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# PYROLYSIS & TORREFACTION OF BIOMASS

# Introduction

- **Pyrolysis** is the decomposition of biomass in the absence of oxidizing agents. Usually at around 300-650$^{0}$C

- **Torrefaction** is similar to Pyrolysis but occurs at lower temperature (around 200-320 $^{0}$C)

- Both techniques utilize the decomposition of biomass to produce valuable products such as: Coke, Syngas, PVC, charcoal and lighter hydrocarbons like gasoline.

# Historical Tid-Bits

- Pyrolysis has been used throughout man's history to produce charcoal using clay Beehive ovens.

- Abraham Gesner used Pyrolysis of coal at 427 $^{0}$C to produce Kerosene (in 1861).  He greatly helped out the whale population by providing an alternative to whale oil.

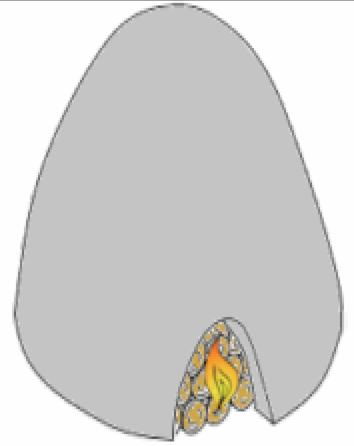

Figure 4.3 Beehive oven for charcoal production through slow pyrolysis of wood

Whale Image Retrived from: http://www.businesspundit.com/wp-content/uploads/2008/12/whale.jpg

# Pyrolysis Process

- In the 'Pyrolysis Process' the body of biomass is heated to the pyrolysis temperature and held at the temperature for a specified time.

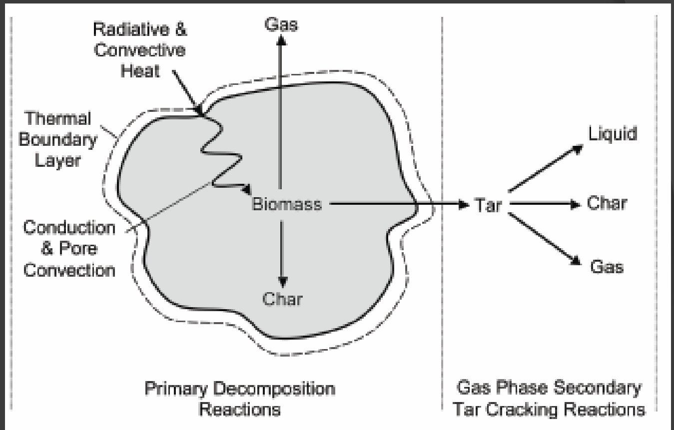

Figure 4.6 Pyrolysis of a biomass particle

The biomass degrades into
**3 constituent yields**:

1) Solid Yield – Char or Carbon
2) Liquid Yield – Tar, Heavy Hydrocarbons and Water
3) Gas Yield – $CO_2$, $H_20$, CO, $C_2H_2$, $C_2H_4$, $C_2H_6$, $C_6H_6$,etc.

# Types of Pyrolysis

- **Slow Pyrolysis** : Primarily to produce Char through Carbonization.

  - Utilizes low temperatures around 400 $^0$C over a long period of time to maximize char formation

  -Oldest form of ‘man-made’ pyrolysis

- **Rapid/Fast Pyrolysis** : Primarily to produce Bio-Oil and Gas

  -Biomass is very rapidly heated (~1000-10,000 $^0$C/s) to a temperature around 650$^0$C-1,000$^0$C depending if bio-oil or gas products are desired.

  -Product gases are quickly removed and quenched ($t<2s$)

- **Pyrolysis in a Medium** – Usually water or Hydrogen

  -Hydrogen is used because the hydrogen molecules bind to the decomposed hydrocarbons in a manner that increases the volatile (gaseous) yield of light hydrocarbons.

  -Water is used to crack biomass in order to produce bio-oil with reduced oxygen content. There is currently a project that (undertaken by a company called ‘Changing World Technology)’ is using this process to convert turkey offal (guts, etc) into hydrocarbons for fuel production.

# Effects of Operating Parameters on Product Yield

- **Heating Rate:**

  -Rapid heating to a moderate temperature (400-600$^0$C) will produce higher volatiles and increased oil production.

  -For example if Esperanto (a grass) is heated at 5$^0$C/min to a temperature of 400-500$^0$C  a typical liquid yield is 45% of the total mass.  If 250$^0$C/min the liquid yield increases to 68.5%.

- **'Pyrolysis Temperature'/Residence Time:**

  -See Figure 4.4

  -Char formation will decrease with increasing temperature.

  -Complex relation between the individual products and the residence time and temperature

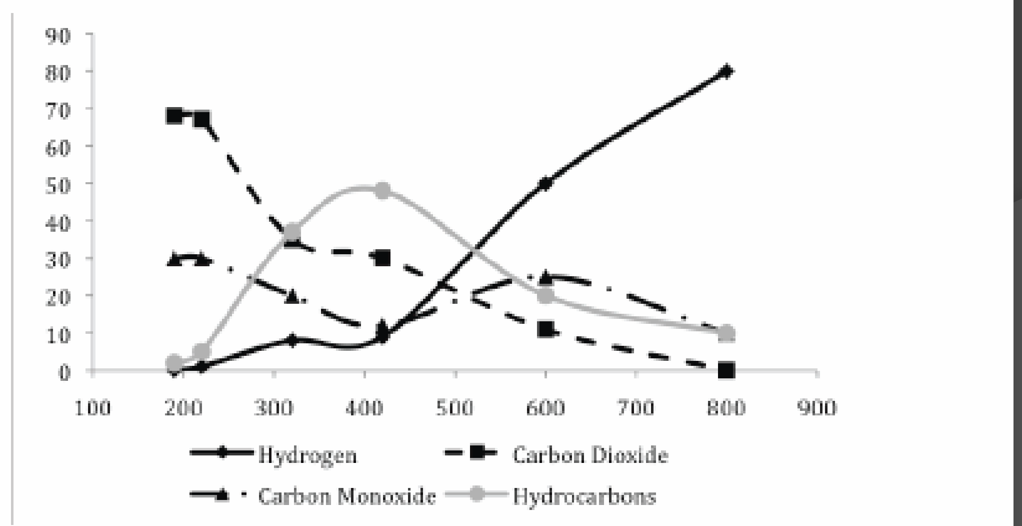


Figure 4.4 Release of gases during dry distillation of wood. Drawn based on data of Nikitin et al., 1962

# Effects of Operating Parameters on Product Yield - Continued

- **Biomass Type:**

  -Major constituents of Biomass are: Cellulose, Hemi-cellulose and Lignin.

  -Cellulose (150-350$^0$C) turns into condensable vapour (tar)

  -Hemi-cellulose (275-350$^0$C) yields primarily non-condensable vapour

  -Lignin (250-500$^0$C) degrades slowly into char and liquid yield

- **Additional Factors:**

  Pressure

  Ambient Gas Composition

  Presence of Mineral Catalysts

# Pyrolysis Kinetics

- Important Factors governing the molecular reactions are: Chemical Kinetics, Heat Transfer and Mass Transfer.

- Physical aspects of the molecular reactions:
  - Three Stages of Pyrolysis
    - Up to 100$^{0}$C the particle's dry out.
    - At 200-600$^{0}$C molecules of biomass decompose into solid and liquid yield along with non-condensable gases. (This is 'Primary Pyrolysis')
    - Vapours are extracted and condense as 'tar' or 'bio-oil' while large molecules continue to crack yielding char at 300-800$^{0}$C. This is called 'Secondary Pyrolysis'.

  - Fine particle sizes offer little resistance to the escape of condensable gases and will therefore lead to a higher liquid yield. Whereas larger particle sizes will provide more resistance to the vapours as they try to escape and will therefore provide more opportunities for the vapours to crack resulting in a higher char yield.

# Pyrolysis Kinetics – cont.

- Chemical Aspects
  - The biomass composition (ie relative levels of Cellulose, Hemi-cellulose and Lignin) effects the final pyrolysis products.
  - There are several theorized 'models' of the reaction processes that describe the interplay of factors like pyrolysis temperature, residence time and heating rate.

- Kinetic Models of Pyrolysis
  - One-Stage global, single reaction models
    - *The pyrolysis is modeled by a one step reaction using experimentally determined factors*
  - *One-Stage, Multi-reaction models:*
    - *Several parallel reactions describe the degradation of biomass into the various yields.*
  - Two-stage semi-global models:
    - *Includes primary and secondary reactions to provide the most detailed results.*

# Heat Transfer in a Pyrolyzer

- During the Pyrolysis process heat is Transferred to the particles primarily through radiation and convection, though some heating techniques use conduction. The primary heat transfer mechanisms are suggested:
  - *Conduction inside the particle*
  - *Convection inside the particle pores*
  - *Convection and radiation from the particle's surface*

- Heat transfer considerations are especially important in the design of the pryolyzer as heating rate plays a large role in the determination of the final products.
  - All pyrolyzers will heat up the heating medium before operation though the medium's vary
    - *Reactor wall (Ablative Reactor)*
    - *Gas (Entrained bed reactor)*
    - *Heat Carrier Solids (Such as those in a fluidized bed)*

- Though most units require heat initially, once the required temperature is reached several exothermic reactions proceed that provide enough heat for the process (Autothermal Reaction).

# Pyrolyzer Design

- Though early pyrolyzers (the beehive ovens) were designed to maximize the production of char, modern units are designed to produce either liquid or gas. Based on the type of products that are desired the designer will select the required heating rates, temperatures and duration of the reaction.
  - Once the previous points are determined an appropriate reactor is selected.

- Reactor Types
  - Fixed Bed
  - Bubbling Bed
  - Circulating Fluidized Bed
  - Entrained Bed
  - Others

*Fluidized beds will provide the fastest heating rates while fixed or moving beds will be slower

# Torrefaction

- Torrefaction is a milder form of pyrolysis carried out at temperatures around 200-300$^0$C. It is primarily used as a pre-treatment of biomass to improve its energy density through drying.
  - During Torrefaction the biomass dries and partially de-volatilizes in such a manner that there is a significant reduction in the Biomass's weight while the energy content is maintained.
  - Biomass darkens and becomes brittle (through the decomposition of the Hemi-cellulose molecules of the biomass).
    - Because Torrefaction makes the biomass brittle and easy to mill it reduces the handling costs. Basically it will allow a strong fibrous material to become brittle like coal so that it may be pulverized for use in a boiler or other reactor.
  - Drops weight of Biomass to 62%-69% of the original mass, though the energy density can increase by 29%-33%
  - Torrefaction will alter the Biomass such that it will absorb less moisture while stored then regular Biomass.

- Advantages
  - Offers cleaner burning fuel with low acid content in the smoke.
  - Absorbs less moisture when stored
  - A higher heating value may be achieved
  - Increases the ease of handling and allows for use in pulverized coal fire boilers

# Torrefaction - Continued

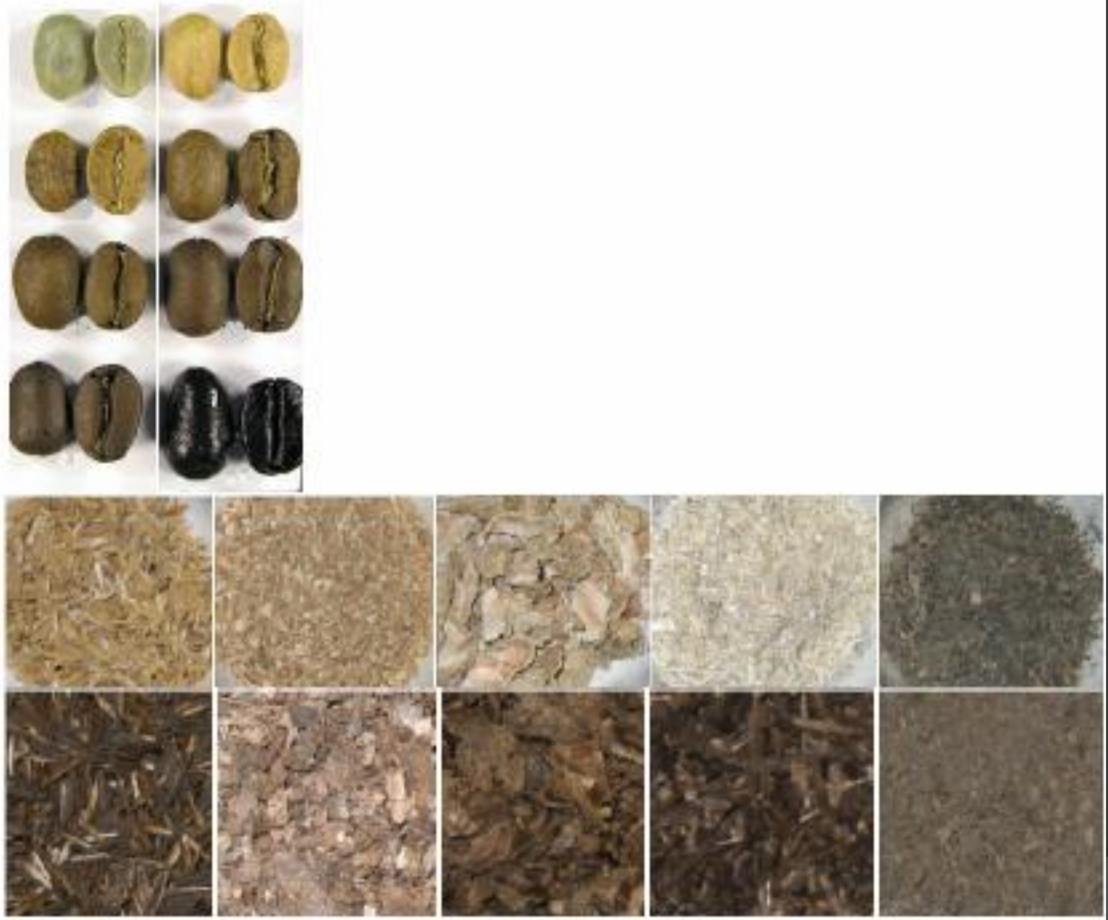

Figure 4.8 Comparison of photographs of several biomass before and after torrefaction. Top row shows raw biomass, rice husk, sawdust, peanut husk, bagasse and water-hyacinth. The bottom shows photograph of the same biomass after torrefaction [From Pimchuai et al., 2009]

# References

The information contained in this presentation was obtained from the self study package "Chapter 4: Pyrolysis & Torrefaction of Biomass"  Written By: Dr. Pabir Basu