DELIVERABLE D1.3:

Report on the possible production processes of organic and hybrid aerogels and comparison with the state of the art

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ABSTRACT

The deliverable 1.3 is written as a knowledge base to perform the work in the project from the very beginning with all the strength and expertise of the partners. From the chemistry to the particle production processes and up-scale issues, it gives an overview of the actual stand of the technics to be used and in which direction we tend to go to adapt them for our purposes.

The first section is discussing the actual stand of the synthetic polymer aerogel market. It reviews the main actors and the main application areas of such aerogels. It also quantifies the expected growth of such market that justifies the necessity for the development of large scale aerogel production capacities.

The state of the art is then drawn in the second section. The chemistry of the different gel systems are described and documented. Particle production processes that have been used or that could be used to produce aerogel particles are reviewed and their main controlling parameters are explained. Finally the drying is also reviewed.

In the third and final section, the scales up possibilities are discussed. Firstly the requirement and bottlenecks of the processes to be used at large scale are defined, giving some decision tools to select the relevant technics from the literature. Then the processes described in the second section are critically assessed regarding their compatibility with the scale up requirements, their compatibility with the different chemistries and the material shapes and sizes they can achieve.
**Definitions**

**Hybrids:** According to IUPAC, hybrids are material composed of an intimate mixture of inorganic components, organic components, or both types of component. The components usually interpenetrate on a scale of less than 1 μm. In that respect, the term ‘hybrid materials’ encompasses also intimate mixtures of purely organic or inorganic materials. However, according to the common usage of the term, hybrid materials are *composites* consisting of two constituents at the nanometer or *molecular* level. Commonly one of these compounds is *inorganic* and the other one *organic* in nature. In this project the term “hybrids” will be used for both organic-organic and organic-inorganic gels and aerogels.

**Aerogel:** An open non-fluid colloidal or polymeric network that is expanded throughout its volume by a gas and which is formed by removing all swelling agents from a gel without substantial volume reduction or network compaction.

**Wet-gel:** This is the most general term to refer to any gel whose pores are filled with a solvent. It is used mostly by the aerogel literature in order to emphasize the contradistinction to the term “aerogel.” The rest of the literature simply refers to wet-gels as “gels.” Special cases of wet-gels are: hydrogels, alcogels, organogels and lyogels.

**Hydrogels:** Gels whose pores are filled with water.

**Alcogels:** Gels whose pores are filled with an alcohol.

**Organogels:** Gels whose pores are filled with an organic solvent. Alcogels are a special case of organogels.

**Lyogels:** In the German definition ([https://de.wikipedia.org/wiki/Gel](https://de.wikipedia.org/wiki/Gel)), this term is practically synonymous to wet-gels. In some older patent literature the term was used synonymously to organogels.

In this project terms “organogels” and “alcogels” are preferred.
1. REVIEW OF THE PRESENT MARKET FOR POLYMER BASED AEROGELS

Aerogels are low-density (typically <0.2 g cm\(^{-3}\)), highly porous (>90% v/v) nanostructured solids. The most common kind of aerogels is based on silica, whose fragility, however, limits its applications (e.g. aerospace exploration, NASA’s Stardust Program and Mars Rovers) [1]. The fragility of silica aerogels has been rectified with polymer-based and polymer-crosslinked aerogels, whereas the surface functionality of pre-formed silica wet-gels networks plays the role of a chemical template that directs accumulation of a nano-thin conformal polymer coating over the entire skeletal framework [2].

Until now a large variety of organic and hybrid (crosslinked) aerogel types exist, mainly based on synthetic organic polymers, including phenolic resins (e.g., resorcinol-formaldehyde) [3], [4], polyureas [5], polyimides [6], [7], polyamides (Kevlar\(^{TM}\)-like) [8], polybenzoxazines [9], poly(acrylonitrile-co-diacylate) [10], polyurethanes [11] as well as polynorbornene and polydicyclopentadiene prepared via Ring Opening Metathesis Polymerization (ROMP) [12].

However commercial production is limited to silica (largest market), carbon and some small amounts of organic aerogel, offered in small quantities. They are available in following forms: irregular monoliths, blankets (combined with other carrier compounds), powder with irregularly shaped particles. Flexible blankets produced by Aspen Aerogels or NanoTech and pipe-insulation materials produced by Cabot are well established in the market. A lot of efforts have been devoted towards production of monolithic aerogels for glazing applications (Airglass). However, for some applications, particles form is beneficial. An important producer here is Dow Corning, which produces silica aerogel powder (irregularly shaped particles) for cosmetic industry [13].

Organic aerogels are not well commercialized so far, only small amount can be ordered, mainly for academic purposes (e.g. via www.aerogel.com). Organic aerogels in form of spherical particles of given particle size distribution are not commercially available at all.

Today, the technology for manufacturing organic aerogel is ready for the next step that will bring them from the lab to large-scale production. Those advances will have to be application-relevant and for this purpose this project will focus on two major classes of materials, aerogels based on natural biopolymers (polysaccharides) and aerogels based on synthetic polymers derived from isocyanates (polyurethanes, polyureas, polyamides) or ROMP-derived (polydicyclopentadiene and polynorbornenes). The global aerogel market was valued at $294.1 million in 2014 and is expected to grow significantly at a compound annual growth rate (CAGR) of around 33% from 2014 to $1598.6 million in 2020. (Global Aerogel Market – Segmented by Type, Application and Geography – Trends and Forecasts, Mordor Intelligence LLP 2016)

By today, the vast majority of market opportunities for aerogels, are linked to their super insulation properties, resulting in applications in oil and gas pipe line insulation, exterior insulation for construction or in high performance apparel e.g. for winter sports. However, today these markets are being served predominantly by silica aerogels with a market share of up to 75%. (World Aerogel
Market – Opportunities and Forecast, 2014-2021, Guru Gopal Mallick (2016) Further, developing markets for aerogels are in electronical components (e.g. capacitors, humidity sensors, fuel cell batteries), foundry technologies (e.g. aerogelic additives and binders) and architecture (e.g. illumination, super light concrete), which require varying material properties. As a result aerogels other than silica-based, including polymer based aerogels, are expected to be the even faster growing segment in the segmentation of aerogels based on raw materials, with a CAGR of 47% in the period from 2014-2020. (Global Aerogel Market – Segmented by Type, Application and Geography – Trends and Forecasts, Mordor Intelligence LLP (2016)) This forecast underlines the necessity for new, aerogels based on synthetic as well as natural polymers, allowing for alternative product properties, serving the growing market need.

Commercially available carbon aerogels, which are prepared from resorcin-formaldehyde by carbonization, are sold by American Aerogel and Aerogel Technologies™, both located in the US. Whereas American Aerogel incorporates their material in vacuum insulation panels, to address high performance thermal packaging systems, Aerogel Technologies sells electrically conductive aerogel monolith for the use as electrodes in supercapacitors or batteries. The market share of these companies is currently unclear.

Furthermore Aerogel Technologies™ sells is monolithic aerogels Airloy™, which are based on synthetic polymers. These are meant to serve as ultra-light alternatives to conventional plastics and ceramics with high strength, stiffness and toughness, with relatively high density as compared to classical aerogel materials. Here again, the share of the global organic aerogel market is unclear.

Organic aerogels in form of spherical particles of given particle size distribution are not commercially available at all.

For the near future a strong increase in capacity for existing organic aerogels is to be expected, accompanied by an increasing variety of raw materials as well as applications.

Today, the technology for manufacturing organic aerogel is ready for the next step that will bring them from the lab to large-scale production. Those advances will have to be application-relevant and for this purpose this project will focus on two major classes of materials, aerogels based on natural biopolymers (polysaccharides) and aerogels based on synthetic polymers derived from isocyanates (polyurethanes, polyureas, polyamides) or ROMP-derived (polydicyclopentadiene and polynorbornenes). Both classes are described below.
2. STATE OF THE ART: PRODUCTION OF ORGANIC AND ORGANIC-INORGANIC HYBRID AEROGELS

2.1. Starting materials and chemistry

2.1.1. Biopolymer based aerogels

There is a growing interest in using biopolymers for aerogel production. Biopolymers from various sources such as alginate, cellulose, lignin, pectin, chitosan, proteins and others have been tested as precursors. Resulting aerogels exhibit both specific inheritable functions of the starting biopolymer and distinctive features of aerogels (open porous structure with high specific surface and pore volume). This synergy of properties has prompted to view biopolymer aerogels as promising candidates for a wide spectrum of applications. Up-to-date reports on biopolymer aerogels describe their potential use for thermal insulation [14]–[19], tissue engineering and regenerative medicine [20], drug delivery systems [21], [22], as catalysts and sensors [23], [24] adsorbents [25]–[27] and as starting materials for carbon aerogels [28], [29] and composite organic-inorganic aerogels [23], [30]. Biopolymer characteristics (molecular weight, composition, degree of branching) as well as introduction of other (bio)polymers and additives have a significant effect on both bulk properties of the aerogels as well as on their porous network. Thus, the major scope of research in biopolymer aerogels is the exploration of relations between aerogel properties and chemical nature of the precursors. The general method of biopolymer aerogel production involves a gelation step in an aqueous or organic solvent medium. Many gelation methods have been developed including thermal and cryogelation, coagulation by changing solvent quality and chemical (including ionotropic) crosslinking. If gelation takes place in an aqueous medium, solvent exchange to an organic solvent, which is miscible with supercritical CO$_2$, is required due to miscibility gap in the CO$_2$/water system. The organic solvent is then washed out with supercritical CO$_2$ leaving behind an aerogel. Solvent exchange is often the most time consuming step and can also lead to gel shrinkage.

Below we describe the state of the art on bio-aerogels made from polysaccharides that will be used in the Nanohybrids project.

2.1.1.1. Alginate-based aerogels

Sodium alginate (simply “alginate” in the following) solution can form a gel when divalent cations are added. These cations, such as Ca$^{2+}$, act as crosslinkers, creating ionic bond between the carboxylate groups of the alginate strands. The subsequent supercritical drying of the alcogels leads to the formation of alginate aerogels [21], [31]–[36]. The transformation of alginate hydrogels into aerogels by supercritical drying opens up a multitude of opportunities into high-value added materials. Different shapes are reported in literature for alginate aerogels: monoliths, beads and microspheres. Production of alginate aerogels as beads (droplet method) and spherical particles of different size (emulsion-gelation) is established on the lab scale. TUHH and BASF have recently shown the way to produce alginate aerogels with extremely low density and thermal conductivity.
Applicability of alginate aerogels for life science applications is proven on the lab scale (TRL 4).

2.1.1.2. Cellulose-based aerogels

Cellulose is an inexhaustible natural polymer; its use is reconsidered in our days due to the discoveries of non-toxic cellulose solvents and the possibilities of making materials with various functionalities due to its large amount of reactive hydroxyl groups on anhydroglucose unit. Cellulose-based aerogels are a new and very promising materials offering a wide range of potential applications from bio-medical and cosmetics (delivery systems, scaffolds) to thermal (insulation) and electro-chemical (when pyrolysed).

Two main ways of making cellulose aerogels are known. Cellulose is dissolved in a direct solvent such as 8% NaOH/water [38], [39], ionic liquid [40]–[43], N-methyl-morpholine N-oxide (NMMO) monohydrate [44], [45], LiCl/DMAc [46] or calcium thiocyanate [47], then coagulated in a non-solvent (water, alcohols) and finally dried in a way that prevents pores collapse, i.e. either via freeze-drying [41], [46], [47], or with sc-CO$_2$ [38]–[40], [42]–[45]). In all cases cited, cellulose “network” is formed during cellulose coagulation either from a solution [40]–[47] or from a physical gel [38], [39].

The second way of making cellulose aerogels is to use cellulose nanofibers, which can be bacterial cellulose [48], [49] or micro- or nano-fibrillated cellulose prepared via mechanical disintegration of the native cellulose [50], [51], often accompanied by the enzymatic and/or chemical treatment. In these cases the starting material is a continuous “non-woven” network of cellulose I nanofibers filled with water. This type of starting material does not allow “flexible” manipulations in terms of processing and we shall not consider it for making cellulose aerogel beads.

Cellulose-II based aerogels as compared with Cellulose-I aerogels have wide pore size distribution, from tens of nanometres to several microns, and rather high specific surface area of several hundreds of m$^2$/g. The density depends essentially on the initial cellulose concentration in solution and on the accuracy in drying and varies from 50 to 200 kg/m$^3$. It is possible to produce additional porosity in cellulose aerogels by “foaming” cellulose solutions using a surfactant [38]. Cellulose-silica composite aerogels, based on the interpenetrating organic-inorganic network was recently reported with very high specific surface area (around 800 m$^2$/g) and improved mechanical properties compared to neat aerogels [52].

Most of cellulose-based aerogels are produced in form of monoliths. Particle production of cellulose aerogels at a lab scale was established recently [39], [53]–[56], [57].

2.1.1.3. Chitin- and Chitosan-based aerogels

Chitin is the second most abundant polymer in nature. Because of its renewable resource, biocompatibility, biodegradability and antimicrobial properties, chitin and its derivatives are widely used in many applications including biomedicine, catalysis, agriculture and purification and
separation techniques. In the context of the Nanohybrids project, it is of note that there is no article reporting the production of chitin aerogel beads, to the best of our knowledge. Chitosan aerogel microparticles will be described in detail below.

Aerogels of chitin can be prepared (1) by reacetylating the chitosan polymer in an aqueous solution, (2) by dispersing chitin nanofibrils or sonicating nanowhiskers in water to form a hydrogel or (3) by the dissolution of chitin and regenerating the gel in solvent usually ethanol.

(1) Robitzer and coworkers [58, 59] prepared chitin aerogels from Squid-pen chitosan by reacetylating the chitosan amine functional groups with acetic anhydride. The resulting hydrogels are washed with ethanol and dried under supercritical CO$_2$ condition.

(2) Heath and co-workers reported on chitin nanowhisker aerogels by sonicating the nanowhiskers in water to form hydrogel [60]. In this process, the nanowhiskers form percolated hydrogen-bonded nets through the sonication-assisted aqueous assembly. The subsequent solvent exchange and supercritical drying leads to the aerogel formation. The chitin nanowhisker aerogels have very low densities (0.043 g/cm$^3$), high porosities (97 %) and surface areas up to 261 m$^2$/g. Tsutsumi et al. [61] recently reported on a method in which the Squid-pen chitin nanofibrils are dispersed in an aqueous solution and the pH is raised to 10 - 11 using sodium hydroxide solution to produce hydrogels. Washing the hydrogels with water and then with ethanol gave alcogels. Using supercritical drying process a highly porous crystalline chitin aerogels with high surface areas up to 289 m$^2$/g is obtained.

(3) In the works [62]-[66], the commonly found solvents for dissolving chitin and producing aerogels are N,N-dimethylacetamide (DMAc)/lithium chloride (LiCl), 1-butyl-3-imidazolium acetate and an aqueous solution of NaOH/urea mixture. Mostly ethanol was used as coagulant bath to regenerate the chitin gels.

Chow et al. [62] reported on the freeze drying technique for the production of porous chitin matrices from DMAc/LiCl solvent system with a high bulk density and low porosity 61 %. Using the same solvent system but employing supercritical drying technique, Tsioptsias and co-workers [66] produced chitin aerogels with a high porosity 91.5 % and high surface area 360 m$^2$/g.

Silva and co-workers [65] produced chitin aerogels using ionic liquid as “green” solvent. Herein chitin is dissolved in ionic liquid, 1-butyl-3-imidazolium acetate. After moulding at 4°C for 1 hour, chitin is regenerated in ethanol. The ionic liquid is removed by soxhlet extraction with ethanol and the subsequent supercritical drying gave aerogels. The monolithic chitin aerogels have very low density (0.039 g/cm$^3$) and high porosity 90 %.

Recently, chitin aerogels are prepared using 11 wt.-% of NaOH, 4 wt.-% of urea and water as the solvent medium and ethanol as coagulant. Ding et al. [63] used supercritical drying technique to produce mechanically strong chitin aerogels with high surface area (366 m$^2$/g) and low density (0.23 – 0.27 g/cm$^3$). Duan and co-workers [64] used freeze drying technique to produce highly porous (porosity of 98.59 %) chitin sponges.
Chitosan is one of the most important derivatives of chitin. When the degree of deacetylation of N-acetyl-glucosamine units in chitin is higher than 50%, the biopolymer is termed chitosan. That means that chitosan is a copolymer of N-acetyl-glucosamine and N-glucosamine units. Due to the presence of more than 50% of N-glucosamine units, the chitosan polymer offers water solubility under mild acidic condition by protonation of amine functional groups ($pK_a = 6.3$). Due to the cationic nature of the chitosan polymer in an acidic aqueous medium, the chitosan gels can be easily prepared by pH inversion using an alkaline medium which causes the coagulation of polymer, increasing the pH value above $pK_a$ and deprotonate the amine functional group. On the other hand, the chitosan gel can be prepared by crosslinking the amine functional groups either ionically with polyelectrolytes or covalently with low-molecular weight electrophilic reagents like aldehydes, acid chlorides, acid anhydrides and epoxides. Washing the hydrogels with alcohols or acetone and subsequent supercritical drying gives aerogels.

Quignard and co-workers [58], [59], [67]–[69] prepared chitosan aerogel beads from squid-pen and crab-shell chitosan with a high degree of amine groups by dissolving chitosan in acetic acid and dripping the solution in a sodium hydroxide solution through a 0.8 mm syringe needle, upon which gelation at the surface immediately sets in and is completed after short storage time in the base solution. Washing with water, exchange with ethanol and subsequently drying with supercritical carbon dioxide leads to chitosan aerogel beads with a fibrillar microstructure, volume shrinkage upon drying of around 50% and specific surface area from 150 to 300 m$^2$/g.

Ionically cross-linked chitosan aerogels are prepared by crosslinking hemicellulose citric acid with chitosan in an aqueous medium which improve the flexibility of the aerogel at room temperature and saline water uptake [70]. Chemically cross-linked chitosan aerogels are prepared by the sol-gel route with different aldehydes (glutaraldehyde, glyoxal and formaldehyde) as cross-linkers [71]–[73]. In principle, it is a kind of Schiff base reaction. The nucleophile of the amine groups in chitosan reacts with electrophile of the aldehyde functional groups. The hydrogels are neutralized with sodium hydroxide and washed with water and alcohol to form alcogels. The supercritical drying of alcogels provide highly porous (surface area in the range from 400 to 845 m$^2$/g) chitosan-based aerogels.

Water soluble derivative of chitosan aerogel is recently reported [74]. An acidic aqueous solution of chitosan is treated with L-glutamic acid to form hydrogel. The solvent exchange is carried out with acetone and then with ethanol and subsequent supercritical drying yielded aerogel of chitosan-L-glutamic acid. This aerogel product improves the solubility of chitosan at neutral and basic pH. Interestingly this derivative of chitosan aerogel is evidenced to show helical structure in DMSO.

Chitosan is used in the preparation of organic-inorganic hybrid aerogels in the form of microbeads. In general, the inorganic components are hybridized with chitosan polymer either by co-gelation or post gelation method [75]–[82]. Chitosan-montmorillonite clay hybrid aerogels microbeads are recently reported [75] in which the organic and inorganic components are mixed together before the gelation (see Section 2.1.3 for details). Montmorillonite is abundant mineral clay having two-dimensional interlayer space. An acidic aqueous solution of chitosan is mixed with sodium salt of...
montmorillonite. Being cationic polymer in the acidic medium, the ammonium ions of chitosan can intercalate the layers of montmorillonite and increase the interlayer spacing. The resulting acidic dispersion is dripped into the alkaline solution so the gel microbeads of chitosan-montmorillonite are formed. Washing and supercritical drying of the hydrogels provide aerogels. Chitosan-silica hybrid aerogels in the form of monoliths [83] are also prepared by this approach. An acidic solution of chitosan and silica precursor are mixed together under stirring and moulded to form gel. After 48 h, the gels are washed with water and ethanol and the supercritical drying provide chitosan-silica hybrid aerogels.

On the other hand, in post gelation method, the gels (hydrogels, alcogels and aerogels in the form of microbeads) of chitosan prepared by dripping method in alkaline solution are utilized in the sol-gel process to form organic-inorganic hybrid microspheres. The gels of chitosan beads are dipped in the precursors of metal oxide sol for 12 to 48 h. So the sol-gel process occurred in the organic matrix of chitosan microbeads to form hybrid microspheres. After washing, the hybrid microspheres are dried by supercritical CO$_2$ yielding organic-inorganic hybrid aerogels microbeads. The presence of inorganic gel in the matrix of chitosan gel resists the usual microbeads shrinkage during drying [76–82].

2.1.2. Synthetic polymer aerogels

Isocyanates are inexpensive starting materials available in bulk quantities and are typically used for the synthesis of polyurethanes and polyureas [10]. However, the isocyanate chemistry is extremely versatile and can be used for other classes of polymers, not typically associated with isocyanates, such as polyimides and polyamides. Considering the cost of the second reagent, which reacts with isocyanates in order to form the aerogel skeletal framework, this project focuses on polyureas, polyurethanes and polyamides.

For all these materials, the same three design rules apply [10]: (a) induce early phase separation of the developing polymer into the tiniest nanoparticles possible; (b) an efficient way to do “(a)” is with small-molecule soluble multifunctional monomers that produce highly-crosslinked, insoluble polymers; and, (c) classic (industrial) methods for polymer synthesis, which frequently rely on oligomeric precursors, may not be the most suitable for aerogel synthesis. Rules (a) and (b) together ensure that phase-separated nanoparticles have high surface functional group density to promote extensive interparticle crosslinking. Eventually, that principle works well even with virtual primary particles (micelles); this was demonstrated with the emulsion gelation of acrylonitrile in water [10].

Next, five systems relevant to the assembly of particles into globular or fibrous nanostructures will be reviewed, focussing on the NanoHybrids requirement. These principles should be extended for production of micro-particles in NanoHybrids.

2.1.2.1. Polyurea (PUA) aerogels

Polyurea aerogels are synthesized via the reaction (1) and (2) presented on the Fig. 2-1, from an
aliphatic (Desmodur N3300A), or an aromatic (Desmodur RE) triisocyanate [5], [84]. Both monomers are supplied in bulk quantities as pure compounds (for full characterization see [5]) by Bayer Corp. These reactions (Fig. 2-1 (1) and (2)) are typically involved in the environmental curing of PUA films, or for foaming polyurethanes [85]; their advantage for aerogel synthesis is the use of water rather than polyamines [86], [87], which can be expensive. The bulk density of PUA aerogels has been varied over a wide range (0.016-0.6 g cm$^{-3}$).

![Triisocyanates](image1)

**Fig. 2-1 Triisocyanates used in the manufacture of polyurea (PUA) aerogels and their reactions**

2.1.2.2. Polyurethane (PU) aerogels

Polyurethane aerogels based on industrial oligomeric diisocyanates and diols using 1,4-diazabicyclo[2.2.2]octane (DABCO) as catalyst are known [88]. Considering the design rules above, the Leventis’ group recent studies of PU aerogels [11] employed: (a) dibutyl tin dilaurate as a Lewis acid catalyst known to induce only polyurethane formation [89]; and, (b) readily available small molecule multifunctional monomers. Thus, Desmodur N3300A and Desmodur RE were employed as triisocyanates, and the group of small molecule aromatic alcohols presented in Fig. 2-2.

![Aromatic alcohols](image2)

**Fig. 2-2 Aromatic alcohols used for polyurethane (PU) aerogel manufacture**

Morphologically, the similarity between silica aerogels and PU aerogels from Desmodur RE triisocyanate and POL triol is striking, however, the latter are much stronger materials with compressive moduli up to 650 MPa and specific energy absorption >100 J g$^{-1}$.

2.1.2.3. Polyamide (PA) aerogels

Polyamides are a class of extremely strong materials, and most notable include Kevlar$^\text{TM}$. Typically polyamides are prepared from diacid chlorides and diamines (eq. 1).

\[
R–\text{COCl} + R’–\text{NH}_2 \rightarrow R–\text{CONHR’} + \text{HCl}
\] (1)
However, that process is not easily adaptable to aerogels, resulting from rather expensive trifunctional monomers required, and from their extreme sensitivity towards moisture. Here, polyamide aerogels will be prepared from inexpensive triisocyanates such as Desmodur N3300A and Desmodur RE with di- or tricarboxylic acids (eq. 2).

\[
R\text{-COOH} + R^\prime\text{-N}=C=O \rightarrow R\text{-CONHR}^\prime + CO_2 \tag{2}
\]

The attractiveness of our system lies with: (1) the use of much less moisture-sensitive isocyanates and insensitive carboxylic acids; (2) replacing expensive triamines with inexpensive triisocyanates; and, (3) \(CO_2\) being the only by-product, in contrast to \(HCl\) of eq. 1. Most importantly, tricarboxylic acids can be replaced with even less expensive boric acid (\(H_3BO_3\)), yielding extremely strong B–N interparticle bonds (eq. 3), which is reflected on the mechanical properties of the resulting aerogels.

\[
B(OH)_3 + 3 R^\prime\text{-N}=C=O \rightarrow B(NHR^\prime)_3 + 3 CO_2 \tag{3}
\]

2.1.2.4. Polyimide (PI) aerogels

Polyimides are a class of engineering plastics, and are pursued for high temperature applications. Polyimides are synthesized commercially by two methods: (a) by condensation (>190 °C) of aromatic dianhydrides and amines (the DuPont route, e.g., Kapton™) [90], or (b) by crosslinking (>300 °C) norbornene end-capped imide oligomers (the PMR route; PMR: polymerization of monomer reactants) [91], [92]. Typically polyimides are not considered isocyanate derivatives like polyurethanes and polyureas.

Polyimide aerogels based on the DuPont route were reported in a 2006 US patent [93]. Alternatively, Leventis et al. have developed a room-temperature method for the synthesis of polyimide aerogels via a rather underutilized reaction of aromatic dianhydrides with multifunctional isocyanates [94]–[96]. Fig. 2-3 compares the mechanistic routes of the two processes and emphasizes that both yield chemically identical products. The main advantages of the isocyanate route are: use of low cost isocyanates; use of no sacrificial reagents (like acetic anhydride and pyridine by the DuPont route); and, \(CO_2\) is the only byproduct (unlike \(HCl\) from the DuPont route). Detailed structural analysis with small angle neutron scattering (SANS) has revealed that materials synthesized in \(N\)-methyl pyrrolidone (NMP) via either route consist of similar size primary (1

\[
4.7/5.8 \text{ nm and } 35/42 \text{ nm, respectively). SEM, however, has shown that } 2^\text{o}- \text{ particles assemble differently: into fibers in the isocyanate route, and into globular aggregates in the amine route. The difference has been attributed to the rigidity of the 7-member intermediate in the isocyanate route (Fig. 2-3).}
\]
Polyimides from isocyanates (PI-ISO)  

\[
\begin{align*}
\text{OCN} & \xrightarrow{\text{room temperature}} \text{NCO} \\
\text{N} & \xrightarrow{\text{room temperature}} \text{N} \\
-2n \text{CO}_2 & \xrightarrow{} \text{N} \\
\end{align*}
\]

Polyimides from amines (PI-AMN)

\[
\begin{align*}
\text{H}_2\text{N} & \xrightarrow{} \text{NH}_2 \\
\text{HOOC} & \xrightarrow{} \text{COOH} \\
\end{align*}
\]

Fig. 2-3 Polyimide (PI) through the isocyanate (PI-ISO) and the amine (PI-AMN) route. \((\text{AcO})_2\text{O}:\) acetic anhydride.

2.1.2.5. ROMP-derived aerogels

Mechanically, polydicyclopentadiene (PDCPD) and polynorbornene (PNB) are extremely strong materials and, because they are pure hydrocarbons, they are also extremely hydrophobic. They are prepared easily from the corresponding monomers via Ring Opening Metathesis Polymerization (ROMP), which comprises a very convenient method to access purely hydrocarbon polymers under mild reaction conditions. Depending on the catalyst, e.g., first or second-generation Grubbs’ catalysts (GC-I and GC-II), the olefins along the polymeric backbone can be all trans, or a mixture of cis and trans (Figure 2-1), respectively [11]. More recently, we discovered that mostly cis-PDCPD wet-gels obtained with a novel catalytic system based on a ditungsten complex \((\text{Na}[\text{W}_2(\mu-\text{Cl})_3\text{Cl}_4(\text{THF})_2])\cdot 3\text{THF},\) referred to as \(W_2\) swell up to 120 times during solvent-exchange in toluene and keep their shape upon deswelling in pure hydrocarbons (e.g., pentane).

Figure 2-1 Ring Opening Metathesis Polymerization (ROMP)
2.1.3. Hybrids

2.1.3.1. Functionalization of aerogel microparticles

To enrich aerogel functionality, various methods have been reported in the literature such as hydrophobization, coating and compaction. Functionalization can be performed at every production step as well as post-processing. Hence, the functionalization should be implemented in the process design as a sub-step or a separate step of the overall process. Here we present a “process-oriented” classification of possible functionalization approaches.

2.1.3.2. Co-gelation approach

Aerogels consisting of organic polymer/inorganic oxide interpenetrating networks were pioneered by Leventis in 2009 using the co-gelation approach, and have been used as precursors to several purely metallic (Fe, Co, Ni, Cu, Sn) and carbide (of Ti, Cr, Hf) aerogels [97]–[99]. Specifically, in 2007 Leventis and his group had reported that resorcinol-formaldehyde gels, which are the most widely used precursors of carbon aerogels, can be synthesized in organic solvents at room temperature using acid (HCl) catalysis [100]. That method cut the base-catalyzed 7-day-long literature method for gelation to a couple of hours. At that point it was realized that since gelation of all hydrated metal ions, [M(H₂O)₆]³⁺, is based on their high acidity (typically pKₐ < 2.0), they could be used as acid-catalysts for the gelation of resorcinol-formaldehyde. Thus, allowing the acidity of such gelling metal ion sols to catalyze co-gelation of resorcinol-formaldehyde has afforded sturdy, monolithic aerogels consisting of interpenetrating networks of resorcinol-formaldehyde / metal oxide nanoparticles. Those monoliths were subsequently pyrolyzed at 800 °C, triggering carbothermal smelting, which gave sturdy monolithic metallic and carbide aerogels [97]–[99]. More recently (2014), this method has been expanded to another class of phenolic resin type of aerogels, that is benzoaxine aerogels [101] interpenetrated with iron oxide nanoparticles [102]. Depending on the smelting temperature (500 to 1300 °C), the behavior of the resulting iron aerogels can be tuned between explosive (≤ 800 °C) and thermite (> 900 °C) [103].

As for biopolymers, silica/biopolymer hybrids represent the most studied case. There are two main strategies to obtain silica/biopolymer hybrids: chemical crosslinking and physical co-gelation. Covalent coupling represents a powerful approach to control the rate of degradation and mechanical properties, but does chemically modify the biopolymer backbone. In order to minimize number of needed chemicals and process steps, and also to avoid possible contamination of the resulting material, an alternative approach, co-gelation, can be used. Co-gelation does not result in the chemical coupling between components, leading to rather interpenetrating structures. Often, however, there is no unambiguous evidence of interpenetrating character of the structure, especially when two or more biopolymers are blended and co-gelled. This should be taken into account as it may lead to inhomogeneous structure and limit reproducibility. However, interactions between components may be strong due to electrostatic attraction arising between silicates and hydroxyl, carboxyl, amine and other groups of the biopolymers.
In case organosilicates are introduced into aqueous biopolymer, due to partial miscibility, the synthesis starts in two-phase emulsion. This can be avoided when prehydrolyzed precursors or water-soluble sodium silicate are used.

Co-gelation of chitosan/silica system is described by many authors [104], [105]. In a typical procedure, acidic chitosan solution is mixed with an organosilane (TMOS, TEOS) and left for hydrolysis and condensation. Gel formation occurs after 12 – 48 h. Thus, to be used in the emulsion-gelation method the gelation time should be drastically reduced. Similar, but much faster process, is observed for cellulose/water glass systems [106].

Chemically crosslinked biopolymer/inorganic gels are known for chitosan gel as it has reactive NH$_2$ group [107]. To the best of our knowledge, alginate and cellulose are not functionalized in this way due to their relative inertness.

Blending with inorganic particles, mainly SiO$_2$, TiO$_2$, Fe$_3$O$_4$ and others, serve the aim of reinforcing the aerogel backbone along with introducing functionality of the mineral component (adsorption, catalytic, photo or magnetic properties), see [108]–[110]. It is important to note that properties of such composites are not just the sum of the properties of the individual components [110], even though no chemical reaction is expected.

2.1.3.3. Functionalization of hydrogels/alcogels

Aqueous media in hydrogels may be used to carry out silica gelation. For instance, Molvinger et al. (2004) performed gelation of TEOS in hydrated chitosan microspheres using NaF as catalyst. Then the beads were washed by distilled water, solvent exchanged and sc-dried.

Last step of the solvent exchange can serve as another opportunity to functionalize the aerogels. Silica chemistry permits sol-gel transformation in many organic solvents which can be afterwards extracted with sc-CO$_2$. In a typical procedure biopolymer alcogel are immersed in a prehydrolyzed precursor in an organic solvent letting it infiltrate the gel. Then, gel particles are moved to another bath with a catalyst to complete the gelation.

Alternatively, alcogels are immersed in an organic solvent that contains an organosilane, water and a catalyst, then rinsed with the solvent and immediately exposed to the sc-drying. Chitosan/silica hybrid aerogel were prepared using this method [36]. Similar and somewhat simpler method is described wherein alcogels were immersed in alcoholic solutions of metallic alkoxides such as Ti(acac)$_2$-2(OiPr)$_3$, Ti(OiPr)$_4$, Zr(OBu)$_4$, Al(OEt)$_3$ followed by rinsing with ethanol and sc-drying [108]. Using this method, cellulose/silica hybrids have been produced [52].

When silica precursor is used in the gelation step, hydrophobic or other functional groups can be grafted to the surface ≡Si–OH groups. Several examples of this approach involve hydrophobization of chitosan/silica alcogels by soaking them in 10 % hexamethyldisilazane (HMDS) followed by sc-drying [83], [104].
2.1.3.4. Functionalization of aerogels

Most traditional aerogels, and most notably those of silica, are fragile materials. That fragility is expressed in the most dramatic way during drying of wet-gels: evaporation of a solvent through the porous network generates capillary forces that in most cases cause collapse of the network. That limitation has been overcome by using drying with supercritical fluids. That drying method has rendered aerogels as an independent class of materials possible. The fragility issue of silica and other inorganic aerogels has been addressed successfully by Leventis with a special class of organic-inorganic hybrid aerogels referred to as polymer-crosslinked (or X-) aerogels [111]–[113]. In those materials, a conformal polymer coating is applied at the wet-gel stage to the skeletal inorganic nanoparticles rendering their interparticle necks wider. The mechanical strength of the inorganic network is increased by up to 300 times, for a nominal increase in bulk density by a factor of 3. The method has been expanded beyond silica to over thirty other metal oxide aerogels from the periodic table [114]. Applications of such aerogels even in ballistic protection have become possible [115]. It has been shown that such polymer-crosslinked networks are also strong enough to withstand the surface tension forces of ambient pressure drying [116].

Subsequently, it was reasoned that since the increase in strength in X-aerogels is attributed to the polymeric crosslinker, purely polymeric aerogels with the same nanostructure and interparticle connectivity as in X-aerogels should have similar mechanical properties. This hypothesis has been confirmed with aerogels synthesized from all major polymeric classes (polyurethanes, polyureas, polyamides, polyimides, phenolic resins including polybenzoxazines, polynorbornene, polydicyclopentadiene etc.) and in many cases the compliance of the polymeric network has allowed drying under ambient pressure without any compromise of the characteristic aerogel properties (low density, high surface area etc.) [117].

Gas-phase modification methods are developed to overcome this limitation. In case of silica/biopolymer hybrid aerogels, gas-phase reactions such as hydrophobizing agents are reported, e.g. exposure of chitosan/silica aerogels to HMDS vapor at elevated [83], [104]. Plasma treatment is an attractive hydrophobization technique recently reported for pure alginate aerogels [118].
2.2. Aerogel production in form of particles: State of the art

Silica and carbon aerogels in the form of microparticles are traditionally obtained from monoliths by milling [119]. However, the resulted particles have arbitrary shape and have a wide particle size distribution, which may be disadvantageous for life-science applications, where the particle size and shape controls many important functions, like active agents release and sensory properties.

Three main ways in making polymer particles can be distinguished:

1) Formation of liquid droplets in gaseous phase with subsequent fall in a bath in which the droplets are gelling/coagulating (dripping, jet cutting, atomization).

2) Emulsion gelation way in which droplets are formed in a liquid phase when two immiscible fluids are mixed.

3) Disruption of gelation by vigorous agitation.

This is illustrated in Fig. 2-4 in which cases a-d correspond to mechanical (or electro-mechanical) “cutting” of solution and case e corresponds to “emulsion” route.

![Fig. 2-4 Schematic presentation of different procedures for the preparation of cellulose beads by different techniques: dripping (a), jet cutting (b), spinning drop atomization (c), spinning disc atomization (d), and dispersion (e). [120].](image)

2.2.1. Formation of liquid droplets in gaseous phase with subsequent fall in a bath, in which the droplets are gelling/coagulating (dripping, jet cutting, atomization).

The main approach here is that when a fluid droplet is falling into a bath, the solution falling is gelling and a “micro-gel” is formed. Gelation can be induced by a chemical reaction in which the cross-linker (which is in the bath) diffuses into the droplet and cross-links the polymer. Another way is temperature induced gelation. Both cases are widely known for making beads based on polysaccharides. It should be noted the case of cellulose is special and will be considered separately below.

The easiest way to be used on the laboratory scale for making beads is “Dripping method”. It consists of dripping a polymer solution from a syringe or pipette into the bath in which gelation will
occurs. On a larger scale other methods are used: jet-cutting, atomisation, spraying and electro-spraying, but the principle is the same. The size of the beads that are formed depends on orifice diameter of the syringe/nozzle, solution and bath viscosities, kinetics of gelation, the distance from the nozzle to the bath, etc.

2.2.1.1. Dripping

2.2.1.1.1. Description of dripping methods

One of the latest achievements in the field of beads formation is the use of monodisperse dripping devices [121], [122]. Main advantages of these dripping devices are: an ability produce droplets with controlled initial trajectories, spherical form, droplets’ sizes in the micrometer range and of course an ability to produce almost identical droplets. However the major part of dripping devices is characterized with low production capacities what is the biggest disadvantage of such devices. But some dripping devices with spinning parts which cut liquid jet may have capacity up to 200 kg/h (on the wet gel basis).

In our days monodisperse dripping is used in different areas of chemical and pharmaceutical industries and is implemented in such processes as microencapsulation, coating, sol production and etc. Currently present on the market monodisperse dripping devices may be divided into the following groups by the way of breaking up liquid jet: electrostatic, ultrasonic and mechanical (Fig. 2-5). There are also dripping devices in which the only driving force is the gravity but these devices are of low capacity and produce big droplets (usually more than 2 mm). Droplet’s diameter for such devices depends mainly on the diameter of an outlet orifice [123].

![Dripping methods](image)

**Fig. 2-5 Dripping methods**

Dripping devices can produce particles with sizes from 20 μm up to 3 mm. Amount of produced droplets for these devices may reach 100,000 droplets per second.

In electrostatic dripping the droplet formation is accelerated by an electrostatic force created by application of electrostatic potential between the outlet orifice (the needle) and the grounding electrode which is placed in certain distance from the outlet orifice. In fact the process of droplets formation is similar to that one which takes place in electrostatic atomization. But because the liquid
is issued through a narrow needle, is supplied without application of any significant gauge pressure and thus forms a single low-velocity straight jet at the outlet orifice produced droplets have got almost the same size. The applied electrical potential can be static or pulsed[124]. This way of atomization is also applicable for spraying liquids with cells. It was shown that high electrical fields do not cause loss of cells’ viability and activity[125].

As in electrostatic atomization there are designs of dripping devices which allow supplying two immiscible liquids at the same time and thus producing micro capsules directly at the outlet orifice[126]. Schematic drawing and photos of such device are shown in the Fig. 2-6.

Fig. 2-6 Microencapsulation by dripping

Main advantages of these devices are simple design, spherical form and narrow size distribution of produced particles and micro capsules, absence of direct contacts between droplets what excludes droplets’ merging and particles agglomeration.

As it was mentioned one of the biggest disadvantages of dripping devices is quite low productivity and the most obvious (and most likely the only) way for scaling up is installation of multiple devices in one housing (chamber) (Fig. 2-7).
The certain drawback of such scale up method is a significant increase of capital and operating costs.

Table 2-1 Dripping capability

<table>
<thead>
<tr>
<th>Method</th>
<th>Droplet size, μm</th>
<th>Typical application</th>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dripping</td>
<td>20-3000</td>
<td>Encapsulation, Medicine, Chemical industry</td>
<td>Uniform droplets, no impact between droplets</td>
<td>Incapable of handling high liquid flow rates, material losses</td>
</tr>
</tbody>
</table>

2.2.1.1.2. Examples of gels or aerogels produced by simple dripping method

Biopolymer aerogel beads (except cellulose)

Recently, the preparation of aerogel beads based on polysaccharides, or bio-aerogel beads, have been reported in the literature at lab scale only. Some examples are given below.

Quignard and co-workers [58], [59], [67]–[69] prepared chitosan aerogel beads from squid-pen and crab-shell chitosan with a high degree of amine groups by dissolving chitosan in acetic acid and dripping the solution in a sodium hydroxide solution through a 0.8 mm syringe needle, upon which gelation at the surface immediately sets in and is completed after short storage time in the base solution. Washing with water, exchange with ethanol and subsequently drying with supercritical carbon dioxide leads to chitosan aerogel beads with a fibrillar microstructure, volume shrinkage upon drying of around 50 % and specific surface area from 150 to 300 m$^2$/g.
Alginate and κ-carrageenan aerogel beads were prepared by *dripping method* (see Fig. 2-8) [32]. Sodium alginate solution is added dropwise at room temperature to a stirred CaCl₂ or CuCl₂. Kappa-carrageenan bead formation is the thermo- and ionotropic gelation of κ-carrageenan hot droplets added into a cold saline (KCl) solution. The subsequent supercritical drying of the gel particles leads to the aerogel formation [32]. The size of aerogel particles varied from few hundreds of microns to few millimetres. The overall volume shrinkage was very high for carrageenan particles (95%), less for chitosan (60%) and low for Ca-alginate (20%). The specific surface area was respectively 200, 330 and 570 m²/g.

![Image of hydrogel and aerogel beads](image_url)

**Fig. 2-8** Optical and SEM images of hydrogel (first column) and aerogel spheres (second column) and of cross-sections of aerogel spheres (third and fourth columns) of Cu-alginate (row a), chitosan (row b) and carrageenan (row c). [32].

Finally, a modification of the process using pulsed electric fields for the atomization of the aqueous precursor solution through the nozzle was reported for the preparation of microsized alginate gel particles [127].

**Cellulose aerogel beads**

The difference between making cellulose beads and other polysaccharide beads is that cellulose is directly coagulated in the bath without gelation. As a result, a network of coagulated cellulose with a non-solvent (water or alcohol) in the pores is formed. This is very different because gelation, if it is physical, can be reversible, and coagulation is an irreversible phase transition.

Cellulose beads already exist on the market for immobilization, purification, separation and filtration purposes mainly in the form of swollen-in-water particles [128]–[130]. There are two approaches in making cellulose beads:

Dissolution of a cellulose derivative (viscose, cellulose esters or ethers) and then cellulose regeneration in a bath, which chemical composition is tuned to perform “de-derivatisation” (hydrolysis, deacetylation, etc.) [53], [131], [132].
For example, cellulose acetate was dissolved in water-miscible organic solvent (acetone or DMSO), then dispersed in a coagulation bath based on water and particles were formed [132]. Cellulose was then regenerated by hydrolysis. The diameter of beads was from 0.15 to 2 mm.

Using NaOH-water-urea, coagulated in water cellulose beads were prepared in ref [133] by dripping solution in water. In wet state the size of beads was around 3 mm. The influence of cellulose concentration, composition of coagulation bath and its temperature on beads geometry (in the wet state) and morphology after drying with sc CO₂ was studied. The specific surface area for various cases is shown in Fig. 2-9. The beads were never dried and sc drying was used only to study specific surface area. The same approach was used to prepare beads based on oxidized cellulose (oxidation performed on ready wet beads) and the release of model drugs from never-dried cellulose was investigated [134].

![Image](image-url)

**Fig. 2-9** The effect of (A) temperature, (B) acid concentration and (C) cellulose concentration on specific surface area of the cellulose beads. If not stated otherwise, the following coagulation conditions were applied: 5% cellulose solution coagulated into 2 M HNO₃ at 25 °C. Lines are given to guide the eye. [133].

Imidazolium-based ionic liquids were used to make cellulose beads [135] via “underwater pelletisation”. In this method, the solution is pushed by a pump or extruder through a die plate, preferably without contact with air, into the non-solvent bath. The solution was at an elevated temperature, e.g., from 50 to 150 °C in order to reduce the viscosity. A knife passes across the holes of the die plate at particular short intervals of time and divides the exiting solution into small portions. Beads of uniform size are generally obtained after drying. The beads can, for example, have an average diameter of from 100 μm to 10 mm, in particular from 0.1 mm to 5 mm or from 0.2 mm to 2 mm. The drying was performed in ambient conditions and although the porosity was not discussed in this patent, we may suppose it was low [136].

To the best of our knowledge only one publication reports on the preparation of cellulose aerogel beads. They were obtained from cellulose-NaOH-water solutions. The beads were made by dripping method. It was shown that the shape of the beads varied from very flat plates to spheres (Fig. 2-10) [39], [136]. The influence of the preparation conditions (cellulose concentration, delay time, bath
temperature, and the distance between the pipette and the bath surface) on the shape of the beads is discussed. Various inorganic powders were encapsulated into cellulose beads and organic-inorganic aerogel particles were prepared (Fig. 2-11).

![Fig. 2-10 Wet cellulose particles (coagulated cellulose in water). [39].](image1)

![Fig. 2-11 Photos and SEM images of TiO$_2$-encapsulated (a, b) and iron-encapsulated (c, d) aerocellulose beads. [39].](image2)

To conclude on the preparation of cellulose beads from cellulose dissolved in direct solvent via dripping method, still a lot of understanding is missing concerning the influence of solvent and processing parameters on beads geometry and morphology.
2.2.1.2. Jet cutting

2.2.1.2.1. Process description of beads production by geniaLab® JetCutter

The preparation of solid particles, like beads with a size between the micro- and millimeter with a high productivity and an economic efficiency is possible by using the JetCutter technology of geniaLab® developed by Vorlop and Berford in 1996 [137].

In principle the technology is based on the mechanical separation of a liquid jet. A rotating wire cuts the liquid jet into equal sized cylinders and these are symmetrically curved during falling down. The spherical shaped beads are collected in a suitable bath. The beads shall not be able to coalesce.

The significant difference to the classical dripping belongs to its high production rates, some kg per hour, and the feasibility to work with highly viscous liquids, dispersions and melts [138] (viscosity of more than 110 Pa·s with a lowest limit of 0.2 Pa·s.). The solution is pressed through a nozzle to reach a high velocity. The typical diameter of such a nozzle is between 0.1 and 1 mm. The stable liquid jet leaves the nozzle and is then cut by a rotating tool into cylindrical shaped parts as depicted in Fig. 2-12 [139].

Fig. 2-12 Schematic sketch of the droplet preparation: with a high velocity a stable liquid jet is leaving the nozzle. A rotating cutting tool mechanically separates the jet into cylindrical shaped parts. Further falling of the cylinders shape them into spheres. The losses are caused by the cutting process and depend on the thickness of the cutting tool [139].

Fig. 2-13 shows the table top unit of a JetCutter Typ S and in Table 2-1 its productivity is listed [140]. The productivity is mainly influenced by two factors: (1) the frequency of generation and (2) the initial sphere diameter.
Fig. 2-13 JetCutter Typ S from geniaLab®, Braunschweig, Germany. Tabletop unit with a 1 L stock solutions reservoir. (http://www.genialab.com/JetCutterS.php)

Table 2-2 Productivity of a JetCutters Typ S in kg/hour using various cutting frequencies [140]

<table>
<thead>
<tr>
<th>Bead diameter [mm]</th>
<th>Production rate at different cutting frequencies in [kg/h]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>f = 5000 Hz</td>
</tr>
<tr>
<td>0.2</td>
<td>0.08</td>
</tr>
<tr>
<td>0.4</td>
<td>0.6</td>
</tr>
<tr>
<td>0.6</td>
<td>2</td>
</tr>
<tr>
<td>0.8</td>
<td>4.8</td>
</tr>
<tr>
<td>1</td>
<td>9.4</td>
</tr>
<tr>
<td>1.5</td>
<td>31.8</td>
</tr>
<tr>
<td>2</td>
<td>75.4</td>
</tr>
<tr>
<td>2.5</td>
<td>147</td>
</tr>
<tr>
<td>3</td>
<td>254</td>
</tr>
</tbody>
</table>

Beside others, the size of droplets using the classical dripping process depends on physical properties like surface tension, density and viscosity of the solution, as well as process parameters like diameter of nozzle and gravity [141]. In contrast the JetCutter process is running independently of such parameters [142].
A specific (and negative) feature of jet cutters is material loss which consists of so called cutting loss and spraying loss (Fig. 2-14). Spraying losses (but not cutting losses) can be minimized by inclining the cutting disk or/and by using smaller cutting wires. Inclination angle depends on a liquid’s flow rate and a frequency of cutter’s rotation.

**Fig. 2-14 Cutting and spraying losses**

The rotating frequency of the cutting tool, representing the number of cylinders, is between 1,000 and 10,000 per second. The surface tension leads to the spherical shape adaption. A snap shoot is given in Fig. 2-15.

**Fig. 2-15 Snap shoot of the cutting process.(http://www.genialab.com/JetCutterS.php)**

The hardening of the spheres is performed during its flight or when diving into a regeneration bath. After a certain time of regeneration the beads can be spooned out.

The efficiency of process parameters is mathematically described by Prüße et al. [142] and [143].
2.2.1.2.2. Examples of gels /aerogels produced by this method

Some examples of produced beads by geniaLab® are shown in Fig. 2-16.

Fig. 2-16 Examples of beads produced by geniaLab®. Left to right: Alginates with encapsulate Fibroblast of mouses $\phi = 320 \, \mu m$; Chitosan $\phi = 500 \, \mu m$; Alginate $\phi = 500 \, \mu m$; Pectin $\phi = 500 \, \mu m$. (http://www.genialab.com/JetCutterS.php)

All these beads are monodispersively sized as shown in Fig. 2-17 [142].

![Distribution of size of alginate beads](http://www.genialab.com/JetCutterS.php)

Fig. 2-17 Distribution of size of alginate beads [144].

For R&D the JetCutters process is mainly used for medical, food and bio catalytic applications. Nowadays gel spheres of alginates are used for drug deposition and release. For example the MRI-contrast media of van Elk et al. or the capsulation of bacteriophages by Choinska-Pulit [145], [146]. In the area of food the JetCutter process is used to depose foodstuffs and supplements [147]. The application of bio catalysis is described by Berensmeier et al., where dextranucrase is immobilised in alginates for the synthesis of oligosaccharides [148]. Metrangolo-Ruiz et al. report on the immobilization of alcoholic dehydrogenase of polyvinylalcohols in the production of chirale hydrophobic alcohols [149].
GeniaLab® itself provides commercially various products based on alginate, chitosan, carrageenan, pectin and cellulose on the market. They are used for food, cleaning and cosmetic stuffs.

Cellulose aerogel beads were prepared for the first time with this method in the frame of “Aerocell” European project (6th framework program). Cellulose was dissolved in 8%NaOH-water and jet-cutted into H₂SO₄ solution. Wet beads were washed from acid in water, water replaced by acetone and cellulose was dried with sc-CO₂[150].

The same jet-cutting technology was used to prepare cellulose aerogel beads starting from a cellulose derivative: this is the case of cellulose carbamate solution which was dissolved in NaOH-water [53]. Beads were made by jet-cutting method by GeniaLab, Germany. Cellulose was regenerated from cellulose carbamate either by thermal treatment or by chemical treatment in acid-salt bath. Beads of about 0.5 mm were formed. They were dried with sc-CO₂. Depending on the polymer concentration the specific surface area varied from 350 to 540 m²/g.

2.2.1.3. Spraying/atomization

2.2.1.3.1. Process description

In our days atomization process is widely used in different industries and applications and became almost irreplaceable for different areas of production. Atomization can be considered as a full disintegration of incompressible liquid stream or jet accompanied by formation of poly- or monodispersed droplets. Theoretical investigations of this complicated hydrodynamic process have been started more than 100 years ago by Lord Rayleigh and have been later developed by many authors [151], [152].

Atomization became a crucial stage for such processes like spray combustion, spray drying, evaporative cooling, spray coating, and drop spraying. One can find a lot of examples of applications in medicine, meteorology, and printing. There are such specific examples of atomization process as cavitational dispersion in surgery for selective removal of tissues. Numerous spray devices have been developed which are generally designated as atomizers, applicators, sprayers, or nozzles. These devices utilize different physical phenomena to initiate disintegration of a solid liquid jet, stream or surface. Result of such disintegration is spray which is generally considered as a multiphase system consisting of big number of droplets (discrete phase) immersed in a gaseous continues phase. Most part of designed devices atomizes liquids by creation of great velocity difference between the liquid and the surrounding gas. Some devices like pressure nozzles and rotary atomizers introduce high-speed liquid jets into stationary or slow moving gaseous phase. Some devices like two-fluid atomizers impact with high-velocity gas on relatively slow moving liquid. There are also a number of other devices which use mechanical, electro-magnetic or other forces to atomize liquids.

Different types of atomizers and nozzles have got their own advantages and disadvantages. They also differ by means of droplets’ sizes and size distribution.

2.2.1.3.1.1. Basics
There are a number of basic processes which a common for all methods of atomization and which lie in the foundation of the liquid disintegration process. These processes are the conversion of bulk liquid into a jet or sheet and the growth of disturbances which ultimately lead to disintegration of the jet or sheet into ligaments and then drops. Evolution of these processes determines characteristics of the resulting spray: mean droplets’ size, droplets velocities, their penetration, shape and size distribution. All these characteristics are strongly influenced by nozzle’s type, size, physical properties of the dispersed liquid (such as viscosity, surface tension and density), physical properties of the gas media in which the liquid is introduced. Basically, atomization occurs as a result of the competition between the stabilizing influences of surface tension and viscosity and the disruptive actions of various internal and external forces. In most cases, turbulence in the liquid, cavitation in the nozzle, and aerodynamic interaction with the surrounding gas, all contribute to atomization. Thus atomization can be considered as a multi-stage process. Once droplets occur after initial breakup of the liquid jet or sheet and because of their instability they as a rule start disintegrating into smaller droplets. The smaller droplets (if instability is still present) undergo further disintegration. This process continues until the stabilizing effect of surface tension becomes larger than the influence of disruptive forces. This means that the drop size characteristics of a spray are governed not only by the drop sizes produced in primary atomization but mainly by the extent to which the largest of these drops are further disintegrated during secondary atomization.

When a high-speed liquid flux interacts with comparatively slow gas phase we can observe following mechanisms of droplets formation:

When the differential velocity between liquid jet and the gas phase is relatively small axisymmetric oscillations in the liquid jet appears causing jet’s disintegration into drops of fairly uniform size. This is so called Rayleigh mechanism of breakup. Oscillations exist on the surface of the jet. Drop diameters are roughly twice the initial jet diameter. Size of droplets becomes bigger if the liquid has higher viscosity. Smaller droplets can be produced by increasing jet’s velocity. At higher velocity the whole jet starts oscillating. In this case it has sinusoidal shape. This regime exists only in quite a narrow range of velocities.

When the velocity difference becomes large enough one can observe waves on the surface of the jet caused by the direct aerodynamic interaction between the jet and the surrounding gas phase. These waves lead to detachments of ligaments from the jet. The ligaments being quite unstable further disintegrate into small droplets. Such droplets are much smaller than the initial jet diameter. At very high relative velocities atomization is complete within a short distance from the discharge orifice. A wide range of drop sizes is produced, the mean drop diameter being considerably less than the initial jet diameter.

These effects were observed and theoretically described firstly by Rayleigh. He considered the simple situation with a laminar jet emerging from a plain orifice. and postulated the growth of small disturbances that produce breakup when the fastest growing disturbance attains a wavelength \(\lambda_{opt}\) of
4.51 \( d \), where \( d \) is the initial jet diameter. After breakup, the cylinder of length 4.51 \( d \) becomes a spherical drop, so that

\[
4.51d \times \left( \frac{\pi}{4} \right) d^2 = \left( \frac{\pi}{6} \right) D^3
\]

and hence \( D \), the drop diameter, is obtained as

\[
D = 1.89d
\]

Fig. 2-18 (a) shows an idealization of Rayleigh breakup for a liquid jet. Experiments show good agreement with Rayleigh’s conclusions but there are also a number of “satellite” drops which are created as the individual cylinders neck down and separate.

Rayleigh took into consideration only surface tension and inertial forces what is in fact not enough. Later Rayleigh’s theory was revised and expanded by Weber who included the effect of air resistance on the disintegration of jets into drops. He found that air friction shortens the optimum wavelength for drop formation. For zero relative velocity he showed that the value of \( \lambda_{opt} \) is 4.44\( d \), which is close to the value of 4.51\( d \) predicted by Rayleigh for this case. For a relative velocity of 15 m/s, Weber showed that \( \lambda_{opt} \) becomes 2.8\( d \) and the drop diameter becomes 1.6\( d \). Thus the effect of relative velocity between the liquid jet and the surrounding air is to reduce the optimum wavelength for jet breakup which results in a smaller drop size.

Weber also examined the effect of liquid viscosity on jet disintegration. He showed that the effect of an increase in viscosity is to increase the optimum wavelength for jet breakup. This can be written as

\[
\lambda_{opt} = 4.44d(1 + 30h)^{0.5}
\]

where

\[
Oh = \mu_L/(\rho_L a d)^{0.5}
\]

\[\text{D1.3 – v1.0} \]

\[\text{NanoHybrids NMP-03-2015 - PUBLIC} \]
This group is sometimes referred to as the Z number, the stability number, or the Ohnesorge number ($Oh$).

The latter expressions concern breakup of liquid jets. But many types of nozzles form liquid sheets which may have flat or conical shape. Although basically the mechanisms which are responsible for sheets breakup are the same as those in case of jets, there are some additional expressions which describe relations between process parameters and droplets sizes.

As for jets in case of high-velocity fluxes energy of fluctuations which are caused by turbulence is high enough to disintegrate liquid sheets into separate ligaments even without any interaction with surrounding gas phase. However, the main reason for sheets breakups is still rapidly growing waves caused by surrounding gas phase. When energy of such waves becomes more than a certain critical value it leads to liquid sheet breakup forming instable ligaments which later disintegrates into separate droplets according to the Rayleigh mechanism. The dependence of the drop sizes produced in this mode of atomization on air and liquid properties can be expressed as

$$\frac{D}{\delta} \approx We^{-0.5}$$  \hspace{1cm} (5)

where $\delta$ is the sheet thickness and $We$ is the Weber number, is $U^2 \rho A \delta/\sigma$.

Almost all atomizing devices which are currently available at the market may be divided into following groups:

- Pressure Jet Atomization
- Fan Spray Atomization
- Twin-fluid Atomization
- Rotary Atomization
- Effervescent Atomization
- Electrostatic Atomization
- Vibration Atomization
- Whistle Atomization

Each of the mentioned methods has got its own advantages and disadvantages which will be discussed further.

But firstly for better understanding of atomization processes taking place in nozzles of different types it is useful to give some relations for produced droplets’ mean diameter here.
For pressure jet swirl atomization mean surface-volumetric diameter can be calculated using Vitmann-Katsnelson-Paleev expression [153]:

$$d_{3,2} = \frac{b}{0.11Re^{0.34}}$$  \hspace{1cm} (6)

$$Re = \frac{4G_{M0}/\pi \rho_{M0} v}{d_c}$$  \hspace{1cm} (7)

$$b = \left[\frac{d_c}{2 \cos(\alpha/2)}\right]\left(1 - \sqrt{1 - \mu \cos(\alpha/2)}\right)$$  \hspace{1cm} (8)

where \(b\) – liquid’s sheet thickness, \(d_c\) – outlet orifice diameter, \(\mu\) – outlet orifice discharge coefficient, \(\alpha\) – spray cone angle.

Nukiyama and Tanasawa expression[151] is quite common for calculations of twin-fluid atomization with internal mixing:

$$d_{3,2} = \left(0.0185/u_0\right)\sqrt{\frac{\sigma_l}{\rho_{M0}}} + 11.245\left(\frac{\mu_l}{\sqrt{\sigma_l \rho_{M0}}}\right)^{0.45}\left(\frac{V_{M0}}{V_G}\right)^{1.5}$$  \hspace{1cm} (9)

where \(u_0\) – initial relative gas-liquid velocity, \(\sigma_l\) – liquid’s surface tension, \(\mu_l\) - liquid’s viscosity, \(V_{M0}\) – liquid volumetric flow rate, \(V_{M0}\) – gas volumetric flow rate.

For atomization of liquids with low viscosity \((\mu_l^2/\rho \sigma_l d_c) < 0.42\) using twin-fluid nozzles with external mixing the following expression for median diameter was offered by Plit et al. [152]:

$$\frac{d_{50}}{d_c} = 0.21\left(\frac{\sigma_l}{\rho w_0^2 d_c}\right)\left(\frac{D_{eff}}{d_c}\right)^{0.7} \left[1 + 520\left(\frac{\mu_l^2}{\rho \sigma_l d_c}\right)^{0.03} (d_c/D_{sc})\right]$$  \hspace{1cm} (10)

For liquids with high viscosity \((\mu_l^2/\rho \sigma_l d_c) > 0.42\) correspondingly:

$$\frac{d_{50}}{d_c} = 0.21\left(\frac{\sigma_l}{\rho w_0^2 d_c}\right)^{0.3}\left(\frac{D_{eff}}{d_c}\right)^{0.7} \left[1 + 2300\left(\frac{\mu_l^2}{\rho \sigma_l d_c}\right)^{0.03} (d_c/D_{sc})^{1.3}\right]$$  \hspace{1cm} (11)

where \(w_0\) – outlet gas velocity, \(D_{eff}\) – effective diameter of gas supplying channels, \(D_{sc}\) – swirling chamber diameter.

For droplet size calculations in rotary atomization an expression provided by Frasser, Eisenklam and Dombrowski[151] [154] is considered as the most reliable:

$$d_{3,2} = 0.55(G_{M0} v_l/d_r)^{0.2} (1/n)^{0.6} (1/\rho M0)^{0.3} (\sigma_l/l)^{0.1}$$  \hspace{1cm} (12)

$$\delta_{\text{max}} = 3d_{3,2}$$  \hspace{1cm} (13)

where \(d_r\) – diameter of the rotor, \(n\) – nozzle’s rotational speed (in rpm), \(l\) – wetted disk perimeter. For rotary atomizers with wing or nozzle disks \(l = zh\) and \(l = z\pi(d_c/2)\) (\(z\) is an amount of wings or channels, \(h\) – wing’s height) correspondingly.
Sauter mean diameter for effervescent atomization can be calculated using the following expression provided by Lund et al. [155]:

\[
d_{3,2} = 3 \sqrt[3]{\frac{3}{2} \sqrt{2\pi d_L^3} \left[1 + \frac{3\mu_i}{\sqrt{\rho_l \sigma_i d_L}}\right]} \tag{14}
\]

where \(d_L\) – diameter of produced ligaments, \(\rho_l\) – liquid’s density.

In ultrasonic atomization Sauter mean diameter is equal to:

\[
d_{3,2} = \frac{0.252}{A} \sqrt[3]{\frac{3V_f \mu \sigma}{\pi D \rho^2 f g \cos \beta_{surf}/2}} \tag{15}
\]

where \(f\) – nozzle’s operating frequency, \(D\) – external nozzle’s surface diameter, \(A\) – ultrasonic waves’ amplitude, \(\beta_{surf}/2\) – angle between vertical axis and atomization surface.
2.2.1.3.1.2. Production of powders and spherical particles via atomization

Atomization process via spraying has been widely used for production of powders, nano-, micro- and macro-scale particles. This process is successfully utilized in spray drying and widely spread in different industries. For food production atomization process is used for milk powder production[156], coffee[157], juice production [158], eggs [159], cereal, spices[160], flavorings, starch and starch derivatives, vitamins, enzymes, stevia, colourings and etc. [161] In pharmaceutical industry atomization is used for production of both active components and accompanying ingredients. A lot of studies have been dedicated to micro-encapsulation and encapsulation via atomization especially in food and pharmaceutical industries [162]–[164].

Besides this atomization process has been successfully utilized for a number of applications where melts’ handling takes place. Dental amalgams are produced using spray atomization. Application of nozzles is typical for production of solid rocket fuels, explosives and flares. Atomization process is involved in production of filters, metallic paints, jewelry-brazing pastes, food additives and batteries.

Varying nozzle types and process parameters it is possible quite significantly affect qualitative and quantitative characteristics of the final product. A lot of companies such as Bosch, Glatt, Buechi, GEA and etc. are currently offering apparatus of different designs and equipped with different nozzles.

2.2.1.3.1.3. Pressure Jet Atomization

Pressure Jet Atomization is the most common method which is currently used for a very wide range of standard problems. In nozzles of this type the pressure created by the pump converts into kinetic energy leading to liquid acceleration to velocities higher than the velocity of surrounding gas phase. Depending on design features of pressure nozzles accelerating liquid’s motion can be organized in different ways which one can split in two groups: linear motion and motion with tangential component. Pressure Jet nozzles may have different number of outlet orifices of dissimilar shape. Pressure Jet Atomization has been studied by many researches like Hiroyasu and Katoda[165], Mock and Ganger [166], Carey [167], Radcliffe[168], Dombrowski et al. [169], [170], Shen and Poulikakos[171] and others [172], [173].

2.2.1.3.1.3.1. Plain-orifice nozzles

This type of nozzles is the most simple and at the same time a quite effective method of liquid’s disintegration[174]. When the pressure is comparatively low the liquid issuing through a cylindrical orifice with a small diameter forms cone-shaped strained flux. When the gauge pressure in the nozzle overcomes the limit of 150kPa the outgoing liquid forms high-velocity jet and rapidly disintegrates into separate droplets. The mean diameter of these droplets and their size distribution significantly depend on many parameters such as nozzle operating conditions, physical properties of the liquid, nozzle design[175]. An increase of the pressure leads to an increase in jet’s velocity, and this respectively causes rise of both turbulence intensity in the fluid and aerodynamical frictional force induced by surrounding gas phase and thus a higher degree of liquid disintegration is reached. High
pressure of injection, low pressure of the surrounding gas phase where injection is carried out, small diameter of the outlet orifice – all these factors guarantee formation of small size droplets. On the other hand an increase of liquid’s viscosity and surface tension leads to higher stability of the jet, i.e. to lower degree of disintegration. High viscosity leads to formation of big droplets, poor atomization, deeper penetration of the jet into the chamber, lower rates of drying or conversion processes. Surface tension prohibits liquid’s surface strain. Density of the liquid affects the degree of droplets’ spread in the surrounding gas phase as the kinetic energy of the jet is one of the most important factors which influence dispersed liquid’s behavior. The angle of the spray cone formed by plain-orifice nozzles as a rule varies from 5° up to 15°. Majorly this angle depends on the turbulence and physical properties (viscosity and surface tension) of the liquid jet and less on diameter and orifice’s diameter to length ratio. An increase of the turbulence leads to an increase of the spray cone angle because of changes of the ration between radial and tangential components of velocity vector towards to the first one.

Atomization process in case of plane-orifice nozzle is quite significantly affected by the flux of the continuous gas phase[176]. This influence relates to the fact that disintegration process doesn’t by the moment when the jet leaves the outlet orifice of the nozzle. Indeed the disintegration process continues in the chamber while droplets’ diameter doesn’t reach certain critical value when further breakup of droplets is not possible any longer. For each particular case this critical value depends on relative velocity between liquid and gas phases. If directions of liquid’s and gas phase’s fluxes are collinear the penetration of the liquid into the chamber becomes deeper and the dispersion process lasts longer what leads to growth of the droplets’ mean diameter. If the fluxes are contrary decrease of droplets’ penetration with simultaneous increases of the spray cone angle and disintegration quality occurs. The gas phase velocity affects both droplets’ formation and evolution processes and degree and quality of the disintegration process. It is worth mentioning that the influence of the gas phase velocity on the disintegration process in case of plain-orifice nozzles can be evaluated only when this velocity is not high enough so that it changes the nature of the atomization process. If the gas phase velocity exceeds this limit the mechanism of the disintegration process may convert into that one which takes place in air-assist (or air-blast, or twin-fluid) atomizers.

Plain-orifice nozzles are widely used for injecting liquids into controlled gas fluxes. These injections can be carried out in both co-current and counter-current manners or with a certain non-zero angle between the nozzle’s axis and the gas flux[177], [178]. One the most successful application of nozzles of this type is a fuel injection into working chambers of diesel engines [179]. Since significant pressure is reached when air-fuel mix compression occurs it is necessary to supply pressure of about 83 – 103 MPa to the nozzle to inject fuel into the combustion chamber with sufficient quality of the atomization process.

2.2.1.3.1.3.2. Pressure-Swirl Atomization

One of limiting factors of application of plain-orifice nozzles for some problems is comparatively narrow angle of the spray cone. And for many real problems it is necessary to have a wide angle. To organize spray cones with such wide angles it is common to use pressure-swirl nozzles which are
also known as simplex nozzles [180]. Nozzles of this type consist of conical swirling chamber with an orifice placed in the vertex of the chamber. Liquid supplies in the chamber through tangential inlet orifices. If the pressure in the liquid is high enough the liquid gains quite high angular velocity and this leads to formation of a vortex with a gas core. Swirling in this way liquid then flows out through the outlet orifice of the swirling chamber and is disintegrated by axial and radial forces with generation of tulip-shaped or conical sheet which undergoes subsequent breakup in separate droplets. Key factors affecting the atomization process in this case most of all are interactions between the liquid and the surrounding gas phase, surface tension of the liquid and viscosity. The angle of the spray cone for this type of nozzles may vary from 30° up to almost 180° depending on the relative values of tangential and axial components of the velocity vector at the outlet of the nozzle and thus can be controlled by varying these values. The size distribution of obtained droplets is the function of the liquid’s pressure and geometrical parameters of the swirling chamber. The smaller the swirling chamber the smaller droplets can be produced. However operating conditions are quite significantly limited in this case. Another disadvantage of this atomization method is instability of the spray cone’s shape because liquid leakages.

Swirling flows are widely used in nozzles and burners for organization of recirculating zones with high speed shears. Centrifugal force is utilized in this type of nozzles for the liquid break up. Tangential and radial components of the velocity vector have got an order of the axial component or even higher. Existing at the present time swirling-pressure nozzle designs can be conventionally separated in two groups basing on the shape of the spray cone: solid-cone nozzles and hollow-cone nozzles (Fig. 2-19). The first type of design provides almost uniform spread of atomized droplets in the volume of the spray cone. For the second type a high concentration of droplets at the periphery of the cone is typical.

The hollow-cone is typical namely for simplex nozzles. The spray cone shape varies depending on the liquid pressure. When the pressure is low the liquid just flows out the nozzle. With a pressure increase the liquid starts escaping in the form of thin pencil-like flux. The cone which appears at the outlet orifice of the nozzle in this case may convert into a sphere because of surface tension forces.

Fig. 2-19 Spray cone types
With the further pressure increase the sphere opens and converts into hollow tulip-shape cone with a rugged edge where the liquid breaks up into big droplets. When the pressure is high the curved surface of the “tulip” straightens and as a result the spray becomes hollow-cone. With cone’s expansion its wall becomes thinner making the cone unstable. The cone starts disintegrating into separate ligaments which then degrade down to small droplets which all together form still easily visible hollow-cone. For inviscid liquids the lowest pressure limit when the atomization still occurs is roughly equal to 100 kPa.

A number of different simplex nozzles which defer from each other mainly by the way of creation of rotational motion in the outgoing jet were designed for various practical applications where one of the stages is a combustion process (Fig. 2-20). Swirling chamber in these nozzles may have conical, spiral or tangential cuts. Last two types may be replaced with guiding blades or orifices. Simplex nozzles of big size are successfully used in boiler-utilizers and industrial kilns and furnaces. Fuel flow in such nozzles may reach 67 kg/min.

Nozzles which have solid-cone spray create relatively big fractions. Besides this droplets which go along the axis of the spray cone are bigger than those which are at the periphery. At the same time it is possible to produce droplets with smaller sizes using nozzles with hollow-cone. However for simplex nozzles liquid’s flow rate is proportional to the square root of the pressure. It means that to double flow rate it is necessary to increase pressure of supplied liquid for four times. Because of this for some cases it is necessary to raise pressure to unacceptable or inexpedient values to reach desirable capacity.

![Simplex nozzles for combustion applications](image)

**Fig. 2-20 Simplex nozzles for combustion applications**
On the other hand for small flow rates the pressure should be so low that the atomization process quality won’t reach the appropriate level. This disadvantage of simple nozzles pushed development of wide-range atomizers such as duplex, dual-orifice and spill-return atomizers [166]–[169] (Fig. 2-21).

These nozzles can easily provide “maximum-minimum flow rate” ratio up to 20 with the operating pressure up to 7 MPa. Thus high quality of atomization is guaranteed within the whole range of flow rates without overcoming normal pressure limits of supplying equipment.

There is a number of other designs of simplex nozzles [181] which provide qualitative dispersion for wide range of flow rates by varying effective flow area.

2.2.1.3.1.4. Fan Spray Atomization

It is worth mentioning that the cross section of spray cones of nozzles mentioned above under normal operating conditions is a circle. If it necessary to obtain a flat elliptical spray cone fan spray nozzles are used (Fig. 2-22).

Fig. 2-21 Duplex, dual-orifice and spill-return atomizers
Fig. 2-22 Fan Spray Atomizer

This type of nozzles may have various designs such as flood nozzles and flat nozzles [182]. In fan spray flood nozzles a jet of a round cross section collides with a curved surface creating wide flat spray cone with almost uniform distribution of relatively big droplets. Nominal spray cone angle for these nozzles is $120^\circ$ or more. In fan spray flat nozzles the outlet orifice looks like V-shape slot cut in a hemisphere which is connected to an inlet channel. Issuing thin liquid jet disintegrates forming flat elliptical spray cone the major axis of which is parallel to the major axis of the outlet orifice. Nozzles of this type are the most spread flat fan atomizers. These nozzles provide perfect atomization and sharply defined spray cone for viscous and non-Newtonian liquids. Flat spray cone may be also achieved by making narrow slots in flat or cylindrical surfaces and supplying the liquid to them in two opposite directions.

It was found out that the trajectory of the flat sheet created by the fan spray nozzle depends on the initial pressure of the supplied liquid, thickness of the sheet and liquid’s surface tension and to a smaller extent on liquid’s density [170]. The sheet’s thickness becomes narrower with the distance from the nozzle’s outlet orifice. Surface tension deforms sheet’s edges what leads to curvy shape of edges with sheet’s expansion. Liquid’s viscosity suppresses sheet edges’ disintegration and as a result bigger droplets are produced. An increase of initial pressure of supplied liquid and/or of assistant air may decrease mean diameter of produced droplets. Ambient pressure insignificantly affect spray cone angle. However an increase of ambient pressure leads to an increase of droplets’ mean diameter since with higher ambient pressure disintegration process occurs closer to the outlet orifice where the sheet is thicker. Fan spray nozzles produce bigger droplets than pressure-swirl nozzles for the same flow rate. However, Lucas fan spray nozzle allows producing small droplets with the mean diameter smaller than 25 $\mu$m even for oils with viscosity $8.5 \times 10^{-6}$ $m^2/s$.

Fan spray nozzles are widely used for different surface coatings[183], in some gas turbines of small sizes [184] and in some other specific applications where flat elliptical spray cone is necessary.
2.2.1.3.1.5. **Twin-fluid atomization**

As it was mentioned above the main disadvantage of swirl-pressure nozzles is poor quality of atomization for low flow rates because of too low differential pressure for those cases when sizes of inlet orifices are chosen in the way to provide maximum capacity for maximum pressure. This problem may be solved by application of duplex, dual-orifice or spill-return atomizers. On the other hand the disintegration process at low inlet pressure may be improved by forcing the system to hydrodynamic instability, which occurs when high-velocity gas flows are utilized.

Twin-fluid atomization is one of the most common methods and applicable in many areas [185]–[191]. Gas (as a rule air) is used to improve and support quality of atomization in the whole range of flow rates. Kinetic energy of high-velocity air flux is used to break up liquid jets into some ligaments which then subsequently disintegrate into separate droplets. Large scale vortexes in the air flux significantly affect the liquid causing destabilization, stretching and fluctuation of the jet. Because of very complicated interactions between the liquid and the air the range of droplets’ sizes obtained with twin-fluid atomization is very broad. There are two types of twin-fluid nozzles divided by means of quantity and velocity of supplied into nozzles gas: with lack of gas and with excess of gas.

For the first group supplied gas flow rate is maintained at the minimum level but there are no restrictions for the inlet pressure. The gas is supplied by a compressor or from a high-pressure vessel flowing through orifices surrounding the liquid jet and creating a high-velocity flux. For the second group of nozzles gas velocity is usually not more than 150 m/s and therefore it is necessary to supply a big amount of the air to provide a good atomization. In addition the gas plays the role of a media which carries dispersed droplets.

In twin-fluid nozzles of the first type the air is necessary to improve atomization process when the fluid flow rate is low creating sufficient injection pressure. However for some nozzle designs the gas supply is necessary for the whole range of operating conditions if atomization quality reached by the nozzle without gas is not high enough. Within the atomization process the influence of the high-velocity gas flux on the liquid may occur both inside and outside the mixing chamber of the nozzle. This method is well suitable for liquids with high viscosity. The spray cone angle can be controlled by varying gas flow rate.

In nozzles with gas excess a big amount of gas is used as a main driving force of disintegration process. Using these nozzles it is possible to produce small droplets in spite of low initial pressure. Besides this fact these nozzles have got quite simple design. Twin-fluid nozzles with gas excess thanks to their advantages over pressure jet nozzles are widely used in different applications where injections in high-pressure chambers are required. This atomization method implies introduction of one or several discrete liquid jets into high-velocity gas flux. These jets while being transported by the gas flux disintegrates into separate droplets. But the process can be carried out in an alternative manner: the liquid jet is transformed into thin flat stripe before interaction with the dispersing gas. This method also became widely applicable. For example the nozzle described in the work [192] is designed basing on this principle. Nozzles where the liquid is supplied in the form of this stripe in
contrast to nozzles where discrete liquid jets are introduced have got one feature which becomes crucial and doubtless advantage for a number of practical applications: using these nozzles it is possible to atomize liquid with uniform spread of droplets inside the chamber where injection occurs. Other twin-fluid nozzles with gas excess create high concentration of droplets along the axis line of the nozzle. However nozzles of this type have got also a certain disadvantage related to the fact that the maximum efficiency of atomization process is reached only when the gas impinges the liquid stripe from both sides what in its turn requires more complicated internal design to organize two separate air fluxes.

2.2.1.3.1.6. Rotary atomization

In the rotary atomization disintegration of the liquid occurs because of high kinetic energy which is transferred from a nozzle’s rotating head. The liquid being dispersed is supplied on the rotating surface as close to the axis of rotation as possible (Fig. 2-23). Because of centrifugal forces the liquid almost uniformly spreads on the surface (in case of continues supply). In case of low flow rate of the liquid being dispersed droplets start appearing in immediate proximity to the edge of the rotating surface. In case of high flow rates ligaments or thin liquid sheet appear on the edge. These ligaments or the liquid sheet then disintegrate into separate droplets. Rotating surfaces may have a form of a flat disk, of a disk with vanes [193], [194], of a cup, of a wheel with slots and etc.

Fig. 2-23 Rotary atomization

The most spread rotary atomizers are atomizers with a rotating cup or a disk. In some cases to organize a spray of a certain form or a controlled transport of dispersed droplets gas/air fluxes supplied in a special manner are used. The rotary atomization is as a rule carried out in cylindrical or conical chambers to create an umbrella-shape spray. A uniform liquid’s supply may be provided by using a nozzle in the form of a cup. Atomizers with a conical cup have got the maximum capacity
among all other rotary atomizers. The diameter of the rotating surface may vary from 25 mm up to 450 mm. Small discs rotate with a high frequency up to 1000 rps, at the same time the frequency of big discs do not overcome 200 rps. The maximum frequency of about 2500 rps was used to disintegrate pressurized liquid by rotating disk [195]. In some practical applications the frequency of rotating nozzle is 50 rps, however to improve quality of the atomization process an additional coaxial air flux is used. When rotary atomizers were applied to spray drying some improvements were introduced which allowed to reach the capacity of 2400 kg/min of initial raw material and high linear velocity of the disk’s edge at the same time. Droplets of 20 μm were produced [196].

Application of rotary atomizers for the spray drying was studied a lot and described in works of such authors as Kayano and Kamiya[193], Tanasawa et al. [194], Hinze and Milborn [197], Christensen and Steely [198], Kitamura and Takahashi [199] and others.

Main ways to improve the atomization quality are: increase of nozzle’s rotational speed, decrease of liquid’s flow rate, usage of nozzles with notches. High liquid’s flow rate leads to that liquid leaves the spinning nozzle in the form of ligaments which disintegrate into droplets with a wide size distribution. One of the ways to increase atomizer’s capacity is to increase diameter of the nozzle proportionally. This way has got the limitation concerns operational difficulties of big size nozzles. Another way is to apply stacked spinners with a large diameter [195]. To reach finer dispersion it is possible to apply an electrical field which is created between the spinning nozzle and the grounding electrode [200]. Thickness and uniformity of the liquid sheet leaving the rotating nozzle can be controlled by varying liquid’s flow rate and/or nozzle’s rotational speed. Additionally to provide uniform produced droplets’ size distribution presence of a significant centrifugal force, an absence of vibrations, a constant flow rate and a smooth nozzle’s surface are required. Atomization quality for liquids with low viscosity as a rule is higher than for viscous liquids.

The problem concerns liquid’s adhesion to the nozzle’s surface is also quite typical for atomizers with a spinning disk. This phenomenon may lead to that an injection velocity at the edge of the disk is much lower than the peripheral speed of the disk. This feature of disk rotary atomizers is the main disadvantage which limits their application only for those regimes when liquid’s flow rate is relatively small. However atomizers equipped with nozzles with vanes haven’t got this disadvantage.

One of the most attractive features of rotary atomizers is the ability to produce droplets with very narrow size distribution what occurs while using small size nozzles with high rotational speed and low flow rates[201]. Mean diameter of produced droplets depends mainly on the rotational speed and the nozzle’s diameter, on the density and the surface tension of the liquid being dispersed and to a lesser extent on the atomizer’s capacity and the liquid’s viscosity. Insignificant dependency of the droplets’ mean diameter on geometrical characteristics of guiding vanes is also worth mentioning. The droplets’ mean diameter varies approximately from 10 up to 200 μm. Rotary atomizers are also very convenient for practical operation because of the possibility to change atomization quality, a rotational speed and flow rate of the liquid, all independently from each other.
Also rotary atomizers were successfully used for dispersion of liquids in a wide range of viscosity [202]–[207].

2.2.1.3.1.7. **Effervescent atomization**

Effervescent atomization appeared as a logical evolution of the atomization technique based on injection of a liquid with a gas dissolved in it. This method (with a dissolved gas) allowed producing very fine droplets with a narrow size distribution. And even a small amount of gas (less than 15% in mole fraction) can significantly improve atomization process. However it is necessary to organize an expansion chamber upstream the nozzle’s outlet orifice to reach the maximum efficiency of such atomization method since bubbles’ growth rate in such systems is very often quite small. Namely effervescent atomization, described by Lefebvre et al. [181] at the first time and which is by its nature close to the method with a dissolved gas, appeared as a result of tries to solve this problem.

In effervescent atomization air or gas is injected through a plain-orifice atomizer in a vessel (or channel) with a liquid being dispersed which is directly connected to the nozzle. In contrast to twin-fluid atomization gas in effervescent atomization is used not to create kinetic energy which is necessary to break up liquid jets. It does not also dissolve in the liquid as it happens in the method described above. Instead of this it just penetrates into the volume of the liquid. Flow rate of the gas is low in this case as well as the differential pressure between the gas and the liquid. The gas pressure is kept almost equal to the liquid pressure to provide only penetration of the gas into the flowing liquid. Then gas bubbles appear in the liquid, and such double-phase system is supplied to the nozzle’s outlet orifice. While issuing from the nozzle’s orifice because of successive explosions of gas bubbles the liquid disintegrates into separate droplets [208]. The disintegration occurs thanks to appearance of blast waves born by bubbles explosions.

In many cases an increase of gas flow rate causes a growth of amount of bubbles and a decrease of produced droplets’ mean diameter. However in practice high quality of atomization can be reached with both low liquid’s initial pressure and low gas flow rate. The atomization process goes well enough even when the liquid’s pressure is much lower than that in pressure atomization. Mean diameter of produce droplets for effervescent atomization is comparable with the corresponding value for twin-fluid atomization with lack of gas and with the same gas-liquid ratio. Thanks to large sizes of orifices and channels effervescent atomizers are to a much less extent liable to plugging. This fact allows using them for dispersion of slurries. Presence of air bubbles is also an advantage for combustion applications since soot formation significantly reduces. Beside this effervescent atomizers have got a simple design, are reliable and cheap.

2.2.1.3.1.8. **Electrostatic Atomization**

In electrostatic atomization the electrical potential difference is created between the liquid being dispersed and the electrode placed in a certain distance from the outlet orifice of the nozzle [209]–[211]. As a result of mutual repulsion of charges appeared on the surface of the liquid the surface becomes instable and disintegrates when the energy of the pressure created by electrostatic forces
exceeds liquid’s surface tension energy. The process of droplets’ formation goes in a continuous manner if the electrical potential is maintained beyond the certain critical value correlated with the liquid’s flow rate. Both alternate and direct current are applicable for creating the electrical potential.

A number of investigations have been made to explain the nature of droplets’ formation in electrostatic atomization, for example [212], [213]. A hypothesis that liquid’s atomization occurs as a result of single droplets’ separation from capillary tips of the liquid was made. However this mechanism hasn’t been proven experimentally. Because of sophisticated nature of the process there is no general theoretically based model of the electrostatic atomization in our days.

The size of produced in electrostatic atomization droplets is a function of applied electrical potential, of size and design of the grounding electrode, of a liquid’s flow rate, a nozzle’s outlet orifice diameter and physical properties of a liquid such as surface tension, permittivity and electrical conductivity [214]–[217]. With an increase of the electrical potential the diameter of produced droplets decreases, at the same time velocities of the liquid and droplets increase and distance between neighbor droplets decreases. If electrical potential’s increase is continued droplets will form a single continuous liquid jet. When the electrical potential overcomes a certain critical value this jet disintegrates into a mist consisting of fine droplets. However it is almost impossible to produce monodisperse sprays using electrostatic atomization. Some experiments with water, sugar solution, hydraulic oil and alcohol also showed that there is an upper limit of electrical conductivity beyond which atomization doesn’t occur any longer. Fine droplets were produced when atomizing liquids with relatively low electrical conductivity. It was also found out that some organic liquids with low dielectric constants are not disintegrated by this method of atomization.

The electrical potential which is required for liquid’s atomization depends on a required nozzle’s capacity and on liquid’s electrical properties. In fact capacity of electrostatic atomization is quite low. This disadvantage of the given method limited its application to electrostatic painting and non-impact printing.

It is worth mentioning that to produce monodisperse sprays it is necessary to keep the liquid’s flow rate at a very low level what brings obvious difficulties for scaling up.

2.2.1.3.1.9. Vibration Atomization

Liquid’s disintegration into separate droplets can occur because of periodical vibrations transferred to the liquid. These vibrations may be created by piezoelectric transducers, acoustic devices or by a direct mechanical impact. Accordingly, vibration atomization may be divided into three categories: ultrasonic atomization, acoustic atomization and mechanical vibration atomization. Each of these three methods differs from the others not only in nozzles’ design but also in droplets’ size distribution.

In ultrasonic atomization high-frequency sound waves are focused on a liquid being dispersed [218]. The liquid may be in a vessel with a generator of vibration placed at the bottom or may be supplied on a vibrating solid surface. High-frequency ultrasonic nozzles are characterized with a low capacity
and with small sizes of produced droplets. They are often used as medical inhalators. Sizes of droplets produced with nozzles with operating frequencies between 10 and 1000 kHz are of about 3-50 μm [195]. Some nozzles allow producing submicron particles; at the same time the others – up to several hundred microns. Originally ultrasonic nozzles were developed for applications in small boilers for domestic heating. But during the last decade ultrasonic nozzles have been used in such industrial areas as pharmaceutics, semiconductor processing, spray drying and etc. [219] One of main and very useful features of ultrasonic nozzles is an ability to organize a very low liquid’s flow rate, what first of all is explained by small amplitude of vibrations created by the generator[195]. For example the capacity of a nozzle with operating frequency of 700 kHz producing droplets of 10 μm is 2.2x10^-3 L/min of an initial solution. Thus produced droplets can be easily introduced into a gas flux and be conveyed by it in the form of uniform mist. Thanks to this feature ultrasonic nozzles are extremely suitable for such applications as coating, humidification and spray drying. Some nozzles can produce very fine droplets (1-5 μm) [220], what is required for a number of pharmaceutical processes and lubricating systems. Another side of the low capacity is a low initial velocity of produced droplets which is also explained by the nature of ultrasonic atomization phenomenon. Low droplets’ velocities guarantee insignificant impact of surrounding gas media on produced droplets and negligible droplets’ deformation. Thus ultrasonic nozzles are acceptable for producing particles with perfect spherical form.

At the same time the low capacity of ultrasonic nozzles is their drawback for a large number of applications. Maximum capacity depends on a diameter of an outlet orifice, a spraying surface area and physical properties of a liquid being dispersed. All these factors also influence quality of liquid’s disintegration what makes process of choosing nozzle’s characteristics quite complicated.

Another disadvantage of some ultrasonic nozzles is inability to install them in all directions. That means that atomization can occur only in the upward direction with some inclination from the vertical axis. This fact makes impossible an installation of ultrasonic nozzles in existing equipment and requires new apparatus design.

Some ultrasonic nozzles are applicable for production of microcapsules. Such nozzles have got two inlets for liquids. And if two immiscible liquids are supplied they form spherical droplets consisting of two layers (Fig. 2-24).
Instead of electrical pulses acoustic waves may be used to create periodical vibrations. In acoustic atomization an oscillator creates signals which are then amplified and transferred to a speaker. A liquid steam flow through a pipe to which vibrations are transmitted by means of a metal rod connected to the speaker’s diaphragm. Because of an influence of these vibrations the liquid stream disintegrates into separate droplets. The diameter of capillaries used in acoustic atomization as a rule varies from 50 up to 1500 μm [195]. The size of produced droplets lies in the range from 100 up to 3000 μm. Signal frequency varies from 0.3 up to 30 kHz.

2.2.1.3.1.10. Whistle atomization

Whistle atomization is also known as acoustic or ultrasonic gas atomization. In the whistle atomization [195], [221] the liquid jet is disintegrated into droplets by direct impact of a high-pressure gas jet what is schematically shown in the Fig. 2-25. Focused gas flux creates inside the nozzle acoustic waves of high energy and high frequency and hence nozzles of this type are called whistle atomizers.
This type of nozzles is characterized by acoustic waves’ operating frequency of about 10 kHz, and the diameter of produced droplets is approximately equal to 50 μm (raw material flow rate up to 75 L/min). However size distribution of droplets produced by this method is quite broad with a standard deviation of about 2.5. Besides this the only way to change produced droplets’ diameters is a modification of nozzle’s design what is of course quite difficult to be implemented in industrial applications.

2.2.1.3.1.11. Summary

To summarize all the mentioned data and to provide a general overview of atomization methods the following table is prepared (Table 2-3).

Table 2-3 Summary table

<table>
<thead>
<tr>
<th>Method</th>
<th>Droplet size, μm</th>
<th>Typical application</th>
<th>Advantages</th>
<th>Limitations</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure atomization</td>
<td>Plain-Orifice</td>
<td>Diesel engines, Jet engine after burners, Ramjets</td>
<td>Simple, rugged, cheap</td>
<td>Narrow spray angle, solid spray cone</td>
</tr>
<tr>
<td></td>
<td>25-250</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Simplex</td>
<td>20-200</td>
<td>Gas turbines, Industrial furnaces</td>
<td>Simple, cheap wide spray angle</td>
<td>High supply pressure, varying spray angle with pressure differential and</td>
</tr>
<tr>
<td>Method</td>
<td>Range</td>
<td>Application</td>
<td>Characteristics</td>
<td>Ambient gas density</td>
</tr>
<tr>
<td>------------------------</td>
<td>--------</td>
<td>----------------------------------------------------------------------------</td>
<td>----------------------------------------------------------------------------------------------------------</td>
<td>--------------------</td>
</tr>
<tr>
<td>Duplex</td>
<td>20-200</td>
<td>Gas turbine combustors</td>
<td>Simple, cheap, wide spray angle, good atomization over a wide range of liquid flow rate</td>
<td>Narrowing spray angle with increasing liquid flow rate</td>
</tr>
<tr>
<td>Dual-Orifice</td>
<td>20-200</td>
<td>A variety of aircraft and industrial gas turbines</td>
<td>Good atomization, turndown ratio 50:1, relatively constant spray angle</td>
<td>Poor atomization in transition range, complexity in design, susceptibility of small passages to blockage</td>
</tr>
<tr>
<td>Spill Return</td>
<td>20-200</td>
<td>A variety of combustors, slurries and fuels of low thermal stability</td>
<td>Simple, good atomization over entire range of liquid flow rates, very large turndown ratio, low risk of blockage due to large passages</td>
<td>Varying spray angle with liquid flow rate, higher power requirements except at maximum discharge</td>
</tr>
<tr>
<td>Fan spray</td>
<td>100-1000</td>
<td>High-pressure painting/coating, Annular combustors</td>
<td>Good atomization, narrow elliptical spray pattern</td>
<td>High supply pressure</td>
</tr>
<tr>
<td>Rotary atomization</td>
<td></td>
<td></td>
<td></td>
<td>Satellite droplets, 360° spray pattern</td>
</tr>
<tr>
<td>Spinning Disk</td>
<td>10-200</td>
<td>Spray drying, Aerial distribution of pesticides, Chemical processing</td>
<td>Good monodispersity of droplets, independent control of atomization quality and liquid flow rate</td>
<td></td>
</tr>
<tr>
<td>Rotary Cup</td>
<td>10-320</td>
<td>Spray drying, Spray cooling</td>
<td>Capable of handling slurries</td>
<td>Possible requirement for air blast around</td>
</tr>
<tr>
<td>Method</td>
<td>Mixing Type</td>
<td>Viscosity Range</td>
<td>Application</td>
<td>Benefits</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>-------------------</td>
<td>-----------------</td>
<td>--------------------------------------</td>
<td>-----------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td><strong>Twin-fluid atomization</strong></td>
<td>Internal mixing</td>
<td>50-500</td>
<td>Industrial furnaces, Industrial gas turbines</td>
<td>Good atomization, low risk of clogging due to large passages, capable of atomizing high-viscosity liquids</td>
</tr>
<tr>
<td><strong>Gas-Assist (lack of gas)</strong></td>
<td>External mixing</td>
<td>10-140</td>
<td>Industrial furnaces, Industrial gas turbines</td>
<td>Good atomization, low risk of clogging due to large holes, capable of atomizing high-viscosity liquids, no risk of liquid backup into air line</td>
</tr>
<tr>
<td><strong>Twin-fluid atomization</strong></td>
<td>Plain-Jet</td>
<td>15-130</td>
<td>Industrial gas turbines</td>
<td>Simple, cheap, good atomization</td>
</tr>
<tr>
<td><strong>Gas-Blast (with excess of gas)</strong></td>
<td>Pre-filming</td>
<td>25-140</td>
<td>Wide range of aircraft and industrial gas turbines</td>
<td>Good atomization especially at high ambient pressures, Wide spray angle</td>
</tr>
<tr>
<td><strong>Effervescent atomization</strong></td>
<td></td>
<td>20-340</td>
<td>Combustion</td>
<td>Simple, reliable, very good atomization, low risk of plugging due to large holes, easy maintenance, beneficial effects on reducing soot formation and exhaust smoke,</td>
</tr>
</tbody>
</table>
2.2.1.3.2. Applicability of nozzles for production of aerogels in the form of spherical particles

2.2.1.3.3. Examples:

Cellulose beads can be made either in form cellulose derivatives followed by cellulose regeneration or ii) from direct cellulose solutions.

Atomization was used to make cellulose beads (not aerogels) made from viscose [54]. The work was done with a slit atomizer and with several nozzle-type atomizers. The influence of the diameter and length of nozzles and of their rotational speed on drop shape and size was studied, as well as of viscose concentration. Viscose was then regenerated into cellulose and dried in ambient conditions. The beads of sizes varying from <0.25 mm to > 1.25 mm were obtained. It should be noted that viscose process is accompanied by ejection of sulphur-containing gases during cellulose regeneration and thus is far from being environmentally friendly.

The second way of making cellulose beads is from cellulose dissolved in direct solvent. They can be Na-OH water, N-methylmorpholine-N-oxide monohydrate, dimethylacetamide/LiCl (DMA/LiCl) or ionic liquids (see details in review [120]

Cellulose beads were also prepared by atomization from cellulose/DMA/LiCl solution [222]. Cellulose solution was transferred from the solvent reservoir to the nozzle by applying pressurized nitrogen, the solutions were atomized into droplets by means of pressurized air jets pointed at the tip of the needle from which the solution protruded and the droplets were collected in a beaker containing isopropanol/water or methanol/water after traveling several inches through open air. Solvent phase inversion was “instantaneous”, and the beads retained their spherical droplet shape. DMAc/LiCl were removed first by washing with alcohol (isopropanol or methanol), and secondly by
exhaustive water washing. The size of wet particles was from 300 to 900 μm. These beads were never dried.

Atomisation as described in [54] was used to make cellulose beads from cellulose dissolved in NaOH-water solution using so-called Biocelsol cellulose dissolution procedure [55]. The beads were dried in the oven; the size varied from 70 to 300 μm and the release of model drug was studied.

Cellulose beads were prepared from cellulose-NaOH-urea solution via electrospraying [223]. Surfactant SDBS or polyvinyl alcohol were added. The beads were dried with freeze-drying method which led to large pores. The diameter of particles was around 1 mm.

2.2.2. Microparticles: Emulsion-Gelation process

The idea that sol may be shaped into spherical particles and then gelled underlies the so-called emulsion gelation method. In this process the gelation reaction takes place in a continuous phase (oil) that is immiscible with the sol. Continuous energy input and surfactants help keeping the sol dispersed in the continuous phase. Once the stable emulsion is formed (sol-in-oil or often referred as to water-in-oil, w/o), chemical and/or physical impact triggers the gelation reaction. After gelation is completed, the gel particles suspended in the oil phase should be separated (recovery process). When gelation takes place in a solvent that is immiscible with supercritical carbon dioxide, the recovery should be followed by a solvent exchange wherein gel fluid is substituted by a light organic solvent (ethanol, acetone). The latter is finally extracted by sc-CO₂.

![Fig. 2-26 Emulsion gelation process for aerogel micro-particles production](image)

In the present report all above described steps will be examined in detail. As the gelation process depends on the nature of precursor, the main focus here is on project-relevant polymers, i.e. alginate, cellulose and chitin/chitosan. In most cases, these polymers undergo the gelation is aqueous media, so that the solvent exchange must be performed prior to drying. It is of note that there is no comprehensive report in the literature presenting all the steps from a sol to an aerogel. This report is aimed to bridge this gap and presents the essential information collected from various sources.
Special attention is called to the potential scalability of each step as to make possible a comparison across the particle production methods (see Section 3).

2.2.2.1. Emulsification and emulsion gelation

The formation of a stable emulsion with subsequent gelation is the central process of the emulsion gelation method. Emulsification and gelation are interrelated and thus will be reviewed together in this section. For short, the terms “continuous phase” and “oil” as well as “dispersed phase” and “water” are used interchangeably.

Generally, there are three ways to combine gelation and emulsification: (i) all components needed for the gelation are premixed and then emulsified; (ii) a precursor is first emulsified followed by addition of *insoluble* in oil trigger; (iii) a precursor is first emulsified followed by addition of *soluble* in oil trigger. These processes are described in detail below.

2.2.2.1.1. All components are premixed

“All-premixed” method consists of mixing all necessary chemicals into a one-phase reacting system (“sol” for inorganic systems). The chemistry should be chosen so that gelation is delayed providing enough time to disperse the system in oil and form a stable emulsion.

This method is exemplified by Alnaief and Smirnova (2011) using silica sol prepared from tetramethylothsilicate (TMOS), methanol, water and hydrochloric acid [224]. Aqueous ammonia is added to the sol as gelation trigger. The reacting mixture is then poured into canola oil and emulsified under continuous stirring. Sol-gel transition took place within 20–30 min and can be detected visually. At this stage the stirring is stopped and gel spheres are left overnight in the oil for aging. The suspension is extracted with sc-CO$_2$ resulting in aerogel microspheres 100 – 2000 µm in diameter (depending on process parameters).

Similar process is applied to aqueous solution of alginate [225]. It relies on well-known internal setting method wherein gelation of alginate/CaCO$_3$ mixture is triggered by addition of slowly hydrolysing pH reducer, glucono-δ-lactone (GDL). Here CaCO$_3$ acts as a source of Ca$^{2+}$ cations, which are liberated into alginate solution during graduate pH reduction caused by the hydrolysis of GDL. Once GDL is admixed, the reacting mixture is poured into paraffin oil (with 1wt% Span 80 as surfactant). The mixture is emulsified using a marine propeller for 30 min at constant stirring rate. Alginate gel microspheres are collected after filtration, solvent exchanged and supercritically dried. By changing the process parameters particle with D$_{90}$ in the range 150 – 1432 µm can be obtained.

To the best of our knowledge these reports are the only examples of the “all premixed” method where all steps towards aerogel are presented. Besides these works, a production procedure for chitosan microspheres is reported by Hassan et al. [226], wherein a premixed chitosan/glutaraldehyde solution is dispersed in mineral oil containing Span 83 using an ultrasound probe. Particles are obtained in the size range 0.3 – 1.4 µm.
Thus, examples of the emulsion gelation using “all-premixed” method are limited to alginate and chitosan systems. It can be however surmised that “all-premixed” method can also be extended over cellulose in NaOH solutions. A study by Qin et al. [227] shows that gelation of cellulose/urea/NaOH system upon addition of epichlorohydrin (ECH) happens in 5–15 min. Gelation time can be adjusted by changing the ECH concentration and temperature. This would eventually enable the premixing of the components and dispersing them in an oil phase.

Chitosan hydrogels could also be formed by crosslinking not only with glutaraldehyde but also with other crosslinkers such as glyoxal or formaldehyde into its aqueous acidic solution [72], [104, p. 215], [228], [229]. For food and pharmaceutical applications another attractive crosslinker, L-glutamic acid, is reported [230]. Similar to the work by Alnaief and Smirnova (2011), hybrid chitosan/silica systems can be gelled as exemplified by Ayers and Hunt [83]. This procedure relies on one-step sol-gel transition of TEOS in the acidic chitosan solution. For adsorption applications chitosan crosslinked by metal polyoxyanions (molybdate, vanadate) may be of interest [231].

When chemical crosslinking of chitosan should be completely avoided, the “all-premixed” method could be realized via graduate pH change. Oppositely to alginate gelation, pH should be increased in the course of the gelation as chitosan is soluble in diluted aqueous acids and gels above pH 7. This can be achieved by addition of urea that undergoes hydrolysis in presence of a specific enzyme (urease), see [232].

2.2.2.1.2. All components are premixed: gelation under physical impact

In one special case of the “all-premixed” method the reacting mixture consist of a single component that undergoes gelation reaction under a physical impact such as heating, cooling, UV radiation or solvent evaporation. In this case, more control over the gelation may be gained. For the project-relevant polymers, preparation of chitosan microspheres is only reported, to our knowledge.

Chitosan microspheres are prepared by Genta et al. using so-called emulsion-evaporation technique [233]. It relies on the solidification of droplets dispersed in a continuous phase while aqueous phase is removed by evaporation. This technique potentially allows to avoid the use of crosslinkers. In brief, chitosan/acetic acid emulsion in paraffin oil with Span 20 is heated up to 60 °C and stirred with a vibromixer under reduced pressure until the solvent was evaporated completely. Particles with D90 between 8 and 15 µm are obtained.

Although there are no complete examples of this method for native alginate and cellulose, some appropriate gelation mechanisms are identified upon literature review. They are briefly reported below.

As for alginate, its thermogelation below room temperature, though evidenced by the viscosity drop, does not result in strong gels [234] and thus is not suitable for the emulsion-gelation. Chemically modified alginate (for instance, via reaction with 2-aminoethyl methacrylate or methacrylic

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anhydride) can be photo-crosslinked via exposure to UV light or laser irradiation within several minutes [235].

Heat-induced gelation of cellulose solutions is also documented. The gelation can be performed with or without crosslinker. In the former case cellulose/NaOH solutions initially prepared at –6 °C can be gelled upon heating to room or higher temperatures [38]. Chemical crosslinking is also combinable with heat-induced gelation in aqueous cellulose/urea/NaOH system as exemplified by Zhou et al. [236] and Chang et al. [237]. In this case a certain amount of ECH is added to the cellulose solution and the mixture was stirred at 25 °C for 1 h. Subsequent heating to 50 °C allows to obtain cellulose hydrogel. Heat-induced gelation is also known for cellulose solutions in calcium thiocyanate [238].

Based on the results from this Section, the features of this “all-premixed” method may be summarized as follows:

1. The method is relatively simple and allows to carefully control the ratio between biopolymer and crosslinker (the latter is insoluble in the oil phase and thus does not leak out from the droplets).

2. In this method the crosslinker is homogeneously dispersed either as fine particles or at molecular level. This provides more homogeneous hydrogel structure than in the external gelation.

3. There is no longer control over the reaction rate once the components are mixed. This means that the reaction kinetics must be carefully studied and the factors such as temperature, composition, influence of surfactant and oil should be thoroughly evaluated. Few comprehensive studies partially address these issues however not in the context of the emulsion gelation. For instance, Kuo and Ma reported the influence of calcium source (CaCO₃, CaSO₄ and their mixtures), alginate and calcium concentration, and temperature on the gelation time. Hence, more fundamental studies are needed to integrate this method with emulsion gelation.

4. In case emulsion-evaporation technique is chosen, partial collapse of the porous network is expected. In the context of the aerogel production, one would rehydrate the particle after the separation from oil. To what extent the porous structure can be recovered remains an open question. Another potential limitation is slow evaporation of the aqueous phase from the emulsion (within 19 h in the study by Genta et al. [233]).

5. In absence of any crosslinker, only cellulose can be gelled under thermal treatment, whereas alginate and chitosan do not undergo gelation under physical impact and should be chemically modified.

6. As soon as gel particles are formed, the energy input (stirring, shaking) must be minimized in order not to damage the freshly formed and weak microparticles [225]. It seems quite challenging to control the gelation on a larger scale as gelation rate is often sensitive to temperature. Thus, possible variation in temperature (e.g. local heating due to stirring) may shade the sol-gel transition and make difficult to find an appropriate emulsification regime.

2.2.2.1.3. Gelation trigger insoluble in oil (emulsion-coalescence method)
This method, also called emulsion-droplet coalescence, is used when the gelation trigger is insoluble in the oil phase. Generally, there are two ways to perform gelation in this case: (i) emulsions of a biopolymer and a trigger are prepared separately and then mixed under stirring; (ii) a trigger is introduced into a beforehand prepared emulsion of a biopolymer. In both modifications droplets of each component collide and coalesce resulting in the particle formation. In practice, a hybrid way is often used. In this case, a lipophilic surfactant is initially present in the oil phase and serves for the stabilization of the w/o emulsion. A mixture of the gelation trigger with a hydrophilic surfactant is then added. Some typical examples are given below.

Alginate microspheres with a diameter between 220 and 350 µm are prepared by Fundueanu et al. [239], [240] starting from an alginate emulsion in dichloroethane (1:4, + 2.5% cellulose acetate butyrate as surfactant). Calcium chloride solution is poured into the emulsion and left under stirring for 10 – 60 min. The authors of the works [241], [242] employed two surfactants to achieve satisfactory results in the preparation of alginate microparticles. In a typical procedure aqueous alginate is dispersed in the oil phase containing a lipophilic surfactant (e.g. Span 85) using a mechanical stirrer. Aqueous solution containing a hydrophilic surfactant (e.g. Tween 85) is then added for the accommodation of the counterion solution. A few minutes later calcium chloride solution is finally added. Using a similar method particles of 5 – 150 µm in diameter are prepared by Lemoine et al. [243], less than 200 µm by Chan et al. [244] and more recently by Yu and Fan [245].

Similar procedure used by Denkbas et al. [246] wherein acidic chitosan is first dispersed in mineral oil/petroleum with a hydrophilic surfactant (Tween 80). Glutaraldehyde is added into the medium under continuous stirring. After 3 hours chitosan microspheres in the size range of 10 – 200 µm are recovered from the suspension.

Lim et al. [247] prepared chitosan microspheres by introducing aqueous sodium hydroxide into beforehand prepared emulsion of chitosan in iso-octane with Span 85 as surfactant. Contrary to the emulsion gelation of alginate with two surfactants, the authors found that the presence of Tween 85 in the counterion solution destabilizes the emulsion and chitosan microspheres cannot be successfully formed. The use of only Span 85 in oil gives satisfactory chitosan microspheres of 250 – 1000 µm in size.

Usually, the gelation trigger is added into the emulsion. In a reverse approach, when the emulsion is poured into the aqueous gelation bath, is also known. Ko et al. [248] dropped a chitosan emulsion in CH₂Cl₂ (2:10, 2% Tween 80) into tripolyphosphate solution by spray gun. After 15 – 60 min, particles with diameters between 500 and 710 µm are recovered.

The emulsion-coalescence method allows for the production of nanoparticles. For instance, by mixing two separately prepared emulsions of chitosan and sodium hydroxide (both in paraffin oil with 5% Arlacel C), Tokumitsu et al. [249] have produced particles in the range of 0.4 – 1 µm.

Immiscible with oil aqueous solution of glutaraldehyde can be used for the chemical crosslinking of chitosan emulsion in mineral oil [250]. The mixture is additionally thermostated at 48 °C to reduce
its viscosity and increase the gelation rate. Particles with $D_{90}$ in the range 6 – 24 µm can be achieved depending on process parameters.

To the best of our knowledge, the sole example of cellulose microparticles obtained via emulsion gelation is the work by Luo and Zhang [251]. An aqueous solution of cellulose/NaOH/urea is dropped in paraffin oil (plus Span 80). The mixture is stirred for few hours and then acidified by the addition of dilute hydrochloric acid. Particles are recovered after phase separation from the lower layer, which is washed with water and acetone [251]. By changing Span 80 content (1–10%), o/w ratio (3:1–10:1) and stirring speed (200–1000 rpm), cellulose microspheres with particle diameter from 5 µm to 1 mm are prepared.

Based on the results from this Section, the following features of the emulsion-coalescence method can be listed:

1. More diverse gelation chemistries can be employed in the emulsion-coalescence method compare to “all-premixed” one, since many gelation reactions occur instantly. Fast gelation kinetics may be beneficial for this method as it allows “freezing” the emulsion droplets.

2. Due to stochastic nature of the droplet coalescence, the ratio between biopolymer and crosslinker is not constant in every single coalescence event, and thus a uniform crosslinking density cannot be guaranteed. An additional separation step would be required to remove an excess of the crosslinker from the oil.

3. When crosslinker solution is introduced in beforehand prepared emulsion, a macroemulsion is formed. Possible agglomeration phenomena may take place due to aggregative instability of the macroemulsion (see Section “homogeneous emulsion gelation” below).

4. Since the gelation only occurs when the second component is added, the emulsification of a precursor can be performed beforehand using any energy-intensive emulsifying devices without a risk of breaking particles. This would allow to produce smaller particles [249] and minimize the impact of the shearing stress on the gel.

5. Second surfactant is often needed to accommodate the crosslinker solution raising a point of the oil and surfactant recovery strategies.

2.2.2.1.4. Gelation trigger soluble in oil (“homogeneous emulsion gelation”)

In some studies it is noted that uniformly distributed crosslinker, i.e. dissolved in oil, is readily available for the reaction on the droplets surface and thus can minimize possible agglomeration phenomena [252]. Difficulties with controlling the particle size as the particles may tend to coagulate into large masses before hardening properly are also stated [253]. To distribute a crosslinker homogeneously, it must be soluble in oil phase. Since high concentrations of crosslinkers in the oil phase are often unachievable, this method relies on the fixing droplet shape by surface hardening. Further crosslinking and complete gelation can be effected by the addition of more crosslinker in
“emulsion-coalescence” manner once the surface hardening has been achieved. Several representative examples of this “homogeneous emulsion gelation” are described below.

Typically, alginate aqueous solution is mixed with a suspension of insoluble calcium salt (carbonate, citrate, monohydrogenophosphate, oxalate or tartrate). The mixture is then dispersed in canola oil (1:5 – 1:6 v/v). Once stable emulsion is obtained (after ca. 15 min), glacial acetic acid dissolved in a small portion of canola oil is added to the emulsion with continued agitation. This liberates Ca$^{2+}$ for gelation of the alginate polyanions. The suspension is mixed with calcium chloride solution (hardening) and left for the partitioning of particles to the aqueous phase. To recover the particles the aqueous phase is filtered and the particles washed with 1% Tween solution [253]–[255]. This procedure gives particles in the range of 200 – 1000 µm. A similar method is used in the recent study by Reis et al. [256]. By optimizing the recovery procedure (see Section “Particle recovery and solvent exchange” for details) spherical particles with a diameter down to 4 µm are prepared.

Several studies are devoted to the gelation of chitosan using the “homogeneous emulsion gelation”. Similar to the above described methods, glutaraldehyde is often employed as crosslinker. As it is insoluble in oil, a solution of glutaraldehyde in toluene is used (solubility 0.096 and 4.4 mg/100mL in hexane and toluene, respectively). In a typical procedure, chitosan in acetic acid is injected in the oil phase under continuous stirring. Span 80 is the commonly used surfactant. Glutaraldehyde solution in toluene is introduced into the emulsion. Reaction lasts for few hours. Sometimes heating is applied to increase the crosslinking rate.

As for particle sizes, the study by Genta et al.[257] reported $D_{90}$ of the chitosan microspheres in the range between 20 and 30 µm. Al-Helw et al. [258] prepared particles with the mean diameter of 274 – 450 µm. Microspheres below 300 µm in diameter are reported by Jameela et al. [259].

In most cases, non-ionic sorbitol-based surfactants are utilized. An interesting feature of the study by Thanoo et al. [252] is the use of the ionic surfactant, sodium dioctyl sulfosuccinate (DOS, HLB = 10.9). Particles in the range 150 – 1200 µm are prepared.

Study by Bugamelli et al. [260] demonstrates an elegant approach towards chitosan microparticles wherein an antioxidant food additive, ascorbyl palmitate (E304), is used as both surfactant and crosslinking agent. On the one hand, due to its amphiphilic properties, ascorbyl palmitate is deposited at the w/o interface and stabilizes the emulsion. On the other hand, it oxidizes during microparticle preparation yielding dehydroascorbyl palmitate, which carbonyl groups form covalent bonds with chitosan amino groups.

Based on the results from this Section, the following features of the emulsion-coalescence method can be listed:

1. Similarly to the “emulsion-coalescence method” diverse gelation chemistries can be employed in the “homogeneous emulsion gelation”. Fast gelation kinetics is not only beneficial but rather prerequisite. Data on partition coefficients of the crosslinker between aqueous and oil phases should be known or estimated.
2. Potential agglomeration phenomena can be avoided due to homogenous distribution of the crosslinker. Emulsification regime should nevertheless be selected so that to minimize the impact of the shearing stress on just hardened gel microparticles.

3. An additional separation step would be required to remove an excess of the crosslinker from the oil.

4. Similarly to the “emulsion-coalescence method” the emulsification of a precursor can be performed beforehand using any energy-intensive emulsifying devices without a risk of breaking particles. Moreover, emulsification can be performed as continuous operation using various readily available high-pressure homogenizers (see next Section). Mixing with the crosslinker can then be accomplished in another vessel.

2.2.2.1.5. High-pressure homogenization

The high-pressure homogenization (HPH) technology was developed for the stabilization of dairy and food emulsions [261]. This process forces a fluid through a narrow gap valve resulting in cavitation, turbulence and high shear stress. These phenomena cause the dispersion of particles or droplets. HPH allows to obtain fine emulsions and longer shelf-life products [262]. In addition, this process is effective for inactivation of pathogenic microorganisms [263]. Nowadays HPH has many applications in pharma, biotechnology, chemical and food industries. Some examples in food industry are proteolysis during cheese production [264], almond milk obtainment [265], soy products treatment for protein modification [266]–[268], processing of plant raw materials [269], juice production for long shelf-life and high-quality products [270], dairy beverage products [271], [272].

Both emulsions and suspensions can be obtained by HPH using mostly the same equipment. But further its application for emulsifying is considered.

HPH commonly consists of high-pressure pump and high-pressure dispersion unit. Dispersion unit can be subdivided into radial diffusers (most frequently), counter-jet dispergators (jet dispergator by Bayer, microfluidizer, nanojet are examples) and axially flown-throw nozzle-aggregates Fig. 2-27 [273]. Homogenizer type affects the size of droplets and size distribution. Thus, radial diffuser usage leads to the highest average droplet diameters. Counter-jet principle allows to obtain much smaller droplets. Finest emulsion can be obtained by nozzle aggregates; the reason is the decrease of the coalescence.
Fig. 2-27 Different types of HPH systems [273]: A) radial diffusers, B) counter-jet dispersators, C) axial flow nozzle system

It is possible to obtain submicron emulsions using HPH. Droplets size reduction increases emulsion stability because of the Laplace pressure. Also droplet size reduction increase interfacial surface area and requires the use of higher surfactant concentrations in order to provide droplets to be rapidly coated during the emulsifying [274]. In the work [275] oil-in-water emulsions (peanut oil) with whey protein isolate as surfactant were obtained and its stability upon frozen storage was checked. Authors use 4.3 wt% of whey protein isolate and at pressure higher than 200 MPa they reach the best emulsion stability for different oil to water ratio. Droplets size can be reduced by increasing the homogenizing pressure and viscosity of the disperse phase [276], these results were shown for vegetable-oil-in-water emulsions obtainment. In another research more complicated dependence of droplets size on pressure was shown [277], droplets size decreases with pressure until 90 MPa and above it droplets diameter increases with pressure and then it remains stable up to 200 MPa. Above 200 MPa diameter decreases again and then increases at 250 MPa. However, final decrease above 300 MPa occurs. In high pressure unit collision and coalescence takes place and it depends on the density of energy, temperature and on all the process parameters. Experimentally determined dependence of droplets size on disperse phase viscosity frequently has an exponential form [278].

Nowadays there is no theory for HPH process description, calculation and for evaluation of the emulsion end properties with process parameters. But there are a lot of empirical investigations for different types of HPH which can be used for energy evaluation [279], [280]. Besides, there are some research on HPH modeling where the best equations are selected for fluid flow calculations [278], [281]–[285]. This examples and results can be used for scale up and design of production based on HPH.
2.2.2.2. Process parameters

Compare to the production of monolithic samples, the emulsion gelation introduces many variables into the overall process. These parameters are: water-to-oil ratio, energy input (stirring rate), geometry of the emulsification setup (e.g. stirrer and vessel geometry), nature and concentration of surfactant, duration of emulsification and regimes.

In most cases these parameters are chosen empirically, the above cited studied lack rationalities behind process parameters used and rather present results based on preliminary process optimization. Unfortunately, the process optimization is only limitedly reported in most the cases.

A study by Lim et al. [247] provides a comprehensive comparison of several gelation techniques, wherein aqueous sodium hydroxide and tripolyphosphate were introduced into beforehand prepared emulsion of chitosan in iso-octane. The following formulation parameters were studied: the concentration of chitosan in acetic acid (1 – 3 wt%), concentration of surfactant (Span 85) in iso-octane (2 – 6 wt%), concentration of sodium hydroxide (0.5 – 3 M), the period of emulsification prior to addition of NaOH (10 – 30 min), the period of stirring after addition of NaOH (2 – 4 h), and the stirring speed (500 – 1500 rpm). Particles of spherical, ellipsoidal and irregularly shape were observed. In some cases the tendency towards aggregation was also noted. In general, the interplay between the process parameters determines the particle morphology and size distribution. The most important conclusions are: (i) an optimum amount of NaOH should be present to obtain sphericity and sufficient integrity; (ii) particles derived from high chitosan concentration are less susceptible to aggregation upon collision; (iii) lengthening the period of emulsification led to a greater tendency to aggregation; (iv) a faster stirring speed gave rise to microspheres of a wider size distribution; (v) an increase in the surfactant concentration resulted in larger though more monodisperse microspheres.

Several studies suggest to use Eq. (1) as a departure point in planning emulsion gelation studies [286], [287]:

\[
d \propto K \frac{D_v V_a \nu_a}{D_s V_o \nu_o} \frac{1}{N C_s} \frac{\gamma}{1} \tag{1}
\]

Here \( d \) is the average particle size, \( K \) is a variable depending on the apparatus geometry (e.g., type and dimension of stirrer), \( D_v \) and \( D_s \) are the diameter of the vessel and of the stirrer, \( V_a \) and \( V_o \) are the volume of the aqueous and of the oil phases, \( \nu_a \) and \( \nu_o \) respective kinematic viscosities, \( N \) is the stirring speed, \( \gamma \) is the surface tension between the two immiscible phases, \( C_s \) is the stabilizer concentration. Below we briefly summarize the most important results on the use of Eq. 1.
Even though after few minutes of the emulsification, the mixture appears to be visually homogeneous, a steady state droplet size distribution is not yet reached. Fig. 2-28 illustrates the time evolution of the emulsion [287].

![Image](image.png)

**Fig. 2-28 The course of droplet formation in an emulsion of aqueous albumin in chloroform-toluene mixed by a constantly powered vortex mixer [287]**

This result suggests that the gelation kinetics in the “all-premixed” should be carefully adjusted not to be too fast. At the same time, “homogeneous emulsion gelation” and “emulsion-coalescence” methods are free from this drawback.

Equation 1 suggests that the particle size depends on the apparatus geometry (constant $K$). The role of this factor is clearly evidenced by Poncelet et al. [253] in the production of alginate particles (“homogeneous emulsion gelation”). At all other conditions being equal, increase from 200 to 500 rpm leads to a decrease in the particle size by a factor of 5.1 for turbine with baffles, whereas only by a factor of 2.7 for marine impeller. This highlights the following two aspects: (i) design of the stirrer should be carefully examined; (ii) detailed technical drawing of the emulsification unit must be reported (almost always missing in the publications).

Water-to-oil ratio is well-known parameter and is often reported. At the lab scale this ratio is between 1:2 and 1:10. Large scale production would evidently pose a question on the optimal ratio as the oil recovery is intended.

Another outcome from the Eq. (1) is that the ratio between aqueous phase and oil phase viscosities should be possibly small when aimed for microparticles. Thus, data on viscosity for both polymer solutions and oil phases are paramount and should be measured and reported. For binary oil phases cubic McAllister equation can be used to estimate kinematic viscosities. Special attention should be put on the viscosity of reactive mixtures when “all-premixed” method is used, as well as on biopolymer/solid precursor for the “homogeneous emulsion gelation”. This data is very scarce impeding quantitative estimations.
Table 2-4 Hydrophilic-lipophilic balance of a range of frequently used surfactants

<table>
<thead>
<tr>
<th>Surfactant</th>
<th>HLB</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyglycerol polryricinoleate</td>
<td>1.5</td>
</tr>
<tr>
<td>Sorbitan trioleate (Span 85)</td>
<td>1.8</td>
</tr>
<tr>
<td>Sorbitan tristearate (Span 65)</td>
<td>2.1</td>
</tr>
<tr>
<td>Sorbitan sesquioleate (Arlacel 83)</td>
<td>3.7</td>
</tr>
<tr>
<td>Glyceryl monostearate</td>
<td>3.8</td>
</tr>
<tr>
<td>Sorbitan monooleate (Span 80)</td>
<td>4.3</td>
</tr>
<tr>
<td>Sorbitan monostearate (Span 60)</td>
<td>4.7</td>
</tr>
<tr>
<td>Sorbitan monopalmitate (Span 40)</td>
<td>6.7</td>
</tr>
<tr>
<td>Sorbitan monolaurate (Span 20)</td>
<td>8.6</td>
</tr>
<tr>
<td>Polyoxyethylene sorbitan tristearate (Tween 65)</td>
<td>10.5</td>
</tr>
<tr>
<td>Polyoxyethylene sorbitan trioleate (Tween 85)</td>
<td>11</td>
</tr>
<tr>
<td>Polysorbate 60 (Tween 60)</td>
<td>14.9</td>
</tr>
<tr>
<td>Polysorbate 80 (Tween 80)</td>
<td>15</td>
</tr>
<tr>
<td>Polysorbate 40 (Tween 40)</td>
<td>15.6</td>
</tr>
<tr>
<td>Polysorbate 20 (Tween 20)</td>
<td>16.7</td>
</tr>
</tbody>
</table>

The fact that the particle size is reciprocal to the stirring speed (rpm) is widely used to modulate it: smaller particles are produced at higher stirring speed. This holds true for the mode of the particle size, however the distribution becomes broader. This effect may lead to the increased mean size at higher stirring rates [288].

The last factor in Eq. (1) depends on the surfactant concentration and the surfactant structure. The latter is often taken into account by using so called hydrophilic-lipophilic balance (HLB). The HLB is a rough measure of the surfactant hydrophilicity (see Table 2-4 for the most used surfactants).

Many empirical studies are devoted to the proper selection of the surfactants based on HLB values. The most common recommendation is that w/o emulsions should be stabilized by surfactants with HLB in the range 3 – 6, whereas o/w are stable in presence of much more polar surfactants (HLB = 8 – 15). Fig. 2-29 depicts the rate of droplet coalescence for one of the most frequently employed system water/paraffin oil [289]. As one can see, even relatively small changes in the HLB may lead to the loss in emulsion stability. Various method are suggested in the literature for the evaluation of emulsion stability such as turbidity, conductivity measurements, using phase inversion temperature and many others (see comprehensive review by McClements [290]). For rapid evaluation one can count down the time needed to observe the very first signs of phase separation in an emulsion of
interest (Fig. 2-30). Although results are rough, they are often in agreement with published data. Thus, this method could be recommended for unexplored systems.

![Graph showing the influence of HLB on emulsion stability](image1)

**Fig. 2-29. Influence of HLB on emulsion stability [289]**

![Graph showing the stability of the alginate/CaCO3/paraffin oil emulsion](image2)

**Fig. 2-30. Stability of the alginate/CaCO3/paraffin oil emulsion as visually evaluated (unpublished results, TUHH)**
2.2.2.3. Particle recovery and solvent exchange

Once the reaction between precursor and crosslinker is completed, the emulsion turns into a suspension. The latter should be separated from oil, subjected to the solvent exchange and supercritically dried. This section deals with first two processes, whereas supercritical drying is described in Section 2.3.

For washing out the oil phase some studies recommend the use of light organic solvents such as hexane [226], [258], petroleum ether [257], dichloromethane/hexane [291] and acetone [292], [293]. As settling velocity of particles is reciprocal to the dynamic viscosity of the continuous phase, solvents like tetrachloromethane may be added prior to centrifugation step to reduced its viscosity [292].

Upon complete oil removal, low boiling solvents can be evaporated to collect the hydrogel particles. Often, however, partitioning into an aqueous solution is employed. This process is based on the fact that hydrophilic particles are accumulated in the denser aqueous phase wherefrom they can be collected and subjected to the solvent exchange. Besides water, various hardening solutions are used in order to complete the crosslinking, in particular, calcium chloride and glutaraldehyde [253], [254]. Tween and glycerol may be added to the aqueous phase [294].

Although the recovery process has a large impact on the yield, particle sphericity and agglomeration, only fragmentary empirical data are present in the literature on this topic. Reis et al. [256] describe the effect of various solvents (acetate buffer, hexane, acetone, iso-propanol, petroleum ether) on the sphericity, particle size and yield of alginate particles (by “homogeneous emulsion gelation”). It is found that washing solutions that compose of organic solvents enable particle separation at lower centrifugal force. Further, dehydrating solvents such as acetone and iso-propanol are revealed to improve the recovery yield. The latter is reported in the range 35 – 70 %. Similar yields in the ranges 66 – 88 and 83 – 87 wt% are reported by Esposito et al. [286] and Bera et al. [295], respectively. Yields greater than 67 % are found by Pavanetto et al. [250].

Little is known about residual oil and organic solvents in resulting particles. Pavanetto et al. [250] used infrared spectroscopy (FT-IR) to detect mineral oil residues. Up to 6.8 % mineral oil are detected in chitosan particles (by “emulsion-coalescence”). This value is rather high and may adversely affect the adsorption capacity of the final aerogels. In food applications, vegetable oil residuals may result in rancidity and must be carefully controlled. Four to nine washing steps are required to ensure complete removal of paraffin oil as confirmed by optical microscopy (presence of oil film is observed), see [256]. Unfortunately, such precautions are rarely taken and should be addressed in this project.

For the aerogel production from biopolymers, solvent exchange must be performed to be able to use sc-drying. Some studies report a positive role of organic solvents at the recovery step as they harden the gel microparticles, dissolve an excess of oil facilitating the separation (easier filtration, lower centrifugal force). However, the exposure of hydrogels to highly concentrated organic solvents (>30
– 50 %) leads to the significant shrinkage and hence poor textural properties of the resulting aerogels. Thus, it is crucial to maintain a balance between the minimal amount of the organic solvent at the recovery step and the maximal amount that gels can tolerate. On the other hand, gel microparticles are less sensitive to the large concentration gradients during the solvent exchange compare to monoliths. Comprehensive studies are required to clarify the interplay in the process parameters.

Another attractive possibility is to extract continuous phase directly with sc-CO$_2$. For that, the following prerequisites must be met: (i) gelation takes place in non-aqueous media; (ii) this media is miscible with sc-CO$_2$ at reasonable pressure ($p$) and temperature ($T$); (iii) oil is miscible with sc-CO$_2$ at reasonable $p$ and $T$. To the best of our knowledge, the only example is the work by Alnaief and Smirnova (2011), wherein silica aerogel is obtained by emulsion gelation of ethanolic sol in canola oil [224]. Both solvents were extracted with sc-CO$_2$ at 40 °C for 8 h (pressure is not specified).

As described above, it is generally not possible to use non-aqueous systems in the gelation of alginate, cellulose and chitin/chitosan. However, gelation in presence of organic solvent such as ethanol and acetone is recently reported for a wide variety of biopolymers such as high-methoxyl and low-methoxyl pectin, alginate, xanthan and guar gums [296], [297]. Sc-drying can immediately be implemented as the next step resulting in monolithic aerogels with reasonably good textural properties. Similar phase separation process is reported for cellulose solutions [298].

In fact, this phase separation process is known in the emulsion gelation of biopolymers for a long time under names “dehydratation” and “hardening” [241], [299]. The role of the solvent is three-fold: to harden the gel microspheres, to reduce viscosity of the contentious phase and to substitute water with the solvent making the sc-drying possible. To the best of our knowledge, such integration is exemplified by García-González et al. [300] using an emulsion of pectin in canola oil. Ethanol is added to the emulsion followed by heating. After cooling to room temperature additional ethanol is introduced, particles are covered, solvent exchanged and sc-dried ($D_{90} = 1100 – 1600$ µm). This method shows that crosslinker-free approach is feasible. Disadvantages are significant oil dilution and rather high solvent consumption.
2.2.3. Disruption of gelation by vigorous agitation

Selected organic polymer aerogels have been produced in powder form by disrupting the gelation process. Owing to the insolubility of the developing polymer, phase-separated polymeric nanoparticles are still formed and aggregate in small-scale into porous agglomerates. Since agitation prevents those agglomerates from assembling into the 3D network of a typical gel, they form precipitates. Necessarily then, the structure within the microparticles comprising that precipitate is akin to an aerogel, which is thus obtained in powder form after drying of the wet precipitate.

2.2.3.1. Process description

Gelation has been halted (disrupted) by two means: dilution of the sol with large amounts of solvent being added just before gelation, or vigorous agitation of the sol. In both cases primary particles are formed and aggregate into higher agglomerates. Those two methods prevent those agglomerates from interacting with one another, thus they are not allowed to form the continuous 3D network of a typical aerogel.

2.2.3.2. Examples

Park et al. [301] made polyurea (PUA) aerogel powders by reacting tetrakis(4-aminophenyl) methane (TAPM) with various alkyl diisocyanates in DMF at room temperature, followed by precipitation of the sol in a large volume of a non-solvent (acetone) that was added just before gelation. The precipitate was washed 3 times with pure acetone and was dried at 150 °C under vacuum. The precipitate consisted of spherical particles, the size of which was larger than the network nanoparticles in their gel state. The latter was measured with dynamic light scattering at about 9-30 nm. After drying, SEM showed that network particles were spherical and their size depended on the chemical identity of the diisocyanate (Fig. 2-31). BET surface areas measured with N$_2$ sorption (19-68 m$^2$ g$^{-1}$) were lower than those measured with CO$_2$ sorption (170-240 m$^2$ g$^{-1}$). On geometric grounds, it was calculated that the BET surface areas corresponded to the external surface area of the particles shown in SEM. Therefore, it was concluded that CO$_2$ is also capable to sample micropores. Those differential gas sorption characteristics render such PUA powders suitable for application in gas separations (e.g., of CO$_2$, N$_2$ and CH$_4$).
Kong et al. [302] produced PUA aerogel powders by mechanical agitation of sols obtained from reaction of toluene-2,4-diisocyanate (TDI) and 4,4'-oxydianiline (ODA) at 30 °C in acetone, and in selected cases also in acetonitrile. The typical total monomer concentration (TDI+ODA) in the sol was 1% w/w. The reaction was run under conditions of precipitation polymerization; therefore powders were compared among themselves, viz. with no reference to monolithic aerogels. All precipitates were collected by centrifugation, washed with acetone and dried at 60 °C to powdery products. No application of vacuum during drying was reported. With no stirring at all, at low stirring rates (100 rpm), or with reciprocating stirring the authors reported fibrous morphologies (Fig. 2-32). In all cases the diameter of the fibers was ≤100 nm. At higher stirring rates (600 rpm) they reported granular polymers. Nanomorphology, however, was a complicated function of several parameters: For example, with no stirring at all, network nanomorphology changed from fibrous to particulate (granular aggregates) by lowering the reaction temperature from 30 to 0 °C. Similarly, using reciprocated stirring, nanomorphology changed from fibrous to particulate by increasing the total monomer concentration (TDI+ODA) from 1 to 5% w/w. Nanofibers were obtained for monomer concentrations lower than 2% w/w. Running the reaction in acetonitrile (all other parameters being the same, reciprocating stirring, [TDI+ODA] = 1% w/w, 30 °C) those authors reported large (5-20 μm in diameter) spherical particles rather than fibers. It is noted that quite analogous observations about the network morphology were reported for PUA aerogels synthesized from a series of aliphatic and aromatic triisocyanates and water in acetone [303] and in acetonitrile [304], however the authors failed to reference and comment.
Q. Wu et al. [105] produced nanofibrous polyimide (PI) powders by mechanical agitation of a gel-like polyamic acid (PAA) product, which was obtained from pyromelitic dianhydride and 4,4’-diaminodiphenylmethane in a mixed solvent of tetrahydrofuran/methanol. Interestingly, rather than a real gel, the gel-like PAA product was a clear glass-like viscous solution that, upon addition of acetone, phase-separated into an opaque-white wet-gel. The authors make a point that a gel-like PAA product was obtained only from the specific monomers; other starting materials yielded only viscous solutions of the corresponding PAAs. Subsequently, acetone was solvent-exchanged with cyclohexane, which was removed under vacuum at about 10 °C yielding PAA aerogels that were step-cured (imidized) by heating successively at 100, 200 and finally at 300 °C. If addition of acetone into the gel-like PAA product was accompanied with vigorous mechanical stirring, the end product was an aerogel powder rather than a monolith (Fig. 2-33). In contrast to the report of Kong et al. on PUA powders (see above), vigorous agitation did not disrupt the microfibrous network structure of the PI, which was found identical both in monoliths and in powders (Fig. 2-33 and Fig. 2-34).
Fig. 2-33 (a) PAA aerogel powder. (b) PI aerogel powder. (c) SEM image of PAA aerogel powder. (d) SEM image of PI aerogel powder.

Fig. 2-34 SEM images of: (a) PAA monolithic aerogels and (b) PI monolithic aerogels after sublimation drying of the gels for 4 days.
2.2.4. Process for synthetic polymer powder production that could potentially lead to aerogels

The literature of isocyanate-derived aerogel powders and particles is not broad. Thus, with an eye on possible future adaption of research on other related areas, our search field was expanded into other particulate matter based on the polymers of interest: polyureas, polyurethanes, polyamides and polyimides. Thereby, our search results have been organized in three sections (2.2.4.1 – 2.2.4.3). The first section is entitled and concerns “Powders of granules, particles and microcapsules that potentially could become relevant to aerogels”. The second section is entitled, concerns and describes “Powders of hybrid materials that potentially could become relevant to aerogels”. Following the IUPAC definition of hybrid materials (material composed of an intimate mixture of inorganic components, organic components, or both types of component), hybrid materials here are combinations of synthetic polymers with other synthetic polymers or with inorganic components like oxides. And finally, the third section is entitled “Powders of porous particles including aerogels”. The first and third sections are divided into subsections concerning polyureas, polyurethanes, polyamides and polyimides, and whenever appropriate each subsection is divided into powders of granules, particles and microcapsules.

2.2.4.1. Powders of granules, particles and microcapsules that potentially could become relevant to aerogels

2.2.4.1.1. Polyureas (PUAs)

2.2.4.1.1.1. Polyurea (PUA) granules

PUA granules have been utilized as carriers for a diverse variety of fillers including fertilizers [305]. PUA content of these particles varied from 0.5 to 15 % w/w, based on the total weight of the encapsulated particles. The process of producing PUA particles, in which fertilizers were encapsulated, comprised of two main steps: (a) formation of isocyanate-coated particles by spraying an aromatic diisocyanate to the fertilizer particles containing at least one water soluble plant nutrient; and, (b) formation of PUA encapsulated fertilizer particles by reacting water with the isocyanate-coated particles obtained from the first step.

2.2.4.1.1.2. Spherical polyurea (PUA) particles

Highly uniform PUA microspheres were prepared by precipitation co-polymerization of isophorone diisocyanate (IPDI) and diethylenetriamine (DETA) in a binary solvent system of water/acetone [306]. A slight decrease in size of microspheres was achieved with increasing the polymerization temperature; at 30 °C, microspheres had an average size at of 2.76 μm, whereas at 50 °C the average size was reduced to 2.05 μm. Increasing the amount of water in the solvent increased the polymerization rate, while the size of the microspheres was reduced. For instance, for a mass ratio of water/acetone of 20/80, the particle size was 3.10 μm, whereas with a mass ratio of 1/1 the size was 2.14 μm, under the same polymerization conditions.
Variable sizes of PUA particles were obtained by using different diamines [307]. Emulsion polymerization of toluene-2,4-diisocyanate (TDI) with different compositions of ethylene diamine (EDA) and 1,6-hexane diamine (HDA) resulted in different particle sizes. The different diamine compositions consisted of EDA, HDA, or a mixture of EDA and HDA (molar ratio 1/1). As the methylene groups in diamines with the same molar ratio increased, the size distribution became narrower. This is related to the fact that EDA was more reactive compared to HDA, and therefore microcapsules obtained from EDA had more urea groups. In addition, the nature of isocyanates affected the size and size distribution of the microspheres. The aliphatic isophorone diisocyanate (IPDI), due to its superior reactivity vs. the aromatic toluene-2,4-diisocyanate (TDI), under emulsion polymerization in the presence of an aqueous solution of polyvinyl alcohol (PVA) resulted in smaller mean particle sizes (3.3 vs 5.6 μm) with narrower size distribution. The mean diameter of the microspheres increased with the increase of the TDI content and their size distribution became broader. Using different molar ratios of IPDI and TDI, such as 1/0, 0.67/0.33, 0.33/0.67, and 0/1, the PUA microcapsules had diameters of 3.3, 3.8, 4.4, and 5.6 μm, respectively [308].

PUA nanoparticles with diameters ranging between 25 and 55 nm were synthesized from oil/water nano-emulsions by an interfacial polycondensation process. Briefly, a defined amount of isophorone diisocyanate (IDPI) was added to the oil/surfactant mixtures; the oily component was saturated with a medium-chain triglyceride (MCT) and Kolliphor®ELP (KELP) was used as surfactant [309]. Then, the aqueous component was added dropwise to these mixtures under continuous stirring at 2500 rpm. Parameters such as concentration of IPDI and polymerization temperature were crucial to control the morphology and size of the KELP PUA nanoparticles from nano-emulsions. Increase of the surfactant content in the oil/surfactant ratio resulted in a decrease of mean diameters.

2.2.4.1.1.3. Polyurea (PUA) micro- or nano-capsules

Micro- or nano-capsules is a prime example showing that the morphology affects the properties of the material. PUA microcapsules have gained a lot of attention as encapsulating systems. The main desired properties of any encapsulation system are: (a) selective control of transport of encapsulated moieties in and out of the shell; and, (b) stability of the shell in order to avoid collapse into the solvent environment. PUA is a good candidate, because it is chemically stable and highly porous. PUA microcapsules can be prepared by precipitation polymerization and interfacial polymerization. Interfacial polymerization includes emulsion polymerization and the microfluidics technique. Particle size can be tuned by modifying the experimental conditions (e.g., polymerization temperature, solvent, stirring rate and/or concentration of monomers).

Polycondensation reaction between a diisocyanate (toluene-2,4-diisocyanate (TDI), or hexamethyl-1,6-diisocyanate (HMDI)) and a polyamine (ethylenediamine (EDA), 1,6-hexamethylenediamine (HMDA), or diethylenetriamine (DETA)) resulted to formation of PUA nanocapsules [310]. PUA nanoparticles obtained by polycondensation at the droplet interface of oil/water nano-emulsions in aqueous solution/non-ionic surfactant/oil systems were obtained using isophorone diisocyanate (IPDI) as monomer [311]. Assuming that IPDI preferably reacted with the hydroxyl-groups of the
surfactant, the effect of Polysorbate-80 as a non-ionic surfactant on the polymerization process was significant and a decrease in surfactant concentration resulted in a decrease in particle diameter. Furthermore, suitable concentrations of the non-ionic surfactant Polysorbate-80 provided a high degree of protection against freezing stress. Lysine-coated PUA nanoparticles [312] with an average diameter of 52±7 nm were synthesized from nano-emulsions by polymerization at the droplet interface using an extremely low concentration of monomer.

PUA nanocapsules of about 100 nm were obtained from nano-emulsions [313] by a two-step method. In the first stage, a nano-emulsion was prepared, by a heating–cooling cycle, in which the oil phase contained an oil soluble monomer (e.g., toluene-2,4-diisocyanate; TDI). In the second stage, a water-soluble monomer and a crosslinker (diethylenetriamine; DETA) were added, leading to formation of a polymeric shell by an interfacial polycondensation reaction. Poly(ethylene glycol)octyl-phenyl ether (OP), a non-ionic surfactant, was the emulsifier. A possible application of the nanocapsules containing hexadecane, dodecane, and/or decane is in the field of thermal energy storage, as phase-change materials (PCM) [313] [314]. PCM is a substance with a high heat of fusion that is capable of storing and releasing large amounts of energy by melting and solidifying. Heat is absorbed or released when the material changes from solid to liquid and vice versa. Thus, when the encapsulated PUA microcapsule reaches the temperature at which it changes phase, it absorbs a large amount of heat at an almost constant temperature until all material becomes liquid.

PUA microcapsules were also prepared in aerosols [315], whereas droplets of toluene-2,4-diisocyanate (TDI) or hexamethylene diisocyanate (HDI) reacted with ethylenediamine (EDA) vapor. Particle size could be tuned by adjusting the temperature of the aerosol generator and the flow rate of the carrier gas. Higher temperatures lead to larger microsphere diameters and different morphology: at 40 °C microcapsule sizes were in the range of 0.4 to 1 μm with spherical morphology, whereas at 80 °C sizes were in the range of 20 to 30 μm with microcapsules having spherical and irregular shape. The aerosol reactions are exceedingly fast and they require no additives (e.g., surfactants or solvents).

Microfluidics has been used as a continuous approach of preparing monodispersed PUA microcapsules [316] [317]. The microcapsule shells were formed by reaction of TDI, dissolved in oil or toluene, with an amine, dissolved in water. Shell thickness increased with increasing amine solubility in the oil phase. Variation of morphology and size was achieved using different amines and oils. PUA microcapsule diameters increased with an increase of the fractional flow rate of the dispersed phase and shell thickness increased with increasing amine solubility in the oil phase. Toluene was the oil phase and amines included polyethylenimine (PEI), ethylenediamine (en), tetraethylenepentamine (TEPA) and 1,6-hexamethylenediamine (HMDA). Diameters were in the range of 55 to 110 μm. The presence of surfactants during synthesis had a notable impact on the microcapsule morphology, mechanical properties, and permeation properties. In the absence of surfactant, shells were formed as smooth layers without a well-defined fine-structure at the nanoscale. Use of surfactant induced formation of a certain sponge-like fine-structure on the microcapsule shell. The morphology of the shell determines the permeation properties.
Microcapsules synthesized from the reaction of a TDI-based poly(isocyanate) pre-polymer with a benzophenone-based amine were filled with a photochromic spiropyran and were dissolved in sunflower oil (core material) [318]. The average microcapsule diameter (by means of optical microscopy) was 148 μm. The microcapsules presented an almost-spherical shape with a uniform shell wall, about 2 μm thick. Such high shell thickness provides sufficient mechanical strength and prevents microcapsules from breaking apart (and therefore leakage of the core material) during processing or after inclusion into a polymeric carrier. These microcapsules are considered suitable candidate materials for the in situ visual detection of mechanical damages by color change. Briefly, the microcapsules are embedded into a photoresist polymer (polyethylene glycol methacrylate photopolymer). After scratching the polymeric coating the embedded microcapsules are broken; the UV-sensitive core material is released and it diffuses into the polymer matrix. Upon exposure to UV-A light, a rapid color change in the region where the damage was made is observed.

PUA microcapsules have been used as encapsulating agents for dyes [319] and essential oils [320] [321] [322]. Poly[(phenyl isocyanate)-co-formaldehyde] (PPI) and toluene-2,4-diisocyanate (TDI) monomers, bearing three and two isocyanate groups, respectively, were used to obtain shell membranes with different crosslinking degrees, by varying the PPI/TDI ratio [320]. The consistency of the shell membrane can be tuned by changing the diamine monomer; hydrazine monohydrate (HH), ethylenediamine (EDA), and butanediamine (BDA) monomers, having two terminal amine groups but different length, modulated membrane stiffness and permeability. PUA microcapsules shells were hard when using HH and more flexible when BDA was used. Mean diameter of microcapsules encapsulating essential oils was in the range of 10-15 μm; size distribution was dependent on the kind of essential oil used in the synthesis. The morphology of PUA microcapsules was similar for all samples, but encapsulation yield depended on the essential oil used. For lemon balm the loading was 40.0 % w/w, for lavender, sage and thyme were 24.6, 50.5 and 31.5% w/w, respectively. Intense investigation has been done for producing perfume-containing microcapsules with a PUA [323] [324] wall that can be used in home or personal care products, and consumer products comprising those microcapsules. The process uses combination of aromatic and aliphatic poly(isocyanates) in specific relative concentrations.

PUA microcapsules have been studied as release carriers for insect pheromones [325]. (Z)-11-hexadecenyl acetate, a sex pheromone component, was used as the model molecule. PUA microcapsules were prepared using TDI as the oil-soluble monomer, DETA as the water-soluble monomer and 0.25% nonylphenol polyethylene glycol ether as the appropriate emulsifier. The dimensions of the PUA microcapsules were in the range of 20 μm. The morphology of the polymeric shell was studied by scanning electron microscopy (SEM) and it seemed to be rough. The PUA shell protected the active agent from rapid evaporative loss and chemical degradation. Although those microcapsules did not meet the desired goal of a constant near-zero-order rate of release, they performed adequately well as carriers for the controlled/sustained release of the pheromone with a dynamic rapid to slowing release lasting for almost 1 month.
Microencapsulated electronic ink [326] was prepared by interfacial polymerization of toluene-2,4-diisocyanate (TDI) and triethylene tetraamine (TETA) in the presence of Pigment Hansa Yellow 10G (negatively charged electrophoretic particles). The microcapsules were regular, transparent, smooth, optically clear and had a wall thickness of around 1.5 µm and an excellent sealing property. The particle size distribution was narrower and the average particle size was smaller with increasing stirring rate. Crucial parameter for their preparation was the presence of emulsifiers, with polyoxyethylene octylphenyl ether (OP-10) showing better results regarding to morphology of particles (compared to polyoxyethylene sorbitan monooleate (Tween 80), polyoxyethylene and sodium dodecyl sulfate (SDS)). The pigment particles were negatively charged and could move reversibly at a constant velocity in the capsules under a block wave AC field (E = ±30 V mm⁻¹), with a response time of about 150 ms. Therefore, it could be applied to pigment-in-dye type electronic ink.

PUA sub-microcapsules with sizes of around 200 nm were prepared using the electrocapillary emulsification method [327] in order to control particle size. PUA capsules were synthesized via interfacial polycondensation between tetraethylenepentamine (TEP) dissolved in an aqueous phase and toluene-2,4-diisocyanate (TDI) dissolved in a mixture of cyclohexane and chloroform. The oil phase contained a lipophilic non-ionic surfactant (sorbitan sesquioleate, SO-15) as an emulsion stabilizer. Highly uniform PUA microcapsules bearing amine groups on the surface were prepared using one single monomer, isophorone diisocyanate (IPDI), via step polymerization with water in water/acetone mixtures [328]. The process did not involve any stirring or shaking. The size was controllable from 2 to 10 µm by changing the IPDI concentration, the water/acetone ratio or the polymerization temperature.

Microcapsules for internal radiation therapies containing metal elements [329], Dy, Ho and Cu, with a diameter of 5 to 10 µm were successfully obtained by interfacial polymerization of a commercially available trisocyanate monomer (Takenate D-110N, Takeda Pharmaceutical Industry, Osaka). The amount of the metal elements loading was measured using a high frequency plasma photoemission apparatus. NiCl₂ as a recyclable catalyst has been encapsulated inside PUA microcapsules [330]. The microcapsules were prepared by interfacial polymerization between diisocyanate monomers (TDI and IPDI) and water with triethylamine as a catalyst in a water-in-oil emulsion system in the presence of the surfactant Span 80. The diameter of the microcapsules depended on the experimental conditions with a range of 3.5 to 22 µm.

Furthermore, microcapsules of PUA were used in catalysis, by entrapping Pd nanoparticles or Pd complexes [331] [332] [333] [334]. PUA was deemed to be a suitable encapsulation matrix by virtue of the ability of the urea functionality to ligate and retain metal species, such as Pd(OAc)₂. The microcapsules were prepared by an in situ interfacial polymerisation approach. The combination of microencapsulated Pd(OAc)₂ is demonstrated to be an efficient and economical catalytic system for batch Suzuki cross couplings at low temperatures in both organic solvents and scCO₂.
Hollow PUA microspheres with uniform morphology [335] were prepared via precipitation polymerization of isophorone diisocyanate (IPDI) in water/acetone mixtures. The procedure involved three steps: at the first step, IPDI reacted with water to form the core particles; the second step included the addition of triethylene tetramine (TETA) and additional IPDI; and, at the last step hollow microspheres were obtained by dissolution of the core template. During this process, different PUA polymers were formed at the first and second steps. At the beginning of the reaction, water reacted with IPDI, producing linear PUA. Crosslinked PUA shells were produced at the second step, via reaction between TETA and IPDI. The different solubility of linear and crosslinked PUA resulted in the formation of hollow microspheres after the dissolution of the core template by immersing the core–shell microspheres in a mixture of acetone/acetic acid at 80 °C for 8 h. The size of PUA microcapsules can be controlled with variations on the experimental conditions (different IPDI concentration, different amount of TETA, different feeding rate of TETA and/or IPDI) and ranges from 3.5 to 7.7 µm.

2.2.4.1.2. Polyurethanes (PUs)

2.2.4.1.2.1. Polyurethane (PU) particles

The emulsion polymerization method has been used to obtain poly(ester urethane urea) microparticles based on poly(propylene glycol) toluene-2,4-diisocyanate terminated pre-polymer (TDI) or poly(propylene oxide)-based tri-isocyanate-terminated pre-polymer (TI). Toluene solutions of either of the above monomers and poly(ε-caprolactone) diol (PCL) were added in an aqueous solution of poly(vinyl alcohol) and the emulsion was stirred at 60 °C. The resulting microparticles were centrifuged, washed with distilled water and air-dried. Their mean size was 24 µm for TDI-based microparticles and 19 µm for TI-based microparticles [336].

PU microparticles, synthesized from castor oil and 4,4’-methylene-di-p-phenyl diisocyanate (MDI), have been formed under shear stress during extrusion processing and successfully reacted with starch to improve their mechanical properties, hydrophobicity and thermal stability [337].

2.2.4.1.2.2. Polyurethane (PU) microcapsules

Pre-polymers synthesized from TDI-based isocyanates and 1,4-butanediol, 1,6-hexanediol or glycerol could encapsulate IPDI in oil-in-water emulsions, using gum Arabic as surfactant and encapsulation agent. When TDI was used as the isocyanate, the average microcapsule size ranged from 0.8 to 3 µm, depending on the polyol used [338], while when TDI-based Desmodur L-75 and 1,4-butanediol were used, the average capsule diameter was 75.8 µm [339]. These microcapsules can find application in self-healing polymers, with IPDI acting as the healing agent.

A PU prepolymer, synthesized from the reaction between TDI and poly(ethylene glycol) (PEG), was mixed with energy storage paraffin and added to a water solution of a non-ionic emulsifier. Addition of 1,4-butanediol (chain-extender) produced paraffin containing PU microcapsules, with diameter...
around 3 μm. These microcapsules have been applied to the Outcast/silk fabric to improve its thermoregulating performance [340].

PU microcapsules containing docosane have been obtained by an oil-in-water emulsion polymerization of PEG and 4,4'-methylene-di-p-phenyl diisocyanate (MDI), using poly(vinyl alcohol) as a surfactant and dibutyl tin dilaurate as a catalyst. The resulting microcapsules had an average diameter of 4 μm and the encapsulation shifted the phase transition temperature of docosane from 42 to 37°C [341].

PU microspheres for drug delivery were prepared via a oil-in-water single-emulsion solvent extraction/evaporation technique. A CH₂Cl₂ solution of the polymer and the drug was added to a water solution of polyvinyl alcohol under vigorous stirring, resulting in a microemulsion. After a given time, the system was opened to allow solvent evaporation. The final product was obtained with centrifugation and particles were washed with water and freeze-dried. The particle diameter ranged from 1 to 100 μm and their encapsulation efficiency from 26.6 to 97.2 %, depending on the polymer and the emulsifier used [342].

Porous CaCO₃ particles have been used as sacrificial templates to form PU microcapsules. The CaCO₃ particles were incubated in a DMF solution of PU, loading the PU in the pores of CaCO₃. The adsorbed PU was crosslinked when the particles were dispersed in hexamethylene diisocyanate (HDI) solution. The particles were immersed in a solution of ethylenediaminetetraacetic acid disodium salt (Na₂EDTA) to remove CaCO₃. The resulting PU microcapsules had similar size with the templating CaCO₃ particles (around 7.2 μm), were dispersable in water and able to absorb hydrophobic substances from organic solutions (e.g., Nile red or coumarin-6 from ethyl acetate) [343, p. 3]

2.2.4.1.3. Polyamides (PAs)

2.2.4.1.3.1. Polyamide (PA) particles

Polyamide (PA) powders were obtained by anionic solution/suspension polymerization of lactams, and were used for removing dyes from wastewater. These powders were synthesized by lactams, such as 2-pirrolidone, ε-caprolactam, or o-laurolactam and they were dispersed in the solvent (a mixture of aliphatic hydrocarbons with boiling point ranging from 120 to 140 °C). The chain initiator (stearoyl isocyanate), was added using a syringe pump, over a certain period (12, 6, or 12 h, respectively, for the three aforementioned lactams), and with constant feeding rate (60 mL h⁻¹). At the end of dosing period the mixture was maintained under stirring for additional 2 h. So obtained polymer particles were transferred into a large amount of methanol, separated through filtration, and then washed several times with methanol. Finally, the powders were subjected to extraction with methanol for 8 h and vacuum-dried. Particle size range of PA powders was 0.1-527.62 mm [344].
2.2.4.1.3.2. Polyamide (PA) microcapsules

Because of their versatile properties, microcapsules have found various applications in the medical and industrial fields. The emulsification technique which employs microporous glass membranes was used to prepare polyamide microcapsules of narrow size distribution. This method also seems promising to get various sizes of the capsules by selecting the pore size of the glass membranes. Microporous glass tubes were made hydrophobic by chemically treating with octadecyltrichlorosilane and trimethylsilane and were then mounted on the membrane emulsification apparatus. Cyclohexane was circulated through the inside of the tube and then the nitrogen gas was applied to the disperse phase. The aqueous disperse phase consisted of piperazine, Na$_2$CO$_3$, dextran and NaCl. The applied gas pressure was raised for the disperse phase to be squeezed through the pores of the glass tube into the circulating cyclohexane. Terephthaloyldichloride was added to the emulsion and the interfacial polymerization was allowed to proceed. The capsules obtained were centrifuged, washed and then transferred into water with aid of surfactant. The aqueous microcapsules were washed repeatedly with water. The obtained PA microcapsules had average pore diameter of 1120 nm [345].

Encapsulation by interfacial polycondensation involves two main stages: (1) emulsification of the organic phase, containing a lipophilic monomer in aqueous medium, and (2) addition of a hydrophilic monomer.

Microcapsules that are composed of an aqueous core and a PA wall and were synthesized via interfacial polycondensation have also been reported. Said microcapsules were prepared in a Sovirel reactor equipped with an impeller stirrer. To the diamine solution (polyoxypropylenediamine (Jeffamine D-230)) was added the solvent mixture (cyclohexane/chlorofom) containing span85 as an emulsifying agent. The mixture was then mechanically emulsified (600 rpm) at room temperature to yield a water-in-oil emulsion. A solution of sebacoyl chloride (CS) in the same solvent mixture was added and stirred for the specified time at 300 rpm. The resulting PA microcapsules were collected by centrifugation, washed with cyclohexane and suspended in water for analysis. Size distribution was between 10 and 100 µm and the mean diameter was around 35 µm [346].

Encapsulation of emulsion droplets via interfacial polycondensation in water as continuous phase has also been used as a method to fabricate PA microcapsules. A cyclohexane/chloroform mixture, containing terephthaloyldichloride, was pre-emulsified into distilled water containing the stabilizer (poly(vinylalcohol) (PVA)), by mechanical stirring at low stirring rate (200 rpm). Then the stirring speed was increased (to 1,200 rpm) to intensify emulsification. The stirrer speed was reduced to 400 rpm and distilled water containing PVA, hexamethylenediamine (HMDA) and diethylenetriamine (DETA) were added to start the interfacial polycondensation. The reaction was allowed to complete. Excess of amine is necessary in order to trap the liberated hydrochloric acid. SEM images showed almost spherical particles with sizes below 100 nm [347].
2.2.4.1.4. Polyimides (PIs)

2.2.4.1.4.1. Polyimide (PI) particles

Dispersion polymerization is an attractive method for producing micro-size polymer particles in a single step process. Using this method, poly(amide acid) microparticles were synthesized by a reaction between benzophenone-3,3,4,4-tetracarboxylic dianhydride (BTDA) and 4,4’-diaminodiphenyl ether (DPE) with stirring at 200 rpm, using polyvinylpyrrolidone as a dispersant, and were subsequently heated to undergo imidization [348]. PI particle sizes increased with increasing temperature, concentration of dispersant, and concentration of monomers.

2.2.4.2. Powders of hybrid materials that potentially could become relevant to aerogels

PUA microcapsules have found tremendous use as self-healing and anticorrosive coatings. The main idea is the release of a healing agent (diisocyanate, oil) in order to prevent corrosion [349]. HDI-filled silica/PUA hybrid microcapsules [350] prepared via a combined strategy of interfacial polymerization and an in situ sol-gel process in an oil-in-water emulsion, exhibited superior thermal stability and solvent resistance. The diameter and shell thickness were linearly related to the agitation rate; microcapsules formed had diameters of 57 to 328 µm and shell thicknesses of 1 to 8 µm. Self-healing anticorrosion coatings based on microcapsules were fabricated on a steel substrate. The anticorrosion performance was attributed to the release of HDI from ruptured microcapsules at scratched areas, followed by HDI reacting with moisture or water to form solid polymer that filled the crack. From a two-step in situ polymerization method using an oil-in-water emulsion technique PUA microcapsules containing linseed oil [351] were produced with dimensions varying from 8 to 45 µm, depending on the stirring rate. The mechanism of the reaction consists of two steps. The first step involved the reaction between urea and formaldehyde, forming methylol urea, and the second step involved a condensation reaction between the molecules of dimethylol urea forming a low molecular weight prepolymer. Further reaction led to the crosslinked polymer; the reaction mixture was adjusted to pH 2-3 at 50-60 °C. In the synthesis of microcapsules, formation and stabilization of emulsion is very critical, and is greatly influenced by the concentration of the emulsifier and the stirring rate, which was varied between 100 and 400 rpm. Higher stirring rates and longer reaction times lead to microcapsules with larger mean diameters.

The aerosol technique was employed for the preparation of uniform colloidal inorganic particles coated with a PUA polymer [315] [352]. Mixed PUA/metal oxide particles were obtained by exposing polymer colloids (TDI or HDI with EDA) to alkoxide (Ti(IV) ethoxide and Al(III) sec-butoxide) vapors (produced by hydrolysis of alkoxide droplets in contact with water vapor). Spherical particles with TiO₂ and Al₂O₃ cores were formed with dimensions somewhat enlarged compared to untreated polymer particles as a consequence of the exposure to alkoxide vapors in the boiler section. Particle sizes ranged from 1 to 10 µm.

Urea-formaldehyde (UF) microcapsules containing dicyclopentadiene (DCPD) as the healing agent were prepared by in situ polymerization in an oil-in-water emulsion. Microcapsules of 10-1000 µm
in diameter were produced by appropriate selection of agitation rate in the range of 200-2000 rpm [353]. The relationship between average diameter and agitation rate is linear in log-log scale. During the polymerization urea and formaldehyde react in the water phase to form a low molecular weight pre-polymer. As its molecular weight increased, the pre-polymer was deposited at the DCPD/water interface. UF ultimately became highly cross-linked and formed the microcapsule shell wall. Microcapsules feature a smooth 160-220 nm inner membrane and a rough, porous outer surface.

Polyamide-polyurea (PA–PUA) hybrid microcapsules with porous membranes have also been fabricated by interfacial polymerization with the use of one surfactant and one co-surfactant. They were prepared from sebacoyl dichloride (SD), toluene-2,4-diisocyanate (TDI), diethylenetriamine, and ethylene diamine. First, an organic phase containing the SD and the TDI was added to the water phase containing sodium dodecyl sulfate (SDS) as a surfactant. The above mixture was mechanically agitated for 20 min with a stirring speed of 800 rpm to yield an oil-in-water emulsion. The stirring speed was then reduced to 400 rpm, and followed the aqueous phase including buffer solution, poly(vinyl alcohol) (PVA) as co-surfactant, diethylene triamine, and ethylene diamine was added to the emulsion in a fixed rate, and then the mixture was further stirred. The emulsification and interfacial polymerization took place at 10 °C. The prepared microcapsules were separated by centrifugation and then they were washed with distilled water. Finally, the hybrid shells were dried at ambient temperature or freeze drying at 0.12 mbar. The frozen microcapsules were dried for ±40 h. Cold and dried samples were ground to obtain powder. Increase of stirring rate led to formation of smaller particles (from 41.23 to 10.04 μm) and narrower distributions. Furthermore, the different drying processes and the content of the surfactant had a significant influence on the variation of particle sizes. Thus, the formed microcapsules were damaged severely by conventional drying at ambient temperature, which was caused due to the pressure difference across the shell while the particle size of the microcapsules decreased with the increase of the surfactant content [354].

Incubation of sodium poly(styrene sulfonate) (PSS) microparticles in a solution of an aliphatic hybrid poly(urethane-amine) resulted in the formation of hollow multilayer microcapsules. The PSS microparticles were templated on CaCO3 and the poly(urethane amine) was synthesized by co-polymerizing 2-methylaziridine with CO2. The produced microcapsules were found suitable for pH/thermally responsive drug delivery [355].

A hybrid PU bearing tetra-aniline pendant units was synthesized by hexamethylene diisocyanate (HMDI) and tetra-aniline diol, the product of functionalization of tetra-aniline amino-group with a diol-group. Said polymer could be self-assembled in an aqueous acetic acid/n-octane emulsion to form microcapsules with varying sizes (165-233 nm) and shell thicknesses (50-120 nm). The smallest and most uniform sized of these particles were obtained when the reaction mixture was stirred more vigorously and for a longer period of time [356].

Hollow waterborne PU microspheres have been obtained by a prepolymer synthesized from isophorone diisocyanate (IDPI), 2,2-bis(hydroxymethyl propionic acid) (DMPA), 1,4-cyclohexanediethanol (CHDM) and terminated by 3-aminopropyltriethoxysilane (APTES). The
pre-polymer was self-crosslinked to form microspheres after water was added in a toluene solution under vigorous stirring, thus hydrolyzing the ethoxy silane groups to silanol groups (Si–OH), which in turn condensed to form a siloxane (Si–O–Si) network structure. The microspheres created had encapsulated toluene droplets, which were removed by heating to leave a cavity within the microspheres. Depending on the toluene/pre-polymer ratio, the microsphere size ranged from 1.6 to 24.825 µm, while the average size of the holes on the microspheres surface was 268 nm [357].

Microencapsulation of dodecane in PA microcapsules was obtained by interfacial polycondensation of p-phenylenediamine (PPD) and sebacoyl chloride (SC) with the use of polyvinyl alcohol (PVA) or Tween 20 as dispersion stabilizers (PVA is actually a protective colloid). The oil solution was prepared from dodecane and SC at room temperature. The organic mixture was added dropwise under vigorous stirring into the aqueous solution containing the dispersion stabilizers. After this addition, the stirring rate was decreased and the amine solution was added to the mixture. The prepared microcapsules were isolated by filtration and washed with distilled water. A significant decrease in the mean diameter of the microcapsules (from 545 to 55 µm) was observed when increasing the stirring speed. The type of stabilizer used also affected particle size, size distribution and surface morphology of the microcapsules. Addition of a small amount of oleic acid to the organic phase improved wall strength significantly. Its slightly amphiphilic nature allowed its positioning at the oil/water interface and its subsequent incorporation in the PA wall during capsule formation. This strategy was much more effective than using a triamine crosslinker [358].

2.2.4.3. Powders of porous particles including aerogels

2.2.4.3.1. Polyureas (PUAs)

Porous polyurea (PUA) granules can be prepared through a simple protocol by precipitation polymerization of isocyanates. By reacting toluene-2,4-diisocyanate (TDI) with water in a water acetone binary solvent system, materials with irregular granular shape in the range of 10 to 20 µm were obtained [359]. Water plays a dual role; of a reactant and of a component of the binary solvent. As a reactant, it reacts with the isocyanate group on TDI molecules to yield CO₂ and amine. The amine molecules generated react with the isocyanate groups to form linear PUA. As a solvent, water causes precipitation of oligomers and the reaction proceeds as precipitation polymerization. Variable granules sizes and properties were achieved when polymerization reactions were carried out at different temperatures and various TDI feeding rates. When the temperature was increased from 30 to 50 °C, specific surface areas decreased from 161.68 to 148.23 m² g⁻¹, and a significant increase of pore volume was noted (from 2.20 to 3.48 cm³ g⁻¹). The resulted porous PUAs were used as absorbents of anionic dyes such as Remazol brilliant blue R (RBBR) and acid fuchsine (AF) [360]. High adsorptions, up to 122.10 mg·g⁻¹ for RBBR and 108.61 mg·g⁻¹ for AF, were reported and the porous PUA materials were easily regenerated by washing with H₂O/EtOH mixtures. Testing of these materials as adsorbents demonstrates that porous PUA can be used in anionic dye removal from aqueous media, and that high performance is maintained after multiple cycles of use.
2.2.4.3.2. Polyamides (PAs)

Porous aromatic PA particles were prepared from $p$-phthalyl chloride and 4,4′-diaminodiphenyl ether in acetone, using the precipitation polymerization method. Distilled water was added in varying amounts to the solution. Distilled water was added in varying amounts to the solution, which was then subjected to ultrasonic irradiation at 45 kHz in a water and ice bath during mixing and for a period of 20 min. The product was extracted by centrifugation and washed with acetone and water. The sample was then dried overnight in a vacuum oven at 100 °C. PA particles obtained were spherical, with a narrow size distribution. The average particle diameter was 712 nm, the surface area was 106.7 m$^2$ g$^{-1}$ and the particles showed high thermal stability (477 °C) [361].

2.2.4.3.3. Polyimides (PIs)

Fabrication of polyimide (PI) aerogel microparticles via a simple method, avoiding scCO$_2$ drying, has also been reported. Poly(amide acid)s were synthesized via the polymerization of pyromellitic dianhydride (PMDA) and 4,4′-oxydianiline (ODA) and were then transformed to polyimide microparticles by heating in an autoclave [362]. The fabricated spherical particles had sizes ranging between 3.6 and 4.9 mm and their surface area was determined as 103 m$^2$ g$^{-1}$.

To maintain a balance between maximizing the gas uptake and achieving good reversibility for adsorbents such as CO$_2$, functional groups, such as triazines, were used as cross-linkers for the synthesis of microporous PI powders. Porous triazine-based PI networks were synthesized by a condensation reaction of 2,4,6-tris(p-aminophenyl)-1,3,5-triazine (TAPT) with various commercially available dianhydrides in m-cresol [362]. All triazine-based PI networks exhibited high thermal stability under air, with particle sizes ranging from 0.05 to 0.5 μm. They also featured remarkable CO$_2$ uptake (0.42 to 2.45 mmol g$^{-1}$) under ambient conditions. The gas selectivity for CO$_2$ over N$_2$ could be increased significantly (from 30.9 to 55.5) by increasing the polarity of the polymer surface. For example, TPIs which contained carbonyl or ether functionalities provided an increased CO$_2$/N$_2$ selectivity ratio [363].

Porous PI nanoparticles were fabricated from poly(amic acid) (PAA) derivatives with poly(acrylic acid) (PAS) as the porogen, using a reprecipitation method and subsequent imidization. The porous nanoparticles were prepared by the reprecipitation method using two PAA precursors. The first one was synthesized by 1,4-bis(3,4-dicarboxytrifluorophenoxy)-tetrafluorobenzene dianhydride (10FEDA) and tetrafluoro-m-phenylenediamine (4FMPD), and the second one was prepared from 3,3′,4,4′-biphenyltetracarboxylic dianhydride (BPDA) and $p$-phenylene diamine (PDA). Pyridine was used as catalyst and acetic anhydride as dehydrating agent. A mixed solution of PAA and porogen was prepared by dissolving a given amount of porogen into a PAA/N-Methyl-2-pyrrolidinone (NMP) solution. The mixed solution of PAA and porogen was injected into vigorously stirred cyclohexane. The subsequent two-step imidization was performed to convert PAA to PI. Chemical imidization occurred by adding a mixture of pyridine and acetic anhydride into the PAA nanoparticle dispersion. After a given time, the chemically imidized PI nanoparticles were separated (using a centrifuge) and dried in vacuo. Finally, they were cured at 270 °C to ensure complete conversion into PI.
nanoparticles, synthesized from BPDA/PDA/PAS, showed higher porosity than those synthesized from 10FEDA/4FMPD/PAS, with pore sizes of 20-100 nm and high thermal stability (400 °C). The number of pores in each PI nanoparticle increased upon increasing the PAS content [364]. The same method was used for PAAs based on 1,2,3,4-cyclobutanetetracarboxylic dianhydride (CBDA) and bis(2,2'-trifluoromethyl)benzidine (TFMB) or 4,4'-(hexafluoroisopropylidene)dipthalic anhydride (6FDA) and 4,4'-oxydianiline (ODA), with poly(sodium-4-styrenesulfonate) (PSS) as the porogen, giving particles with similar sizes [365].
2.3. Drying process

Drying process is the last and the most critical step in the aerogel production. The gel is a highly porous structure in which the pores are filled with a liquid. The fraction of the volume of the liquid to the volume of the gel is generally more than 0.95. Removal of the liquid solvent from the pores is termed drying. It is desirable to preserve the pore volume of the matrix, minimize shrinkage of the matrix and prevent collapse of the pores during drying to obtain aerogels with desirable properties for a wide variety of applications.

There are mainly three methods which are used to dry the wet gels which are:

1. Ambient pressure drying combined with matrix strengthening mechanisms

2. Freeze drying

3. Supercritical drying.

A diagram showing the change in the state of solvent during each different drying technique is given in Fig. 2-35. An overview about each drying technique is included below.

![State diagram showing the routes of different drying methods](image-url)
2.3.1. Ambient Pressure Drying

Ambient pressure drying is the process of drying the wet gels by evaporating their pore liquid at ambient pressures and typical temperatures from room temperatures up to 200 °C. [366]. It is highly challenging as the porous structure of the wet gels cannot withstand the large capillary forces created inside the pores at the liquid-vapor interface during the evaporation of the pore liquid [367]. If the wet gel is dried under ambient conditions without a control mechanism, they can shrink significantly causing them to lose all their porous structure. Consequently, in order to use this method, it should be combined with surface treatment [368], network strengthening [369] and/or use of an aprotic solvent to reduce surface tension [370] to minimize the capillary forces [371]. Based on the surface treatment approach, Smith et al. developed a technique based on “springback effect” to keep the porous structure intact after ambient pressure drying. The method involves both the modification of the surface and the strengthening of the network [372]. The patent for this technique was issued in 1996 [373]. This technique involves the reaction of organic compounds with the hydroxyl groups of the internal surface of alcogels after the solvent exchange steps resulting in hydrophobic aerogels. During ambient pressure drying, these organic groups enable the re-expansion of the wet gel without any crack in the structure [374]. Another approach to prepare wet gels capable to keep their porous structure during ambient pressure drying was to age the gels in alkoxide/alcohol solutions to strengthen the microstructure [375] or to use different precursor such as MTMS for the gel preparation [376]. In another study which is carried out by Leventis et al., polymer cross-linked aerogels were prepared which are able to withstand the capillary pressure [377]. Cabot Aerogel is now using this ambient pressure drying technique combined with surface treatment to produce aerogel particles with irregular shapes with the name of Lumira® (formerly Nanogel®).

Although various approaches were undertaken to use ambient pressure drying for the production of aerogels, the preparation of wet gels using this method is more time consuming and a difficult process. Furthermore, there is not any example for organic aerogels at least on a large scale. The most probable reason is that biopolymers are intrinsically hydrophilic.

2.3.2. Freeze Drying

Freeze drying is another possible route to dry the wet gels [371]. Primarily, the solvent inside the pores is frozen by lowering the temperature to under the freezing point of the solvent. Subsequently, the pressure is reduced below the sublimation pressure at this temperature generally by pulling vacuum on the system. The solvent sublimes and is removed from the pores. The solvent thus passes from a solid phase to a gas phase without the formation a liquid-vapor interface. Once the solvent is removed the system is pressurized and the sample is brought back to room temperature.

Freezing might damage the nanostructured gels as freezing could lead to the growth of crystals and development of stress inside the pores leading to a possible fracture of the matrix. If the solvent is water, the situation is more difficult since water expands when it freezes. This may destroy the pore structure. Moreover, if the solvent is an alcohol, another difficulty arises such as achieving the
freezing temperature ($T_f$ of ethanol is 160 K as an example) [378]. There are also other disadvantages such as the lengthening of the aging period to obtain a stable network, or time consuming sublimation steps [371], [378]. Even though it is used on a laboratory scale and there are commercial freeze drying equipment, freeze drying of aerogels is not practiced on a commercial scale.

2.3.3. Supercritical Drying

Supercritical fluid technology is another method which can be used for drying the wet gels. A fluid reaches its supercritical state when it is compressed and heated above its critical temperature and pressure. Supercritical fluids (SCFs) have liquid-like densities and gas-like viscosities [379]. Moreover, the diffusion coefficients in supercritical fluids are higher than in liquids making those materials very promising in various applications. Typical values for thermophysical properties of liquid, supercritical fluid and gas is given in Table 2-5 for comparison of these 3 states.

![Table 2-5 Thermophysical Properties of a liquid, a SCF and a gas [349]](http://example.com/table25.png)

<table>
<thead>
<tr>
<th></th>
<th>Liquid</th>
<th>SCF</th>
<th>Gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm$^3$)</td>
<td>0.6 – 1.6</td>
<td>0.2 – 0.9</td>
<td>(0.6 – 2) × 10$^{-3}$</td>
</tr>
<tr>
<td>Viscosity (Pa·s)</td>
<td>$10^{-3}$</td>
<td>(1 – 9) × 10$^{-5}$</td>
<td>(1 – 3) × 10$^{-5}$</td>
</tr>
<tr>
<td>Diffusivity (m$^2$/s)</td>
<td>$10^{-9}$</td>
<td>(2 – 7) × 10$^{-8}$</td>
<td>(1 – 4) × 10$^{-5}$</td>
</tr>
</tbody>
</table>

The critical properties of various fluids are given in Table 2-6. Among those, supercritical carbon dioxide (sc-CO$_2$) is very attractive as it has relatively easily accessible critical conditions, is nontoxic, environmentally friendly, widely available and cheap.

![Table 2-6 Critical temperatures and pressures of selected solvents](http://example.com/table26.png)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Critical Temperature (K)</th>
<th>Critical Pressure (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>508.1</td>
<td>4.7</td>
</tr>
<tr>
<td>Methanol</td>
<td>512</td>
<td>8.09</td>
</tr>
<tr>
<td>Water</td>
<td>647.3</td>
<td>22.06</td>
</tr>
<tr>
<td>Ethanol</td>
<td>514</td>
<td>6.3</td>
</tr>
<tr>
<td>Carbon dioxide</td>
<td>304.2</td>
<td>7.38</td>
</tr>
<tr>
<td>Ethane</td>
<td>305.7</td>
<td>4.91</td>
</tr>
<tr>
<td>Propane</td>
<td>300</td>
<td>4.26</td>
</tr>
</tbody>
</table>
As a result of these favorable properties, sc-CO$_2$ has been in use on an industrial scale since the early 1970s primarily for extraction of target compounds from solid and liquid matrices. [379]. The sc-CO$_2$ is mainly used for the extraction of caffeine from coffee, extraction of bitter acids from hops, for extraction of spices and essential oils [380].

To show at what scale the supercritical extraction is now operated, a list of the some commercialized supercritical extraction plants with some extractor sizes (if available) is given in Table 2-7. These data clearly indicate that supercritical fluid technology is practiced at industrial scale for a wide variety of purposes.

<table>
<thead>
<tr>
<th>Application</th>
<th>Location</th>
<th>Extractor Size &amp; Quantity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decaffeination of coffee</td>
<td>Kaffee HAG AG, Bremen Germany</td>
<td></td>
</tr>
<tr>
<td></td>
<td>General Foods, Houston, Texas</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hermsen, Bremen, Germany</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Jacobs Suchard, Bremen, Germany</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SKW-Trostberg, Poszzillo, Italy</td>
<td>360 L</td>
</tr>
<tr>
<td>Hops extraction</td>
<td>Pfizer Hops Extraction, Sydney, Nebraska</td>
<td>200L, 500L</td>
</tr>
<tr>
<td></td>
<td>Hopfenextraktion, HVG, Barth, Raiser &amp; Co</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SKW Trostberg, Munchsmunster, Germany</td>
<td>650 L</td>
</tr>
<tr>
<td></td>
<td>Natal Cane By-Products Ltd., Merebank, South Africa</td>
<td>1000 L</td>
</tr>
<tr>
<td></td>
<td>Barth &amp; Co., Wolnzach, Germany</td>
<td>4000L x5</td>
</tr>
<tr>
<td></td>
<td>Hops Extraction Corp. of America, Yakima, Washington</td>
<td></td>
</tr>
<tr>
<td></td>
<td>J.I. Haas, Inc., Yakima, Washington</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pitt-Des Moines, Inc., Pittsburgh, USA</td>
<td>3000L x4</td>
</tr>
<tr>
<td></td>
<td>Carlton, United Breweries, United Kingdom</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NORAC, Canada</td>
<td>250 L x4</td>
</tr>
<tr>
<td>Color extraction / Red</td>
<td>Mohri Oil Mills, Japan Fuji Flavor, Japan</td>
<td>200 L, 300L x2</td>
</tr>
<tr>
<td>Product</td>
<td>Supplier</td>
<td>Capacity</td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>--------------------------------------------------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td>Pepper</td>
<td>Natal Cane By-Products Ltd., Merebank, South Africa</td>
<td>200 L</td>
</tr>
<tr>
<td></td>
<td>Sumitomo Seiko, Japan</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Yasuma (Mitsubishi Kokoki facility), Japan</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Hasegawa Koryo, Japan</td>
<td>500L ×2</td>
</tr>
<tr>
<td></td>
<td>Takasago Foods (Mitsubishi Kokoki facility), Japan</td>
<td></td>
</tr>
<tr>
<td>Extraction of flavors, aroma, spices</td>
<td>Camilli Albert &amp; Louie, Grasse, France</td>
<td>5.8 L</td>
</tr>
<tr>
<td></td>
<td>Soda Flavor Co., Japan</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Guangxia Toothpaste, China</td>
<td>500L ×3, 3500L ×3, 1500L ×3</td>
</tr>
<tr>
<td></td>
<td>Flavex, Rehlingen, Germany</td>
<td>70L</td>
</tr>
<tr>
<td></td>
<td>Flavors extraction Flavex GmbH, Rehlingen, Germany</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Raps &amp; Co., Kulmbach, Germany</td>
<td>500L ×3</td>
</tr>
<tr>
<td></td>
<td>Shaanxi Jia De Agriculture Eng. Co., Ltd., China</td>
<td>500 L ×2</td>
</tr>
<tr>
<td>Nicotine extraction</td>
<td>Philip Morris, Hopewell, Virginia</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nippon Tobacco, Japan</td>
<td>200 L</td>
</tr>
<tr>
<td>Tea decaffeination</td>
<td>SKW-Trostberg, Munchmuenster, Germany</td>
<td></td>
</tr>
<tr>
<td>Hops extraction and spices</td>
<td>SKW-Trostberg, Munchmuenster, Germany</td>
<td>200 L</td>
</tr>
<tr>
<td></td>
<td>Pauls &amp; White, Reigat, United Kingdom</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nan Fang Flour Mill, China</td>
<td>300 L ×2</td>
</tr>
</tbody>
</table>

Even though the primary application area of scCO₂ on an industrial scale has been the food industry due to the nontoxic nature of CO₂ compared to toxic organic solvents, scCO₂ is also attracting increased attention for production of specialty materials. There is already a plant in Denmark developed by Natex for impregnation of wood with biocides.

One of the most important potential applications of supercritical extraction is supercritical drying which is also the third method used for the removal of solvents from the wet gels to obtain aerogels. This drying technique was firstly developed by Kistler in 1930s [381]. Supercritical drying can be
performed not only with supercritical carbon dioxide [382] (low temperature supercritical drying technique or COLD process) [367] but also with organic solvents at their critical state (high temperature supercritical drying technique or HOT process) [383].

High temperature supercritical drying technique involves the use of a supercritical solvent which is usually an alcohol. The process requires high pressures and temperature to reach the supercritical states of those solvents (Table 2-6). The wet gel is placed inside a high pressure vessel with an excess amount of solvent and the vessel is sealed. Subsequently, the temperature in the vessel is increased above the critical temperature of the solvent. After reaching the equilibrium at those conditions, the system is depressurized isothermally (since the temperature is above the critical point of the solvent, there is no vapor-liquid boundary). During depressurization, the fluid is first released in its supercritical state and then in its gaseous state leading to pressure reduction in the system as the solvent is completely removed by diffusion [378]. Finally, the aerogel is taken out after the reduction of temperature to room temperature. The necessity of high temperatures presents a disadvantage of this method as solvents are flammable at this temperature and organic aerogels might be damaged at those conditions. Actually, an autoclave which was filled with supercritical methanol exploded and partially destroyed the buildings of the company Airglass AB in Sweden in 1984 showing the risk of this process for large scale application [378], [383]. Consequently, there is no commercial facility which uses HOT process.

To reduce the time required for the supercritical drying process, “rapid extraction method” was also proposed in which the wet gel was directly obtained inside the high pressure vessel using the conditions of HOT process. This method was primarily investigated by Poco et al. [384] and then also by several research groups [385], [386]. This method is a one-step process from the precursor to aerogels which could be completed in as little as 3 to 8 hours [387]. However, the use of high temperature and high pressures was highly challenging and thus limited the applicability of this technique.

Alternatively, low temperature supercritical drying technique involves the use of supercritical CO\textsubscript{2} which has a low critical point temperature compared to the alcohols filling the pores. The pore liquid can be extracted with CO\textsubscript{2} either in liquid or in supercritical state. It has been shown that this method does not require any further purification steps. The technique also fulfills the standards of quality and safety of industry [388]. In this process, the wet gel is placed inside of a high pressure vessel where it is heated and pressurized with carbon dioxide to a pressure and temperature slightly above the critical point. Pure supercritical carbon dioxide is continuously pumped into the vessel to extract the solvent from the pores. After the drying is complete, the system is depressurized to atmospheric pressure. During this stage, the temperature of the vessel is kept above the critical temperature to prevent the creation of a vapor-liquid interface and then the aerogel is collected from the high pressure vessel.

Among supercritical drying techniques used for the production of aerogels, the low temperature supercritical drying with scCO\textsubscript{2} is the most attractive at small and large scales as the process reduces
the amount of solvent used, is environmentally friendly since it uses CO₂ which is nontoxic, nonflammable and which does not leave any residue in the matrix as stated before.

Consequently, Aspen Aerogels as one of the leaders in this field manufactures a variety of flexible aerogel based products for insulation which are already in the market using this supercritical fluid technology. Their production scheme can be seen in Fig. 2-36. Primarily, the sol is prepared as it is usually done for a native aerogel production. Then, this sol is sprayed onto a roll of dry fiber blanket and heated until the gelation occurs. This blanket is rolled up and then placed inside of a tank filled with an aging solution. The blanket roll is then subjected to supercritical drying with CO₂. Finally, the roll is again heated to remove any solvent remaining inside the blankets.

![Fig. 2-36 Aerogel blanket production process of Aspen Aerogels](image)

Even though there is no industrial scale plant in operation for production of aerogel particles as there is for blankets (Aspen Aerogels), it is certain that the process can be adapted to produce aerogel particles quickly and crack free at an industrial scale. On a laboratory scale, it was shown that the process is applicable to dry nanoporous alginate microspheres with different mean diameters ranging from 25 µm to few hundred microns [225] and silica aerogel microparticles with mean particle diameters ranging from 200 µm to few millimeters [224]. Starch aerogel particles with a mean diameter of around 400 to 800 µm were also dried using the same method [389].

The problem, which might arise when handling nano-sized aerogels while placing them in and taking out of the vessel, was solved at lab scale by using filter paper. Aerogel particles were primarily placed inside a box made out of filter paper and then placed inside the high pressure vessel for supercritical drying. Depressurization rate is also another important parameter for preserving the regular shape of particles and their porous structure as high depressurization rates leading to a fast
cooling of the system could also damage the structure of particles as it does for monoliths. Temperature and pressure of the supercritical drying process are important points to be considered while drying the particles, especially organic ones which might be affected with high temperatures. Moreover, supercritical drying of particles might also be advantageous as the process would require much less time compared to large wet gel blocks since drying is primarily diffusion controlled. In the study of Gonzalez and Smirnova, it was shown that the drying time required for starch aerogel particles (mean diameter 400-800 µm) was about 1 hour compared to the drying time for cylindrical starch aerogels (length: 3.2 cm, diameter: 1.2 cm) which was more than 4 hours [389]. It was also seen that spherical alginate aerogels with a diameter of 4 mm were completely dried in less than 2 hours.

In conclusion, supercritical drying with carbon dioxide at an industrial scale should be preferable over the other methods. The existence of several industrial plants using supercritical extraction technology for various applications (Table 2-7) shows that this process can be scaled up from laboratory to industrial scale. The use of pilot plants would also help to optimize the process before any industrial scale application by investigating the effect of several parameters such as the temperature, pressure and flow rate on the structure of the final material. The use of multiple extractors instead of a single one should also be investigated by cost and efficiency analysis. The extraction could be started consecutively in multiple extractors. While the extraction continues in an extractor, another one could be depressurized and be prepared for the next process. This extraction cycle should then be optimized to manage the duration of each process and to be able to increase the productivity of the plant.

Although supercritical drying is sometimes seen as a time consuming and also a costly process due to high pressure equipment, this misconception can most likely be attributed to the studies in the literature on drying of silica aerogel monolithic blocks which were a few centimeters thick. Drying aerogel particles or powders would reduce this time requirement diminishing the operational costs. Moreover, recent developments on mathematical modeling on the supercritical drying to provide insight into material development, scale-up and optimization of the aerogel manufacturing have shown that the process is open to optimization for cost reduction purposes [382], [382], [390]. Unfortunately, supercritical drying is a complex process consisting of different steps (some of them are also coupled) such as diffusion of CO₂ into the solvent inside the pores; volume expansion of the solvent; spillage of the solvent from the pores into the flowing stream; counter diffusion of the solvent and sc-CO₂ inside the pores; mass transfer of the solvent from the gel-CO₂ interface to the flowing stream; convection in the flowing stream; shrinkage and thus volume change of the gel during the drying process. Thus, developing mathematical models is not an easy task as they should take into account these phenomena as much as possible to be able to consider all the related effects such as pore contraction, pore liquid spillage, solvent volume expansion and solvent flow in the apparatus. Consequently, the model would allow to plan and optimize the large scale production plants towards the desired aerogel properties and costs. One of the key parameters to this end would be the external mass transfer coefficient which might be primarily estimated using the correlations in
the literature developed for extraction from packed beds. Subsequently, new correlations should be
developed using the results of laboratory scale tests. As a result, these correlations might be used to
predict drying times in pilot and industrial scale vessels. Another important parameter in these
models is the diffusion coefficient which is usually suggested to be composition dependent. Using
the Vignes correlation would be a good choice for initial estimates; however, it is also necessary to
measure it or find it based on experimental results of supercritical drying for more accurate
predictions on large scale. Axial dispersion which might be significant in packed beds is also another
important phenomena to consider in those models especially at a large scale. On the other hand, the
effect of other important parameters of the drying process such as temperature, pressure and flow
rate on the drying times could be predicted by these models. These models could also be modified to
mimic various experimental conditions involving different kind of aerogels, extraction vessels with
different sizes and/or different solvents. Thus, if all the important parameters are carefully analyzed,
the model predictions might as well be used to scale up the lab scale experiments and also to
optimize large scale supercritical drying processes reducing the required time and expenses.

There are only few works presented in the world’s publications in which attempts were made to the
supercritical drying process scale up. Semi-continuous supercritical drying technique was proposed
in [391]. Alcogel microparticles suspension in alcoholic medium is introduced into the reactor
through a special nozzle at CO₂ inlet without the reactor opening. Thus, the number of required steps
during the process is reduced. In another study [392] the supercritical drying process was modeled by
CFD and the efficiency criterion was proposed. These studies can provide a starting point for the
supercritical drying process scale up and the industrial technologies development, including
continuous.

The drying process might also be costly if drying times are long as the process would require a lot of
supplies. Thus, it may be more economical to recycle the CO₂ during the run. Efficient separation of
CO₂ and extracted solvent from the high pressure extraction vessel would be needed for recirculating
CO₂ back to the extraction vessel. There are several methods which might be used for this kind of
separation which would depend on the nature of the solvent and its concentration in scCO₂. The use
of a pressure separator after the extraction vessel or a distillation column might be some options. The
concentration of solvent in the CO₂ stream that is recycled back to the extractor should be as low as
possible and thus should not result in a decrease in extraction efficiency due to a reduced
concentration gradient. A good cost and efficiency analysis should be carefully carried out as the
composition of the exit stream also changes through the process which might affect the separation.
Furthermore, an inefficient separation for recycling might increase the costs rather than reducing it.
3. Scale up possibility

3.1. Requirement and bottle neck

Bottlenecks and requirements

As described above in Sections 1 and 2, aerogel production of silica aerogel mats is already carried out at industrial scale, so that commercial feasibility of a sol-gel process in combination with supercritical extraction has been principally shown.

A tentative production scheme for organic aerogel particles is shown in Fig. 3.1 including rough estimates for quantities involved in case of a total volume of 1000 t/a aerogel. In an initial step, gel components are produced in a mixing unit and transferred to a gel particle preparation unit where they are combined to form gel particles. The most suitable technology or technologies for producing particles of the desired size is investigated within the project. After formation of gel particles, a potential ageing step is required to complete the gelation reaction. Insufficient gel ageing could lead to inferior product properties, inferior mechanical stability of the gel, which could lead to gel damage in the process, or release of unreacted contaminants from the gel into the process complicating waste purification and recycling. In the case of a hydrogel precursor, the water contained within the gel needs to be replaced with an organic solvent prior to the supercritical extraction step. This step occurs in a solvent exchange unit. The solvent exchange potentially has to proceed in several steps since hydrogels can collapse in case of direct exchange from water to organic solvent. For both hydrogel and organogel particles, a hydrophobization and/or functionalization step could be required, which could also be carried out in the solvent exchange unit. The obtained organogel particles are then transferred to the supercritical extraction unit where aerogel particles are obtained via supercritical extraction with CO₂. Following extraction, residual organic solvent might need to be removed from the aerogel in a drying step.

From a quantitative point of view, the following steps will be the most challenging:

- Solvent exchange and/or functionalization of organogel: Large volumetric excesses for maintaining concentration gradients and due to slow diffusion processes. Furthermore, for bio-based hydrogels, direct solvent exchange from water to an organic solvent can lead to material collapse so that multi-step solvent exchange across several water/solvent ratios is required further increasing duration and solvent volume. Due to the large volumes involved, purification of the corresponding outlet streams i.e. separating water and unreacted material from solvent will be challenging. Measures for accelerating diffusion and maintaining high concentration gradients should be investigated. Solvents should be chosen in such a way as to avoid azeotrope formation with water in order to both reduce water content in organogels and to simplify solvent purification.

- Purification of CO₂ outlet after supercritical extraction due to large solvent volume

- Recompression of large amounts of CO₂ after supercritical extraction and solvent separation
• Gel ageing: Long ageing times lead to large intermediate storage volume for ageing.

• Production of small gel particles (diameter <50 µm) in sufficient quantity and quality (monodispersity).

• Final drying step (solvent emissions, particle drying technology)

Furthermore, the following general critical aspects need to be considered:

• Contaminants that are released from hydro-, lyo- and aerogel particles could form complex mixtures with unknown effects on plant equipment (corrosion, explosion protection) and purification behaviour (multi-phase mixtures) and need to be avoided. Ideally, the gel formulations need to be tuned in such a way that no contaminants are released into any of the process outlet streams. Outlet stream purification is also critical for recycling efficiency and thus economic viability (solvent and CO₂ recycling). CO₂ losses could also be critical for lifecycle or sustainability analyses. Waste water from hydrogel production needs to be recycled or more purified before release into the environment.

• In the case of food products, the process needs to comply with the respective requirements thus increasing investment and process cost.

• Particle handling (transport) within and after the process needs to be considered.

• Explosion protection: Due to the use of organic solvent and the production of fine particles (µm), the process equipment will likely require explosion protection, which increases investment cost.

The gel material should fulfill the following requirements:

• For material handling, the following points should be addressed:

  o Hydro-, lyo and aerogel particles should be spherical to facilitate particle handling processes (pumping etc.).

  o Hydro-, lyo and aerogel particles should not aggregate/clump (particle handling).

  o Viscosities of starting materials should match in order to enable sufficient mixing.

  o Hydro-, lyo and aerogel particles should be mechanically robust and self-supporting since very likely reactors will be oriented vertically to simplify particle transport (entry through top, exit through bottom).

• Investment cost could be reduced by the following aspects:

  o The hydrogel should gel and age as fast as possible to avoid additional ageing units or to reduce reactor usage.
The solvent exchange from hydro- to organogel needs to be as fast as possible in as few steps as possible i.e. the gel should tolerate solvent exchange well (critical).

The hydro-, lyo- and aerogel should not release contaminants into waste streams (water, solvent or CO₂) in order to avoid additional purification steps (critical). Furthermore:

- Ingredients or wash streams should not contain corrosive materials to reduce equipment cost (e.g. stainless steel)
- Ingredients or wash streams should not contain toxic materials to avoid corresponding safety measures.
- Solvents with low explosion class/high flash point should be chosen if possible to avoid corresponding explosion protection (investment cost).
- Hydro-, lyo and aerogel should exhibit a certain temperature resistance, since most processes can be accelerated via heating (e.g. solvent exchange, supercritical extraction).

Fig. 3-1: Potential production process for organic-aerogel particles.
3.2. Conclusion on the potential compatibility of processes with scale-up and aerogel chemistries within the Nanohybrids project

Table 3-1 Overview about the processes applicable for production of gel particles (to be later dried to obtain an aerogel)

<table>
<thead>
<tr>
<th></th>
<th>JetCutter</th>
<th>Emulsion gelation</th>
<th>Spraying</th>
<th>Dripping</th>
<th>Vigorous agitation during gelation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Particle size</strong></td>
<td>0.2-10 mm</td>
<td>10-500 µm</td>
<td>1 – 500 µm</td>
<td>0.2-10 mm</td>
<td>1-100 µm</td>
</tr>
<tr>
<td><strong>Scale of the process (productivity)</strong></td>
<td>Technical scale (several kg/hour)</td>
<td>Technical scale possible</td>
<td>Productivity depends on the nozzle</td>
<td>Lab</td>
<td>Technical scale possible</td>
</tr>
<tr>
<td><strong>Needs of additives</strong></td>
<td>No</td>
<td>Yes: surfactants, oil</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td><strong>Special advantages</strong></td>
<td>Versatile systems, simple, commercially available apparatus; monodispersed particles</td>
<td>Simple apparatus</td>
<td>Particle size can be regulated by stirring and surfactants</td>
<td>Different sizes possible depending on the nozzle</td>
<td>Very simple</td>
</tr>
<tr>
<td><strong>Specific problems</strong></td>
<td>Not suitable for small particles</td>
<td>Washing of oil; Polydispersed particles</td>
<td>Clogging, polydispersed particles</td>
<td>Limited productivity</td>
<td>Batch process; Irregular shapes</td>
</tr>
<tr>
<td><strong>Possible to use for polysaccharides?</strong></td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Possible to use for organic polymer aerogels?</strong></td>
<td>Unlikely</td>
<td>Yes</td>
<td>Unlikely</td>
<td>Unlikely</td>
<td>Yes</td>
</tr>
<tr>
<td><strong>Main know how in NanoHybrids consortium</strong></td>
<td>DLR</td>
<td>TUHH + MUCTR (high pressure homogenizer)</td>
<td>MUCTR</td>
<td>KOC ARMINES</td>
<td>UPAT, UoA</td>
</tr>
</tbody>
</table>
3.2.1. Dripping

Dripping process, i.e. making beads by dripping a solution into a bath in which polymer will either gel or coagulate, with a syringe or pipette, is an easy way to study and understand the influence of various parameters (polymer concentration, solvent, solution viscosity, parameters of the bath) on the formation of beads – their size, shape and morphology. This is an inevitable step when a new system is prepared and would make a background for further up-scaling steps.

On a larger scale, “dripping” method must be extended to spraying, jet-cutting or atomisation. Certainly, the processing parameters will have to be adjusted according to the method used.

In order to apply those methods to synthetic polymer aerogels, the gelation process has to be fast enough and be completed within the short time interval between droplet formation and collection. The reaction of organic monomers at sufficiently low concentrations to form gels suitable for aerogels is a rather slow process, which typically takes from minutes to hours to complete, even at elevated temperatures.

3.2.2. Jet cutting

The JetCutting process has been successfully employed for the preparation of micrometer and millimetre sized beads. Especially for biopolymer solutions of high viscosity the JetCutting process is recommended in terms of monodispersity and productivity. The productivity in the range of hundreds of kg per hour seems adequate considering the amount of beads needed for a pilot plant. In addition to that the JetCutter technology is already approved for large scale by GeniaLab®. Even though the JetCutter seems to be an appropriate choice for biopolymer solutions of high viscosity it lacks in terms of productivity for solutions of viscosities lower than 200 – 300 Pa.s. The reason is increasing spray loss with decreasing viscosity.

Jet cutting is a very high throughput process where the time between formation and collection of sol droplets is very short. The gelation process has to be completed within that time interval. Although the droplet receiving bath can be operated at elevated temperatures, and, conceivably, droplets can be heated ‘in-flight’ in order to accelerate the gelation reaction, it is unlikely that gelation of polyureas, polyamides and polyurethanes can ever become fast enough for jet cutting to become a viable approach to those types of aerogel powders.

3.2.3. General conclusions and recommendations on the emulsion gelation

In this method, agitation creates steady-state conditions, whereas sol-droplets are kept in suspension indefinitely, or as long as needed for the gelation reaction within the sol-droplets to be completed. Therefore, the success of this method for making isocyanate-derived polymeric aerogels is predicated upon choosing a solvent for the continuous phase of the suspension that is not miscible with the sol. For a typical DMF-based sol, that continuous phase might be based on a hydrocarbon like hexane.
Furthermore, based on the information presented above and requirements catalogue (Deliverables 1.1 and 1.2), the following conclusions and recommendations can be drawn:

1. The smallest particle size for the emulsion gelation is 1 – 5 µm, the largest is up to 1500 µm. Spherical particles can be obtained in most cases. Thus, these values are in the range of what is required for food applications (see D.1.2, Section 5). As for adsorption applications, the particle size are too small to be used as humidity adsorbents in drying units (D 1.1, Section 2), but matches the range required for filtering devices for personal protection (D 1.1, Section 3).

2. Influence of process parameters should be carefully examined using physical and/or design of experiments approaches. Necessary physico-chemical data (densities, viscosities, partition coefficients, gelation rates; their temperature dependence) should be acquired prior to process design.

3. All three emulsion gelation methods allow for the preparation microparticles from project-relevant polymers as supported by above given examples. Preference should be given to the processes which involve the minimal number of reagents and allows for possible simple particle recovery and regain of oil and organic solvents.

4. Design of the emulsification unit should be thoroughly documented. High sensitivity of the particles characteristics is expected, thus process parameters should be carefully controlled.

5. Functionalization should be considered as a part of the integral process. Monolithic samples should first be tested to demonstrate that functionalization have a desired effect.

3.2.4. Disruption of gelation by vigorous agitation

This method of forming aerogel particles can be considered as a simplification over the emulsion gelation process in that it does not use a second immiscible solvent as a continuous phase. In fact, it can be applied with any organic, inorganic and biopolymer gel. In the latter case, the gel must be well formed first. It can be also applied to all hybrid gels that are formed via a one-step, one-pot process. Fig. 3-2 demonstrates the setup for a 1L scale production of wet-gel polyurea (PUA) powder by the method of vigorous agitation; it also includes picture of a silicon carbide aerogel powder synthesized by this method.
Fig. 3-2 Left: 1L setup for preparation of PUA aerogel powder (Paraskevopoulou, Leventis, unpublished results). Right: An example of a PUA aerogel powder prepared by utilizing the method of vigorous agitation.

The particle size depends on the rate of stirring, and in some cases—most notably with PUA—the rate of agitation may also affect the network morphology within particles, changing for example from fibrous to particulate. Like the emulsion gelation process, this is a batch process, but unlike the former it yields spheroidal rather than perfectly spherical particles. Fig. 3-3 shows such a PUA aerogel particle obtained by vigorous agitation of an acetone sol consisting of an aliphatic triisocyanate (Desmodur N3300), water and triethylamine as catalyst.

Fig. 3-3 SEM at two different magnifications of a particle of a PUA aerogel powder made by disrupting gelation of an acetone sol with vigorous agitation. BET surface area: 162 m² g⁻¹. (Paraskevopoulou, Leventis, unpublished results).
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