Chemical Conversions

Lecture 15 – Biomass Parts to Products

Explosives are an unusual area of biomass chemistry, but an important one. Many of the first commercial explosives were based on wood, cellulose and glycerin that had been reacted with nitric acid. This produced things like nitrocellulose and nitroglycerin that became major industrial chemicals for road building, medicine, and mining. Energetic chemicals can be very dangerous, but they also represent a very unique and powerful use of biomass chemistry that cannot be easily mimicked by fossil fuel chemistry. From the bioenergy perspective, they have the potential to convert fairly small amounts of biomass into fairly large sources of energy. For example, 14g of an explosive called RDX can be used to generate 100 kV electric pulses. With just a small amount of current this is ~ 130 horsepower. Comparatively, 16g of nitrocellulose can propel a .50 caliber round with the same energy as a 4,500 lb F-150 truck moving 10 mph. Lots and lots of energy contained in a very small package.

Imagine if we could generate electricity or power from the controlled use of energetic materials produced from biomass. This is an area with a great deal of potential.

Week 6 – Chemical Conversions
-Learning Objectives-

- Explain the chemical conversion of biomass.
- Identify things in your day to day life that use chemical conversions of biomass.

Biomass Conversion Pathways

- Mechanical Conversions – normal everyday conditions
  - Crushing oil seeds and algae
  - Densification
  - Chipping and grinding
- Thermal Conversions – over 400 ˚C
  - Combustion (excess oxygen produces excess heat)
  - Gasification (heat with some oxygen)
  - Pyrolysis (heat with no oxygen)
- Chemical Conversions – under 400 ˚C
  - Biomass breakdown to components (acid, base, solvent, enzyme)
  - Biomass components to fuels & chemicals (endless possibilities)
  - Oil Conversions
- Biological Conversions – mild, wet conditions
  - Fermentations (microbes without oxygen)
  - Photosynthetic organisms and animals

This week we are covering chemical conversions, our third biomass conversion pathway type.

Chemical Conversion Products

- Cellulose, Lignin, Hemicellulose, and Extractives
- Sugars – monosaccharides and disaccharides
- Furfurals and other C5 aromatics
- Benzene, Xylene, Toluene, and other C6 aromatics

4 BR405 - Lecture 1 - Overview 4/12/2016

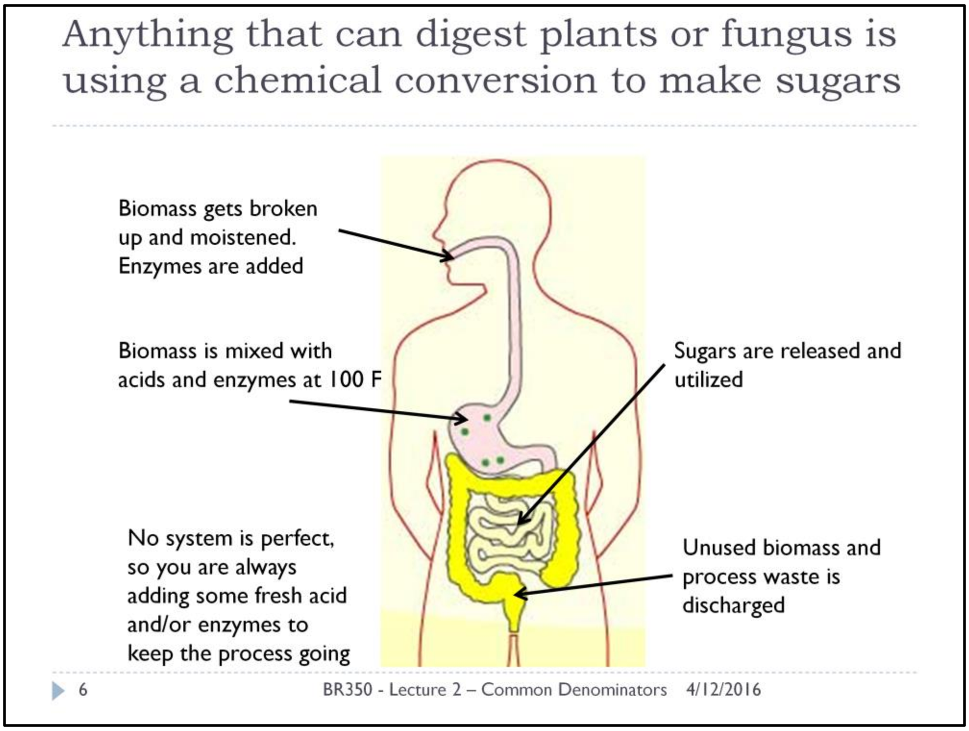
In biomass-to-parts we covered turning biomass into cellulose, lignin and hemicellulose. In biomass parts-to-products we will cover turning cellulose, lignin and hemicellulose into sugars and various chemicals.

Breakdown Cellulose, Hemicellulose, and Lignin into sugars and chemicals

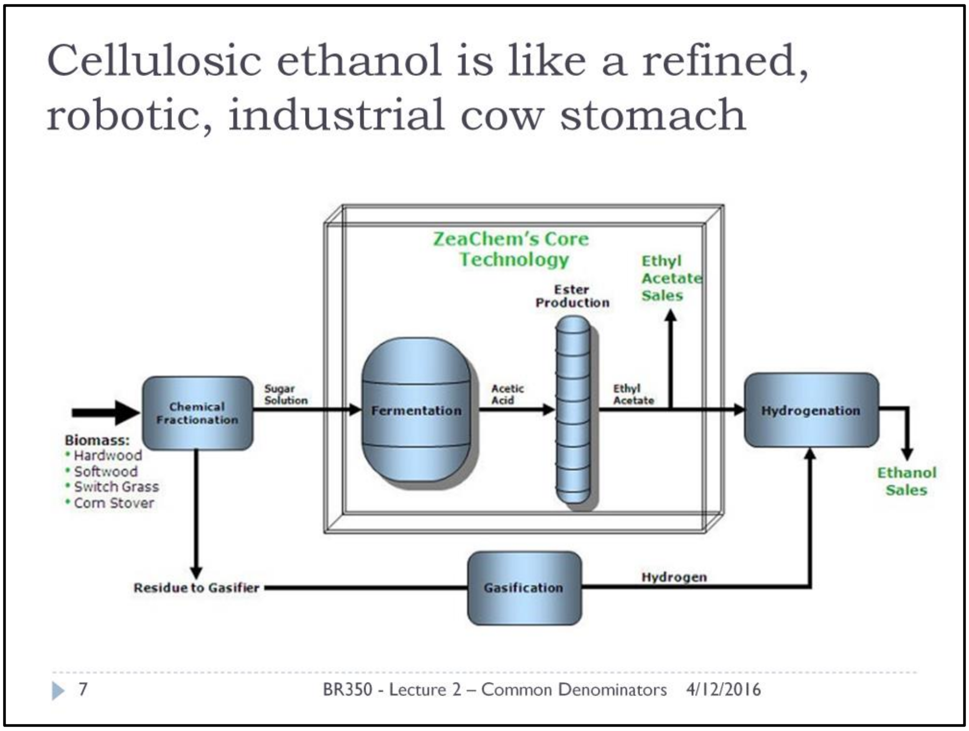
Acids – hydrochloric, sulfuric, acetic, sulfurous
Enzymes – cellulase, xylanase, lignase
Catalysts – zeolites, alumina, cobalt, nickel, copper
Oxidation – hydroxides, singlet O2, ozone, etc

All of these breakdown processes are basically similar to digestive processes

It turns out that many of the chemical processes you can use to break biomass into its pieces can also be used to break those pieces into sugars and chemicals. We will review acid, enzyme, catalyst and oxidation methods that can break down cellulose, lignin and hemicellulose.

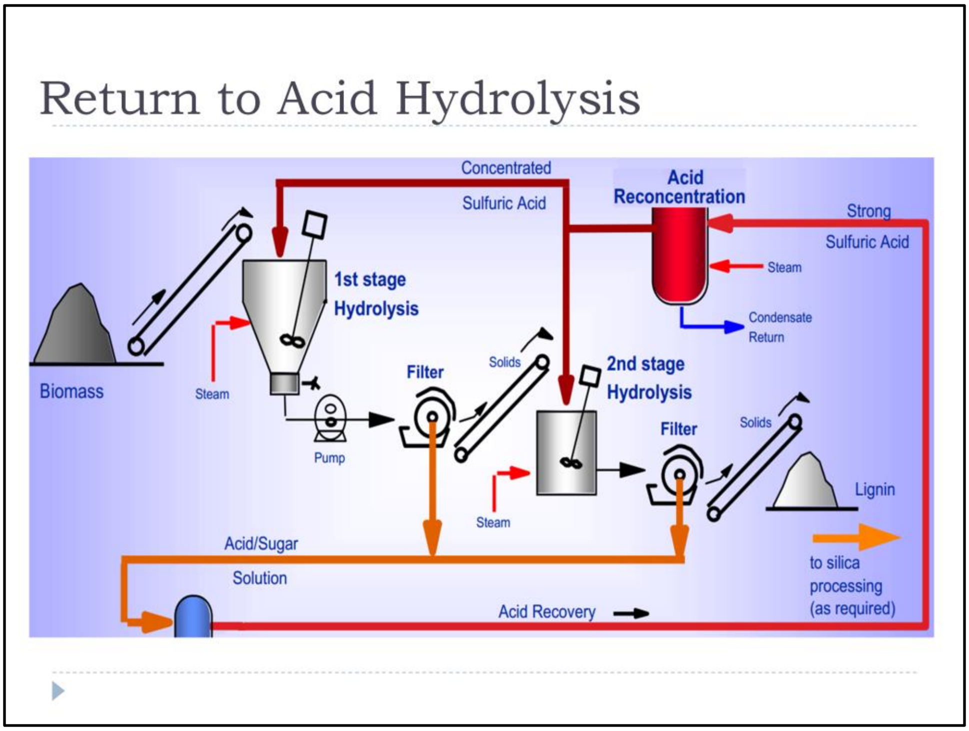


I am going to repeat this analogy because it is important. We are all using biomass chemical conversions right now and we have recently done a biomass mechanical conversion. Every time you cut your food to eat it and every time you chew it before swallowing you are doing a mechanical conversion. You reduced to size to get it into the reactor (your mouth). Then you chewed it so that it could be broken down easier in your stomach, so technically you had to perform two mechanical conversions. Likewise, two chemical conversions also occurred – as soon you began chewing the biomass, you began adding enzymes (a fancy protein chemical) to the biomass to begin the breakdown process. Then, after you swallowed the biomass it was conveyed down your throat and into a special reactor, where it began the second chemical conversion by being broken down in a 98 °F HCL bath, also known as your stomach. The biomass is broken down enough by these mechanical and chemical conversions that it can be used as a source of nutrition for living organisms like us – thank goodness it's designed so well.



Just like the digestion analogy, cellulose …..

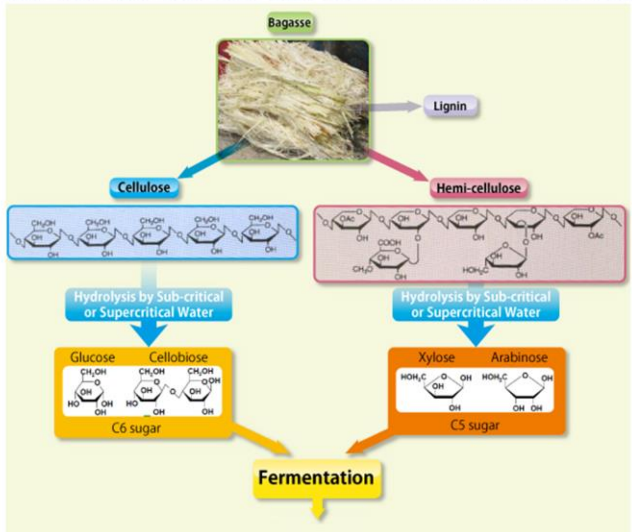
An over-simplification, but accurate and provides an example just about everyone can get



BlueFire Renewables - http://bfreinc.com/

This looks like a repeat because it is. One of the reasons acid hydrolysis with hydrochloric and sulfuric acid is compelling is that the same chemical can be used to both break the biomass into its parts and also to break the cellulose fiber into sugars. The conditions of both reactions are different and it is necessary to separate the solid fibers, but the fact that both processes can use the same reactive chemical is ideal because it means less overall steps, which often improves economics. You take the cellulose fibers that were produced from one acid bath and you soak them in a second acid bath until they turn into sugar. Then you recycle all the acid and the process continues to produce sugar and lignin from biomass.

Different Options with Water Hydrolysis

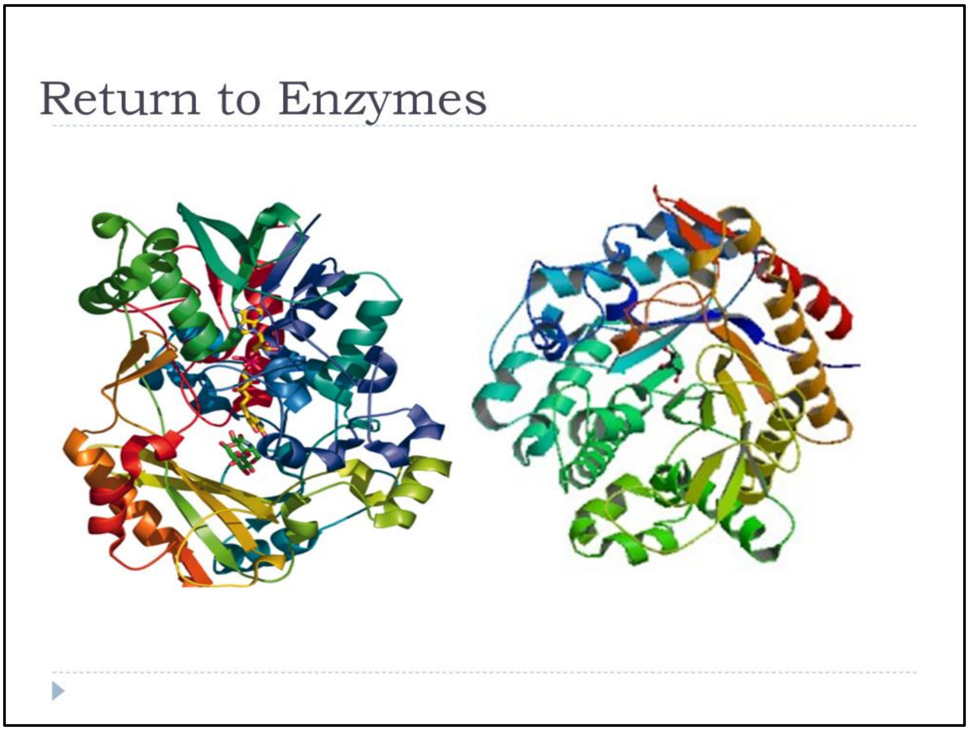


9 BR350 - Lecture 2 – Common Denominators 4/12/2016

http://renmatix.com/

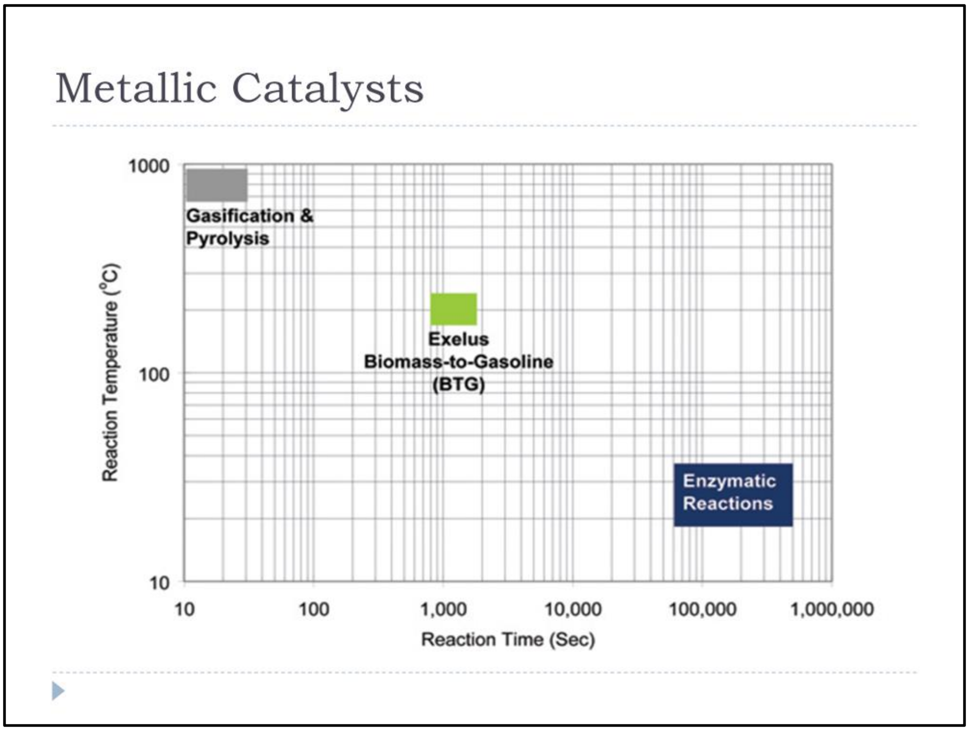
http://www.asiabiomass.jp/english/topics/1101_01.html

A recent development in the bioenergy industry has been hydrolysis without acid. Instead of acid it is possible to use sub-critical or supercritical water to break cellulose fibers down into sugars. This process has the added benefit of being able to break hemicellulose down into sugars as well. Sub-critical and supercritical water reactors require extremely high pressures so this can be a complicated and expensive process, but it is also very clean and sustainable which is extremely compelling compared to using acids. If this process proves to be economic at commercial scales it will certainly play a large role in many bioenergy developments.



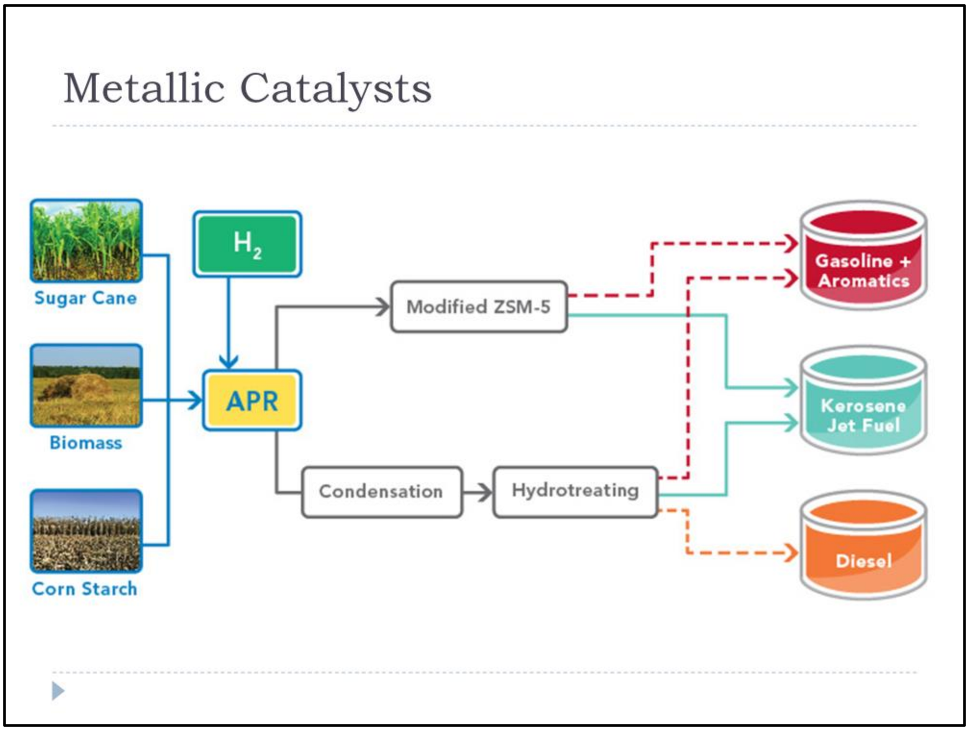
Novozymes - http://www.novozymes.com
Codexis - http://www.codexis.com/

Enzymes are like nanobots – if we ever get to the point of designing little nanobots that perform work as a result of some kind of external stimulus or condition, I bet they will look like enzymes. Like we discussed, enzymes are a very expensive chemical because they have to be harvested from microbes, plants or animals and then purified. Despite this expense, they are absolutely worth the money in many cases. They are extremely efficient and exact catalysts capable of supporting chemical reactions that would be nearly impossible in so few steps without them. They work at room temperature, very moderate conditions, and they can break cellulose and lignin down very effectively. In some ways enzymes represent the ultimate chemical reactant because of their abilities, however maybe like a nanobot, they can break easily if the conditions become too extreme or something chemical damages them. The challenge with enzymes is their price and how easily they can be damaged, but if you can get past those challenges they are hard to beat.



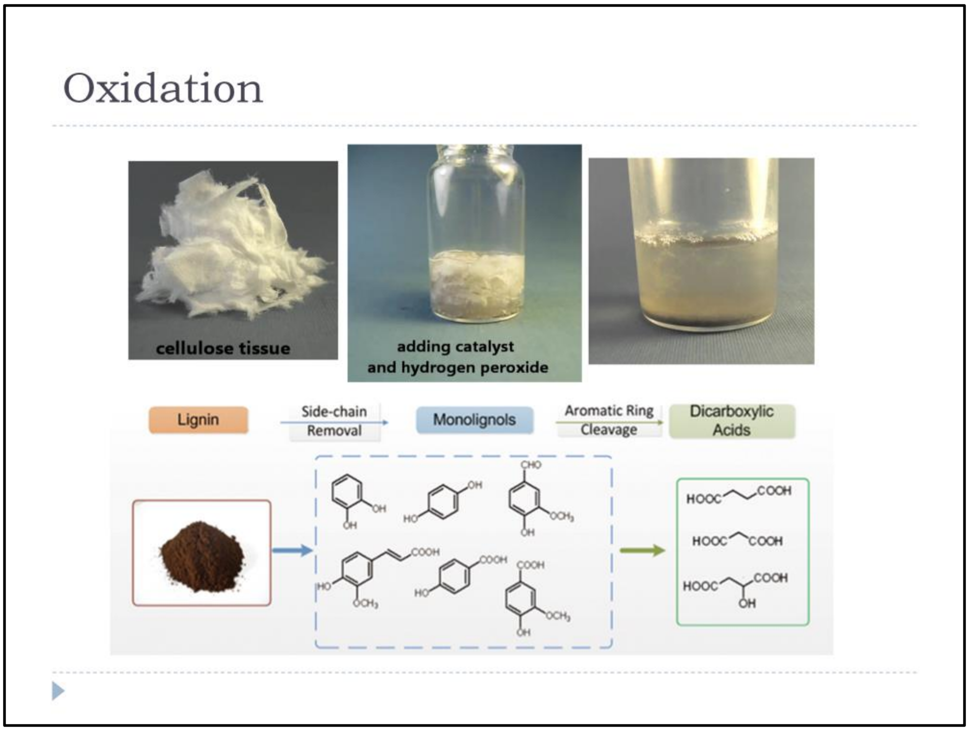
Exelus - http://www.exelusinc.com

Metallic catalysts are what oil refineries use. They are often made of metals like aluminum, nickel, cobalt, ruthenium and palladium. Just about every transition metal on the periodic table has been found to show catalytic activity on some aspect of biomass chemistry. Metallic catalysts are usually used in the form of beads or powders and they are mixed with the chemical that needs to be altered. Under various conditions different metallic catalysts can cause a variety of reactions that can turn cellulose into sugars, acids or even aromatics like gasoline. The strength of metallic catalysts is that they are tougher and cheaper than enzymes, the weakness is that are not as precise or efficient. There are always tradeoffs.



Virent - http://www.virent.com/

Of the chemical conversion methods discussed so far metallic catalysts have the greatest potential to make gasoline from biomass. They are capable of selectively supporting the desired reactions to turn cellulose and lignin components into gasoline. To the extent that these reactions can be done with very little external hydrogen they could become a commercial reality in the near future. Alternatively many of the same processes can be used to generate valuable chemicals instead of gasoline, which may make more sense in the long run.



http://www.hydrogenlink.com/biomassdegradation

Zaluska, A., and L. Zaluski. "New catalytic complexes for metal hydride systems." Journal of alloys and compounds 404 (2005): 706-711.

Ma, Ruoshui, Mond Guo, and Xiao Zhang. "Selective Conversion of Biorefinery Lignin into Dicarboxylic Acids." ChemSusChem 7.2 (2014): 412-415.

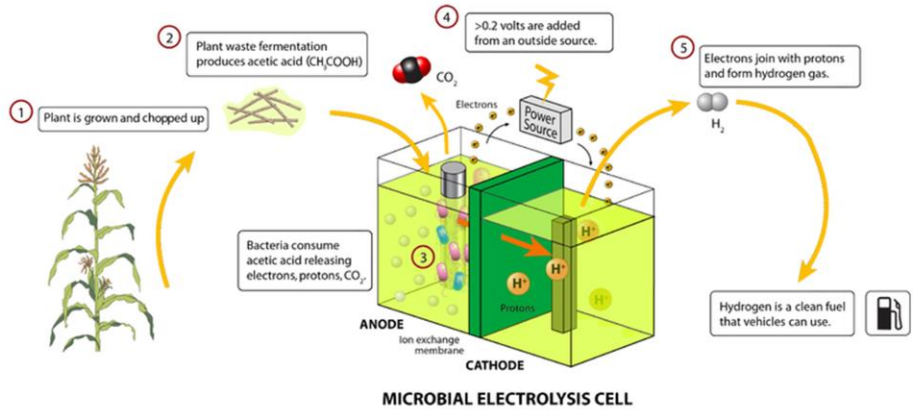
There has been a considerable amount of research since the 1980's on using reactive oxygen as singlet oxygen, ozone and hydroxyl radicals to break down lignin and cellulose into sugars and chemicals. This is a very exciting area of development because it has the promise of being affordable and working at reasonable reactor conditions. The hydrogen link development I previously shared is a recent example of this. They are able to use catalysts like NaBH4, LiAlH4, or NaAlH4 and reactants like H2O2 to generate hydroxyl radicals that quickly and cleanly break down cellulose and lignin. A similar development that is specifically targeting lignin is hoping to produce dicarboxylic acids through highly selective chalcopyrite-catalyzed oxidations. This reaction also takes advantage of reactivity of H2O2 and its ability to generate hydroxyl radicals. There are related developments that have occurred using ozone and singlet oxygen as well. This is a very high growth, high potential area of chemical conversions.

Biomass to Parts & Parts to Products Overview

- Large biomass molecules are chemically degraded into smaller molecules (just like pulping)
- Choice of chemicals (Acids, Enzymes, Catalysts) determines products and conditions
- Challenging to recover chemicals and separate out products

We have covered a lot of material, so in closing I want to review three major aspects of chemical conversions; read slides …

Next Lecture – Oil Conversions and Syngas Conversions



http://www.futureforall.org/energy/microbial_fuelcells.htm

http://en.wikipedia.org/wiki/Microbial_fuel_cell

http://www.microbialfuelcell.org/www/

Microbial fuel cells can generate electricity from any place with wastewater and/or aquatic sediments. They can technically be powered by any source of biomass or waste that can be fermented or composted and unlike alcohol production the fermentation doesn't have to be nearly as controlled or fast. To learn more about this technology please visit the attached links.