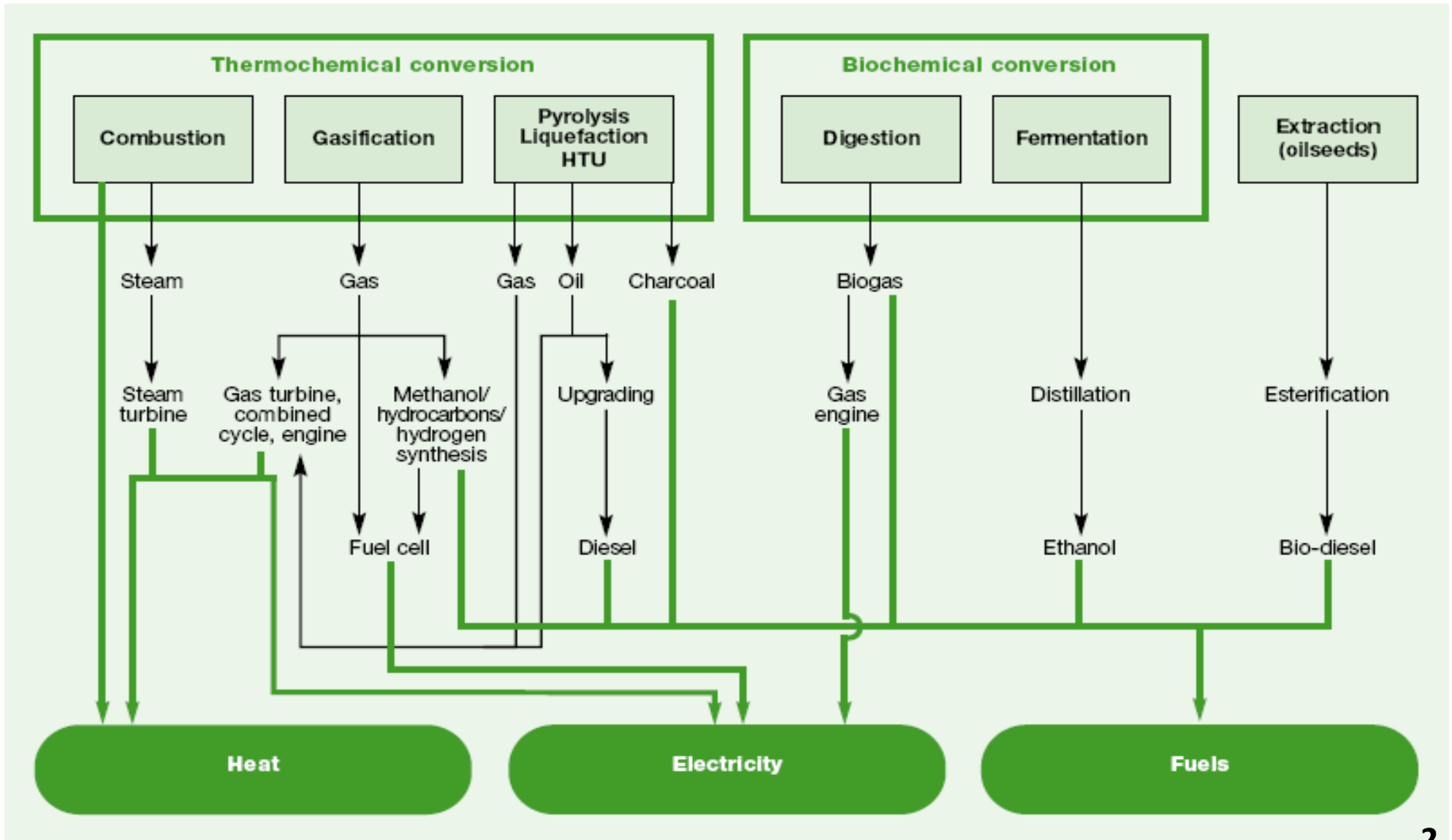


Thermochemical and Hydrothermal Conversion Processes

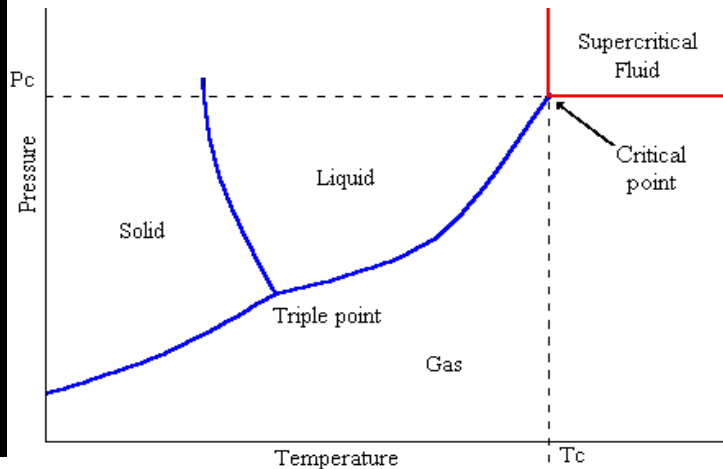
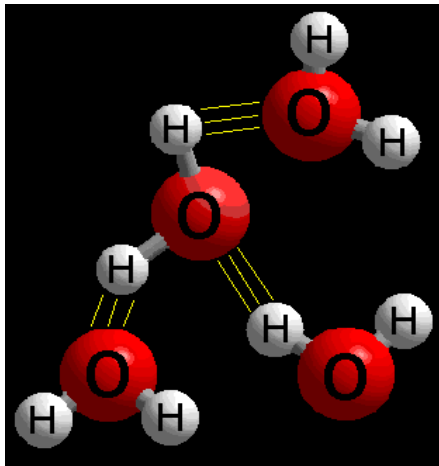
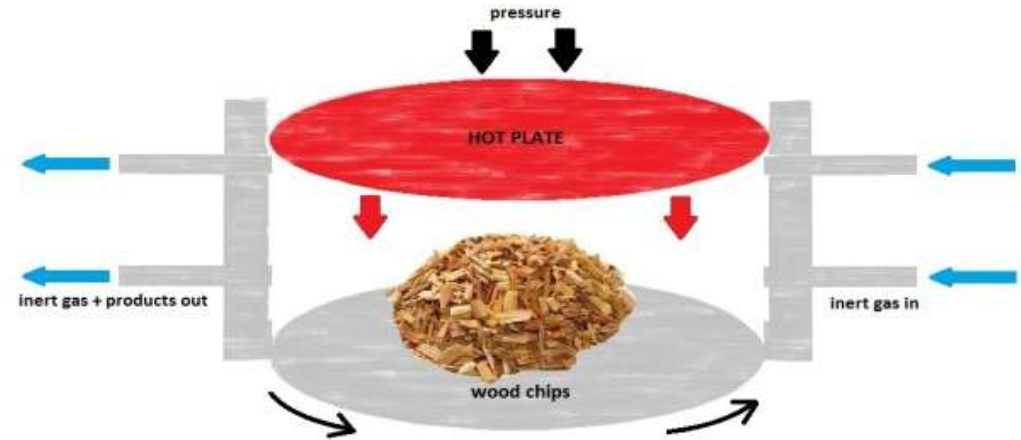
Fernando Resende
School of Environmental and Forest Sciences
University of Washington

Biomass to Fuels/Energy



Thermochemical/Hydrothermal Conversion of Biomass

Low Moisture Biomass (~10 wt %):
✓ Ablative Pyrolysis of Beetle-killed Trees



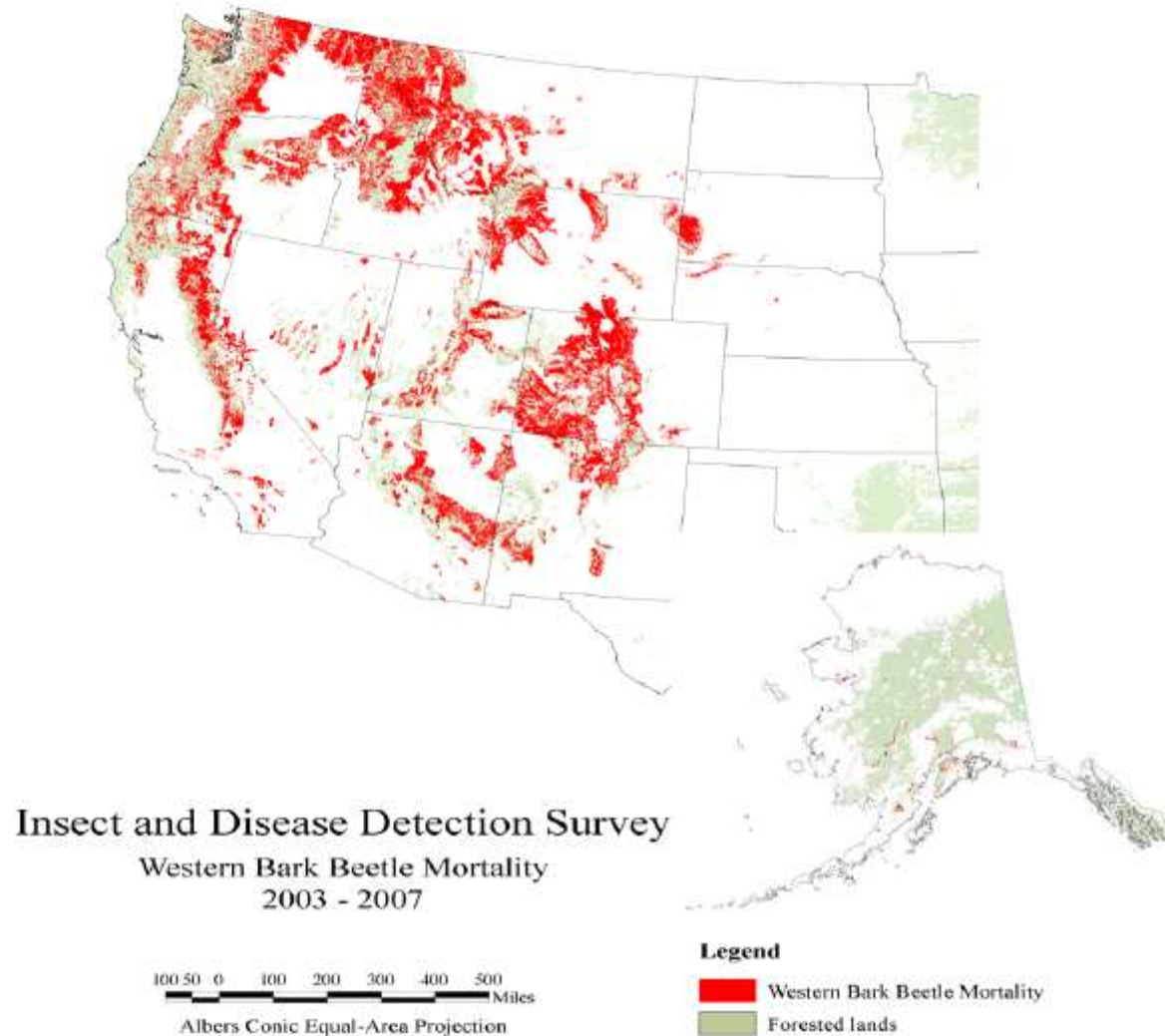
High moisture biomass (> 40 wt %):

✓ Hydrothermal Gasification/Liquefaction of Biomass

The beetle-killed trees problem

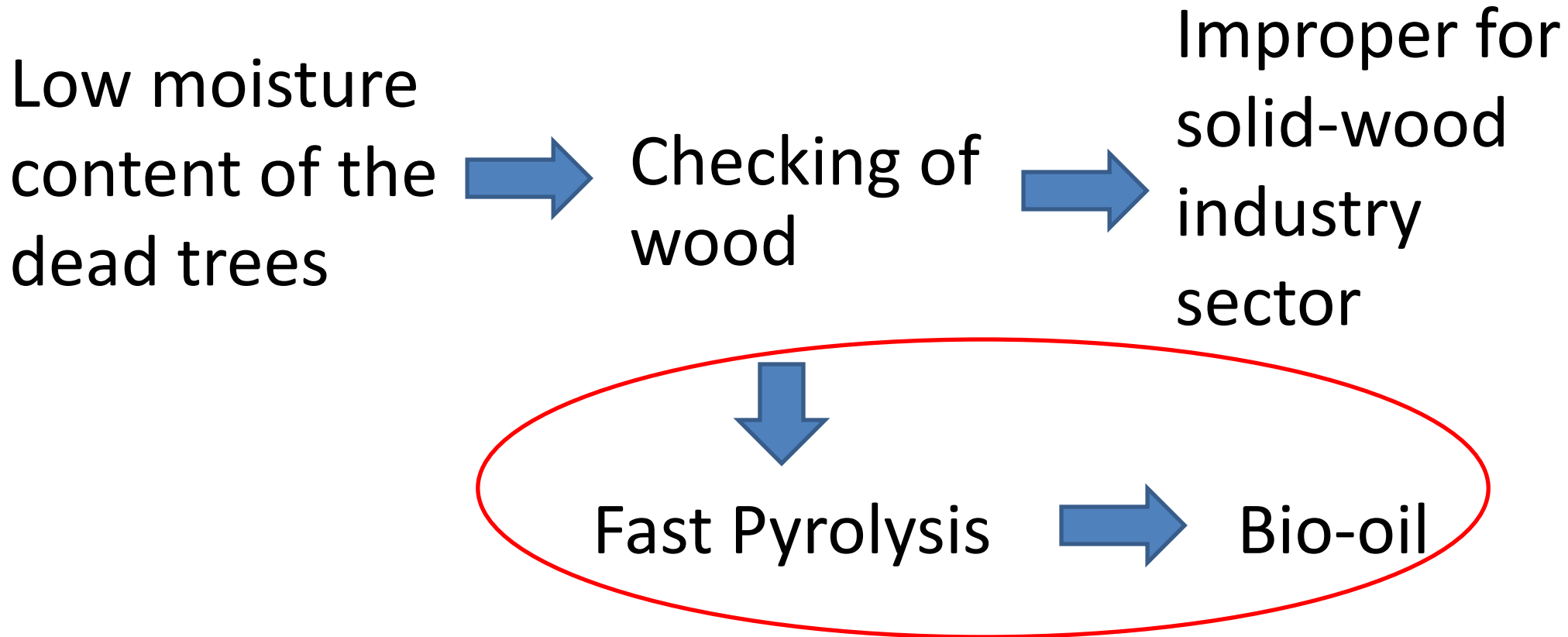


- MPB attacking Lodgepole pine: drought, warmer winters, aging forest
- More than 10 million acres of west forest affected
- Trees mortality causes a fire hazard
- Disposal methods include piling and burning (wastes energy, carbon and nutrients)



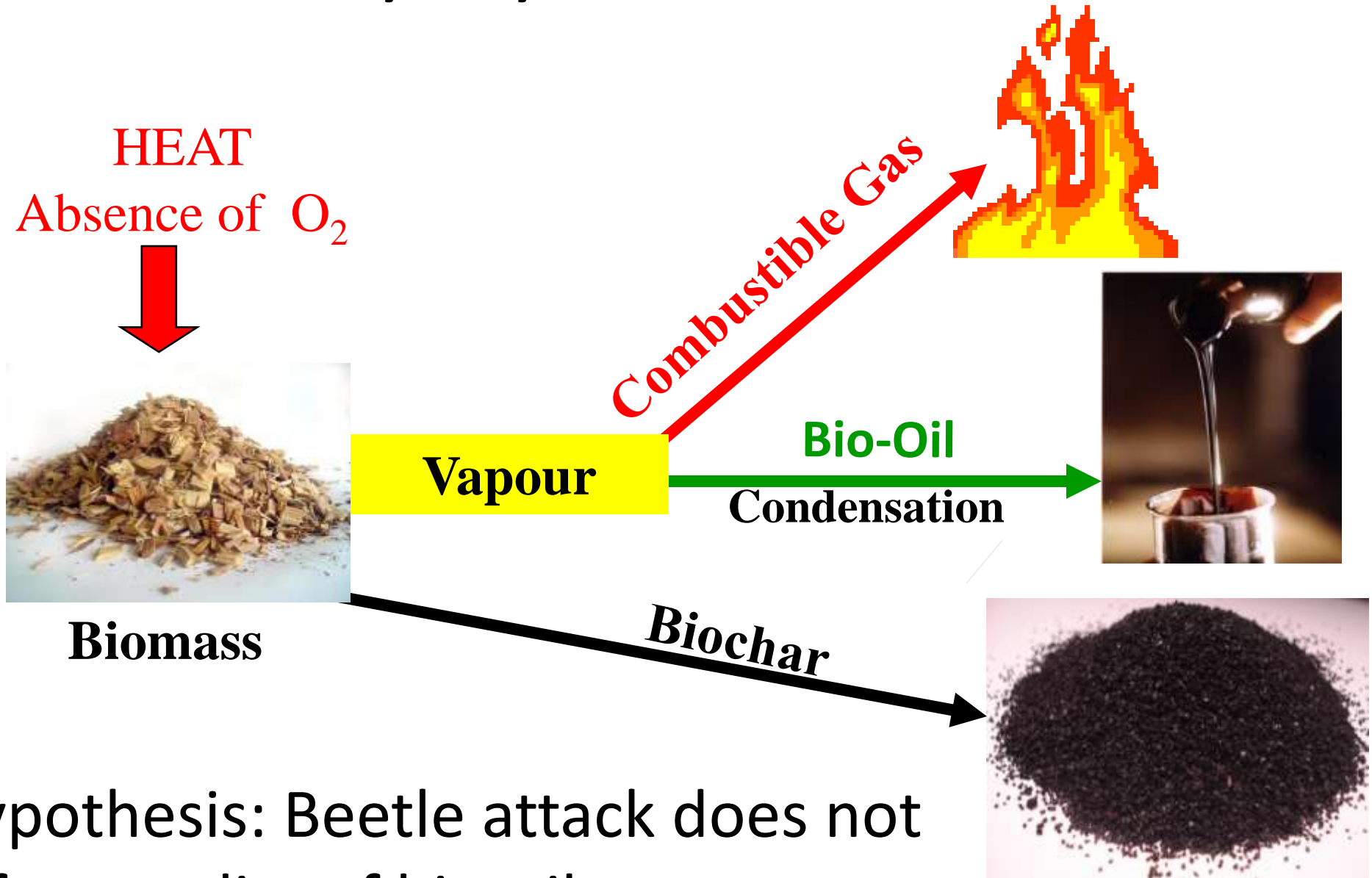
Western Forest Leadership Coalition, "Western Bark Beetle Assessment: A Framework for Cooperative Forest Stewardship", 2009 Update.

Applications for beetle-killed trees



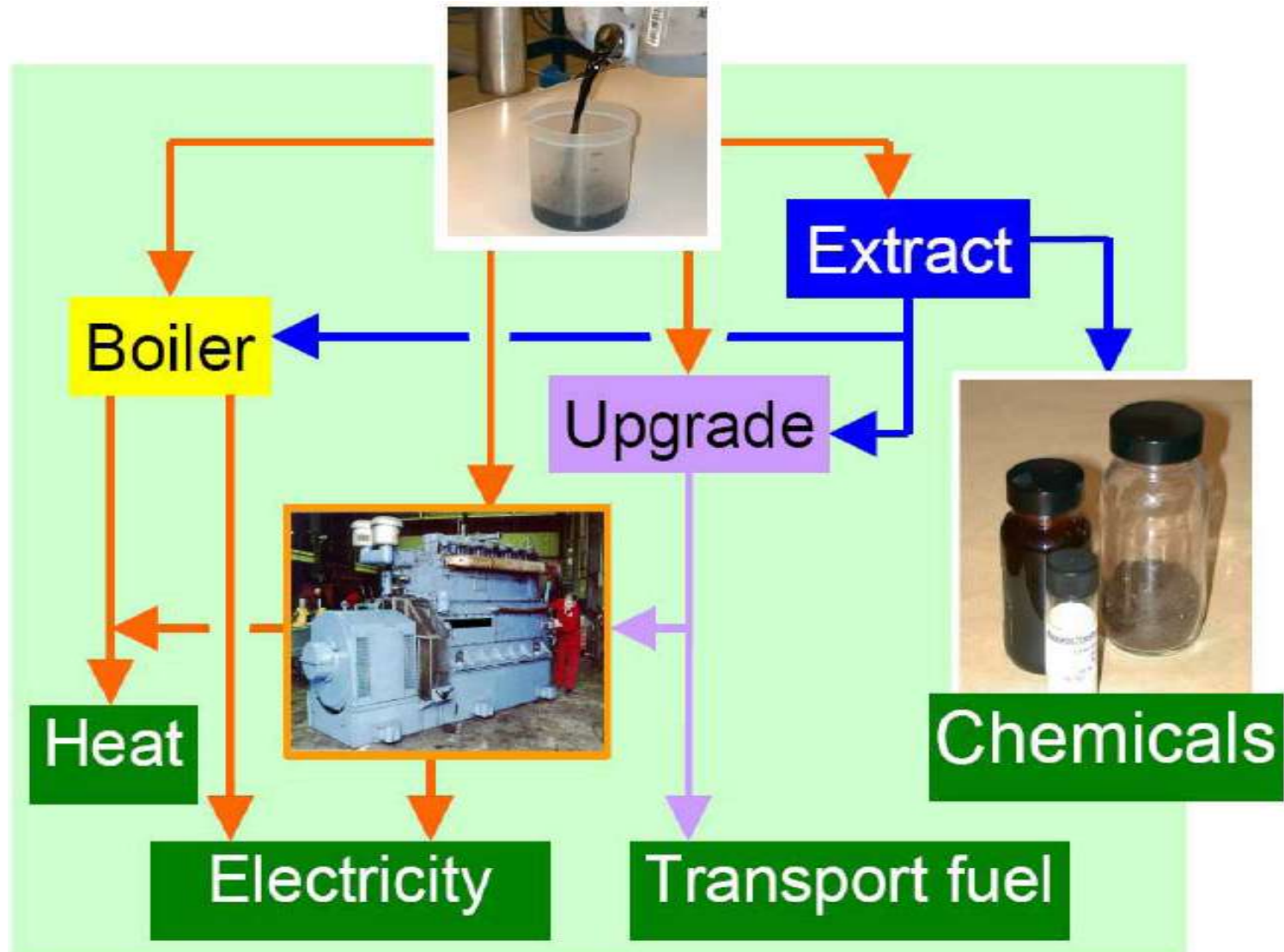
Opportunity to reduce the volume of dead trees and produce a high-value product

Pyrolysis of biomass

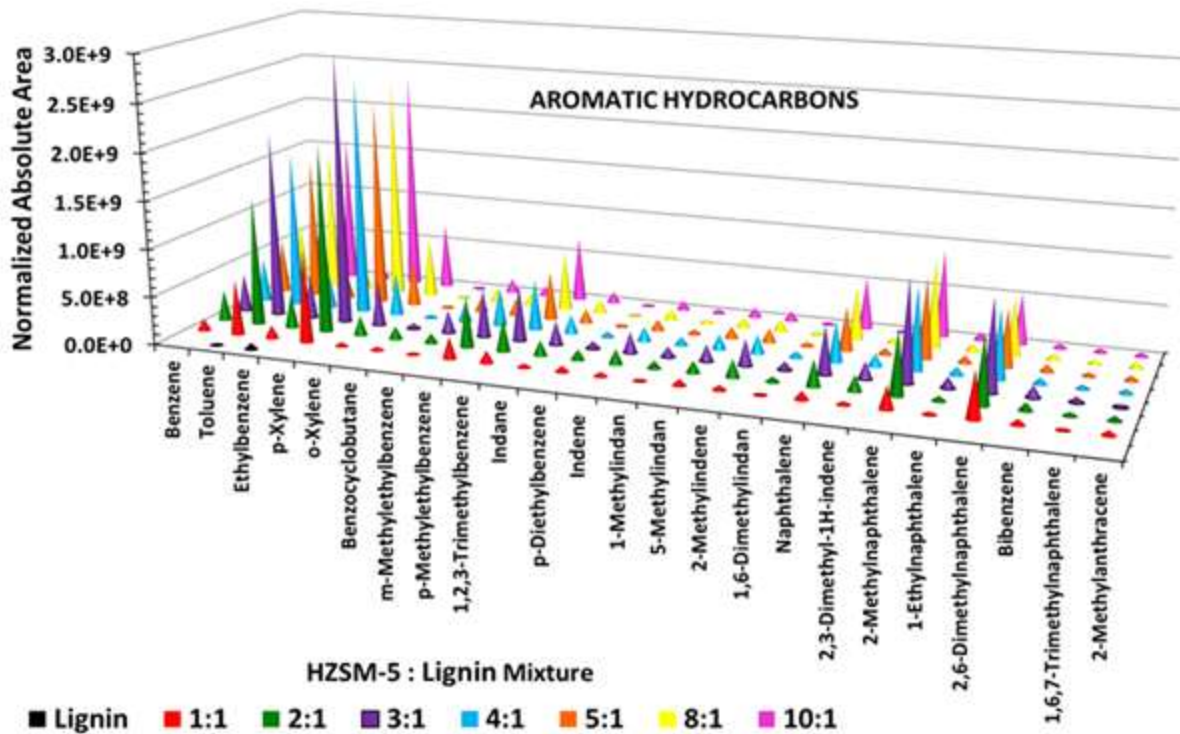


Hypothesis: Beetle attack does not affect quality of bio-oil

Bio-oil as a liquid fuel for transportation?



Catalytic Fast Pyrolysis with a zeolite catalyst



Products:

CO

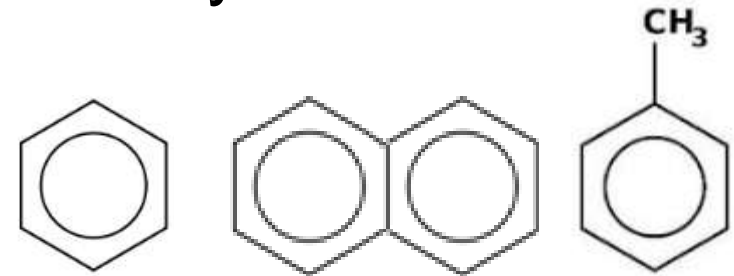
CO₂

Char

water

Aromatic

Hydrocarbons

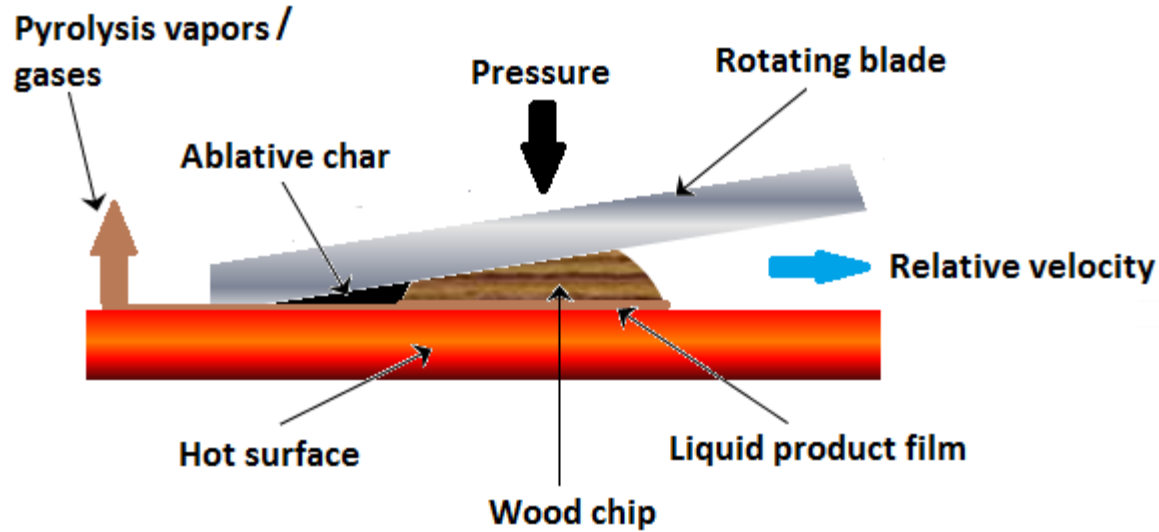


Mobile Pyrolysis Units

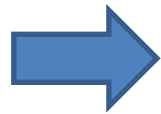
- Mobile units: reduce transportation costs for low-density biomass (50 dry tons/day)
- Bio-char can be used on-site as soil-amendment
- Process economics depends on bio-oil yield: 70 gal/ton is needed for feasibility (73 wt % conversion)
- Grinding estimated to be 7 % of costs



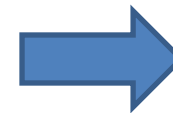
Ablative Pyrolysis: “Melting butter in a frying pan”



Reaction rate not limited by heat transfer through particle



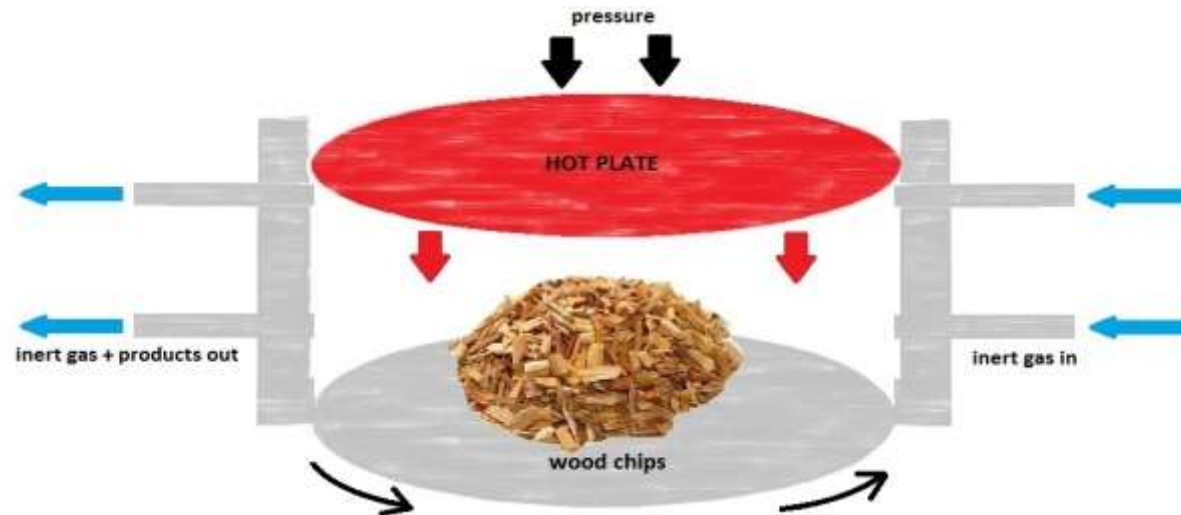
no upper limit to particle size



Reduced grinding costs

- Up to 81 wt % conversion has been observed
- Low reactor volume (only appropriate for small scales)
- Low capital and operational costs

An ablative pyrolysis reactor for beetle-killed trees



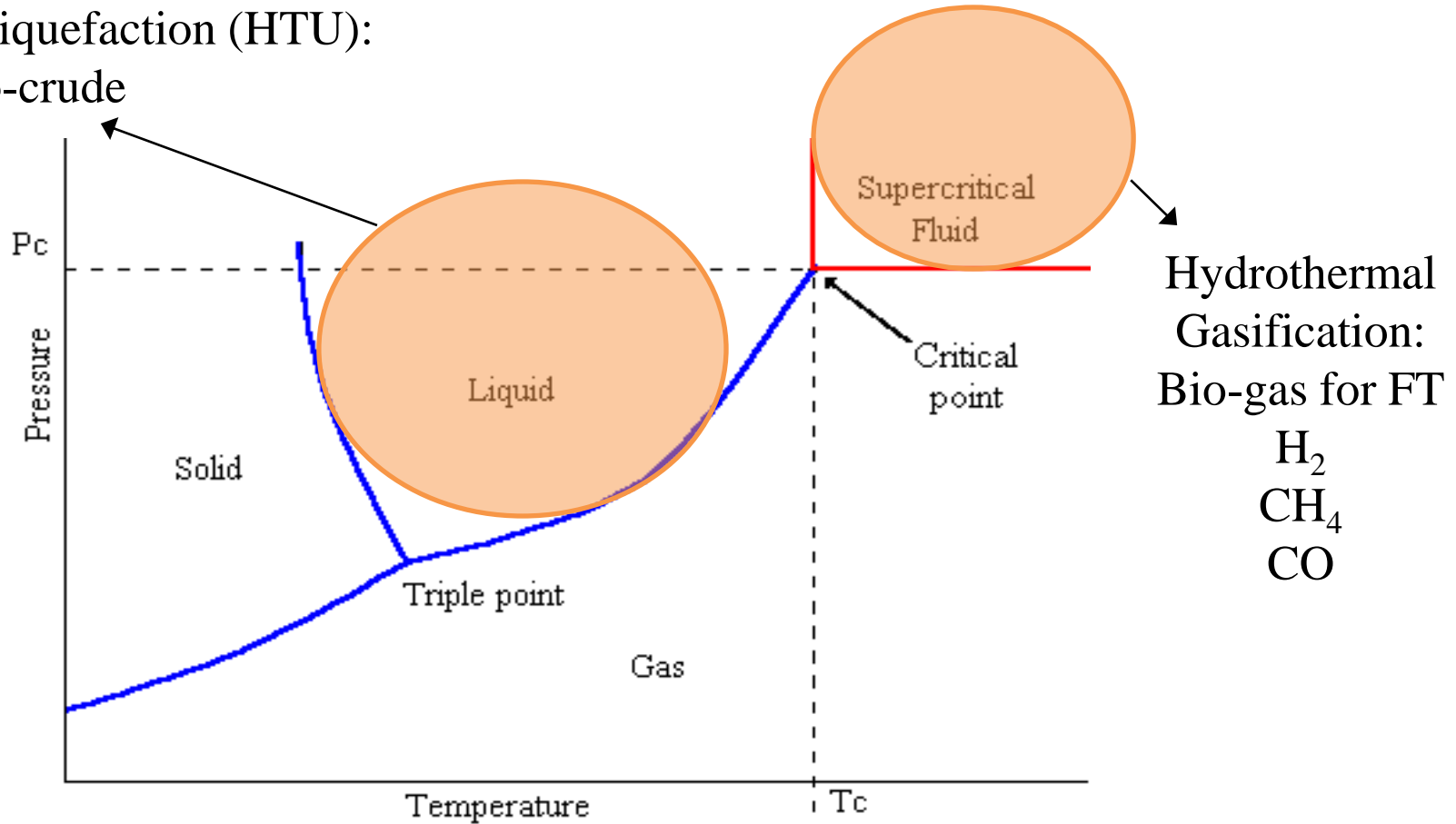
- Influence of decay stage on the quality of the bio-oil?
- What are the variables that control process yields?
- How to keep the bio-oil over 73 wt %?
- What is the maximum size of wood chips allowable?
- Does the low-density of the wood affect the ablative process?
- What is an optimum reactor design for the conversion?

Applications for High Moisture Biomass

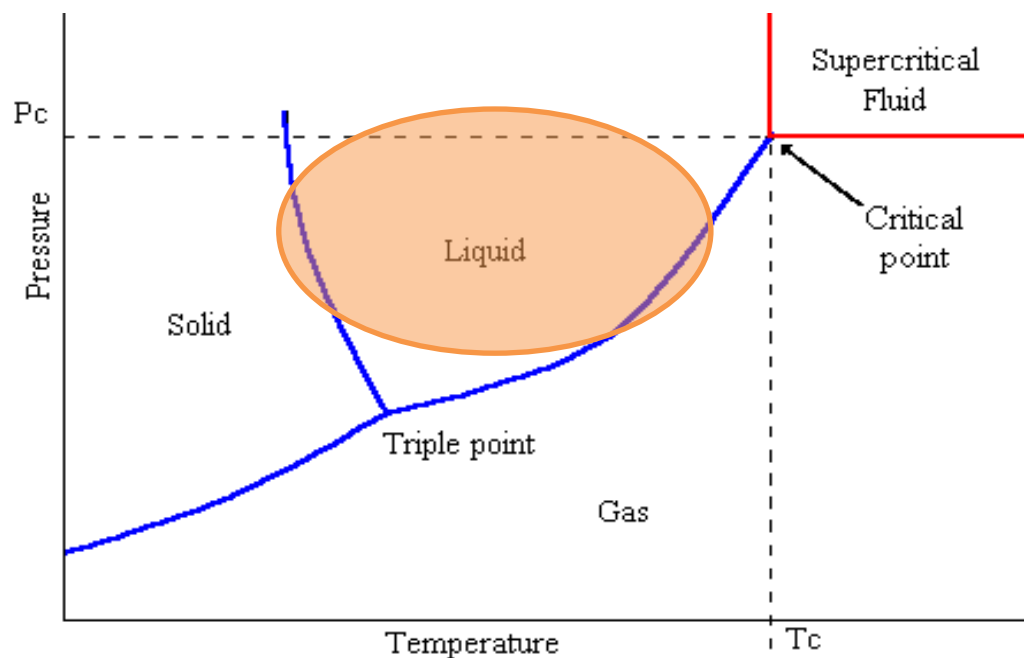
Water as a solvent:
Avoids the drying step

Hydrothermal Liquefaction (HTU):

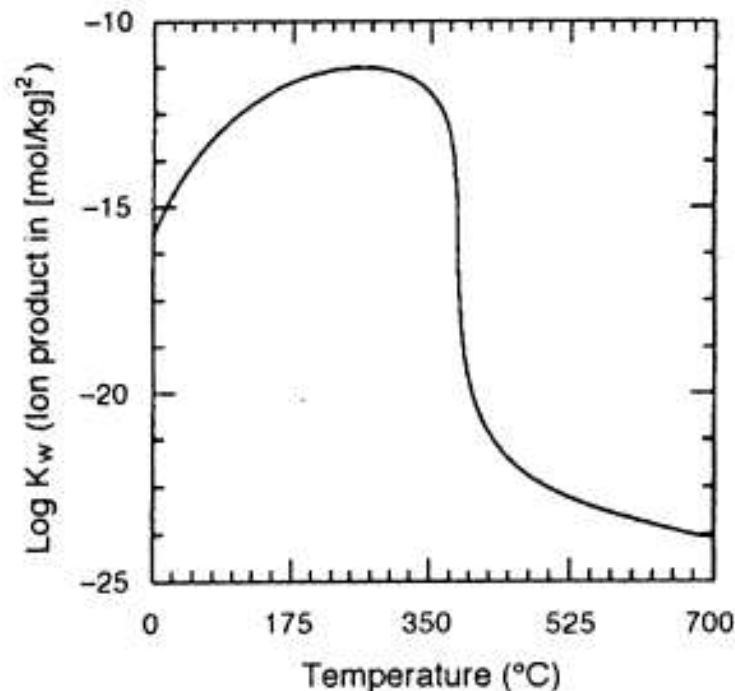
Bio-crude



Hydrothermal Liquefaction (Hydrothermal Upgrade, HTU)



K_w increases 1,000 at 200-300°C



Temperature: 280-380°C
Pressure: 5-40 MPa

Water self-ionization:
 $2 \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{OH}^-$

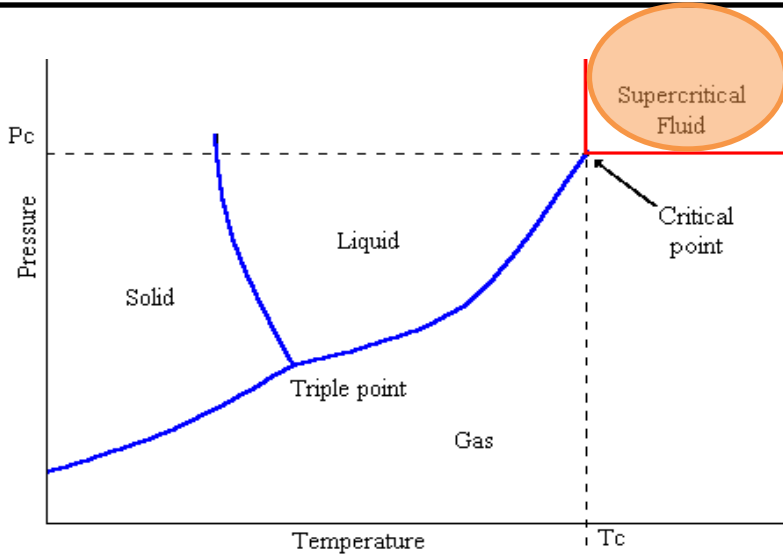
Wood liquefied at 340°C



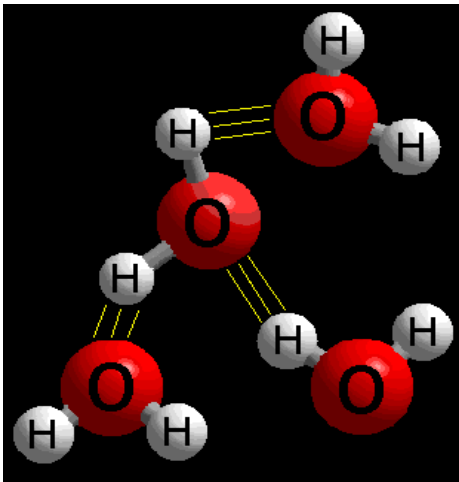
Time, min 0 1 2 3 4 5

Peterson, A.A.; Vogel, F.; Lachange, R.P.; Froling, M.; Antal, M.J.Jr.; Tester, J.W.; "Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies", Energy & Environmental Science, 2008, 1, 32-65 **14**

Hydrothermal Gasification (SCWG)



Water above 374°C and 22 MPa



Properties of Supercritical Water:

High Temperature and Pressure



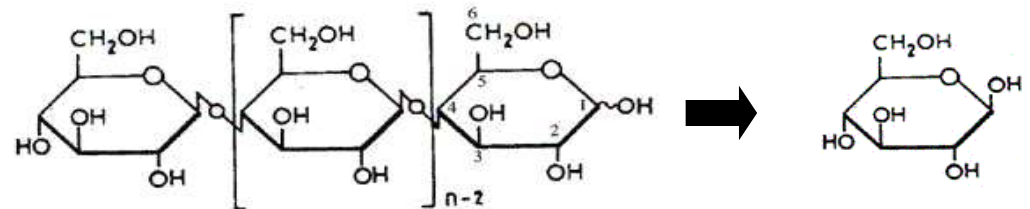
Weakens H bonds



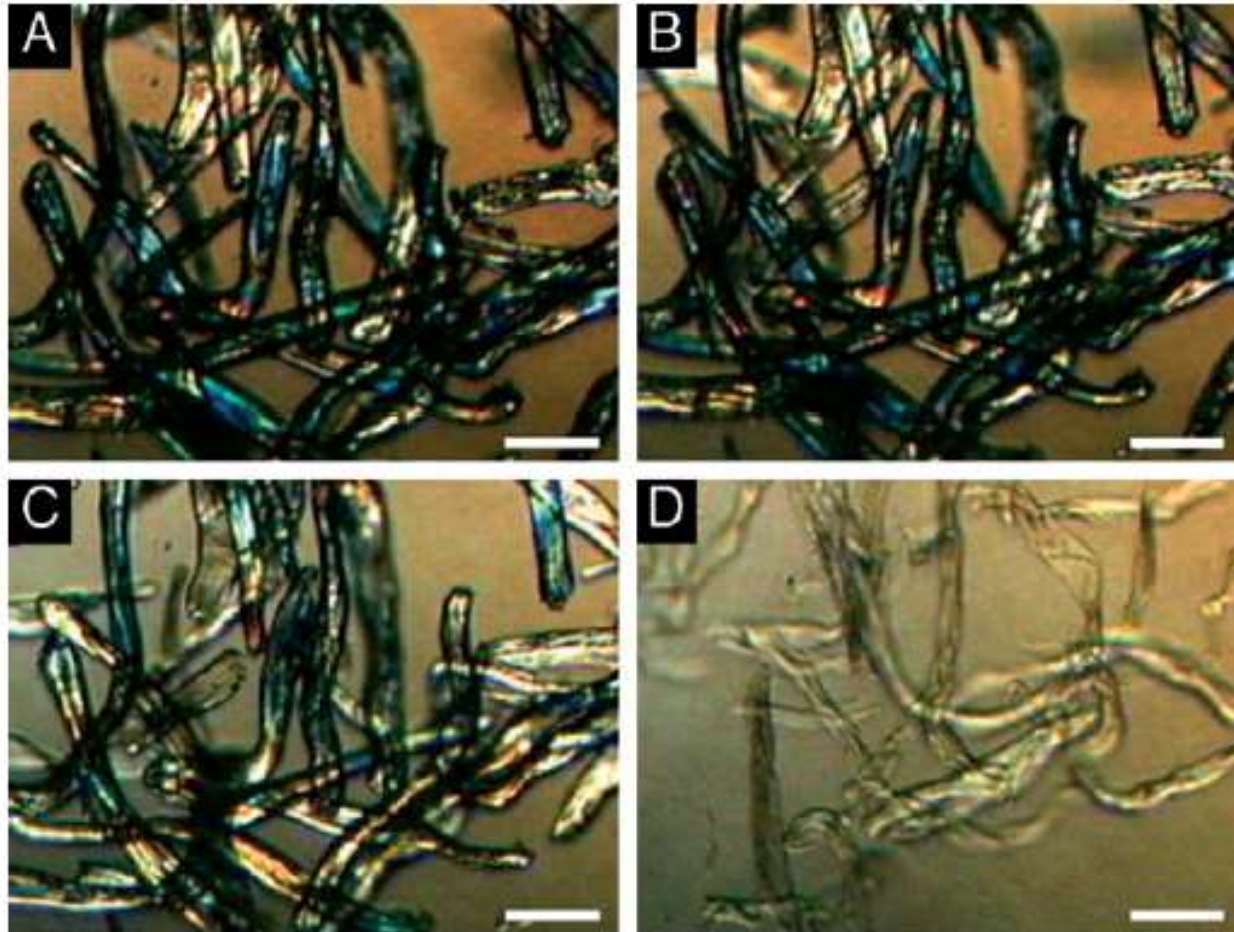
Decreases dielectric constant



Dissolves organic compounds:



Cellulose dissolving in hot compressed water



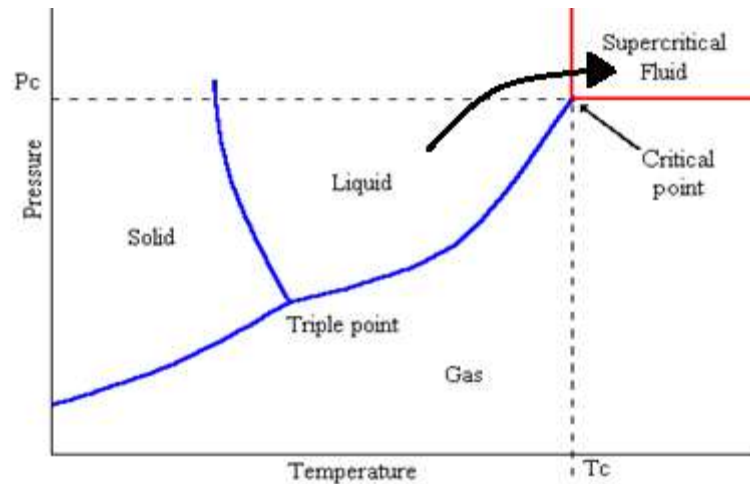
S. Deguchi, K. Tsujii and K. Horikoshi, Cooking cellulose in hot and compressed water, *Chem. Commun.*, 2006, 3293–3295.

Supercritical Water Gasification (SCWG)

Water as solvent:

- Avoids the drying step
- H₂ rich gas can be produced via the water-gas shift reaction:
$$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$$

(water is also a reactant)
- Avoids phase change (no latent heat)



Energy Efficiency

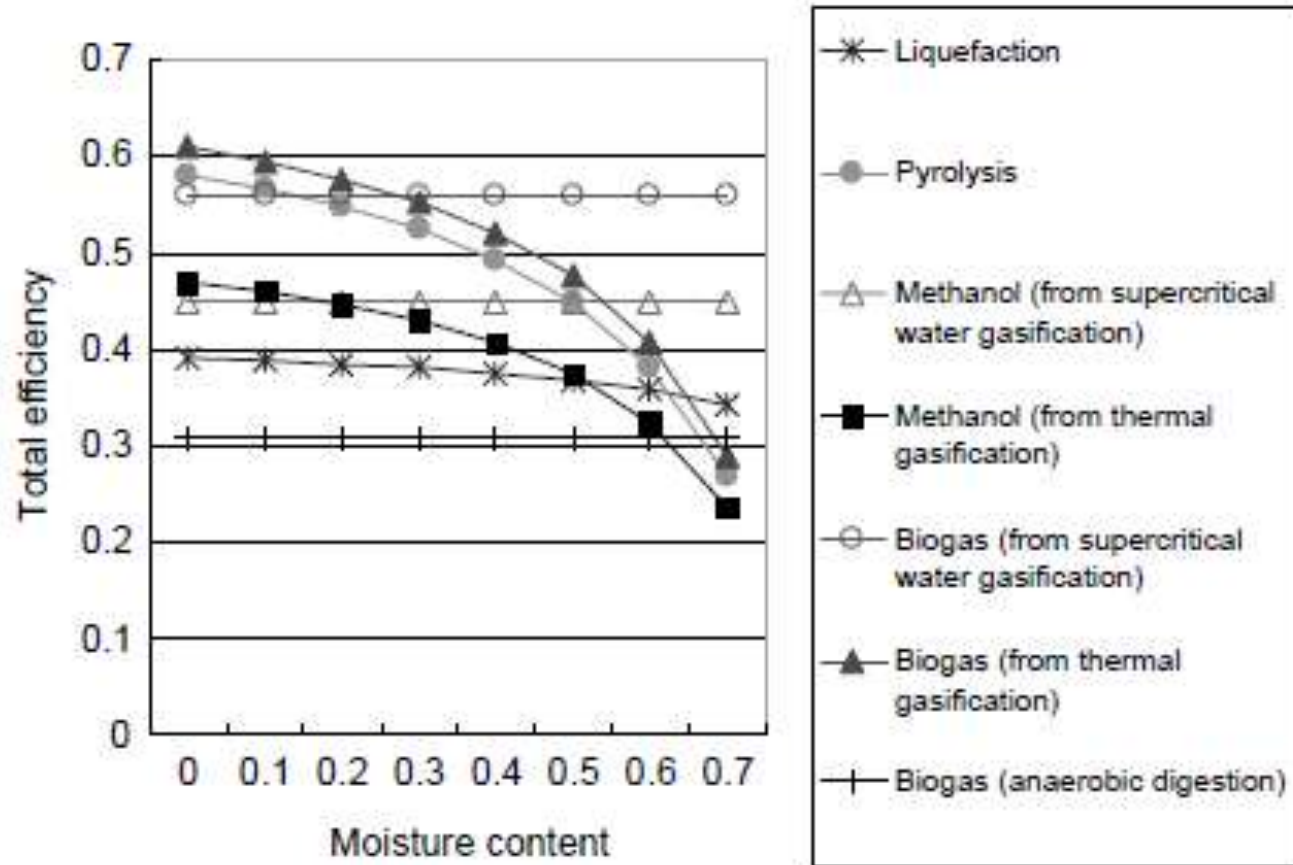


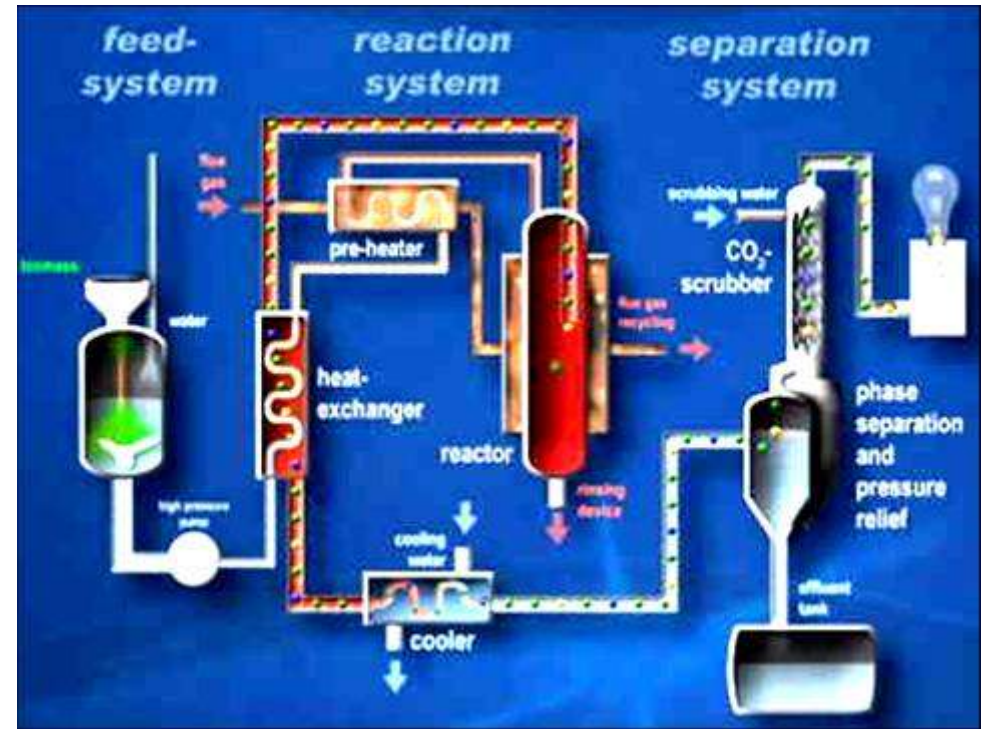
Fig. 4. Total efficiency of heat utilization processes versus biomass moisture content.

Yoshida, Y.; Dowaki, K.; Matsumura, Y.; Matsubishi, R.; Li, D.; Ishitani, H.; Komiyama, H.; "Comprehensive Comparison of efficiency and CO₂ emissions between biomass energy conversion technologies – position of supercritical water gasification in biomass technologies", Biomass and Bioenergy, 25, 2003, 257-272.

Questions?

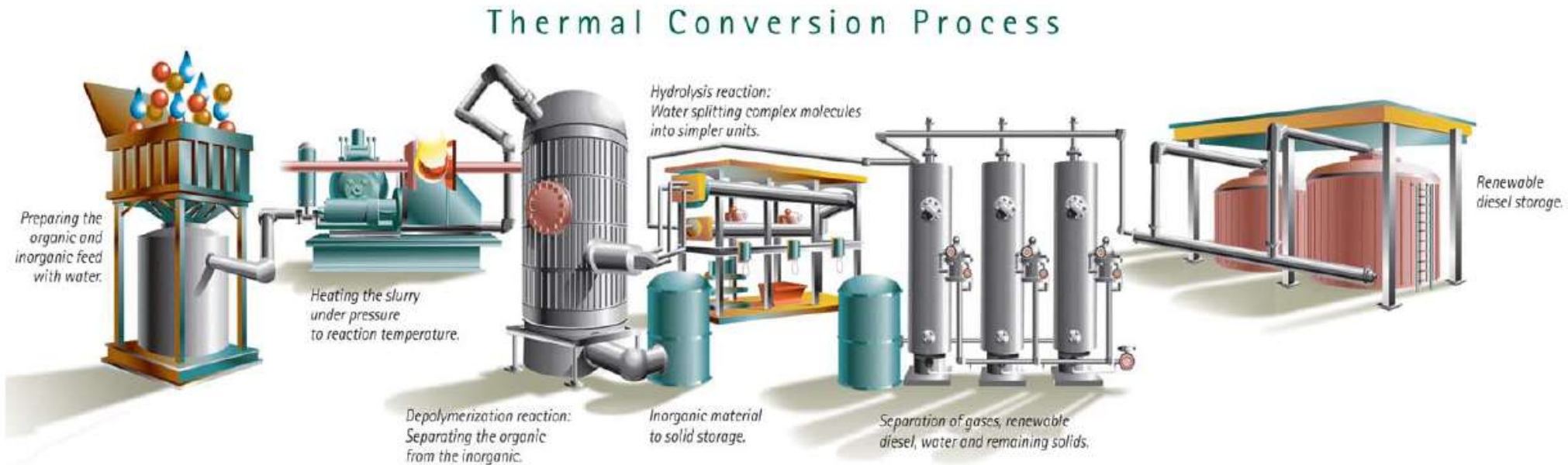
VERENA Gasification Plant, Germany

- 100 kg/h
- 700°C, 350 bar
- Residual biomass from the food and beverage industry, sludge



Hydrothermal Liquefaction Plant

Changing World Technologies (CWT, Carthage, Missouri)



- ✓ Converts wastes from turkey production (fatty acids) into diesel and fertilizers
- ✓ Fatty acids have chain lengths similar to gasoline and diesel (15-20 carbons)
 - ✓ Elimination of carboxyl group results in diesel