feet part 2 bar pressure for sealing the tubes. Inside the reactor has default state (0.2 bar overpressure) while filling, but during the whole procedure it changes constantly with change of temperature, since it is air tight sealed.

Temperature

The tube bundle reactor (R1000), the mixing vessel (B1010) and the catalyst purge feed vessel (B1013) can be tempered and are isolated. The rest of the installation doesn't have temperature control, and has therefore ambient temperature. Since the pilot hall doesn't have any isolation, these temperatures changed substantially during the year.

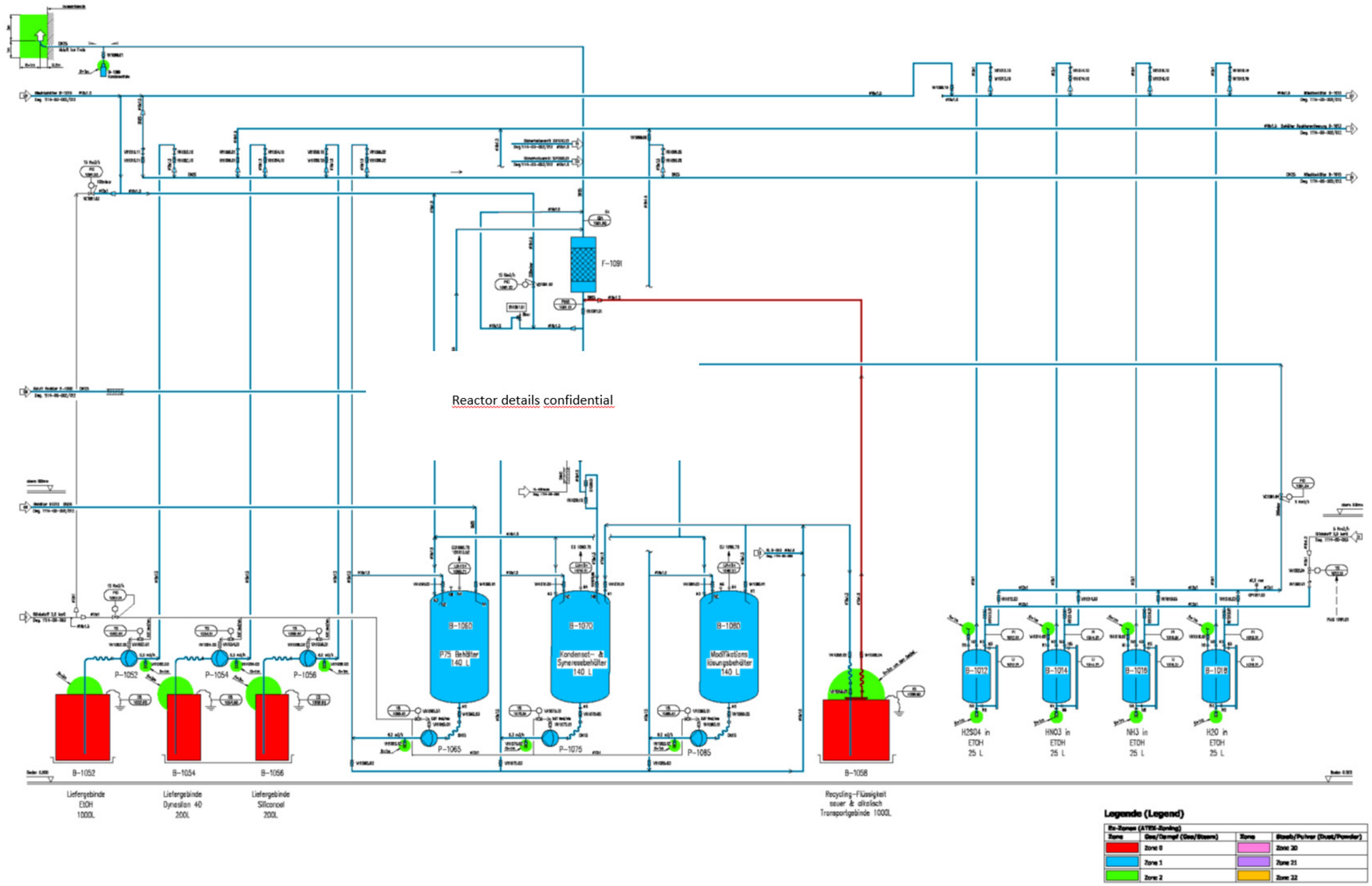


Figure 8: Proces flow chart of the 80 L pilot plant with tanks, condenser, exhaust and coloured ATEX classification.

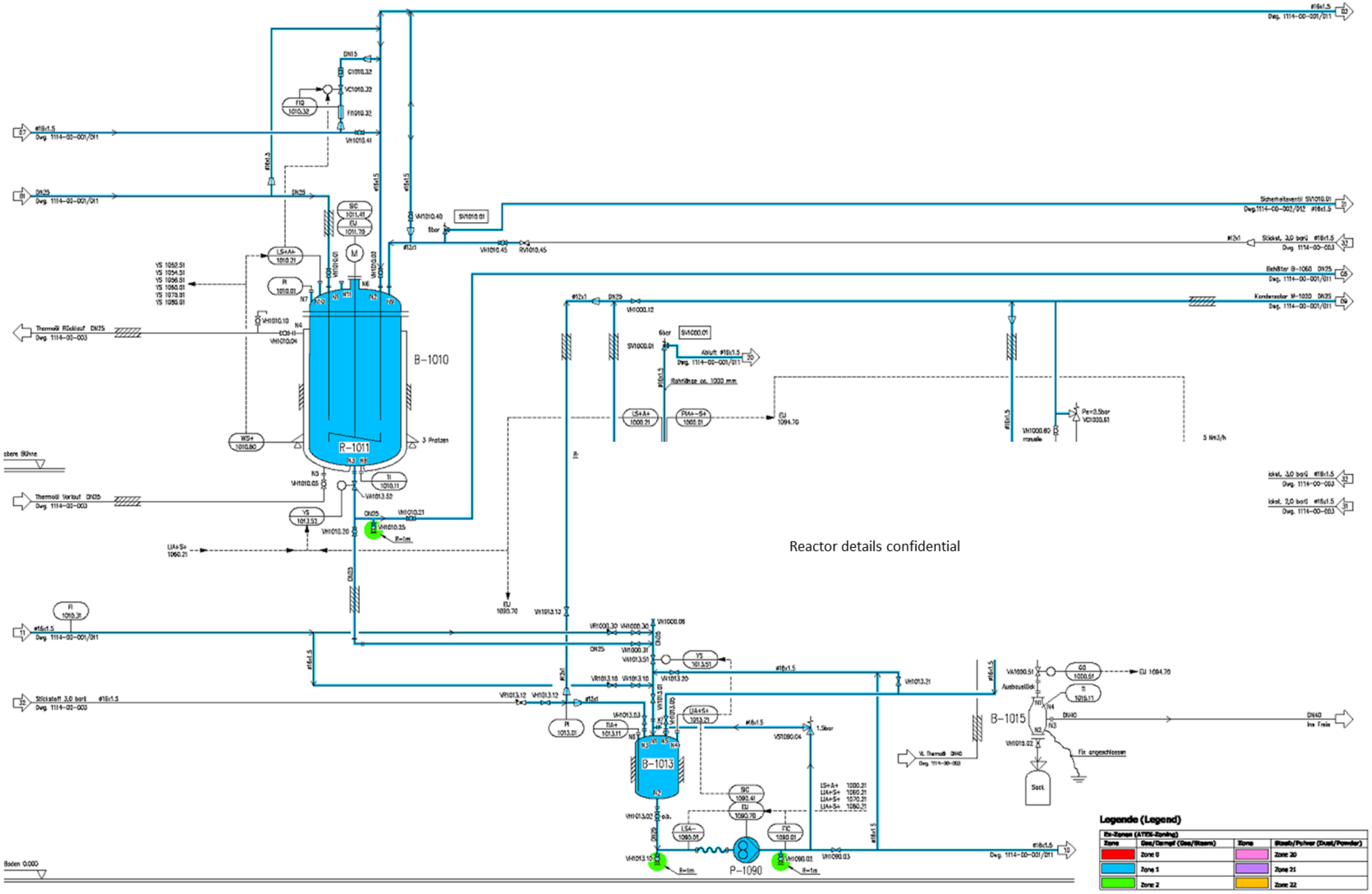


Figure 9: Process flow chart of the 80 L pilot plant focused on the tube bundle reactor, the mixing vessel (B1010) and the catalyst purge feed vessel (B1013) with coloured ATEX classification.

3 Procedures and methodology

The aerogel is manufactured using the one-pot-recipe [8,21,22] developed in small scale in the single tube experiments in the laboratory. The optimized chemical recipe results in recognition values that are characteristic to the material and required for industrial usage (e.g. envelope density). During the upscaling steps, this values were used as references to validate the process during optimization steps. In this work, the focus was on construction, commissioning, operation and optimization of the pilot facility for the production of silica aerogel granulate. Most of the optimization steps were done in the small scale attempts, to explore parameters like time, temperature and pressure or small changes in the recipe that were needed for successful material. While the optimization process was ongoing, the large pilot facility was commissioned and prepared for operation. As soon as the reactor was ready, trials were done in large scale to find the next steps that had to be adjusted to the large production. A flexible procedure took place adapted to the conditions, where smaller experiments were done in single tubes in lab scale, smaller scale experiments in 1ZR or in large scale production in the 80 L reactor to find optimal conditions and workflow.

3.1 Description of a production cycle in the facility

A typical process flow in the 1ZR is shown in *Figure 10* and can be directly applied to the 80 L pilot. Since the majority of the process for the 1ZR and the 80 L reactor is directly transferable, in the following it is described for the large scale facility, unless other stated. The individual steps are described in more detail in the following subchapters.

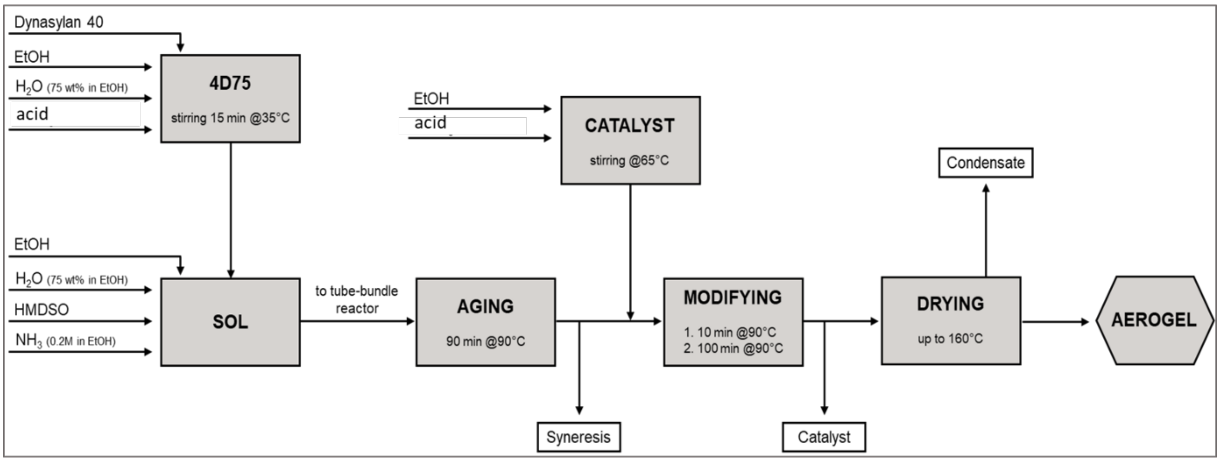


Figure 10: Production flow for the industrial aerogel manufacturing using the one pot recipe.

As a first step the sol precursor has to be prepared, which is referred to as P75, or 4D75, since we used Dynasilan ® 40 and not TEOS as it can be found in literature[23]. The sol precursor can be stored multiple weeks in this form and therefore prepared in a step before the actual production starts. The sol will be put for gelation and aging, which is often done in the same process, as the sol gels within the correct conditions and, if let at the same conditions, it ages. During the aging process, the gel body shrinks and syneresis liquid is built. This is removed after aging is ended and the catalyst for modification is added. The modification steps requires a rinsing step, why it's usually refreshed or recirculated after a short time, before the actual reaction time for modification starts. When the modification is completed, excess catalyst is removed and the liquid trapped inside the gel distilled of during the drying, therefore called condensate.

During the process in large scale facility, different parameter change in the tube bundle reactor (R1000) and were used to monitor the reaction; temperature and nitrogen flow were set, pressure change and condensate were given from the settings. The syneresis liquid yield showed the reproducibility of the aging step. The used amount of modification solution gave an idea about the shrinkage of the gel. *Figure 11* shows an example of batch 10, how the different parameters change. For this run (*Figure 11*), from 8:00 to 9:30, the reactor was preheated, rinsed and dried, which can be seen on the elevated temperature. The sudden change in nitrogen flow and the slight increase in condensate comes from the rinsing and drying. From 9:30 to 10:15 the reactor was equilibrated and the heating up to 100 °C started, while the sol was prepared. The slight drop in the temperature indicates the reactor filling. After that, the reactor was sealed and as soon as 100 °C was reached, it was kept for 50 min for aging, from approx. 11:00 to 11:50. The pressure change around 12:00 indicates the start of the modifications cycles (as the pressure compensation is carried out by hand), until the end, where the temperature is increased to 110 °C around 13:45. After that, the pressure was released, liquids were removed and the drying started. At around 15:25 the reactor cooling started (see also: *Figure 16: Overview from Batch 1 to 22 in large scale facility*).

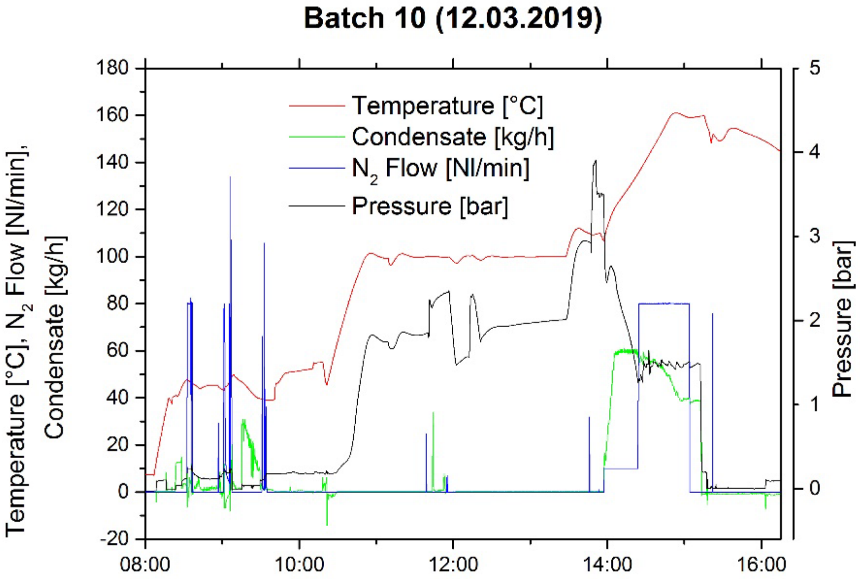


Figure 11: Temperature, condensate, nitrogen flow and pressure plotted against time for Batch 10 in the 80 L reactor to produce aerogel.

3.1.1 Formulations

For the aerogel production the following chemicals are needed: strong mineral acid; 29 % Ammonia solution (NH_4OH); deionized Water (H_2O); anhydrous Ethanol with 2% MEK (EtOH); Dynasilan ® 40 (D40); Hexamethyldisiloxane (HMDSO).

To fill the catalysts and water tanks (B1012, B1014, B1016, B1018) the solution had to be prepared separately using the recipes as in *Table 1* described. The Chemicals were prepared using 25 L canisters, where the chemicals were dosed using a balance or a measuring cylinder. The equipment was always handled while grounded.

Table 1: Chemical composition for filling the acid/ base catalyst and water tanks.

B1012 [mineral acid 1]	EtOH /kg	20-30
	acid /mL	50-200
B1014 [mineral acid 2]	EtOH /kg	20-30
	acid /ml	1500-2500
B1016 [0.2 M NH_4OH]	EtOH /kg	22.68
	NH_3 29% /mL	399.00
B1018 [75/25 wt% H_2O/EtOH]	EtOH /kg	6.25
	H_2O /kg	18.75

For the sol-gel process and drying at ambient pressure three solutions are needed (*Table 2*). The precursor for the sol is a stable solution that can be kept for several weeks and therefore can be prepared in larger quantities for more batches. On the contrary, the sol is not stable anymore, especially after addition of the base, and therefore should be in place for gelation that usually takes only minutes to happen. The modification solution is added after the gelation and aging process is finished, it further strengthens the gel and provides hydrophobicity.

Table 2: Recipe for Precursor, Sol and Modification (Mod) solution to make aerogels in the 1ZR and the 80 L reactor.

		D40 /g	EtOH /mL	Acid /mL	H_20 /mL	Prec. /mL	HMDSO /mL	NH_4OH 2 M /mL	Acid /mL
1ZR	Precursor	345.6	389.25	0.11	54.48				
	Sol		193.08		14.28	144.81	144.81	3.02	
	Mod								250
		D40 /kg	EtOH /kg	Acid 1	H_20 /kg	Prec. /kg	HMDSO /kg	NH_4OH 0.2 M /kg	Acid 2
80 L	Precursor	48.87	36.03	4.83	10.27				
	Sol		30.55		4.21	29.64	24.47	2.65	
	Mod		24.30						3.93

3.1.2 Sol precursor (4D75/ P75) production

The silica source for the process is a concentrated colloidal suspension of silica particles produced by acid-catalyzed hydrolysis condensation of tetraethoxysilanes [23]. For the 1ZR experiments the D 40, and EtOH get mixed and heated up to 35 °C. first the acid is added and then slowly the water, the mixture is stirred at 35 °C for 15 min, after the next day, this solution can be used for up to 2 months. The same procedure can be applied to the 80 L reactor, the ingredients are fed into the mixing vessel (B1010) in the same order. In large scale, the precursor amount was always prepared for a bit more than three runs and stored in the mixture reservoir (B1060).

3.1.3 Sol preparation, reactor filling and gelation

The sol preparation for the 1ZR was done using a flask, adding EtOH, precursor and H_2O, mixing at room temperature with 280 rpm. After dissolving, the HMDSO was added and the solution was brought to the 1ZR. The NH_4OH was added, after 1ZR was prepared for filling, so the sol could be transferred immediately after dissolving the base. After filling the smaller scale reactor it was closed and heating started. Leftover were kept at ambient to check for the gelation.

For the large scale reactor, the same sequence of chemicals was used, but the preparation took place in the mixing vessel (B1010) at ambient temperature with 280 rpm stirring. To make sure, that the reactor always was filled exactly to the same level (to exclude volume errors from temperature changes), a little bit too much sol was prepared to fill it until overflow. The addition of NH_4OH, filling of reactor and discharging the overflow was done automatically, so the gel could never gel at the wrong place. To control the filling of the reactor the liquid level switch (Liquiphant) was used. The leftovers were collected in acid in the catalyst purge feed vessel (B1013) to prevent from gelling and then transferred to waste or recycling.

3.1.4 Aging

Aging is an important step in the sol gel chemistry, as is helps to strengthen the gel structure. During a process called Ostwald ripening, the specific surface area decreases with increased aging time. More time and temperature leads to a lower bulk density, higher pore size and volume for ambient dried gels [17,24]. The aging is a required process, but the overall time can be reduced by using more temperature and pressure, which can be provided by the tube bundle reactor. The aging step takes 90 min at 90 °C and the pressure usually goes up to 1.3 (±0.1) bar. The waiting time during the aging is used to prepare everything for the next modification step.

3.1.5 Modification step

As the gelation and aging step is completed, the HMDSO in the gel included gets activated using acid [21,22]. Therefore the modification solution contains a strong mineral acid that promotes the hydrolysis of HMDSO and generated trimethyl groups, whose apolar and aprotic functionality makes the surface of the gel hydrophobic when attached. The acid content is determined by the base to neutralize and the activation for HMDSO needed, but shouldn't be too high as hydrolysis and condensation reaction could be reversed to certain extend and solubilize the gel.

The modification happens at the similar pressure and same temperature as the aging. The acid and the EtOH is brought to the mixing vessel (B1010) above the reactor and mixed at 150 rpm and 65 °C. As the syneresis liquid is removed from the tube bundle reactor (R1000) the mixing vessel is brought to the same pressure as the reactor. The corresponding valves are opened to fill the reactor with the modification solution until the liquid level switch indicates overflow. The first round of modification serves as a rinsing step and is therefore last 10 min. After this time, the modification solution is released and reintroduced to promote a homogenous distribution, this time for 100 min at 90 °C at 1.5 (±0.1) bar. The process in the 1ZR reactor was performed the same, but the filling and the emptying was done by hand using bottles. The pressure was usually a little bit higher towards the end of the modification step. The modification step has been more modified towards the end of the series (Batch 32 – 36) towards a more cycling process, where the same solution was circled through the reactor (R1000) and the catalyst purge feed vessel (B1013) in time intervals.

3.1.6 Drying, in situ and external

To dry the gel inside the reactor (R1000) it was thought to heat up the reactor (R1000) to 150 °C or even higher and a high flow rate of (preheated) nitrogen gas carries away the evaporating solvents. Therefore a condenser (W1020) was provided to trap the evaporated solvents and the temperature of the reactor is controlled using a Lauda heating system in combination with a thermo oil. In this state of the pilot facility, the nitrogen couldn't get preheated, and therefore had to be used in ambient temperature with heating provided to the gel by the heat exchanger only. Although the drying was adopted from 1ZR experiments, where this strategy worked well, several issues were recognized in the large scale and could not be eliminated.

The large pilot performed very well with respect to the gel preparation process (production of precursor solutions, sol-gel process, aging, hydrophobization. During the operation of the large pilot facility, it became clear that, despite significant trials and efforts, in situ drying did not allow us to produce materials within product specifications. Hence, an alternative, scalable drying technology was identified, and a pilot drying installation rented towards the end of the project. Extensive drying parameter studies were carried out using gels produced in the pilot, and materials for sampling were subsequently produced using the combination of the gel synthesis pilot and the pilot drying installation.

3.2 Characterization techniques

Different Techniques were used to evaluate the procedure and methods used in the process. *Table 3* shows the summary of the used devices and techniques in the process and in the following the devices are described with their specifications.

Most of the recipe that can be used for our process has already been intensively studied [21,22]. Therefore the intermediate steps to get to the gel, i.e. pore volume or surface area affected by the chemical composition did not need complex experimental series. Only small adjustments in regards to previous recipes had to be studied, like the time needed for chemicals to diffuse within the tubular geometry. Most of the time, the process was evaluated checking the parameters during the run (i.e. pressure change and liquid yield) and the final dried material. Mostly the density was used to compare different batches, as this parameter proved as a good first indicator for the overall impression of the material. If the final material was too dense or too brittle, the lambda value as the nitrogen sorption wouldn't be good either. If the material showed good quality, the particle size distribution gave an idea if the drying process was too destructive for the material.

Table 3: List of different characterization techniques

Measurement	Device	Analyt
Tap density	Measuring cylinder and balance	Aerogel
Envelope density	Sand Pycnometre	Aerogel
Partcile Size Distribution	Sieves	Aerogel
Lambda value	Guarded hot plate measurement	Aerogel
Nitrogen sorption, Pore Volume, Surface area	3 Flex Surface characterization analyzer	Aerogel
^{1}H-NMR	NMR spectrometer	Solvent recovery

3.2.1 NMR spectroscopy

NMR spectra were acquired on a Bruker Avance III HD NMR spectrometer equipped with a 9.4 T wide-bore magnet, corresponding to Larmor frequencies of 400.2 and 100.6 for ^{1}H and ^{13}C, respectively.

3.2.2 Tap density

To measure the tap density, a polymethylpentene measuring cylinder (Nalgene ® 100 mL) and a balance are used. The aerogel to measure has to be overturned in the box, to avoid granular convection. The tarra of the measuring cylinder has to be measured, and filled with aerogel granulate two third. To prevent from loss, the cylinder is closed by hand and tapped to an even surface approx.. 20 times, until the level of the material was constant. Volume and weight of the material is measured, from which the tap density can be calculated. This measurement had always been repeated at least three times. To measure the tap density is a simple and easy method to determine quality, after appearance and haptics already show a good material. Since the tap density is also depended on the particle size distribution it can only be used in a continues process, where it can be assumed the particle size distribution is similar.

3.2.3 Envelope density

The envelope density (ρ) was obtained by a Geopyc 1360 (Micromeritics). A 12.7 mm diameter chamber was used to measure with a consolidation pressure of 4 N. 10 cycles were carried out for each measurement. The envelope density is always the first one to be measured for aerogel granulate. Only if the parameters show good quality, further analytics are done.

3.2.4 Guarded hot-plate measurements

The packed bed thermal conductivity of small samples was determined using a custom built guarded hot plate device (measuring zone of 25 × 25 mm2) which was designed for small samples of low conduct ivity materials. One side of the asymmetric configuration was heated to 30°C with the other side cooled to 12°C. Packed granulate bed thermal conductivities were measured on a mixture of aerogel granulate (2-4 mm) with aerogel powder (crushed aerogel granulate) in a 1.7/1 mass ratio. The mixture was loaded into a 60x50x13 mm3 frame sealed at the bottom with a thin polymer film. The thermal conductivity of the larger, pilot-produced sample was also measured using a large guarded hot plate device according to SN EN 12667 and ISO 8302. Two 490x490x50 mm 3 frames were filled with silica aerogel granulate before they were closed with a thin polymer film. The two frames filled with aerogel granulate lie horizontally sandwiched between the hotplate and the two cooling plates, and are surrounded by a thick layer of thermal insulation.

3.2.5 Nitrogen sorption analysis

The surface area (S_{BET}) and pore structure were characterized by nitrogen sorption analysis. A sample (particle size ≈3 mm) of measured mass (typically ≈100 mg) was placed in a glass tube and degassed under vacuum to a pressure of 0.016 mbar for 20 h at 100 °C (heating rate of 10 °C min−1). The samples were weighed again and the nitrogen sorption isotherms analyzed in a Micromeritics 3Flex instrument with P/P 0 ranging from 0.001 to 0.998 in 30 steps, equilibration times of 10 s for each incremental nitrogen addition, a minimum of 600 s per incremental step, leading to a total run time of ≈20 h. The analysis used the BET model to extract the surface area S_{BET}.

4 Results and discussion

4.1 Single tubes and single cell reactor (1ZR)

The new production concept is based on a tube-like geometry of the gel bodies that enables for a very fast heat transfer to the gel, which is critical to speed up the sol-gel and hydrophobization process. The viablity of this approach for the rapid production of silica gels/aerogels was verified at the smaller scale before implementation in a large pilot facility.

Table 4: Overview single tube experiments

Series	Goals	Results
1	Reduction of water, 29% HMDSO	Samples density in range 0.10-0.12g/cm^3
2	Reduction of water, 25% HMDSO	Samples denser than 0.13 g/cm^3
3	Reduction of water, 27% HMDSO	Optimal amount of HMDSO
4	Aging and modification time study	2h + 2h best results
5	Influence of water in modification solution	Less water better results
6	Diffusion time of acid during modification	
7	Modification with acid at 120°C	Materials too dense
8	Melamine addition to decrease ammonia conc.	Further exp. needed
9	Hydrolysis with phosphoric acid	Did not work

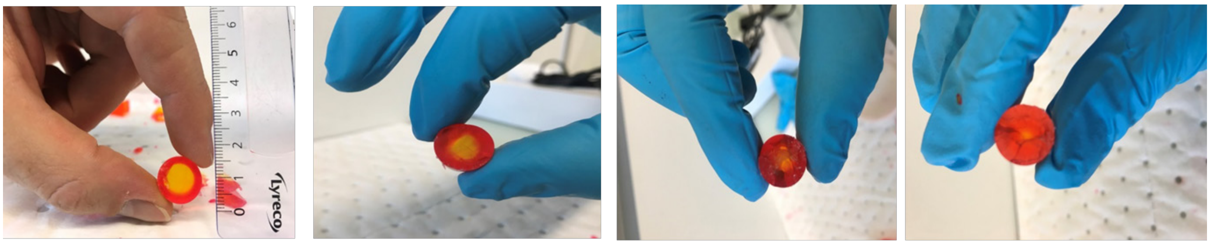
The experimental series started with single tube experiments in laboratory scale. *Table 4* gives an overview of the conducted experiments and in the following the most important findings are described. *Table 5* and *Figure 13* shows the parameters for experimental series 6 and the result.

Table 5: Example for an experimental series (6 a to l) from single tubes, where the influence of a specific acid as modification agent was observed for different modification times. For this series, an aging and modification temperature of 105 °C was applied.

Sample	P750 [ml]	Ethanol [ml]	water [ml]	HMDSO [ml]	2 M NH_3 [ml]	Modification / Acid catalyst	Aging time
6a	12	16	1.183	12	0.25	2.5 ml of 0.125 M acid 1h	0.5h
6b						2.5 ml of 0.125 M acid 1.5h	0.5h
6c						2.5 ml of 0.125 M acid 2h	0.5h
6d						2.5 ml of 0.125 M acid 1h	1h
6e						2.5 ml of 0.125 M acid 1.5h	1h
6f						2.5 ml of 0.125 M acid 2h	1h
6g						2.5 ml of 0.125 M acid 1h	1.5h
6h						2.5 ml of 0.125 M acid 1.5h	1.5h
6i						2.5 ml of 0.125 M acid 2h	1.5h
6j						2.5 ml of 0.125 M acid 1h	2h
6k						2.5 ml of 0.125 M acid 1.5h	2h
6l						2.5 ml of 0.125 M acid 2h	2h

Figure 13: Heating oil bath with lab scaled sample containers (top) and resulting silica aerogel granulate samples.

The sol-gel process was optimized in terms of processing time in the lab, where a variety of chemical conditions (concentrations of reagents and catalysts) could be varied simultaneously (*Figure 13*). The production of a high quality aerogel with low density requires sufficient mechanical strength and sufficient surface hydrophobization to promote spring-back (recovery of volume) after the shrinkage due to the strong capillary forces during the evaporative drying process. At the same time, for economical production, we want to minimize the aging time and hydrophobization time to increase the throughput of a production facility. In order to reconcile these conflicting requirements and be able to produce strong, well-hydrophobized silica gels using short aging and hydrophobization times, it is paramount to identify the optimum combination of processing conditions (chemistry, temperature, pressure, time). In total 9 series of such experiments were carried out to find the optimum conditions and all samples analyzed in terms of density. Hydrophobization efficiency is limited by the infiltration of the (acidic) hydrophobization catalyst, which activates the HMDSO hydrophobization agent that is already inside the gel (*Figure 1*). A series of lab scale experiments were carried out with methyl orange as pH indicator to visually follow the hydrophobization process as a function of time (*Figure 14*).



Gel after 15 min

Gel after 30 min

Gel after 45 min

Gel after 60 min

Figure 12: Diffusion of the acidic hydrophobization catalyst monitored by the methyl-orange pH indicator (yellow= basic, red= acidic).

Table 6: Comparison of several batches from the 1ZR.

Sample	Density $[g/cm^3]$	Thermal conductivity [mV/m*K]
Batch 7	0,166	
Batch 8	0,194	
Batch 9	0,123	
Batch 10	0,103	
Batch 12	0,107	18,9
Batch 13	0,124	17,4
Batch 14	0,125	17,9

Parallel to the single tube experiments, already the first Experiments in the 1ZR were conducted. The first set of experiments in the 1ZR consisted of parameter studies to optimize the silica aerogel quality (envelope density at or below 0.120 g/cm^3, thermal conductivity of the particle bed around 18 mW/(m.K). After some initial trials, proof-of-concept was achieved for Batches 12-14. In *Table 7* the envelope density and thermal conductivity are listed, these experiments were conducted all completely in the 1ZR reactor: filling with sol, gelation and aging, modification and the drying.

Overall there were about 60 Experiments conducted in the 1ZR, but after this first Experiments the large scale facility was commissioned. Later on experiments were done parallel to the operation in the 80 L reactor for double confirmation, e.g. use the prepared sol precursor from the pilot in the 1ZR. To investigate if the tubes could have a larger diameter for an industrial scale facility, it was also possible to exchange the tube in the 1ZR. In the end, there have been over 40 batches run in the 1ZR whose purpose mainly was, to confirm procedures in the large scale and if there something didn't work e.g. if it was the chemicals used, or the pilot facility. In the end, this also helped to find out, that external drying will lead to better material.

A best process, based on the design of the lab scale experiments was then implemented on the 1ZR reactor with the following conclusions:

- Whole process in tubes with 20 mm diameter can be done in 5 hours, including drying
- In tubes with 25 mm diameter, the process can be done in 5 hour 35 min, including drying
- Sol/process optimized with different mineral acids for catalyst activation
- Diffusion of acid during modification strongly depends on temperature, further possibility to accelerate the whole process
- Good density aerogel samples, within material specifications, are obtained when flow rate of hot nitrogen during drying is minimum 7 l/min

Based on these promising results, the decision was taken to move forward with a large pilot installation based on this production concept.

4.2 Large pilot reactor ("Nautilus")

Following the conceptualizing, the pilot plant was realized as in *Figure 15 a-j* is shown.

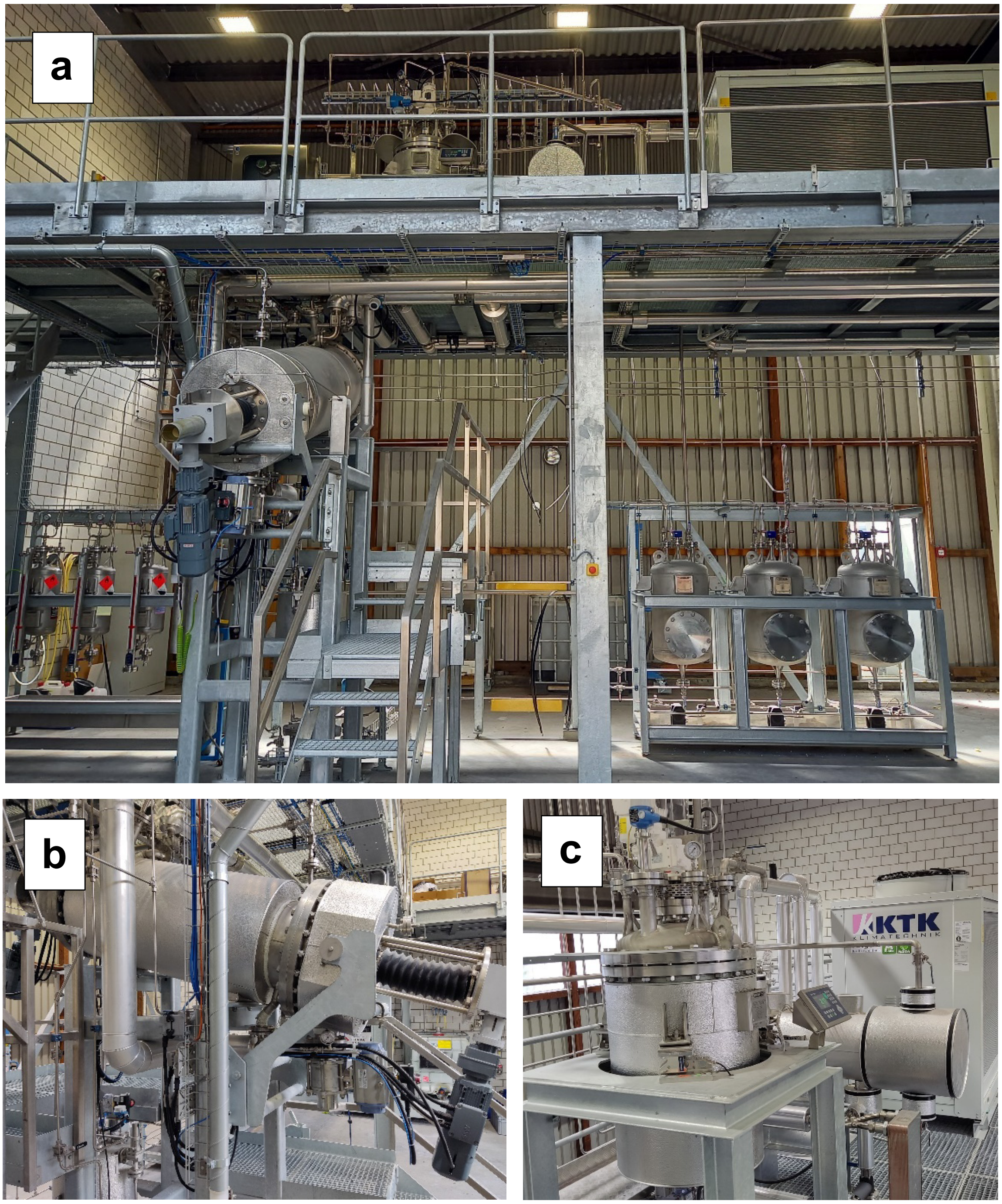


Figure 14: Silica aerogel granulate production facility at Empa. a) Overview of the pilot plant situated at Empa. On the 2nd floor the mixing vessel is located next to the condenser and the cooling system to the right side. On the middle floor is the sol-gel reactor. The catalyst purge feed vessel is underneath it on the ground floor. Right on that the mixture reservoirs can be seen and on the very left the vessels for minor components. b) Sol-gel reactor vessel. c) Sol mixing vessel. ***(continues)***

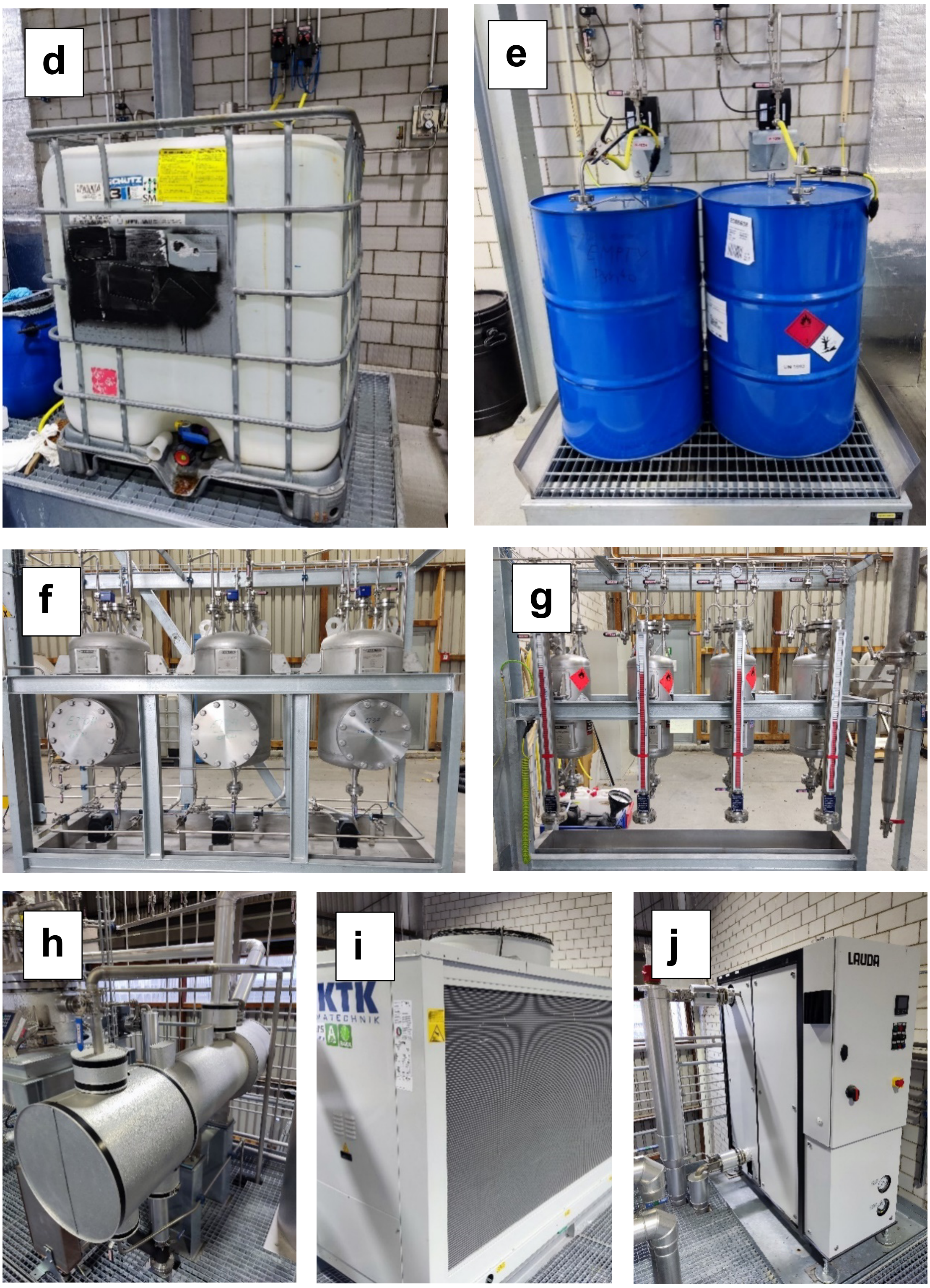
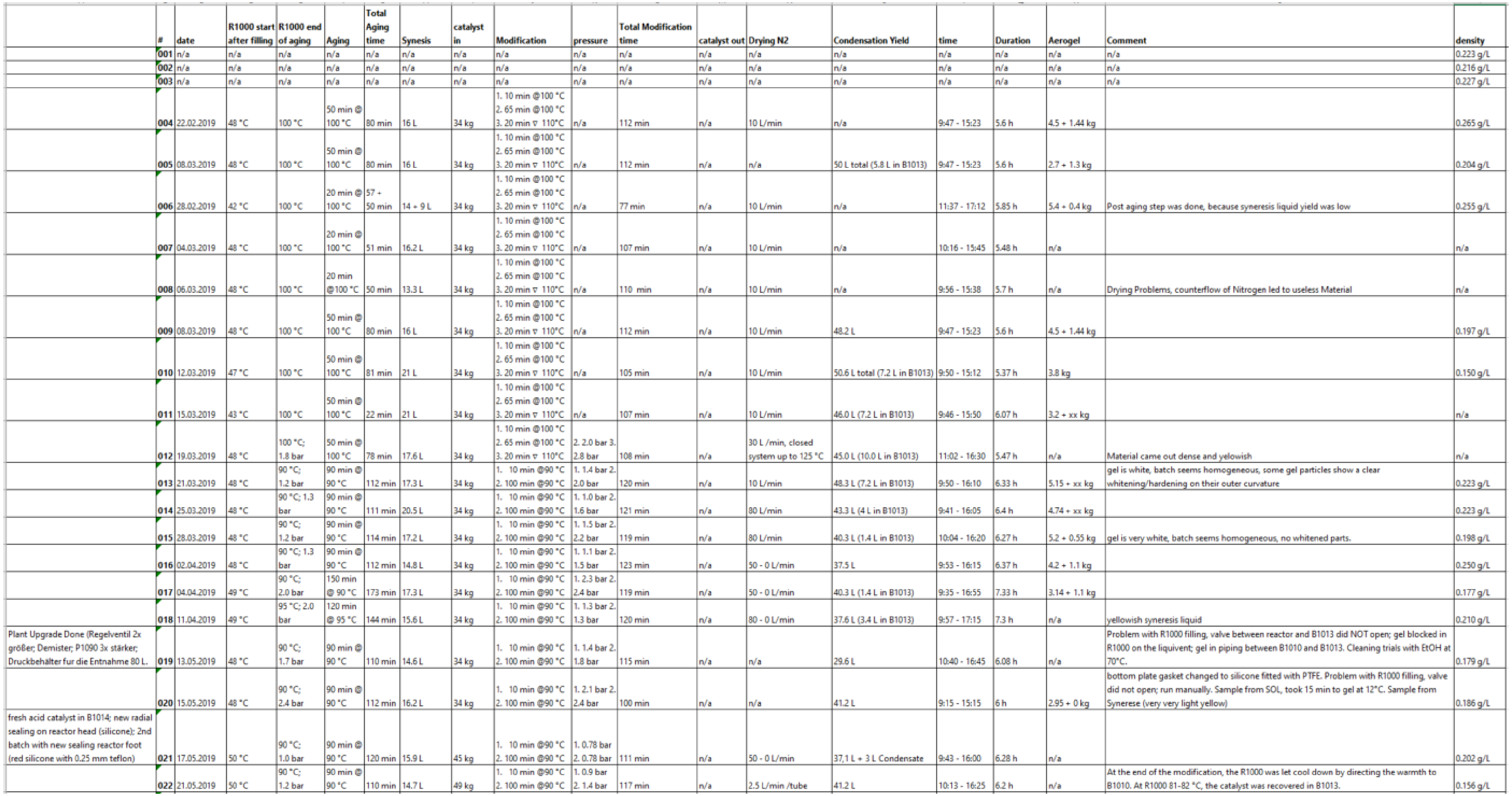


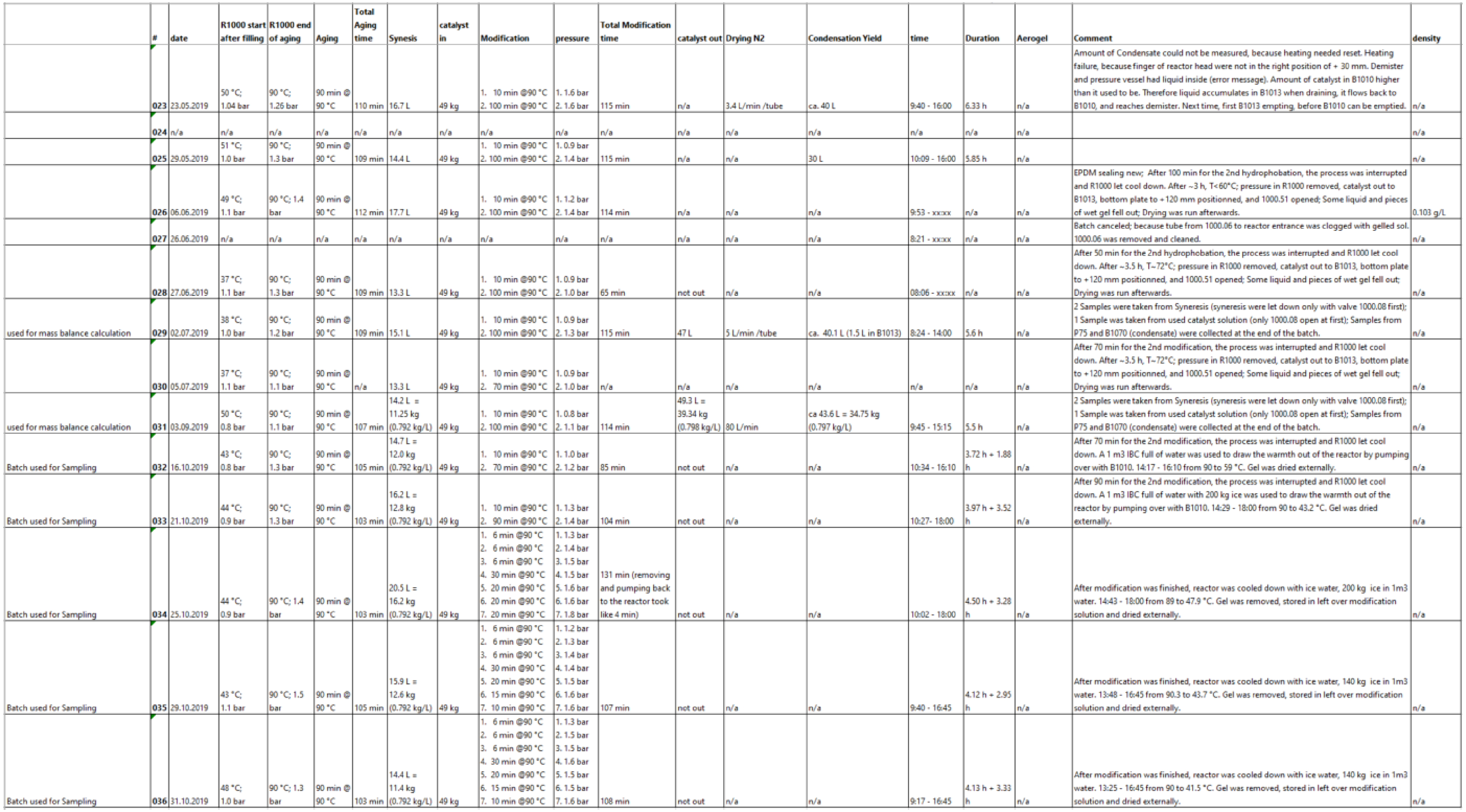
Figure 15 ***(continued)****. d-e) Raw materials, solvents and waste containers, f) Mixture reservoirs. g) Minor component vessels. h) Condenser. i) heating system. j) Cooling aggregate.*

4.2.1 Experiments targeting in situ drying



	#	date	R1000 start after filling	R1000 end of aging	Aging	Total Aging time	Synesis	catalyst in	Modification	pressure	Total Modification time	catalyst out	Drying N2	Condensation Yield	time	Duration	Aerogel	Comment	density
	001	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.223 g/L
	002	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.216 g/L
	003	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	0.227 g/L
	004	22.02.2019	48 °C	100 °C	50 min @ 100 °C	80 min	16 L	34 kg	1. 10 min @100 °C 2. 65 min @100 °C 3. 20 min ▿ 110°C	n/a	112 min	n/a	10 L/min	n/a	9:47 - 15:23	5.6 h	4.5 + 1.44 kg		0.265 g/L
	005	08.03.2019	48 °C	100 °C	50 min @ 100 °C	80 min	16 L	34 kg	1. 10 min @100 °C 2. 65 min @100 °C 3. 20 min ▿ 110°C	n/a	112 min	n/a	n/a	50 L total (5.8 L in B1013)	9:47 - 15:23	5.6 h	2.7 + 1.3 kg		0.204 g/L
	006	28.02.2019	42 °C	100 °C	20 min @ 100 °C	57 + 50 min	14 + 9 L	34 kg	1. 10 min @100 °C 2. 65 min @100 °C 3. 20 min ▿ 110°C	n/a	77 min	n/a	10 L/min	n/a	11:37 - 17:12	5.85 h	5.4 + 0.4 kg	Post aging step was done, because syneresis liquid yield was low	0.255 g/L
	007	04.03.2019	48 °C	100 °C	20 min @ 100 °C	51 min	16.2 L	34 kg	1. 10 min @100 °C 2. 65 min @100 °C 3. 20 min ▿ 110°C	n/a	107 min	n/a	10 L/min	n/a	10:16 - 15:45	5.48 h	n/a		n/a
	008	06.03.2019	48 °C	100 °C	20 min @100 °C	50 min	13.3 L	34 kg	1. 10 min @100 °C 2. 65 min @100 °C 3. 20 min ▿ 110°C	n/a	110 min	n/a	10 L/min	n/a	9:56 - 15:38	5.7 h	n/a	Drying Problems, counterflow of Nitrogen led to useless Material	n/a
	009	08.03.2019	48 °C	100 °C	50 min @ 100 °C	80 min	16 L	34 kg	1. 10 min @100 °C 2. 65 min @100 °C 3. 20 min ▿ 110°C	n/a	112 min	n/a	10 L/min	48.2 L	9:47 - 15:23	5.6 h	4.5 + 1.44 kg		0.197 g/L
	010	12.03.2019	47 °C	100 °C	50 min @ 100 °C	81 min	21 L	34 kg	1. 10 min @100 °C 2. 65 min @100 °C 3. 20 min ▿ 110°C	n/a	105 min	n/a	10 L/min	50.6 L total (7.2 L in B1013)	9:50 - 15:12	5.37 h	3.8 kg		0.150 g/L
	011	15.03.2019	43 °C	100 °C	50 min @ 100 °C	22 min	21 L	34 kg	1. 10 min @100 °C 2. 65 min @100 °C 3. 20 min ▿ 110°C	n/a	107 min	n/a	10 L/min	46.0 L (7.2 L in B1013)	9:46 - 15:50	6.07 h	3.2 + xx kg		n/a
	012	19.03.2019	48 °C	100 °C; 1.8 bar	50 min @ 100 °C	78 min	17.6 L	34 kg	1. 10 min @100 °C 2. 65 min @100 °C 3. 20 min ▿ 110°C	2. 2.0 bar 3. 2.8 bar	108 min	n/a	30 L /min, closed system up to 125 °C	45.0 L (10.0 L in B1013)	11:02 - 16:30	5.47 h	n/a	Material came out dense and yelowish	n/a
	013	21.03.2019	48 °C	90 °C; 1.2 bar	90 min @ 90 °C	112 min	17.3 L	34 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 1.4 bar 2. 2.0 bar	120 min	n/a	10 L/min	48.3 L (7.2 L in B1013)	9:50 - 16:10	6.33 h	5.15 + xx kg	gel is white, batch seems homogeneous, some gel particles show a clear whitening/hardening on their outer curvature	0.223 g/L
	014	25.03.2019	48 °C	90 °C; 1.3 bar	90 min @ 90 °C	111 min	20.5 L	34 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 1.0 bar 2. 1.6 bar	121 min	n/a	80 L/min	43.3 L (4 L in B1013)	9:41 - 16:05	6.4 h	4.74 + xx kg		0.223 g/L
	015	28.03.2019	48 °C	90 °C; 1.2 bar	90 min @ 90 °C	114 min	17.2 L	34 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 1.5 bar 2. 2.2 bar	119 min	n/a	80 L/min	40.3 L (1.4 L in B1013)	10:04 - 16:20	6.27 h	5.2 + 0.55 kg	gel is very white, batch seems homogeneous, no whitened parts.	0.198 g/L
	016	02.04.2019	48 °C	90 °C; 1.3 bar	90 min @ 90 °C	112 min	14.8 L	34 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 1.1 bar 2. 1.5 bar	123 min	n/a	50 - 0 L/min	37.5 L	9:53 - 16:15	6.37 h	4.2 + 1.1 kg		0.250 g/L
	017	04.04.2019	49 °C	90 °C; 2.0 bar	150 min @ 90 °C	173 min	17.3 L	34 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 2.3 bar 2. 2.4 bar	119 min	n/a	50 - 0 L/min	40.3 L (1.4 L in B1013)	9:35 - 16:55	7.33 h	3.14 + 1.1 kg		0.177 g/L
	018	11.04.2019	49 °C	95 °C; 2.0 bar	120 min @ 95 °C	144 min	15.6 L	34 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 1.3 bar 2. 1.3 bar	120 min	n/a	80 - 0 L/min	37.6 L (3.4 L in B1013)	9:57 - 17:15	7.3 h	n/a	yellowish syneresis liquid	0.210 g/L
Plant Upgrade Done (Regelventil 2x größer; Demister; P1090 3x stärker; Druckbehälter fur die Entnahme 80 L.	**019**	13.05.2019	48 °C	90 °C; 1.7 bar	90 min @ 90 °C	110 min	14.6 L	34 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 1.4 bar 2. 1.8 bar	115 min	n/a	n/a	29.6 L	10:40 - 16:45	6.08 h	n/a	Problem with R1000 filling, valve between reactor and B1013 did NOT open; gel blocked in R1000 on the liquivent; gel in piping between B1010 and B1013. Cleaning trials with EtOH at 70°C.	0.179 g/L
	020	15.05.2019	48 °C	90 °C; 2.4 bar	90 min @ 90 °C	112 min	16.2 L	34 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 2.1 bar 2. 2.4 bar	100 min	n/a	n/a	41.2 L	9:15 - 15:15	6 h	2.95 + 0 kg	bottom plate gasket changed to silicone fitted with PTFE. Problem with R1000 filling, valve did not open; run manually. Sample from SOL, took 15 min to gel at 12°C. Sample from Synerese (very very light yellow)	0.186 g/L
fresh acid catalyst in B1014; new radial sealing on reactor head (silicone); 2nd batch with new sealing reactor foot (red silicone with 0.25 mm teflon)	**021**	17.05.2019	50 °C	90 °C; 1.0 bar	90 min @ 90 °C	120 min	15.9 L	45 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 0.78 bar 2. 0.78 bar	111 min	n/a	50 - 0 L/min	37,1 L + 3 L Condensate	9:43 - 16:00	6.28 h	n/a		0.202 g/L
	022	21.05.2019	50 °C	90 °C; 1.2 bar	90 min @ 90 °C	110 min	14.7 L	49 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 0.9 bar 2. 1.4 bar	117 min	n/a	2.5 L/min /tube	41.2 L	10:13 - 16:25	6.2 h	n/a	At the end of the modification, the R1000 was let cool down by directing the warmth to B1010. At R1000 81-82 °C, the catalyst was recovered in B1013.	0.156 g/L

Figure 15: Overview from Batch 1 to 22 in large scale facility with envelope density and comments



	#	date	R1000 start after filling	R1000 end of aging	Aging	Total Aging time	Synesis	catalyst in	Modification	pressure	Total Modification time	catalyst out	Drying N2	Condensation Yield	time	Duration	Aerogel	Comment	density
	023	23.05.2019	50 °C; 1.04 bar	90 °C; 1.26 bar	90 min @ 90 °C	110 min	16.7 L	49 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 1.6 bar 2. 1.6 bar	115 min	n/a	3.4 L/min /tube	ca. 40 L	9:40 - 16:00	6.33 h	n/a	Amount of Condensate could not be measured, because heating needed reset. Heating failure, because finger of reactor head were not in the right position of + 30 mm. Demister and pressure vessel had liquid inside (error message). Amount of catalyst in B1010 higher than it used to be. Therefore liquid accumulates in B1013 when draining, it flows back to B1010, and reaches demister. Next time, first B1013 empting, before B1010 can be emptied.	n/a
	024	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a		n/a
	025	29.05.2019	51 °C; 1.0 bar	90 °C; 1.3 bar	90 min @ 90 °C	109 min	14.4 L	49 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 0.9 bar 2. 1.4 bar	115 min	n/a	n/a	30 L	10:09 - 16:00	5.85 h	n/a		n/a
	026	06.06.2019	49 °C; 1.1 bar	90 °C; 1.4 bar	90 min @ 90 °C	112 min	17.7 L	49 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 1.2 bar 2. 1.4 bar	114 min	n/a	n/a	n/a	9:53 - xx:xx	n/a	n/a	EPDM sealing new; After 100 min for the 2nd hydrophobation, the process was interrupted and R1000 let cool down. After ~3 h, T<60°C; pressure in R1000 removed, catalyst out to B1013, bottom plate to +120 mm positionned, and 1000.51 opened; Some liquid and pieces of wet gel fell out; Drying was run afterwards.	0.103 g/L
	027	26.06.2019	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	8:21 - xx:xx	n/a	n/a	Batch canceled; because tube from 1000.06 to reactor entrance was clogged with gelled sol. 1000.06 was removed and cleaned.	n/a
	028	27.06.2019	37 °C; 1.1 bar	90 °C; 1.3 bar	90 min @ 90 °C	109 min	13.3 L	49 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 0.9 bar 2. 1.0 bar	65 min	not out	n/a	n/a	08:06 - xx:xx	n/a	n/a	After 50 min for the 2nd hydrophobation, the process was interrupted and R1000 let cool down. After ~3.5 h, T~72°C; pressure in R1000 removed, catalyst out to B1013, bottom plate to +120 mm positionned, and 1000.51 opened; Some liquid and pieces of wet gel fell out; Drying was run afterwards.	n/a
used for mass balance calculation	**029**	02.07.2019	38 °C; 1.0 bar	90 °C; 1.2 bar	90 min @ 90 °C	109 min	15.1 L	49 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 0.9 bar 2. 1.3 bar	115 min	47 L	5 L/min /tube	ca. 40.1 L (1.5 L in B1013)	8:24 - 14:00	5.6 h	n/a	2 Samples were taken from Syneresis (syneresis were let down only with valve 1000.08 first); 1 Sample was taken from used catalyst solution (only 1000.08 open at first); Samples from P75 and B1070 (condensate) were collected at the end of the batch.	n/a
	030	05.07.2019	37 °C; 1.1 bar	90 °C; 1.1 bar	90 min @ 90 °C	n/a	13.3 L	49 kg	1. 10 min @90 °C 2. 70 min @90 °C	1. 0.9 bar 2. 1.0 bar	n/a	n/a	n/a	n/a	n/a	n/a	n/a	After 70 min for the 2nd modification, the process was interrupted and R1000 let cool down. After ~3.5 h, T~72°C; pressure in R1000 removed, catalyst out to B1013, bottom plate to +120 mm positionned, and 1000.51 opened; Some liquid and pieces of wet gel fell out; Drying was run afterwards.	n/a
used for mass balance calculation	**031**	03.09.2019	50 °C; 0.8 bar	90 °C; 1.1 bar	90 min @ 90 °C	107 min	14.2 L = 11.25 kg (0.792 kg/L)	49 kg	1. 10 min @90 °C 2. 100 min @90 °C	1. 0.8 bar 2. 1.1 bar	114 min	49.3 L = 39.34 kg (0.798 kg/L)	80 L/min	ca 43.6 L = 34.75 kg (0.797 kg/L)	9:45 - 15:15	5.5 h	n/a	2 Samples were taken from Syneresis (syneresis were let down only with valve 1000.08 first); 1 Sample was taken from used catalyst solution (only 1000.08 open at first); Samples from P75 and B1070 (condensate) were collected at the end of the batch.	n/a
Batch used for Sampling	**032**	16.10.2019	43 °C; 0.8 bar	90 °C; 1.3 bar	90 min @ 90 °C	105 min	14.7 L = 12.0 kg (0.792 kg/L)	49 kg	1. 10 min @90 °C 2. 70 min @90 °C	1. 1.0 bar 2. 1.2 bar	85 min	not out	n/a	n/a	10:34 - 16:10	3.72 h + 1.88 h	n/a	After 70 min for the 2nd modification, the process was interrupted and R1000 let cool down. A 1 m3 IBC full of water was used to draw the warmth out of the reactor by pumping over with B1010. 14:17 - 16:10 from 90 to 59 °C. Gel was dried externally.	n/a
Batch used for Sampling	**033**	21.10.2019	44 °C; 0.9 bar	90 °C; 1.3 bar	90 min @ 90 °C	103 min	16.2 L = 12.8 kg (0.792 kg/L)	49 kg	1. 10 min @90 °C 2. 90 min @90 °C	1. 1.3 bar 2. 1.4 bar	104 min	not out	n/a	n/a	10:27- 18:00	3.97 h + 3.52 h	n/a	After 90 min for the 2nd modification, the process was interrupted and R1000 let cool down. A 1 m3 IBC full of water with 200 kg ice was used to draw the warmth out of the reactor by pumping over with B1010. 14:29 - 18:00 from 90 to 43.2 °C. Gel was dried externally.	n/a
Batch used for Sampling	**034**	25.10.2019	44 °C; 0.9 bar	90 °C; 1.4 bar	90 min @ 90 °C	103 min	20.5 L = 16.2 kg (0.792 kg/L)	49 kg	1. 6 min @90 °C 2. 6 min @90 °C 3. 6 min @90 °C 4. 30 min @90 °C 5. 20 min @90 °C 6. 20 min @90 °C 7. 20 min @90 °C	1. 1.3 bar 2. 1.4 bar 3. 1.5 bar 4. 1.5 bar 5. 1.6 bar 6. 1.6 bar 7. 1.8 bar	131 min (removing and pumping back to the reactor took like 4 min)	not out	n/a	n/a	10:02 - 18:00	4.50 h + 3.28 h	n/a	After modification was finished, reactor was cooled down with ice water, 200 kg ice in 1m3 water. 14:43 - 18:00 from 89 to 47.9 °C. Gel was removed, stored in left over modification solution and dried externally.	n/a
Batch used for Sampling	**035**	29.10.2019	43 °C; 1.1 bar	90 °C; 1.5 bar	90 min @ 90 °C	105 min	15.9 L = 12.6 kg (0.792 kg/L)	49 kg	1. 6 min @90 °C 2. 6 min @90 °C 3. 6 min @90 °C 4. 30 min @90 °C 5. 20 min @90 °C 6. 15 min @90 °C 7. 10 min @90 °C	1. 1.2 bar 2. 1.3 bar 3. 1.4 bar 4. 1.4 bar 5. 1.5 bar 6. 1.6 bar 7. 1.6 bar	107 min	not out	n/a	n/a	9:40 - 16:45	4.12 h + 2.95 h	n/a	After modification was finished, reactor was cooled down with ice water, 140 kg ice in 1m3 water. 13:48 - 16:45 from 90.3 to 43.7 °C. Gel was removed, stored in left over modification solution and dried externally.	n/a
Batch used for Sampling	**036**	31.10.2019	48 °C; 1.0 bar	90 °C; 1.3 bar	90 min @ 90 °C	103 min	14.4 L = 11.4 kg (0.792 kg/L)	49 kg	1. 6 min @90 °C 2. 6 min @90 °C 3. 6 min @90 °C 4. 30 min @90 °C 5. 20 min @90 °C 6. 15 min @90 °C 7. 10 min @90 °C	1. 1.3 bar 2. 1.5 bar 3. 1.5 bar 4. 1.6 bar 5. 1.5 bar 6. 1.5 bar 7. 1.6 bar	108 min	not out	n/a	n/a	9:17 - 16:45	4.13 h + 3.33 h	n/a	After modification was finished, reactor was cooled down with ice water, 140 kg ice in 1m3 water. 13:25 - 16:45 from 90 to 41.5 °C. Gel was removed, stored in left over modification solution and dried externally.	n/a

Figure 16 (continuing): Overview from Batch 23 to 36 in large scale facility with envelope density and comments

Overall 36 batches have been carried in the large scale facility during the BFE project (*Figure 16*). Despite many tries, and including modifications to the pilot facility to improve heating rate and nitrogen gas flow during drying. A homogenous material within specifications could not be produced by the in situ drying protocol. After it was not possible to achieve the desired densities, the gels from the last five batches have been removed from the pilot before drying, so they could be dried externally. In order to do that, other parameters had to been studied, e.g. how to storage. More to this in the following chapter.

4.2.2 Return to external drying

Because of the success with the all-in-one approach (including drying) with the 1ZR reactor, the main pilot plant also has been designed with this goal in mind. Following commissioning, a large number of experiments have been carried out to optimize materials quality. Unfortunately, the excellent materials qualities (low density) reached with the 1ZR reactor (See section 4.1) did not translate directly to the large pilot installation. After multiple months of (mostly fruitless) optimization attempts, and some modifications to the plant to try and remedy the problems (See section 4.2.1), it was decided to forego the in situ drying step, but rather to carry out the sol-gel and hydrophobization steps in the reactor, extract the solvent-containing silica gel, and carry out the drying using alternative methods. Following this decision, proof-of-concept could be reached very quickly: fast and reproducible production of hydrophobized silica gels with excellent material properties (sufficiently low density) after (external) evaporative drying. The new approach with external drying has the following disadvantages:

- Additional drying apparatus/technology required.
- Required transfer of solvent containing gel from synthesis reactor to drying apparatus, VOC emissions need to be eliminated.
- A scalable industrial drying technology needs to be found and tested.
- However, production cost and cycle considerations highlighted the following advantages
- Drying period not part of cycle time for main production reactor: shorter cycle time means higher throughput for a given reactor volume.
- Promising industrial drying technology is available commercially.

A careful cost analysis revealed that the advantage of shorter reactor cycle times have a massive benefit towards reducing CAPEX, and would outweigh the cost of an external drying installation. Hence, a variety of possible drying techniques were evaluated. For the most promising drying technique, a transportable pilot installation was rented from the same supplier that builds large industrial installations. This pilot installation has only a limited capacity (up to 3 L of material) but closely mimics the conditions and processes on a larger industrial installation.

A large number of drying experiments were carried out, both on laboratory produced test materials, materials produced in 1ZR and materials produced in Nautilus to elucidate the effect of drying temperature, nitrogen flow rate, specific loading of the dryer, gel storage conditions etc. The effect of the storage of the gels in the modification solution was analyzed, because the discharging of the gels is assisted by the liquid, as it helps sweeping the solids from the sol-gel reactor, which leads to a lot of liquid in between the wet gels. Different measurements have shown that this does not affect the density of the gels (*Figure 20*). The effect of mass loading during drying was studied to optimize the capacity, a certain cut off can be found in every drying process (*Figure 19*). Drying temperature, time and gas flow are crucial parameters for the final density of the Aerogel (*Figure 18*, *Figure 21*).

The dried aerogel product consists aerogel particles in excess of 1 mm, with a very limited fraction of dust. Several full a aerogel batches from Nautilus (>50 L) were dried to provide materials for internal and external quality control and sampling to prospective partners and clients and proof of concept.

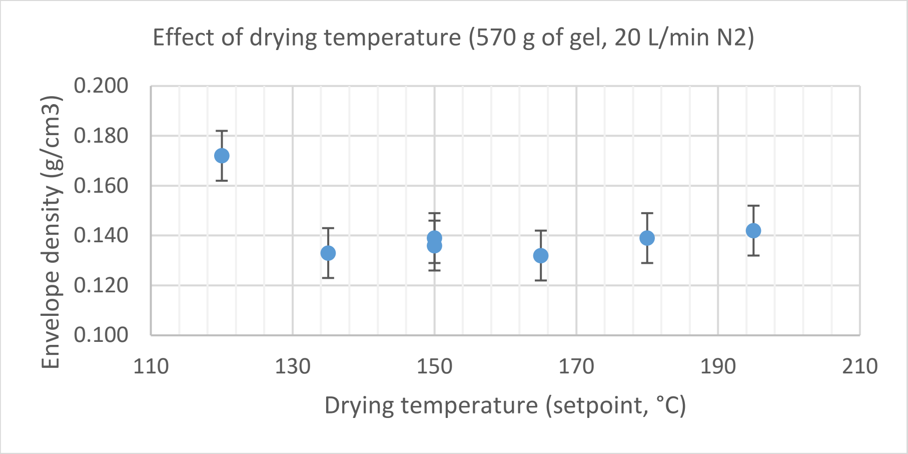


Figure 18: Wide plateau in drying temperature. Higher densities at very low or very high drying temperatures.

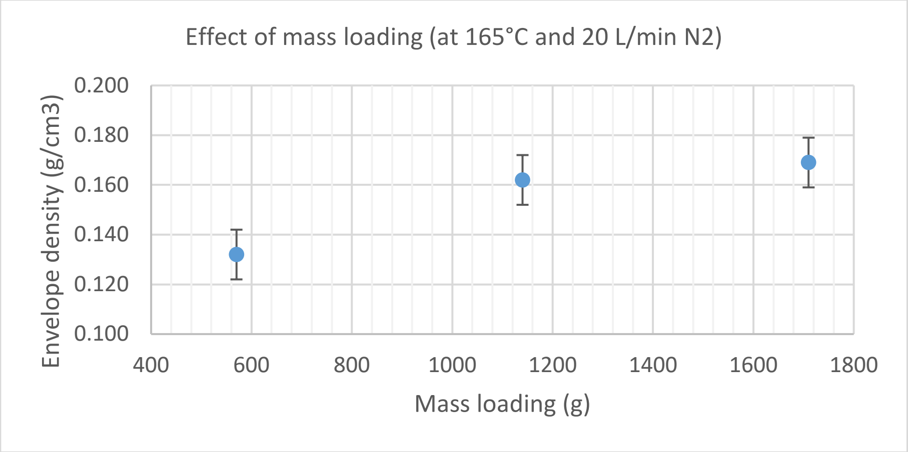


Figure 17: Difficulty to maintain low aerogel density at high loading of product into drier.

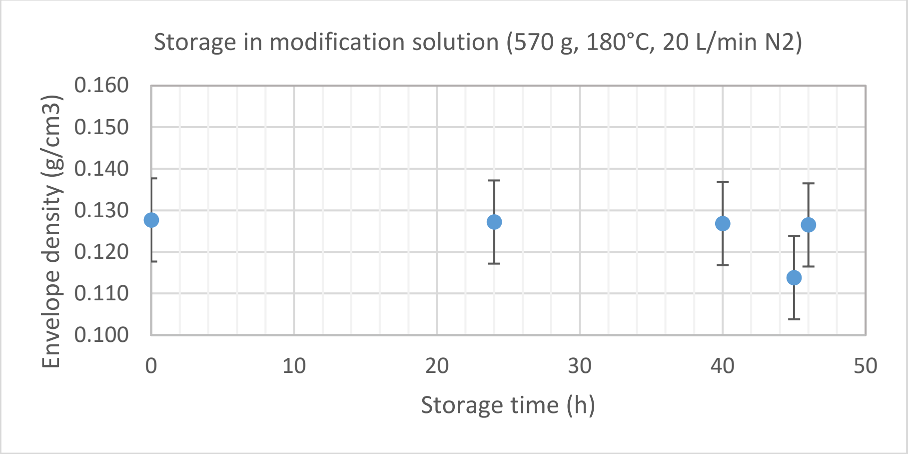


Figure 16: No effect of gel storage on aerogel density.

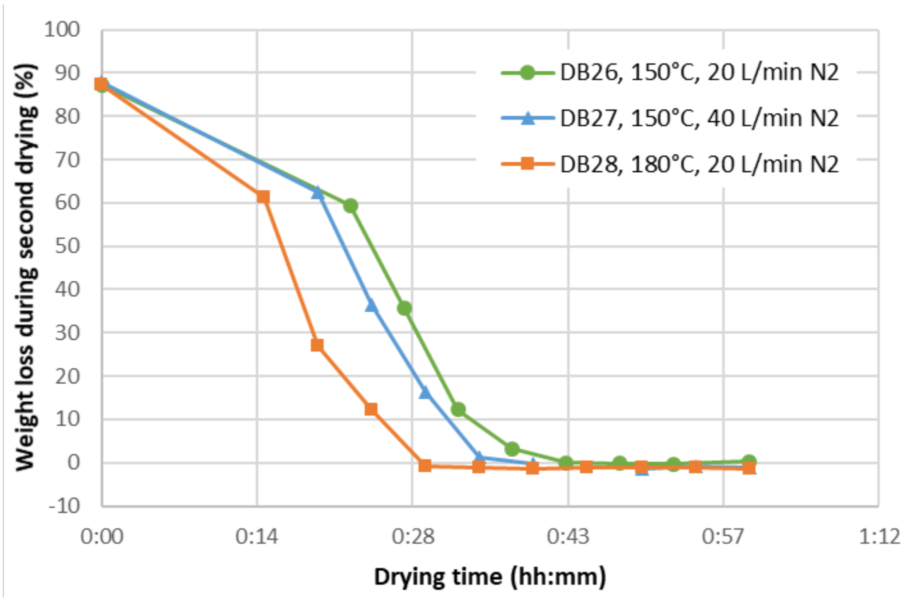


Figure 19: Drying completed between 30 and 45 minutes, depending on temperature and gas flow rate.

4.2.3 Material specifications

The aerogel properties can be tuned by tailoring the sol composition and/or the processing conditions. The values below correspond to the typical material produced at the pilot scale.

Envelope density: 0.110 g/cm^3
Tap density: 0.065-0.070 g/cm^3
BET surface area: >700 m^2/g
Thermal conductivity of particle bed at 20°C: 19 mW/(m.K)
Thermal stability determined by thermogravimetry analysis (TGA):
    up to 260°C in air
    up to 300°C in N$_2$
Core hydrophobic, water contact angle: 146-156°
Particle size distribution (tunable, example only)

Particle Size	Fraction (%)
<1 mm	18.4
1-2 mm	21.2
2-3.15 mm	25.6
3.15-4 mm	17.7
>4 mm	17.1

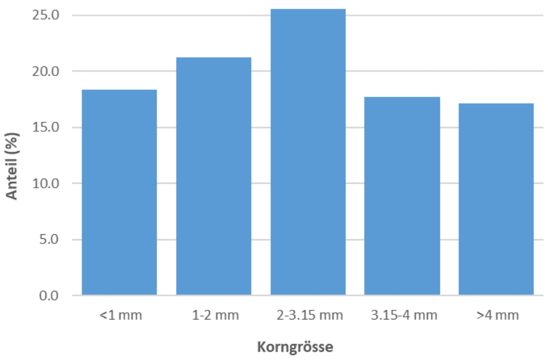


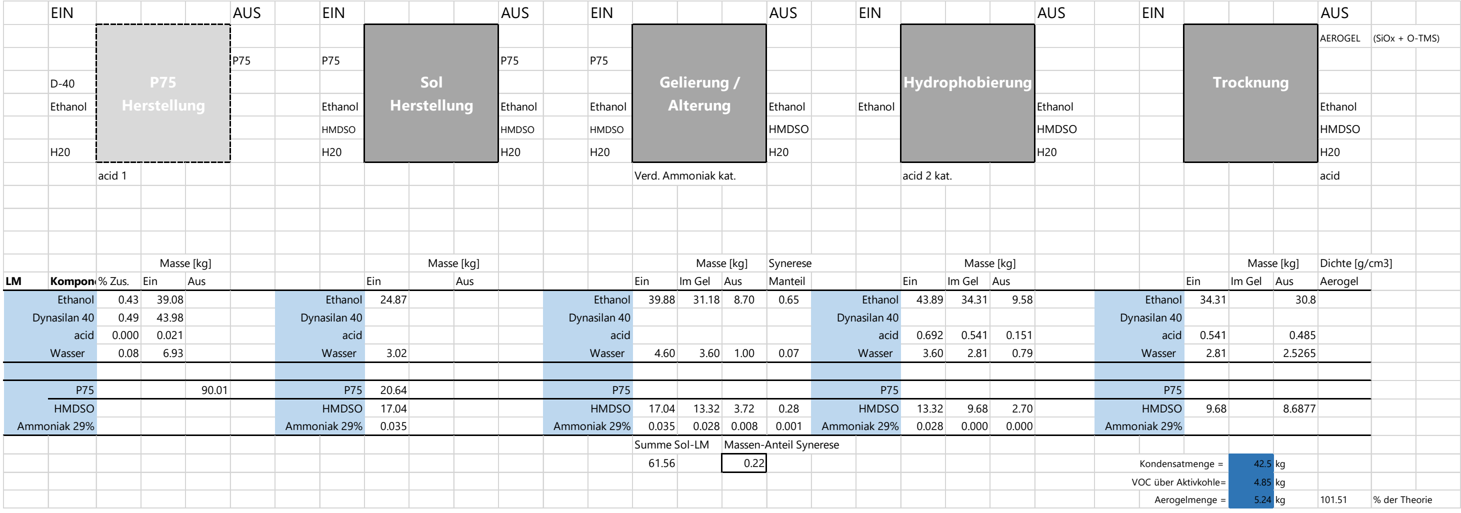
Figure 20 Particle size distribution

4.2.4 Process time reduction

Reducing processing time is a key variable to optimize the process in terms of production cost, because it defines the size/number of the reactors required to reach a certain annual capacity and has therefore very large CAPEX implications. At the same time, sufficiently long aging times [20,25,26] and hydrophobization times [27-29] are a pre-requisite to produce silica aerogels within the targeted specifications. By optimizing the systems chemistry (concentrations of acid and base catalysts in particular) and processing conditions (temperature and time), we succeeded in reducing reactor residence time to three hours.

4.2.5 System mass balance

Several steps have to be considered calculating the mass balance for the large scale facility. *Figure 23* shows the overview from the process. Since the P75 production always was done for several batches in the overview the components were regarded as % Zus.



LM	Kompon	% Zus.	Masse [kg] Ein	Masse [kg] Aus
	Ethanol	0.43	39.08	
	Dynasilan 40	0.49	43.98	
	acid	0.000	0.021	
	Wasser	0.08	6.93	
	P75			90.01
	HMDSO			
	Ammoniak 29%			

	Masse [kg] Ein	Masse [kg] Aus
Ethanol	24.87	
Dynasilan 40		
acid		
Wasser	3.02	
P75	20.64	
HMDSO	17.04	
Ammoniak 29%	0.035	

	Masse [kg] Ein	Masse [kg] Im Gel	Masse [kg] Aus	Synerese Manteil
Ethanol	39.88	31.18	8.70	0.65
Dynasilan 40				
acid				
Wasser	4.60	3.60	1.00	0.07
P75				
HMDSO	17.04	13.32	3.72	0.28
Ammoniak 29%	0.035	0.028	0.008	0.001
	Summe Sol-LM		Massen-Anteil Synerese	
	61.56		0.22	

	Masse [kg] Ein	Masse [kg] Im Gel	Masse [kg] Aus
Ethanol	43.89	34.31	9.58
Dynasilan 40			
acid	0.692	0.541	0.151
Wasser	3.60	2.81	0.79
P75			
HMDSO	13.32	9.68	2.70
Ammoniak 29%	0.028	0.000	0.000

	Masse [kg] Ein	Masse [kg] Im Gel	Masse [kg] Aus	Dichte [g/cm3] Aerogel
Ethanol	34.31		30.8	
Dynasilan 40				
acid	0.541		0.485	
Wasser	2.81		2.5265	
P75				
HMDSO	9.68		8.6877	
Ammoniak 29%				

Kondensatmenge = 42.5 kg
VOC über Aktivkohle= 4.85 kg
Aerogelmenge = 5.24 kg 101.51 % der Theorie

Figure 21: Mass balance for the process in the large scale facility.

In addition of this mass balance, some components have to be added. On one hand, per Batch around 15 to 20 kg of Ethanol is used for rinsing the facility. Note that these washing cycles are carried in the pilot facility to avoid the build-up of deposits because the installation is left empty between cycles. In the planned production facility, the operation is planned in a 24/7 cycle, which eliminates the washing requirement almost entirely. In addition, washing ethanol can be added to the recycling streams there.
Per drying of one batch, approx. one third of a nitrogen bundle (600 L) is consumed. During this pilot drying experiments, the nitrogen was not recycled in a closed loop but vented. In the planned production facility, the washing cycles with ethanol have the nitrogen is recycled in a closed loop after the condenser.

4.2.6 Life cycle considerations

Projected cost and resource efficiency (LCA and LCC) cannot be validated based on the pilot installation alone, because the sustainability and the cost of the final production critically depends on the actual implementation of the industrial installation. For example, the size of the installation, the location of the installation (transport cost and resources), the selection of raw materials providers, and the sourcing of the energy (electricity mix) all have major effects on the overall sustainability of the process. In additions, synergies with existing facilities on the site of production, for example due to the backwards or forwards integration of raw materials and solvent streams, may strongly impact cost, in addition to the sustainability. Because of these difficulties, and because of the longer than expected times required to elaborate and implement the new production concept, no detailed LCA analysis was carried out. However, the piloting activities did confirm the assumptions that were made during the LCA of the Empa one-pot process before project start. Most notably, even though the engineering of the pilot concept has changes substantially from that envisioned at the start of the project, the actual mass and heat flow balances did not change significantly, with only minor modification in chemical recipe and only minor changes in the temperature conditions during the process. In addition, the pilot confirmed the feasibility to scale-up the one-pot production recipe to pre-industrial scale, with process durations in line with the most optimistic assumptions. Because the assumptions were confirmed, and because a new analysis only makes sense once a production, rather than pilot facility has been constructed, the results of the preliminary analysis remain the best estimate of the process efficiency (Figures 1, 23) [21] until an actual industrial production plant is constructed and analyzed in detail. The description of the assumptions and methodology for the LCA analysis can be found in the Supplementary Information of reference 21, available in open access at https://onlinelibrary.wiley.com/doi/full/10.1002/anie.201700836. The approximately 35% better performance of the one-pot process is related to the more effective use of resources, particularly the reduced use of solvents, and the increased ease of solvent recycling without the need for purification (see Section 4.2.7).

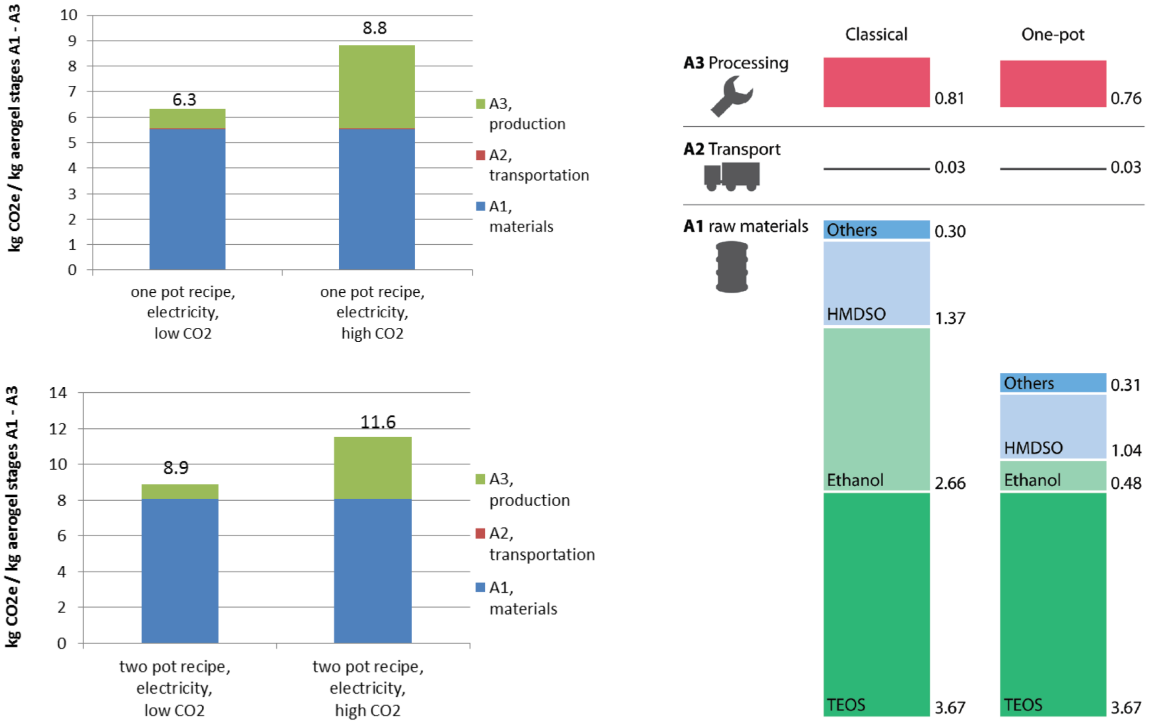


Figure 22: LCA of silica aerogel production. (left) CO_2e emissions for the project Empa one-pot (top) and conventional two-pot production (bottom) for two different types of electricity sources. (right) Direct comparison of one-pot and two-pot production processes (low CO_2 electricity scenario).

4.2.7 Solvent recycling

One of the main potential advantages of the Empa one-pot technology is that recovered solvents (syneresis liquid, used catalyst solution, condensate) display a composition of the three main reagents (EtOH, HMDSO, water) in a ratio that approaches those needed for the synthesis (*Figure 1*). Thus, a large fraction of solvent can be re-used with only little purification step, acid-base neutralization, which reduces cost and processing energy substantially. Because of the cost/complexity with running the large Nautilus pilot plant, such recycling experiments were carried out on a combination of the Nautilus and the smaller 1ZR reactor. A first experiment was carried out on Nautilus, followed by an experiment on the 1ZR reactor using the solvents from the Nautilus pilot.

The material quality achieved corresponded to the targeted density below 0.120 g/cm^3, even after recycling without complete purification up to 100% of the syneresis liquid, 100% of the catalyst solution, and 46% of the condensate.

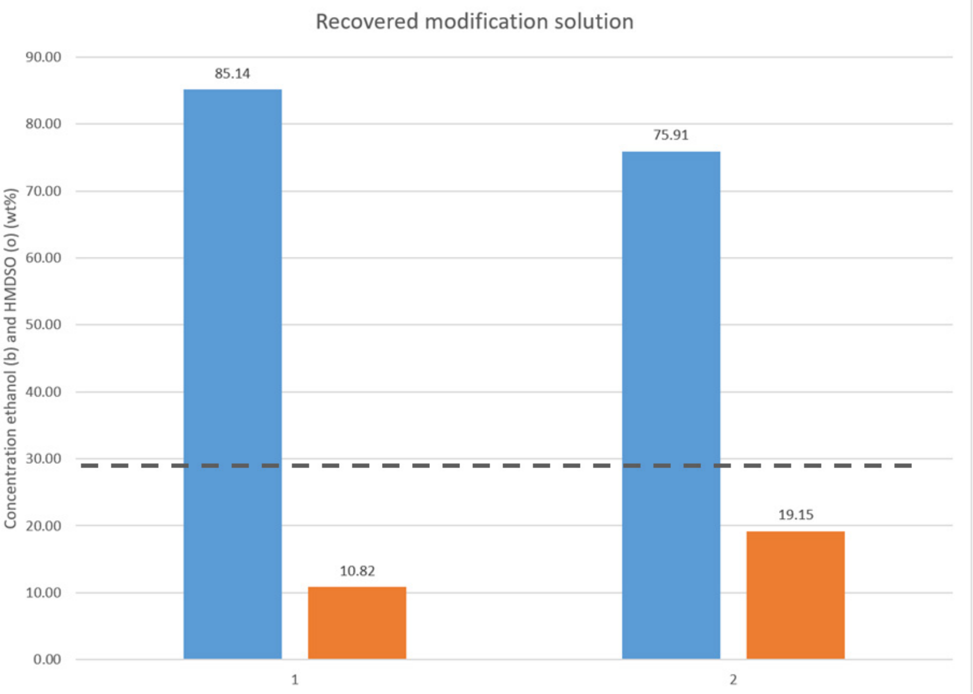


Figure 234: Catalyst solution composition during re-use/recycling over 2 cycles (blue: ethanol, orange: HMDSO). The line denotes the composition of the sol. Starting composition was neat ethanol. The dotted line denotes the composition of the sol.

The aerogel production process is a net consumer of HMDSO (consumed to hydrophobize the silica aerogels) and a net producer of ethanol (produced through hydrolysis and condensation of the tetraethoxysilane (TEOS) precursor, added as part of the P750 PEDS silica source). Thus, a full recycling without purification is not possible and a small fraction of solvent needs to be purified (HMDSO separated from water). Ethanol-water separation is an industrially very well established process (Pervaporation) and can easily be outsourced industrially, but HMDSO-ethanol separation is much less common. We tested the recovery of HMDSO from the condensate, which is a ternary HMDSO (15%) – ethanol (82%) –water (3%) mixture by taking advantage of the immiscibility between HMDSO and water (*Figure 24*). For these separations, water is added to the condensate to trigger a phase separation: HMDSO-ethanol in upper phase, ethanol-water in lower phase and the compositions are analyzed by quantitative ^{1}H NMR (*Figure 25*). Regardless of the amount of water added, the upper phase contains >95% HMDSO with minor traces of ethanol. However, the lower phase contains significant amounts of HMDSO at lower amounts of added water (up to 5%). Because the volume of the lower phase is much larger, this adds up to >40% of total HMDSO. Thus, for an optimized recovery of HMDSO, water needs to be added in ca. 1/1 ratio to the condensate, leading to >90% recovery of a nearly pure HMDSO phase, and a 50% solution of ethanol in water.

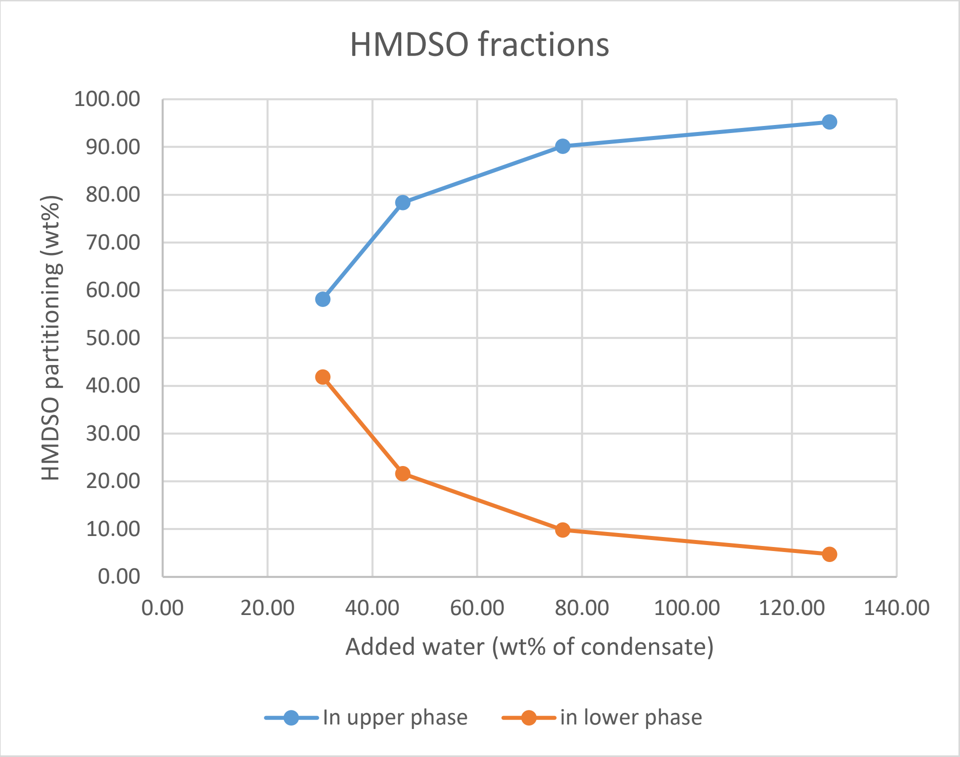


Figure 24: HMDSO amounts retained in upper and lower phase after the addition of water to trigger phase separation.

4.2.8 Comparison of tube-bundle reactor to conventional stirred reactor concepts

The proposed aerogel production concept is different from conventional aerogel production technologies in terms of its chemical formulations, for example the use of pre-polymerized TEOS precursors and, in particular, the inclusion of the (inactive) hydrophobization agent in the sol, followed by later acid-catalyzed activation. The advantages of this have been described above. Here, we briefly evaluation the difference between a tube-bundle reactor to conventional stirred reactor concepts.

At small pilot scale, the same chemical process was implemented prior to the project. In this system, which was pre-industrial and far from optimized, the sol was gelled inside a barrel. After gelation, the gel itself effectively eliminates convection and heat and mass transport are very slow and limited by diffusion. As a result, aging and hydrophobization times were very long with overall production times in excess of 48 hours.

The traditional approach to accelerate heat and mass transport is to break up the gel body in smaller pieces and employ a stirred reactor. To the best of our knowledge, this is also the type of approach currently in use by commercial silica aerogel manufacturers. Such an approach can indeed effectively increase heat and mass transport and reduce processing times, but has several drawbacks. Breaking up the gel body generates fine particulate matter (aerogel powder after further processing) with reduced value in the market and stirring speeds need to be selected carefully to avoid excess fine fractions. In addition, a large diameter stirred reactor is much more difficult to operate at an overpressure and operation above the boiling point of the relevant solvents becomes more difficult, which limits reaction kinetics and extends the required processing times.

By contrast, tube bundle reactors are designed a priori as heat exchanger, which maximizes heat transport, and operation at elevated pressure is straightforward. The tubular design produces gel rods with a one-dimensional geometry that minimizes heat and mass transport into the gel bodies, without requiring an explicit crushing or particle size reduction step. Overall, this concept allows for the fastest possible processing times. On the downside, even tube bundle reactors are being used in industry, they are far less common than simple stirred reactors and their use does add cost and complexity.

4.2.9 Cost considerations

Production costs cannot be calculated directly based on the pilot facility, which is not optimized in terms of reactor volume, staffing requirements, automation and throughput. In addition, raw materials costs are different for purchases on the kg-ton scale for the pilot compared to the 100s of ton scale for a production facility. However, the technical innovations in the pilot project have been the basis for the design of a production facility, and based on this design, costs can be estimated. Note that the actual production cost for this planned facility depend strongly on the boundary conditions (capacity location, salary cost, possible integration into industry park, greenfield versus existing buildings, etc.)

The scenario for which costs are calculated here corresponds to a production facility with a capacity of on the order of 10'000 m^3 per year, operated in a 24/7 cycle and Swiss levels of salary cost for the plant operators, management and maintenance teams. A production scenario for a smaller installation was not evaluated because of the increasing inefficiencies at smaller scale. Larger production capacities could be more effective, but where not considered here because of market risk assessments.

The scenario for which costs are estimated entails an implementation of the production plant as part of a larger chemistry/manufacturing park, where some of the parks overall facilities can be used (nitrogen supply, fire safety, delivery of goods and chemicals), but an industry-standard, user-fee for these facilities has been included in the cost calculations. Also included are the costs associated with the rent/modification of the building. The projected costs also include the necessary periphery, including storage tanks, mixing vessels, drying installation, condenser, packaging of final product in big bags. The exact number is confidential, but based on the engineering design, capital expenses amount to a sum between 10 and 20 Mio CHF.

Based on the engineering design of the facility, informed by this project's pilot facility, and based on the processing durations and conditions, the silica aerogel production cost is estimated at 600-1200 CHF/m^3, depending on sizing and implementation scenario, which is on the order of 50% of current bulk pricing from current producers. The production cost includes a linear write-off of the CAPEX over 10 years (15-25%), raw materials (45-65%), and the OPEX which include salary costs, energy, maintenance, rent and usage fees to the chemical park (20-35%), but do not include costs associated with sales and marketing.

This relatively low cost result from the combination of a fast throughput in the installation enabled by the tube bundle reactor design (which leads to a large capacity for a relatively modest CAPEX), and the efficient use of raw materials that enables recycling without purification to a large extent due to the one-pot process. For comparison, current high volume pricing of silica aerogel granulate is on the order of 2000-3000 CHF/m^3, but with significant fluctuations because the market is not well established with very few reliable manufacturers.

4.3 Overview of project progress

Below, we provide a timeline of the important achievements reached during this project:

October 2017	BFE P&D project start
December 2017	1ZR reactor construction completed
February 2018	Proof-of-concept on 1ZR reactor: all-in-one production
July 2018	Optimization (1ZR, 25mm upgrade and lab)
October 2018	Pilot hall modifications completed
November 2018	Start of construction of large pilot installation ("Nautilus")
January 2019	Nautilus commissioned
July 2019	In situ drying in Nautilus not successful, decision external drying
August 2019	Proof-of-concept on in Nautilus: with external drying (3h+1h drying)
September 2019	Proof-of-concept on solvent separation
September 2019	Pilot drying installation arrived on Empa Campus
September 2019	BFE P&D project end
November 2019	Pilot drying finished, sampling materials produced and distributed

5 Conclusions

Compared to the initial proposal, the project has followed and pursued a significantly different approach. Originally foreseen was to simulate a continuous production tunnel by constructing a single block/cross section and mimicking the spatial-temporal evolution of temperature, pressure and composition in the tunnel by a temporal evolution of temperature, pressure and composition in the single reactor. During the project, this continuous tunnel concept was foregone because:

- Engineering challenges with the tunnel concept (gel-liquid separation, movement of gel blocks through tunnel, transfers).
- The high risk/difficulties to progress with a single large installation: decision to construct a production facility is very binary: there is a (large) minimum size at which such a tunnel can be constructed meaning substantial CAPEX and commitment.
- Non-modular concept makes it difficult to match production capacity and output to demand/sales.
- The new concept is based on a modular design and, initially was thought to enable an all-in-one approach. The latter was proven effective at the small pilot scale, but has been shown not feasible at the large scale (despite the expenditure of great efforts and modifications to the pilot). Thus, a combined process with external drying is now the preferred route, leading to a process with the following overall characteristics:
- Batch process rather than continuous.
- Modular design: smaller production installation possible (with lower CAPEX), possibility to replicate later if demand increases.
- Gelation, aging, hydrophobization in reactor optimized for heat transfer. Processing times in reactor limited to 3 hours. These short times in the reactor increase throughput.
- Gels removed for external drying, scalable and commercially available drying technology tested at small scale, but with a realistic type of pilot installation.

Because of this change in direction, time was expended at verifying the concept on a smaller scale (1ZR). In addition, the final reactor volume of the large pilot plant was smaller than initially planned (80L instead of 200L). As a result, the scheduled volumes of production have not been reached within this project, but materials within specification for sampling has been produced. In addition, the pilot activities were not completed early enough to update the LCA analysis and to draw definitive conclusions about the heat and energy flows in the system.

In our view, these deviations are compensated by the advantages of the new concept (maximized heat transfer, minimal cycle times, modular concept that is easier to transfer to an industrial production line). In addition, the pilot line that was constructed has a very high engineering maturity and a high similarity to a future production facility. Thus, many more of the engineering challenges have been solved at the pilot stage than would have been according to the original proposal.

The status at the end of the BFE project is that the Empa one-pot technology [21,22] has been validated and implemented at the pilot-scale using mature engineering concepts that can be translated directly to the design of a production facility. The tube bundle reactor concept, which maximizes heat and mass transport and hence minimizes residence time and maximizes throughput, combined with the one-pot chemistry, which minimizes solvent consumption and removes to a large extent the need for solvent purification before re-use, represents a silica aerogel production process that is both resource- and cost-effective. As a result, projected production costs are about 30-50% of current bulk pricing for a production facility based on this combination of innovations.

6 Outlook and next steps

The next step after this project is the design, construction and commissioning of a large industrial installation (not at the site of Empa, but by a materials/chemical manufacturer). The engineering office (Swiss) who has designed the 1ZR and Nautilus installations has finalized the detailed engineering of such an installation, taking into consideration the boundary conditions of a possible implementation site. This design is informed by the critical progress made during this BFE project and builds on the essential lessons learnt (both positive and negative) over the last two years. No further support from BFE P&D for a follow-up, larger silica aerogel granulate pilot installation will be necessary or requested.

During this project, an industry partner has provided some of the knowhow and man-power to the pilot installation, and they are a possible implementation partner. In addition, talks are ongoing with other players in the industry, including those that can integrate the silica aerogel production in their own current activities (backwards or forwards integration). The final decision about the technology transfer options is currently under consideration.

Aside from our active pursuit of implementing the specific technology, the project also highlights general aspects of silica aerogel production, its industrial implementation and the overall market. Even with the improved efficiency and throughput, silica aerogel at a competitive price point can only be produced at scale, i.e. with an installation that has a capacity of at least several 1000 m^3 per year. Any facility below this will inevitably run into higher CAPEX, OPEX and materials costs (normalized to the capacity). This represents a substantial barrier to industrial implementation, because it makes it very difficult to start with a small production to test the market, for example to evaluate the response of the market (in terms of growth and growth rate) to a reduction in cost. The gains in efficiency shown for our process can lower this barrier by lowering the CAPEX and OPEX requirements, but not eliminate it completely. The requirement for substantial initial investments, combined with the uncertainty of the price-responsiveness of the market is the key challenge and most likely requires partnerships across the value chain to overcome.

At the same time, the current insecurity about the silica aerogel granulate supply, with few credible manufacturers, may hampers the development of aerogel-based products and solutions. There is currently a very active start-up scene in the silica aerogel field, and also many larger chemical and materials manufacturers hold an expending portfolio of patents on silica aerogel production processes. The emergence of additional credible manufacturers would be a much needed addition to the market.

7 National and international cooperation

There are no Swiss project partners within this BFE P&D project, but multiple Swiss companies are involved in the project as contractors. The piloting activities (design and construction planning) have been conducted in close collaboration with a Swiss Engineering office, specializing in mechanical engineering, construction of apparatuses, and installation planning. Both the 1ZR and the large engineering pilot have been designed and planned as a close collaboration between the Empa team and the engineering office. Many of the components of the pilot are sourced from Swiss suppliers. For example, the control systems are purchased from BRP Automation AG and the flow control systems from Burkert Schweiz AG.

The pilot activities have been carried out in part together with a European chemical manufacturer (Identity confidential) who provided expertise, certain components, and labor to the project. This partner may play a key role in the final implementation of the project results, but the final decision on the way forward has not been taken.

Sample materials have been supplied to potential silica aerogel customers in Switzerland and abroad for evaluation with their solutions.

8 Communication

This project targets the industrial production of silica aerogels. Premature communication to the wider public may interfere with this main objective. However, there has been intense communication with targeted stakeholder across the value chain, e.g. raw materials supply, equipment manufacturers, potential customers, etc.

9 Publications

This project targets the industrial production of silica aerogels. Depending on the outcome of the technology transfer and implementation, parts of the project results, or even the overall production concept may be published in the chemical, materials or chemical engineering scientific literature at a later date.

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