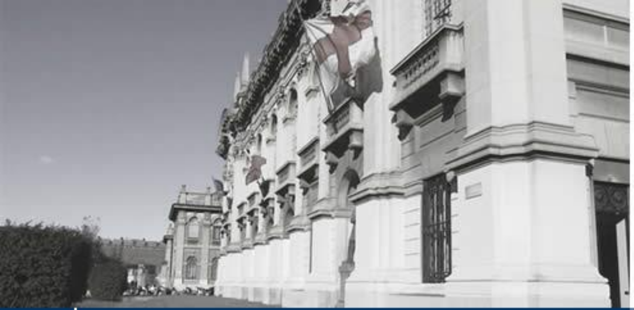


School of Industrial and Information Engineering

Course 096125 (095857)

Introduction to Green and Sustainable Chemistry

POLITECNICO DI MILANO

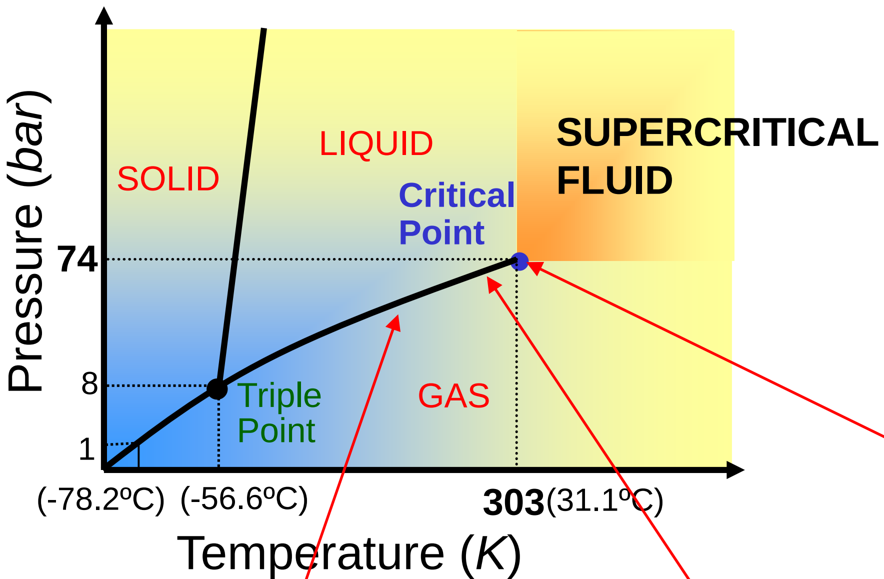
Supercritical Solvents (CO_2, H_2O).

Prof. Attilio Citterio

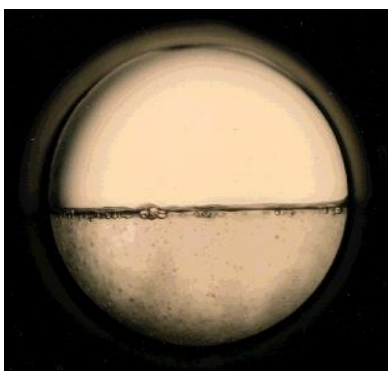
Dipartimento CMIC “Giulio Natta”

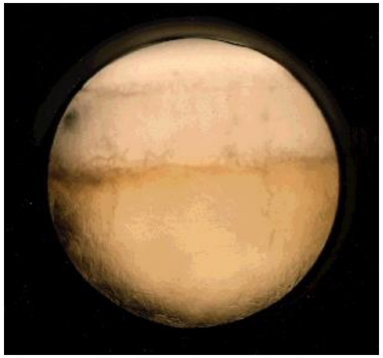
https://iscamapweb.chem.polimi.it/citterio/it/education/course-topics/

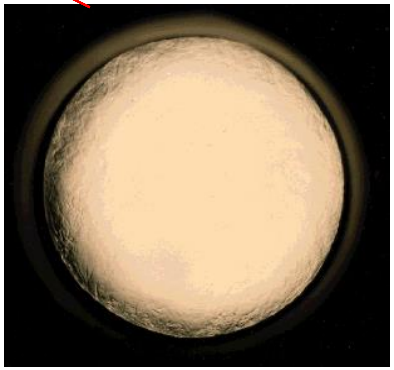
Supercritical Fluids.



- 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.

	Gas	SCF	Liquid
Density ($g \cdot cm^{-3}$)	10^{-3}	0.1-1	1
Viscosity ($g \cdot cm^{-1} \cdot s^{-1}$)	10^{-4}	10^{-3}-10^{-4}	10^{-2}
Diff. Coeff. ($cm^2 \cdot s^{-1}$)	10^{-2}-10^{-1}	10^{-4}-10^{-3}	10^{-5}

Common Supercritical Fluids.

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:

Carbon dioxide	T_c = 31.1 °C	P_c = 73.8 *bar*
Fluoroform	T_c = 25.9 °C	P_c = 48.2 *bar*
Water	T_c = 374.0 °C	P_c = 220.6 *bar*
Ammonia	T_c = 132.4 °C	P_c = 113.2 *bar*
Ethane	T_c = 32.2 °C	P_c = 48.7 *bar*
Methanol	T_c = 239.5 °C	P_c = 8.08 *MPa*

CO_2 is unpolar $\therefore$ high volumes and pressure are necessary to liquefy (high energetic costs). Co-solvents are added to increase the polarity.

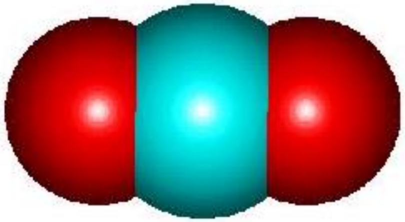
Water becomes SC at higher temperatures and pressures than CO_2.

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

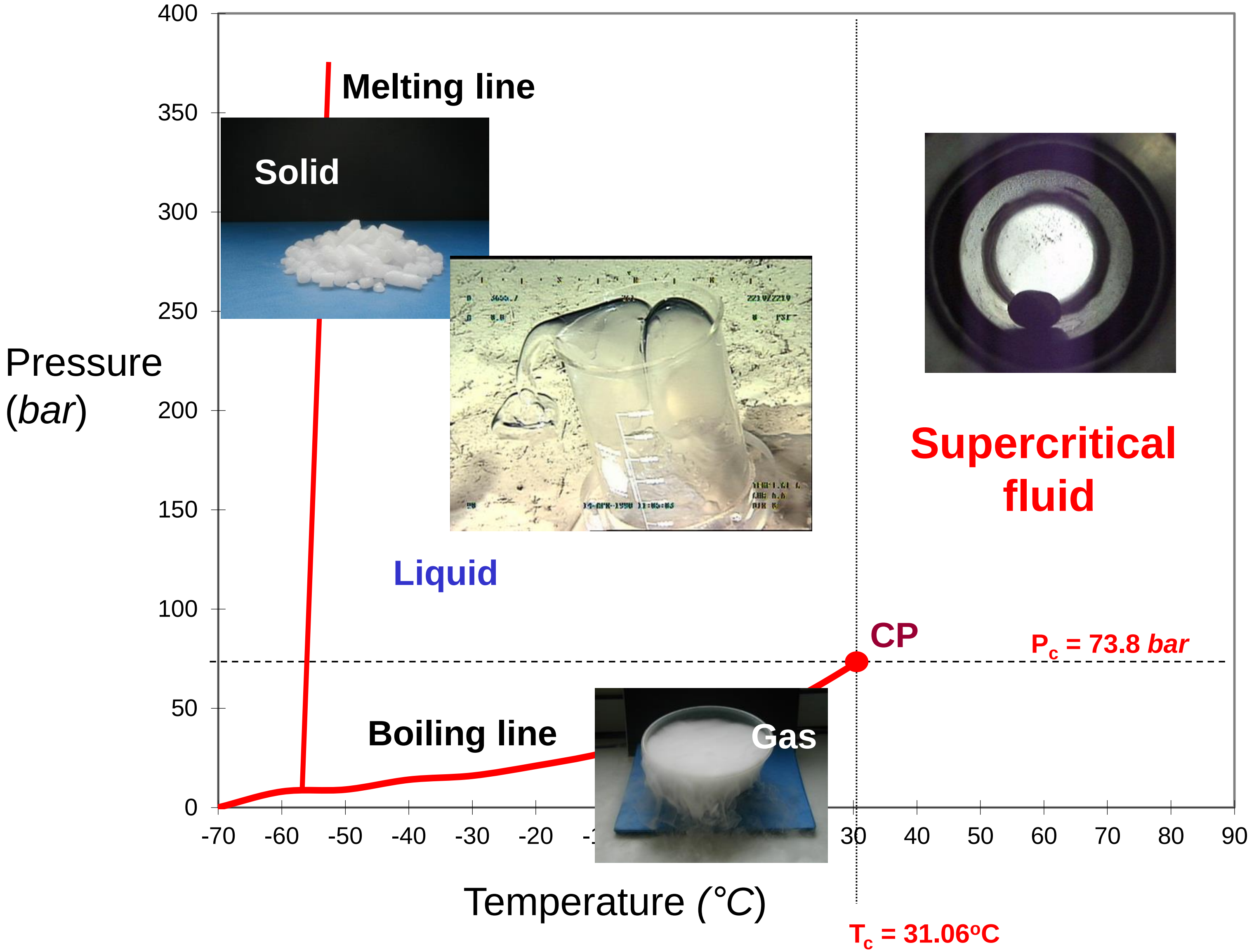
A.A. Clifford in “Supercritical Fluids”. Eds. E. Kiran and J.M.H. Levet Sengers, kluver Academic Publishers. 1994, 449-479.
P.G. Jessop, T. Ikaraya and R. Noyori. Science, 1995, 269, 1065: see also: P.G. Jessop. T. Ikariya and R. Noyori, *Nature, 1994, 368, 231.*
D.M. Eaton, K.D. Barle, C.M. Rayner and A.A. Clifford, *.Journal of High Resolution Chromatography,* 1993, 16, 66.

Carbon Dioxide (CO_2).

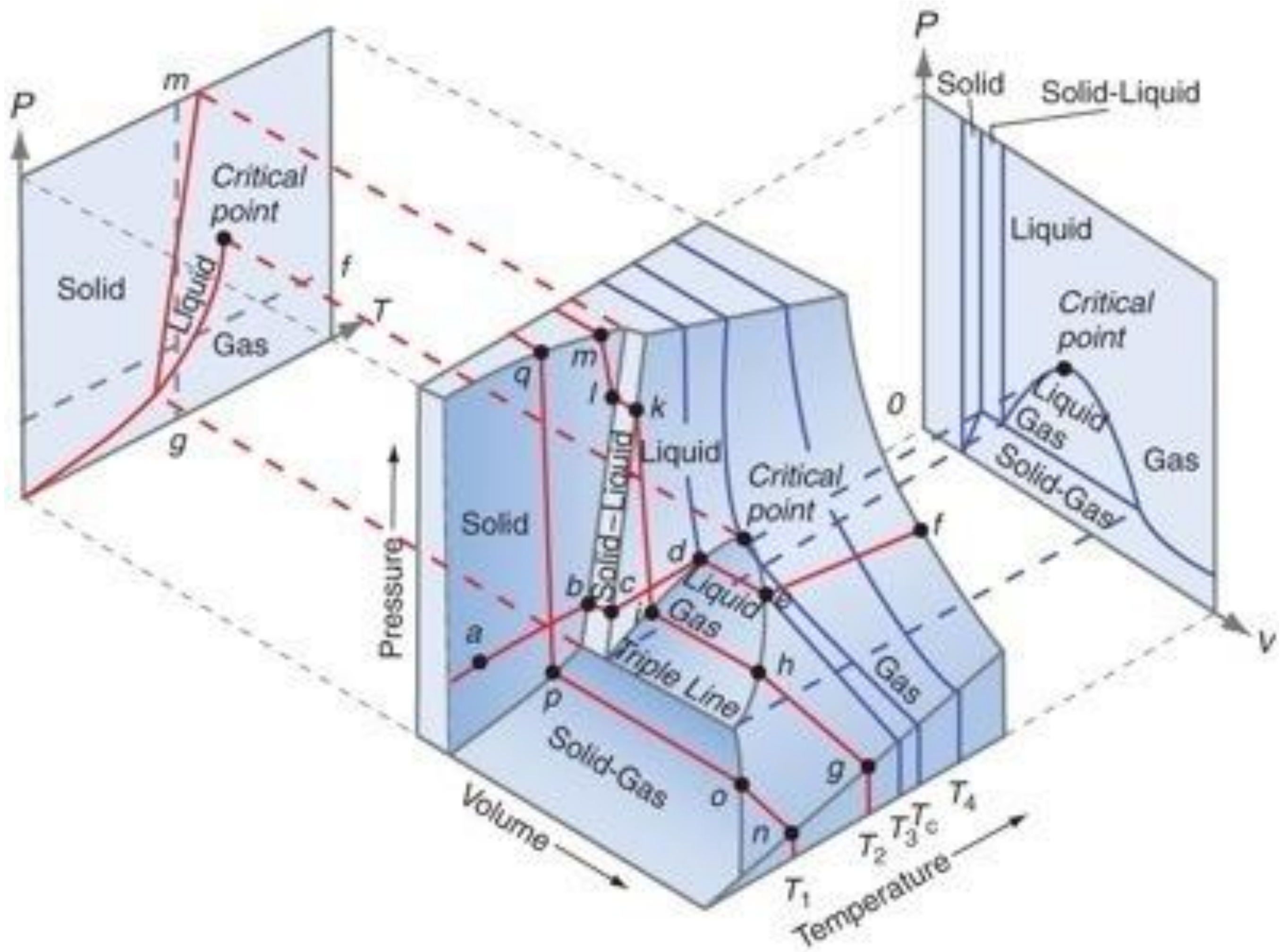


- Similar advantages to water:
  - Natural, cheap,
  - Plentiful (0.04% of atmosphere and now rising!)
  - Available in >99.9% pure form, €90/$110 per 25 *kg*.
  - By-product of brewing, ammonia synthesis, combustion
  - Non-flammable
  - TLV = 5000 *ppm*
- Supply chain and related technology already 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 CO_2 ;
  - 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 CO_2.



Pure CO_2 PTV Diagram and Projections.



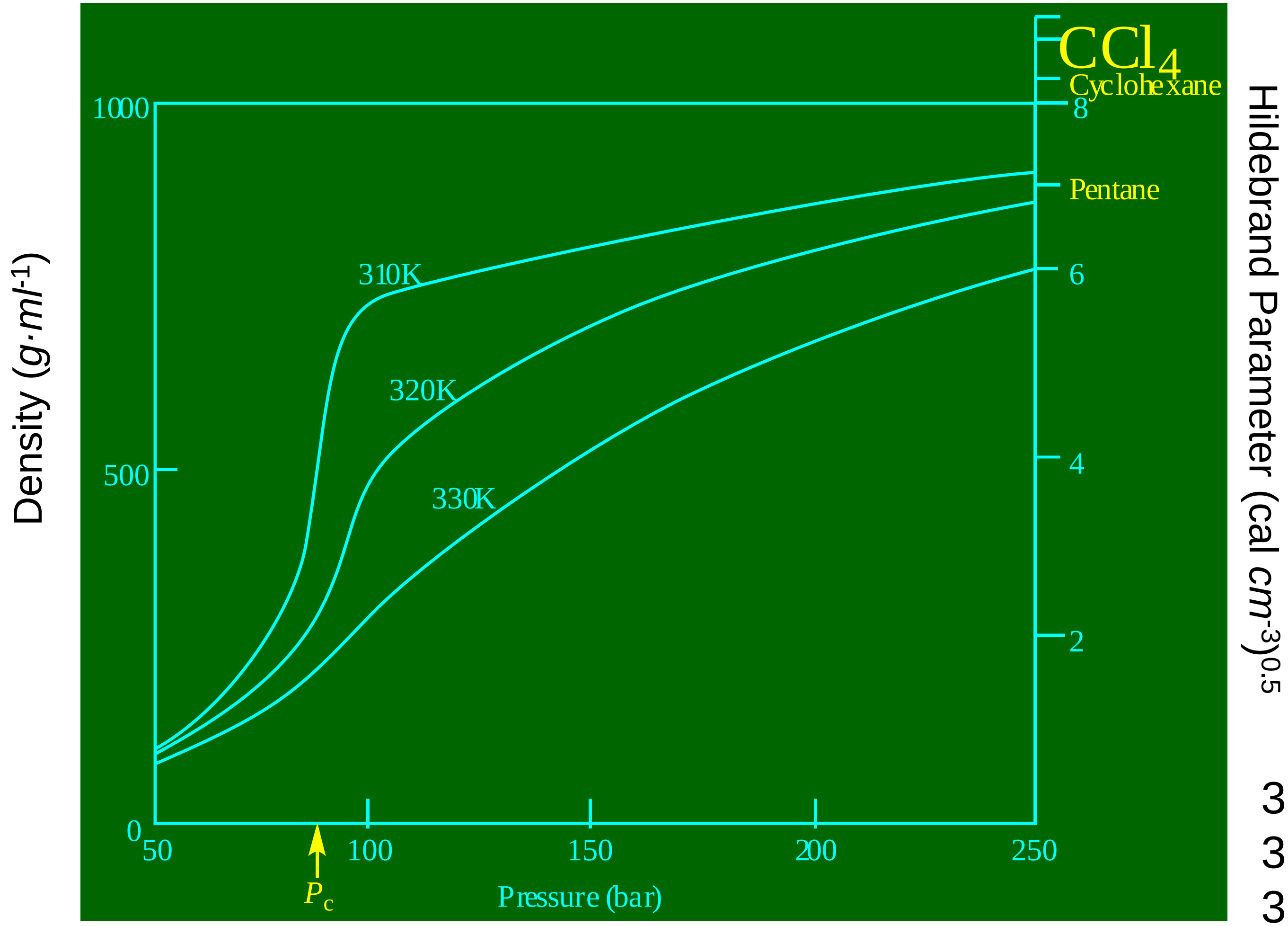
Other Advantages of $scCO_2$.

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

  ← →
  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 CO_2 from Pressure.



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

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_2O), can be exploited synthetically

Current Consumer Related Applications of CO_2 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 $scCO_2$

Spray painting process use $scCO_2$ to reduce VOC emissions (>'80%).

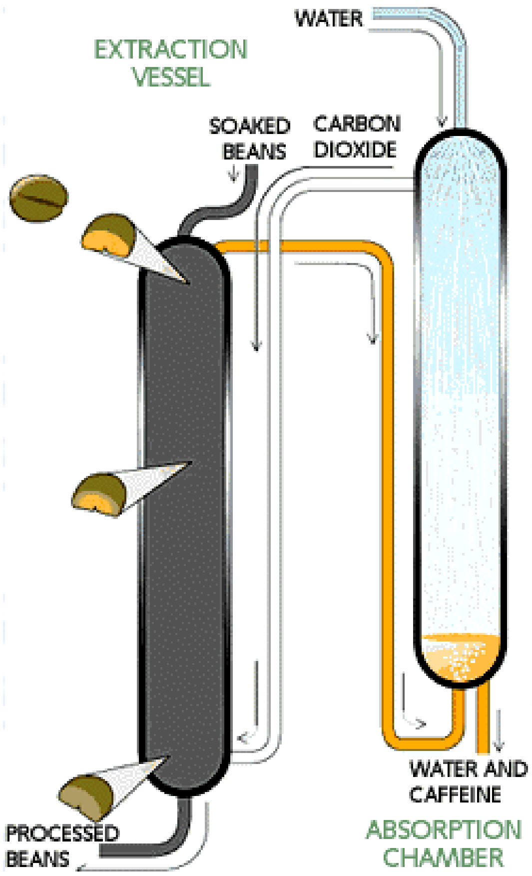
Known are also some continuous synthesis which use sc-fluids with capacity of up to 1000 tonnes per year.

But Also:

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

http://www.thomas-swan.co.uk/

Decaffeination Process.



SOAKING green coffee beans in water doubles their size, allowing the caffeine to dissolve into water inside the bean.

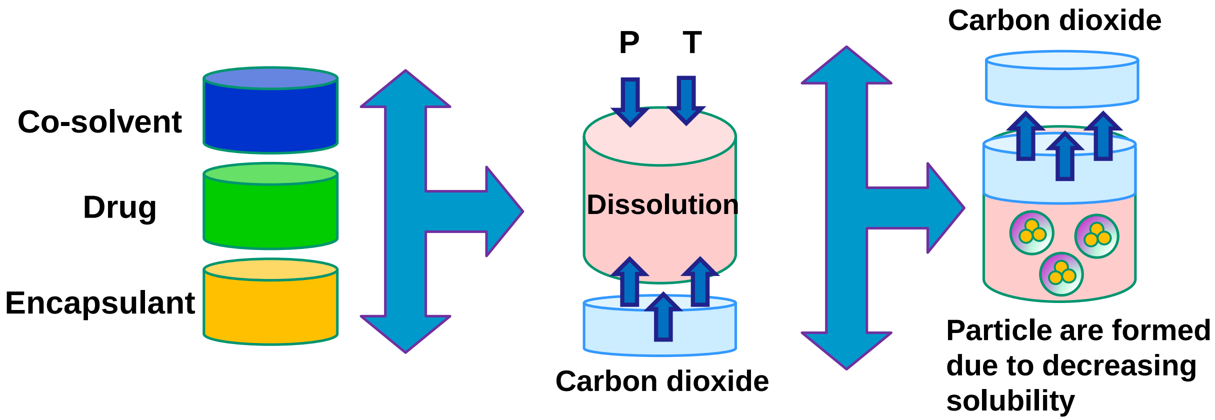
CAFFEINE REMOVAL occurs in an extraction vessel. Caffeine diffuses into this supercritical carbon dioxide, along with some water.

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.

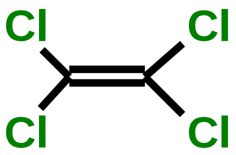
- Two main complementary techniques:
  - ❖ RESS – Rapid expansion of supercritical solution
  - ❖ SAS – Solvent/AntiSolvent Precipitation
- Allow for the processing of a wide range of materials into solid phases with useful properties and morphologies, e.g. pharmaceuticals, protein macroparticles, explosives.



- J.W. Tom, G.B. Lim, P.G. Debenedetti and R.K. Prud'homme, in Supercritical Fluid Engineering Science - Fundamentals and Applications, F. Kiran, J.F. Brennecke Eds., ACS Symposium Series 514, 1993, chapter 11.
- P.G. Debenedetti, Supercritical Fluids - Fundamentals for Application, Eds. E Kiran and J.M.H. Levelt Sengers, 1994, Kluwer Academic Publishers, 1994, pp. 719-729.

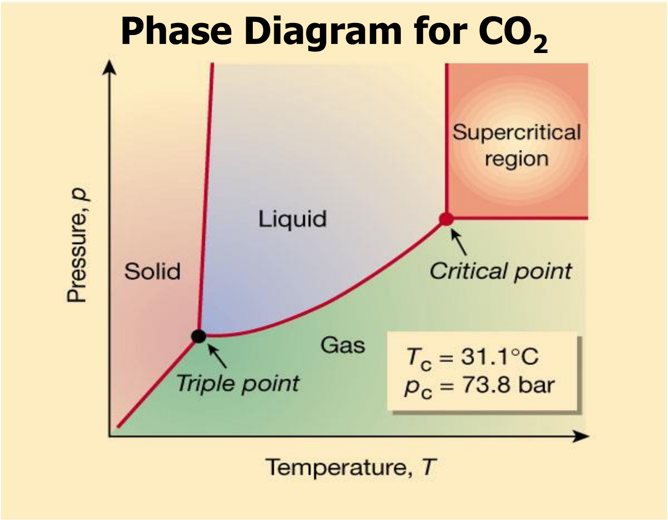
Dry Cleaning with $scCO_2$.

- 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 CO_2
- Requires surfactant (to be recycled)

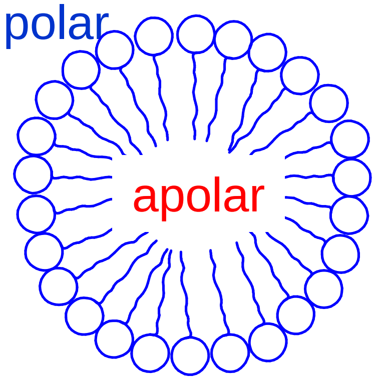


Dry Cleaning with $scCO_2$.

- 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.

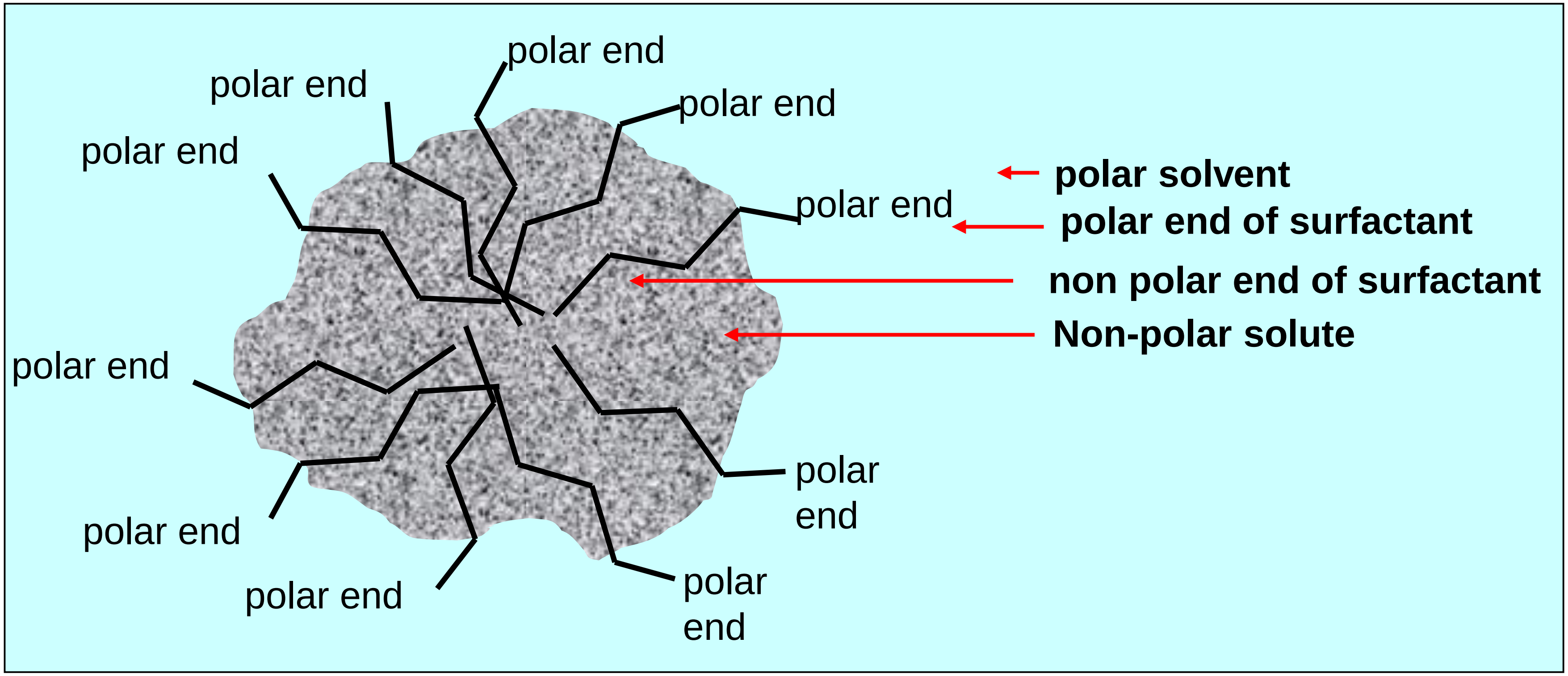
Surfactants.

- 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.



Scheme of a micelle

Micelle Structure of a Surfactant.



Natural and Synthetic Surfactants.

Natural

- Biodegradable
- Commonly soft
- Expensive

e.g.:

- esters of fatty acids
- ethoxylate alcohols
- alcohol ether sulfates
- esters of sucrose

Synthetic

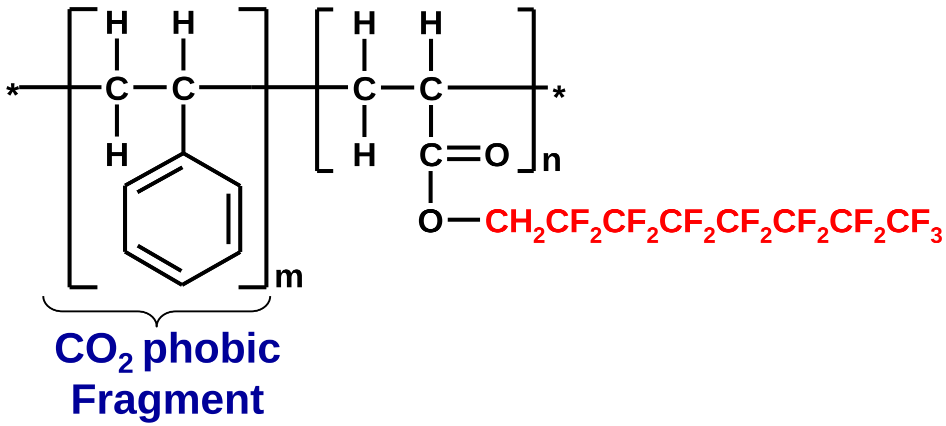
- Frequently not very bio-degradable
- Economic
- Wide variety/activity

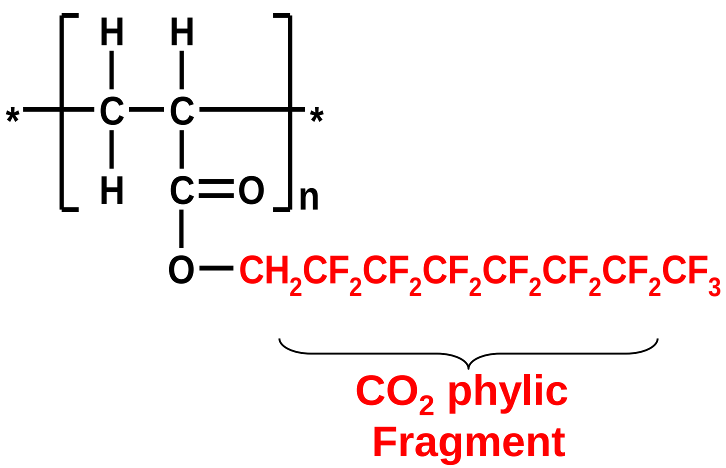
e.g.:

- alkyl benzene sulfonates
- ethoxylate alcohols
- alkyl phenol ethoxylates
- quaternary ammonium salt

Surfactants for LCO_2 or $scCO_2$.

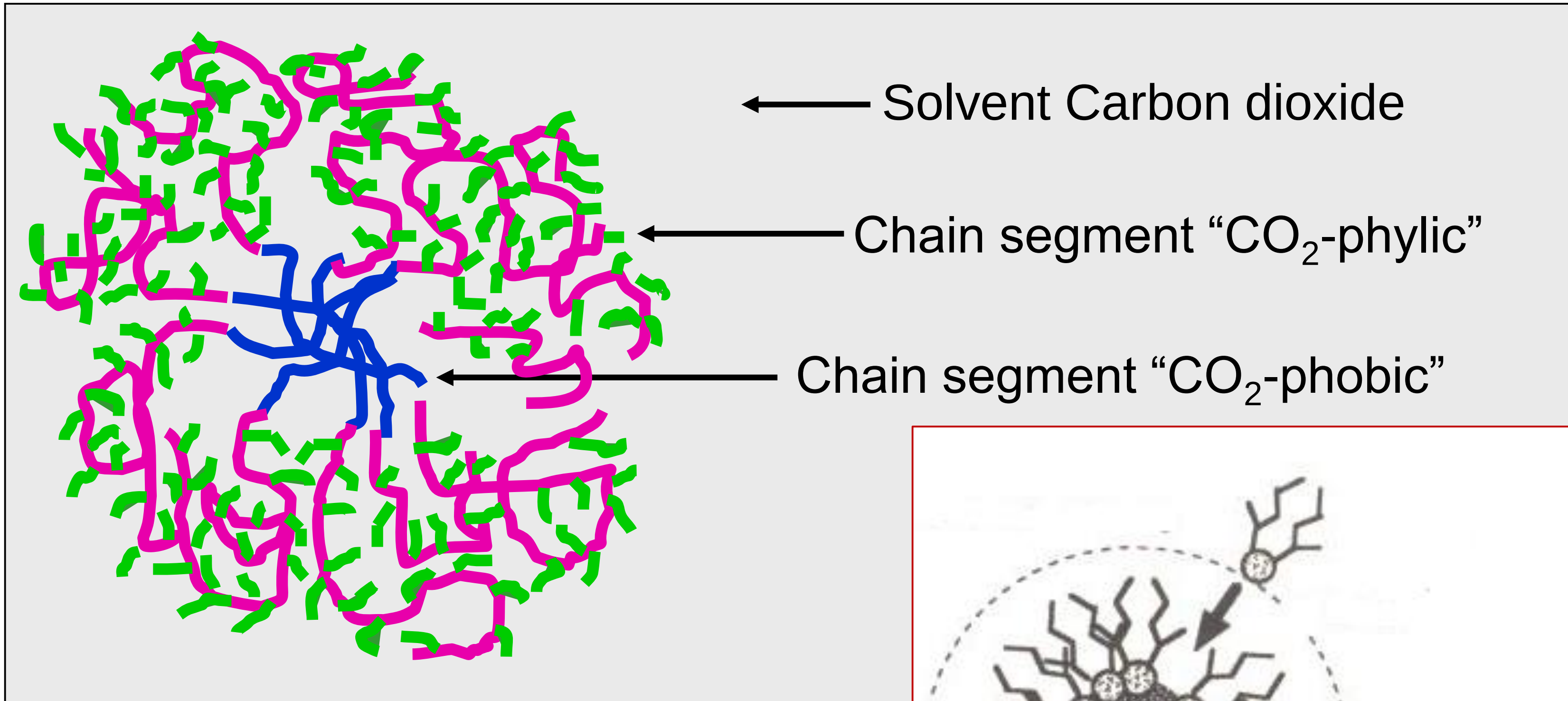
- Must have both CO_2-philic (CO_2 loving) and CO_2 -phobic functionality.
- In 1994, Joseph M. DeSimone of the University of Nord Carolina State University published his discovery that polyacrylate polymers having perfluorinated residues are soluble in liquid or supercritical CO_2 present surfactant properties if they contain aromatic groups (copolymers).

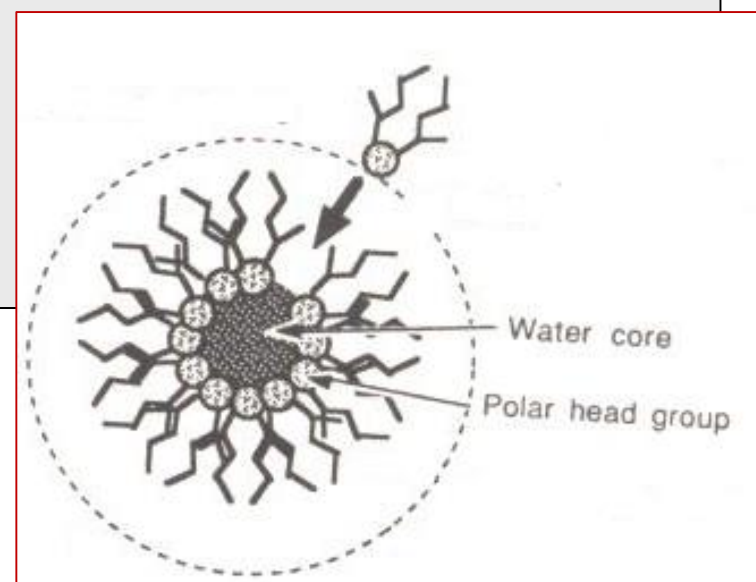




J.L. Kendall, D.A. Canelas, J.L. Young and J.M. DeSimone, *Chem. Rev*., 1999, **99**, 2663.

Micelle Structure for a CO_2 Surfactant.





Supercritical CO_2 Surfactants.

Surfactant Type	Solubility (wt.%)		Emulsion Morphology		γ Range
	CO_2	H_2O	(Stability in h)	Max. W_o	(mN/m)
$CF_3O(CF_2CF_2O)_{7-15}OCF_2COOH$	>3	<0.1	(5 sec – 54 min) W/C	13.9	1.6-3.4
$HOOCCF_2O(CF_2CF_2O)_{2-7}OCF_2COOH$	~2	-	W/C	8.5	-

K.P. Johnston et al., *J. Dispersion Sci. and Tech.*, 2002, **23**: p. 81.

Other Industrial Uses of $scCO_2$.

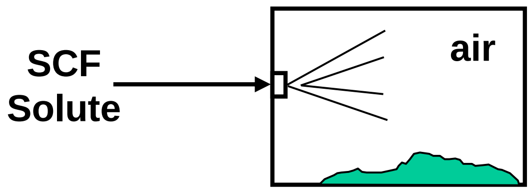
Union Carbide Technology

- 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.

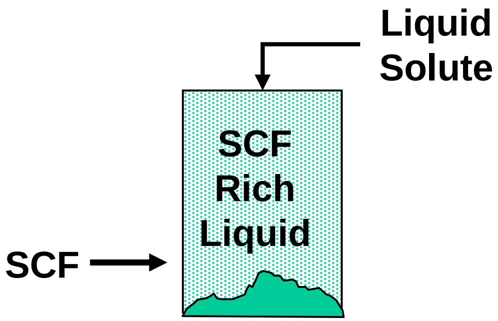
Chem. Eng. News, June 14 1999, 77 (24), 13.

R.S. Oakes, A.A. Clifford and C.M. Rayner, *J. Chem. Soc., Perkin Trans. 1, 2001*, 917.

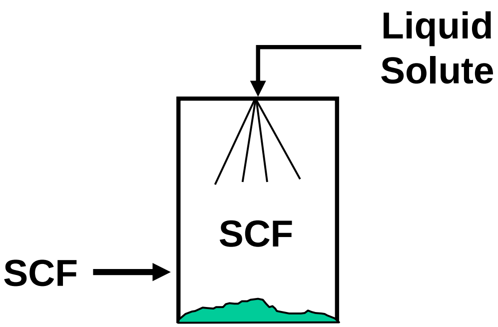
Technologies for Coating by $scCO_2$.



Rapid Expansion of Supercritical Solutions (RESS)



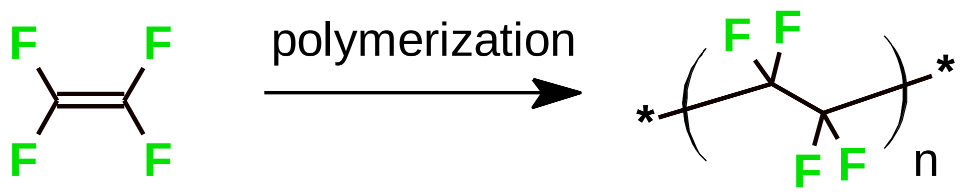
Gas Anti-Solvent (GAS)



Precipitation with a Compressed Anti-solvent (PCA)

Chemical Synthesis in $scCO_2$.

- Fluoropolymer (e.g. Teflon) synthesis:



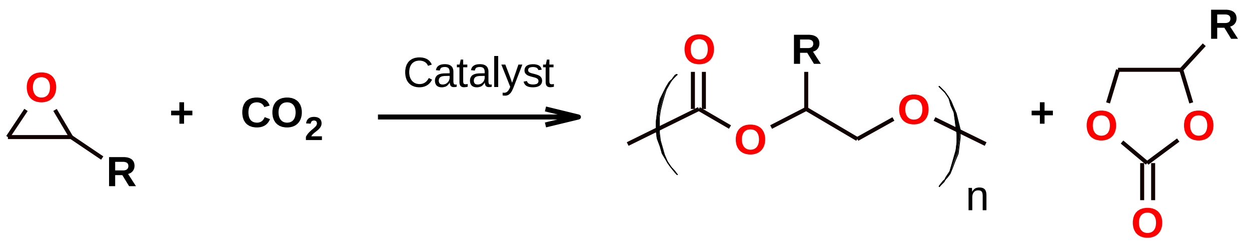
  - Extremely important polymers
  - Dupont $40M development facility
  - Previous methods used CFCs
  - Easy polymer isolation and drying, and minimal waste

Chem. Eng. News, April 26 1999, 77 (17), 10

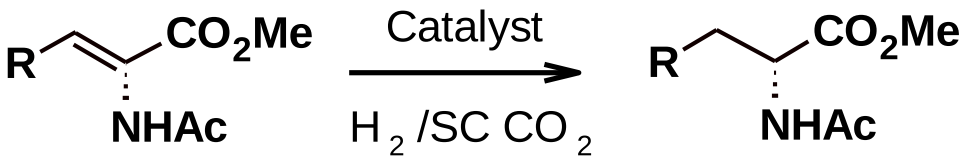
Reactions in $scCO_2$.

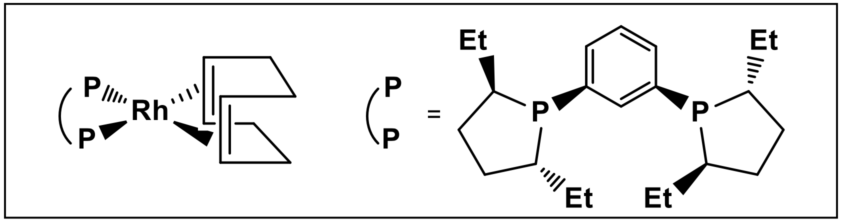
Homogeneous Catalytic Reactions in Supercritical CO_2 :

- Catalytic copolymerization of CO_2 with Epoxides



- Asymmetric Catalytic Hydrogenation of Enamides

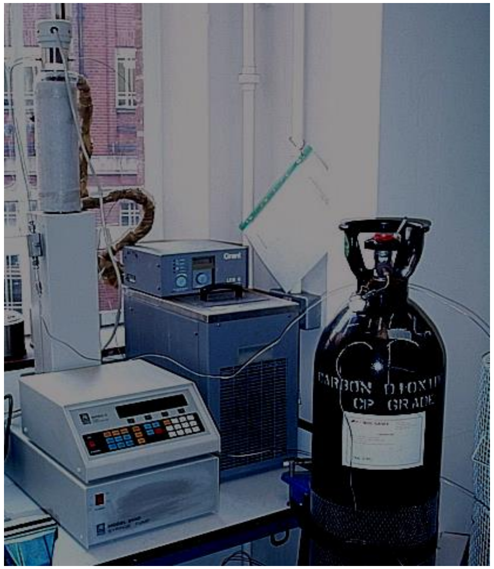


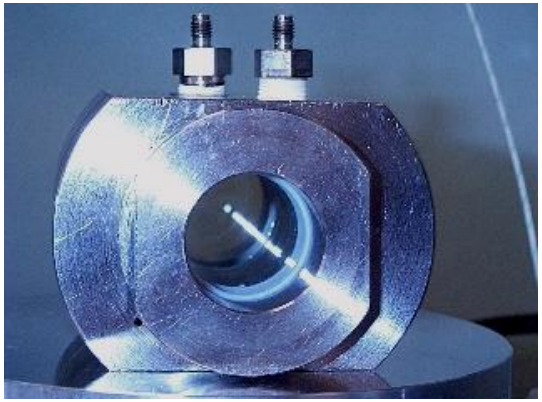


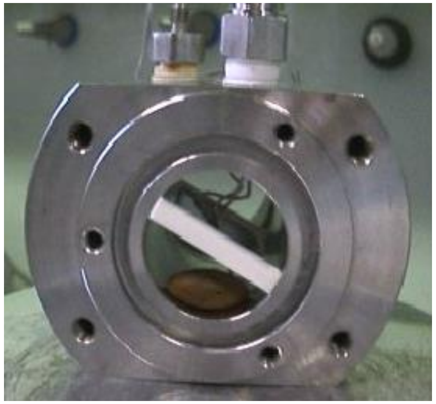
Tumas, Los Alamos National Laboratory

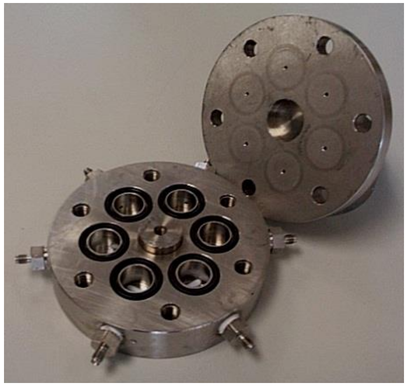
Lab $scCO_2$ Reactors.

Lab Equipment Design with $scCO_2$.









Supercritical CO_2 Extraction.

Very soluble	Sparingly soluble	Insoluble
non-polar and moderately polar molecules <500 MW	**Chlorophyll, waxes and carotenoids**	**Sugars, proteins Tannins, amino acids, pesticides**
Examples: Triterpenoids, alkaloids, lipids <C22	**Oleic acid, dodecanol**	**Waxes**

Factors influencing extraction efficiency

Temperature | Pressure | Solubility

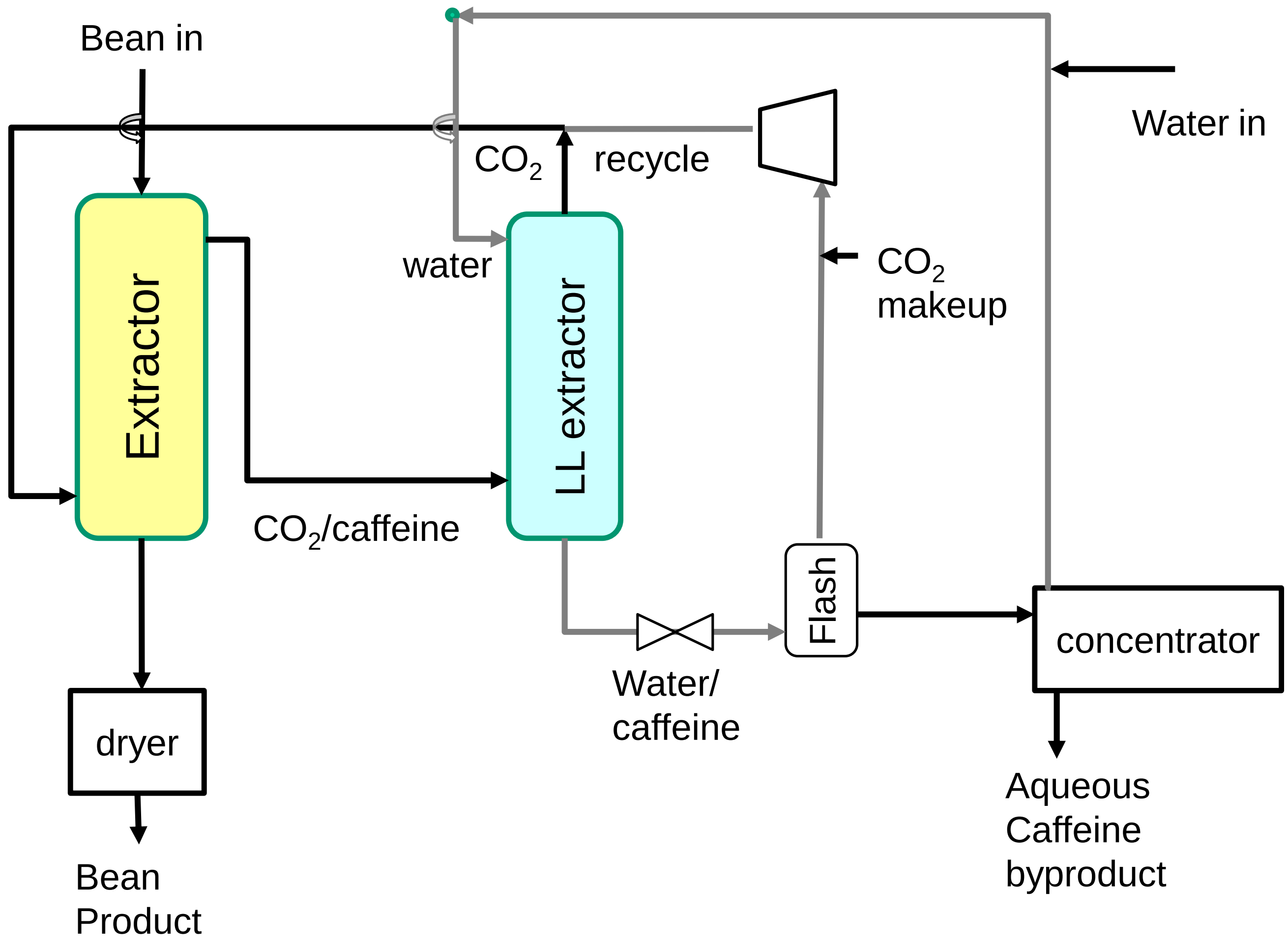
Structure and particle size of raw material

Mass of CO_2 per mass of raw material

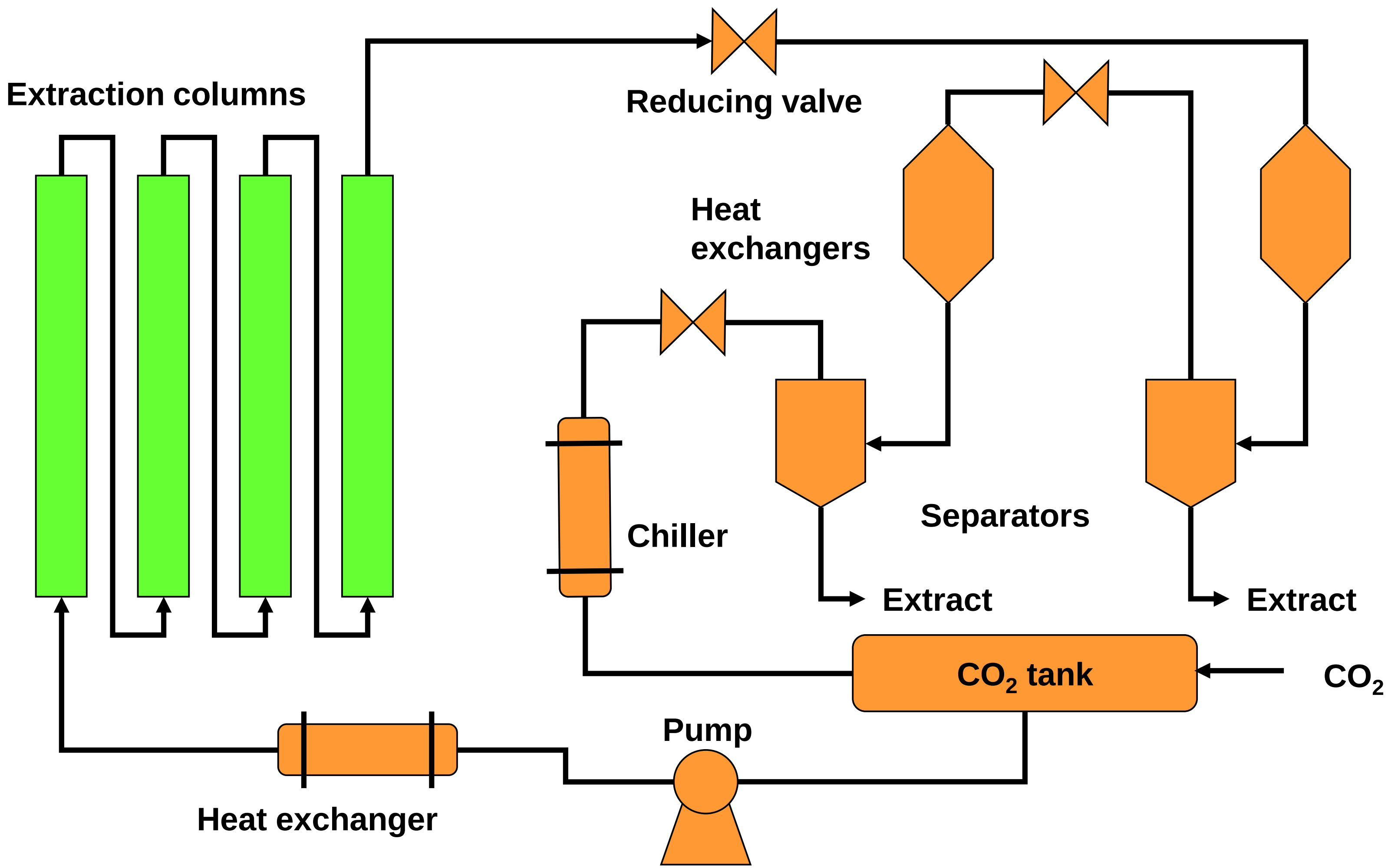
Liquid CO_2 Extraction with Entrainers.

- Very small additions of entrainer modify the extraction characteristics of CO_2
- Alcohols (including water), ketones and hydrocarbons are most commonly used
- Entrainers modify the polarity and solvating properties of liquid CO_2
- Some compounds behave as surfactant agents.

Liquid CO_2 Extraction Circuit.



Supercritical CO_2 Extraction Circuit.



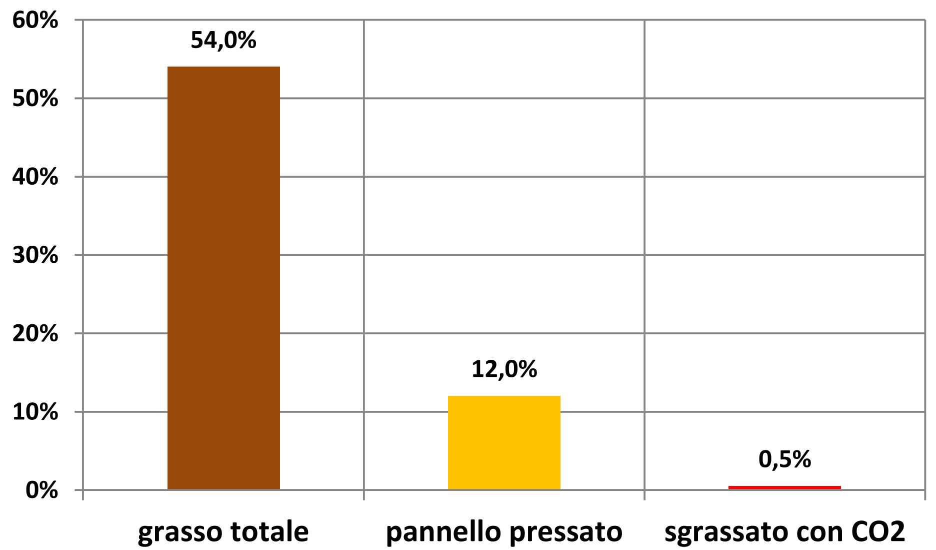
Industrial Extraction with CO_2.

- 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

EVONIK INDUSTRIES



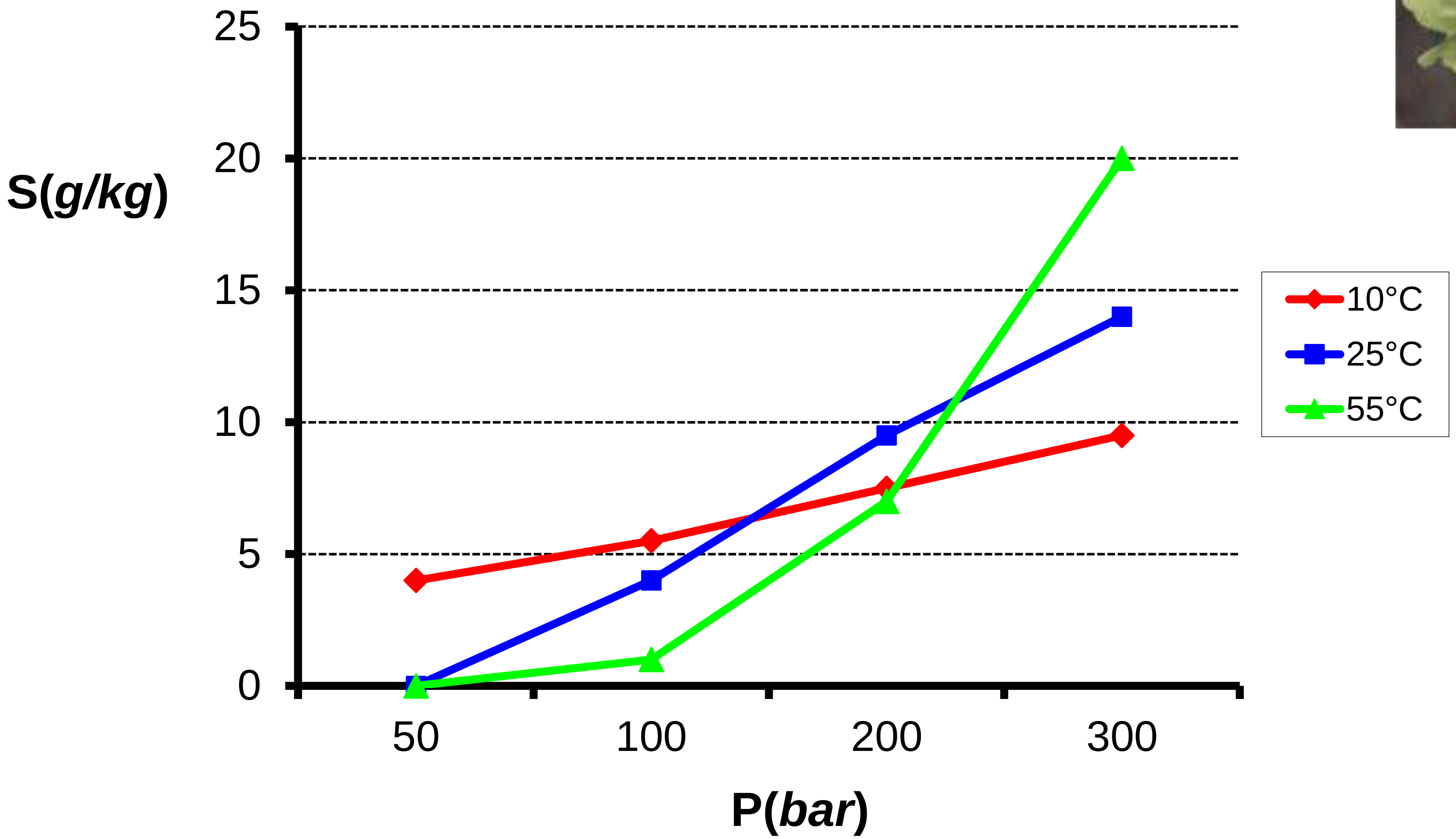
Extraction of Lipids and Aroma with CO_2.

- Triglycerides have limited solubility in LCO_2
- $ScCO_2$ almost exclusively used for fat and oil extraction
- CO_2 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 LCO_2 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 CO_2 extracts when compared to steam distilled oils

Extraction of Lipids with CO_2
(*Oenothera biennis* - Evening primrose).

Extracts consist of a variety of fatty acids, including the non-essential ω-6 polyunstaturated fatty acid γ-linolenic acid (GLA), the essential ω-6 polyunstaturated fatty acid linoleic acid (LA), oleic acid, palmitic acid, and stearic acid.

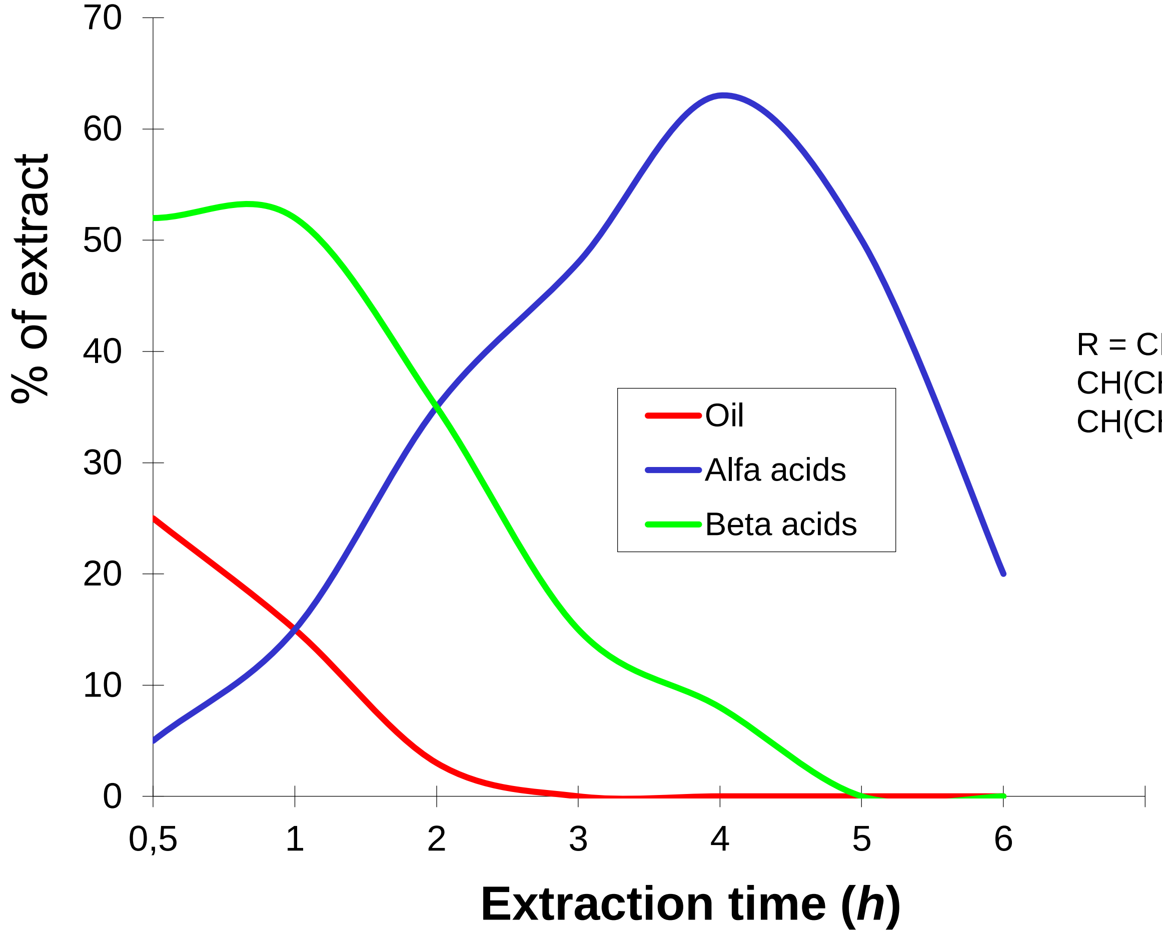


Liquid CO_2 – Selectivity in the Hop Extraction.

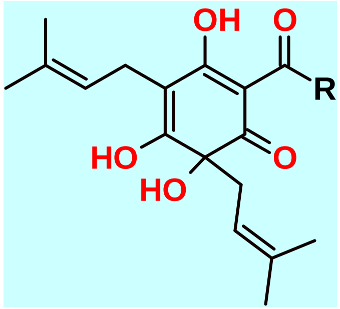
	CH_2Cl_2	Ethanol	Liquid CO_2
Alfa acids	35-45%	30-40%	40-50%
Beta acids	15-20%	10-15%	18-40%
Other soft resins	3-8%	3-8%	5-20%
Hard resins	2-5%	2-10%	None
Olio volatile	1-3%	1-2%	2-8%
Fats and Waxes	1-2%	Traces	0-5%
Tannins	Traces	1-5%	None
Chlorophyll	<1%	Traces	None
Inorganic salts	<1%	0.5-1%	Traces
Residual solvents	<1%	0.01-0.1%	None
Water	Traces	1-5%	1-5%
Typical yield	28%	38%	19%

(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. .

Hop Extraction with LCO_2.

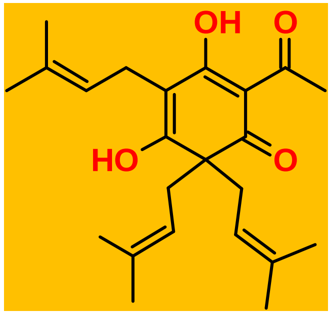


α-acids* (humulones)



R = $CH_2CH(CH_3)_2$	humulone	lupulone
$CH(CH_3)_2$	cohumulone	colupulone
$CH(CH_3)CH_2CH_3$	adhumulone	adlupulone

β-acids (lupulones)

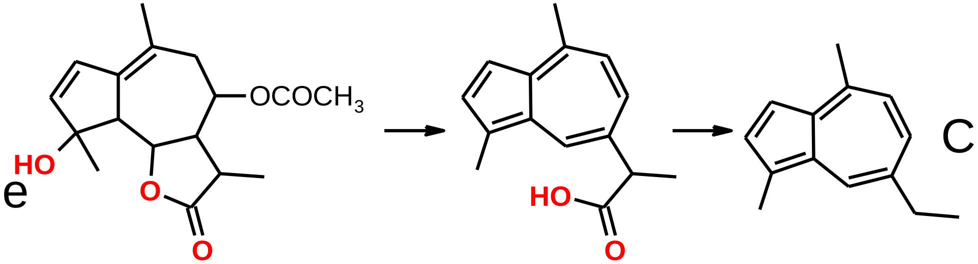


*La frazione di composti dell'estratto precipitati con $Pb(OAc)_2$ è detta acidi alfa.

Matricaria recutita: Composition and Formation of Chamazulene Oil During Steam Distillation.

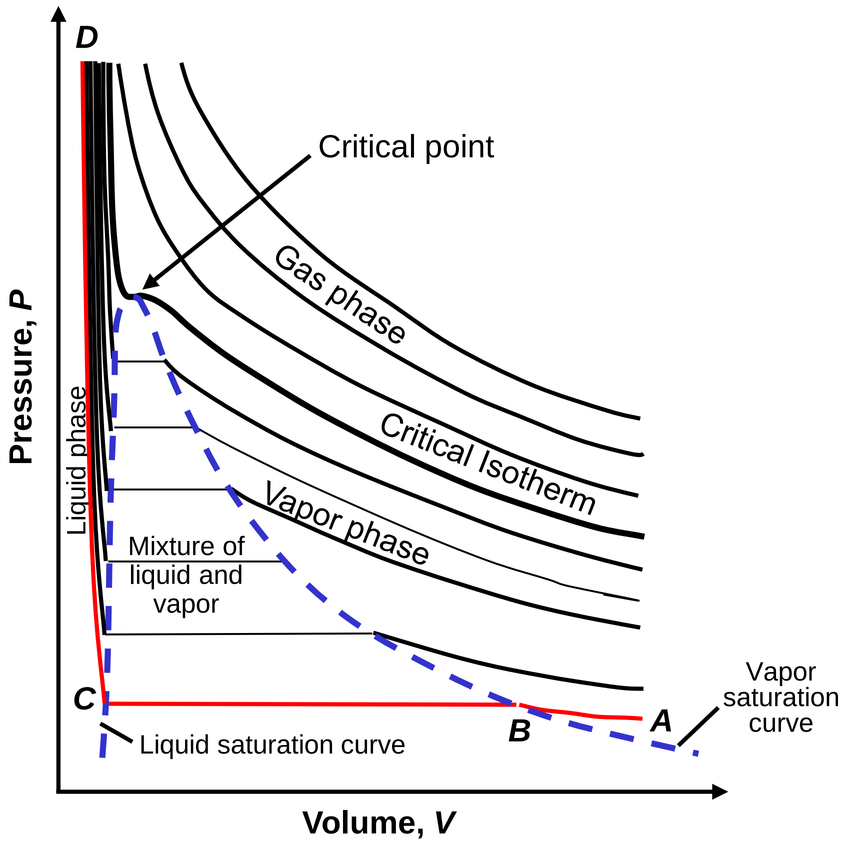
	Steam distilled %	Liquid CO_2 %
β-farnesene	18.4	14.5
spathulenol	<0.1	1.5
α-bisabolol oxide B	19.4	4.6
α-bisabolone oxide A	12.0	3.1
α-bisabolol	<0.1	3.7
chamazulene	15.4	1.3
α-bisabolol oxide A	9.9	23.5
Dicycloethers (MW 200)	2.7	37.8
Colour	Blue	Yellow

Matricine
pro-chamazulene



Chamazulene
(artifact)

Supercritical Water.



Critical point

P ≈ 22 MPa and T = 374^o 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:

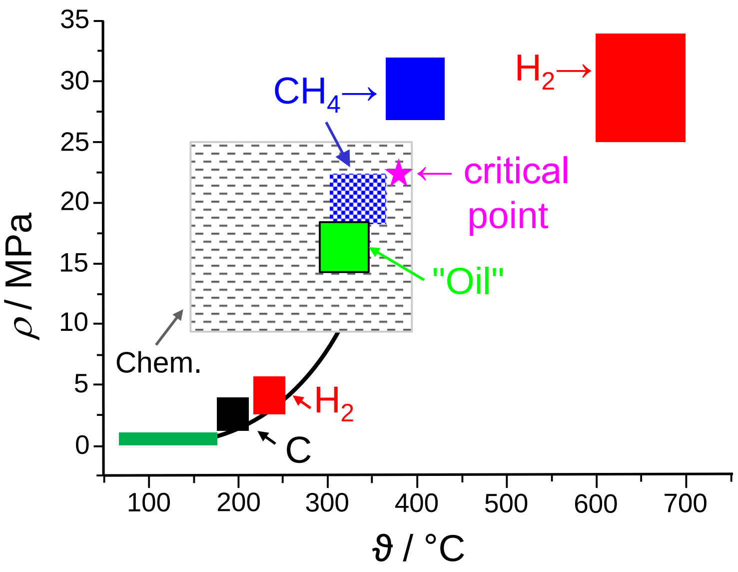
Liquid like density

Gas like viscosity.

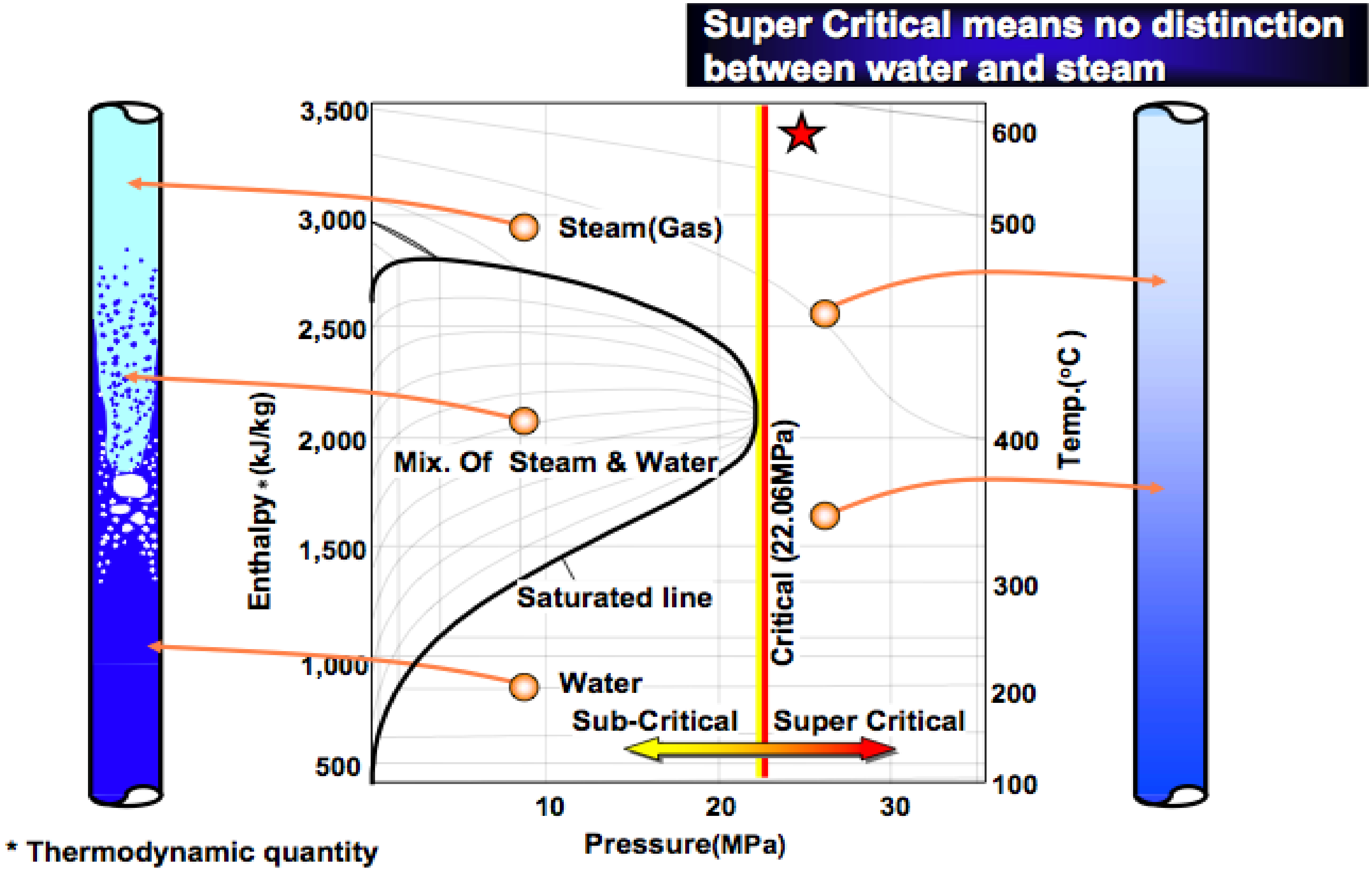
Supercritical Water (2).

	Normal	Subcritical	Supercritical	
T / °C	20	100	374	500
P / *MPa*	0.1	0.1	22.1	50
ε_r	78	30	2	14
pK_w	14	12	20	13

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.

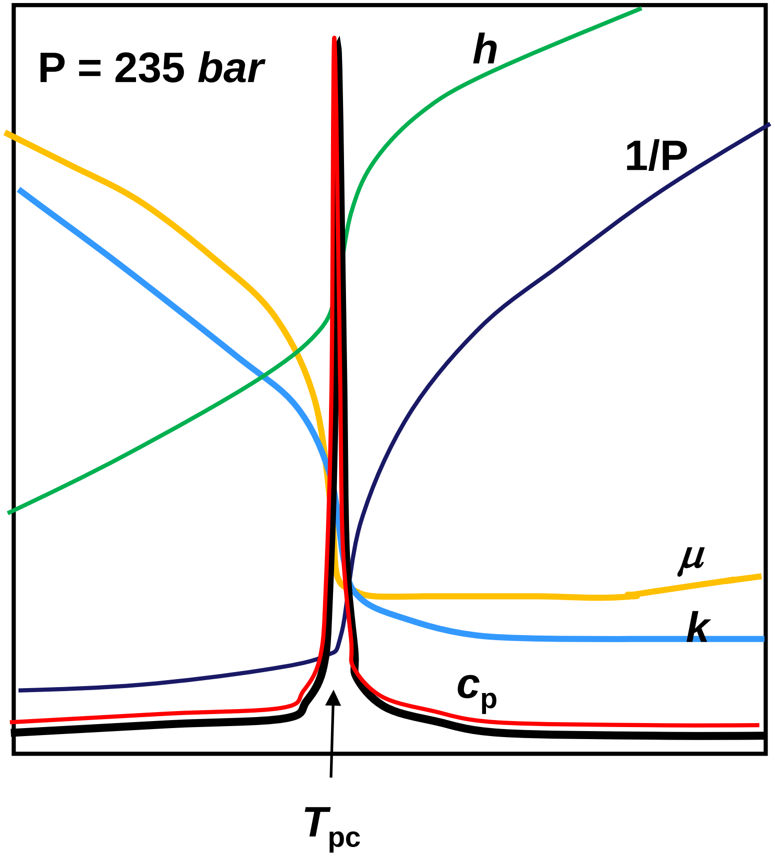


Supercritical Water (3).



Thermal Physical Properties at Critical Temperature.

- Properties variation as C_p, *k*, *h* and *μ* 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 *μ* and k is noticed.

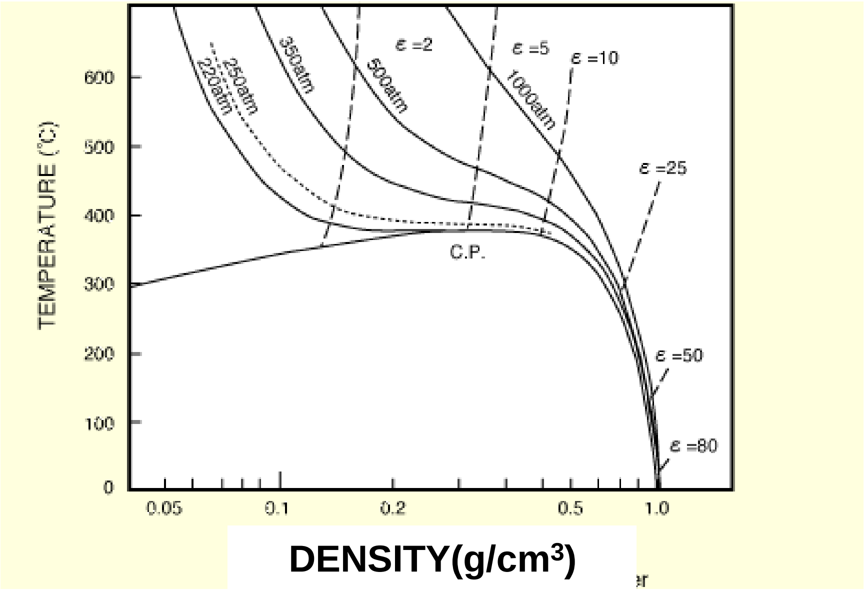


Water Properties Variation with Temperature

SC-Water.

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 (ε = 1.8), and polar solvents, i.e. methanol (ε = 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.



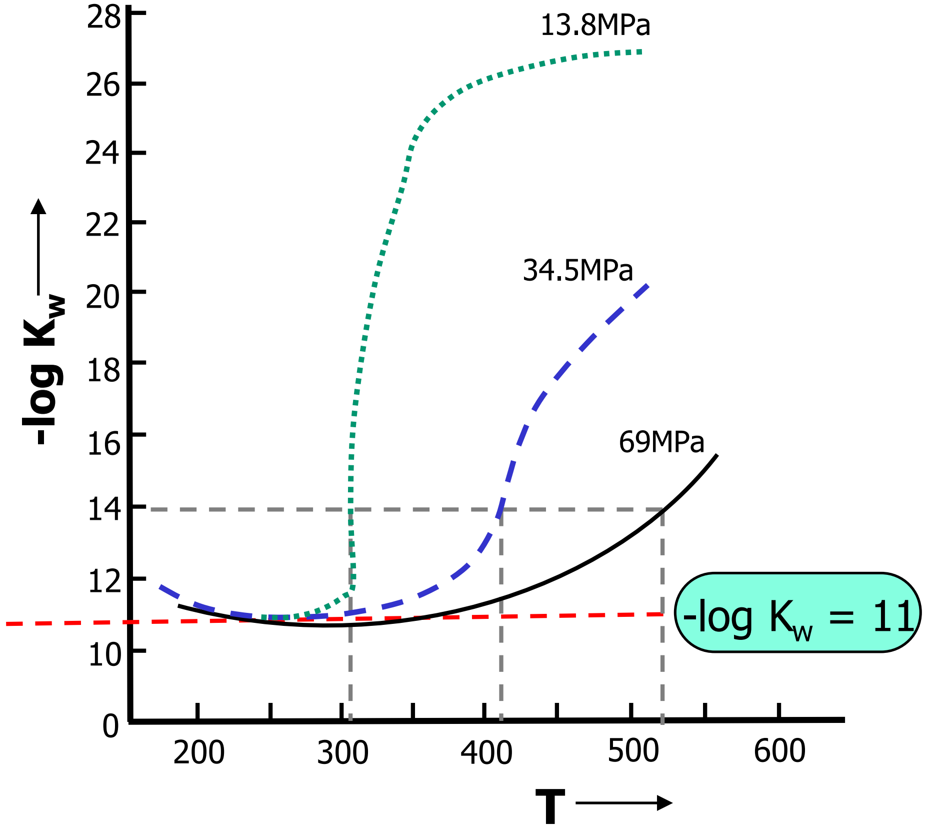
Relative dielectric constant of organic compounds	
- Propane	1.6
- Hexane	1.8
- Heptane	1.9
- CCl_4	2.2
- Benzene	2.3
- Acetone	20.7
- Ethanol	24.5
- Methanol	32.6

SC-Water (2).

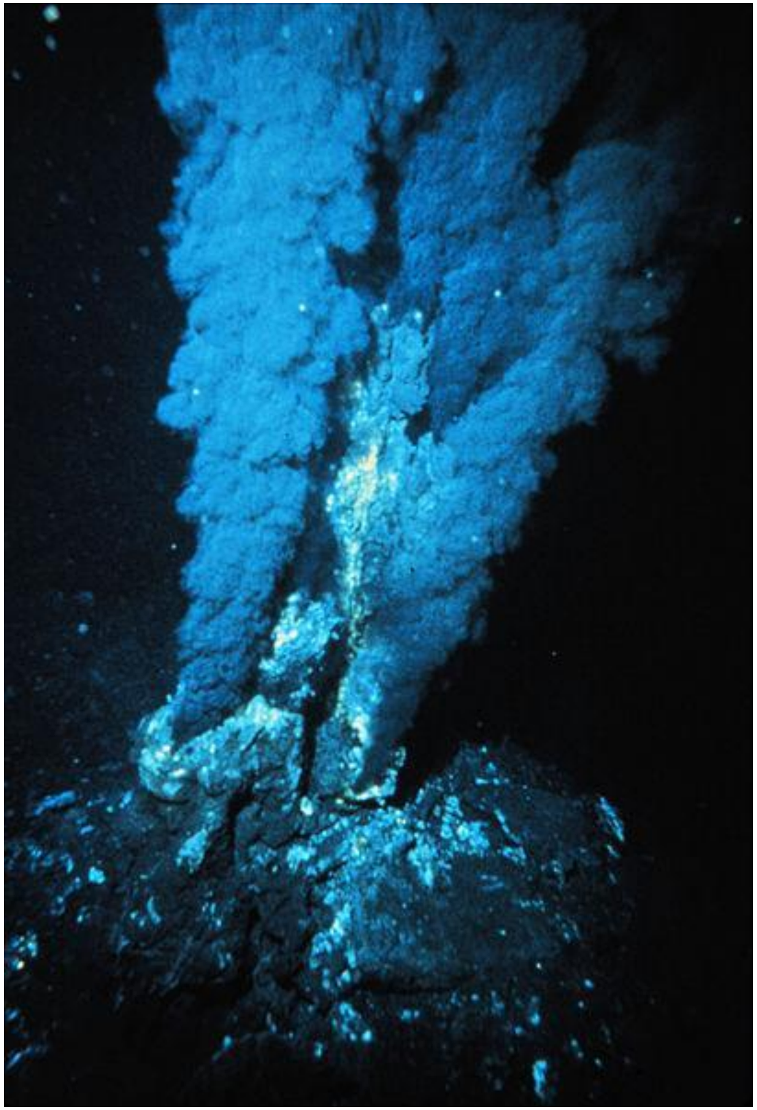
Water ionic product behaviour
$K_w=[H^+][OH^-]$;

- at 25°C and P = 1 *atm*, K_w is $1\times10^{-14}(mol/l)^2$.
- At higher temperature and pressure conditions, this value increase. At 34.5 *MPa* pressure, a maximum value of 1×10^{-11} $(mol/l)^2$ is reached (minimum – log K_w) near 300°C.

  Under these conditions, we have $[H^+] = 3\times10^{-6}$ *mol/l*, with an increase of about 30 times of concentration at room conditions. SC-water can be a potential acid catalyst.



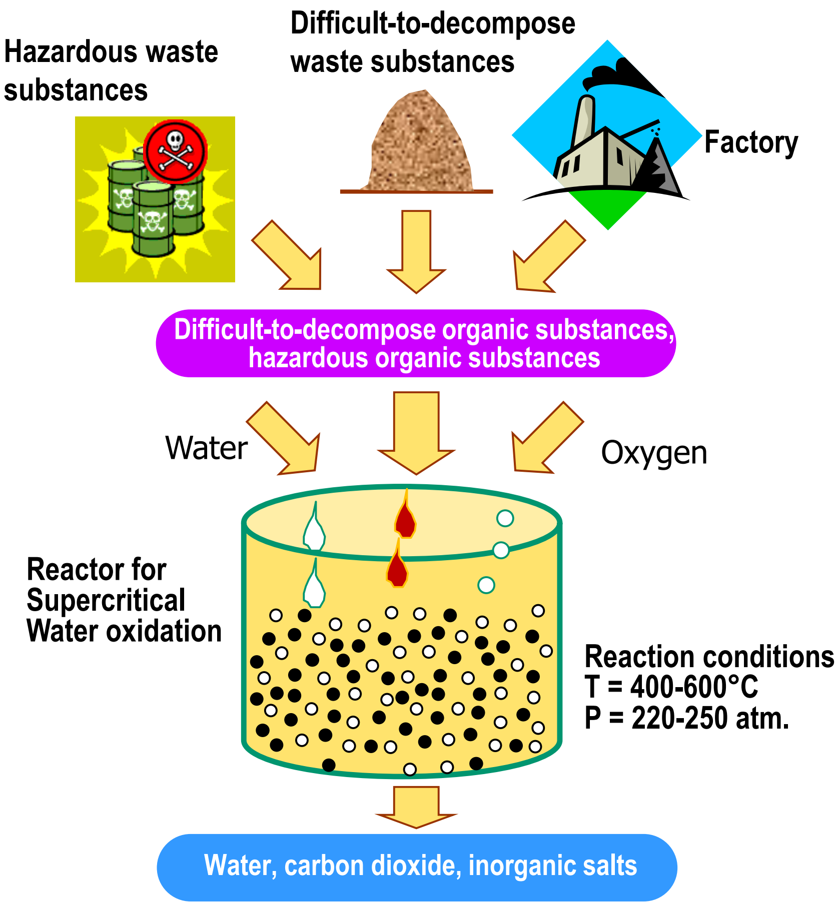
Black Smokers & Supercritical Water.



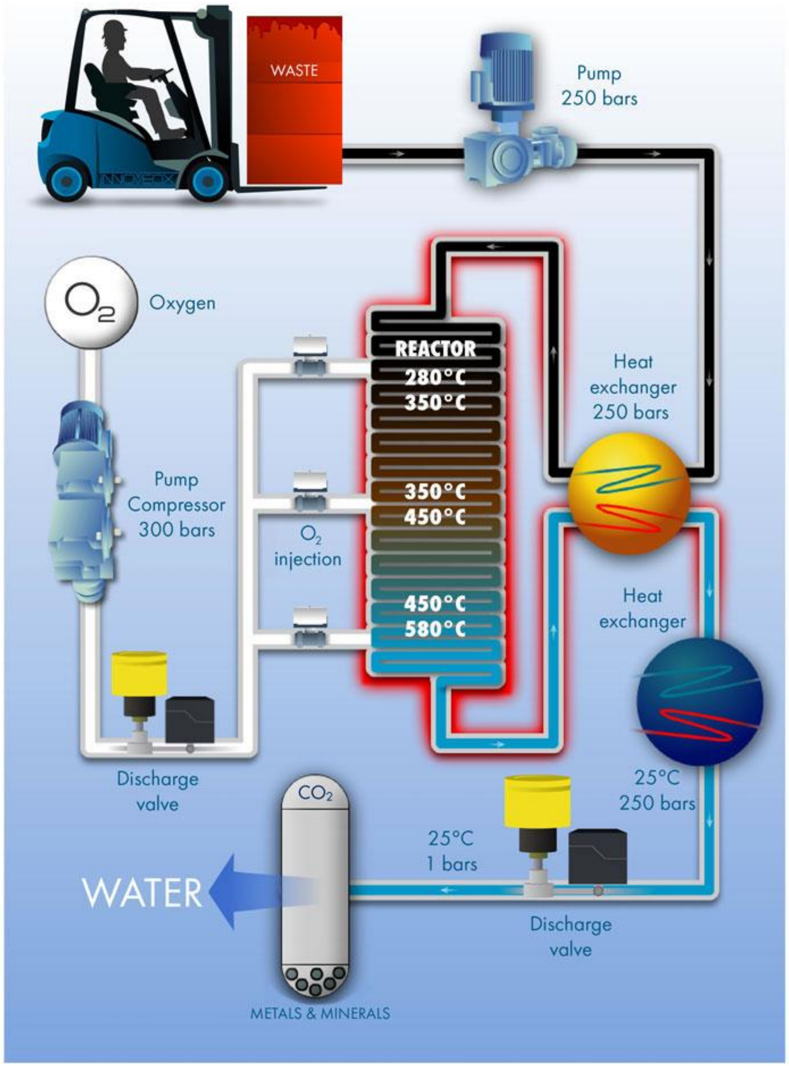
- Located just south of the Equator, at the southern end of the mid-Atlantic Ridge
- 3 kilometers beneath the surface of the ocean
- Temperatures measured between 407°C – 464°C by remotely operated submersibles
- Immense pressure & temperature combine to create an anomaly that has both liquid and vapor qualities
- Provide essential nutrients to locally adapted organisms, microbes, & phytoplankton.

Waste Treatment by Oxidation in Supercritical Water.

- Technology able to complete decomposition of all types of recalcitrant compounds in short time, producing CO_2, H_2O 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