Basic Chemistry & Overview

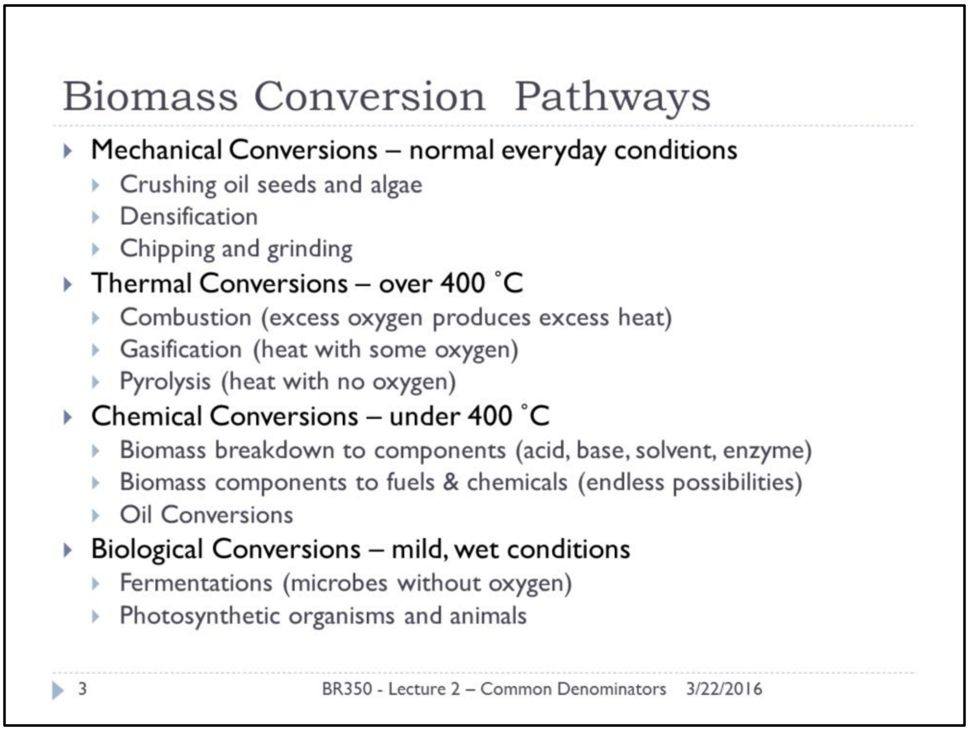
Lecture 9 – Bioenergy Industry Overview

As we begin our discussion about bioenergy conversion processes that are used and will be used industrially, I would like everyone to consider some of the irony around biofuels for vehicles and the horse-drawn carriage. I have attached a link with some amusing images that you can look at if you like. Armies of people, spend millions of dollars a year, trying to recreate what a horse does chemically and mechanically. In some ways a horse is the ultimate bioenergy powered vehicle – grass and water go in, power and locomotion come out. Sure the efficiency isn't great, and you have to keep fueling it even when you aren't using it. But, it certainly is powered by biomass and capable of allowing us to drive around. Worth thinking about.

http://en.paperblog.com/just-say-neigh-10-modern-horse-drawn-carriages-256085/

Week 3 – Basic Chemistry & Overview
-Learning Objectives-

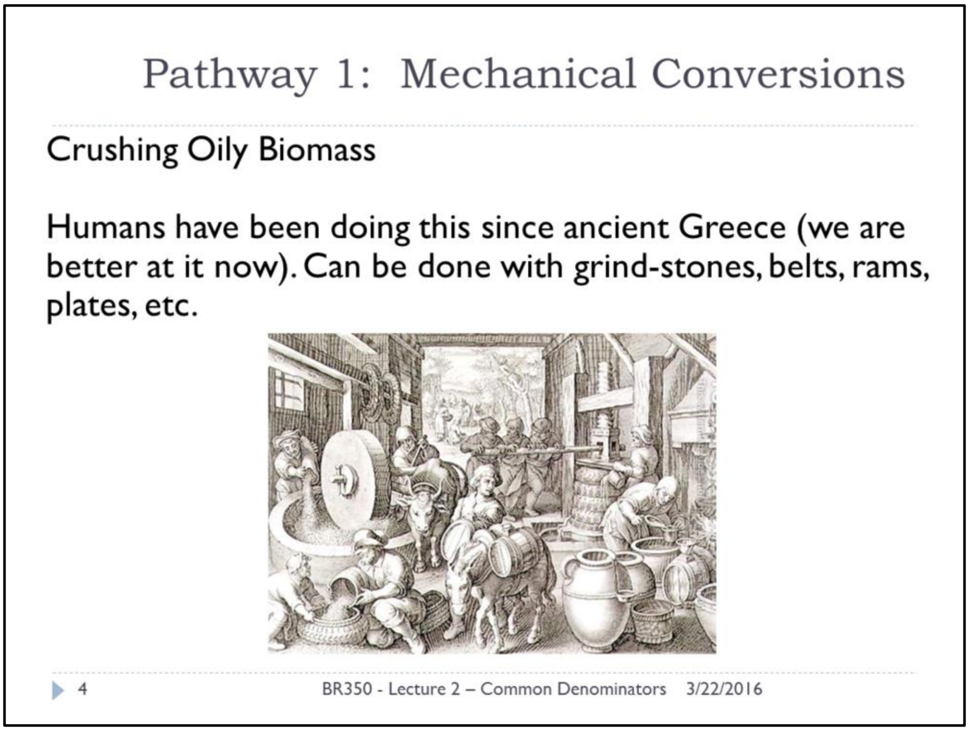
- Recall the 4 common denominators of the bioenergy industry and list their subsets.
- Recognize the basic chemical characteristics of biomass and fuels.
- Describe what makes a good fuel



Most bioenergy ideas and businesses use combinations of different conversion processes and then come up with a cool name for it that get attention (marketable).

When someone tells you about a bioenergy conversion process, you need to be able to identify the basic parts. There are generally only four basic possibilities; Thermal Conversions, Chemical Conversions, Biological Conversions and Mechanical Conversions.

Almost every known bioenergy process will fall into one or more of these categories. You will not be responsible for understanding all of the various details of each conversion type, but you will be responsible for developing a basic understanding that allows you to identify them when evaluating bioenergy news and developments.



The first pathway we will learn about is mechanical conversions. These include crushing oily biomass, densification, chipping and grinding, and drying.

This is an especially important conversion because biomass is a solid. That means it almost always has to be turned into a different kind of solid, liquid or gas to be used. This is much harder from a conversion perspective than the challenges you face when your feedstock is a liquid or a gas.

You must consider the changes a tree has to go through to become a piece of paper. Sure chemical reactions are used to make the pulp, but otherwise 90% of the entire process from tree to paper is mechanical and it is very complicated and expensive. Unfortunately, many new bioenergy companies overlook the importance and challenges of mechanical conversion and it leads to their downfall. A good understanding of mechanical conversions is an important part of understanding how to utilize biomass for bioenergy.

Pathway 1: Mechanical Conversions

Densification

As a non-compressed solid, natural biomass is not very energy dense compared to oils and coal.
Pellets are ~ double the energy content of wood.

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Turning low density unpredictable biomass into high density predictable biomass makes a better fuel and allows us to make better wood stoves and engineer more advanced wood heating systems.

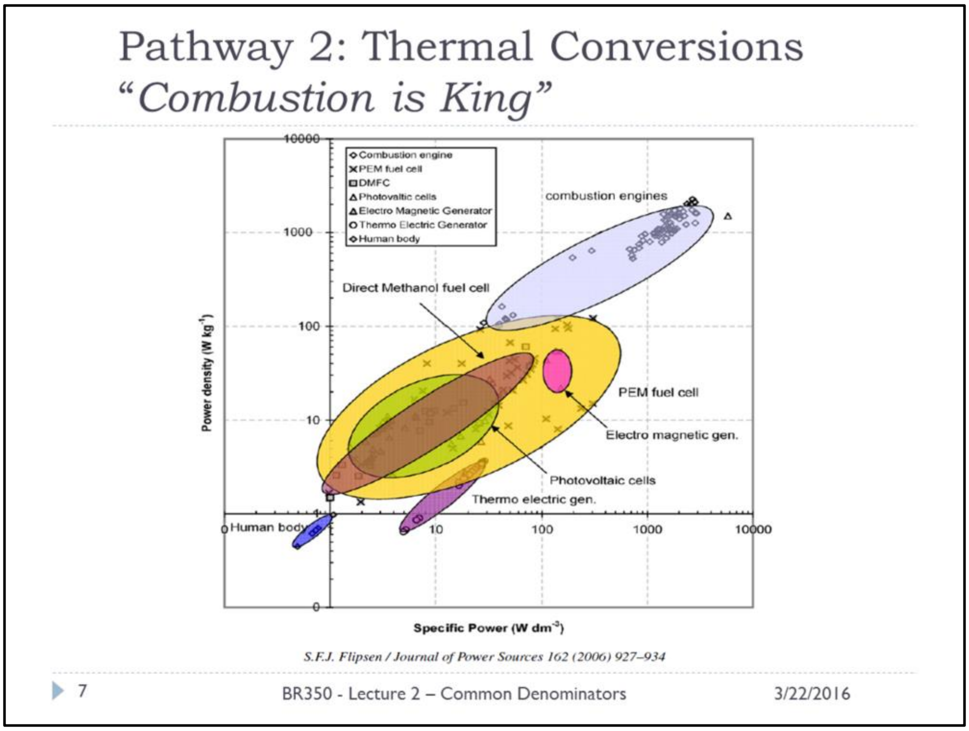
Densification has become an extremely important part of the bioenergy community. We now ship hundreds of millions of dollars in wood pellets to Europe every year.

Pathway 1: Mechanical Conversions

Chipping and Grinding

You can't send a log or a corn stalk into a reactor or a pellet mill, so large biomass has to be turned into small biomass

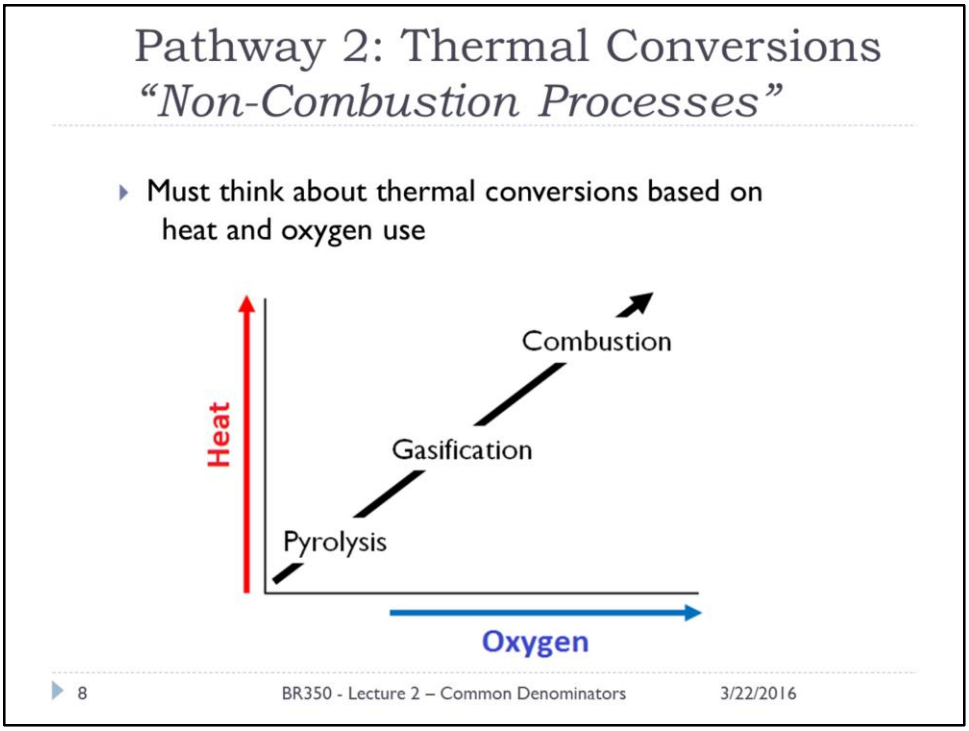
Turning big biomass into small biomass is absolutely required. Trees have to be reduced in size to be transported, and logs have to be reduced in size to be used for building. In the bioenergy world this dramatically increases the price of the biomass, but it is a cost that must be paid to use biomass. So, we will spend some time talking about this technology.



The second pathway we will learn about is thermal conversions. Thermal conversions and mechanical conversions make up the bulk of biomass conversions that occur in the world at any given moment. From a chemical perspective, thermal conversions are the hammer. They are pretty insensitive about the source of carbon, but what they make can be messy.

Without question the most important conversions from an energy perspective are thermal because of combustion. We live on a planet full of oxygen and combustion is king when it comes to making energy.

Oxidation is one of the easiest, cheapest and most powerful chemical reactions on earth. Its dominance in heat and energy production is not chance. No other technology currently comes close in terms of power density and specific power. To the extent that we can gain more control of oxidation reactions (like fuel cells), thermochemical processes will continue to play an important role in our energy future.



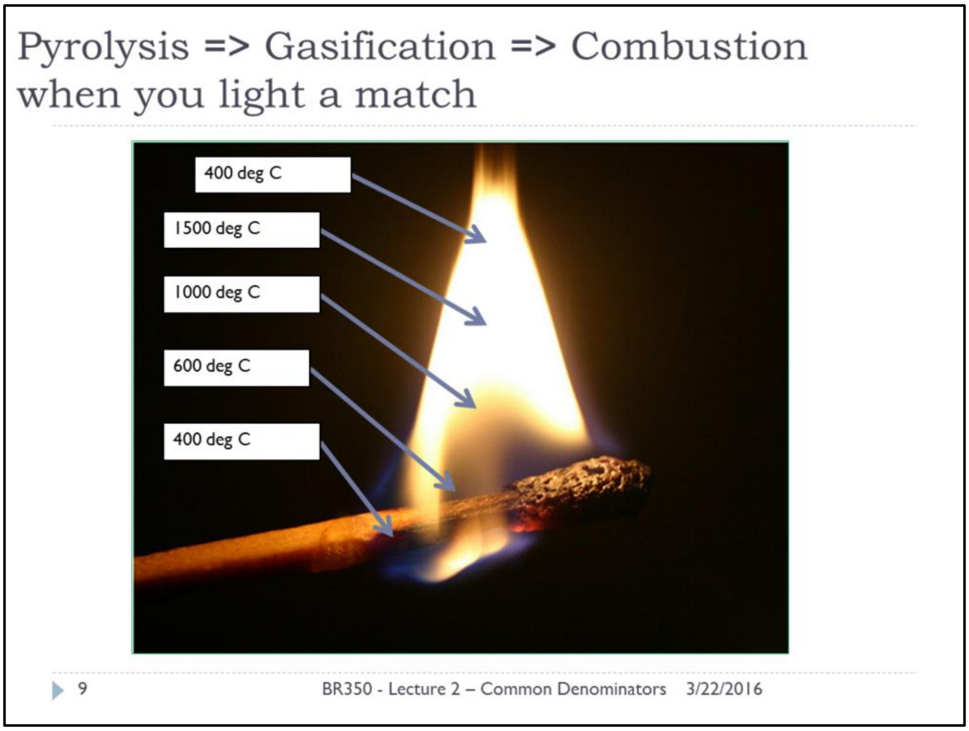
From this point forward, when we think about thermal conversions it will be important to think about heat and oxygen. This is because heat and oxygen almost completely control what kind of thermal conversion will occur. As you add more oxygen and more heat to the process you get different types of thermal conversion.

The lowest level of conversion is pyrolysis. It requires no oxygen and just enough heat to start getting biomass molecules to break, so around 400C.

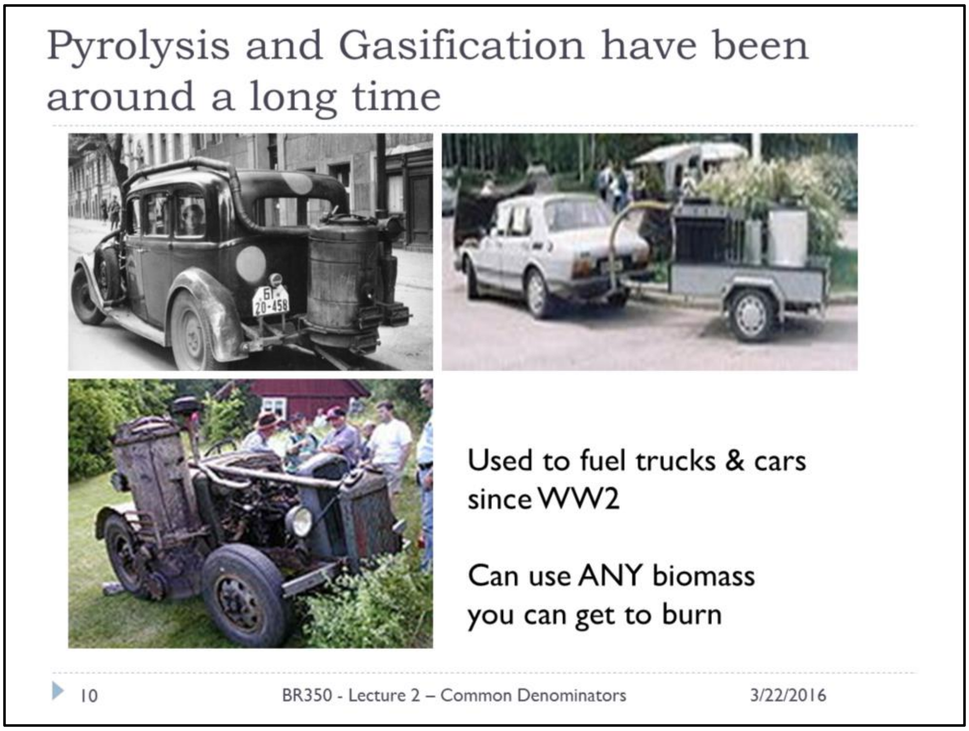
The middle level of conversion gasification. It requires more heat than pyrolysis, but more importantly it requires the addition of a small amount of oxygen. Not enough to combust, but enough to lead to the formation of partially oxidized gas products.

The highest level of conversion is combustion. When you give the system all the oxygen it can handle and enough heat to set it off, it combusts like a match.

Another interpretation of this graph has to do with heat release. Assuming the temperature of the system is in the pyrolysis zone of 400C or more, the addition of oxygen will cause the biomass to leave pyrolysis and go to gasification and then with more oxygen, move onto combustion. However, each thermal process releases heat as well. So in pyrolysis a small amount of heat is generated. Then in gasification more heat is generated, and in combustion the most heat is generated.

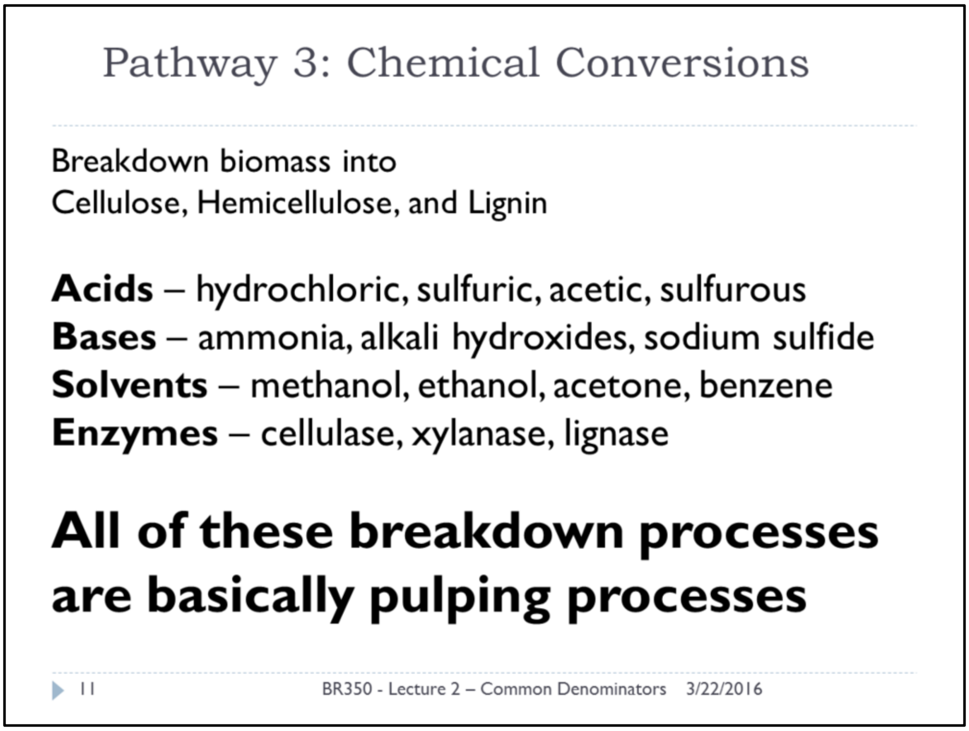


Every time you strike a match you achieve ~ 1500 degrees C *(melting point of steel). I am always amazed that every time I look at a candle or light a match, I am looking at a reaction that is generating temperatures of 1500 degrees C, that is over 2700 degrees F. Considering this, helps us appreciate how much potential energy is available in carbon.*



Pyrolysis and gas ….

When we discussed history we discussed the use of biomass in WW2 for powering vehicles. This was a thermal conversion that turned biomass into a vapor form that could be used by internal combustion engines. The exact thermal conversion was usually something called gasification, but occasionally is was something called pyrolysis. We will learn about both.



Pathway 3 is chemical conversions and it will be split into two parts; breaking biomass down into its pieces, cell …..

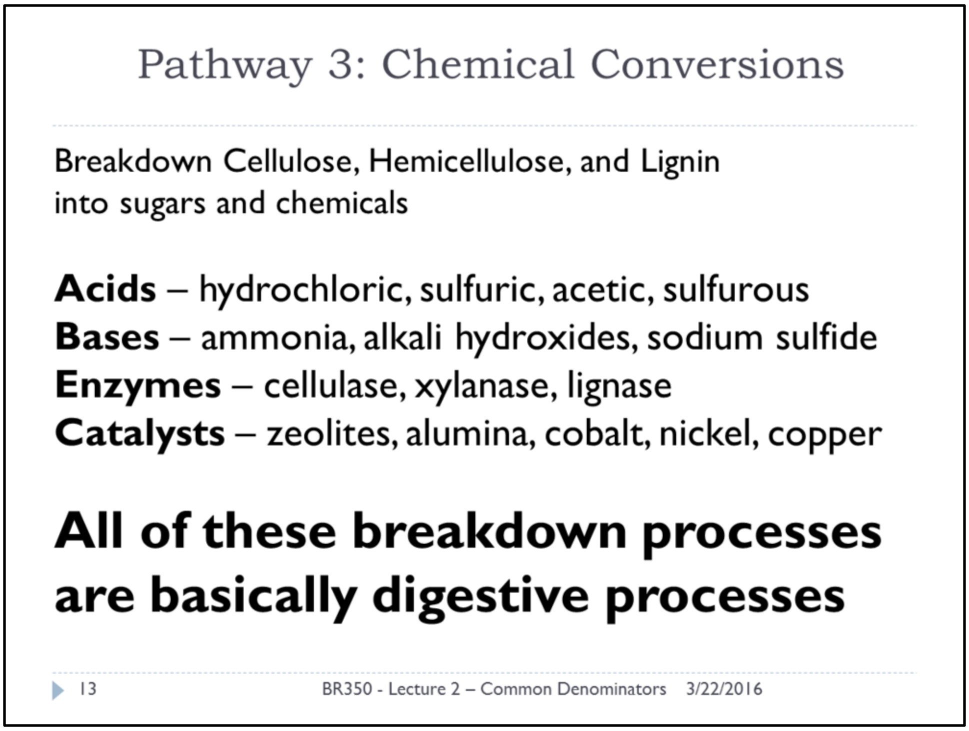
And breaking those pieces down into chemicals and fuels. From the chemical perspective chemical conversions are like the knife (as opposed to the thermal hammer). Chemical conversions are more sensitive to the type of biomass, but the are accurate and precise like a knife, and as a result they can produce 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.

Biomass is largely composed of cell walls and these cell walls can be disassembled elegantly using acids, bases, alcohols, ketones and other solvents. Biochemical processes can be complicated, but acids and solvents are powerful and work based on kinetics that are predictable and can be modeled with impressive confidence. To the extent that reasonably homogenous feedstocks are utilized, these processes will always be competitive in the production of biofuels and biochemical.

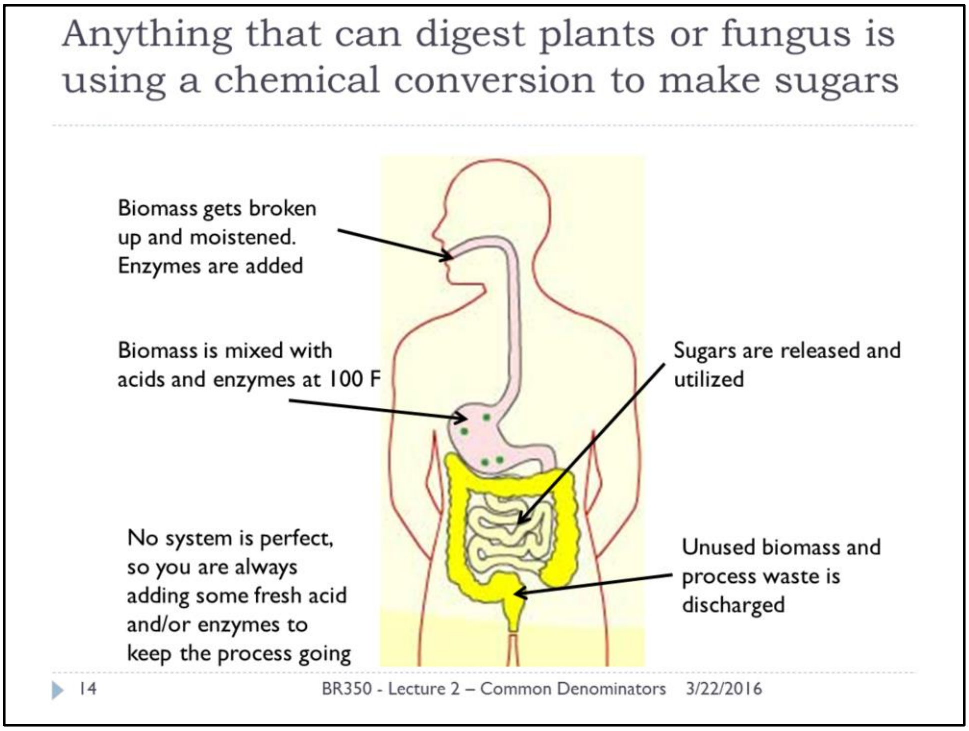
We have been pulping wood since the 1850's

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.

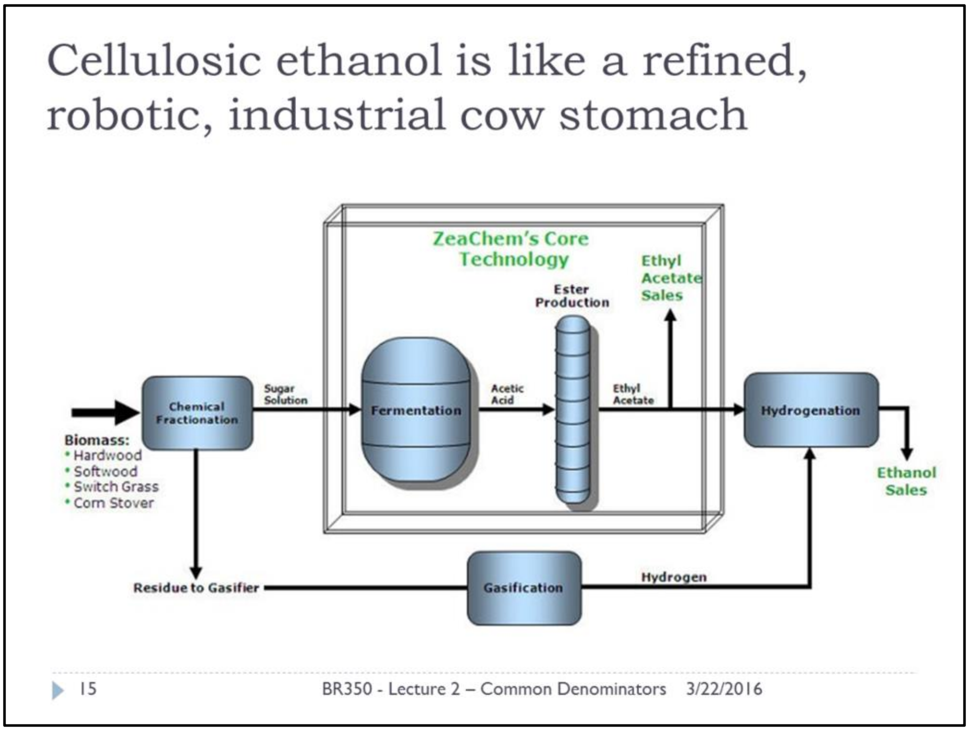


Once we break down the biomass into the cellulose, hemicellulose and lignin, we usually have to break those components down even further to get what we want which is chemicals and fuels that function in our existing systems.

One of the chemicals in highest demand is sugar another one is phenol and a third is furfural. I may have mentioned this before, but we are addicted to organic chemistry, so better ways of producing certain organic chemicals are always of interest and chemical conversions are very good at making very high quality chemicals.



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 its designed so well.



Just like the digestion analogy, cellulose …..

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

Pathway 3: Chemical Conversions

Oil Conversions are a unique aspect of chemical conversion

- Biodiesel
- Renewable Diesel
- Hydrogenated Vegetable Oil
- Soap

Oils and fats are a special biomass fraction and generally expensive to produce.

Breaking biomass into its parts and breaking those parts into chemicals and fuels really focuses on the biomass cell wall. But, as we have discussed, biomass isn't all cell wall and it can be squeezed to produce oils in some cases. These oils get turned into fuels using their own class of chemical conversions.

Biodiesel is a trans-esterification, so it actually adds more oxygen to the fatty acid.

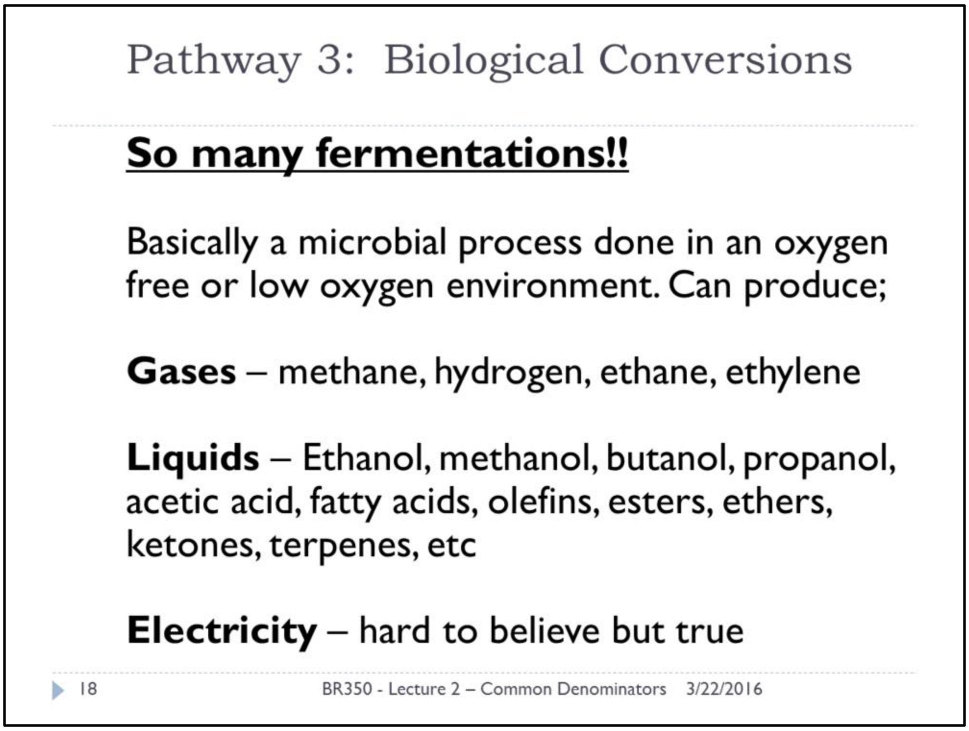
Renewable diesel is produced by any chemical process that removes the oxygen from the natural fat/oil and makes a paraffin or olefin. This is like high tech, super charged vegetable oil hydrogenation.

Hydrogenated vegetable oil has been supporting heart attacks for 50 years at least. Makes great fuel.

Soap is good.

Best available oil source is canola ~ 100 gal/acre on a good year

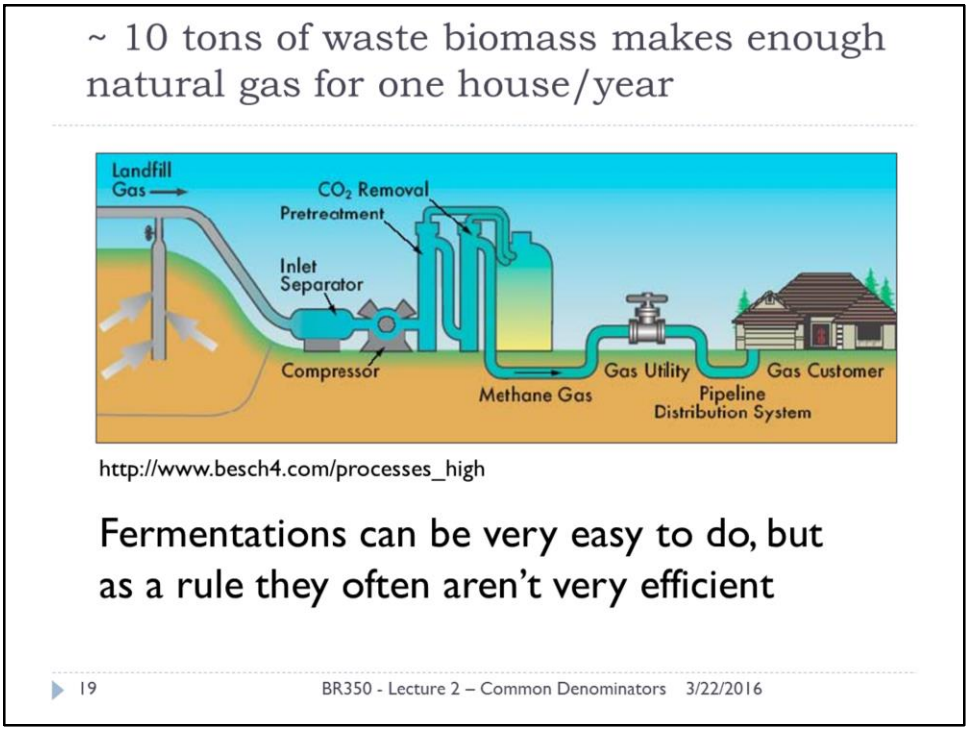
Canola is a great oil plant, but 100 gal/acre doesn't seem like that much unless you are a farmer.



Pathway 4 is biological conversions and it will be split into fermentations, photosynthetic organism and animals.

From the chemical perspective biological conversions are like having an aquarium. It is technically an ecosystem, so you have to consider all the angles and how things will get along. You have to keep everything alive by feeding it and making sure the conditions are correct, and most importantly you have to keep it wet. Living things don’t do dry well, so biological conversions range from wet to completely submerged, like your aquarium, water is a must.

Of the biological conversions available to us, arguably fermentation is used the most for chemicals production. Fermentation is generally the act of feeding microbes in a low O2 environment so that they will start producing things we want. A lot of microbes can live in O2 rich or O2 lean environments, but they produce very different things depending on what they are living in and when its low O2 they start using fermentation pathways. Fermentation can produce a very wide range of products from an ever wider range of microbes.



A very common fermentation is anaerobic digestion like what happens at your local landfill or in your compost pile.

According to the EPA each American generates approximately 1 ton waste/year, depending on how you look at it this is either a tremendous source of gas or an unsustainable situation.

Pathway 3: Biological Conversions

Photosynthetic organisms and animals

Certain microbes, plants, and animals are capable of this. Considerable genetic engineering being done to create more/better options

Algae – oily algae, algae that secrete alcohols and oils
Plants – tapping trees for syrup or oils, oilseed crops
Animals – fat, shellac, tunicates, and insect oils

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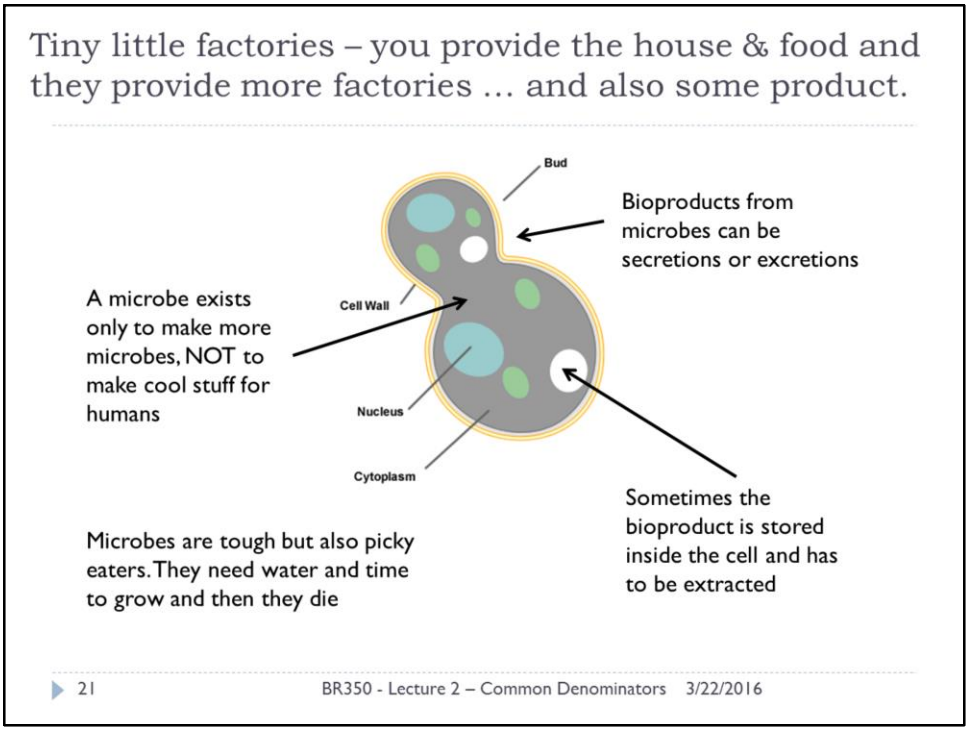
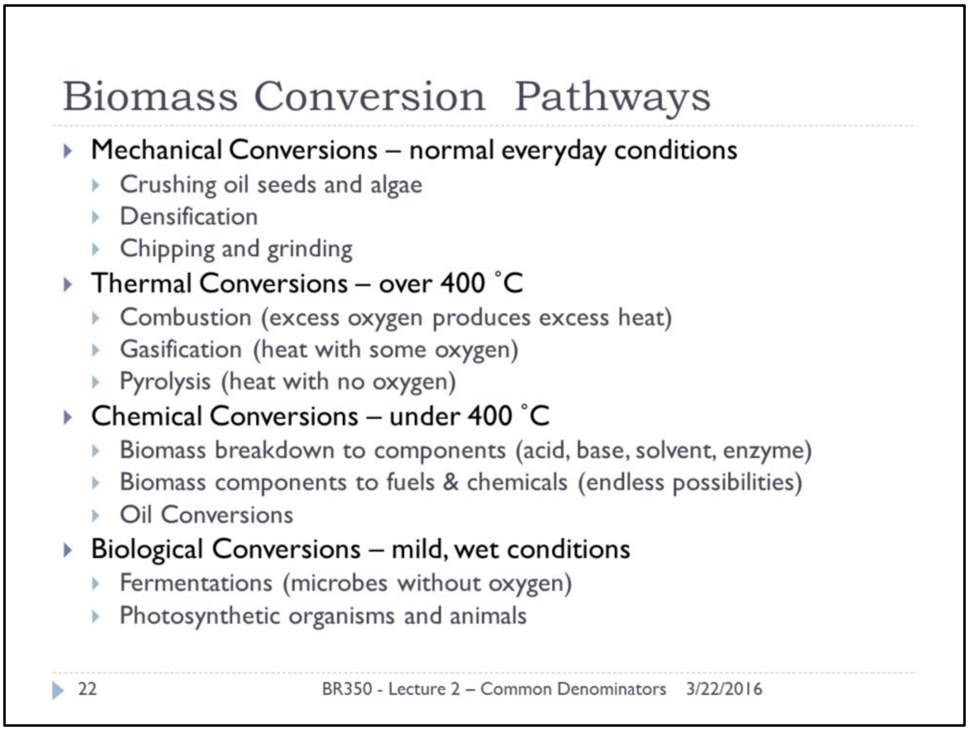
Photosynthetic organisms like algae and plants do not need to be fed sugar or kept in a low O2 environment like fermentation microbes. They produce their own sugars using photosynthesis and they do not really need O2 as much as they need CO2. Photosynthetic organisms can be high tech like algae used for fuels/oil or low tech like canola and peanut plants that are used to produce vegetable oils.

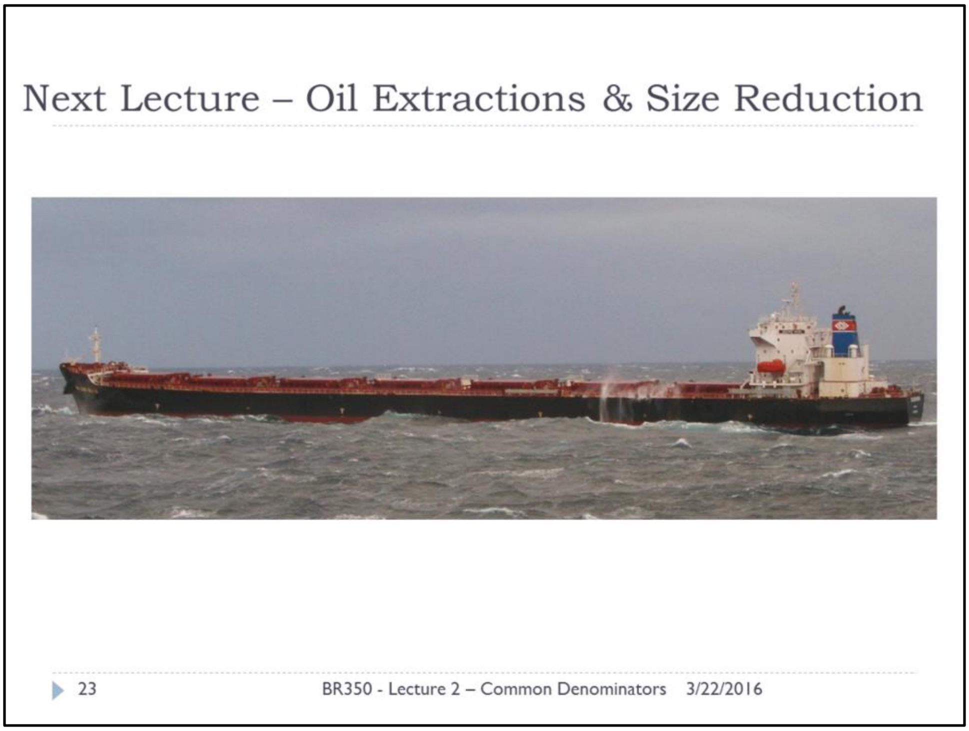
Likewise, animals are their own class because they require O2 and can be fed more complicated forms of biomass that haven’t yet been turned into sugar. Mammals tend to produce oils in the form of fats which are often converted into oils after harvesting. Insects have long been used to produce chemicals and are quickly gaining interest as a source of oils as well. The noble tunicate a funky looking slimy filter feeder found in cold oceans may also become a fascinating new source of cellulose sugars. Like grains, animals are often overlooked in all the bioenergy media and this is unfortunate because they currently play a role and will likely continue to play an increasing role in the biological conversion of biomass into useful chemicals and fuels.



It is imperative that we remember when we use biological conversions that living things do not exist to produce things for us. They can produce things for us if we feed them and provide a healthy environment, but they exist to replicate not to make chemicals. We find chemicals in and around certain living things, but they are by no means an engineered process like chemical and thermal conversions.



Please review.



We always think about petroleum oil spills, but never about vegetable oil spills. Veggie oil can be just as harmful to marine life as petroleum if it is spilled in major quantities. To date there have been very few of these spills. But, it is still worth thinking about. Oil is oil regardless of whether it is from a fossil or vegetable source. When you have a chance please take a look at the attached links that describe a vegetable oil spill scare that happened in AK years ago.

http://gantdaily.com/2010/12/07/alaska-oil-spill-fears-ease-as-freighter-nears-harbor/

http://dec.alaska.gov/spar/perp/response/sum_fy11/101203201/101203201_index.htm