

Microalgae to Biofuels Using Sub-and Supercritical Water Technology

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Energy Technology Partnership Forum
Williamsburg, VA

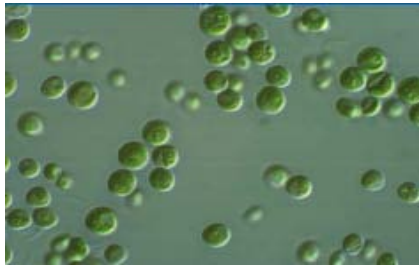
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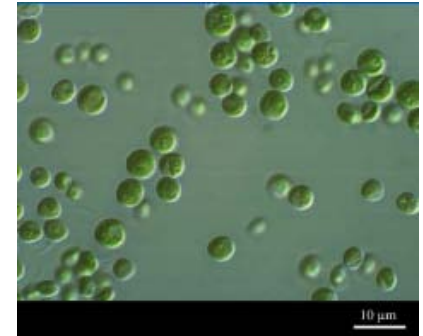
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Microalgae

Microalgae employ photosynthesis to convert sunlight and CO₂ into energy and possess several advantages:

- Higher productivity
- Rapid growth rate
- Grows in wastewater effluent /salt water streams
- Does not require arable land
- Requires less water than energy crops
- Can utilize CO₂-rich flue emissions



Microalgae comprise:

Proteins, Carbohydrates, and Lipids

Comparison of oil yields from other biomass

Crop	Oil Yield Gallons/Acre/year
Soybeans	48
Sunflower	102
Jatropha	202
Oil Palm	635
Algae	1000 - 6500

Source: Adapted from Chisti 2007

➔ **Oil content is usually between 20-50 wt%**

Major Challenges in the Processing of Microalgae

1. Dewatering



- It is not uncommon to have less than one gram of algae per liter (dry basis) of water.
- Energy required for the dewatering process may account for more than 75% of the total energy consumption.
- Typical thermal dryers use significantly more energy per kilogram of evaporated water (3.3–3.9 MJ/kg)

Can microalgae be converted to biofuels without drying / dewatering ?

Major Challenges in the Processing of Microalgae

2. High Nitrogen Content

Alga Species	Protein	Carbohydrates	Lipids
<i>Chlamydomonas reinhardtii</i>	48	17	21
<i>Chlorella vulgaris</i>	51-58	12-17	14-22
<i>Euglena gracilis</i>	39-61	14-18	14-20
<i>Porphyridium cruentum</i>	28-39	40-57	9-14
<i>Scenedesmus obliquus</i>	50-56	10-17	12-14
<i>Spirulina platensis</i>	46-63	8-14	4-9

- Nitrogen content varies between 4 to 8 wt% of the dry biomass
- NO_x emission and losses of nitrogen fertilizer are a matter of great concern

3. Diverse Composition

- More than 50,000 species of microalgae are reported to exist

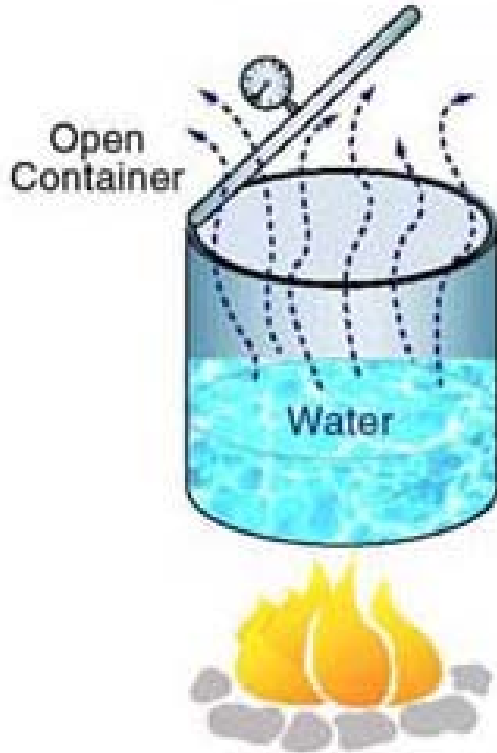
Important to develop processes for the 100% utilization of algal biomass components which can produce fungible fuel and biobased products

Can Water be Used Advantageously?

Capitalize on the extraordinary solvent properties of water at elevated temperature for extracting bioactive compounds and converting algae to liquid fuels.

- Green and Sustainable Chemistry

Supercritical Water ?



Water Heated in an Open Container



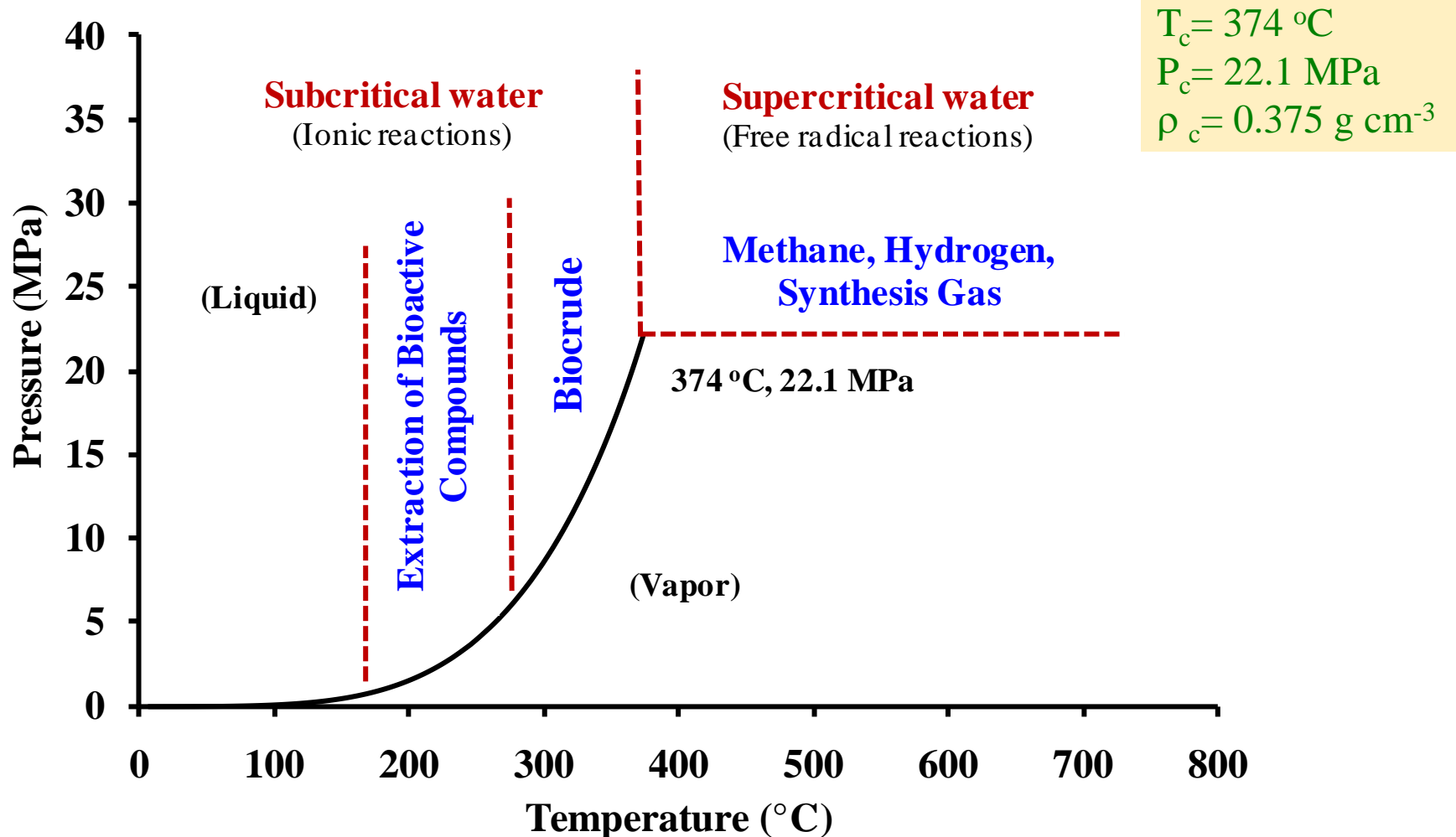
Water Heated in a Closed Container

In closed container, density of the liquid water decreases and the density of the water vapor increases. *Densities Equalizes*



Supercritical Water

Tuning Water Properties for Biofuels Application



Sub- and Subcritical Water as a Reaction Medium

Decreased ↓

Density

Dielectric constant

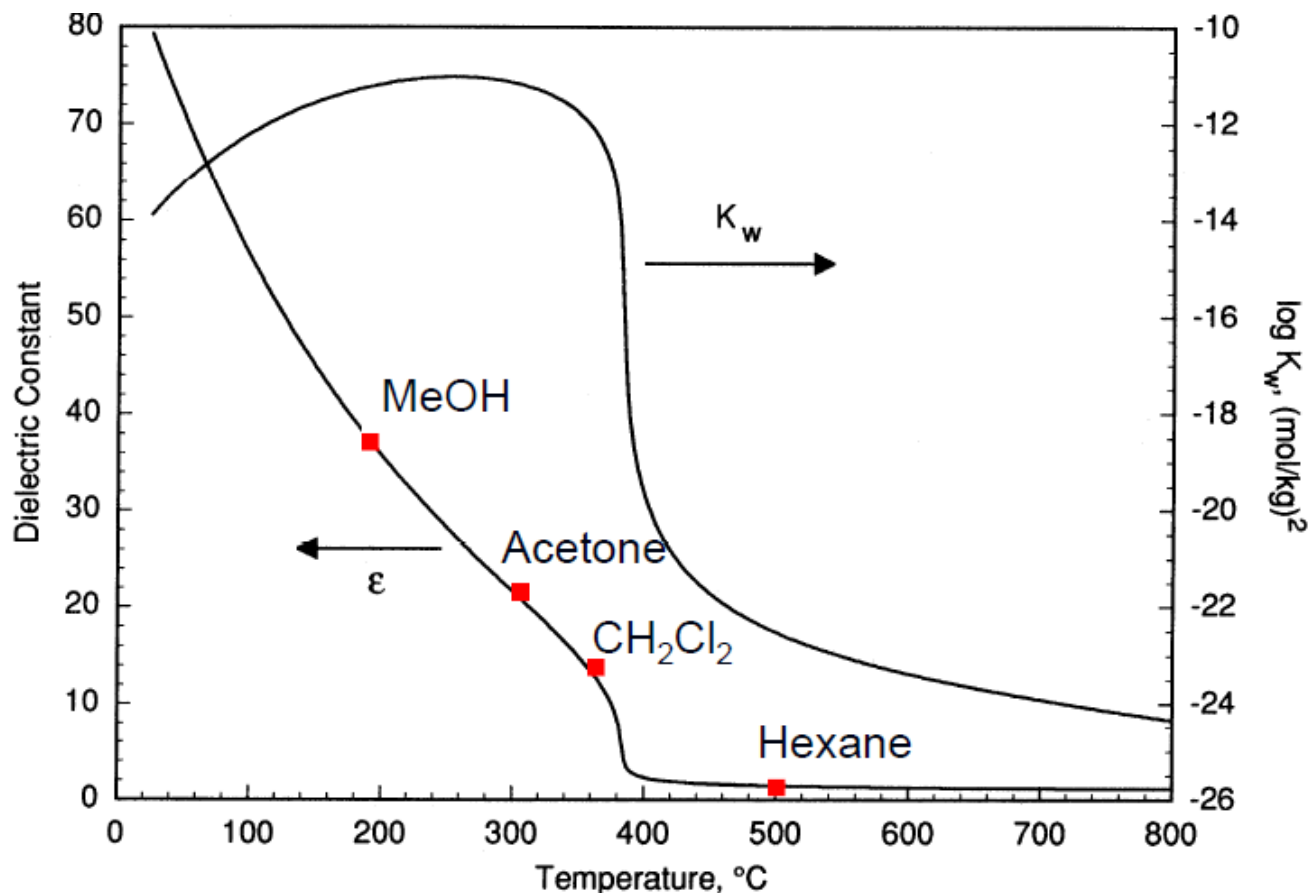
Viscosity

Increased ↑

Ionization constant

Diffusivity

Tunable properties



Advantages and Challenges

Advantages

- ✓ No drying of biomass
- ✓ Not dependent on the type of biomass
- ✓ Reduced mass transfer resistance
- ✓ Flexibility for the type of fuels (solid, liquid, and gas)
- ✓ Easier product separation

Challenges

- ❑ Biomass feeding at high pressure specially for lab scale studies
- ❑ Salt precipitation and corrosion

Development of Two Stage Process

Stage 1: Subcritical Water Extraction

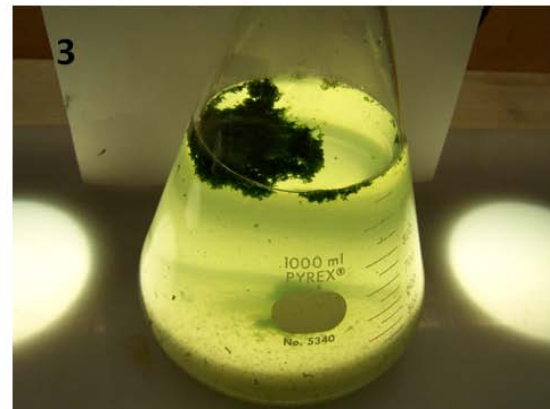
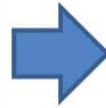
- Protein and Amino acid Extraction

Stage 2: Supercritical Water Gasification

- High Heating Value Clean Synthesis Gas
(CO & H₂)

Microalgae (*Scenedesmus sp.*) in Closed Bioreactor

Environment Laboratory at Kaufman Hall, CEE, ODU



Essential Amino Acid in *Scenedesmus sp* Compared to Soy

mg of amino acid/g of essential amino acids

Essential amino acid	Soy	Scenedesmus sp
Leu	170	123
Lys	160	230
Phe	110	100
Tyr	80	74
Met	30	43
Cys	30	243
Tre	85	84
Val	130	61
Ile	120	42
Tri	15	NA

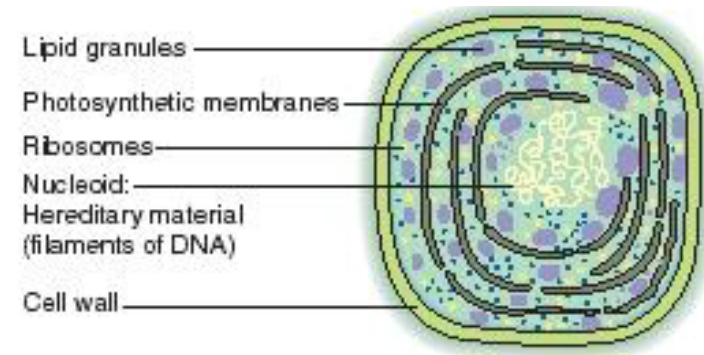
Protein quality in *Scenedesmus sp* is very good

Stage 1: Subcritical Water Extraction

Can subcritical water extraction process provide a commercially viable alternative to conventional methods of protein and amino acid extraction?

Classical methods:

- ✓ Alkali hydrolysis + acid precipitation
- ✓ Enzymatic extraction
- ✓ Supercritical carbon dioxide



http://www.scienceclarified.com/images/uesc_01_img0027.jpg

Disruption of cell wall

Subcritical Water Extraction

To develop and optimize the process and conditions:

- Biopolymers hydrolysis in subcritical water is very sensitive to residence time (few seconds to few minutes)

Fast Reaction Kinetics

Inorganic elements typically contained in ash can be removed from microalgae using subcritical water:

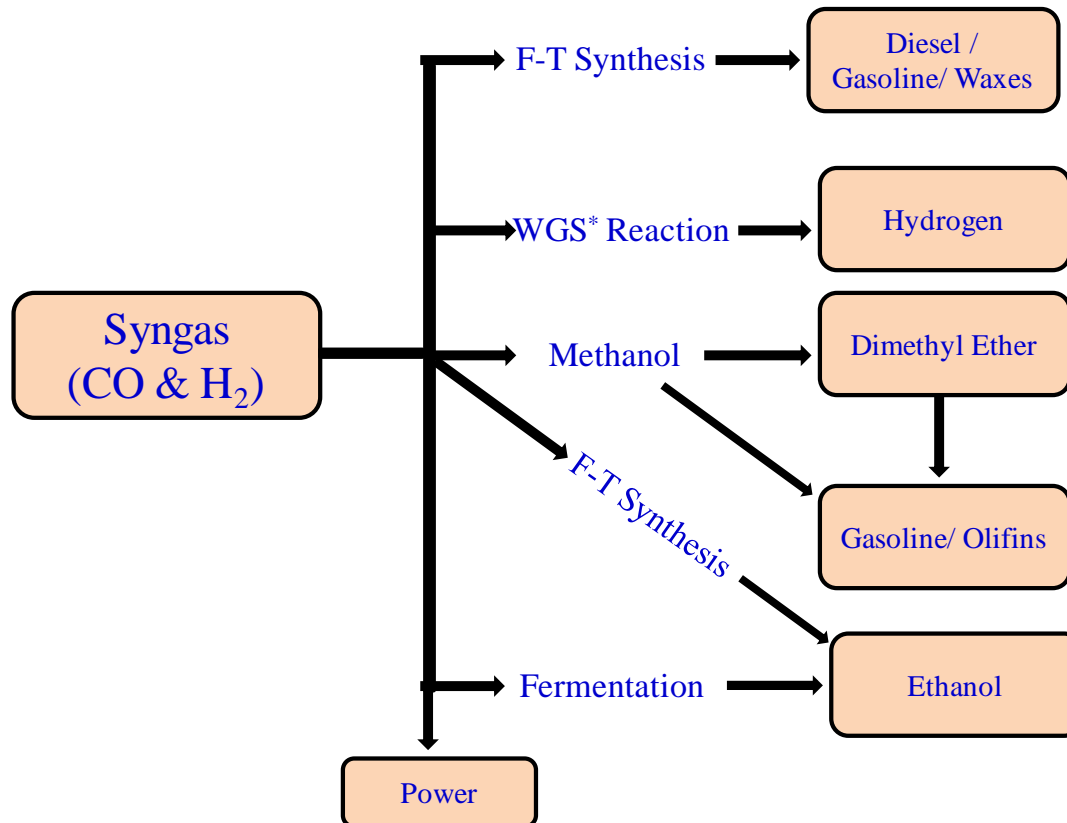
- Typical ash content = 5 to 10% dry basis

Inorganic Removal

Stage 2: Supercritical Water Gasification

- High Heating Value Clean Synthesis Gas (CO & H₂)

Syngas Conversion to Fuels and Chemicals



WGS: Water-Gas Shift Reaction: $\text{CO}_{(g)} + \text{H}_2\text{O}_{(v)} \leftrightarrow \text{CO}_{2(g)} + \text{H}_{2(g)}$

Supercritical Water Gasification: Goal

Lower density promotes free-radical reactions = favorable for gasification

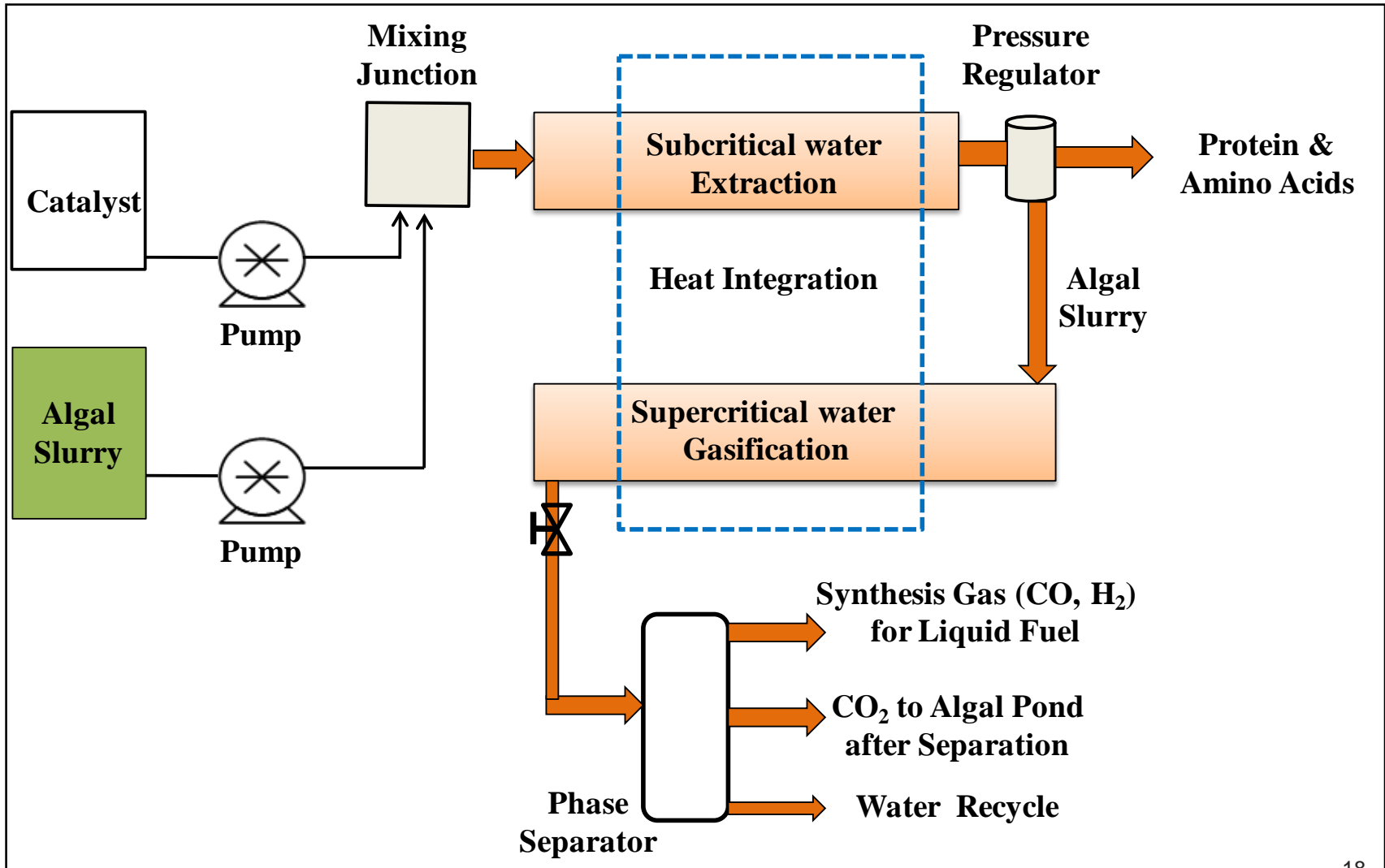
GOAL:

- Develop a continuous flow process to produce high heating value clean synthesis gas from nitrogen free biomass.
- Optimize the ratio of H₂ and CO during supercritical water gasification for liquid fuel production
- Development of low cost catalyst to moderate the gasification conditions

Advantages over Traditional Gasification:

- Wet feedstock
- Higher gasification efficiency at comparatively low temperatures (400-700⁰C) with less tar formation
- Cleaner gas with less tar, char, and dust in synthesis gas
- Synthesis gas is produced directly at high pressure
- Possibility of nutrients recycling present in the aqueous phase

Integrated Process Goal



Energy Balance: A Recent Study

Ref: L. Xu et al. *Bioresource Technology* 102 (2011) 5113–5122

Wet versus Dry Process

The performance indicators considered in this study is the overall energy balance with fossil energy ratio (FER) based on 1 ton of dry microalgae

$$\text{FER} = \frac{\text{HHV}_{\text{biofuel}}}{E_{\text{input}}} \left[\frac{\text{GJ products}}{\text{GJ fossil energy input}} \right]$$

Wet Process Products

- Biodiesel
- Glycerol
- Pyrolysis Oil
- Producer Gas

Dry Process Products

- Green Diesel
- Hydrogen
- Producer Gas
- CO₂ recycling

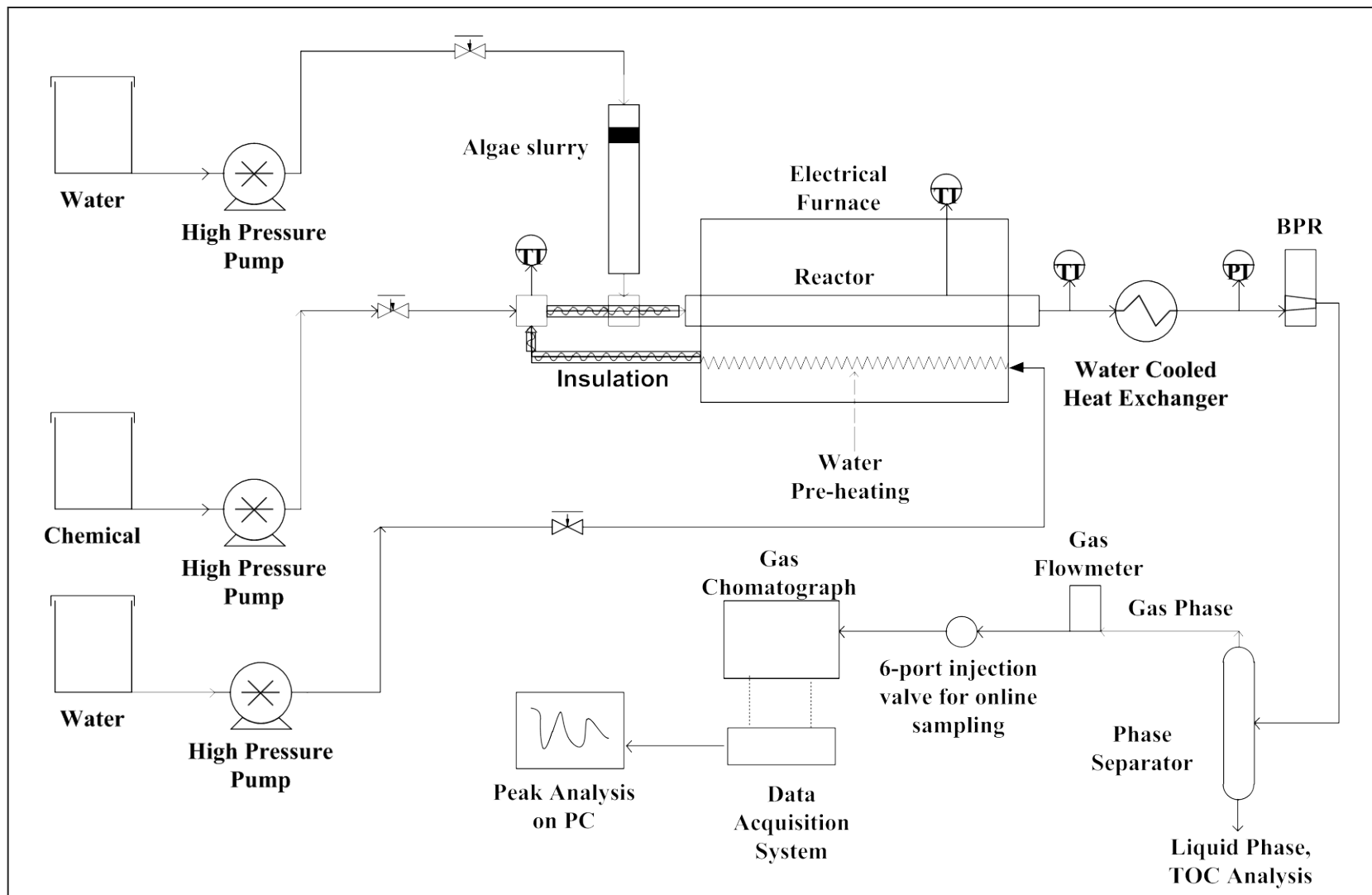
Energy Balance

Fuel Type	FER
Dry Process	1.50
Wet Process	1.37

- Short term, the dry route is more interesting because of a higher FER
- Long term, the wet route has more potential because of producing biofuels with a higher value
- ✓ In case of a batch reactor, no pumping cost, just the reactor heating cost.
- ✓ In a continuous reactor, the algae slurry needs to be pressurized using a pump before it is heated up to a proper temperature,
- ✓ The energy needed for the pump is negligible compared to the heat input.

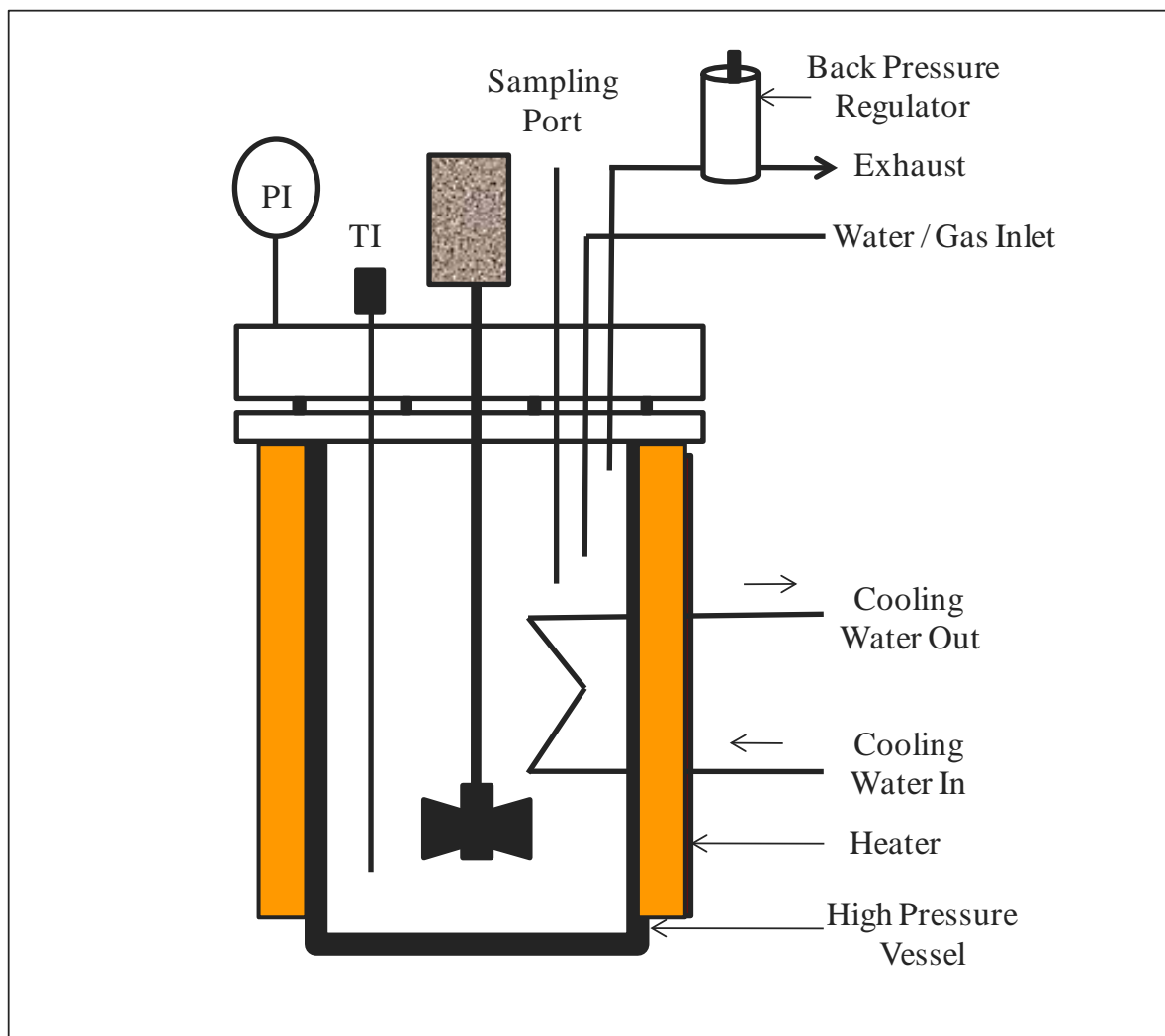
Biofuels Research Facility in Room 243D, Kaufman Hall, ODU

Bench Scale Continuous Flow Set up



Biofuels Research Facility in Room 243D, Kaufman Hall, ODU

Batch Reactor (500 ml, 500°C, 5000 psi)



Biofuels Research Facility in Room 243D, Kaufman Hall, ODU

The laboratory is focused on the hydrothermal and thermochemical conversion processes of biomass for biofuels. The important instruments:

- Ion chromatography system (ICS 5000) for carbohydrate, anions, and amino acid analysis provision.
- Foss digester with integrated programmable unit connected with a distillation unit
- BET surface area and pore volume analyzer (Quantachrome NOVA),
- UV-Vis Spectrophotometer, Total carbon/nitrogen (TOC/NOC) analyzer, Particle size analyzer, Zeta potential.
- IR based moisture analyzer and many small conventional analytical instruments

Thank You!!