DUALFUEL

Biological Conversions

Lecture 17 – Fermentations

http://www.valtra.com/dual-fuel.aspx
http://www.valtra.com/268.aspx

This week we are moving on from chemical conversions to biological conversions.

When you have a chance please look up the Valtra biogas tractor. This is a fairly recent development and potentially interesting for animal farmers and other types of farmers that have large anaerobe digesters producing biogas. Much like some of the previous considerations about using oil crops to generate oil, to support a farmer's fuel needs, this is a way to use decomposable biomass waste to generate natural gas that can also be used to support a farmer's fuel needs. It isn't just oil crops for biodiesel, or sugar crops for ethanol anymore, now we can also use biomass waste to generate compressed natural gas that can be used in engines. Any bioenergy technology that can support fuel needs in the rural areas where biomass is often grown are worth taking a close look at. Having a tractor that can use a modern engine and be powered by something you produce pretty easily from your waste biomass is a great thing.

Week 7 – Biological Conversions
-Learning Objectives-

- Explain the biological conversion of biomass.
- Identify things in your day to day life that use biological 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 biological conversions, our fourth biomass conversion pathway type.

So Many Fermentations!!

Basically a microbial process done in an oxygen free or low oxygen environment that starts with sugars and ends with chemicals. Can produce;

Gases – methane, hydrogen, ethane, ethylene

Liquids – Ethanol, methanol, butanol, propanol, acetic acid, fatty acids, olefins, esters, ethers, ketones, terpenes, etc.

Electricity – hard to believe but true

Pathway Four is biological conversions and it will be split into fermentations, photosynthetic organisms 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 they will start producing things we want. A lot of microbes can live in O2 rich or O2 lean environments. They produce very different things depending on what they are living in and when it’s low O2 they start using fermentation pathways. Fermentations can produce a very wide range of products from an even wider range of microbes.

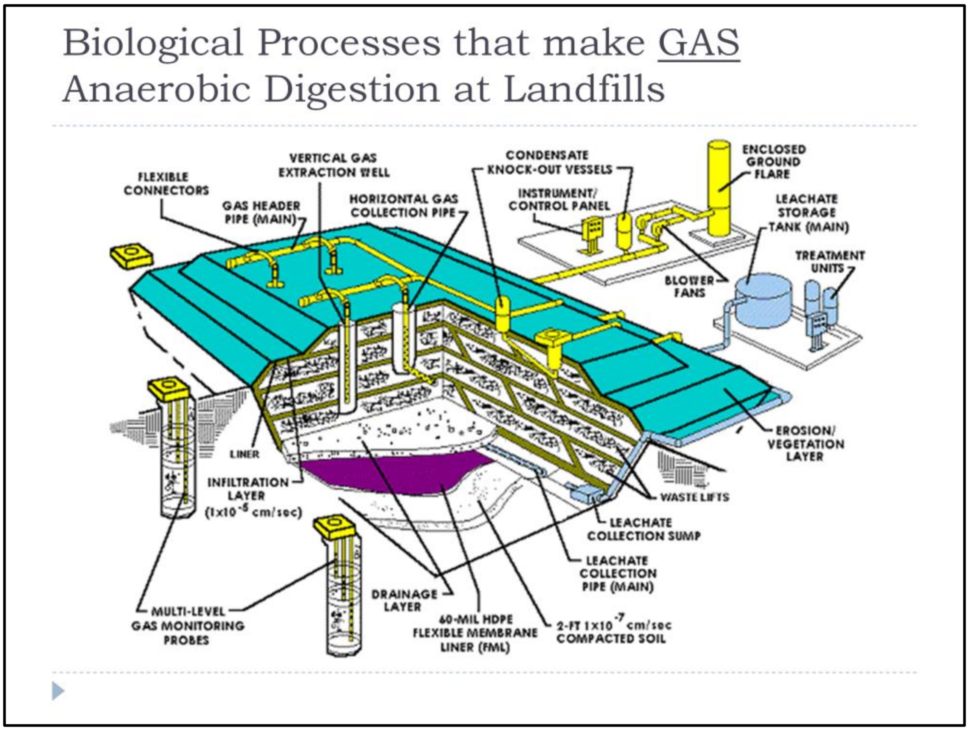
Fermentation is a continuum

1. Free sugars get converted into acids, alcohols, and CO_2 (flexible O_2 conditions)
2. Acids, alcohols, and CO_2 get converted into acetates and acetic acid (low to no O_2 conditions) - acetogens
3. Acetic acid and acetates get converted into methane and CO_2 (no O_2 allowed) - methanogens

It is important that you think about fermentation as a continuum because you may find that a lot of things seem to be fermentations and this can make it clearer. An easy way to think about it is apple juice. When you ferment apple juice microbes eat the easy sugar and make alcohols, acids and tough sugars. If the microbe you used was yeast and you stop here, you have a nice hard cider. If the microbe was something other than yeast and you let it go a little longer, the microbe ecology changes and you become acetogenic. Acetogenic bacteria are very effective at eating everything marginally edible and will consume all the alcohols, acids and tough sugars from the alcohol step. They combine these with CO2 and they generate acetates and acids, largely acetic and propionic. So, the gist of it is, if you let the hard cider ferment a little longer you end up with apple cider vinegar. Now, while we generally stop here from a food perspective, we don't have to, and the final step is methanogenesis.

Methanogens hate O2 and love acetic acid, it is their preferred feedstock. So, if I spike my apple cider vinegar with some aged compost and wait a few days, I will make an anaerobic digester and it will start to produce methane. So think of fermentations as a continuum; easy sugar turns to hard cider, hard cider turns to vinegar, and vinegar turns to methane.

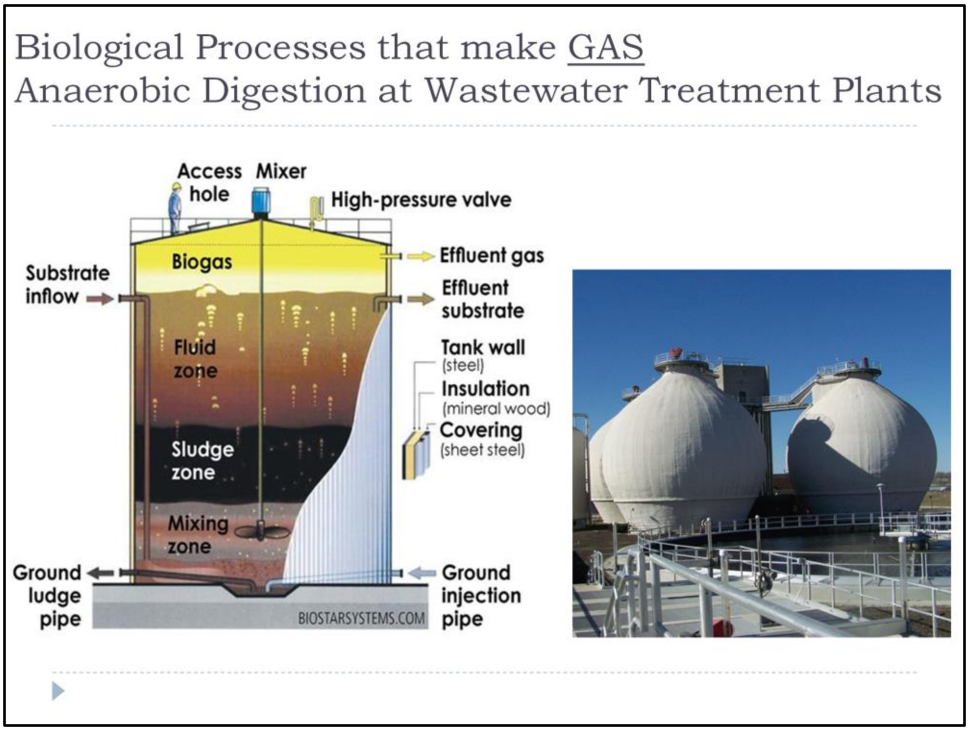
As a side note, the oxygen aspect can be confusing. Fermentation, as a microbial process, does not require O2, but fermentation reactors sometimes utilize O2 to attain the appropriate growth/reaction rates or culture dynamics. This is because different microbes respond to O2 differently, some are tolerant and some are not, and for most the presence of O2 changes what they produce. To be safe, always start thinking about fermentations as an O2 free process that requires sugar to feed the microbes. When you are ready to make things more complex, then its worth considering what happens when some O2 is introduced.



http://www.calrecycle.ca.gov/Archive/IWMBAR/2000/enforcement/

Anaerobic just means without oxygen, and digestion is another way of saying decompose or breakdown. So anaerobic digestion means the O2 free breakdown of biomass and other digestible things. The primary products of anaerobic digestion are CO2 and methane.

This is an elaborate image of a modern landfill. Today's advanced landfills seem less like piles of trash and more like integrated bioreactors for decomposition and the production of methane. The trash is the feedstock and the landfill is engineered to be isolated from the environment as much as possible. Within its walls, there are watering systems to keep things moist, water recycling, a network of tubes and pumps to remove gas, and a wide variety of sensors to help control and optimize the system. Considered from this angle, a modern landfill really is a large bioreactor using microbes to generate biogas. The especially interesting thing is that in many cases this biogas is just wasted instead of captured and used.



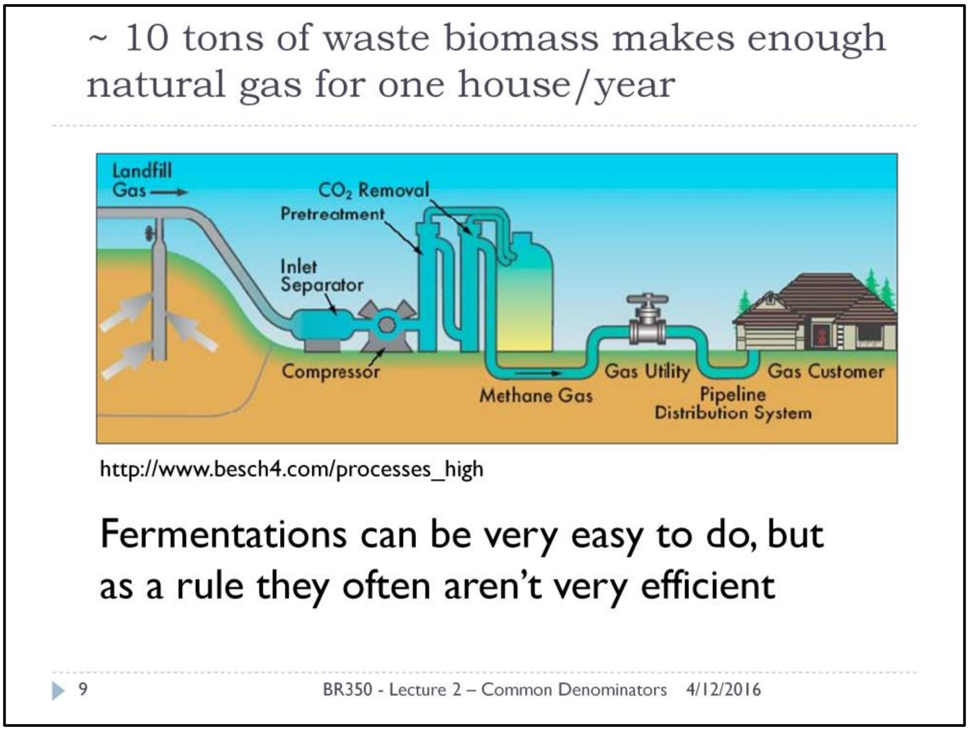
http://www.bizjournals.com/kansascity/print-edition/2011/02/04/biostar-systems-digester-will.html?page=all
https://lincoln.ne.gov/city/pworks/waste/wstwater/treat/

The anaerobic digestion (AD) that happens at a wastewater treatment plant (WWTP) is more involved than what happens at a landfill. Anytime you drive by a WWTP and see big white balls or tanks with dome tops, you are probably looking at an AD. Using AD at WWTP has become almost standard practice if they are large enough. They decrease the level of solid waste or sludge that is generated by converting a portion of it into biogas which is composed primarily of CO2 and methane. This biogas can be used to generate steam or electricity depending on the WWTP's needs. However, much like landfill gas it is often just flared to dispose of it.

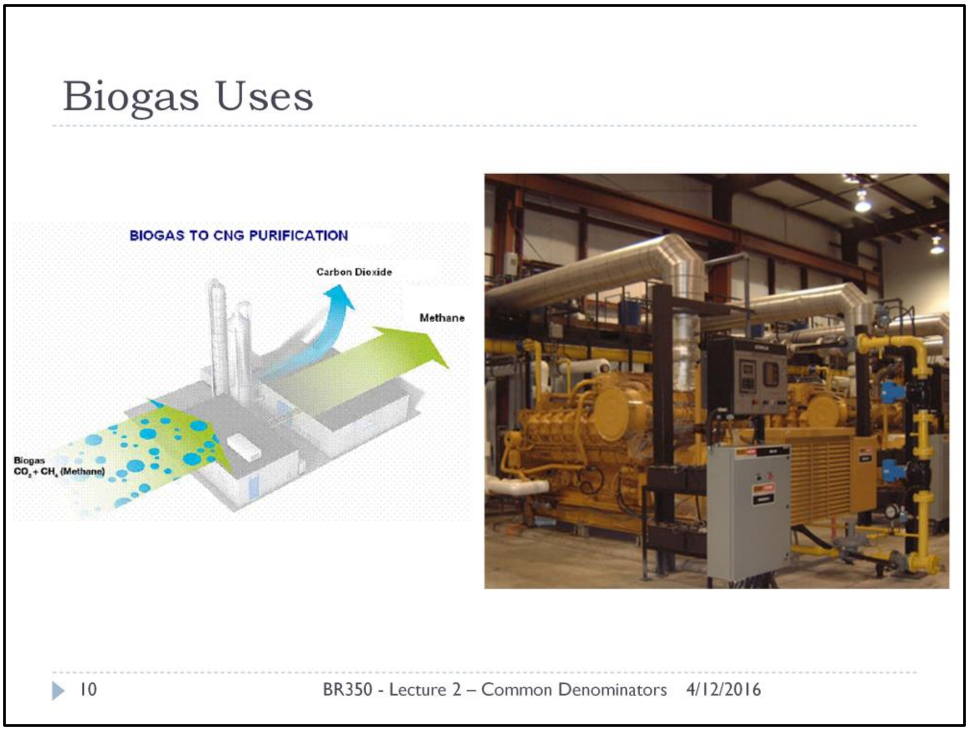
Biological Processes that make GAS
Anaerobic Digestion at Dairies and Hog Farms

http://extension.missouri.edu/p/EQ389

Animal farms generate a lot of waste in the form of manure. They fill huge ponds and tanks with manure and then they have to figure out what top do with it. Some gets applied to fields as fertilizer, but generally that only gets rid of a small portion, so the rest has to be converted into something more stable and less toxic. This can be done with an AD, just like what is done at a WWTP. Just like at a WWTP, when this is done it generates biogas. This is why a biogas tractor is so interesting – with more farm needs for biogas it is possible that less biogas will have to be flared and wasted and instead could be used to support the farm.

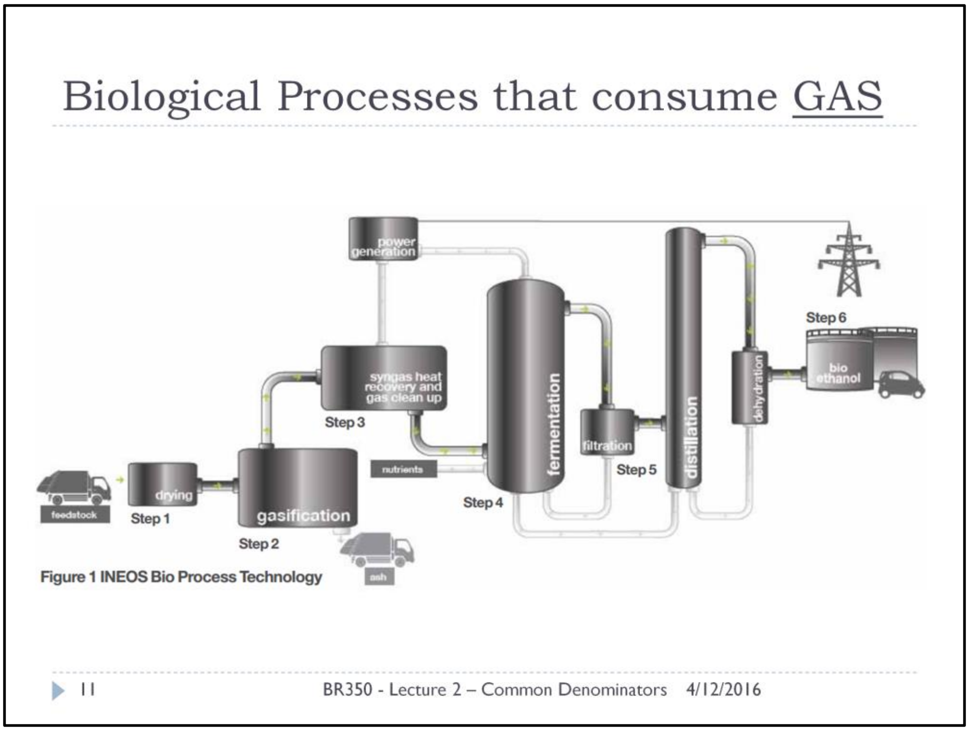


According to the EPA, each American generates approximately 1 ton waste/year and depending on how you look at it this is either a tremendous source of gas or an unsustainable situation. If it takes 10 tons of waste to support one household then either than household needs to have 10 people in it generating 1 ton/year or it needs to be collecting the trash from the neighbors. It's still worth thinking about because 1 ton/year is no joke, but AD it probably wouldn't completely replace the need for natural gas by itself, it would take additional sources of energy as well.



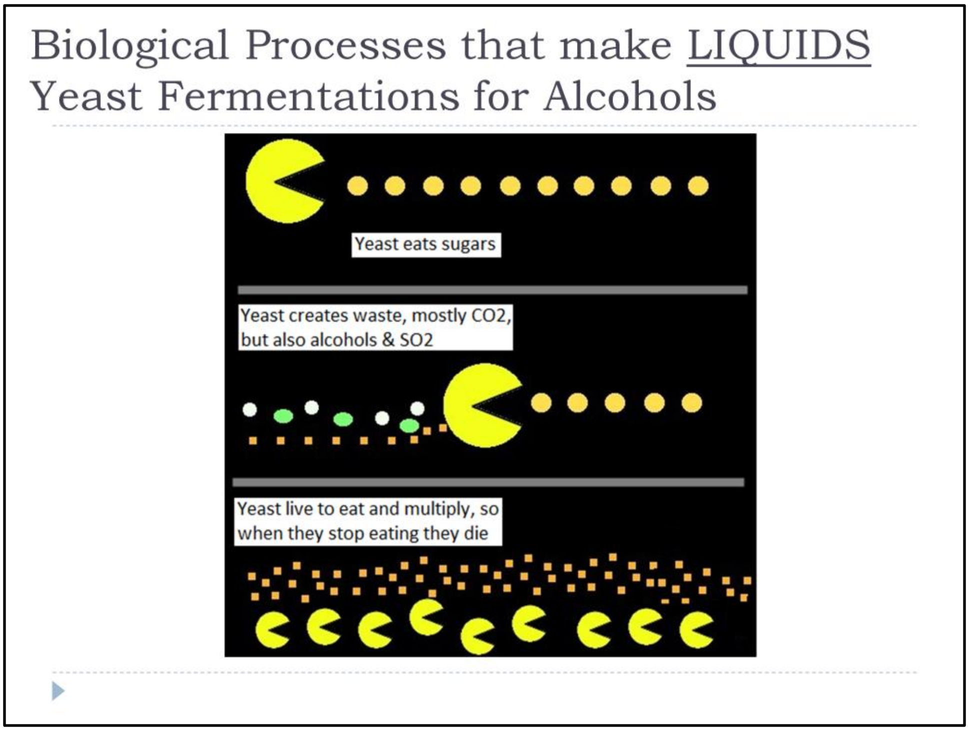
http://sprebiogas.com/bio_cng.htm
http://www.global-greenhouse-warming.com/landfill-gas.html

An exciting new trend for biogas is upgrading it to compressed natural gas. All that is required for this is removal of the water and CO2 which leaves pretty huge quality methane. This methane can then be compressed and used for heating, power or even vehicles. As gas separation and purification technologies continue to improve, bio-natural gas is expected to play a larger role in our natural gas infrastructure.



http://www.ineos.com/businesses/ineos-bio/technology/
http://www.kiverdi.com/home.htm

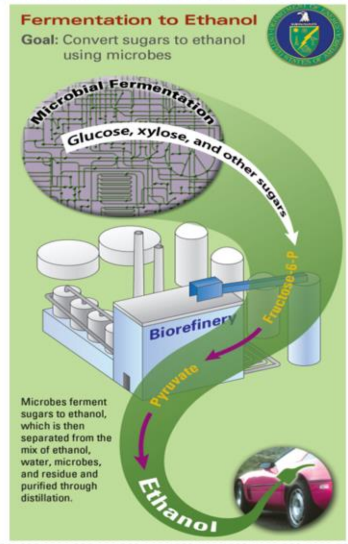
We just looked at several different ways that microbes are used by society to generate gas products, but equally exciting are some of the microbes that are being used to consume gas products. The first commercial cellulosic ethanol plant in the world is actually based on syngas fermentation. The syngas is produced from biomass waste and then it is fed to special microbes that consumes the syngas and excretes ethanol. Syngas fermentations have been studied heavily in the U.S. since the early 80’s an it is exciting that this technology was utilized in the first cellulosic ethanol facility. The company that built it is INEOS bio and the plant is located in Florida. It is worth looking up if you have a chance.



http://www.brewersfriend.com/2010/09/25/pacman-yeast-eureka/

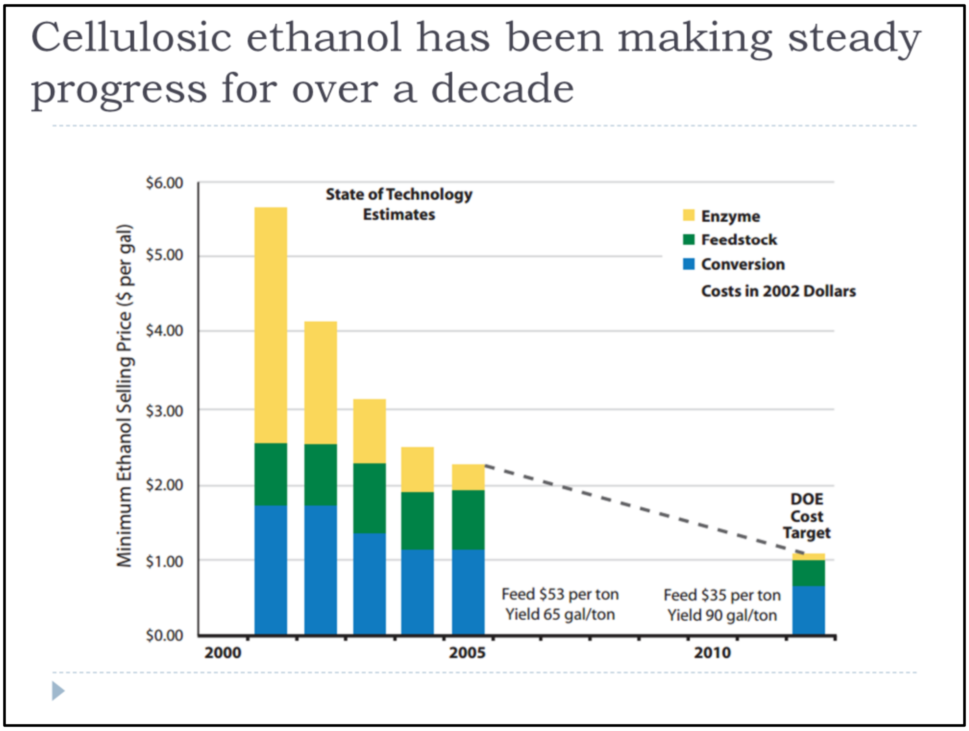
Now we'll move away from fermentation gas products and talk about fermentation liquid products. In general, the Pacman image here does a pretty good job. The yeast is Pacman and the sugars are those little orange balls. The yeast eats the sugars and as it eats them is generates wastes and one of those wastes is ethanol. Technically, most of the carbon the yeast eats become CO_2 and more yeast, but a portion also turns into ethanol which is good because that is what we want. When there are too many yeast and not enough food, the conditions collapse and the yeast die. They don't live very long, so fairly soon after it is no longer reasonable for them to reproduce, they stop living.

Cellulosic ethanol uses a normal glucose fermentation – yay for yeast!



http://genomicscience.energy.gov/biofuels/placemat.html

Yeast have played a big role in human history – bread, beer and wine are part of a lot of stories. Traditional cellulosic ethanol also uses yeast, just like the yeast you could use for bread and beer. Cellulosic ethanol yeast are often more specialized than that, but those common yeasts available to all of us at the grocery store would still work at some level. The hardest part about cellulosic ethanol isn't making the microbe make ethanol, its figuring out how to turn the cellulosic biomass into sugars that you can feed the microbe. Economically turning the cellulose in sugars a microbe wants to eat has taken more than a decade of hard work by thousands and thousands of people.

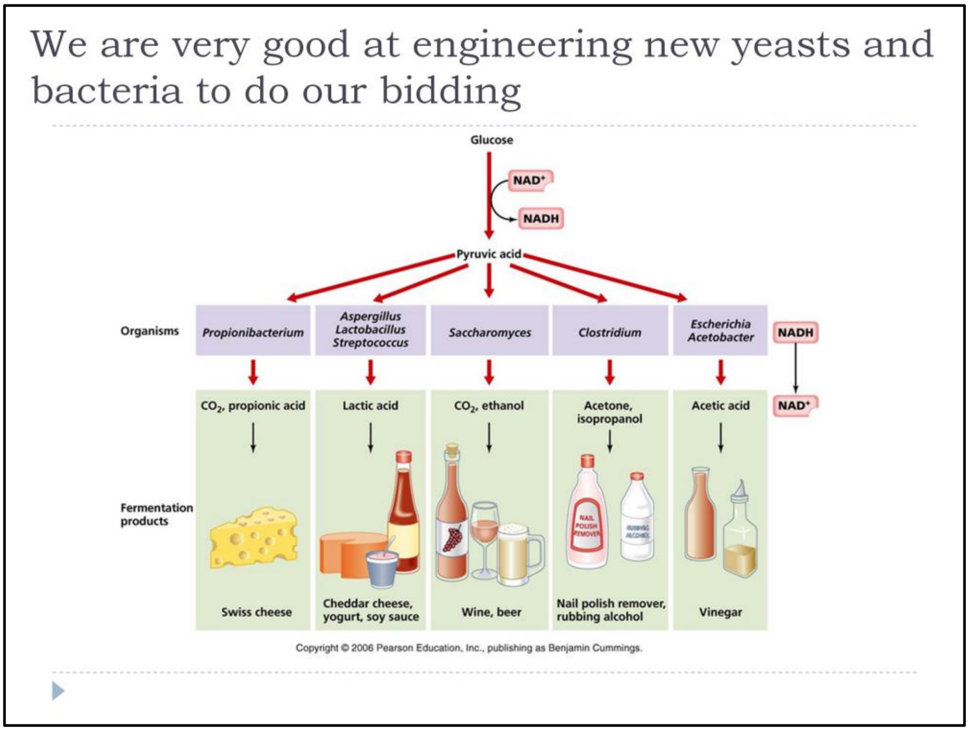


http://www.nrel.gov/biomass/pdfs/40742.pdf

Cellulosic ethanol is finally here! There are two official commercial plants; INEOS in Florida – July 2013 and Beta Renewables in Italy – Oct 2013.

Two more plants are supposed to be open and functional this coming fall, the POET plant and the Abengoa plant, both located in the Midwest.

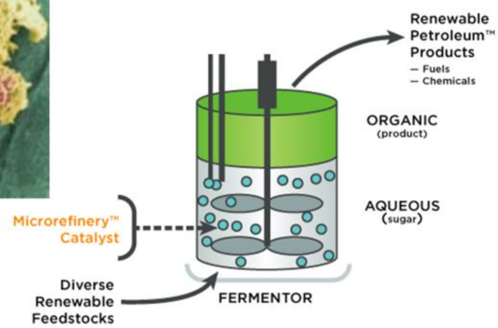
There is a joke that cellulosic ethanol has been five years away for 20 years, but its not longer a joke, and that is exciting. Enzyme costs have plummeted and operations have become more efficient and now it is economic to do what was once just a neat idea. It will be interesting to see what other bioenergy developments occur because of this paradigm change.



Read slide

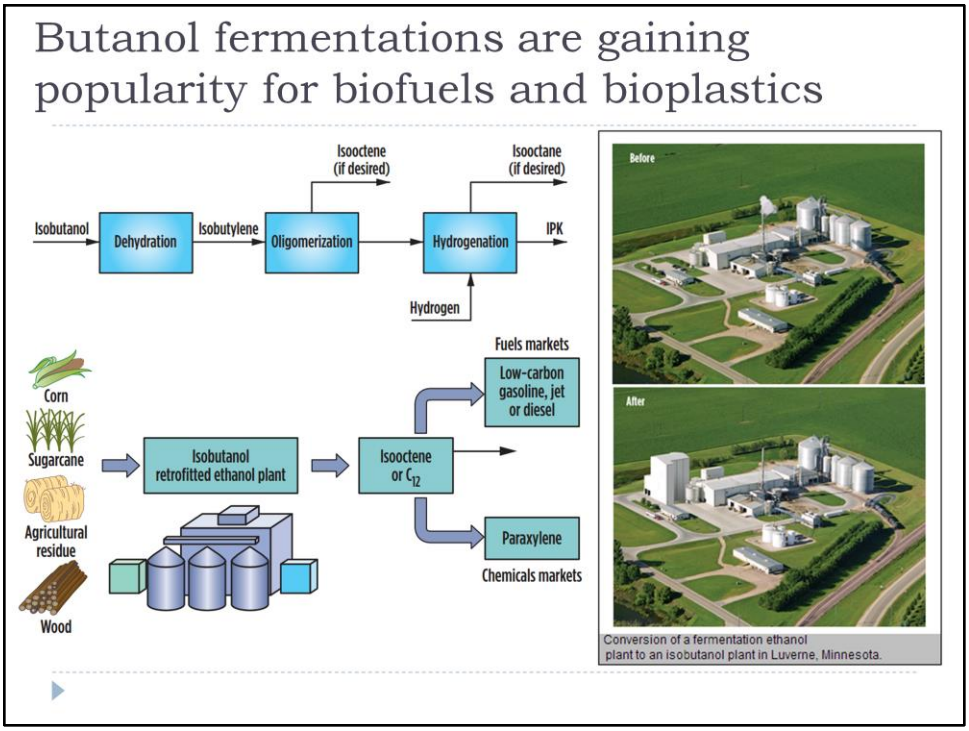
Many of the delicious foods in the grocery store today are based on biological conversions. Cheese, yogurt, soy sauce, pepperoni, salami, wine, beer and vinegar are a few of the more well known products, but there are many more. The production of these products is big business, so there is a large market for improved microbes and bioreactors that make more, faster and cheaper. The industrial microbiology field is constantly advancing and growing

Most of the bioenergy community uses yeast, but bacteria are getting better and better



LS9 http://www.ls9.com/

So far we have talked primarily about yeast which are a fungus. However, in addition to yeast there are some big developments happening with bacteria. A lot of the foods described in the previous slide are bacterial and while yeast are very useful, they are also somewhat limiting compared to bacteria. Bacteria grow faster and have the potential to produce a much wider suite of products than yeast. They also eat more things and live in a wider range of conditions. As a result bacterial conversions are becoming more and more popular of bioenergy. A good example of this is a company called LS9. It has engineered E. coli bacteria that produce long chain fatty acids. They were founded in 2005, have been able to secure 10's of millions in investment, and are working hard to develop other E. coli strains for various fuels and chemicals.

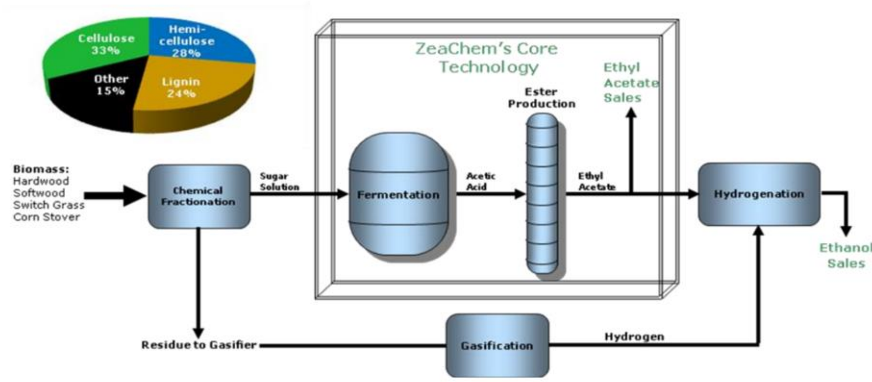


http://www.hydrocarbonprocessing.com/Article/3081332/Bio-isobutanol-The-next-generation-biofuel.html

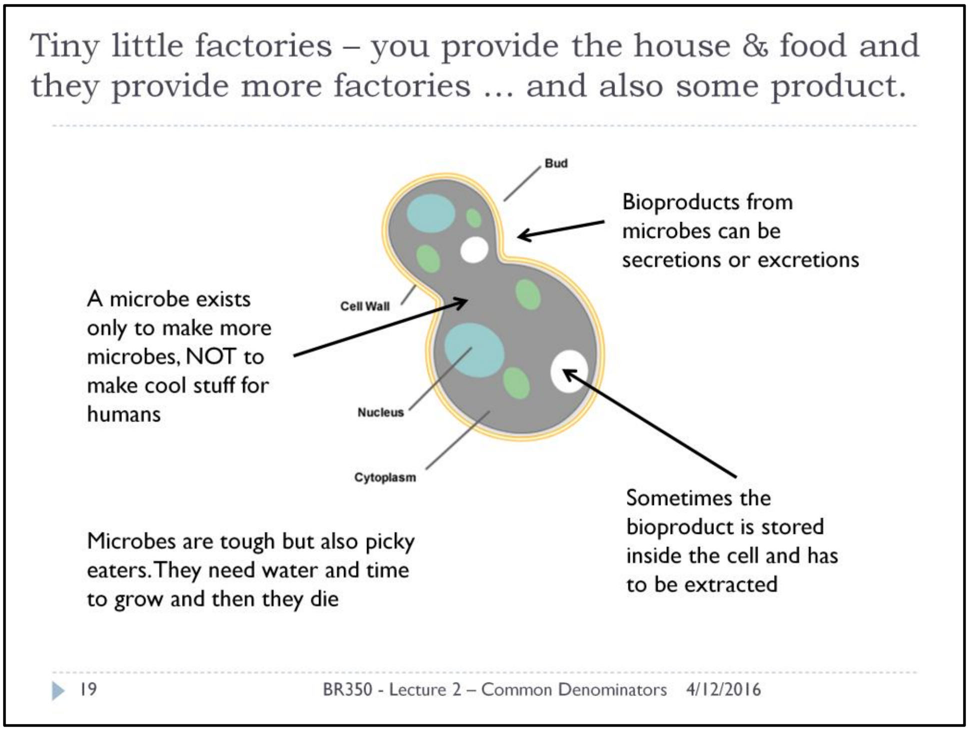
Bio butanol has been a fast moving bioenergy area for about 10 years now. It uses a bacteria called clostridium instead of a yeast, but otherwise uses pretty much all the same processes as a corn ethanol facility. The great thing about butanol is that it is quite a bit more valuable than ethanol and it can technically be used as a drop in gasoline substitute. However, its worth more as a chemical than a fuel, so its role as a biofuel might not be as clear as some think. The fact that butanol technology can take advantage of 90% of the equipment at a corn ethanol facility is a huge deal. If the market for ethanol gets soft and these facilities close down, it is very possible they could become economic again by generating butanol instead of ethanol. The future for butanol seems fairly robust

Cellulosic acetic acid fermentations show tremendous commercial promise

- No CO2 waste products, instead of CO2 and alcohols, you get only acetic acid.
- Can use both cellulose (glucose) and hemicellulose (xylose)

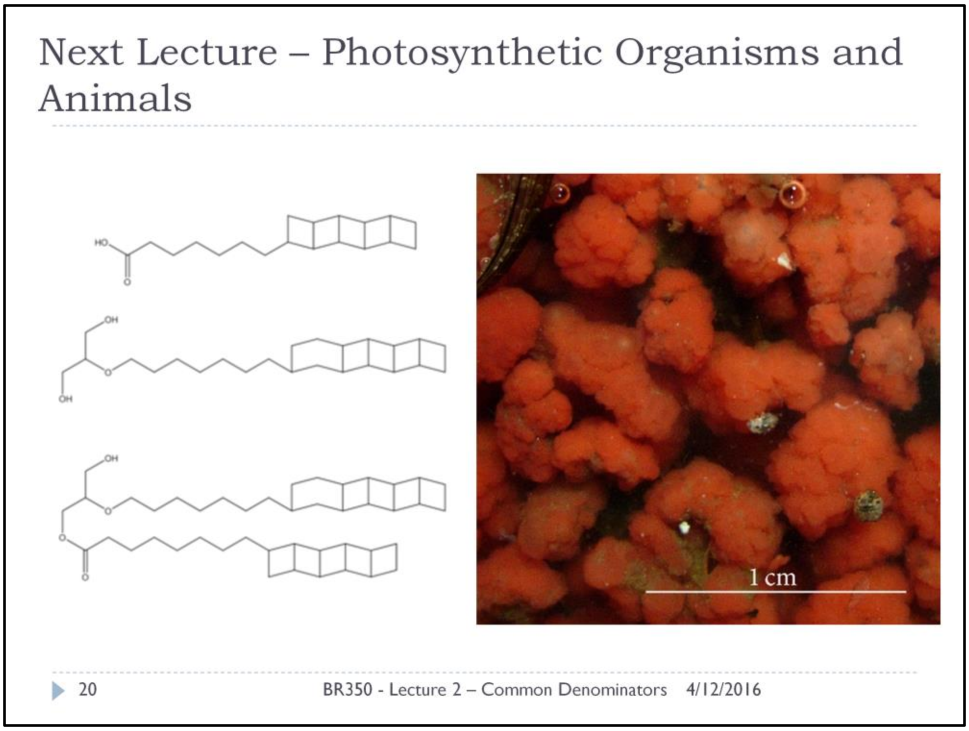


Another fascinating microbial development is the use of acetogens, the bacteria that make the vinegar. The acetic acid in vinegar is what gives it that bite. So, if you are making vinegar you are making acetic acid. The first neat thing about acetogens is that they are willing to eat a much wider variety of things than a yeast, so you don't have to throw away so much biomass. The second neat thing is they don't generate CO2 like yeast and methanogens. They convert more of the sugar into desired products than either yeasts or methanogens. Companies like Zeachem that are using clever, underappreciated aspects of fermentation have a lot to gain from the efficiencies offered by acetoigenic processes. This will be an area to watch closely in the future.



Microbes are ….

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.



http://biotechind2.altervista.org/lezioni/anammox/research.html
http://news.sciencemag.org/2002/10/toxin-eating-bugs-reveal-their-secret

When you have a chance please visit some of the attached links and learn about anammox bacteria and the super neat molecule ladderane.

Ladderanes (or their derivatives) hold potential as a novel next-generation biofuel and for material science applications. These highly energetic molecules, with a carbon backbone consisting of linear cyclobutane rings are part of special membranes in anammox bacteria. Fuels and energetic materials made out of ladderanes would have outstanding performance, so figuring out how to get bacteria to produce this chemical for us is an area of intense interest for many. This is a perfect example of a chemical that is much easier for us to get from a microbe than to try and make ourselves in the lab.