Supercritical Fluid Solvents

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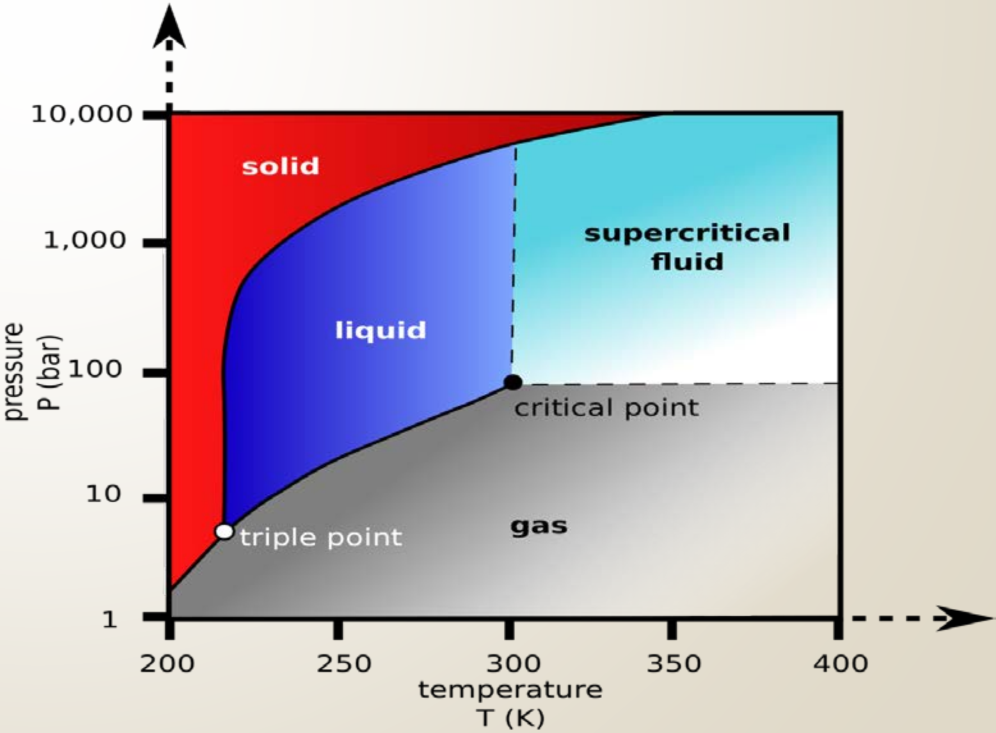
Overview

- What is a Supercritical Fluid?
- Organic vs. Supercritical Fluids
- Supercritical CO_2
- Supercritical H_2O
- Conclusions

What are Supercritical Fluids?

- Fluid at a temperature and pressure above the critical point

- Liquid and gaseous states are indistinguishable



Evolution of a Supercritical Fluid

- https://www.youtube.com/watch?v=GEr3NxsPTOA

Organic Solvents

- Traditionally organic solvents used
- Industries:
  - Chemicals
  - Pharmaceuticals
  - Disposal of hazardous chemicals
- Not environmentally friendly:
  - Toxic, flammable, pollutants

Supercritical Solvents

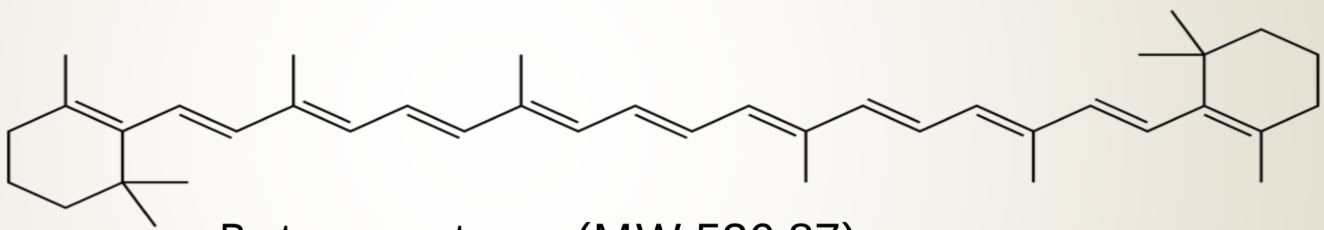
- Environmentally Benign
- Most common- CO_2 and H_2O
- Easily recycled
- High selectivity
- Tunability
  - Density, viscosity, diffusivity

What's the Demand?

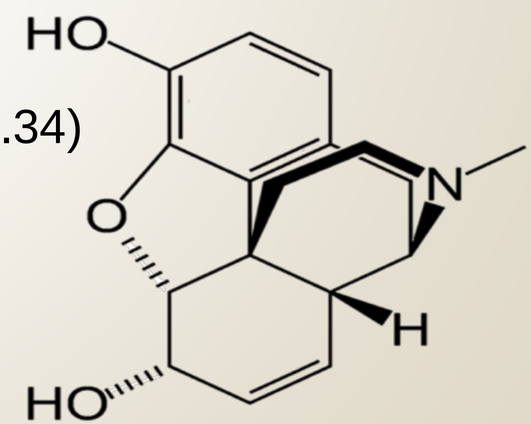
- Demand stems from rising standards in the food and drug industries.
- Extraction with SCF's can often yield upwards of 90% pure product
  - Higher market values
- Traditional extractions use toxic organic solvents like chloroform, dichloromethane, and ethyl acetate
  - scCO_2 is completely non-toxic and environmentally benign
  - scCO_2 is also 100% recoverable and recyclable

Supercritical CO_2 in Food Technology

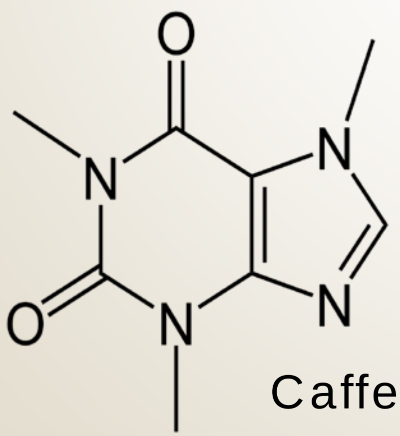
- Supercritical CO_2 is used in the extraction of oils, terpenes, aromatics, natural colorants, and recently cholesterol. Common extracts:



Beta-carotene (MW 536.87)



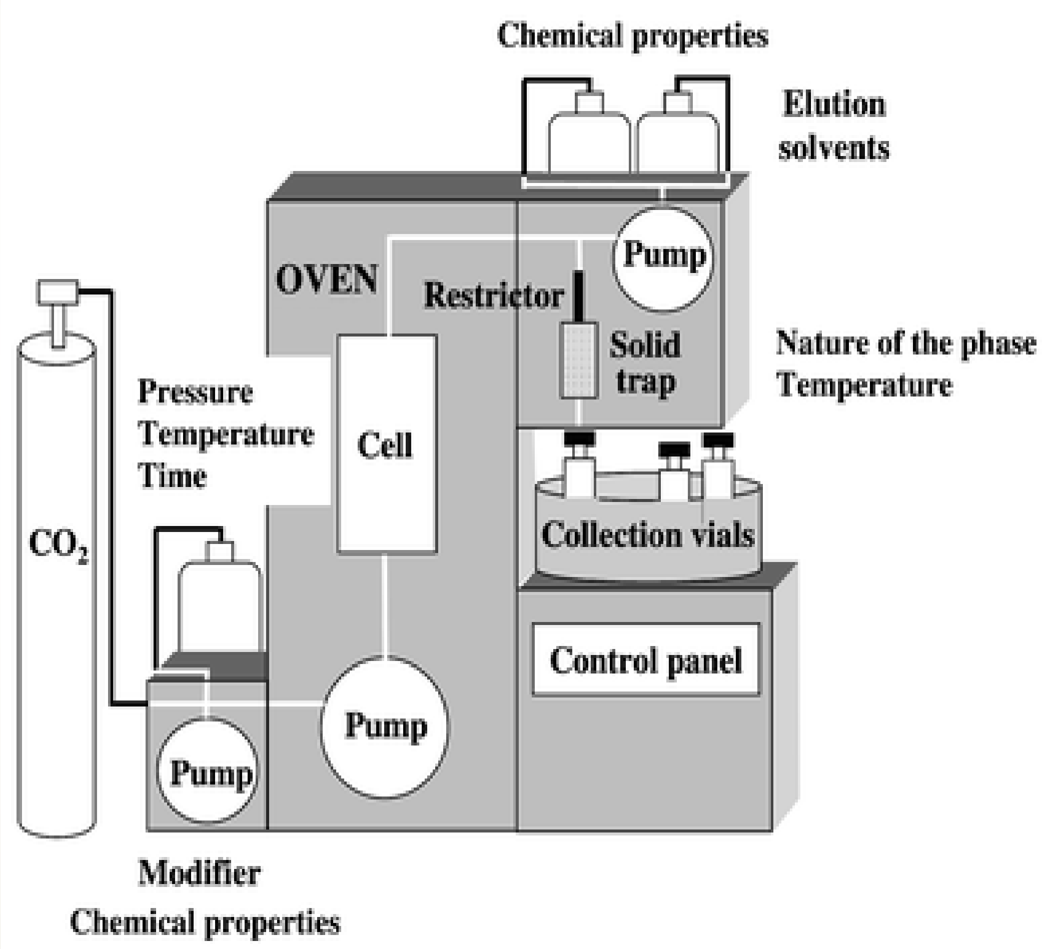
Morphine (MW 285.34)



Caffeine (MW 194.19)

Extraction Basic Principles

- Solvent is pressurized
- Sample introduced to extractor
- Solvent flows through sample
- Waste (solids) discarded
- Flow-through captured
- Solvent recycled



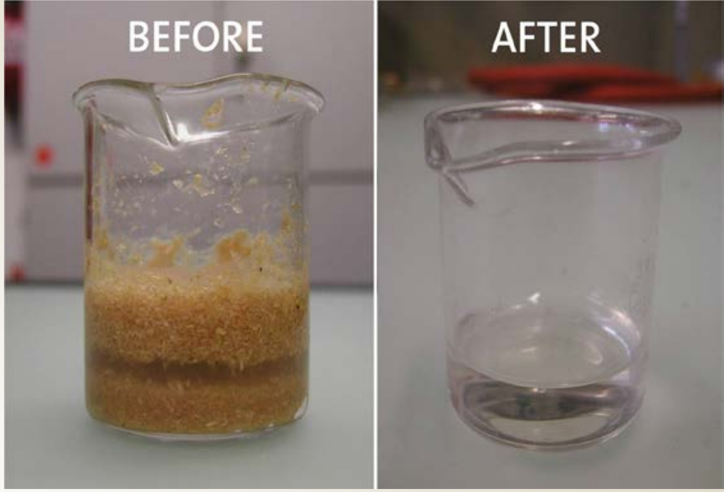
So why isn't $scCO_2$ in mass use?

- Only high-cost, low-volume reaction tanks exist
- No financial incentive
  - Coffee and pharmaceutical industries are the only large markets
- $scCO_2$ extraction is only useful on things with relatively low molecular weights
  - Not practical for use in industrial polymerization reactions
  - Co-solvents such as ethanol are sometimes necessary with higher MW compounds, which pose their own green issues

Supercritical Water (scW)

- Temperature: 380-700 C
- Pressure: 25-40 MPa
- Potential use in several fields
  - Conversion & pretreatment of biomass
  - Supercritical oxidation
  - Organic and inorganic chemistry
  - Energy transfer medium (nuclear & geothermal)
- Serious energy and corrosion challenges with its use

Conversion of Biomass



- Main goal of SCW usage
- SCW gasification of biomass
  - Used with wet biomass (>80% water weight)
  - Reaction occurs by forcing biomass slurry into supercritical state
  - Reaction creates syn-gas
  - At 400° C methane is main product
  - At 650° C hydrogen is main product
- Gaseous products can be tuned by pressure and temperature
- CO_2 dissolves in SCW, only hydrogen and methane collected gases

VERENA Plant in Karlsruhe, Germany

- Biomass turned into slurry
- Preheated to near critical conditions
- Feed into nickel alloy reactor
- Pressure and temperature increase, SCWG occurs
- H_2 & methane collected
- Depressurized & CO_2 vented

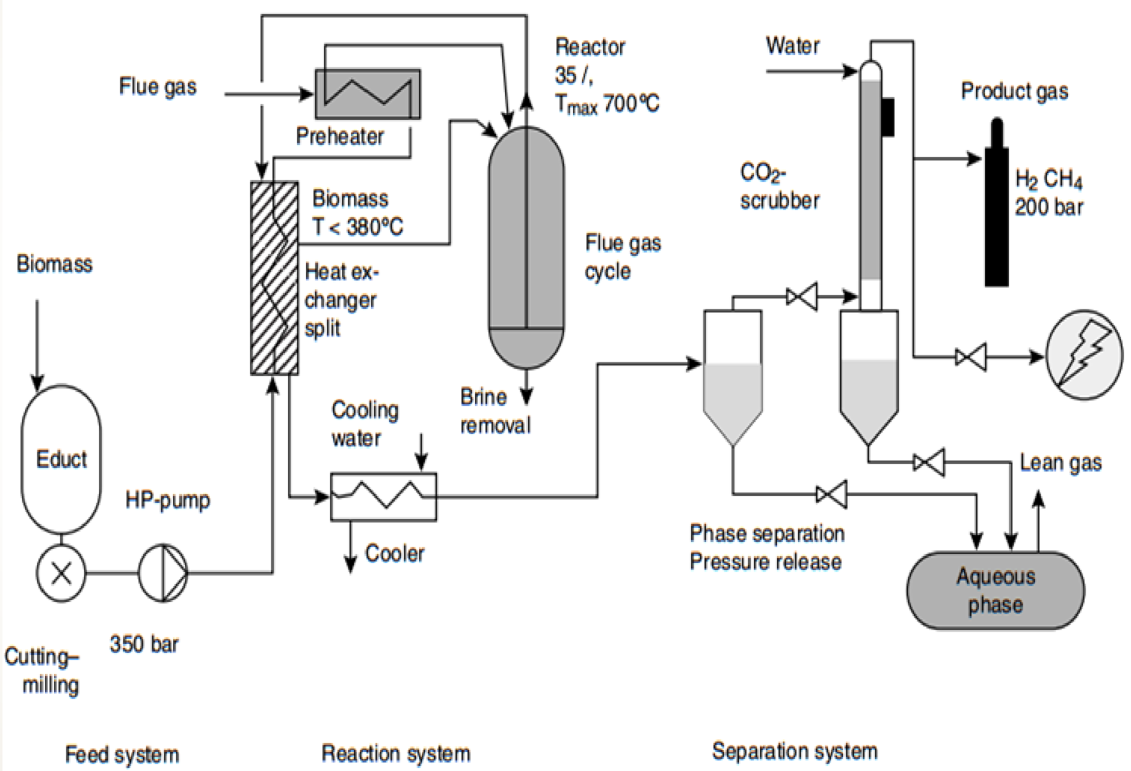
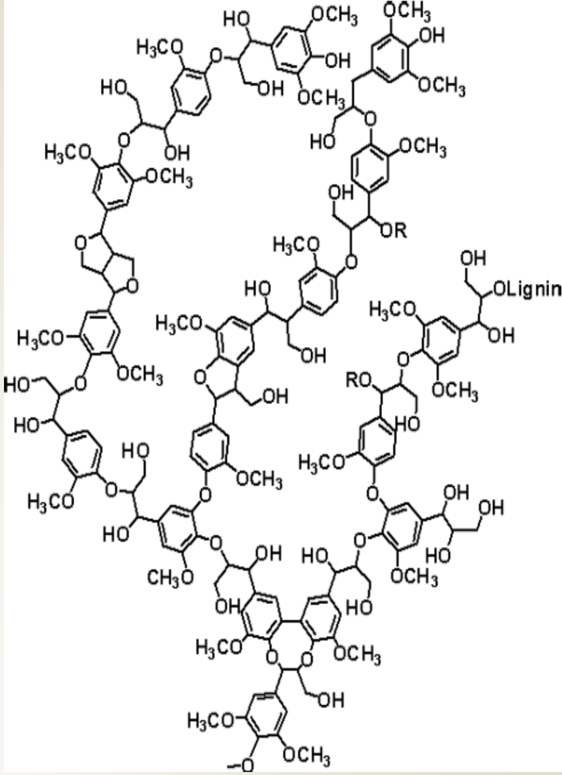


FIGURE 5.1 Schematics of the VERENA demonstration plant. Adapted with permission from Ref. [9].

scW Biomass Pretreatment



- Lignin in plant material prevents enzymatic attack
  - Hydroxyaromatic polymer
  - Cellulose contains 10-25% ligning
  - Prevents fermentation into ethanol
- scW pretreatment can be a solution
  - Hydrolyzes polymeric lignin with CO_2 as acid catalyst
  - Under mild scW conditions (400 C and 25 MPa)
- After scW pretreatment the biomass had a much higher conversion to ethanol

Supercritical Water Oxidation

- Used to destroy hazardous materials
- Oxidation occurs in homogenous phase
  - Extremely fast
  - Near complete oxidation
  - Environmentally friendly/neutral products
- Process is self-sustaining with respect to energy
  - Oxidation is exothermic
  - Heat generated is enough to meet energy requirements
  - Excess heat energy available for power generation

SCWO Process

- Four primary steps
  - Feed preparation
  - Reaction
  - Salt separation
  - Heat recovery
- Oxygen source
  - Air
  - Liquid O_2
  - Hydrogen Peroxide

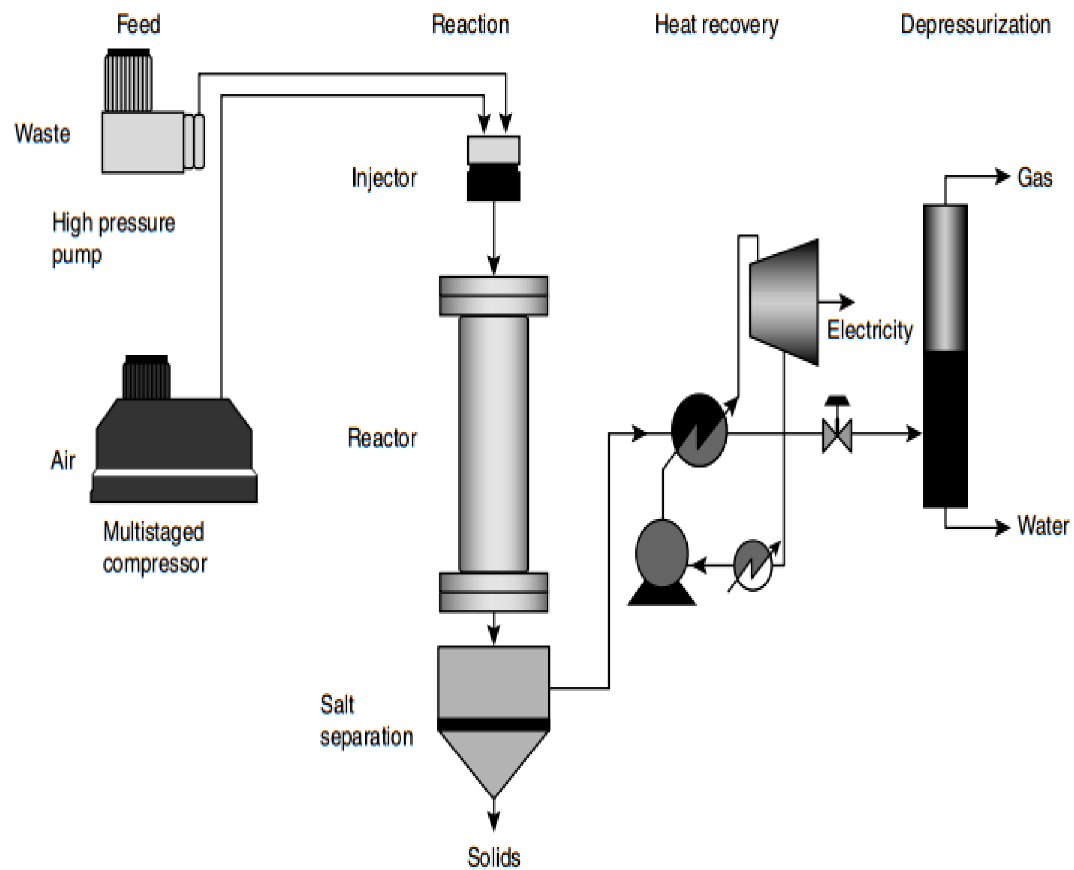


FIGURE 5.2 Schematics of an SCWO plant. Adapted with permission from Ref. [36].

Conclusions

- Drawbacks
  - Potential extreme corrosion problems (scW)
    - Reactors made of exotic alloys
  - Energy intensive
  - Must be run as batch process
  - Cannot be used with high MW substances
    - Thermal degradation
  - scW cannot be used in pharmaceuticals

Conclusions cont.

- Benefits
  - Unique properties
  - Oxidize hazardous chemicals (scW)
  - No catalyst for H_2 production from biomass (scW)
  - Little to no organic waste
  - Recyclable
  - Fast diffusion, low viscosity
  - Environmentally benign
  - Less separations
  - Large availability

Questions?

Sources

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