APPLICATION REPORT

High pressure reactor
Chemical Extraction / Purification, Nanotechnology and Chemical Synthesis

Supercritical Fluids
Green chemistry with highpreactors

The fields of application for Berghof highpreactor are chemical reactions proceeding at increased temperature and pressure demand with a maximum at 260°C/200bar which can be found in various sectors of chemical engineering. Ideal reaction conditions are realized due to the modern and diverse design of highpreactor. In the present series of highpreactor Application Reports an overview on selected research topics is given. The intention is not to provide exhausted scientific information but an introduction to various topics for our customers. All application reports are based on scientific articles published mainly by Berghof highpreactor users. Original literature is cited at the end for further reading.

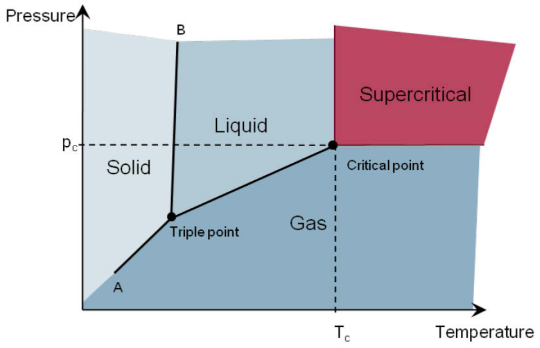
1 Supercritical Fluids

With respect to sustainability and green chemistry, there is a worldwide request for processes being independent from hazardous, expensive, and environmentally harmful organic solvents. Supercritical fluids have the potential of being a gentle alternative that can substitute or eliminate most of the commonly used organic solvents. Moreover, due to the outstanding properties of supercritical fluids, many important industrial processes can be run more cost-effective.

In general, a supercritical fluid (SCF) can be defined as any substance at temperature and pressure above its critical point.

The phase diagram depicts the relationship of pressure (p), temperature (T) and the state of aggregation at certain conditions. The vapor pressure boundary curve separates liquid and gas phase (A) whereas the sublimation boundary curve separates solid and liquid phase (B). The curves meet at the so-called triple point where all three phases are in equilibrium under certain p and T conditions. In the phase diagram, the boundary curve between liquid and gas state is finite and characterized by a maximum (critical point). In contrast, the solid-liquid boundary curve is characterized by an infinite run of the curve.

As temperature and pressure increase, the liquid density decreases and gas density increases. At the near critical point the properties of liquid and gas phase start to converge. Finally, at the critical point, liquid and gas phase become one homogenous phase. A distinction between the two states is not possible anymore.



Phase diagram

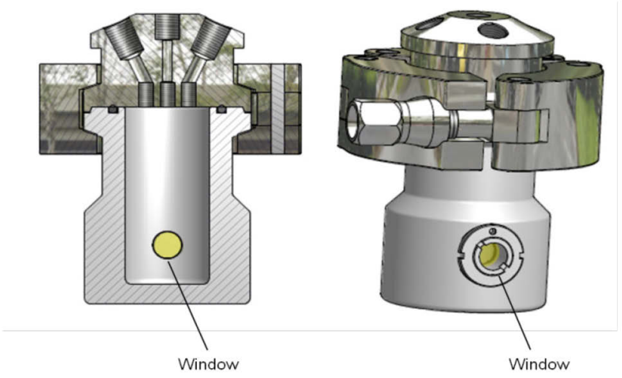
A component whose temperature reaches the critical point is neither in gaseous nor in liquid phase. Consequently, fluids in the supercritical region exhibit outstanding properties similar to those of gases or liquids, respectively. For example, a higher density (comparable with organic liquids) is attended by an increased solubility, low viscosity, decreased surface tension, and higher diffusion coefficients which favor mass transport processes.

Properties of different physical states

Physical state	Density [g/cm^3]	Viscosity [g/cm/s]	Diffusivity [cm^2/s]
Gas p=1bar, T=15-30°C	10^{-3}	10^{-4}	0.1-0.4
Liquid p=1bar, T=15-30°C	1	10^{-2}	10^{-6}
Supercritical Fluid $p=p_c$, $T \approx T_c$	0.2-0.5	10^{-4}	10^{-3}

Modification of temperature and pressure enable further “fine-tuning” of many properties of SCF. For instance, due to pressure dependence of the dielectric coefficient (ε), the selectivity of chemical reactions can be controlled. SCF can be completely and residue-free removed from the process which additionally makes them highly attractive. By post-reactional depressurization, SCF lose their solvent properties and can be removed in gaseous state. Considering this, cost-intensive solvent separation and recovery can be avoided.

There is a growing interest in applying SCF in many fields of chemical engineering (e.g. pharmaceutical industry, food industry, chemical industry, restoration). Berghof highpreactor can be used for varying processes performed at supercritical conditions. Mostly, reactions using supercritical carbon dioxide, supercritical ammonia or subcritical water are performed. But nevertheless, Berghof highpreactor are also suitable for a couple of other substances where reactions are performed at increased temperature and pressure demand with a maximum at 260°C / 200 bar. Moreover, the modular design of highpreactor enables customer specific solutions. For example, phase transition of supercritical fluids can be observed by using a window reactor. For this, the stainless steel reactor contains windows of various materials, e.g. sapphire or quartz glass, depending on customers’ requirements.



Design drawing of a Berghof high pressure reactor with window

Within the scope of this report, just the most important reactants (CO2, NH3, H2O) are considered.

Critical Parameters

Substance	T_c [°C]	p_c [bar]	p_c [g/cm^3]*
Carbon dioxide	31.1	72.8	0.468
Ammonia	132.4	111.3	0.235
Water	374.2	217.6	0.325
Methanol	239.4	79.78	0.272
Propene	91.9	45.6	0.233
Butane	151.97	37.34	0.228
Ethane	32.3	48.2	0.203
Hydrogen sulfide	100.4	88.2	0.31
Sulfur dioxide	157.7	77.8	0.524
Ethanol	240.9	60.57	0.276
Sulfur hexafluoride	45.6	37.1	0.734

*Density

1.1 Supercritical Carbon Dioxide

Supercritical CO2 can be regarded as the most popular green solvent. It is characterized by relative low critical data (T_c=31 °C, p_c=73 bar). Moreover, it shows low viscosity, high diffusivity and low surface tension enabling easy penetration through porous material. SC-CO_2 offers a lot of industrial advantages, e.g. it is environmentally benign, non-toxic, non-flammable, non-corrosive, easy available, it operates under mild conditions and is relatively cheap. Residual CO_2 can be easily separated from the process and reused. Therefore, processes using SC-CO_2 are low energy consuming and do not contribute to greenhouse emission.

The most famous process using SC-CO_2 is the extraction of caffeine from unroasted coffee beans (decaffeination). Since 25 years it is the method of choice and successfully replaced the employment of organic solvents (mainly benzene or methylenchloride). But, there are many more application examples where SC-CO_2 is applied in food industries.

→ De-alcoholization of beverages
→ De-fatting of food
→ Parboiled rice by SC-CO2
→ Extraction of tocopherole for food and pharma industries

The role of SC-CO_2 in biomedical application is constantly growing. Improvements of therapeutic strategies depend on target drug delivery. Researchers are focused on synthesis strategies obtaining possibilities to control the selectivity, size or morphology of nano-sized particles. Most of the existing approaches are limited by severe reaction conditions also affecting the cellular uptake and metabolism. Novel techniques by using SC-CO_2 offer clean and effective methods for drug preparation. Recently, SC-CO_2 also became a hot topic in biomedicine where it is used in tissue engineering.

In the wide field on nanoparticle preparation, SC-CO_2 is suitable for catalytic reactions. One possibility to synthesize nanoparticles represents hydrogenation (see also application report “Biomass derived chemicals and applications”). But, hydrogen alone shows limited solubility in organic solvents. In combination with SC-CO_2 as a carrier, hydrogen has improved mass transfer rates. Therefore, it is transported much easier into liquid phase which enables the synthesis.

The adjustable density, depending on the variation of pressure and temperature, enables to imitate organic solvents whose polarities range from n-pentane (low density) to pyridine (high density). Furthermore, due to high diffusivity, it can easily enter active centers in e.g. metal nanoparticles.

Another promising approach presents the so called carbon dioxide explosion (see also application report “Biofuels” and “Biomass Treatment”). Pretreatment of lignocellulosic biomass is the crucial step to obtain cellulose and its monosaccharide components (saccharification), which can be economically fermented into ethanol. Here, the organic raw material is kept at pressure of 74 bar at around 31 °C under supercritical CO_2 for minutes to hours. The lignocellulosic structures are penetrated by steam under pressure leading to condensation of the steam and wetting of the material. Following, acetyl groups of the hemicellulose fraction hydrolyse by forming organic acids which in turn catalyze the depolymerization of hemicellulose. During the sudden pressure release, the moisture within the lignocellulosic structures evaporates immediately. The expansion of the vapor exerts shear forces on the structures leading to breakdown of the lignocellulosic structures.

1.2 Supercritical Ammonia

Ammonia passes into a SCF at pressure and temperature of 111bar and 132 °C, respectively. Within this range the thermophysical properties are similar to those of supercritical water.

Researchers take advantage of this by performing reactions which are not working well in supercritical water. Furthermore, chemical reactions can be performed under milder conditions and enable highly selective conversions.

Ammonia vs. Supercritical Ammonia

Parameter	Ammonia	Supercritical Ammonia
T [°C]	-33	132.4
p [bar]	1	111.3
ρ [g/cm3]*	0.682	0.235
ε**	16.9	3
pKa***	33	-
η [mPa*s]	$22.5*10^{-2}$	$23.9*10^{-3}$

*Density
**Dielectric constant
***Acid dissociation constant

Mostly, supercritical ammonia is used as a solvent in various chemical syntheses. Advantageous is the relatively low temperature and pressure demand in comparison to classical synthesis routes. For instance, it is used to selectively produce metal nitrides or to support silylation reactions.

Additionally, supercritical ammonia is an important reagent for the synthesis of nanoparticles. Due to the outstanding properties, it enables the control of size, morphology and chemical composition of materials.

Classically, amines can be synthesized using azides as precursors. Due to the toxicity of the substance alternative methods are favored. Ammonolysis reaction using supercritical ammonia results in good yield and represents a relatively environmental friendly method which is performed under mild conditions.

Benzene derivatives are an important additive in polymer production or also colour industry. Conventionally, they are synthesized by a complex hydration reaction. The direct ammonolysis with supercritical ammonia offers an interesting alternative for the functionalization of aromatic compounds.

It has already been mentioned, that the treatment of lignocellulosic raw material is an important prerequisite for biofuel production. Beside SC-CO_2, also ammonia can be applied. During the so-called ammonia fiber explosion (AFEX) the lignin content is reduced and hemicellulose is partially removed while cellulose becomes decrystallized. Biomass is exposed at alkaline pH to liquid ammonia at 90-120°C for several minutes. Afterwards, the pressure is suddenly released. The structure of the biomass is changed, resulting in enhanced water holding capacity and digestibility. However, due to remaining residues of lignin fragments on the cellulosic surface, subsequent water washing is necessary what increases the amount of waste water. Liquid ammonia, used during the process, can be recovered and reused to 99%. Here, the cost for ammonia and the recycling of the reagent are a major drawback. Furthermore, up to now, AFEX pretreatment was shown just to be efficient for lignocellulosic material with low lignin content (see also application report “Biomass treatment”).

1.3 Supercritical Water (liquid hot water)

Hydrothermal processes using water near or above the critical point are of great interest and are highly attractive for manifold applications. It has been shown, that many substances change its properties when changing temperature and pressure. But, water holds a special position among all other SCFs.

Water vs. Supercritical Water

Parameter	Water	Supercritical Water
T [°C]	25	374.2
p [bar]	1	217.6
ρ [g/cm3]*	0.997	0.325
ε**	78.5	5.9
pKa***	14	19.4
η [mPa*s]	0.89	0.03

In general, water is a polar molecule whose hydrogen bond network opposes to align in an applied electric field. Therefore, water is characterized by a relatively high dielectric constant of 79 at 25 °C. When increasing the temperature, molecules move more intense and hydrogen bonds disrupt. The heat capacity increases two to six-fold since more energy has to be supplied to break the hydrogen bonds. The anomalous behavior of water near or above the critical point is mainly caused by the breakage of hydrogen bonds and their proximate ability to move freely. Additionally, the density of water at increased temperatures is lowered, resulting in greater spacing between water molecules and less effective hydrogen bonding. Hence, the dielectric constant decreases with increasing temperature. At 220 °C the dielectric constant decreases to 33, like methanol at room temperature. A further increase of the temperature leads to further decrease of the dielectric constant, until at the critical point it amounts to 6. These values are typical for nonpolar hydrocarbon solvents, e.g. hexane. In the temperature range of 50-100 °C water can solve polar compounds. But at increased temperature (>100 °C) nonpolar compounds can be extracted.
The dissociation constant (pK) can be defined as the product of hydronium ($H3O^+$) and hydroxide (OH^-) ions. With increasing temperature the dissociation constant increases (14 at 25 °C vs. 19 at 374 °C) which affects drastically the solvation properties of water. The concentration of $H3O^+$ is 100 times larger than in water at 25 °C causing a lower pH value. Therefore, water near or above the critical point can act as a strong acid.

Due to the strong corrosive environment, working with special alloys is normally essential. Berghof highpreactor are stainless steel reactors protected from bases and acids with a several millimeter thick PTFE lining. PTFE is characterized by its outstanding chemical resistance against many corrosives. No special and expensive alloys, like Hastelloy have to be used what drastically reduces the initial cost. A further advantage is the complete PTFE lining which assures a hermetically sealing of the reactor. All parts being in contact with the liquid phase are protected from corrosive substances. Berghof highpreactor can be employed for reactions mainly in the subcritical range up to 260 °C.

PTFE-lining of Berghof reactors offers protection against corrosive media

Due to the anomalous behavior of water near or above the critical point it is a useful reagent or catalyst in organic synthesis. Additionally, using liquid hot water is an environmentally friendly and economic process for the detoxification and remediation of organic waste. Since the human population keeps on growing and industrialized countries are rapidly developing, the search for highly effective and “green” methods for waste treatment will remain a hot topic in the future.

1.4 Application examples

SCF expose outstanding properties which make them downright attractive for various applications. Many of the developed processes are already successfully performed on commercial scale. But nevertheless, the improvement and further development of novel approaches in terms of sustainability and green chemistry, has a high potential for future scientific work.

For most applications, researchers take advantage of the solubility of SCFs in gaseous and condensed phase. At increased temperatures, SCFs show reduced viscosity and reduced surface tension making them a useful tool for the penetration into small pores and structures. Due to plentiful application examples, just a small overview of recent developments is given.

Supercritical Fluid Extraction (SFE)

Supercritical fluid extraction can be regarded as the most commonly used method. It is the method of choice for manifold applications in food industry where extracts can be obtained without degradation (e.g. flavors).

The process can be described as the separation of extract and matrix by using SCF (mainly CO_2) as extracting solvent. It comprises the extraction of natural materials, e.g. decaffeination, defatting, producing extracts from hops, fruits or spices, but as well the treatment of other solids, e.g. cork treatment for wine bottles. Normally, SCF flows through a fixed bed containing the solid substrate. Following, the solvent is removed from the extract by reducing the temperature and pressure. Additionally, extraction from solids can be performed by desorption, drying or cleaning. For instance, aerogels can be obtained by SFE with application as catalyst or carriers for pharmaceuticals. Moreover, SFE is a suitable method for detoxification, e.g. biocide contaminants can be gently separated from wood.

Impregnation

The impregnation of materials using SCF can be applied in various industrial sectors. A fast and easy penetration into solid materials makes them highly attractive in wood and textile industry. For instance, wood can be easily impregnated causing functionalization and target property changing. Furthermore, textiles can be dyed or leather can gently be tanned. Here, SCF offers an environmentally friendly and economic efficient method as treatment times, water consumption and the subsequent pollution are reduced. But nevertheless, up to date dyeing of natural fibers cannot be efficiently performed on industrial scale. Supercritical carbon dioxide seems to be not powerful enough to break hydrogen bonds which hinders the diffusion of dyes into the structures. Berghof highpreactor can support this sector to find appropriate solvents or to improve already established techniques.

Material Science

SCFs can be used in material science to functionalize sorbent with different catalyst, chelating agent or pharmaceutical active substances. Specific properties of microporous structures (e.g. zeolites, activated carbon, Al_2O_3) can be achieved by impregnation using SCFs. Mostly, the treatment is performed in liquid phase by dip coating or spraying. A homogeneous dispersion of the fluid can be expected due to its improved surface tension properties. Drying can be neglected since the fluid returns into gas phase upon pressure release. The technique reveals a high potential for applications with thermolabile or oxidation sensitive materials.

Nanotechnology

SCFs are applied to synthesize special functionalized nanostructured materials, e.g. nanorods, nanowires or polymers impregnated with nanoparticles. The structures exhibit enhanced properties making them suitable for microelectronics, energy conversion, sensing devices, microoptics or in catalysis.
Moreover, pharmaceutical industry benefits from the possibility to synthesize particles with target design and properties.

Chemical Synthesis

The outstanding properties of SCFs make them a powerful tool to replace organic solvents in chemical processes.

For instance, SCFs facilitate polymer processing by reducing the viscosity and interfacial tension of the material.

SCF can act as an antisolvent during crystallization processes by reducing the solubility of substances in solvents. Small variations in temperature and pressure enable the control of particle size and morphology and thus the preparation of desired structures. The solvent can easily be separated by reducing the pressure what reduces substance impurities. The technique has high potential for the preparation of precursors for high-tech ceramics (see also application report “Solvothermal / hydrothermal synthesis and application examples”) and pharmaceutical substances with narrow particle size distribution.

The application of SCFs for chemical synthesis can increase the selectivity of the product. Here, SCFs act as solvents whose properties, e.g. diffusivity or mass transfer can be adjusted according to the desired synthesis strategy. The use of expensive and toxic solvents is needless and higher yields can be achieved.

There are manifold already commercially performed SCF applications. But, the call for sustainable synthesis strategies will be intensified in the next year’s opening up a huge potential for SCF research. Berghof highpreactor support ongoing research for reactions with a pressure and temperature demand with maximum at 260 °C / 300 bar. Especially, researchers take advantage of the complete PTFE lining. The excellent chemical resistance of PTFE against most acids and bases enables safe and easy working under extreme corrosive conditions. The use of expensive special alloys is not necessary.

2 Literature Overview

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