Topic Six

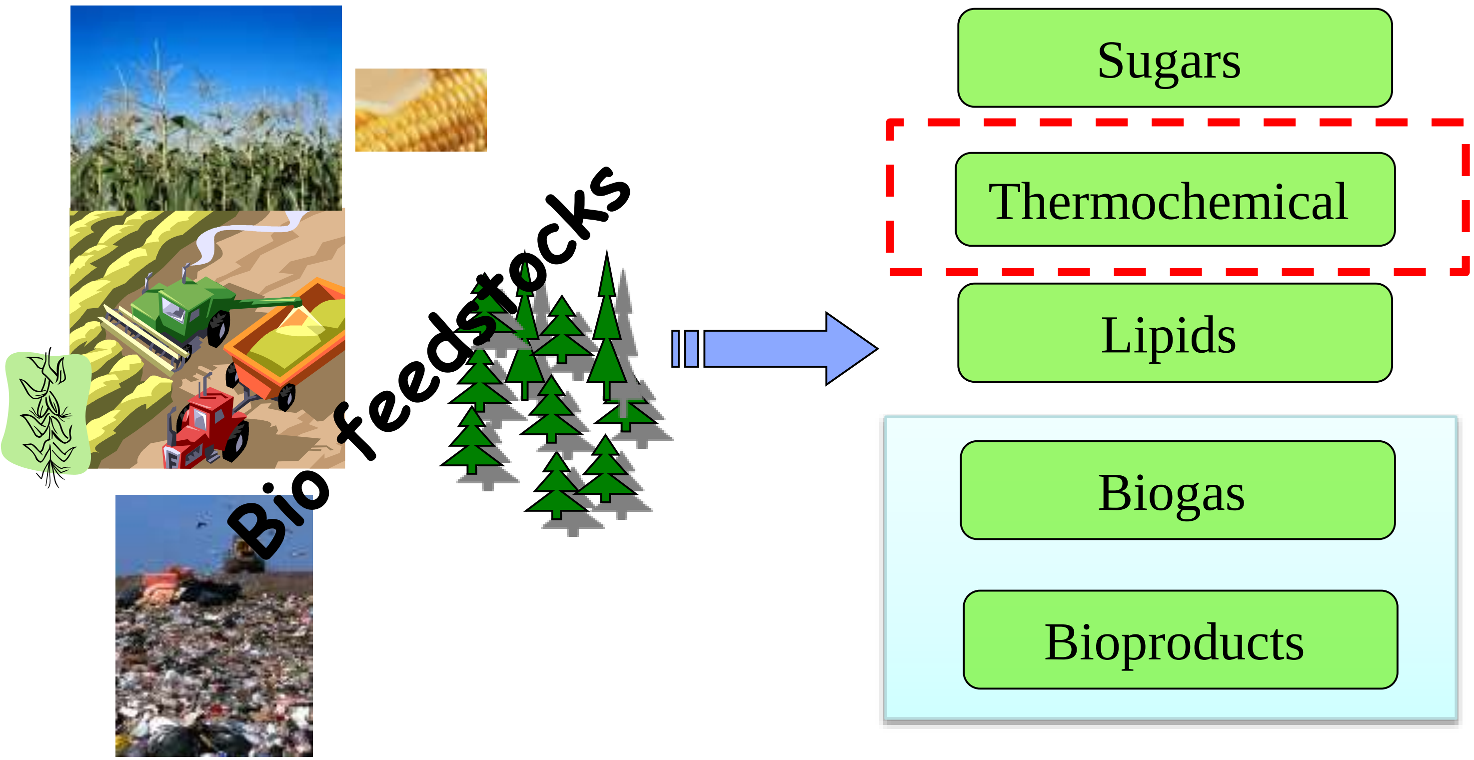
Thermochemical Conversion Technologies for Processing Bio-feedstocks into Fuels and Chemicals

Lecture Twelve-Thirteen

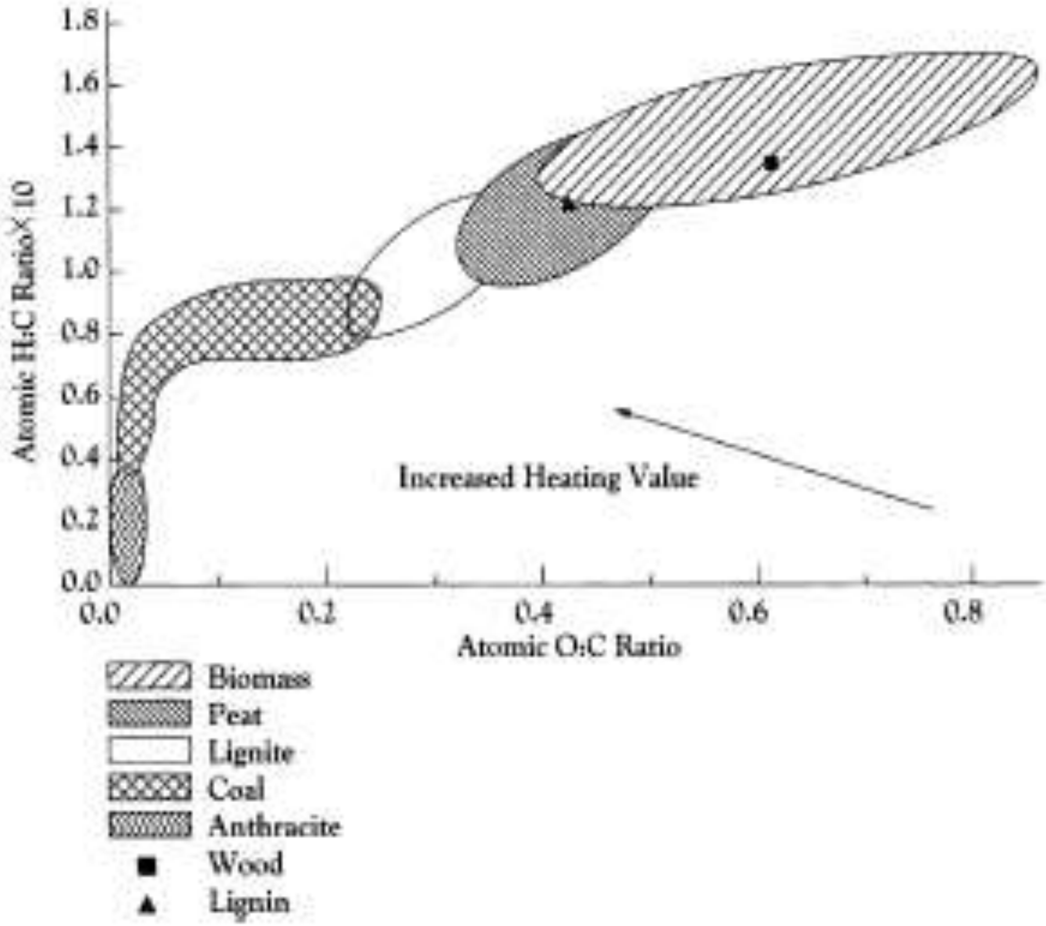
Thermochemical Conversion Technologies

Technologies for Conversion of Bio-feedstock

Technologies for conversion of biomass can be divided into five platforms (Biomass Program, DOE Classification)

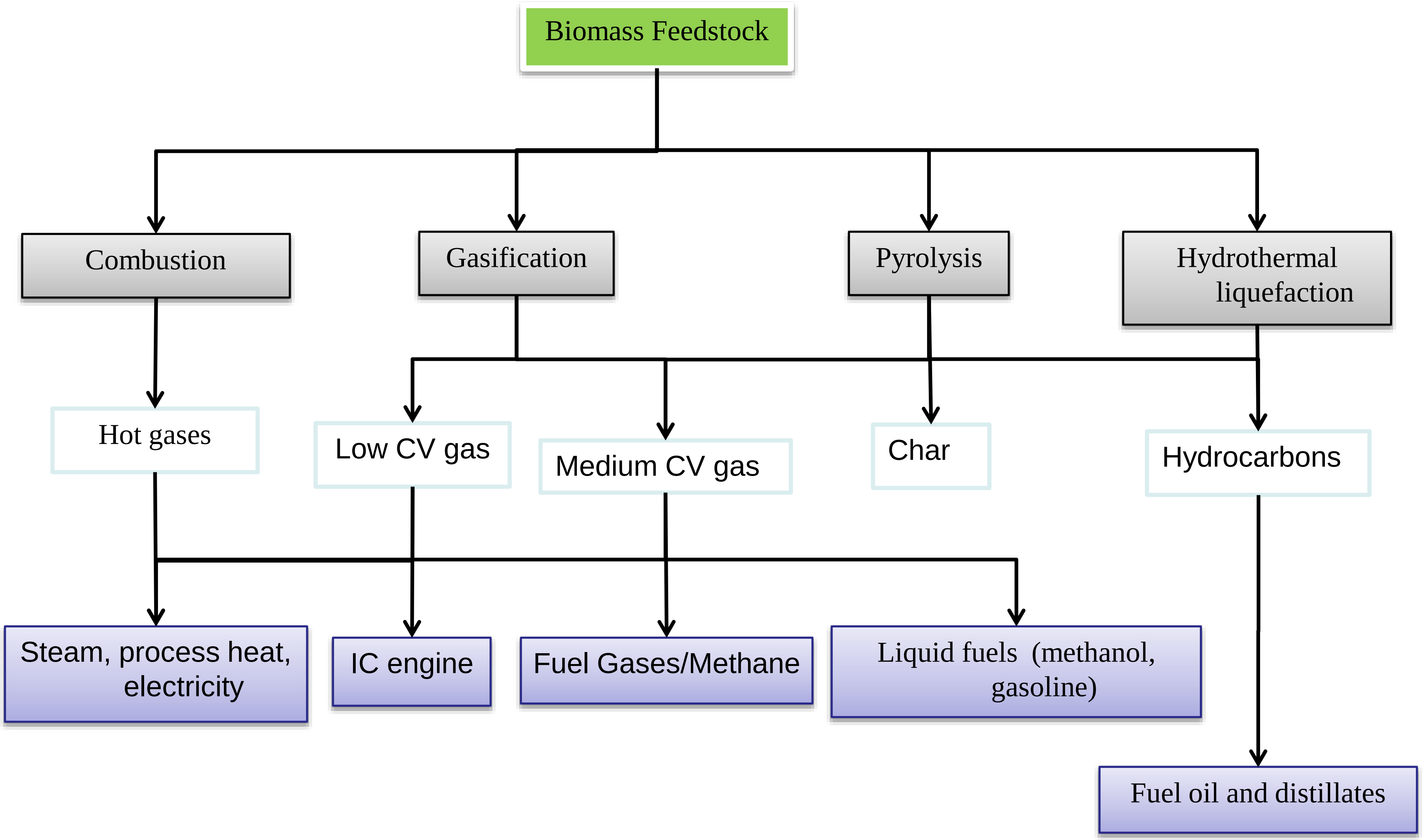


Technologies for Conversion of Bio-feedstock

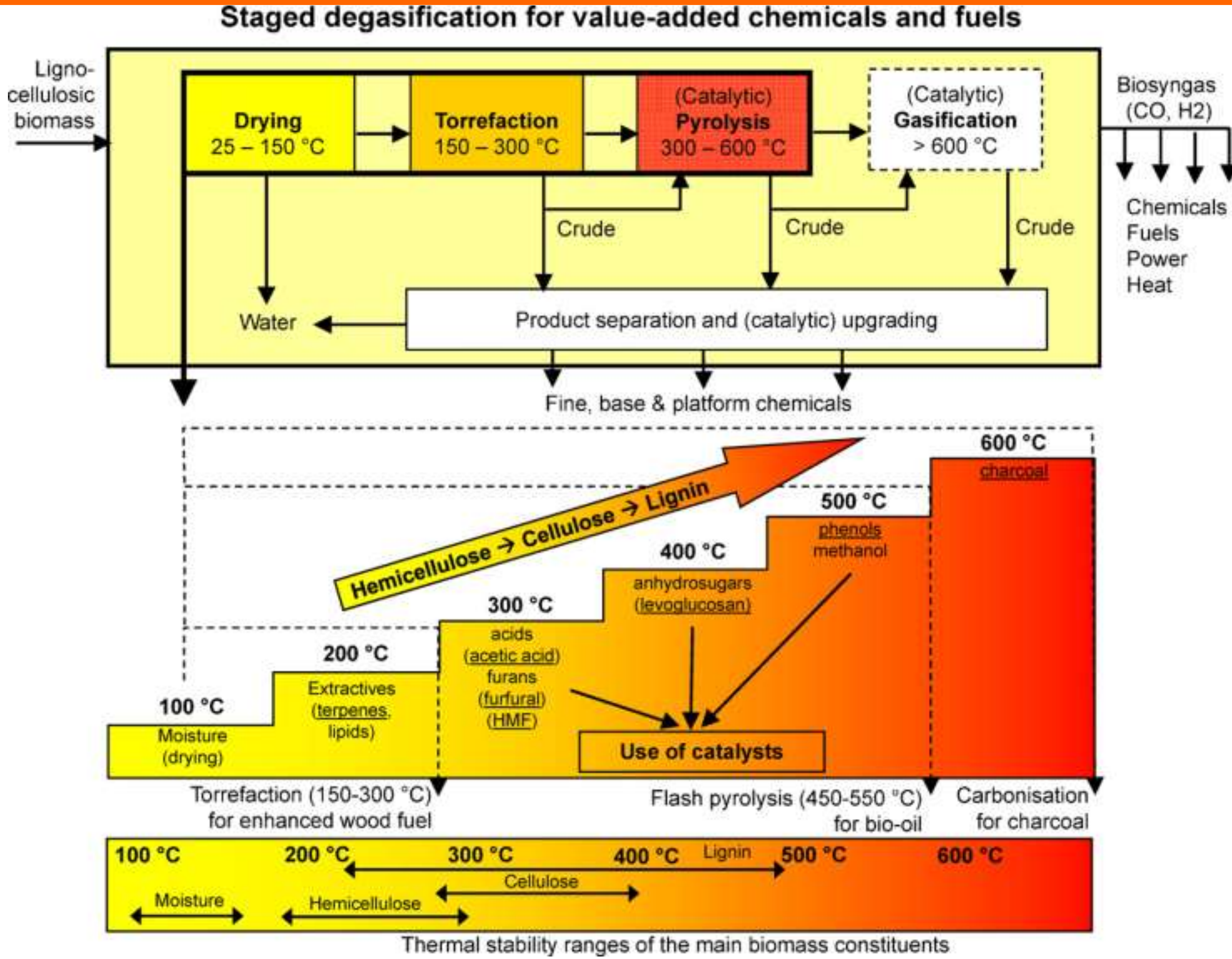


Van Krevelen Diagram (used for comparing biomass and fossil fuels)

Thermochemical Platform



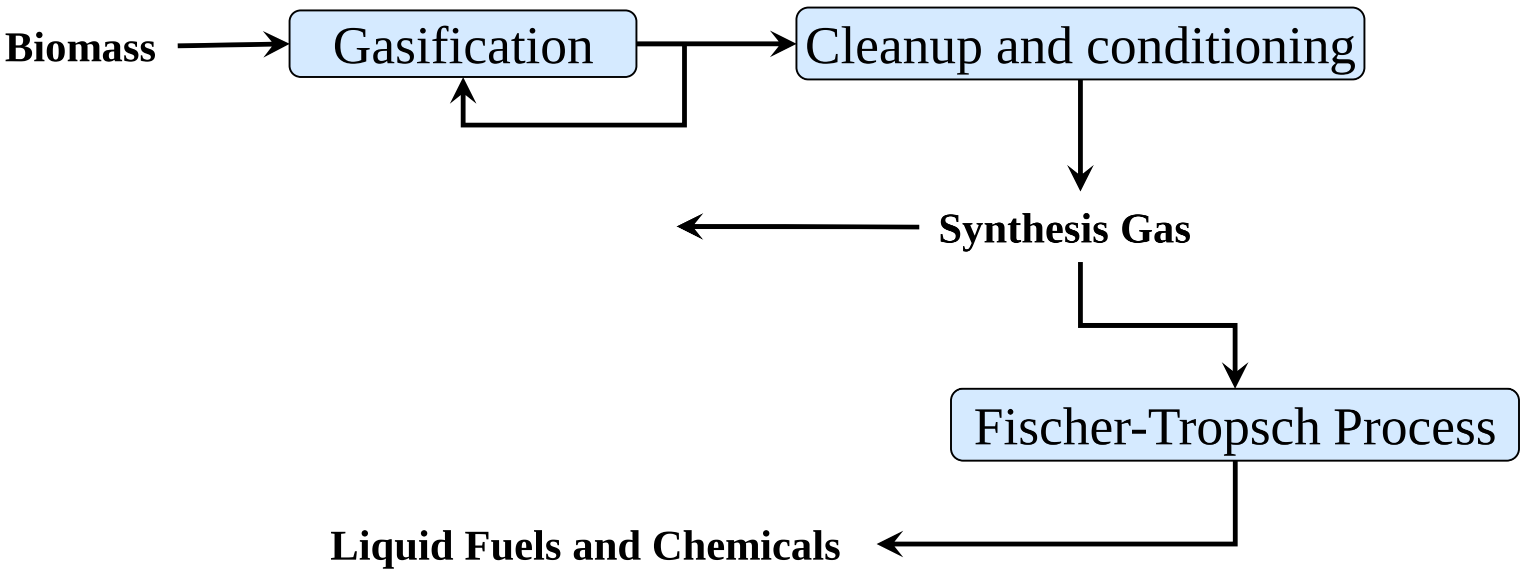
Thermochemical Platform



Thermochemical Platform

Four types of thermochemical processes

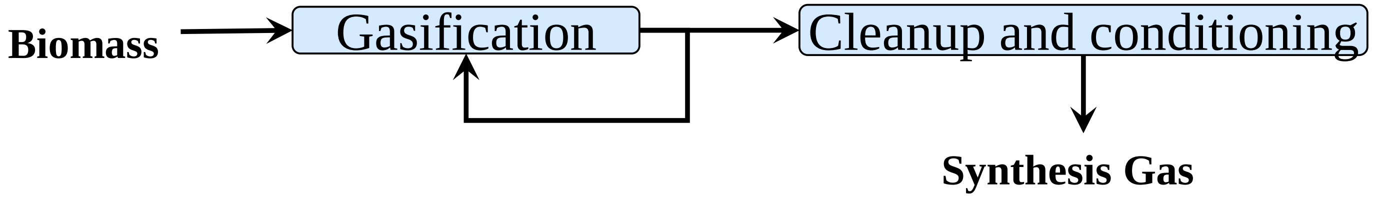
- Gasification: Heating of biomass in limited /no oxygen conditions produces synthesis gas (syn gas) consisting a mixture of CO and H_2



Gasifier Feedstocks

One of the primary reasons for interest in gasifier technology is that multiple feedstocks with different compositions can be used to produce a standard product. Some of the feedstock important characteristics are:

- Moisture content: <30% ideal range.
- Ash content: Clinker formation above 5%.
- Volatile compounds: Operation of gasifier to deconstruct tars and other hydrocarbons.
- Particle size: 10-20% of the hearth diameter.



Gasifier Reaction Chemistry

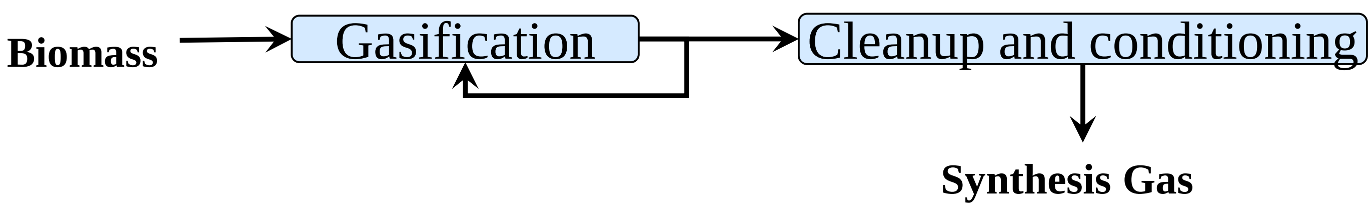
Main reactions

- Partial oxidation: $C + 0.5\ O_2 \leftrightarrow CO$ $\Delta H = -268$ MJ/kg mole
- Complete oxidation: $C + O_2 \leftrightarrow CO_2$ $\Delta H = -406$ MJ/kg mole
- Water gas reaction: $C + H_2O \leftrightarrow CO + H_2$ $\Delta H = +118$ MJ/kg mole

Subsidiary reactions

- Water gas shift reaction: $CO + H_2O \leftrightarrow CO_2 + H_2$ $\Delta H = -42$ MJ/kg mole
- Methane formation: $CO_2 + 3H_2 \leftrightarrow CH_4 + H_2O$ $\Delta H = -88$ MJ/kg mole

Extent of above equilibrium reactions is dependent on the temperature and pressure inside gasifier and therefore can regulated by changing operating conditions.



Gasifier Product Gases

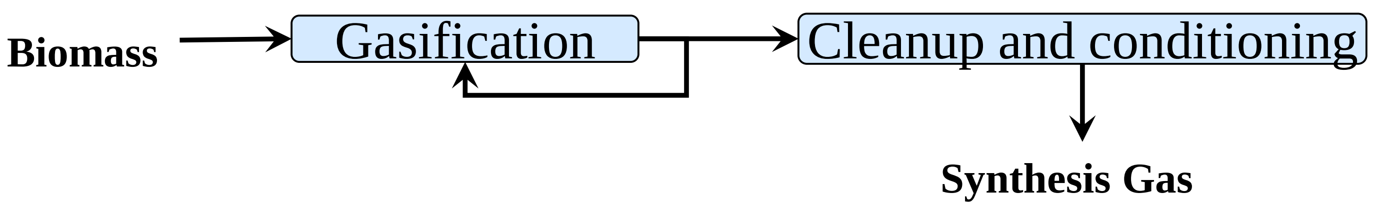
Three main types based on calorific value (CV)

Product Calorific Value Oxidant

- Low CV 4-6 MJ/Nm^3 Air and steam/air
- Medium CV 12-18 MJ/Nm^3 Oxygen (10-15 MJ/Nm^3) and steam (13-20 MJ/Nm^3)
- High CV 40 MJ/Nm^3 H_2 and hydrogenation

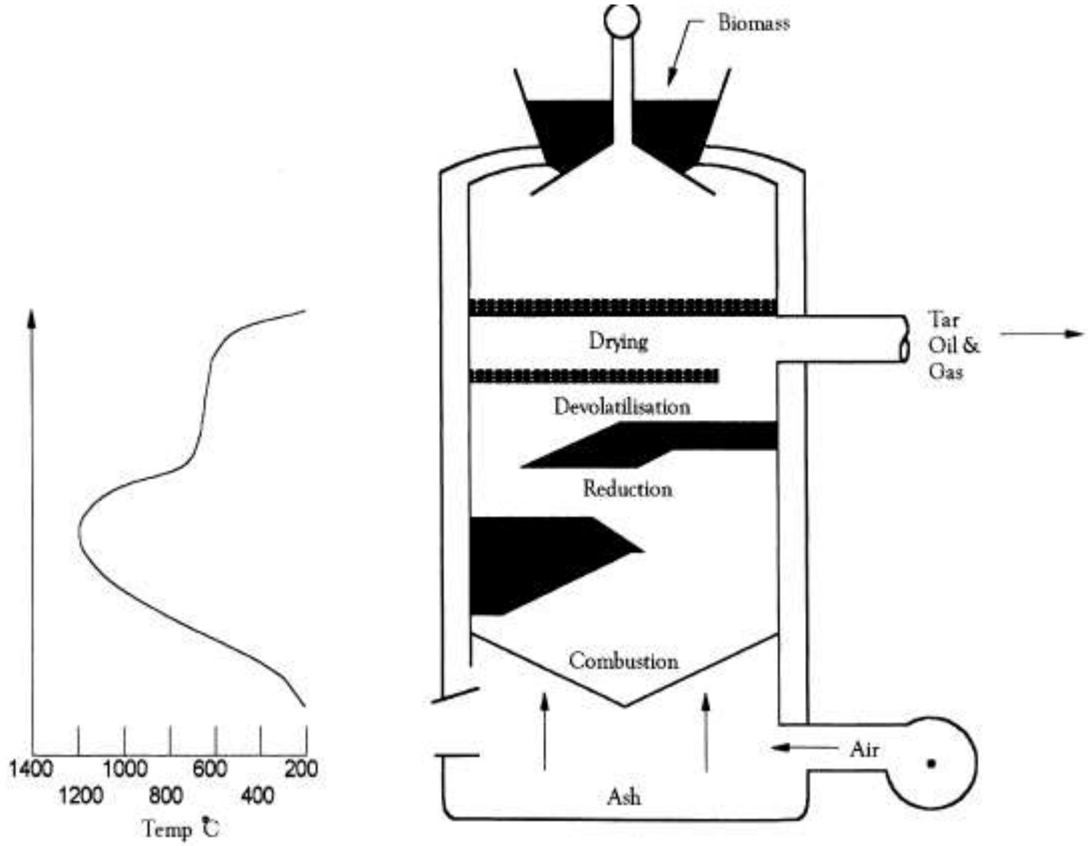
Natural gas 36 MJ/Nm^3

Low CV gas can be combusted directly in engines while Medium and high CV products can be used for subsequent conversion (using Fisher-Tropsch or similar process) into methane and methanol.



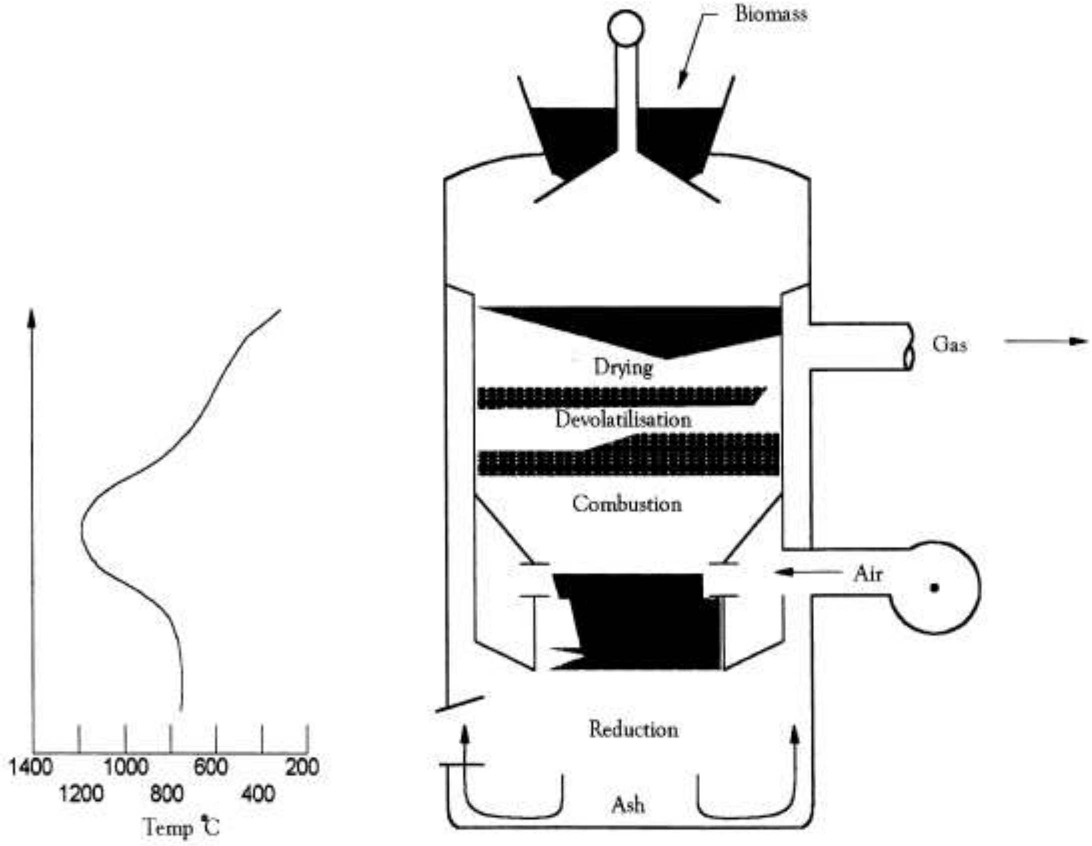
Classification of Gasifiers

Fixed bed Updraft Gasifiers: In countercurrent gasifiers, air and feed move in opposite directions. Produces gas with lower particulates but higher tar content.



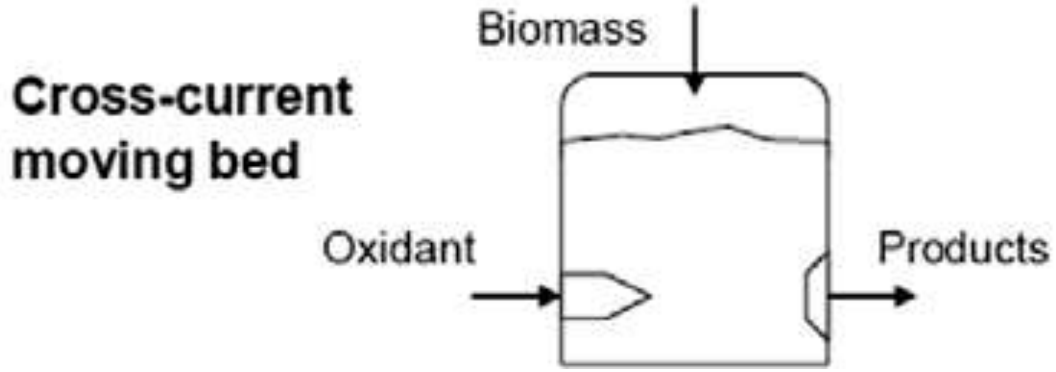
Classification of Gasifiers

Fixed bed Downdraft Gasifiers: Also called cocurrent gasifiers, feed and air move in the same direction in this gasifier. Partial cracking of tars because the gases pass through hot zone. Gas exit temperature is ~900-1000°C.



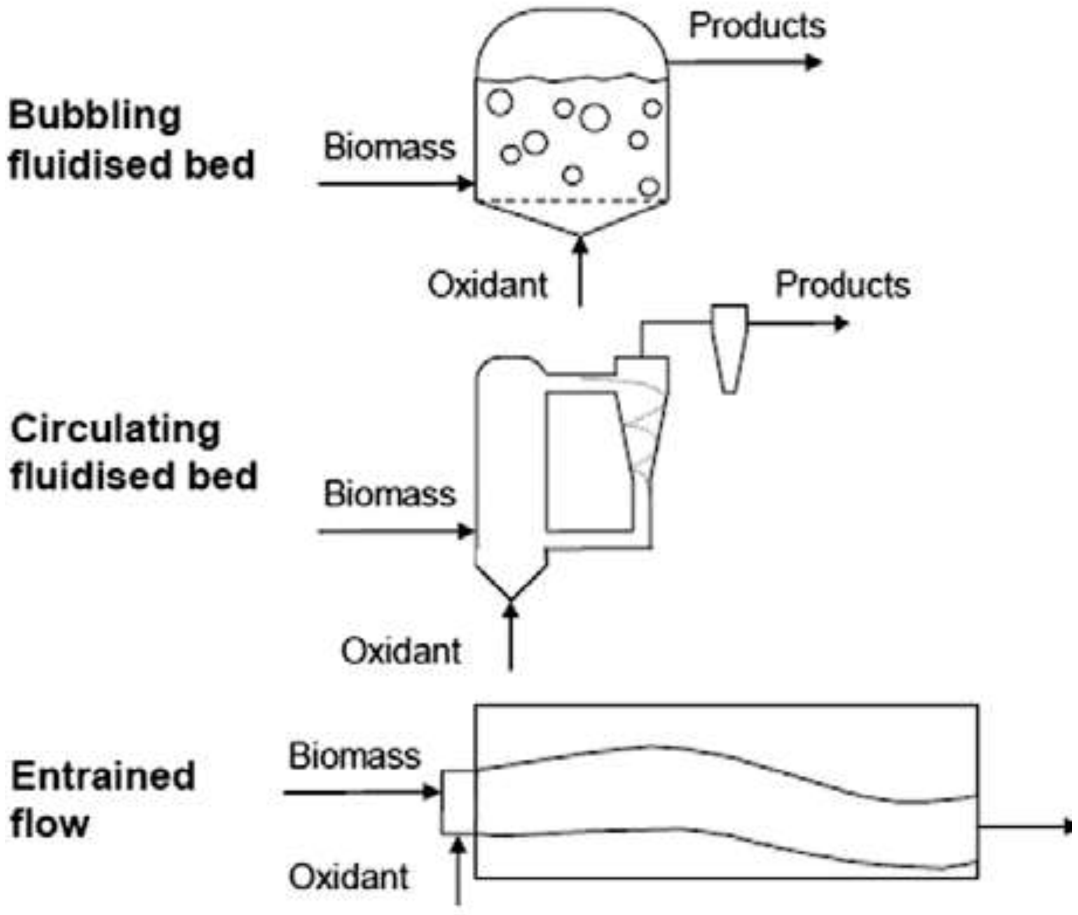
Classification of Gasifiers

Fixed bed Cross flow Gasifiers: In the cross flow gasifiers, air is injected perpendicular to the feed flow.



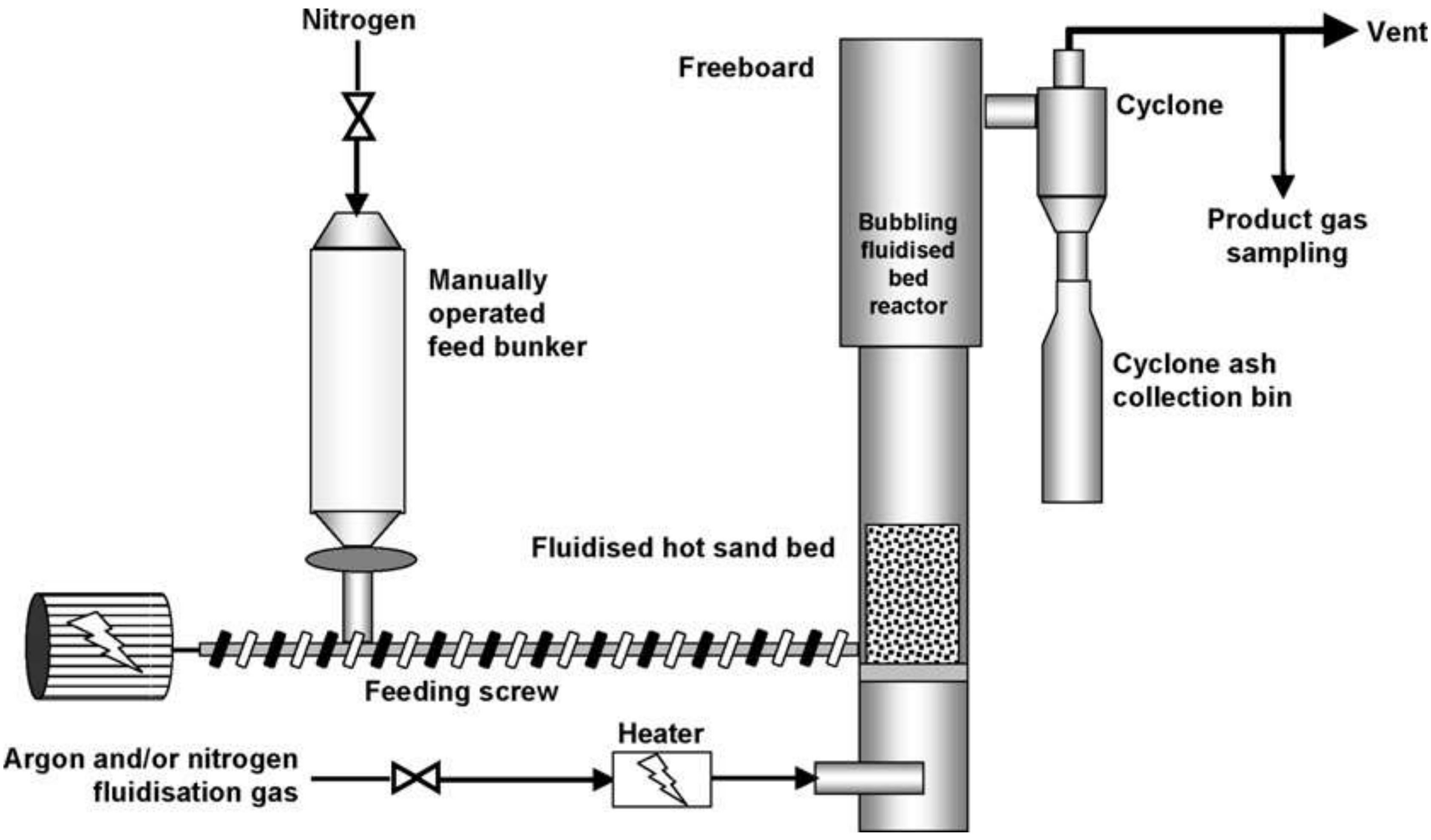
Classification of Gasifiers

Fluidized bed Gasifiers: Bubbled and circulating fluidized bed and entrained flow.



Classification of Gasifiers

Bubbling bed Gasifiers



Gasifier Performance Characteristics

- Particulates, tar, nitrogen, sulfur and alkali compounds are some of the impurities that must be cleaned from the product gas.
- Hot and cold cleaning of product gas.
- Catalytic cracking (800-900°C) or thermal cracking (900-1100°C) are used to reduce tar into low molecular weight compounds.
- Typical fixed bed gasifier product gas composition with air as oxidant is: 40-50% N2, 15-20% H2, 10-15% CO, 10-15% CO_2 and 3-5% H_2 (CV: 4-6MJ/Nm^3).

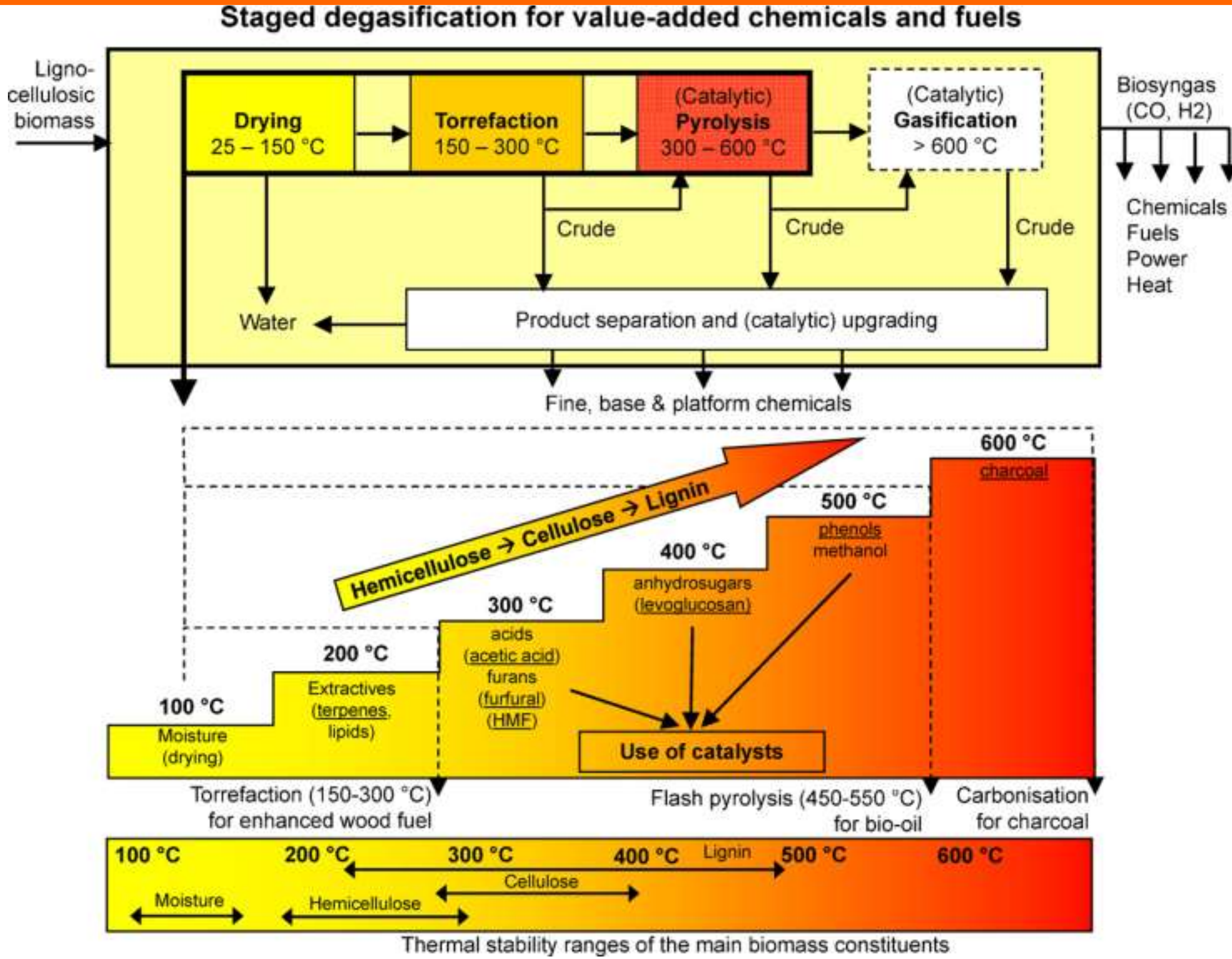
Gasifier Performance Characteristics

- Fixed bed gasifiers are simpler in design compared to fluidized bed gasifiers.
- Fixed bed gasifiers (counter current) produce gas with relatively high tar content and low CV.
- Fluidized bed has uniform temperature distribution however, it is more complex than a fixed bed gasifier.
- Slagging of bed is a major concern in operation of fluidized bed gasifiers.
- Fixed bed, down draft gasifier produces lowest tar in product gas.

Summary of Gasifiers

Advantages	Disadvantages
Fixed/moving bed, updraft	
Simple, inexpensive process	Large tar production
Exit gas temperature about 250 °C	Potential channeling
Operates satisfactorily under pressure	Potential bridging
High carbon conversion efficiency	Small feed size
Low dust levels in gas	Potential clinkering
High thermal efficiency	
Fixed/moving bed, downdraft	
Simple process	Minimum feed size
Only traces of tar in product gas	Limited ash content allowable in feed
	Limits to scale up capacity
	Potential for bridging and clinkering
Fluidised bed	
Flexible feed rate and composition	Operating temperature limited by ash clinkering
High ash fuels acceptable	
Able to pressurize	High product gas temperature
High CH_4 in product gas	High tar and fines content in gas
High volumetric capacity	Possibility of high C content in fly ash
Easy temperature control	
Circulating fluidised bed	
Flexible process	Corrosion and attrition problems
Up to 850 °C operating temperature	Poor operational control using biomass
Double fluidised bed	
Oxygen not required	More tar due to lower bed temperature
High CH_4 due to low bed Temperature	Difficult to operate under pressure
Temperature limit in the oxidiser	
Entrained bed	
Very low in tar and CO_2	Low in CH_4
Flexible to feedstock	Extreme feedstock size reduction required
Exit gas temperature	Complex operational control
	Carbon loss with ash
	Ash slagging

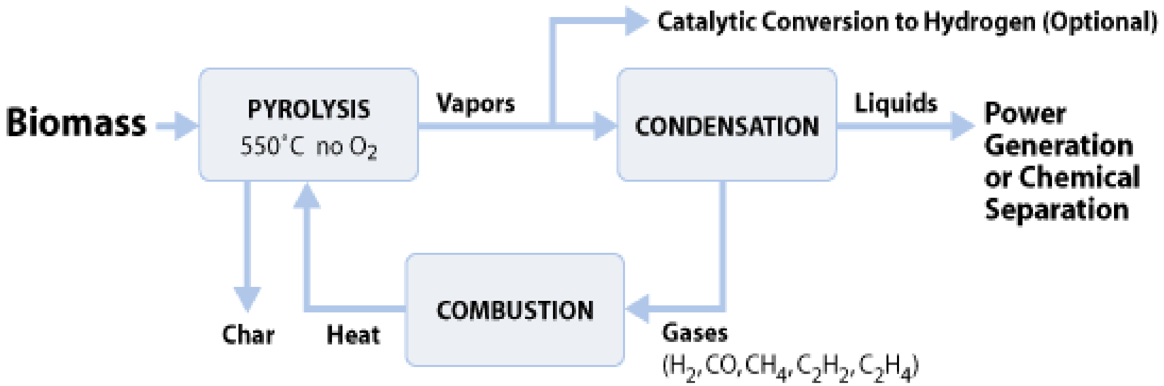
Thermochemical Platform



Thermochemical Platform

Three types of thermochemical processes

• Pyrolysis: Oil is produced by heating solid biomass under high temperature in the absence of oxygen. More suitable for woody biomass that has relatively less moisture content



• Direct hydrothermal liquefaction: This process is similar to pyrolysis, except that it occurs in presence of water at high temperatures (525-600K) and pressures (5-20MPa) generally in presence of catalysts. Suitable for feedstocks that have high moisture content. Ex. Animal manure and municipal waste

Pyrolysis Definitions

- **ASABE**

  Thermochemical conversion process (usually conducted at 400 to 600^o C or 752 to 1112^o F) **in the absence of oxygen**. Pyrolysis of carbon rich feedstocks produces a bio-oil along with some solids (char), and some gases (methane, carbon monoxide, carbon dioxide). The proportions of the products are largely dependent on factors such as operating temperature, pressure, oxygen content and feedstock characteristics.

- **DOE/ NERL**

  The breaking apart of complex molecules by heating in the absence of oxygen, producing solid, liquid, and gaseous fuels.

- **PyNe (IEA Bioenergy Task 34 for Pyrolysis)**

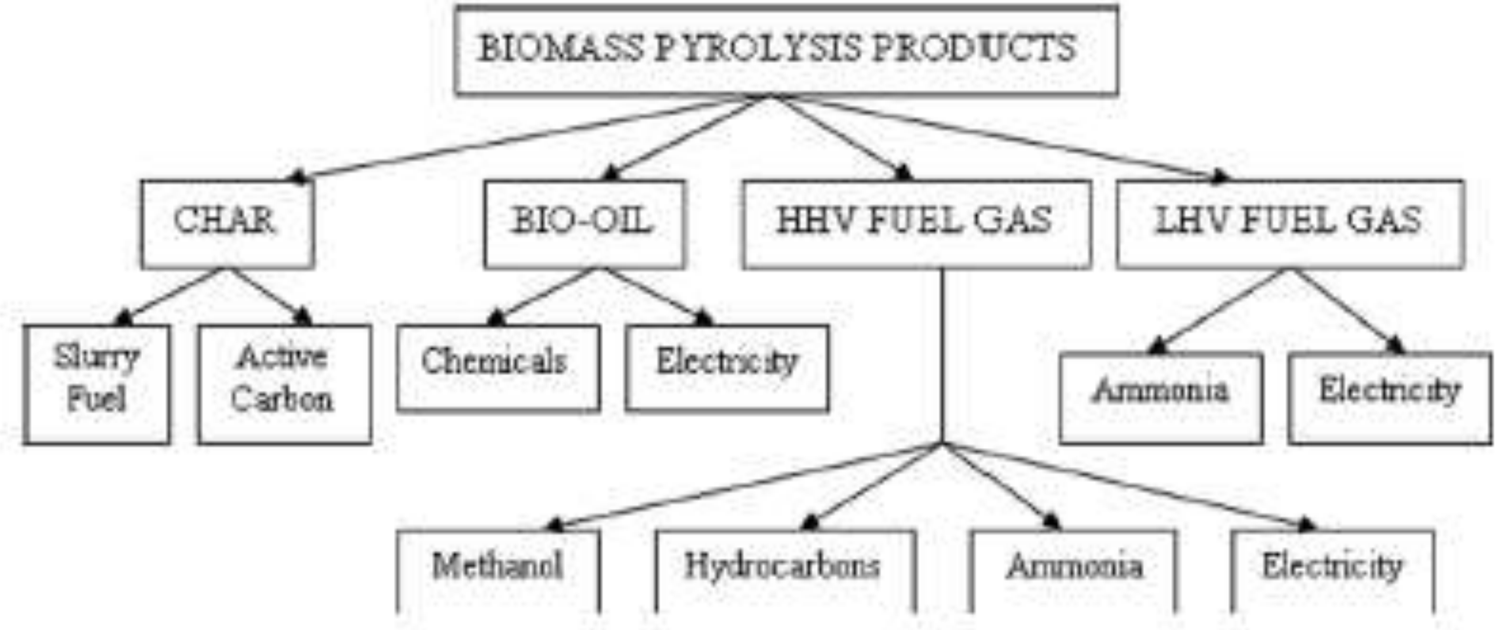
  Pyrolysis is thermal decomposition occurring in the absence of oxygen. It is always also the first step in combustion and gasification processes where it is followed by total or partial oxidation of the primary products.

- **Other**

  A thermal destruction of organic matters at elevated temperatures with no or little oxygen present to produce gases, bio-oil, and char.

Courtesy: BEEMS project

Pyrolysis Overview

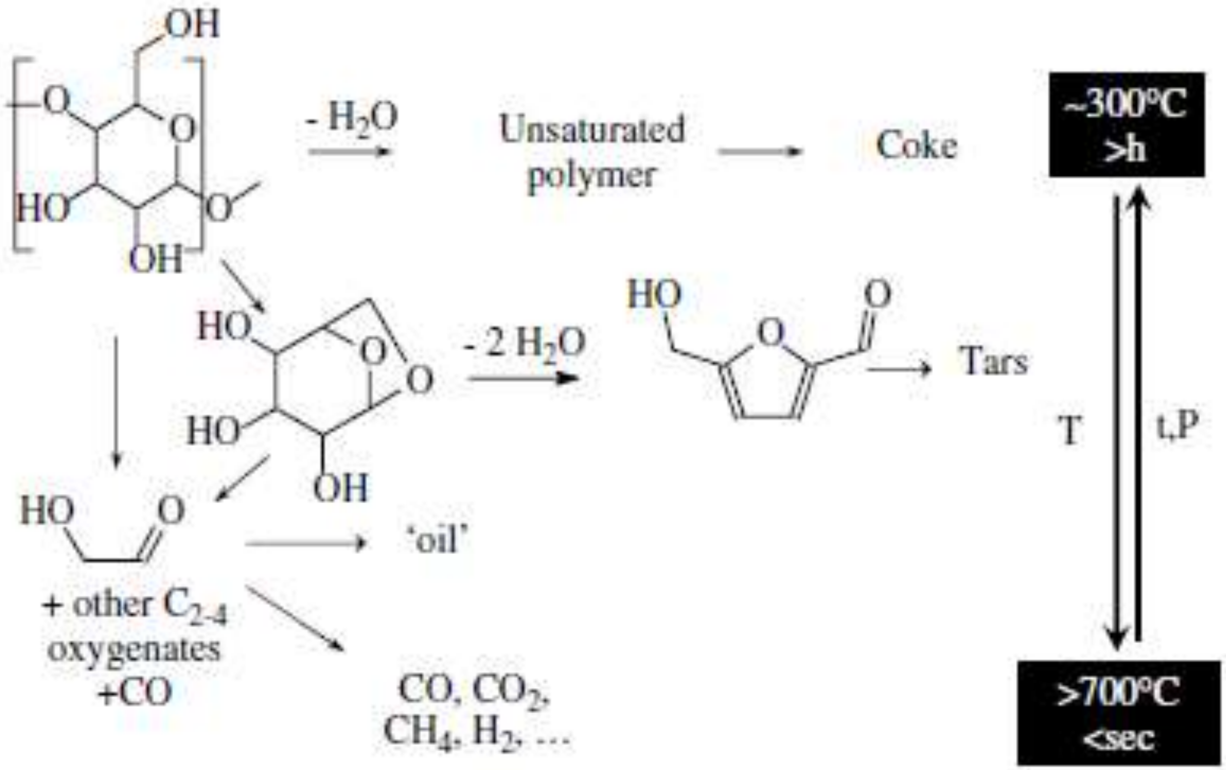


Advantages of Pyrolysis Process

- Utilize renewable resources through carbon neutral route – *environmental potential*
- Utilizes waste materials such as lumber processing waste (barks, sawdust, forest thinnings, etc), ag residues (straws, manure, etc) – *economic potential*
- Energy self-sustaining – *economic potential*
- Convert low energy in biomass into high energy density liquid fuels – *environmental & economic potentials*
- Potentially produced chemicals from bio-based resources – *environmental and economic potentials*
- Relatively simple equipment and low capital cost – *Amenable for distributed processing.*

Courtesy: BEEMS project

Pyrolysis Reaction Chemistry



Pyrolysis Reactions

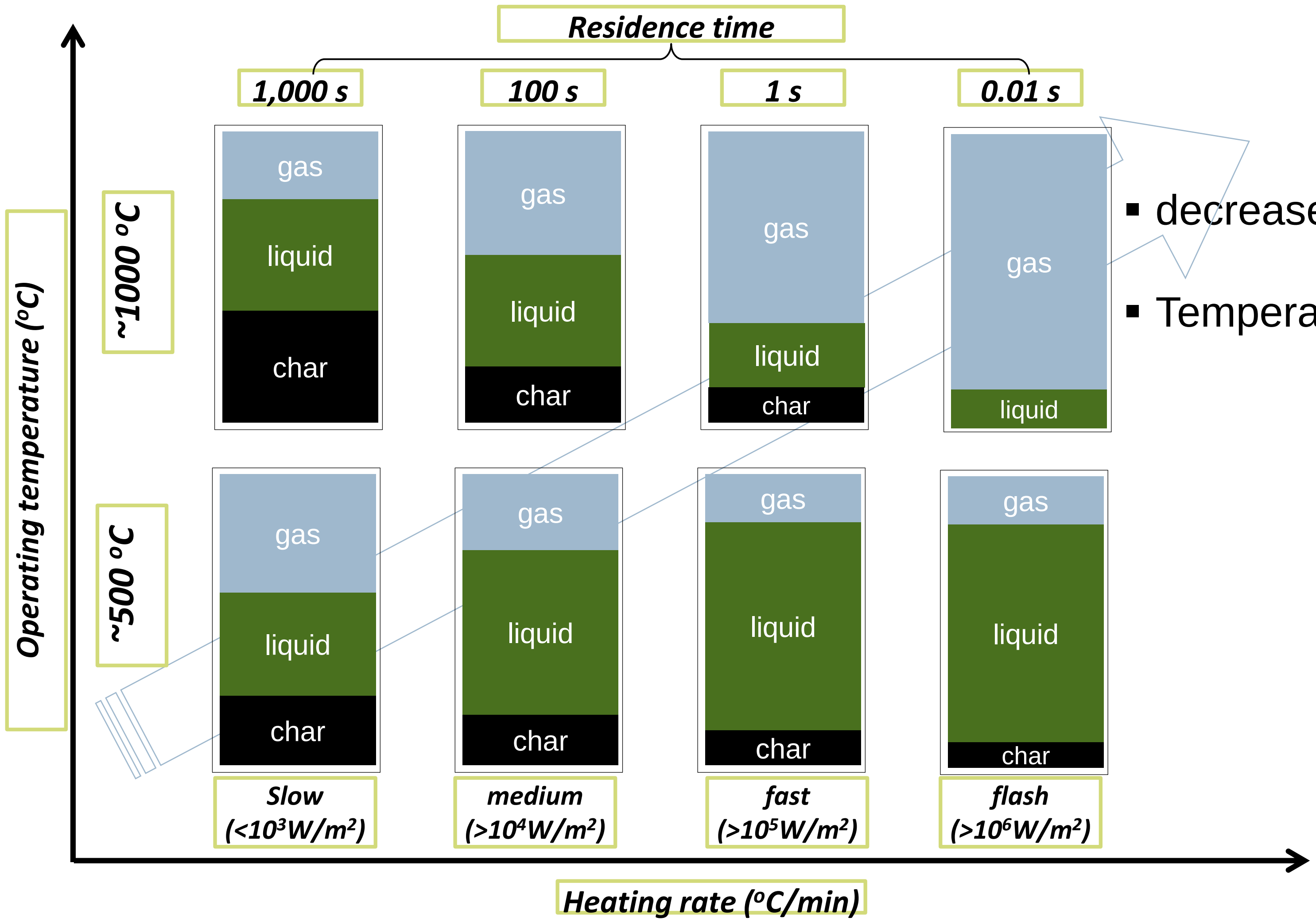
Condition	Process	Products
<575K	Free radical formation, elimination of water and depolymerization.	Formation of carbonyl and carboxyl, evolution of CO and CO2 and mainly a charred residue
575-725	Breaking of glycosidic linkages of polysaccharides by substitution	Mixture of levoglucosan, anhydrides and oligosaccharides in the form of a tar fraction.
>725	Dehydration, rearrangement and fission of sugar units.	Formation of carbonyl compounds such as acetaldehyde, glyoxal and acrolein.
>775	A mixture of all above processes.	A mixture of all above products
Condensation	Unsaturated products condense and cleave to the char	A highly reactive char residue containing trapped free radicals.

Classification of Pyrolysis

Pyrolysis technology	Solid residence time (s)	Heating rate (K/s)	Particle size (mm)	Temperature (K)
Conventional	450-550	0.1-1	5-50	550-950
Fast	0.5-10	10-200	<1	850-1250
Flash	<0.5	>1000	<0.2	1050-1300

Process	Conditions	Product yields (%)		
		Liquid	Char	Gas
Fast	~775K, short hot vapor residence time ~1s	75	12	13
Intermediate	~775 K, moderate hot vapor residence time 10-20s	50	20	30
Slow (Carbonization)	~675K, very long solids residence time	30	35	35
Gasification	~1075K, long vapor residence time	5	10	85

Classification of Pyrolysis

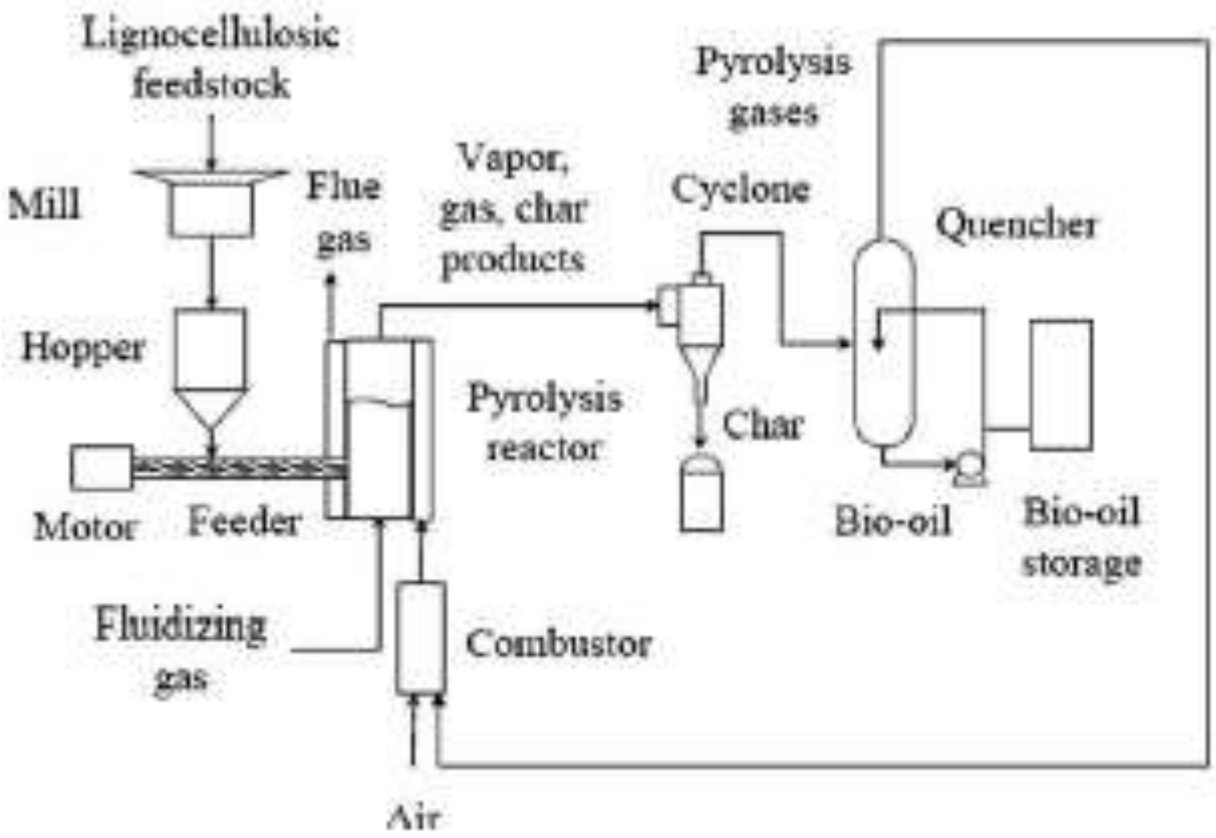


- decrease in time
- Temperature increase

Courtesy: BEEMS project

Classification of Pyrolysis

Fast pyrolysis system



Pyrolysis Products

Composition of pyrolysis liquid

Major components	Mass (%)
Water	20-30
Lignin fragments, insoluble pyrolytic lignin	15-30
Aldehydes, formaldehyde, glyoxal, methylglyoxal	10-20
Carboxylic acids, formic acid, propionic, butyric, pentanoic, hexanoic, glycolic (hydroxyacetic)	10-15
Carbohydrates, cellobiose, α-o-levoglucosan,oligosaccharides, 1,6-anhydroglucofuranose	5-10
Phenols, phenol, cresols, guaiacols, syringols	2-5
Furfurals	1-4
Alcohols, methanol, ethanol	2-5
Ketones, acetol (1-hydroxy-2-propanone),cyclepentanone	1-5

Pyrolysis Products

Comparison of wood bio-oil and Diesel properties .

	Bio-oil	No 2. Diesel fuel
Moisture content	15-30	n.a.
pH	2.5	1
Specific gravity	1.20	0.847
Elemental analysis (% wt)		
C	55-58	86
H	5.5-7.0	11.1
O	35-40	0
N	0-0.2	1
S	n.d.	0.8
HHV (MJ/kg) as produced	16-19	44.7
Viscosity	40-100cp (315K. 25% water)	<2.39(325K)

Pyrolysis Products: Bio-oil Upgrading

- Bio-oil upgrading is very challenging because of
  - High water and acid content (corrosive)
  - High instability, oxidatively and thermally

- Physical treatments
  - Char removal via filtration
  - Emulsification with hydrocarbons for stability
  - Fractionation.
- Chemical treatments
  - Esterification – reaction with alcohol to form esters (remember that bio-oil is acidic)
  - Catalytic de-oxygenation / hydrogenation – to remove oxygen and saturate instable chemicals
  - Thermal cracking for more volatile chemicals
  - Syngas production / gasification

Courtesy: BEEMS project

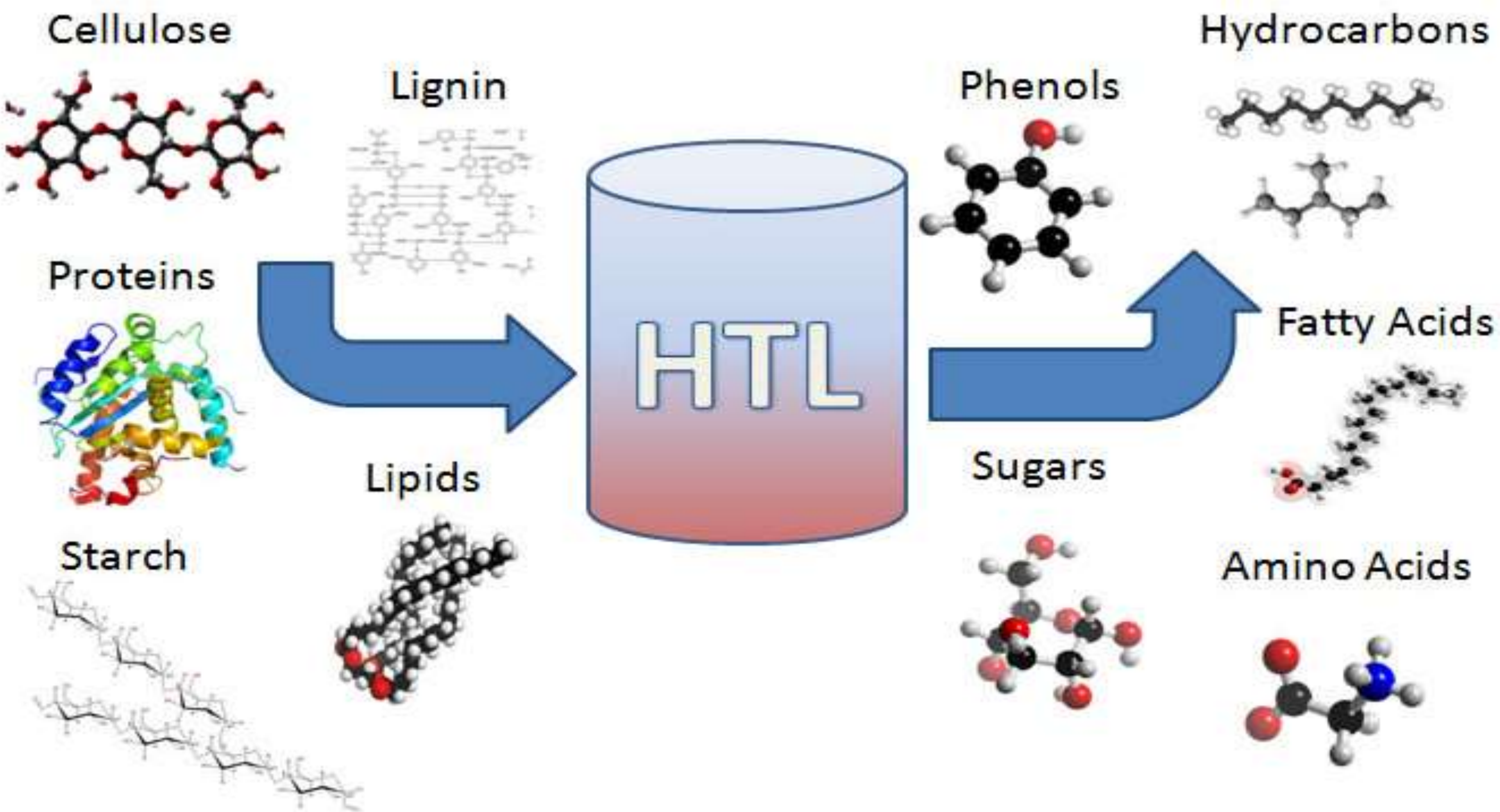
Pyrolysis Products: Bio-oil Upgrading

Chemical treatments that are needed:

- **Catalytic de-oxygenation / hydrogenation**
  - To remove oxygen (completely/partially) and saturate unstable chemicals
  - To stabilize chemicals by saturating with hydrogen
  - Requires supply of significant amount of hydrogen and specialty catalysts (such as Co/Mo/sulfide, oxides of Ni, Co, & Mo), and expensive processing facilities
  - Chemicals in bio-oil may be toxic to catalysts thus reducing their effectiveness.
- **Esterification**
  - To react acids with alcohol to form esters (***remember that bio-oil is very acidic***)
- **Thermal cracking** for more volatile chemicals
- **Physical extraction** of chemicals, such as phenols

Courtesy: BEEMS project

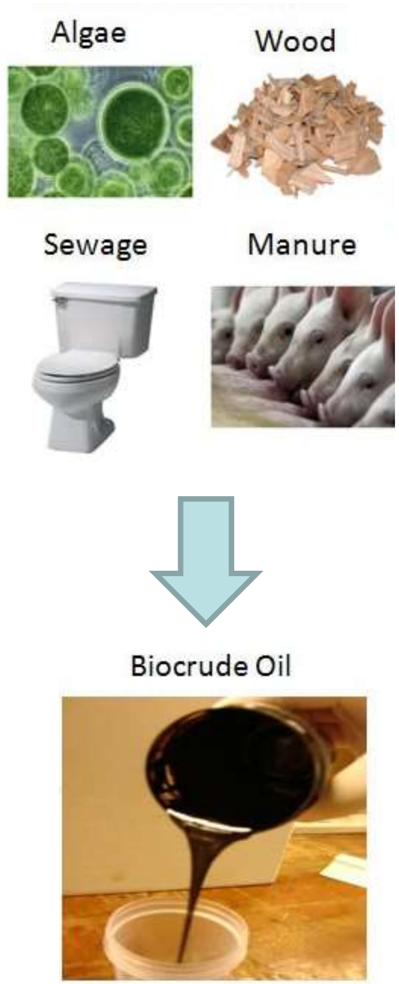
Overview of Hydrothermal Liquefaction



Organic Material → Conversion → Hydrocarbon & Monomer Products

Advantages of Hydrothermal Liquefaction

- Accommodation of water.
  - Single phase system avoids enthalpedic loses of vaporization and/or distillation of water.
- Robust conversion process.
  - A wide variety of organic feedstocks.
  - Gaseous or liquid products.
- Advantageous subcritical conditions.
  - Tunable reaction conditions aide efficiency.
  - Catalytic effect of water enhances conversion.
- Sterilization of product stream.
  - Bio-hazard handling.
    - Bird flu, H1N1, Mad Cow, ect.
    - 22D destruction of infectious prions. (0.1^22 survive)



Continuous Catalytic Hydrothermal Conversion System

- Fast heating element to solve the fouling problem, large reactor to prevent plugging.

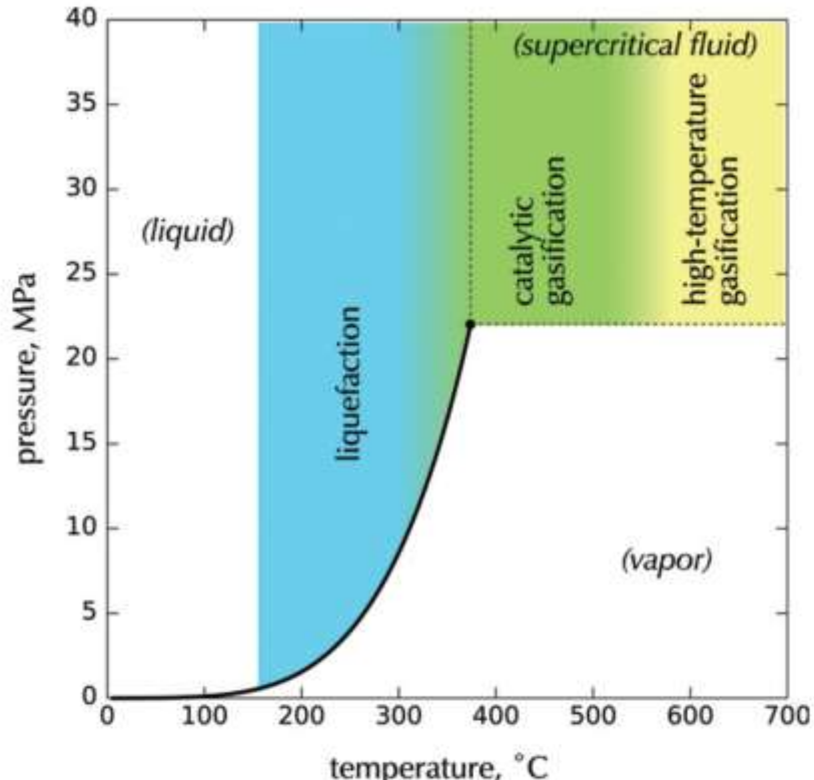
esy: BEEMS project

Hydrothermal Processing: Basics

- Replicate & enhance the extreme environmental conditions which transformed ancient biomass into petroleum crude.
- **Three** major conversion realms.

1. *Liquefaction/pyrolysis*
   - Moderate temperature with suitable pressures to keep water in liquid state
2. *Catalytic Gasification*
   - Partial gasification and thermolysis at high temperature
3. *High-temperature Gasification*
   - Complete thermolysis and non-catalytic reformation occurs

- Critical pt. of H_20 : 374 ˚C @ 22MPa



*Source: P*eterson, A. A., Vogel, F., Lachance, R. P., Froling, M., Antal, M. J., & Tester, J. W. (2008). Thermochemical biofuel production in hydrothermal media: A review of sub- and supercritical water technologies. *Energy and Environmental Science*, 32-65.

Hydrothermal Liquefaction

- This process is similar to pyrolysis, except that it occurs in presence of water at high temperatures (525-600K) and pressures (5-20MPa) generally in presence of catalysts. Suitable for feedstocks that have high moisture content.
    - Above the critical temperature (373.95 C) and pressure (22.064 MPa) has reduced dielectric constant. This enables solvation of small organic molecules and allows organic reactions to occur in single phase.
    - At higher temperature (>280C) ionization of water decreases leading to higher hydronium ion concentrations accelerating the rates of acid-catalyzed decomposition reactions.
    - Hydrothermal processing at lower temperatures (~200C) leads to formation of hydrochar. Higher temperatures (~350 C) leads to bio-oil formation. Higher temperatures (~600C) lead to formation of gaseous products (syngas).

Hydrothermal Liquefaction

- Catalysts are used to improve the yields of bio-oils.
  - Na_2CO_3 is the most common homogeneous catalyst used.
  - Heterogeneous catalysts (based on Ni and Ru metals and alloys)

Table 4. Upgrading conditions for optimizing various bio-crude properties and the relative importance of the different process variables

Property	Optimal conditions	Relative importance of factors investigated
wt% O (low)	530 °C, 6 h, Mo_2C, 20%	T > catalyst loading > t > catalyst type
wt% N (low)	530 °C, 6 h, HZSM-5, 10%	T > t > catalyst loading > catalyst type
H/C (high)	430 °C, 2 h, Pt/C, 10%	T > t > catalyst type > catalyst loading
O/C (low)	530 °C, 6 h, Mo_2C, 20%	T > catalyst loading > t > catalyst type
N/C (low)	530 °C, 6 h, Pt/C, 10%	T > t > catalyst loading > catalyst type
HHV (high)	430 °C, 6 h, Mo_2C, 20%	T > catalyst loading > t > catalyst type
Total area % of fatty acids (low)	530 °C, 6 h, HZSM-5, 20%	T > catalyst type > t > catalyst loading
Total area % of saturated compounds (high)	430 °C, 4 h, Mo_2C, 10%	T > catalyst type > catalyst loading > t
Total area % of N-containing compounds (low)	530 °C, 2 h, HZSM-5, 10%	T > catalyst type > t > catalyst loading
Total area % of N,O-containing compounds (low)	530 °C, 6 h, HZSM-5, 10%	T > catalyst type > t > catalyst loading

Note: Reprinted by permission of The Royal Society of Chemistry. Duan P, Savage PE. Catalytic treatment of crude algal bio-oil in supercritical water: optimization studies. Energy Environ Sci. 2011; 4:1447–1456. doi:10.1039/C0EE00343C.

Ref: Yeh et al. 2012.

Hydrothermal Liquefaction

- **Mechanism of hydrothermal liquefaction**
  - formate formation from carbonate

$$Na_2CO_3 + H_2O + CO \rightarrow 2HCO_2Na + CO_2$$

sodium carbonate *sodium formate*

  - dehydration of hydroxyl groups to carbonyl compounds via enols, and Reduction of carbonyl group to an alcohol

$$HCO_2Na + C_6H_{10}O_5 \rightarrow C_6H_{10}O_4 + NaHCO_3$$

woody biomass *oil* *bicarbonate*

$$H_2 + C_6H_{10}O_5 \rightarrow C_6H_{10}O_4 + H_2O$$

  - Regeneration of formate

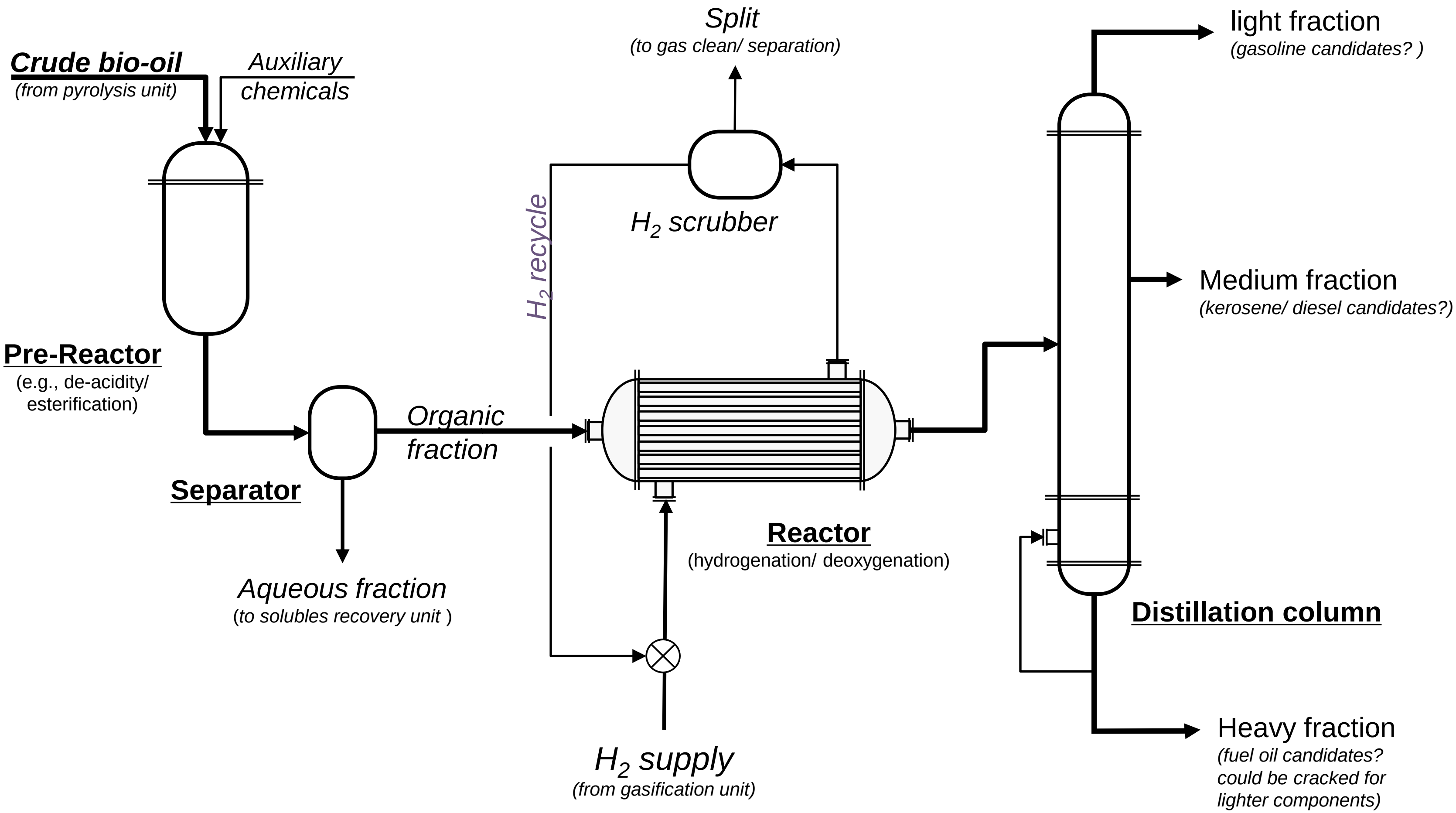
$$NaHCO_3 + CO \rightarrow HCO_2Na + CO_2$$

  - Regeneration of hydrogen

$$HCO_2Na + H_2O \rightarrow NaHCO_3 + H_2$$

Courtesy: BEEMS project

Pyrolysis Products: Bio-oil Upgrading



Courtesy: BEEMS project

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10. Youtube video on Gasifies Experimental Kit: http://www.youtube.com/watch?v=MRMFTzqzWhw&feature=youtu.be

Thank you