Supercritical Solvents (CO₂, H₂O)

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Supercritical Fluids

- Above 31.1 °C and 73 atm ($T_{cr}$ and $P_{cr}$) carbon dioxide behaves as a supercritical fluid and shows properties of both a liquid and a gas.
- It fills the container, like a gas, and dissolves substances like a liquid.
- Once the critical temperature and pressure have been reached the two distinct phases of liquid and gas are no longer visible. The meniscus can no longer be seen. One homogenous phase called the "supercritical fluid" phase occurs.

With an increase in temperature the meniscus begins to diminish.

The liquid density falls due to expansion and the gas density rises as more of the substance evaporates.
Comparison of Physical and Transport Properties of Gases, Liquids and SCFs

<table>
<thead>
<tr>
<th>Property</th>
<th>Gas</th>
<th>SCF</th>
<th>Liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density ($g \cdot cm^{-3}$)</td>
<td>$10^{-3}$</td>
<td>0.1-1</td>
<td>1</td>
</tr>
<tr>
<td>Viscosity ($g \cdot cm^{-1} \cdot s^{-1}$)</td>
<td>$10^{-4}$</td>
<td>$10^{-3}$-$10^{-4}$</td>
<td>$10^{-2}$</td>
</tr>
<tr>
<td>Diff. Coeff. ($cm^2 \cdot s^{-1}$)</td>
<td>$10^{-2}$-$10^{-1}$</td>
<td>$10^{-4}$-$10^{-3}$</td>
<td>$10^{-5}$</td>
</tr>
</tbody>
</table>
A supercritical fluid (SCF) is any substance at a temperature and pressure above its critical values. Critical temperature is the temperature above which a pure gas cannot be liquefied regardless pressure values. They have properties intermediate between gases and liquids, which can be controlled by both temperature and pressure. Typical critical data are:

<table>
<thead>
<tr>
<th>Substance</th>
<th>$T_c$ (°C)</th>
<th>$P_c$ (bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>31.1</td>
<td>73.8</td>
</tr>
<tr>
<td>Fluoroform</td>
<td>25.9</td>
<td>48.2</td>
</tr>
<tr>
<td>Water</td>
<td>374.0</td>
<td>220.6</td>
</tr>
<tr>
<td>Ammonia</td>
<td>132.4</td>
<td>113.2</td>
</tr>
<tr>
<td>Ethane</td>
<td>32.2</td>
<td>48.7</td>
</tr>
<tr>
<td>Methanol</td>
<td>239.5</td>
<td>8.08</td>
</tr>
</tbody>
</table>

CO$_2$ is unpolar $\therefore$ high volumes and pressure are necessary to liquefy (high energetic costs). Co-solvents are added to increase the polarity.

Water becomes SC at higher temperatures and pressures than CO$_2$. 

Why Use sc-Fluids?

- Increased mass transport
- Gases are totally miscible
- No surface tension
- Excellent for infusion and extraction
- Inert and non-toxic
- Inexpensive fluids
- Environmentally compatible
- Solvent is tuneable with pressure

P.G. Jessop, T. Ikaraya and R. Noyori. Science, 1995, 269, 1065: see also:
Carbon Dioxide (CO₂)

- Similar advantages to water:
  - Natural, cheap,
  - Plentiful (0.04% of atmosphere and now rising!)
  - Available in >99.9% pure form, €90/$110 per 25 kg.
  - By-product of brewing, ammonia synthesis, combustion
  - Non-flammable
  - TLV = 5000 ppm

- Supply chain and related technology already established.
- Non-toxic and properties well understood
  - Asphyxiant at high concentrations (excludes oxygen from lungs)
- Easily removed and recycled, and can be disposed of with no net increase in global CO₂
  - Simple product isolation by evaporation, to 100% dryness.
- No solvent effluent, renewable
- Potential for product processing (extraction, particle formation, chromatography, etc.)
Pressure-Temperature Phase Diagram for CO₂

- Solid
- Liquid
- Boiling line
- Melting line
- Gas
- Supercritical fluid

Pressure (bar)

Temperature (°C)

Pressure-temperature phase diagram showing the phase transitions of carbon dioxide. The critical point (CP) is indicated with the critical pressure (P_c = 73.8 bar) and temperature (T_c = 31.06°C).
Pure CO$_2$ PTV Diagram and Projections
Other Advantages of scCO$_2$

- Carbon dioxide is a **non polar molecule** since the dipoles of the two bonds cancel one another.

  ![CO2 structure](O=C=O)

- **High compressibility**
  - Large change in solvent properties for relatively small change in pressure – infinite range of solvent properties available (low viscosity and zero surface tension)
  - Ability to tune solvent to favour a particular reaction pathway simply by optimising temperature or pressure (tuneable density)

- Cosolvents can further **modify solvent properties** (“Tunable” properties)

- **High diffusivity** offers potential for increase reaction rates.

- **Potential for homogeneous catalytic processes.**
  - High solubility of light gases, some catalysts and substrates; bring all together in single homogeneous phase (*hydrocarbons and derivatives with less than 20 carbon atoms, but not big molecules, i.e. oils, waxes, fats, polymers, proteins, sugars*)

- **Inert to oxidation;** resistant to reduction
  - Excellent medium for oxidation and reduction reactions.
Change of Solvent Power of CO₂ from Pressure

Density (g·m⁻¹)

Hildebrand Parameter (cal cm⁻³)⁰.₅

310 K = 37 °C
320 K = 47 °C
330 K = 57 °C

Pc Pressure (bar)
Problems using scCO$_2$

- Moderate pressures required
  - Standard HPLC apparatus used in lab, reactors made of stainless steel, many commercially available.
  - Can be expensive for large scale work

- Weak solvent
  - Relatively non-polar, but high quadrupole moment. Use of co-solvents (MeOH, MeCN, THF, toluene)
  - CO$_2$ exhibits a low dielectric constant, low polarizability/volume
  - Simple modification of reagents to improve solubility

- Energy considerations
  - Compression of CO$_2$ requires energy
  - Energy consumption reduced minimal decompression and recycling

- CO$_2$ is a Lewis acid - reacts in the presence of good nucleophiles
  - Often reversible (acid behaviour in H$_2$O), can be exploited synthetically
Current Consumer Related Applications of CO₂ Technology

• Carbonated drinks
• Leavening agents in baking
• Solvent extraction
  • Decaffeinating coffee and tea
  • Extracting bitterness from hops to make beer
  • Defatting cocoa powder
  • Extracting spices and aromatic plants
• Surface coating
• Fumigation (1% in air will eliminate pests in greenhouses)
• Degreasing and dry cleaning applications
• Welding
• pH control (e.g. effluent streams, pulp and paper mills)
• Refrigeration (dry ice, mechanical systems)
• Fire extinguishers
• Life jackets
Can sc-Fluids be Scaled up?

One of the biggest chemical reactions (polyethylene production) is carried out under SC conditions.

Natural products such as Caffeine and hops extract are obtained using scCO₂.

Spray painting process use scCO₂ to reduce VOC emissions (>’80%).

Known are also some continuous synthesis which use sc-fluids with capacity of up to 1000 tonnes per year.

But Also:

- Textile dyeing
- 157 nm photoresist processing
- Self assembly
- Nanoparticles

http://www.thomas-swan.co.uk/
SOAKING green coffee beans in water doubles their size, allowing the caffeine to dissolve into water inside the bean.

CAFFEINE REMOVAL occurs in an extraction vessel. Caffeine diffuses into this supercritical carbon dioxide, along with some water.

DECAFFEINATED BEANS at the bottom of the vessel are removed, dried and roasted.

RECOVERY of dissolved caffeine occurs in an absorption chamber. A shower of water droplets leaches the caffeine out of the supercritical carbon dioxide.
Particle Formation

- Two main complementary techniques:
  - RESS – Rapid expansion of supercritical solution
  - SAS – Solvent/AntiSolvent Precipitation

- Allow for the processing of a wide range of materials into solid phases with useful properties and morphologies, e.g. pharmaceuticals, protein macroparticles, explosives.

Dry Cleaning with scCO₂

- Current methods use perchloroethylene

  1.5 Million tons used per year (North America)
  - Hazardous air pollutant and suspected carcinogen
  - Contaminates drinking water supplies
  - Contributes to photochemical smog
  - <5% recycled
  - Requires heating to remove solvent residues
  - Characteristic odour

- New process use liquid CO₂
- Requires surfactant (to be recycled)
Dry Cleaning with scCO$_2$

- No unpleasant odors
- No heat required for drying – energy efficient and kinder on clothes
- Possible tax credits and reduced regulatory monitoring
- Utilizes same CO$_2$ used by food and drink distributors
- Related technology also used for degreasing (e.g. metal parts), semiconductor photoresist removal and spin coating.
- Is a relevant byproduct of biorefinery industry
Surfactants

- A molecule that contains a polar portion and a non polar portion.
- A surfactant can interact with both polar and non polar molecules.
- A surfactant increases the solubility of the otherwise insoluble substances.
- In water, surfactant molecules tend to cluster into a spherical geometry
  - non polar ends on the inside of the sphere
  - polar ends on the outside
- These clusters are called micelles.
Micelle Structure of a Surfactant

Polar solvent
Polar end of surfactant
Non-polar end of surfactant
Non-polar solute
Natural

- Biodegradable
- Commonly soft
- Expensive

e.g.:
- esters of fatty acids
- ethoxylate alcohols
- alcohol ether sulfates
- esters of sucrose

Synthetic

- Frequently not very biodegradable
- Economic
- Wide variety/activity

e.g.:
- alkyl benzene sulfonates
- ethoxylate alcohols
- alkyl phenol ethoxylates
- quaternary ammonium salt
Surfactants for LCO$_2$ or scCO$_2$

- Must have both CO$_2$-philic (CO$_2$ loving) and CO$_2$-phobic functionality.
- In 1994, Joseph M. DeSimone of the University of North Carolina State University published his discovery that polyacrylate polymers having perfluorinated residues are soluble in liquid or supercritical CO$_2$ present surfactant properties if they contain aromatic groups (copolymers).

Micelle Structure for a CO₂ Surfactant

Solvent Carbon dioxide

Chain segment “CO₂-phylic”

Chain segment “CO₂-phobic”
## Supercritical CO₂ Surfactants

<table>
<thead>
<tr>
<th>Surfactant Type</th>
<th>Solubility (wt.%)</th>
<th>Emulsion Morphology</th>
<th>γ Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂ H₂O</td>
<td></td>
<td><strong>(Stability in h)</strong></td>
<td>Max. W₀ (mN/m)</td>
</tr>
<tr>
<td>CF₃O(CF₂CF₂O)₇₋₁₅OCF₂COOH</td>
<td>&gt;3</td>
<td>&lt;0.1</td>
<td>13.9</td>
</tr>
<tr>
<td>HOOCCF₂O(CF₂CF₂O)₂₋₇OCF₂COOH</td>
<td>~2</td>
<td>-</td>
<td>8.5</td>
</tr>
</tbody>
</table>

Other Industrial Uses of scCO$_2$

Union Carbide Technology

- Solution for surface coating
- Replaces 40-90% of VOCs with CO$_2$.
  - Coatings on aerospace parts
  - Adhesion promoters on plastics

Food Industry

- Chocolate biscuits
- Extraction of natural materials (Essential oils and fragrances)
- Additives

CO$_2$ Refrigeration

- scCO$_2$ SCF chromatography

Technologies for Coating by scCO₂

Rapid Expansion of Supercritical Solutions (RESS)

Gas Anti-Solvent (GAS)

Precipitation with a Compressed Anti-solvent (PCA)
Chemical Synthesis in scCO$_2$

- Fluoropolymer (e.g. Teflon) synthesis

- Extremely important polymers
- Dupont $40M$ development facility
- Previous methods used CFCs
- Easy polymer isolation and drying, and minimal waste

*Fluoropolymer (e.g. Teflon) synthesis

\[
\text{polymerization} \quad \rightarrow \quad \left( \begin{array}{c}
F \\
F \\
F \\
F \\
\end{array} \right)_n
\]

Homogeneous Catalytic Reactions in Supercritical CO$_2$:

- Catalytic copolymerization of CO$_2$ with Epoxides

\[
\begin{align*}
\text{O} & \quad \text{CO}_2 \\
\text{R} & \quad \text{O} \\
\end{align*}
\]

\[
\text{Catalyst} \quad \rightarrow \quad \begin{array}{c}
\text{O} \\
\text{R} \\
\text{O} \\
\text{O}
\end{array}
\]

\[
\text{Catalyst} \quad + \quad \text{R CO}_2\text{Me} \quad \text{NHAc} \\
\text{H}_2/\text{SC CO}_2 \\
\text{R CO}_2\text{Me} \quad \text{NHAc}
\]

- Asymmetric Catalytic Hydrogenation of Enamides

Tumas, Los Alamos National Laboratory
Lab scCO$_2$ Reactors
Lab Equipment Design with scCO₂
### Supercritical CO₂ Extraction

**Factors influencing extraction efficiency**

- Temperature
- Pressure
- Solubility
- Structure and particle size of raw material
- Mass of CO₂ per mass of raw material

<table>
<thead>
<tr>
<th>Solubility</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Very soluble</td>
<td>Chlorophyll, waxes</td>
</tr>
<tr>
<td></td>
<td>and carotenoids</td>
</tr>
<tr>
<td>Sparsely soluble</td>
<td>Sugars, proteins</td>
</tr>
<tr>
<td></td>
<td>Tannins, amino acids, pesticides</td>
</tr>
<tr>
<td>Insoluble</td>
<td>Oleic acid, dodecanol</td>
</tr>
<tr>
<td></td>
<td>Waxes</td>
</tr>
</tbody>
</table>

- Non-polar and moderately polar molecules: <500 MW

- Examples: Triterpenoids, alkaloids, lipids <C22
Liquid CO₂ Extraction with Entrainers

- Very small additions of entrainer modify the extraction characteristics of CO₂
- Alcohols (including water), ketones and hydrocarbons are most commonly used
- Entrainers modify the polarity and solvating properties of liquid CO₂
- Some compounds behave as surfactant agents.
Liquid CO₂ Extraction Circuit

- Bean in
- Extractor
- LL extractor
- Flash
- Concentrator
- Water in
- CO₂ recycle
- Water/makeup
- CO₂/caffeine
- Water/caffeine
- Aqueous Caffeine byproduct
- Dryer
- Bean
- Product
Supercritical CO$_2$ Extraction Circuit
Industrial Extraction with CO$_2$

- Decaffeination of Tea and Coffee - SCO$_2$
- Extraction of Hops - LCO$_2$ and SCO$_2$
- Defatting of cocoa powder - SCO$_2$
- Extraction of oil seeds - SCO$_2$
- Extraction of spices and aromatic plants - LCO$_2$ and SCO$_2$

Cocoa defatting (2009)

Complete removal of fat (<0.5%), no loss of polyphenols, no solvent residues

![Graph showing the removal of fat in cocoa](image-url)
Extraction of Lipids and Aroma with CO₂

- **Triglycerides** have limited solubility in LCO₂
- ScCO₂ almost exclusively used for fat and oil extraction
- CO₂ extraction reduces post extraction processing
- Oils have lower aroma, colour, free fatty acids and peroxide value
- Resulting residue can be used for animal feed

- Extraction with LCO₂ produces **products with an aroma** which closely resembles the starting material
- Extraction at 10°C or less minimises degradation of labile molecules and the formation of undesirable ‘off-notes’
- A greater proportion of higher molecular weight compounds are normally found in CO₂ extracts when compared to steam distilled oils
Extracts consist of a variety of fatty acids, including the non-essential ω-6 polyunsaturated fatty acid γ-linolenic acid (GLA), the essential ω-6 polyunsaturated fatty acid linoleic acid (LA), oleic acid, palmitic acid, and stearic acid.
## Liquid CO₂ – Selectivity in the Hop Extraction

(The extraction process maintains integrity of hop components (unchanged from pellet resinous compounds)
The extract represents approximately 25% of the original mass of the pellet.

<table>
<thead>
<tr>
<th>Component</th>
<th>CH₂Cl₂ %</th>
<th>Ethanol %</th>
<th>Liquid CO₂ %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfa acids</td>
<td>35-45%</td>
<td>30-40%</td>
<td>40-50%</td>
</tr>
<tr>
<td>Beta acids</td>
<td>15-20%</td>
<td>10-15%</td>
<td>18-40%</td>
</tr>
<tr>
<td>Other soft resins</td>
<td>3-8%</td>
<td>3-8%</td>
<td>5-20%</td>
</tr>
<tr>
<td>Hard resins</td>
<td>2-5%</td>
<td>2-10%</td>
<td>None</td>
</tr>
<tr>
<td>Olio volatile</td>
<td>1-3%</td>
<td>1-2%</td>
<td>2-8%</td>
</tr>
<tr>
<td>Fats and Waxes</td>
<td>1-2%</td>
<td>Traces</td>
<td>0-5%</td>
</tr>
<tr>
<td>Tannins</td>
<td>Traces</td>
<td>1-5%</td>
<td>None</td>
</tr>
<tr>
<td>Chlorophyll</td>
<td>&lt;1%</td>
<td>Traces</td>
<td>None</td>
</tr>
<tr>
<td>Inorganic salts</td>
<td>&lt;1%</td>
<td>0.5-1%</td>
<td>Traces</td>
</tr>
<tr>
<td>Residual solvents</td>
<td>&lt;1%</td>
<td>0.01-0.1%</td>
<td>None</td>
</tr>
<tr>
<td>Water</td>
<td>Traces</td>
<td>1-5%</td>
<td>1-5%</td>
</tr>
<tr>
<td>Typical yield</td>
<td>28%</td>
<td>38%</td>
<td>19%</td>
</tr>
</tbody>
</table>
Hop Extraction with LCO₂

La frazione di composti dell'estratto precipitati con Pb(OAc)₂ è detta acidi alfa.

α-acids* (humulones)

β-acids (lupulones)

R = CH₂CH(CH₃)₂  humulone  lupulone
CH(CH₃)₂  cohumulone  colupulone
CH(CH₃)CH₂CH₃  adhumulone  adlupulone

*La frazione di composti dell'estratto precipitati con Pb(OAc)₂ è detta acidi alfa.
### Matricaria recutita: Composition and Formation of Chamazulene Oil During Steam Distillation

<table>
<thead>
<tr>
<th></th>
<th>Steam distilled (%)</th>
<th>Liquid CO₂ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-farnesene</td>
<td>18.4</td>
<td>14.5</td>
</tr>
<tr>
<td>spathulenol</td>
<td>&lt;0.1</td>
<td>1.5</td>
</tr>
<tr>
<td>α-bisabolol oxide B</td>
<td>19.4</td>
<td>4.6</td>
</tr>
<tr>
<td>α-bisabolone oxide A</td>
<td>12.0</td>
<td>3.1</td>
</tr>
<tr>
<td>α-bisabolol</td>
<td>&lt;0.1</td>
<td>3.7</td>
</tr>
<tr>
<td>chamazulene</td>
<td>15.4</td>
<td>1.3</td>
</tr>
<tr>
<td>α-bisabolol oxide A</td>
<td>9.9</td>
<td>23.5</td>
</tr>
<tr>
<td>Dicycloethers (MW 200)</td>
<td>2.7</td>
<td>37.8</td>
</tr>
<tr>
<td>Colour</td>
<td>Blue</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

Matricine → pro-chamazulene → Chamazulene (artifact)
Critical point
$P \approx 22 \text{ MPa and } T = 374^\circ \text{ C}.$

Below critical Point Temperature
Isotherm shows discontinuity. Especially on intersection with saturation line.

Above Critical point
Isotherm shows no discontinuity SCW is in gas like state.

Gives:
Liquid like density
Gas like viscosity
A process in water at raised temperatures and pressures is called a hydrothermal process. The concept comes originally from the geology. The picture on the left shows a simplified overview about different hydrothermal processes and includes the vapour pressure curve of the water.
Supercritical Water

Super Critical means no distinction between water and steam.

- Steam (Gas)
- Mix. Of Steam & Water
- Saturated line
- Water
- Sub-Critical
- Super Critical

Enthalpy *(kJ/kg)*

Pressure (MPa)

Temp. (°C)

* Thermodynamic quantity
Thermal Physical Properties at Critical Temperature

- Properties variation as $C_p$, $k$, $h$ and $\mu$ are indicated in figure.
- Large properties variation noticed in pseudo-critical region.
- The large increase in convective coefficient is indicated near pseudo-critical line.
- The steep decrease in $\mu$ and $k$ is noticed.

Water Properties Variation with Temperature

$P = 235$ bar

$T_{pc}$

$1/P$, $\mu$, $k$, $c_p$
Dielectric constant of water dependent from temperature/pressure. SC-Water present a dielectric constant between 2 and 30, similar to nonpolar solvents, i.e. hexane ($\varepsilon = 1.8$), and polar solvents, i.e. methanol ($\varepsilon = 32.6$).

Therefore, with SC-Water is possible dissolve organic compounds insoluble in water at ambient condition. Salts have instead low solubility in these conditions.
Water ionic product behaviour

\( K_w = [H^+][OH^-] \);

- at 25°C and P = 1 atm, \( K_w \) is \( 1 \times 10^{-14} \text{(mol/l)}^2 \).

- At higher temperature and pressure conditions, this value increase. At 34.5 MPa pressure, a maximum value of \( 1 \times 10^{-11} \text{(mol/l)}^2 \) is reached (minimum – log \( K_w \)) near 300°C.

Under these conditions, we have \([H^+] = 3 \times 10^{-6} \text{ mol/l}\), with an increase of about 30 times of concentration at room conditions. SC-water can be a potential acid catalyst.
Black Smokers & Supercritical Water

- Located just south of the Equator, at the southern end of the mid-Atlantic Ridge
- 3 kilometers beneath the surface of the ocean
- Temperatures measured between 407°C – 464°C by remotely operated submersibles
- Immense pressure & temperature combine to create an anomaly that has both liquid and vapor qualities
- Provide essential nutrients to locally adapted organisms, microbes, & phytoplankton.
Technology able to complete decomposition of all types of recalcitrant compounds in short time, producing CO$_2$, H$_2$O and inorganic salts.

Main problems arise from corrosion phenomena associated to higher acidity of water in SC conditions.
Oxidations in SC-Water

Equipment for oxidation in supercritical water

Attilio Citterio