



IIT ROORKEE



NPTEL ONLINE
CERTIFICATION COURSE

WASTE TO ENERGY CONVERSION

ENERGY PRODUCTION FROM WASTES THROUGH PYROLYSIS-1

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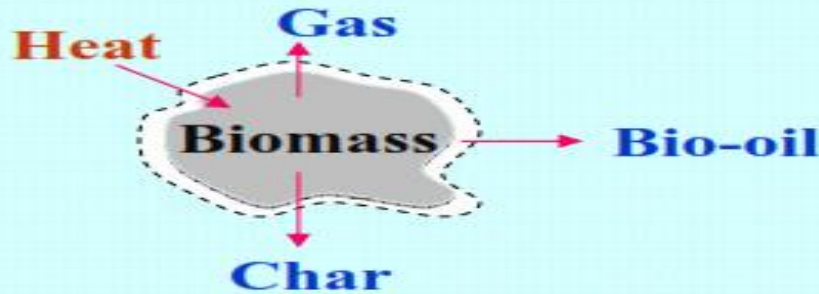
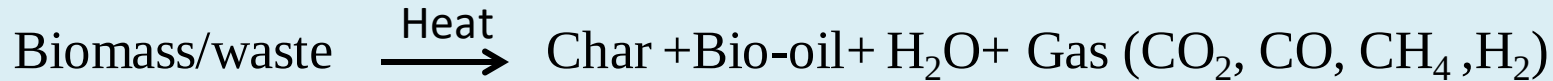
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Pyrolysis

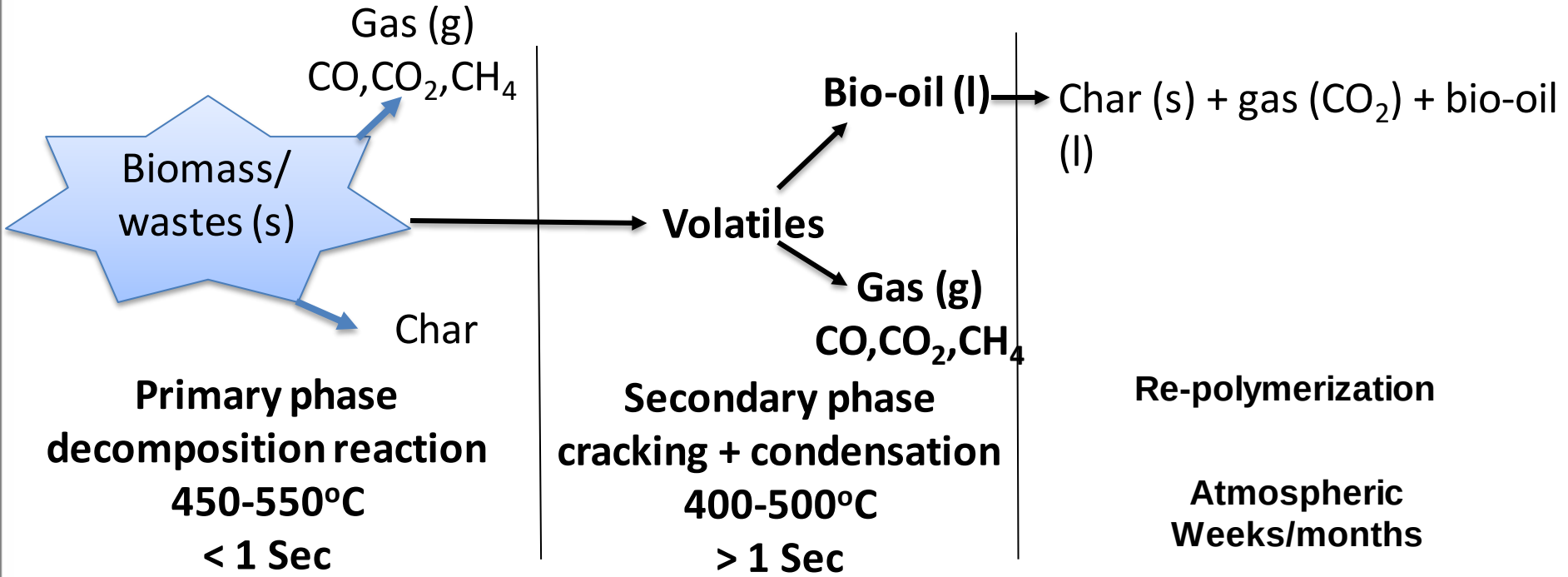
Definition of pyrolysis

- Pyrolysis = pyro (fire) + lysis (cutting)
- Thermal decomposition of carbonaceous material by the heat in absence of oxygen



- It is the first step of gasification and combustion process
- It is the only thermochemical process which converts different types of biomass and organic wastes into solid, liquid and gaseous fuel

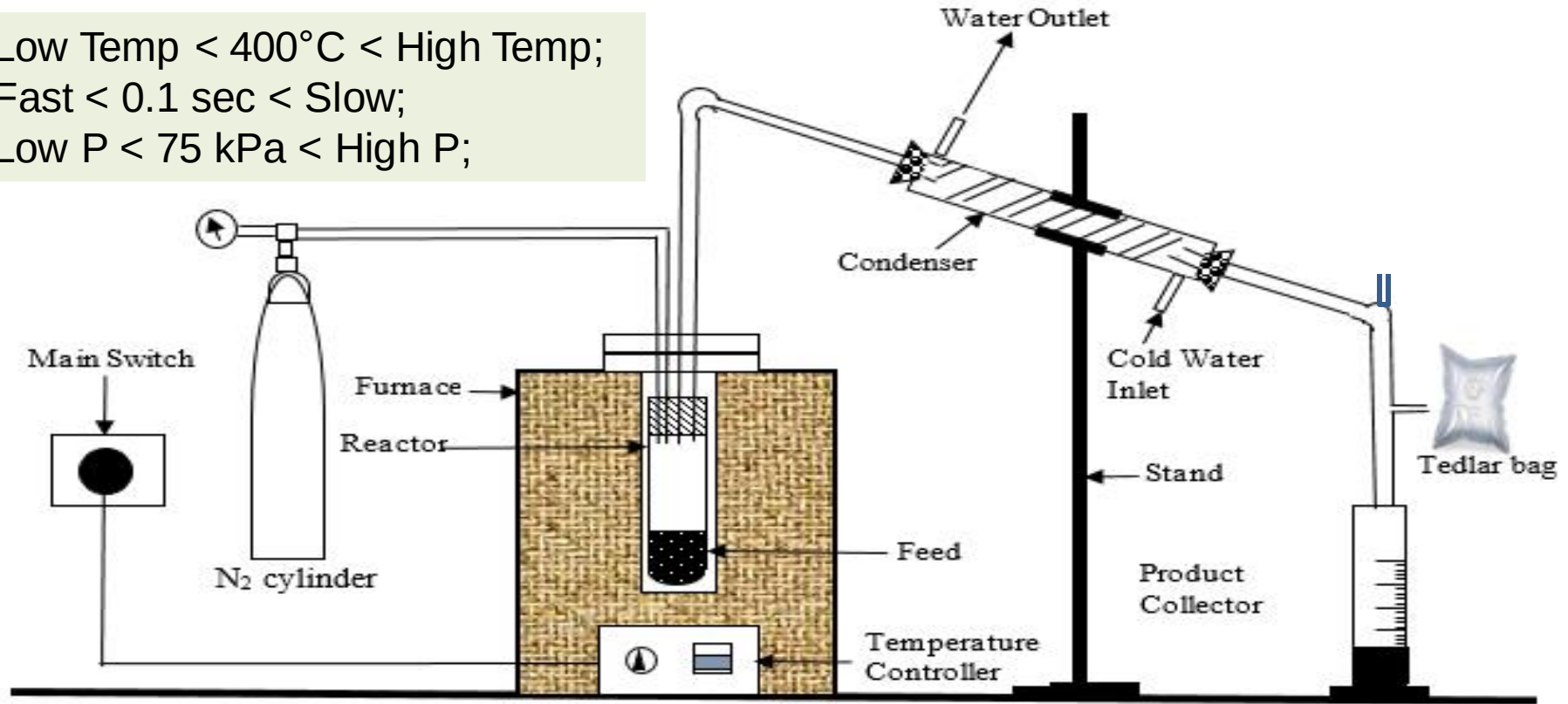
Pyrolysis Mechanism



- Product's selectivity depends on operating conditions such as
- ✓ Temperature
 - ✓ Residence time
 - ✓ Heating rate
 - ✓ Feed size

Systemic Flow diagram of semi batch pyrolysis reactor

Low Temp $< 400^{\circ}\text{C}$ $<$ High Temp;
Fast $< 0.1 \text{ sec}$ $<$ Slow;
Low P $< 75 \text{ kPa}$ $<$ High P;



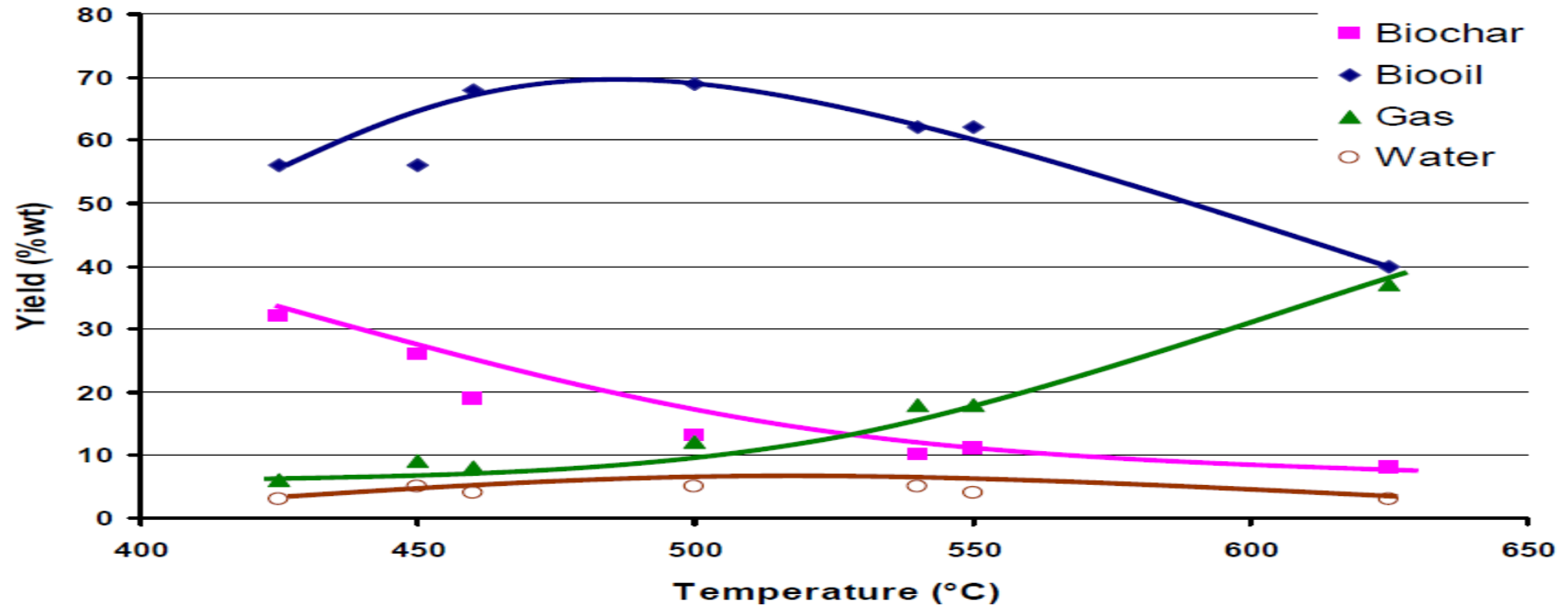
Typical biomass pyrolysis technologies, conditions, and major products

Technology	Temperature Range (° C)	Heating rate	Residence time	Main Products
Carbonization	350-500	Very low	Hours to days	Charcoal
Slow pyrolysis	400-600	Medium	5 to 30 min	Char and gases
	~ 450	Low	Hours	Charcoal, liquid and gases
Fast Pyrolysis	400-650	High	0.5 to 5 seconds	Liquids and gases

Typical biomass pyrolysis technologies, conditions, and major products

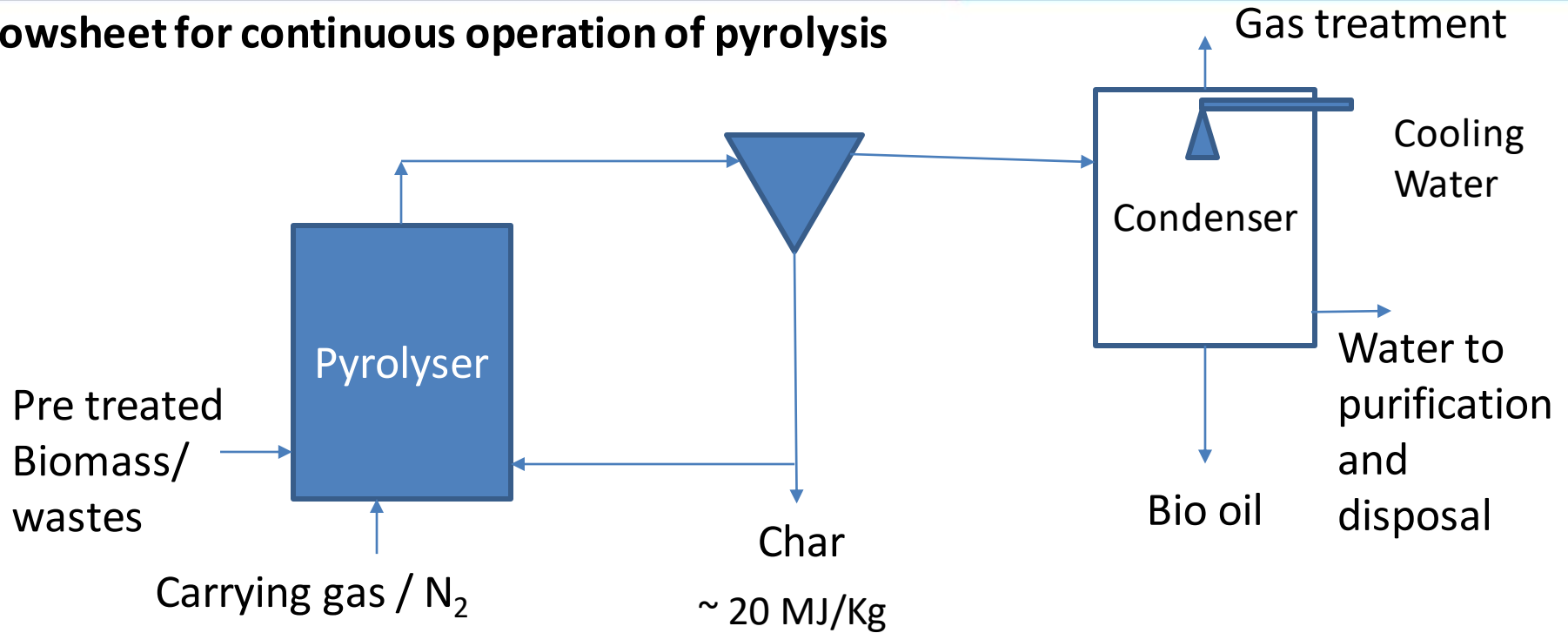
Technology	Temperature Range (° C)	Heating rate	Residence time	Main Products
Flash Pyrolysis	400-650	High	0.1 to 2 seconds	Liquids and gases
	650-900	High	<1 second	Liquids and gases
Ultra Pyrolysis	1000	Very high	<0.5 seconds	Chemicals and gases
Vacuum Pyrolysis	350-400	Medium	2-30 seconds	Liquids
Hydrolysis	<500	High	<10 seconds	Liquids
Methanopyrolysis	>700	High	<10 seconds	Liquids

Relative proportions of end products in pyrolysis of biomass



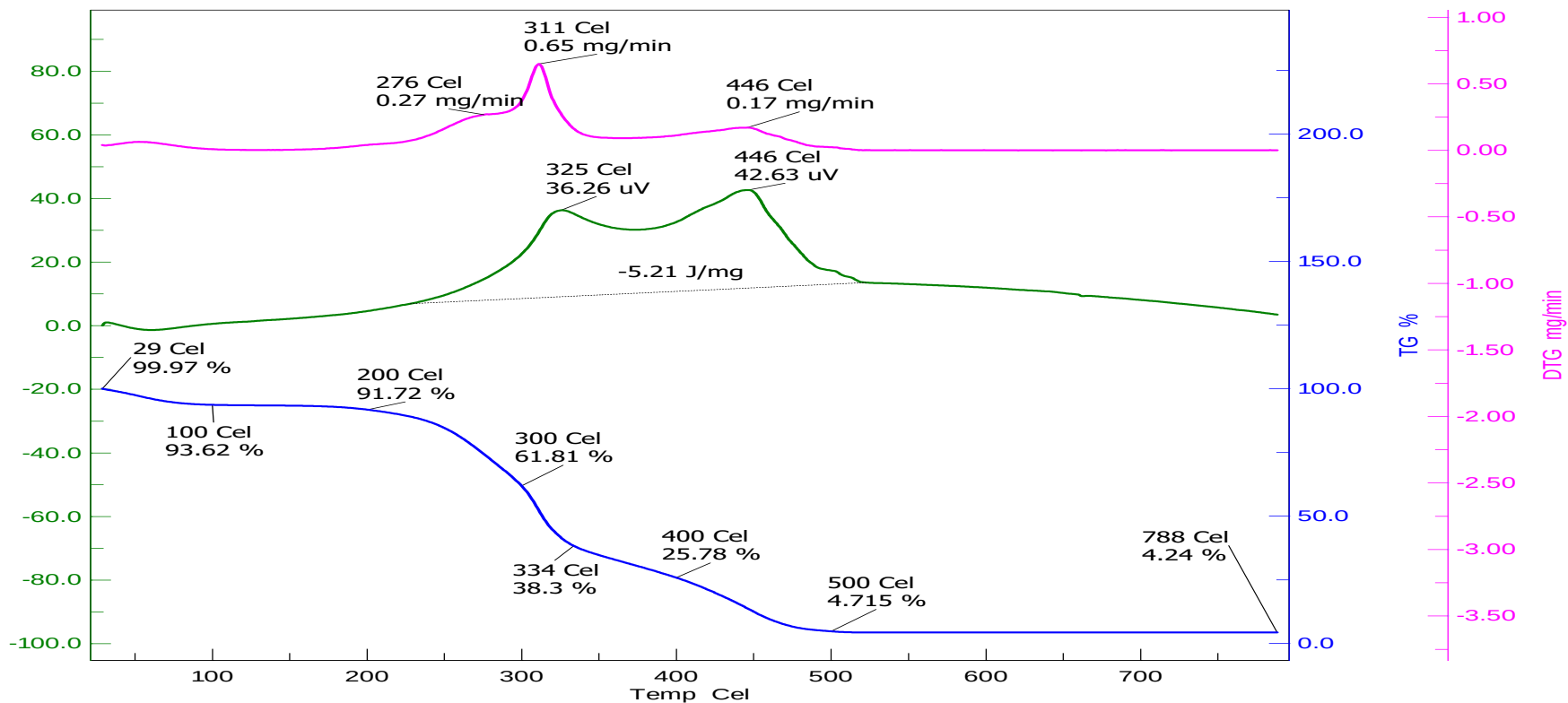
Jahirul et al. 2012, Energies, 5(12), 4952-5001; doi:10.3390/en5124952

Flowsheet for continuous operation of pyrolysis



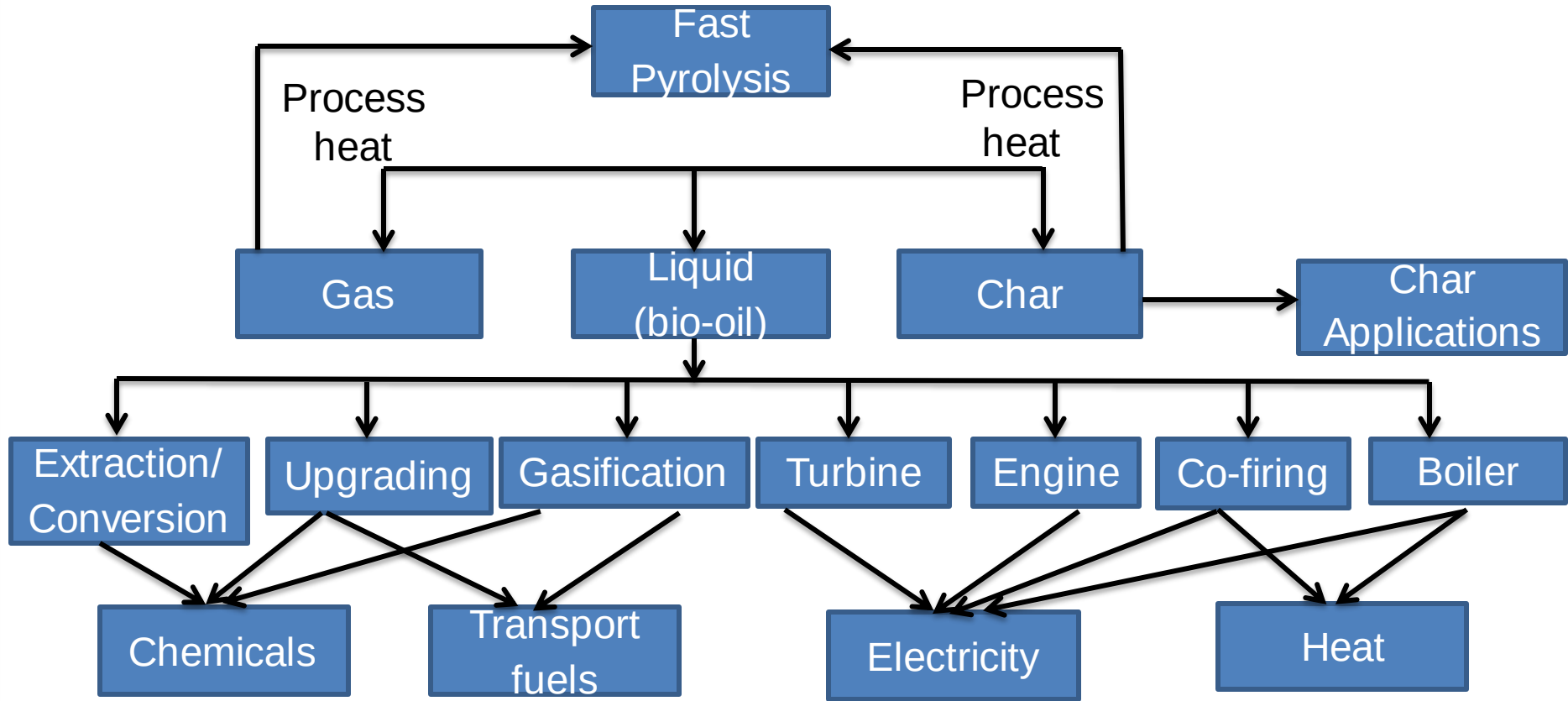
A number of reactions such as cracking, dehydration, dehydrogenation, isomerization, aromatization and condensation take place during pyrolysis (Vamvuka, 2011)

Kinetic evaluation of pyrolysis



TG/DTG/DTA curve sugarcane bagasse in the N₂ atmosphere at heating rate of 10°/min

Applications of pyrolysis products



Various chemicals and fuels from pyrolysis bio-oil

Some chemicals fuels form pyrolysis bio oil are:

Chemicals

Resins

Fertilizer

Flavours

Adhesives

Acetic acid

Industries feedstocks

Fuels

Hydrogen

Upgraded HDO

Fuel via syngas



Some properties of pyrolysis bio-oil and their reasons

Properties		Reasons
Appearance	Dark red-brown to dark green	Micro-carbon and chemical composition in oil
Odor	Distinctive odor an acrid smoky smell	Lower molecular weight aldehydes and acids
Density	Very high compared to fossil fuel Pyrolysis bio-oil: 1.2 kg/liter Fossil oil: 0.85 kg/liter	High moisture and heavy molecule contamination
Viscosity	Can vary from as low as 25 centistokes (cSt) to as high as 1000 cSt	Wide range of feedstock, water content and the amount of light ends collected
Heating value	Significantly lower than fossil oil	High oxygen content



Some properties of pyrolysis bio-oil and their reasons

Properties		Reasons
Aging	Viscosity increase, Volatility decrease, Phase separation and Deposition of gum occur with time	Complex structure with acids, aldehydes, alcohols, sugars, furfural and furans etc. due to the degradation of cellulose and hemicellulose ; phenols, guaiacols, syringols, vanilline, various aromatic compounds and high molecular weight water insoluble compounds from lignin degradation
Miscibility	Miscible with polar solvent but totally immiscible with petroleum fuel	Polar in nature

Comparison of typical bio-oil and diesel characteristics

Physical Property	Bio-oil	Diesel	Comments
Water content (wt.%)	15–30	0.05	Due to original moisture in feedstock; dehydration reaction; and storage Water reduces the heating value and viscosity
Oxygen content (wt.%)	35-40	0	It leads to the lower energy density and immiscibility with hydrocarbon fuels
Low pH	2.5	-	Large amounts of carboxylic acids, such as acetic and formic acids
Viscosity (@ 50°C) cP	40-100	4	Important for fuel injection system and combustion properties of fuel
HHV (MJ/kg)	16-19	45	Low HHV due to high oxygen content
Ash content (wt.%)	0-0.2	0.01	Alkali metals in ash can causes corrosion problem



Advantages and disadvantages of Bio oil

Advantages

- Carbon neutrality
- Utilizes otherwise waste biomass
- Possibility of utilization in small-scale power generation systems as well as use in large power stations
- Storability and transportability of liquid fuel
- High-energy density compared to biomass gasification fuel
- Potential of using pyrolysis liquid in existing power plants



Disadvantages of pyrolysis oil and some issues

- Oxygen content results in low energy density
- Bio-oil is unstable due to more oxygen content
- It can swell and soften natural or synthetic rubbers and corrode the metal component
- New deoxygenating catalyst need to be developed that are greater than 95% selective
- Technical requirements for converting biomass to high yields of liquid bio-oil
- Reactor designs capable of meeting technical requirements
- Product specifications and standards that need to be established
- Applications for using bio-oil in existing or modified end use devices
- Environmental, safety, and health issues



Pyrolysis bio oil upgradation

Physical methods

- Filtration for char removal
- Emulsification with hydrocarbons
- Solvent addition

Chemical Methods

- Reaction with alcohols
- Catalytic deoxygenation
 - Hydrotreating
 - Catalytic (zeolite) vapor cracking

- Bio-oil contains heavy compounds with long carbon chain, low H/C ratio and high O/C ratio.
- Upgrading is done to remove oxygenated compounds responsible for reducing the quality of the bio- oil either through hydrotreating or catalytic cracking.
- Hydrotreating is performed at a temperature of around 350°C, under high pressure of hydrogen, in presence of heterogeneous Co–Mo, Ni–Mo based cat.



Catalytic pyrolysis

Catalytic pyrolysis is operated at atmospheric pressure, wide variety of catalyst available based on the product needed and can be integrated in the unit used for pyrolysis (Zhang et al., 2009a; French and Czernik, 2010; Park et al., 2011).

The main aim of catalytic cracking is to reduce acidity, viscosity, oxygen content, increase heating value and produce low carbon chain compounds.

Zeolite based catalyst which contains the suitable porous structure and acidic properties are often used for biomass pyrolysis (Bulushev and Ross, 2011)

Some catalyst used in the past for biomass pyrolysis are Si-SBA-15, Al-SBA-15 (Cho et al., 2011); ZSM-5 zeolite (López et al., 2011); H-ZSM-5-28 and H-ZSM-5-80 (Azeez et al., 2011); H-ZSM-5 (Agblevor et al., 2010b); nickel, cobalt, iron, and gallium-substituted ZSM-5 (French and Czernik, 2010) etc.



Thanks...

