

Green Chemistry for Biofuels

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Overview

- ☉ Sustainable Production of Energy, Materials, and Chemicals
- ☉ Hydrothermal/Solvothermal approach - Use high-temperature liquid water and supercritical fluids for chemical reactions and extraction
- ☉ Green Chemistry - renewable feedstocks, safer solvents

Why Water?

- Abundant
- Non-toxic
- Non-flammable
- Inexpensive
- Naturally present in biomass
- Needs of science - chemistry in/with water under-explored
- Diverse applications - geochemistry, nuclear power, engineered systems

Introduction to High-Temperature Water (HTW)

HTW: Liquid H₂O at 200 – 350°C ($T_C = 374^\circ\text{C}$)

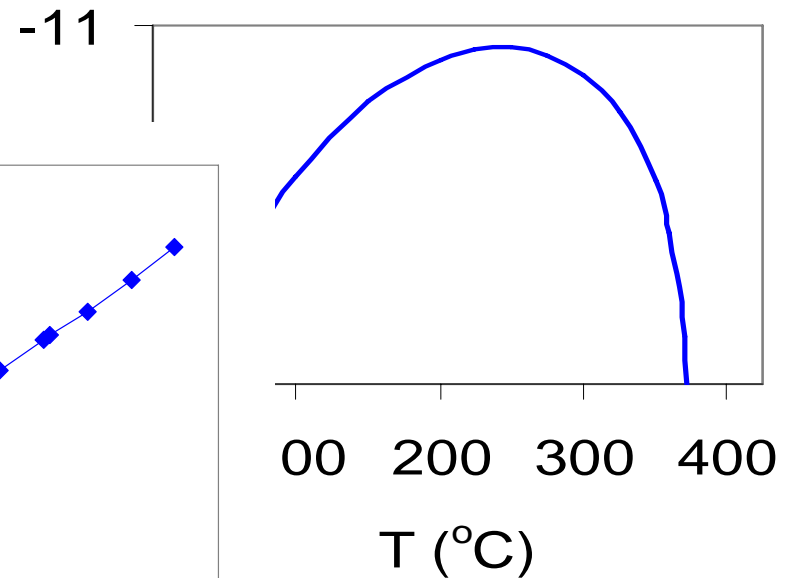
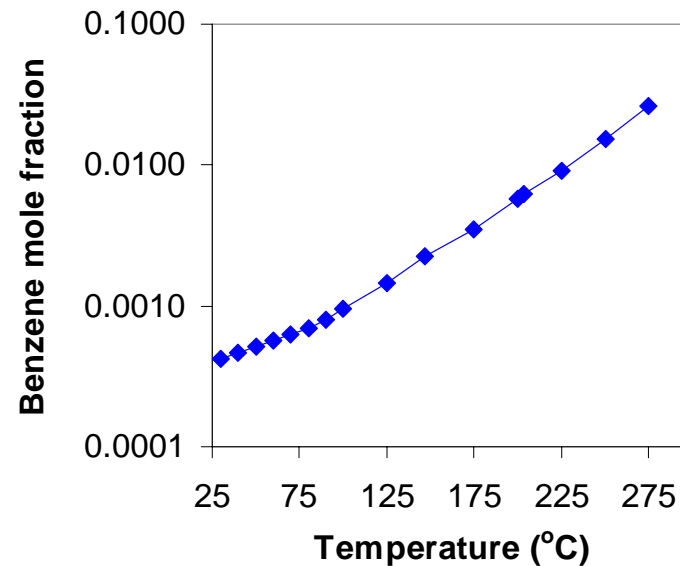
Properties of HTW different from room-temperature water

- Fewer and less persistent H-bonds
- Lower dielectric constant

→ Increased solubility of org

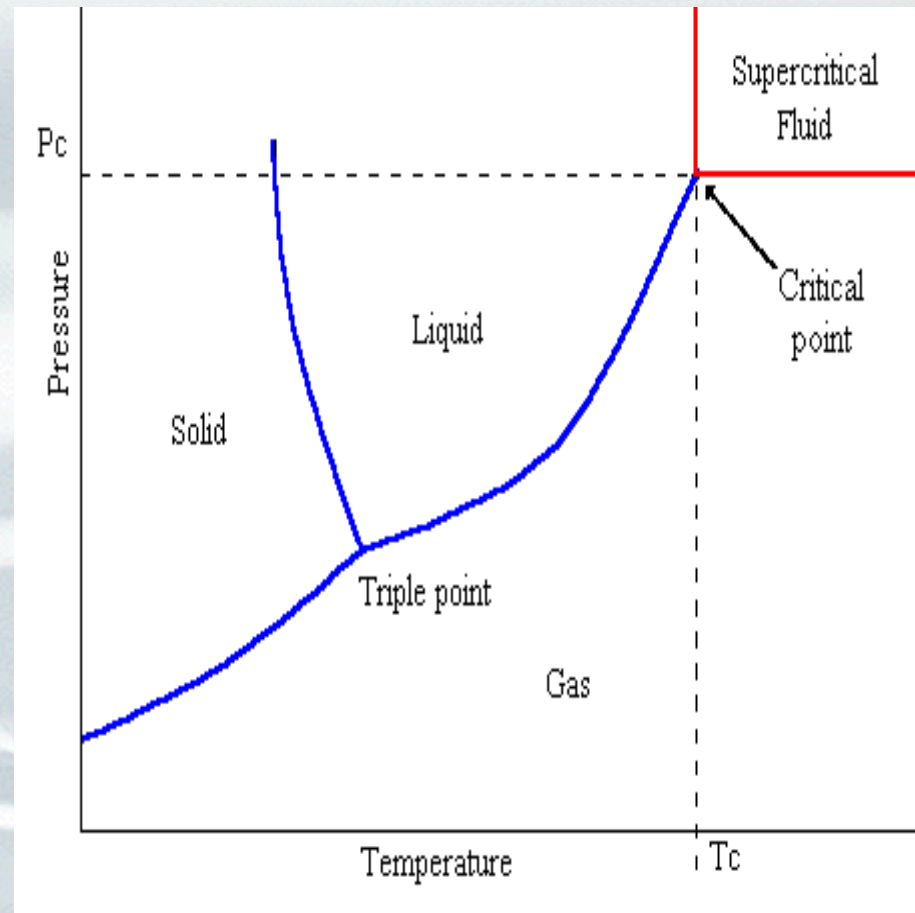
- Higher $K_W = (\text{H}^+)(\text{OH}^-)$

→ Conventio
catalyzes rea



Why Supercritical Fluids?

- Solubility and phase behavior
 - Multi-phase system can become one phase
- Solvothermal reactions occur
- Opportunities for new reaction pathways
- Manipulate solvent properties by tuning P



Renewable Energy - Biomass to Biofuels

- Sustainable Energy (Liquid & gaseous fuels from biomass)
- Hydrothermal & Solvothermal Processing
 - Hydrothermal liquefaction
 - Hydrothermal gasification
 - Solvothermal biodiesel synthesis

Drivers for Renewable Energy

- Energy supply - meet growing global demand
- Energy security - less reliance on imports
- Energy cost - keep prices low
- Climate change - reduce CO₂ emissions



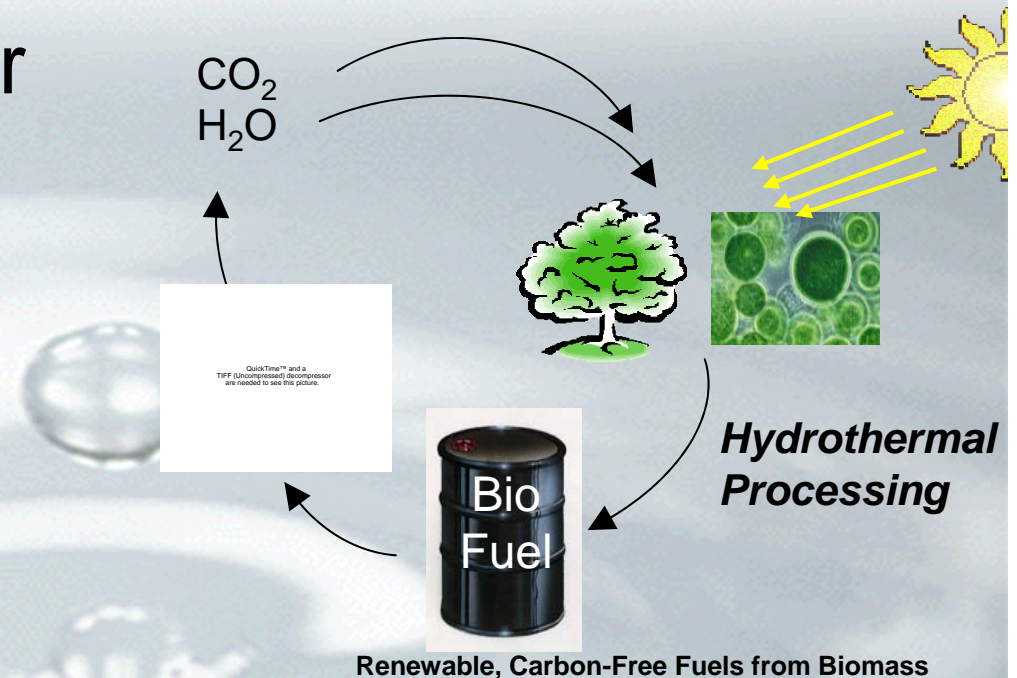
Hydrothermal Liquefaction of Biomass

Hydrothermal Liquefaction

- Different approach for producing renewable liquid biofuels

- not corn ethanol
- not cellulosic ethanol
- not biodiesel
- not “green” gasoline
- not “green” diesel

- Break down the bio-macromolecules in biomass in hot (~ 300 °C) liquid water (hydrolysis, pyrolysis, dehydration, natural acid catalysis)



Renewable, Carbon-Free Fuels from Biomass

Hydrothermal Liquefaction

- No need for organic solvents for oil extraction
- No need to dry wet biomass
 - no/less dewatering required for microalgae
 - no energy demand for drying, centrifuge
- Feedstock agnostic
 - ethanol production needs sugars (carbohydrates)
 - biodiesel & “green” diesel production needs triglycerides
- Best suited for wet biomass
 - cherry processing waste
 - microalgae!

Microalgae

- Wet biomass
- Can have very high oil content
- No food vs. fuel competition
- High photosynthetic efficiency
- High biomass growth rates
 - ~ 5000 gal/acre (~ 500 gal/acre for terrestrial biomass)
- Can grow in salt water (reduce fresh water needed)

Microalgae

- Water provides structural support
 - No lignin (recalcitrant part of terrestrial plants - difficult to break down)
- Could be co-located with waste water treatment plant and/or fossil-fuel fired power plant (biological CO₂ sequestration)

Microalgae

- ~ 100+ start-up companies
- ~ 70% focus on algae growth, GMO
- Fewer focus on extraction of oil
- Standard approach is dewatering, lipid extraction (with hexane), and oil processing to make biodiesel or “green” diesel
 - \$\$\$\$, organic solvents, acids, bases
 - Let’s use a green chemistry approach!

Hydrothermal Liquefaction of Microalgae

Hydrolysis reactions decompose the biomacromolecules

- Proteins \longrightarrow Amino Acids
- Carbohydrates \longrightarrow Sugars
- Lipids \longrightarrow Fatty acids



Microalgae Hydrothermal Liquefaction

