

Thermal Conversions

Lecture 12 – Combustion & Gasification

This micro lecture is on combustion and gasification.

When you have an opportunity please visit attached link for turbine biofuel and watch their YouTube video as well. This is a fascinating spin on thermal conversions because instead of worrying about extractions on an oil rich algae, they just use the entire algal cell as fuel. It turns out that dried algae powder has the right density and size to be aerosolized and then fed into a turbine as a fuel vapor. The oil content provides a high BTU value and the algal cell wall just adds to it. They are currently continuing trials to see if algal powder might someday be able to fuel commercial airplanes. This is a very clever thermal application for algal.

<http://www.turbinebiofuel.com/index.html>

<https://www.youtube.com/watch?v=w5pTHj-oRVY>

Week 5 – Thermal Conversions

-Learning Objectives-

- ▶ Explain the thermal conversion of biomass.

- ▶ Identify things in your day to day life that use thermal 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 thermal conversions, our second biomass conversion pathway type.

Thermal Conversion Products

- ▶ Pyrolysis Oil (bio-oil), Pyrolysis Gas (pygas, pyrogas)
- ▶ Torrefied wood (biocoal), Charcoal (biochar)
- ▶ Producer Gas & Town Gas (pyrolysis gas + syngas)
- ▶ Syngas



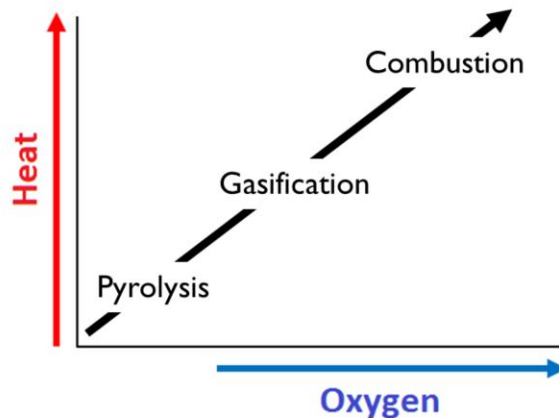
▶ 4

BR405 - Lecture I - Overview 3/22/2016

There are many different types of thermal conversion products. Thermal conversions can be used to produce solid, liquid, and gaseous products and a wide variety of each type depending on reaction conditions. Unfortunately, it can also be a very confusing field because a lot of the same products have different names that would lead you to believe they are not even related. Some of the names of common products are shared here and as you learn more about thermal conversions you will better understand what they are.

Thermal Conversion of Biomass **DEPENDS ON HEAT AND OXYGEN**

- ▶ Must think about thermal conversions based on heat and oxygen use



I am going to repeat myself here because this is important. 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, just 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 into 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 then in combustion the most heat is generated.

Thermal Conversion of Biomass

~ **DEFINED BY THE DESIRED PRODUCT**

Pyrolysis makes
Liquids & Solids



Gasification
makes Gas



Combustion
makes Heat



The type of thermal conversion is defined by the desired product. If you want heat, you want to use combustion. If you want gas you probably want gasification. If you want liquids and solids, pyrolysis is most ideal. None of the conversions is really good at making things other than its primary product, so it makes the most sense to figure out what the desirable product is and then find the appropriate process.

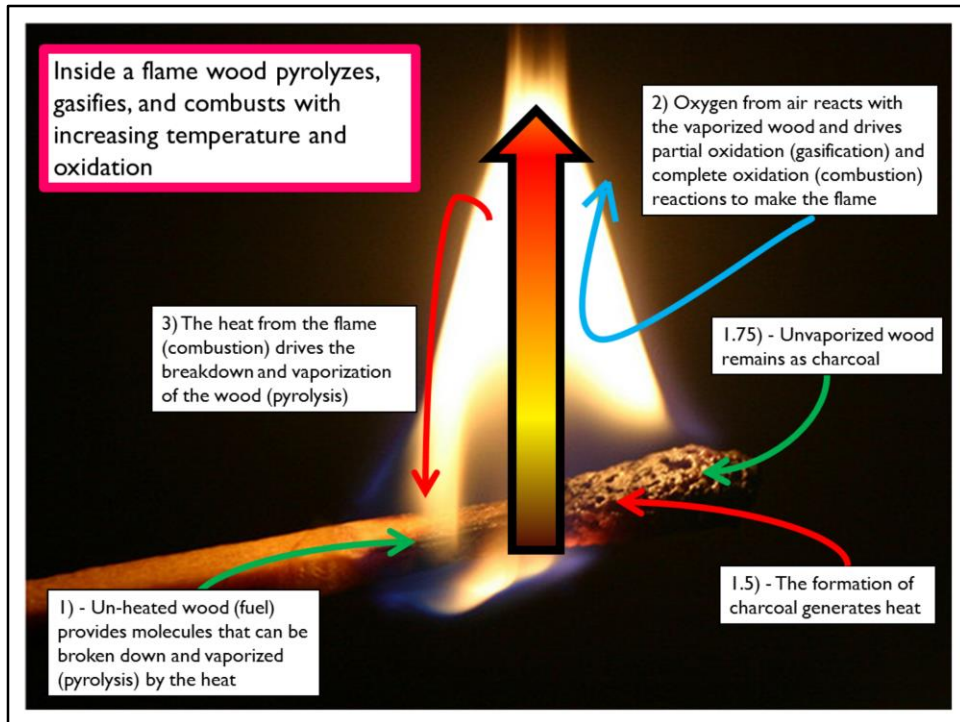
Thermal Conversions of Biomass **DO NOT OCCUR IN ISOLATION**

- ▶ All 3 occur at some level every time you cook food or start a fire








Thermal conversion of biomass.

It is almost impossible to separate biomass pyrolysis, gasification and combustion entirely. All thermal conversions are optimized for a type of thermal conversion based on a desired product, but that only means that of the various products, the primary product is produced the most. It never means it is the only product. Remember, thermal conversions are a hammer and their products are often a little chemically messy.



So back to the match. Inside the match flame, wood pyrolysis, gasifies and combusts with increasing temperature and oxidation. It cycles much the way it is shown in the figure. It costs energy (heat) to break wood down into a gas through pyrolysis, but as soon as O_2 is reacted with the gas, enough heat is generated from the formation of CO_2 and H_2O to continue vaporizing the wood. So, the cycle continues and the match burns through its wood until it is all gone and the match goes out.

Important Definitions

- ▶ O_2 is Oxygen 
- ▶ CO_2 is Carbon Dioxide 
- ▶ H_2O is Water 
- ▶ CO is Carbon Monoxide 
- ▶ H_2 is Hydrogen 
- ▶ CH_4 is Methane (natural gas)
- ▶ E_a is Activation Energy

To do thermal conversions justice we have to do a little more chemistry type stuff. In order to make the diagrams and slides clear we need to review what the chemical notation and molecular models mean. Please take a moment to read through this list and get acquainted with these very important chemicals and notation.

Combustion Can Explain a Lot



- ▶ Breaking bonds **requires** heat
- ▶ Forming bonds **generates** heat

- ▶ CO₂ and H₂O formation **generates** lots of heat
- ▶ CO and H₂ formation **generates** less heat
- ▶ CO₂ and H₂O breakage **require** heat

- ▶ Pyrolysis **requires** lots of heat
- ▶ Gasification is partial oxidation, **generates** some heat
- ▶ Combustion is complete oxidation, **generates** lots of heat

Thinking about combustion can explain pretty much every thermal conversion. We will use the equation shown above to bracket all three types of thermal conversion and show how they relate and how they are different in terms of chemical bonds, chemical products, and heat production.

Pyrolysis is Heating with Little to No O₂

Carbon (Biomass) + ~~X~~₂ + E_a = Bio-oil & Biochar

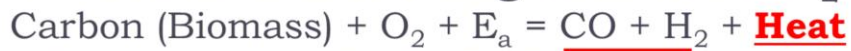
- ▶ Breaking bonds **requires** heat
- ▶ Forming bonds **generates** heat

- ▶ CO₂ and H₂O formation **generates** lots of heat
- ▶ CO and H₂ formation **generates** less heat
- ▶ CO₂ and H₂O breakage **require** heat

- ▶ Pyrolysis **requires** lots of heat
- ▶ Gasification is partial oxidation, **generates** some heat
- ▶ Combustion is complete oxidation, **generates** lots of heat

Pyrolysis is heating with little to no O₂. You still have E_a, but you don't get O₂, so pyrolysis doesn't get the benefit of forming oxygen bonds to make heat like the other conversions. Instead, pyrolysis is all about breaking bonds, so overall pyrolysis requires lots of heat and does not generate it in excess.

Gasification is Heating with Some O₂



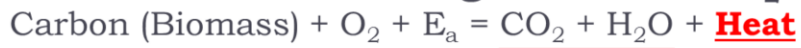
- ▶ Breaking bonds **requires** heat
- ▶ Forming bonds **generates** heat

- ▶ CO₂ and H₂O formation **generates** lots of heat
- ▶ CO and H₂ formation **generates** less heat
- ▶ CO₂ and H₂O breakage **require** heat

- ▶ Pyrolysis **requires** lots of heat
- ▶ Gasification is partial oxidation, **generates** some heat
- ▶ Combustion is complete oxidation, **generates** lots of heat

Gasification is heating with O₂, but not enough O₂ to make CO₂ and H₂O. Instead gasification forms CO and H₂. Therefore it gets some of the heat benefit of the bond formation, but not much. Gasification certainly generates more heat than pyrolysis and in fact can generate quite a bit of heat if properly controlled, but not enough heat to be a self sustaining reaction like combustion. Gasification is right in the middle between pyrolysis and combustion.

Combustion is Heating and Excess O₂



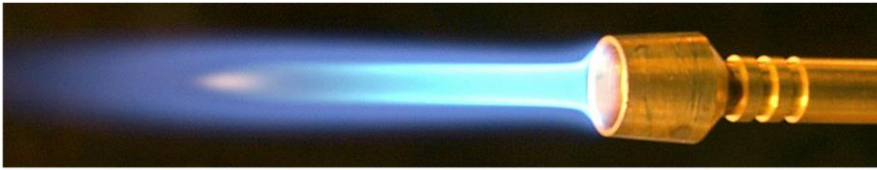
- ▶ Breaking bonds **requires** heat
- ▶ Forming bonds **generates** heat
- ▶ CO₂ and H₂O formation **generates** lots of heat
- ▶ CO and H₂ formation **generates** less heat
- ▶ CO₂ and H₂O breakage **require** heat
- ▶ Pyrolysis **requires** lots of heat
- ▶ Gasification is partial oxidation, **generates** some heat
- ▶ Combustion is complete oxidation, **generates** lots of heat

Combustion is heating with enough O₂ to get maximum bond formation from the production of CO₂ and H₂O. This generates by far the most heat and enough heat in fact to be a self sustaining reaction as long as fuel is provided – just like the match.

Combustion – primarily for the production of heat (and light)

- ▶ Campfires, gas stoves, matches, lamps, etc
- ▶ Gas turbine and Coal/steam turbine power plants
- ▶ Hot air, hot water, steam, hot oil, etc

All of us have probably started a fire and initiated combustion at some point in our lives

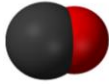


Humans use combustion primarily for heat and light. This includes ... read slides

If you really want to get crazy, look into why light is formed from a flame and how the colors change when combusting different things. Another good puzzle is where the heat comes from. An increasing number of researchers believe like Einstein that chemical reactions are capable of converting mass to energy at a very low level and that is why they generate heat. The opposing camp says that this is impossible and has no explanation for the heat. It is a debate that will likely continue until we have the technology to prove otherwise.

Combustion Products are from “Complete Oxidation”

CO



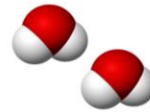
H₂



CO₂



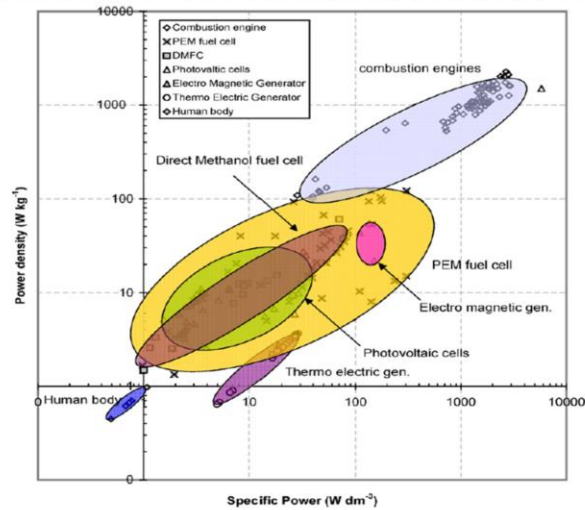
H₂O



- CO₂ and H₂O are the primary products, but CO and H₂ are also generated along with some pyrolysis vapors.
- The production of heat and light are linked. The level of light is directly related to the level of energy that is released during combustion

In general it is important that you remember that combustion products happen because of complete oxidation. That means they are primarily CO₂ and H₂O instead of CO and H₂. It is also important to consider what is being burned. If it is carbon based these will almost always be the products, but if it is not carbon based then there can be a variety of other oxidation products like Sulfur oxides, nitrogen oxides, and chlorides.

At the moment “*Combustion is King*” for energy production on earth



S.F.J. Flipsen / Journal of Power Sources 162 (2006) 927–934

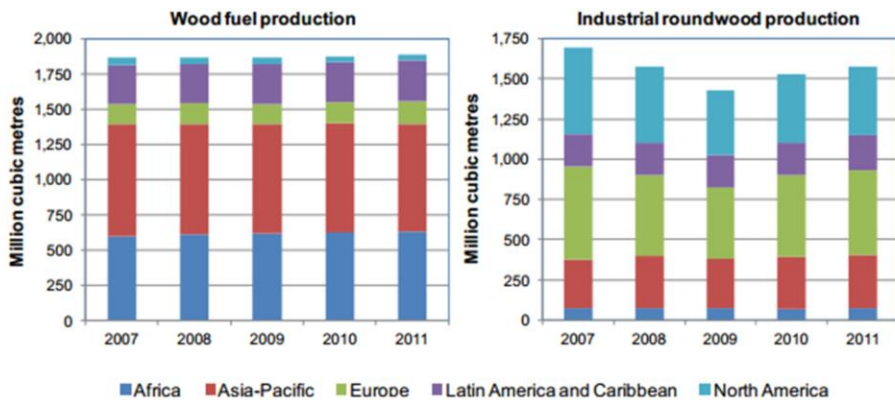
▶ 16

BR350 - Lecture 2 – Common Denominators

3/22/2016

I am going to repeat myself again because this figure makes a very important statement about combustion. Despite its age and simplicity, combustion is an ideal energy production reaction on earth. Without question the most widespread conversion from an energy perspective is combustion. We live on a planet full of oxygen and combustion is king when it comes to making energy.

Combustion is the greatest use of wood in the world



▶ 17

BR350 - Lecture 2 – Common Denominators 3/22/2016

FAO 2011 Global Forest Products Facts and Figures

Nearly 60% of all the wood produced in the world was used for fuel in 2012. 60% is an awful lot of wood and its hard to believe here in NA since we burn so much fossil fuel. However, in a lot of the world wood is the only available carbon source and it is vital for cooking food and providing warmth.

http://www.fao.org/fileadmin/user_upload/newsroom/docs/2011%20GFP%20Facts%20and%20Figures.pdf

Gasification – primarily to make gas products (syngas, producer gas, etc)

- ▶ Fixed Bed
- ▶ Moving Bed
- ▶ Air, Oxygen or Steam driven

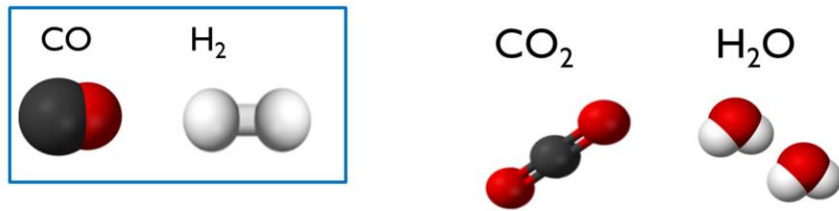
Gasification happens in a meat smoker and when you throw water on a fire



Gasification is primarily used to produce gas, particularly a type of gas known as syngas.

This can be done using a variety of different type of reactor configurations know as fixed bed or moving bed. The process can also be air blown, oxygen blown or steam blown. Believe-it-or-not, but when you have a campfire and you throw water on it suddenly you generate quite a bit of hydrogen because for a moment before the fire goes out you are primarily gasifying instead of combusting. Gasification also happens in a meat smoker as you try to find a balance between the pyrolysis that makes the meat taste good and the gasification that keeps the fire going.

Gasification Products are from “Partial Oxidation”



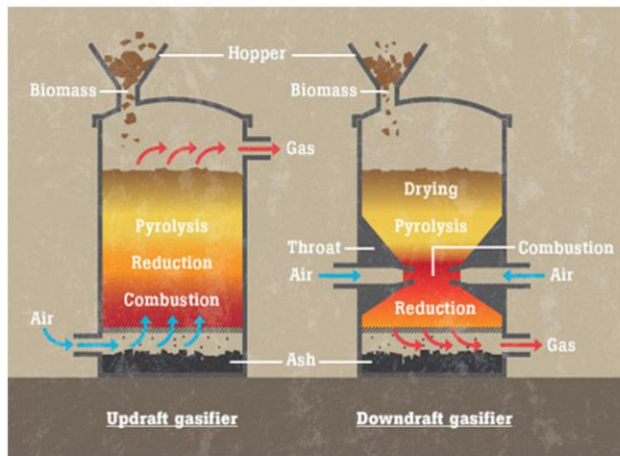
- Synthesis gas (syngas), town gas, water gas, producer gas, coal gas, illumination gas, etc
- These gas products are defined by having high levels of CO and H₂, but they all contain different levels of pyrolysis vapors
- **Syngas is strictly defined as only CO, H₂, CO₂, and H₂O**

These are the products of gasification, under ideal gasification conditions, only partial oxidation products would be formed so no CO₂ or H₂O would be formed (complete oxidation products) just CO and H₂.

Syngas is primarily used for catalysis. It can also be used in turbines for electricity, but its most common use is currently for catalysis and the production of other chemicals like methanol, dimethyl ether, acetone, formaldehyde and paraffin. The most important components of syngas for making chemicals are carbon monoxide and hydrogen.

If you recall from the history lectures, Syngas was used for home heating/cooking before natural gas as late as the 1950's. Humans have been using syngas since the 1800's.

Fixed Bed Gasification



- 1) Notice where air can enter
- 2) Notice where product gas exits

Nexterra – <http://www.nexterra.ca/>

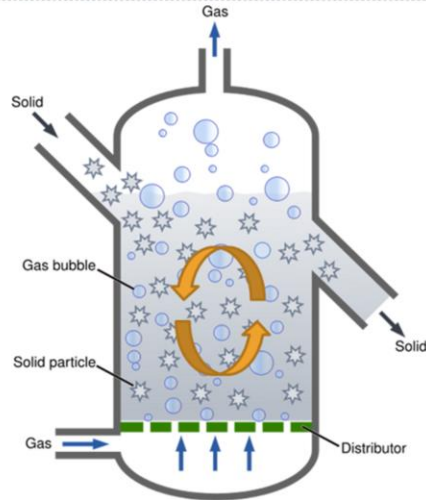
This is an example of the two most common types of fixed bed gasification.

If the reaction is done by bottom up conversion it is updraft. If the reaction is done by top down conversion it is downdraft. Updraft can convert wet fuel but makes low quality gas. Downdraft needs drier fuel and makes better quality gas. Downdraft make a product high in syngas, updraft makes a product high in pyrolysis vapors.

The choice of gasifier design needs to be made based on the available biomass and the desired product. There are types of fixed beds other than updraft and downdraft, but they are by far the most common, largely due to their simplicity.

Moving Bed Gasification

- ▶ Can be fluidized beds, entrained flow, vortex beds
- ▶ This technology allows South Africa to produce all of its fuels from coal

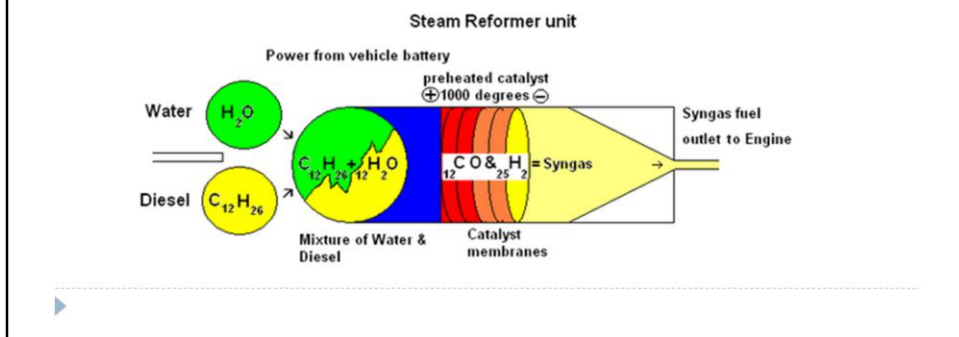


TRI – <http://www.tri-inc.net>

This is an illustration of fluidized bed gasification. Moving the biomass and the bed during the conversion supports much greater conversion efficiencies of biomass to gas (85-95% carbon conversion). Fluidized beds are much more complex and expensive than fixed beds, but their efficiency is higher, the quality of the gas is better, and they can be scaled up much larger than a fixed bed is capable of. So, like all other bioenergy technologies there are tradeoffs depending on the size and type of the biomass resource and the amount and type of product that needs to be generated.

If you could get the campfire hot enough you could spray water on it instead of blow air

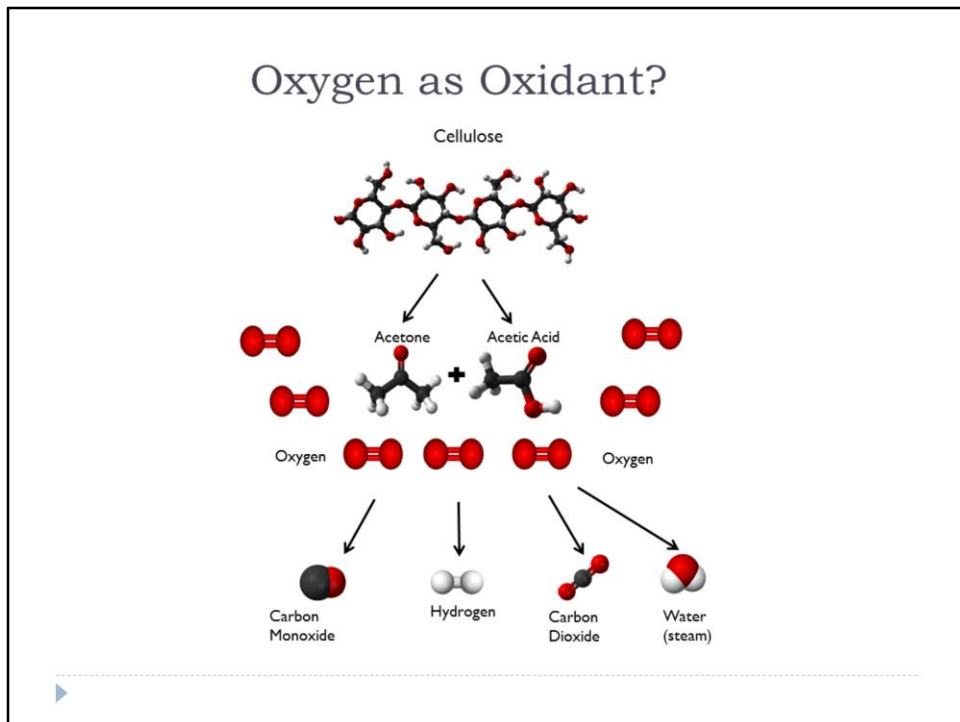
- 1) Burning biomass is commonly done with air to supply oxygen as an “oxidant”
- 2) Air is not the only source of oxygen; water (H_2O) and carbon dioxide (CO_2) can both be used to burn biomass



So, back to the campfire. If you ,,,,

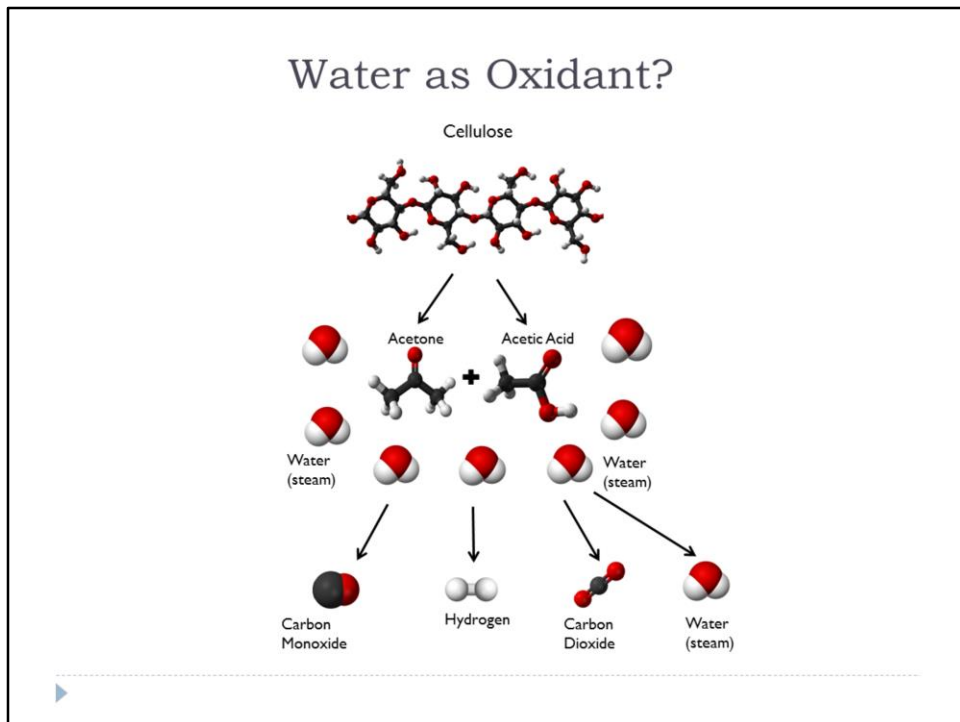
Read slides ...

<http://push.pickensplan.com/profiles/blogs/understand-fuel-reformers-and>



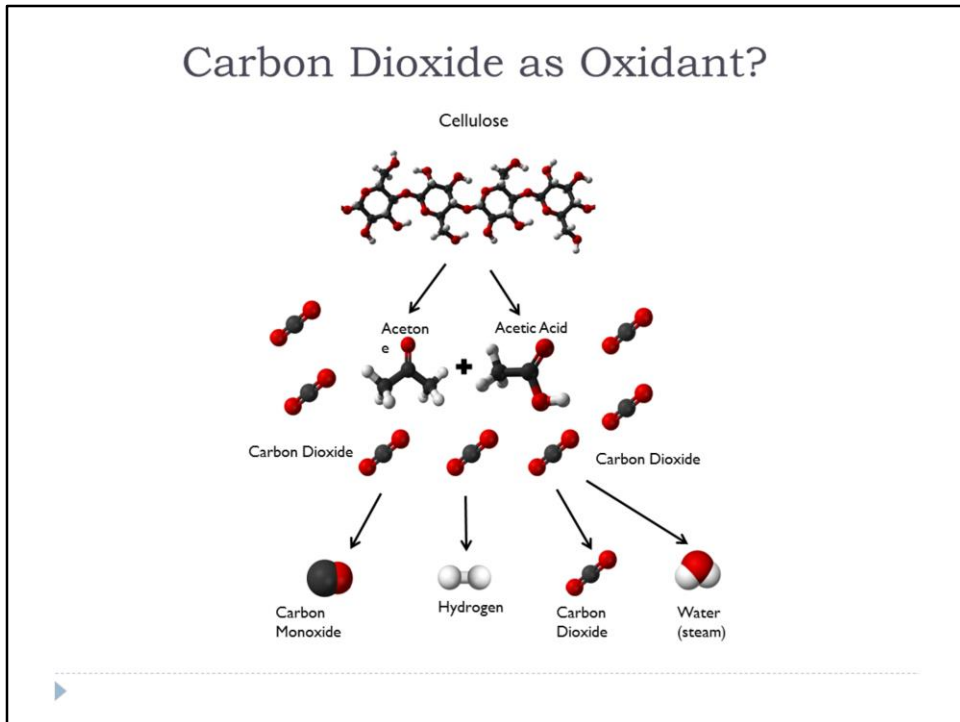
This is an illustration of cellulose breaking into common pyrolysis products acetone and acetic acid - addition of heat causes pyrolysis.

These products react with oxygen as an oxidant to form CO, CO₂ and H₂ – the addition of the oxygen causes gasification.



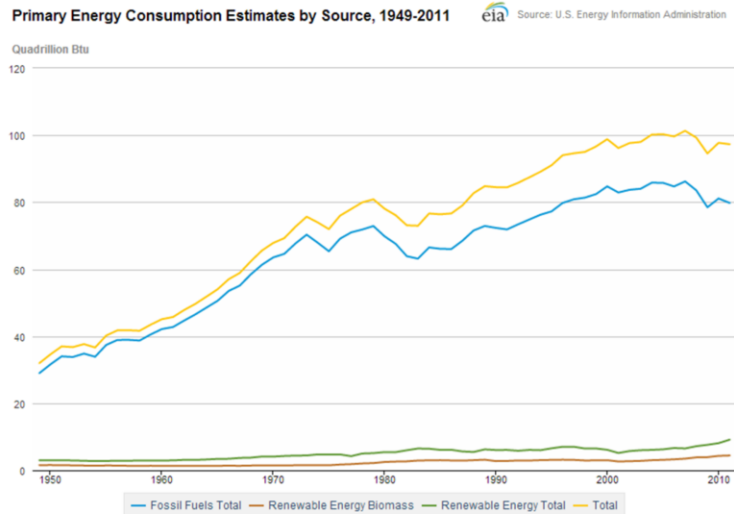
These products react with water as an oxidant to form CO , CO_2 , and H_2 – the addition of the water causes gasification. This is called steam reforming.

Carbon Dioxide as Oxidant?



These products react with CO₂ as an oxidant to form CO, CO₂ and H₂ – the addition of the CO₂ causes gasification. This is called dry reforming.

Next Lecture – Pyrolysis & Liquefaction



▶ 26

BR350 - Lecture 2 – Common Denominators 3/22/2016

<http://www.eia.gov/renewable/data.cfm#biomass>

When you have an opportunity please visit the attached DOE EIA link on biomass. I would like you to spend some time looking at the data available on this website and making some graphs using the available tools. It is very interesting to consider how much biomass we use for energy compared to fossil fuels and how much of our renewable energy comes from biomass alone.