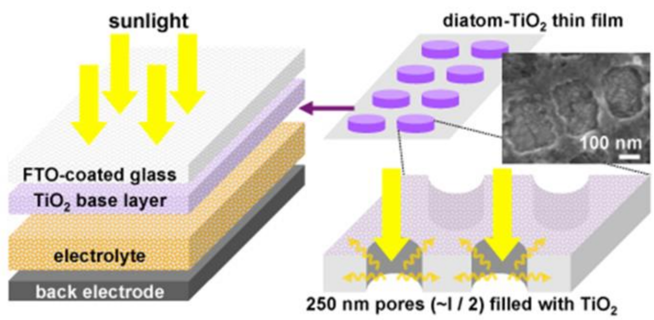


Chemical Conversions

Lecture 14 – Biomass to Parts

Today’s fun bioenergy fact is about plankton-powered solar cells, specifically a type of plankton known as diatoms. The same plankton that live in the ocean and are eaten by whales have become an interesting new bioenergy platform. It turns out that solar cells can be constructed out of diatoms that have been designed to build shells out of semiconductor materials. By controlled feeding of alternative substrates, such as soluble germanium or titanium to living diatom cells, semiconductor materials can be inserted into the diatom biosilica. This process imparts optoelectronic properties to diatoms shell that allow it to be used in solar cells. This is a very neat idea for sustainable electronics, so if you have a chance, please visit the attached link and learn more about it.

http://oregonstate.edu/engr/rorrer/

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

There are a lot of chemical conversion products. They range from cell wall polymers like cellulose and lignin, to much smaller things like sugars and chemicals like furfural. We will not be able to cover all of these, but it is important to appreciate the wide range of commodity, specialty and fine chemicals that can be produced from biomass using chemical conversion processes

Breakdown biomass into Cellulose, Hemicellulose, and Lignin

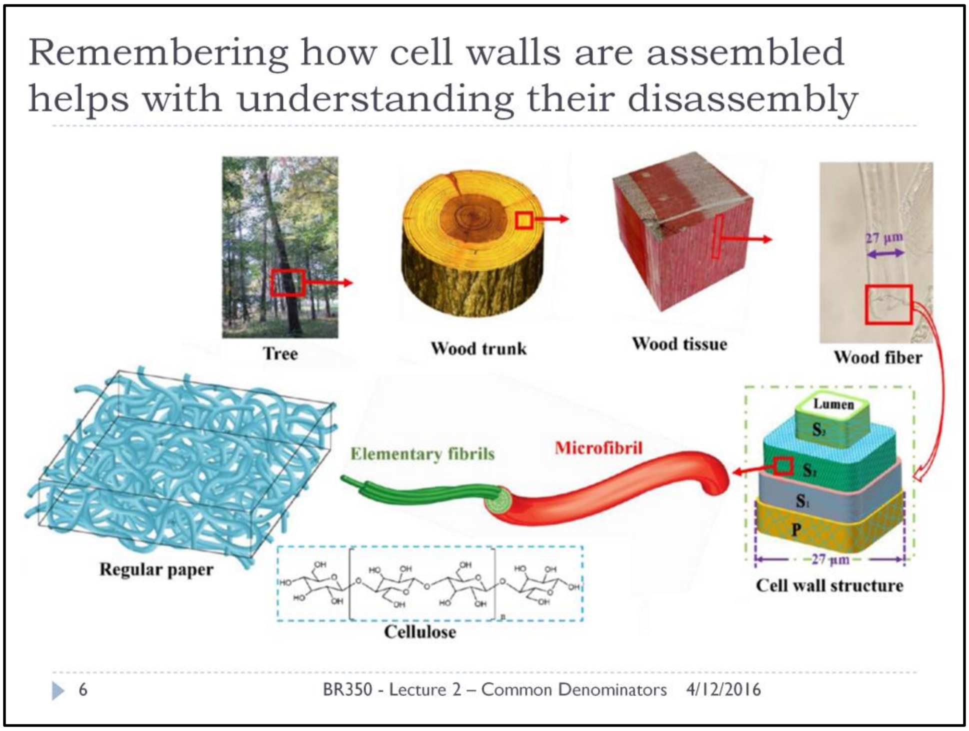
Acids – hydrochloric, sulfuric, acetic, sulfurous
Bases – ammonia, alkali hydroxides, sodium sulfide
Solvents – methanol, ethanol, acetone, benzene
Enzymes – inside plants & produced by fungus

All of these breakdown processes are basically pulping processes

Remember, from a chemical perspective chemical conversions are like the knife (as opposed to the thermal hammer). Chemical conversions are more sensitive to the type of biomass, but the are accurate and precise like a knife, and as a result they can produce a very high quality predictable product.

This pathway is important because we can expose biomass to many different kinds of chemicals and conditions and to get it to turn into a variety of things. It is important that you have a general appreciation for what some of those chemicals, conditions and steps are so that you can better understand the developments in the bioenergy industry.

In general biomass is broken into its parts using acids, bases, solvents or enzymes. It is interesting to consider that we have been chemically breaking biomass into its parts for well over 100 years, so a lot of these ideas are not new, but back then they didn't have the technology we have today, so we can do a lot more with those ideas. It is very likely that from time to time I will mention a chemical or a process that you have never heard before. If that happens and it is not explained in a slide, please look it up on the Internet to familiarize yourself so that you are not left confused.



Fang, Zhiqiang, et al. "Novel Nanostructured Paper with Ultrahigh Transparency and Ultrahigh Haze for Solar Cells." Nano letters 14.2 (2014): 765-773.

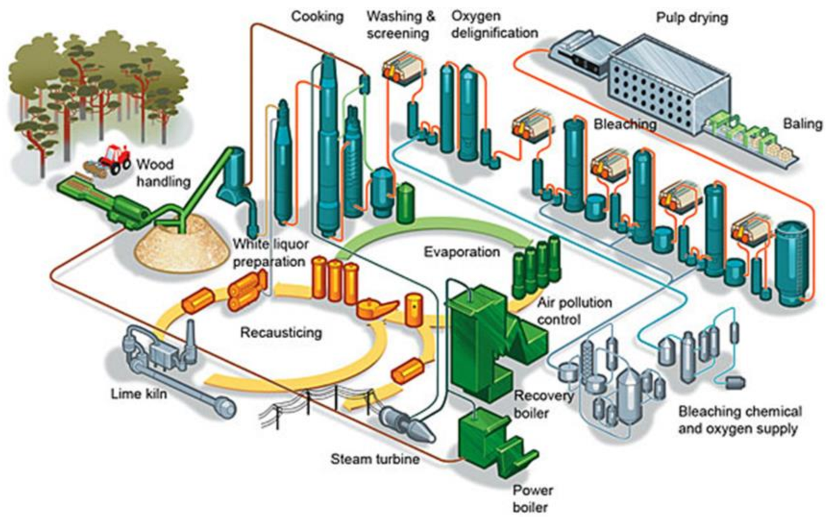
Chemical processes get complex because, unlike thermal processes, they have a lot of steps. To help with this complexity it is important to remember what biomass looks like cellularly and chemically. Most of the time we practice chemical conversions, we are trying to isolate and collect the elementary fibrils shown in this image. These fibers are used to make paper and they are composed of cellulose. So, all of the processes discussed in this biomass-to-parts lecture are related to removing all the cellular stuff around the fibers so that we can have piles of just the pure fiber to work with.

We have been disassembling cell walls by pulping wood for paper since the 1850's

http://w3.upm-kymmene.com/upm/internet/cms/upmmma.nsf/lupGraphics/Botnia_Fray%20Bentos%20mill_1.jpg/$file/Botnia_Fray%20Bentos%20mill_1.jpg

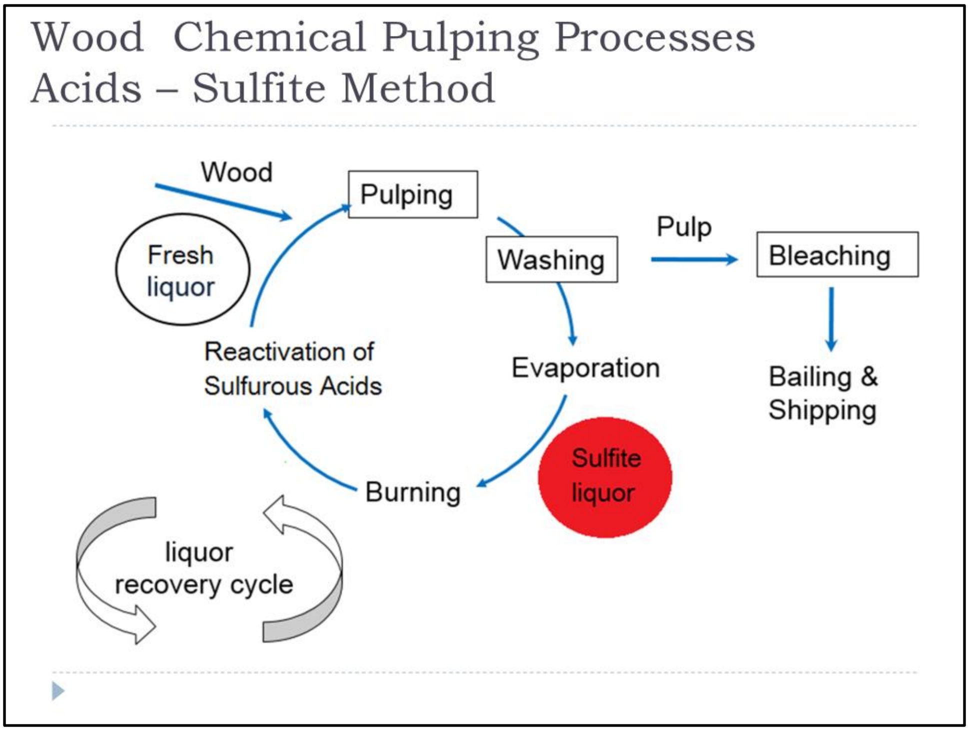
Like we previously discussed, we have been using chemical conversions to turn biomass into useful products for a very long time. The conversion of wood chips into cellulose pulp for paper is a chemical conversion known as pulping. You can pulp any kind of plant biomass to produce cellulose, but not all the cellulose is good for making paper.

Pulping wood for paper is the largest biorefining industry on earth



http://www.metsopaper.com/paper/MPwGeneral.nsf/WebWID/WTB-061228-2256F-E7612/$File/Total_scope_with_large_text.jpg

This is a figure that shows more of the details associated with pulping process. Wood comes in, it is mixed with reactive chemicals, and then the cell wall is broken down into its pieces. The fiber is kept and the rest is sent to a recovery boiler where the non fiber cell matter and the reacted chemicals are burned together to recover the reactive chemicals. Then the reactive chemicals are recycled, reactivated and sent back to be mixed with fresh wood.



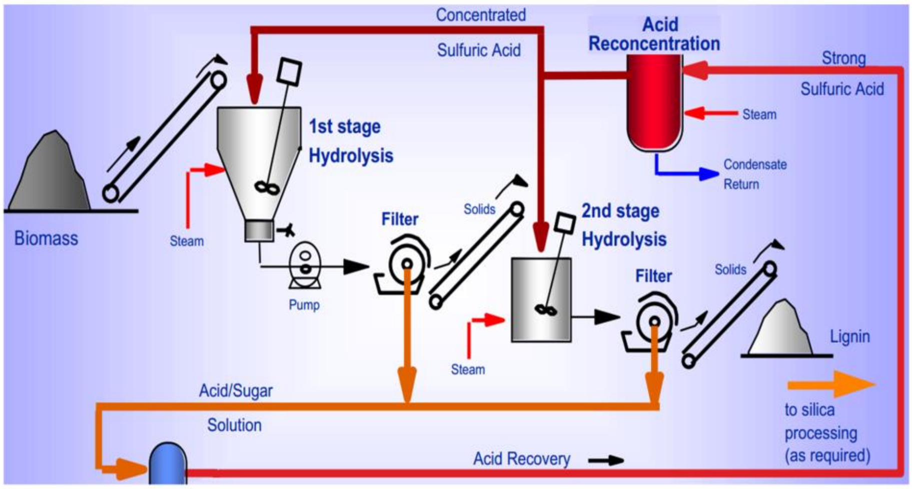
http://www.knowpulp.com/

There are two main types of wood pulping: an acid process known as the sulfite pulping, and a base process known as Kraft pulping. They are very similar in many ways, but different in some important ways as well.

The sulfite process produces wood pulp that is almost pure cellulose fiber by using various salts of sulfurous acid to extract the lignin from wood chips in large pressure vessels called digesters. These pulping chemicals are known as liquor. The pulp is in contact with the pulping chemicals for 4 to 14 hours and at temperatures ranging from 130 to 160 °C. The spent cooking liquor from sulfite pulping is usually called red liquor or sulfite liquor and it can be burned in a recovery boiler to recover the inorganic chemicals for reuse, or it can be neutralized to recover the useful byproducts of pulping. The opportunity to recover useful byproducts from the spent cooking liquor through neutralizing is an interesting aspect of sulfite pulping. It also generates a higher quality lignin and has a potentially higher pulp yield depending on how it is done.

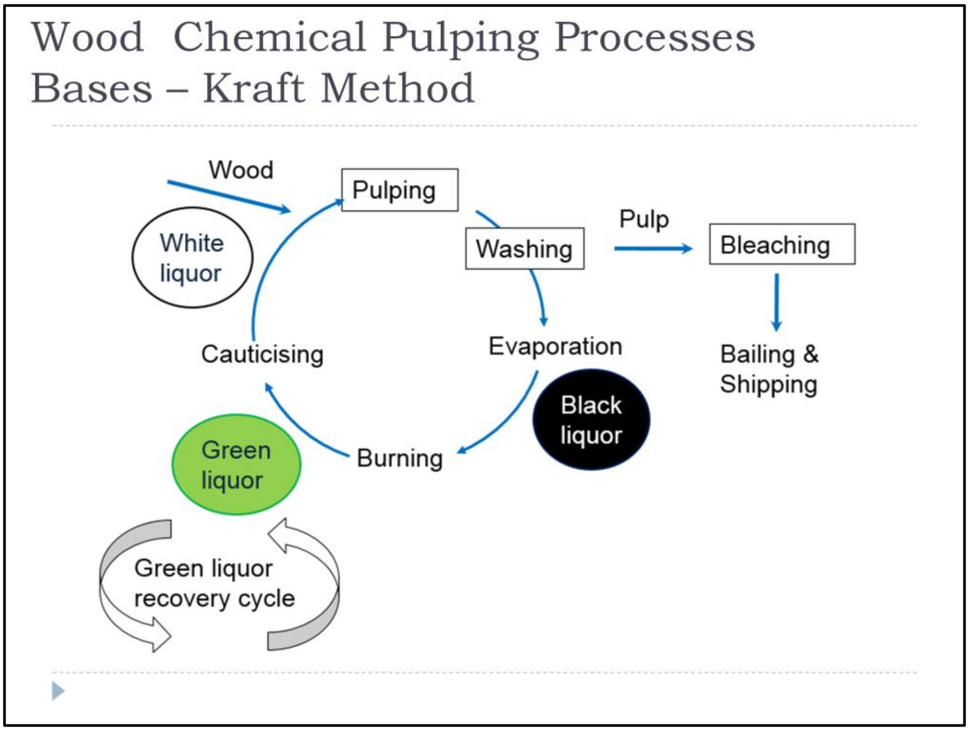
However, the cellulose fiber it generates is often weaker, so it is mostly a specialty process today compared to Kraft pulping.

Acids - Acid Hydrolysis



BlueFire Renewables - http://bfreinc.com/

Outright acid hydrolysis using hydrochloric acid or sulfuric acid is another option very similar to sulfite pulping. You basically mix biomass with acid and then increase the temperature. This separates the fiber part from the other parts and then you can collect the fiber part and use it for producing sugars. After the fiber part is removed from the acid bath, the acid can be recovered and reused. The image shown is a flow diagram that explains how this works

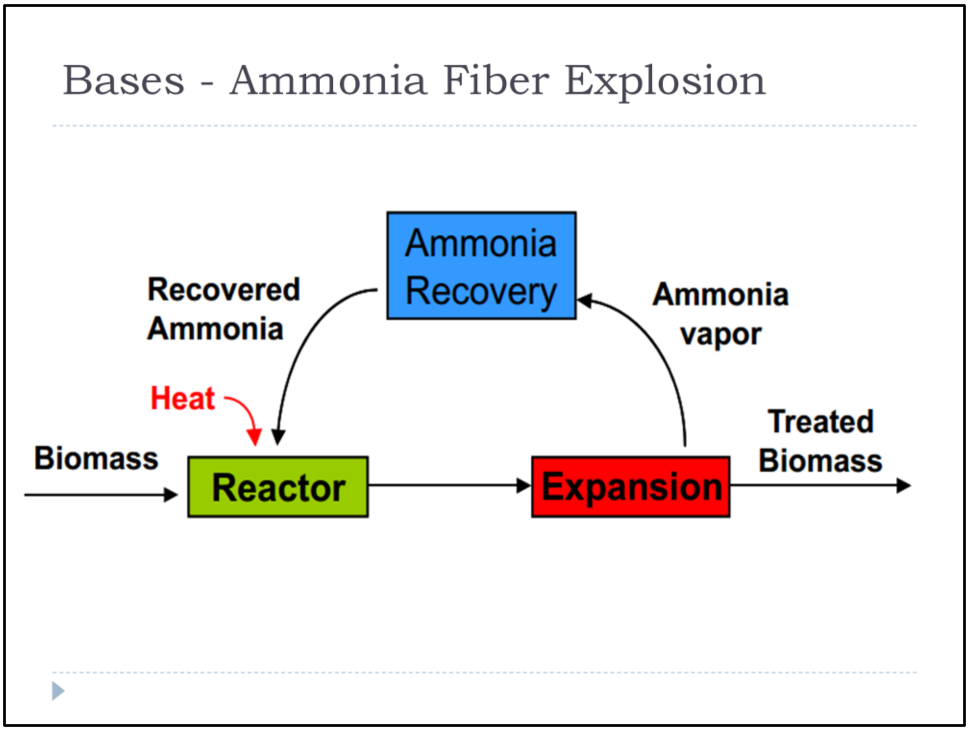


http://www.knowpulp.com/

http://www.getfilings.com/sec-filings/100226/MERCER-INTERNATIONAL-INC_10-K/

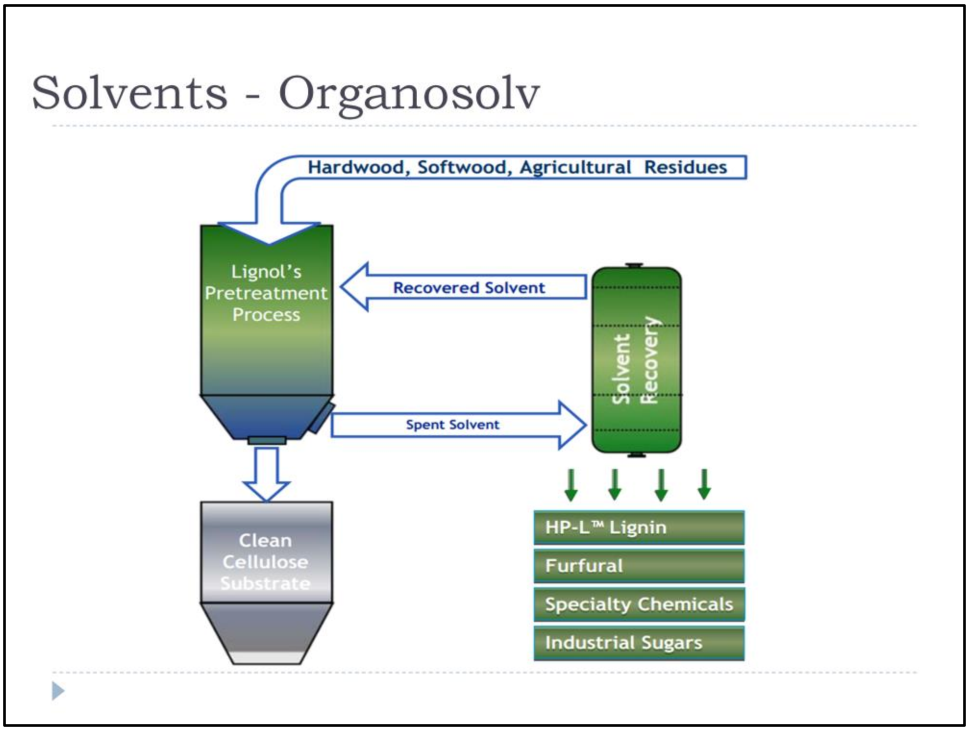
The Kraft process produces wood pulp that is almost pure cellulose fiber by using a mixture of sodium hydroxide and sodium sulfide, known as white liquor, to break the bonds that link lignin to the cellulose. Like sulfite pulping, this is done in large pressure vessels called digesters. The pulp is in contact with the pulping chemicals for 2-3 hours and at temperatures ranging from 170 to 180 °C. Under these conditions lignin and hemicellulose degrade to give fragments that are soluble in the strongly basic liquid. The solid pulp is collected and washed and the spent cooking liquor, known as black liquor, is concentrated and burned in a recovery boiler to recover the inorganic chemicals for reuse.

The Kraft process is by far the most popular commercial pulping method. It works on many different kinds of biomass, it generates a very strong pulp, and in many ways it is a less complicated process than sulfite pulping because of materials and emissions considerations.



AFEX - http://www.mbi.org/mbi-technologies.html

Ammonia fiber explosion, also known as AFEX, is another based driven process to reduce biomass to its parts. One of its strengths is that it is fairly simple. All you do is soak the biomass in ammonia while the temperature and pressure are increased. Once you get to the desired pressure, the pressure is rapidly released resulting in an explosive expansion. This explosion literally tears the cellulose fiber from the lignin and leaves you with a biomass that is much more degradable and digestible than what it was before the AFEX treatment. This process does not leave you with a pile of pure cellulose fiber, but its speed and simplicity make it a good process for a variety of small scale bioenergy ideas.

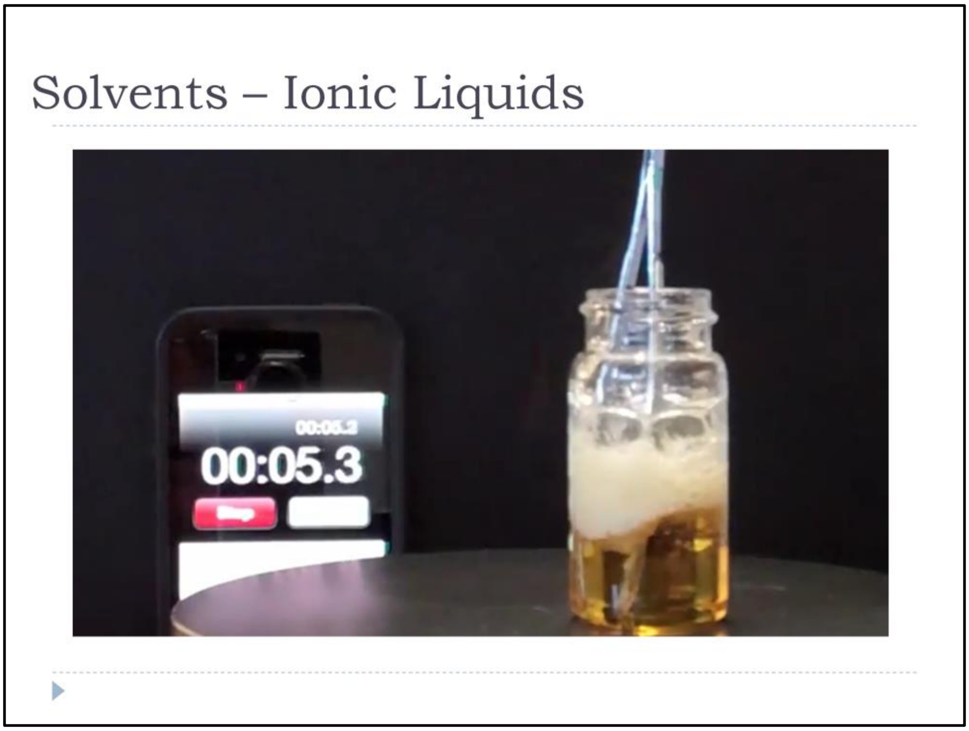


Lignol - http://www.lignol.ca/

http://www.lignol.ca/investors.html

Organosolv pulping has been around since the 1970's and instead of acids and bases, it uses solvents. Remember, a solvent is a chemical that can be used to dissolve something and turn it into a liquid solution. Unlike an acid or a base, solvents don't generally damage or modify the chemistry of the thing that dissolves, they just rearrange the molecules so that they can become a liquid solution.

Just like normal pulping, biomass is mixed with the solvent in a reactor at temperature of between 140-220 °C for several hours. This causes the lignin and the cellulose fiber to be separated and because no acid or base modifications occur, the lignin, hemicellulose and cellulose are extremely pure, much purer than can be achieved with normal pulping. Solvents used include acetone, methanol, ethanol, butanol, ethylene glycol, formic acid and acetic acid. The major disadvantage of organosolv pulping is the pressure. Solvents tend to have very low boiling points, so when you get them hot it takes a lot of pressure to contain them and this makes the process very expensive. Solvents that don't require high pressures and that don't dissolve in water are preferred – at the moment ethanol and butanol are two of the most popular.



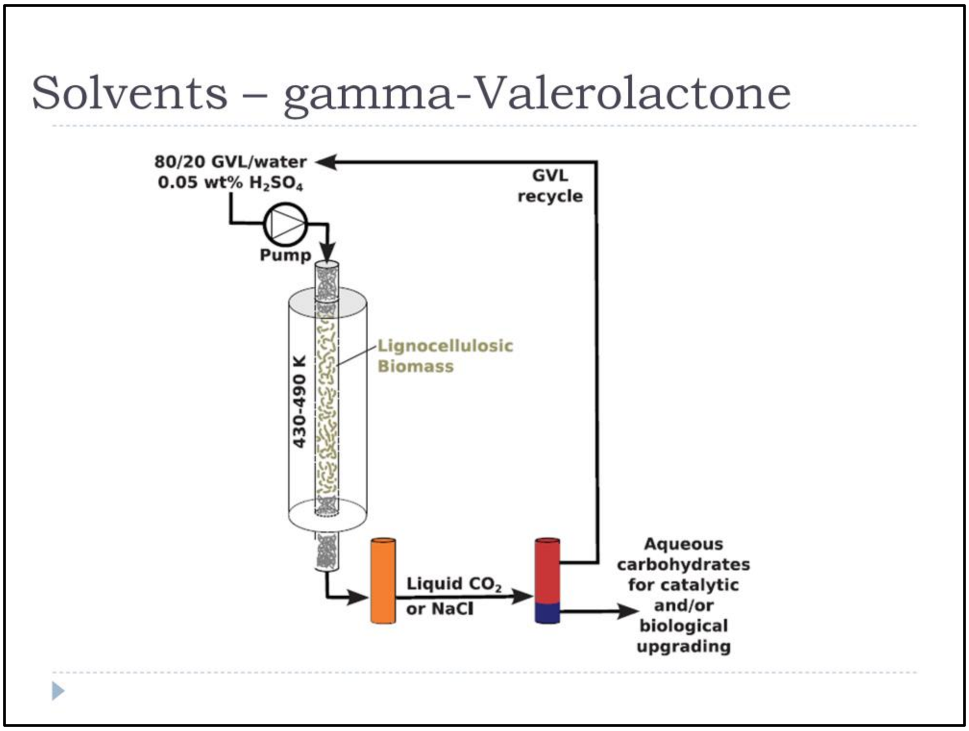
http://secondcriterion.wordpress.com/2012/05/03/video-and-research-highlight-dissolving-cellulose-in-ionic-liquids-for-biofuels/

http://hyraxenergy.com/

http://www2.lbl.gov/tt/techs/lbnl3117.html

One of the most fascinating recent developments in the chemical separation of cell wall components has been something called ionic liquids. Ionic liquids are generally liquid organic salts any salt that can melt without decomposing or vaporizing is usually called an ionic liquid. Ionic liquids are outrageous solvents capable of dissolving a very wide variety of things very fast. The image shown is of a cotton ball being dissolved in an ionic liquid at room temperature in five seconds. Think about how many hours the pulping processes took and you can see why ionic liquids are so exciting.

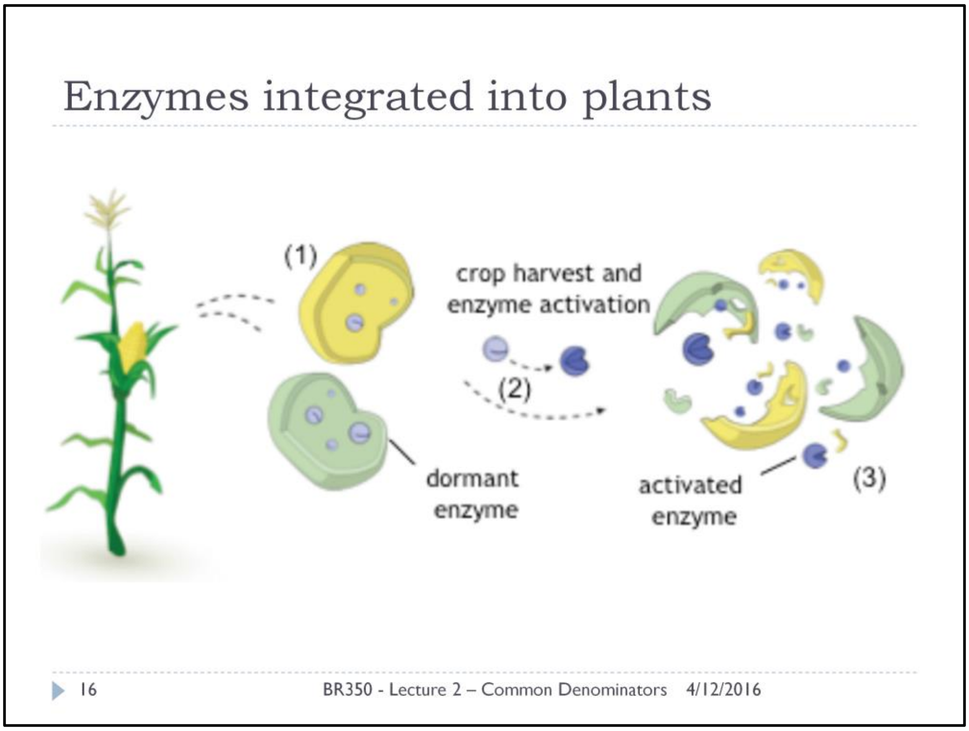
The problem with them is that they are very expensive and we do not have very many efficient methods for recovering them after they have dissolved the biomass. Fortunately this is changing and an increasing number of scientists are developing methods for recovering most of the ionic liquids used in the conversion so they can be reused. This will be a technology to watch closely.



Science. 2014 Jan 17;343(6168):277-80. doi: 10.1126/science.1246748.
Nonenzymatic sugar production from biomass using biomass-derived γ-valerolactone.
Luterbacher JS1, Rand JM, Alonso DM, Han J, Youngquist JT, Maravelias CT, Pfleger BF, Dumesic JA.

Another very exciting solvent is something called gamma-valerolactone or GVL. What is exciting about it is that, like ionic liquids, it can be used to dissolve biomass into its parts at fairly low temperatures and pressures. It is not as low as ionic liquids, but much better than traditional pulping. As a bonus, GVL is pretty easy to recycle and it is much cheaper than ionic liquids.

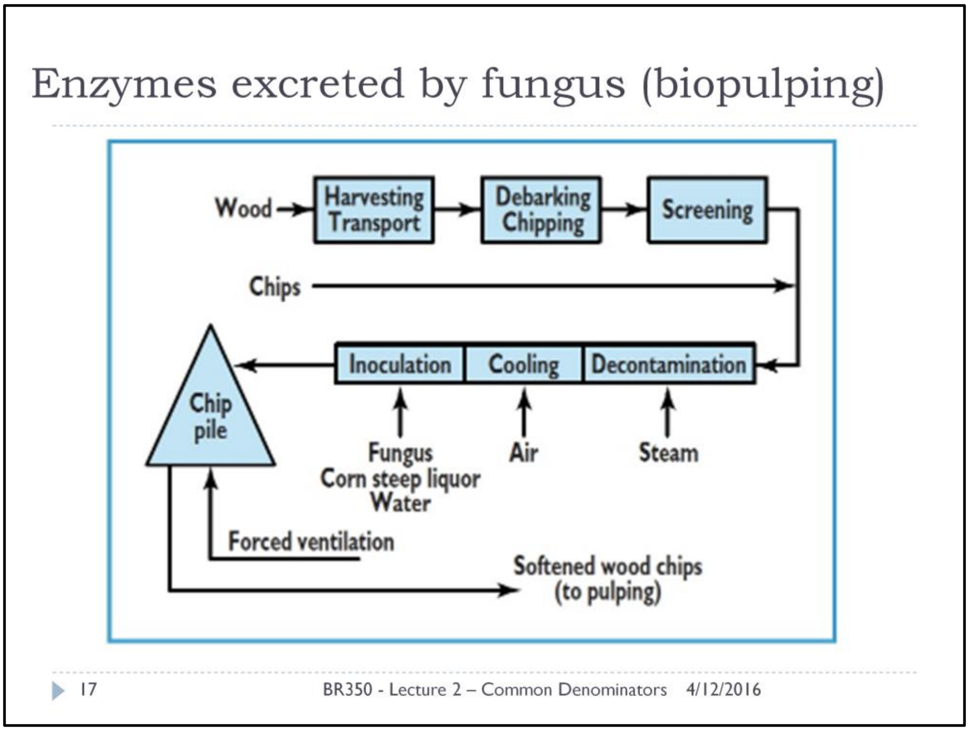
However, the most interesting thing about GVL is that a certain amount is actually produced during the biomass decomposition process, so it’s like breaking the biomass down with a biomass breakdown product. This kind of chemical looping is a chemical engineering dream because it allows the process to be more flexible and economic than normal. The only other chemical that has shown this type of promise is methanol, but to use methanol requires much higher temps and pressures than GVL needs, so GVL is a significant advancement.



Agrivida – http://www.agrivida.com/

Genetically engineering crops to decompose themselves when they are harvested is not practiced by very many people, but it's hard not be a little excited about it. Enzymes are a very expensive chemical because they have to be harvested from microbes, plants or animals and then purified. The traditional approach has been to add enzymes to the biomass and let the enzyme start breaking things down. However, if the plant that needs to be broken down has been genetically engineered to have the desired enzyme, then you can skip buying the expensive enzyme, which would be great. A company called Agrivida is working on this right now.

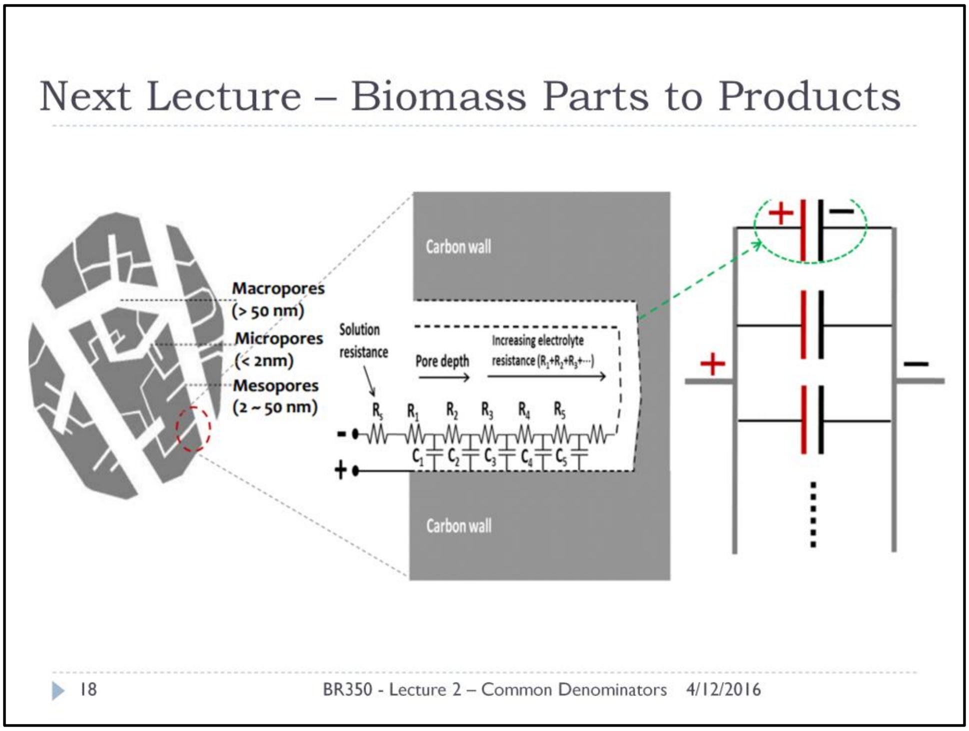
The crops produce dormant enzymes embedded within the plant. These embedded dormant enzymes are activated under specific post harvest conditions and the activated enzymes degrade the cell wall. This approach greatly reduces enzyme, energy, chemical and capital costs normally associated with using biomass.



Canam, Thomas, et al. "Pretreatment of Lignocellulosic Biomass Using Microorganisms: Approaches, Advantages, and Limitations." (2013).

http://www.biopulping.com/2.html

Another way to use enzymes is to get a fungus to excrete them for you. When this is used to break down biomass it is known as biopulping. Currently biopulping treats wood chips with a natural wood-decaying fungus prior to mechanical pulping. This process saves substantial amounts of electricity, reduces the environmental impact of pulping, and enhances economic competitiveness. It is not really done at commercial scale yet, but it is a very interesting approach that is already some what employed in the production of silage for livestock. This is an area with a lot of potential, as long as the proposed application is okay with the long wait times required for the microbe chemicals to do their work.



http://news.illinois.edu/news/13/1023supercapacitors_JunhuaJiang.html

Jiang, Junhua, et al. "Highly ordered macroporous woody biochar with ultra-high carbon content as supercapacitor electrodes." Electrochimica Acta 113 (2013): 481-489.

When you have an opportunity please visit the attached link on biochar supercapacitors. The image looks complex and probably a little confusing, but what it is trying to communicate is that wood anatomy is showing a lot of potential for use in supercapacitors if the wood is very carefully turned into biochar. This is exciting because supercapacitors are a booming industry and wood is much more sustainable and economic than the current materials we rely on. Biochar supercapacitors have demonstrated promising capacity and durability comparable to existing advanced carbon materials. Notably, biochars have good conductivity, electrochemical stability and an interesting pore network that makes them a promising energy and environmental materials.