Hydrothermal Liquefaction

After this module you will be able to…

- Summarize the HTL process
- Identify the effect that feedstock, experimental factors, and catalysts may have on the final product
- Identify the goal product of an HTL Reaction

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References

[1] Toor, S. S., Rosendahl, L., & Rudolf, A. (2011). Hydrothermal Liquefaction of Biomass: A Review of Subcritical Water Technologies. *Energy*, 2328-2342.

[2] Chen, W.H., Lin, B.J, Huang, M.Y., Chang, J. S. (2015). Thermochemical conversion of microalgal biomass into biofuels: A review. *Bioresource Technology*, *184*, 314 - 327.

[3] Perez, Martin. Liquefaction of Algae for Bio-oil Production. Chemistry, undergraduate thesis. Texas A&M University: Commerce, TX, 2020.

Introduction to HTL of Microalgae

Microalgae is a promising potential energy source to replace fossil fuels. All of the carbon in biomass comes from the atmosphere which is then released back into the atmosphere when it is burned. Compared to burning fossil fuels, the overall net difference of carbon in the atmosphere is zero making biomass a carbon neutral energy source. Algal biomass is a renewable source of energy that grows rapidly. Algal biomass is potentially a better alternative to other biomass such as corn because it is not a food source for humans or livestock.

Hydrothermal liquefaction (HTL) is a medium temperature (300-350ºC) and high pressure (5-20MPa) process that converts wet biomass into various biofuels. HTL takes place in subcritical water which is shown in the phase diagram in figure 1. In it's subcritical phase water has quite unique properties and acts as both a reactant and a catalyst in the reaction.

At the subcritical point, water becomes less viscous and the solubility of organic substances increases. Typically water-insoluble molecules are now soluble in water because the dielectric constant of water decreases at its subcritical phase. At 25ºC and 0.1MPa the dielectric constant of water is $78Fm^{-1}$ while at 350ºC and 20MPa the dielectric constant is $20Fm^{-1}$. This also has some effect on the solubility of ionic compounds as water becomes less polar at its subcritical point.

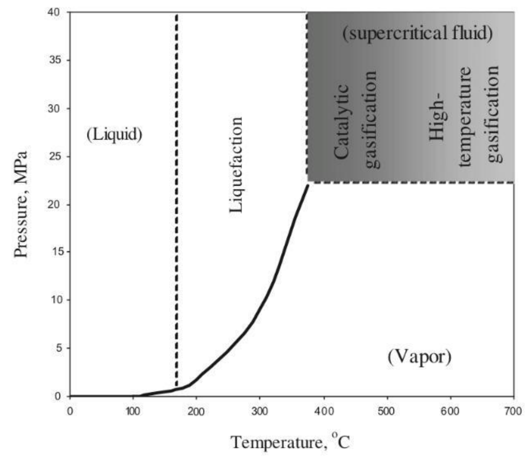

Figure 1. The phase diagram of water.[1]

The reaction mechanism for HTL reactions depends highly on the feedstock source, reaction conditions, and catalyst use. In general, an HTL reaction goes through three main steps:

1. Depolymerization of large bio macromolecules
2. Decomposition of monomer units
3. Recombination of reactive fragments

Ideally, the final reaction products maximize bio-oils within the boiling point range below 700ºC. Additionally the heteroatom content must be considered, specifically nitrogen and sulfur, as they can contribute to pollution as they are burned.

Products & Feedstock

Products

Characterization of the products of an HTL reaction is a critical step. The following methods and instruments are used to characterize the product:

- **Yield.** The yield can be determined by measuring the mass before and after the reaction using the reactions shown. This value is typically divided into solid/ash, bio-oil, and gaseous phases.
- **Elemental composition.** The elemental composition of a bio-oil sample is determined by using a CHN or CHNOS Analyzer.. Ideally, the amount of nitrogen and sulfur in the bio-oil is minimized in order to create a fuel that does not generate NO_X and SO_X pollutants when burned.

$$Bio\ oil\ yeild\ (wt\%) = \frac{W_{bio-oil}}{W_{biomass}} x100$$

$$Solid\ yeild\ (wt\%) = \frac{W_{residue}}{W_{biomass}} x100$$

$$Gaseous\ yeild\ (wt\%) = 100 - \frac{W_{bio-oil} + W_{residue}}{W_{biomass}} x100$$

$$Conversion\ (\%) = 100 - Solid\ yeild$$

- **Higher heating value (HHV).** HHV is the amount of heat produced during combustion. The larger the HHV the more potential energy is stored in the sample and the more effective the fuel. HHV can be obtained experimentally through calorimetry experiments or mathematically through the formula below:

$$HHV = (0.3491 \times C) + (1.1783 \times H) - (0.1034 \times O) - (0.0151 \times N) - (0.1005 \times S)$$

- **Boiling points.** The distribution of boiling points is determined by using thermogravimetric analysis (TGA).. The boiling point ranges of various fuels is shown in the table below:

Type of Fuel	**Boiling Point (ºC)**
Bottle gas and chemicals	25 - 110
Gasoline	110 - 200
Jet fuel, stove fuel, and diesel oil	200 - 300
Lubricating oil for engines, ship fuel, and machine oil	300 - 400
Lubricants and candles, ship fuel	400 - 550
Ship fuel, factory fuel, and central heating	550 - 700
Asphalt and roofing	700 - 800

Table 1. Boiling point range of fuel.[3]

- **Compound Identification.** The major compounds in the product can be determined by gas chromatography-mass spectrometry.

Feedstock

Biomass can describe a wide variety of materials but each material is a combination of carbohydrates, lignin, proteins, and lipids. Compositions of biomass can be seen in Table 2.

Materials	Protein (wt%)	Lipid (wt%)	Carbohydrate (wt%)	Lignin (wt%)	Others (wt%)
Chlorella vulgaris	29.00	49.50	19.70	0	1.8
Spirulinaplatensis	48.36	13.30	30.21	0	8.13
White poplar	0	0	74.6	23.1	2.3

Table 2. Compositional analysis of various feedstocks, adapted from [1] and [2].

Each biomass component reacts differently under hydrothermal conditions. Some of what is known is summarized below:

- **Carbohydrates** depolymerize to form glucose and other saccharides.

- **Lignins** depolymerize to form phenols and methoxy phenols. They produce a significant amount of solid residue.

- **Proteins** depolymerize into amino acids and then typically undergo one of two processes. Amino acids undergo deamination to produce ammonia and organic acids or they undergo decarboxylation to produce carbonic acid and amines.

- **Lipids** depolymerize into free fatty acids which can further degrade into long-chain hydrocarbons which is a good source of bio-oil fuel.

Experimental Set-up

The success of an HTL experiment depends on the reaction conditions used. The most significant reaction conditions include temperature, holding time, and catalyst use.

Temperature

In general, an increase in temperature tends to increase bio-oil yield within the subcritical condition. Ligins are usually more successfully converted into bio-oils at lower temperatures (<250ºC) while carbohydrates and proteins are more successful at higher temperatures (300-375ºC).

Holding Time

The holding time is the amount of time a temperature remains constant during liquefaction. It does not include the amount of time to heat up and cool down the reaction vessel. The holding time usually remains below 60 minutes. The holding time needs to be considered in conjunction with the temperature. It is most likely true that the optimal holding time differs depending on the reaction temperature.

Catalysts

Catalysts are used to lower the activation energy of the reaction thus allowing the reaction to proceed faster. Common HTL catalysts include alkali salts and metals but other catalysts are being considered. As you will see in the next unit, catalysts can lower the reaction temperature and influence the final products of the reaction.

Check Quiz: HTL

1. Which of the following is not a characteristic of algal biomass?
   a. carbon neutral energy source
   b. food source for humans and livestock
   c. renewable energy source
   d. biomass that grows rapidly

2. In its subcritical phase, water is able to dissolve more organic substances. This is the result of the change in which property of water?
   a. Lower viscosity
   b. Decreased dielectric constant
   c. Increased temperature
   d. Increased pressure

3. The final bio-oil product should have which of the following properties? Choose all that apply.
   a. Boiling points below 700ºC
   b. Colorless
   c. High viscosity
   d. Low heteroatom content

4. Consider the following data. Determine the percent yield of each phase.
   Initial mass of biomass = 10.00 mg
   Final mass of solid/ash = 2.24mg
   Final mass of bio-oil = 5.71 mg

5. The elemental composition of a bio-oil product is shown below. Determine the HHV of the oil.

Bio-oil	C	H	N	O	S

Sample A	65.47 %	9.30%	7.33%	17.34 %	0.56%

6. Match each property below with the type of feedstock most likely to be associated with it. The types of feedstocks include carbohydrates, lignins, proteins, and lipids.
    a. Depolymerize into fatty acids _____________
    b. Produce a significant amount of solid residue _____________
    c. Depolymerize to form glucose _____________
    d. Ultimately can produce amines _____________
    e. May degrade into long-chain hydrocarbons _____________
    f. Depolymerize to form phenols _____________
    g. Depolymerize to form amino acids _____________

7. Consider the composition of white poplar as shown in table 2. What temperature would you recommend to convert the majority of its composition into bio-oil using HTL?
    a. 175ºC
    b. 250ºC
    c. 325ºC
    d. 450ºC

8. Consider the following data from an HTL reaction. Determine the holding time of this reaction.
    Reaction vessel turned on: 9:30am
    Reaction vessel reached temp. at 340ºC: 10:15am
    Reaction vessel turned off: 11:00am
    Reaction vessel cooled off: 11:30am

Check Quiz Answers

1. **Answer B**: One of the benefits of algas biomass as a fuel source is that it is NOT a food source for humans or livestock. Therefore it will not deplete or compete with human and livestock food.

2. **Answer B**: A decreased dielectric constant decreases the polar character of water. As the polarity of water decreases, more nonpolar substances are able to dissolve. Water also experiences lower viscosity at its subcritical phase but that is not a direct cause of increased solubility of organic molecules. An increase in temperature and pressure from room temperature causes water to be in its subcritical phase.

3. **Answers A & D**: Two of the main goals of generating bio-oil is to produce a bio-oil that fits the current needs of society. That would require the bio-oil to have a boiling point below 700ºC and have a low heteroatom content.

4. **Solid/Ash = 22.4%** **Bio-oil = 57.1%** **Gaseous = 20.5%**

   Solid Yield = (2.24mg/10.00mg) *100
   Bio-oil Yield = (5.71mg/10.00mg)*100
   Gaseous Yield=100 - [(2.24mg + 5.71mg)/10.00mg]*100

5. **HHV = 31.85 kJ/g**

   HHV = (0.3491 x 65.47%) + (1.1783 x 9.30%) - (0.1034 x 17.34%) - (0.0151 x 7.33%) - (0.1005 x 0.56%)

6. **Answers**: a. Lipid; b. Ligin; c. Carbohydrates; d. Proteins; e. Lipids; f. Ligins; g. Proteins

7. **Answer C**: White poplar is primarily composed of carbohydrates (74.6%). Carbohydrates are known to be more successfully converted to bio-oil at higher temperatures, between 300-375ºC. Although an actual experiment may show this to be inefficient for this sample, it is a good place to start your investigation.

8. **Answer: 45 minutes**; Holding time is defined as the time the temperature remains constant not including the heating up or cooling down time. The reaction remained at a constant temperature from 10:15am - 11:00am.