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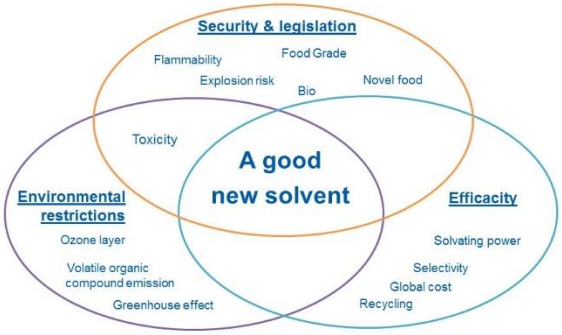
Subcritical water

Subcritical water is liquid water under pressure at temperatures above usual boiling point, 100 °C (212 °F). It is also known as "subcritical water" or "pressurized hot water." At subcritical state, water is maintained in liquid form by apply pressure. Therefore, the liquid water is in equilibrium with vapor at the saturated vapor pressure. Some properties changes take place:

- ✓ ⇗ Solvating power,
- ✓ ⇘ Viscosity and surface tension,
- ✓ ⇗ diffusivity,
- ✓ ⇘ Polarity,
- ✓ ⇗ Self-ionization of water ➔ Light acidification (acid hydrolysis).
- ✓ The duration of extraction is reduced and the solvent volume too ➔ the extract is more concentrated!

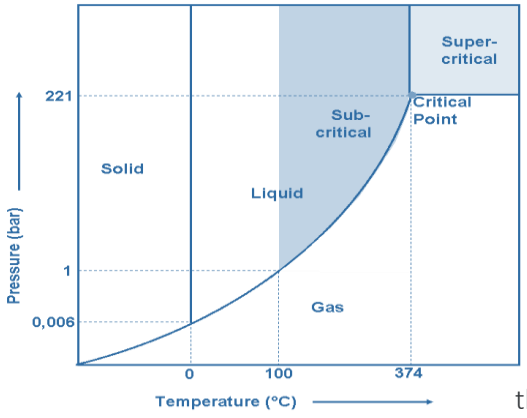
Several words are related to subcritical water: superheated water, pressurized water, …



ALTERNATIVE TO POLAR PETROCHEMICAL SOLVENT

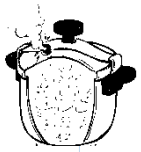
Water in the subcritical state is an alternative to polar liquids and semi-polar solvents such as methanol, ethanol, and acetone.

Additional benefits are associated with its use:



✓ *No toxicity, "green" solvent*
✓ *No residual organic solvent in the final product/extract*
✓ *Non-flammable, non-explosive: less expensive installation (ATEX zone not necessary)*
✓ *Modulation of properties by adjusting the temperature of assay - high temperature allows chemical modification of the material (e.g. hydrolysis)*

The extraction is generally processed at temperatures from 120 ° C to 160 ° C with sufficient pressure (10-20 bar) to maintain the water in liquid state.



The dissociation constant (Kw) of water increases with temperature, this implies that the pH changes to lower pH values.
Because the ionic strength of hydronium and hydroxide ions is higher than at ambient temperature, hydronium ions act as catalyst in reactions.
Hydrolysis of biomass: amino acids, unsaturated fatty acids, polysaccharides…

EXTRACTION PRINCIPLE - SUBCRITICAL WATER

This extraction method uses the new properties of water, at subcritical state which enable the solubilization of less polar compounds. The more the temperature increases, the more the polarity decreases.

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Two systems exist:

- Static Mode: The raw material is wetted with ambient water. Then, the mixture is subjected to high pressure and high temperature followed by cooling with emptying of the liquid phase which contains the interest molecules.
- Dynamic mode: the raw material is introduced into a pressurized extraction autoclave. Preheated water is pumped and percolates through this fixed bed, dissolving and carrying with it interest molecules.

LAB AND PILOT PLANTS

CELABOR has two scales of plants: lab scale and pilot scale

Volumes:	10 – 20 ml	⇨ 5L
Max temperature of extraction:	200 °C	⇨ 200°C
Max pressure of extraction:	200 bars	⇨ 250 bars
Automatization:	Yes	⇨ Yes
Ratio solid to solvent:	1/10	⇨ 1/5

Depending on the temperature of extraction, it is possible to target a type of molecules (e.g. high temperature - polysaccharides are hydrolyzed)

APPLICATIONS

Subcritical water Extraction can be compared to an aqueous-alcoholic extraction or an acetone/water extraction.

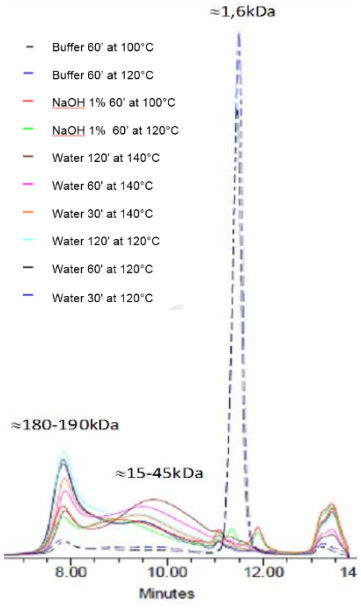

Figure1: High Pressure Size Exclusion Chromatography (HPSEC). Higher T° leads to smaller size molecules

Examples of applications:

- Insoluble fibers Extraction (e.g. hemicellulose, lignin,…)
- Antioxidant molecules (e.g. polyphenols,…)
- Proteins Extraction
- …

CELABOR's **projects** in which subcritical water was used:

✓Byproval (New valorization pathway for fruit/vegetable waste by a combination of extraction and biogas production) http://www.byproval.eu/
✓Salichem (saline plants uses for chemicals and energy production) http://www.salichem.eu/
✓Subwex (Subcritical water as a green solvent for extraction of plants) http://www.cornet-subwex.eu/
✓Walaid (hemicellulose, lignin,…)
✓Walextract (antioxidants, eg : polyphenols,…)
✓Private projects
✓…

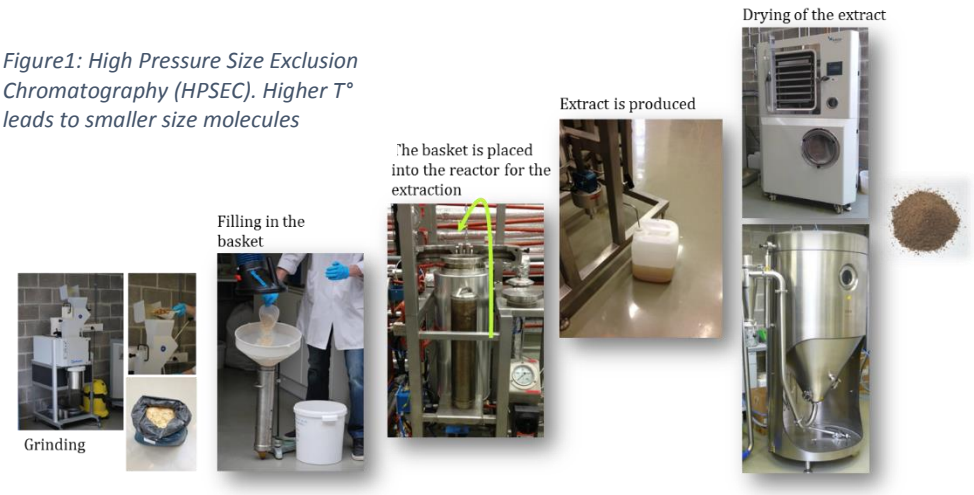

Figure 2: extraction pilot for subcritical water use. A: water tank; B: Reactor; C: extract collector