Supercritical Fluid Solvents

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Overview

- What is a Supercritical Fluid?
- Organic vs. Supercritical Fluids
- Supercritical CO₂
- Supercritical H₂O
- 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 - CO₂ and H₂O
- 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 CO₂ in Food Technology

- Supercritical CO₂ 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
- H₂ & methane collected
- Depressurized & CO₂ vented
Lignin in plant material prevents enzymatic attack
- Hydroxyaromatic polymer
- Cellulose contains 10-25% lignin
- 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 H₂ production from biomass (scW)
- Little to no organic waste
- Recyclable
- Fast diffusion, low viscosity
- Environmentally benign
- Less separations
- Large availability
Questions?
Sources

Background Info Sources:
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- http://www3.nd.edu/~enviro/supercritical.html

scW Sources:
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- Lignin pic: http://www.lignoworks.ca/sites/default/files/what-is-lignin.png

sc CO₂ Sources:
- Food Technology: http://fst.sagepub.com.lib-ezproxy.tamu.edu:2048/content/8/5/269.full.pdf+html
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