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FACULTY OF
BIOSCIENCE ENGINEERING

DEPARTMENT GREEN CHEMISTRY AND TECHNOLOGY
RESEARCH GROUP - THERMOCHEMICAL CONVERSION OF BIOMASS

INTRODUCTION TO FAST PYROLYSIS: HOW DOES IT WORK AND WHY IT SHOULD BE USED

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Bio4Products Webinar: “From biomass to biobased products:
#2 Developing a pyrolysis-based biorefinery”

BIO4PRODUCTS
Creating sustainable resources for process industry

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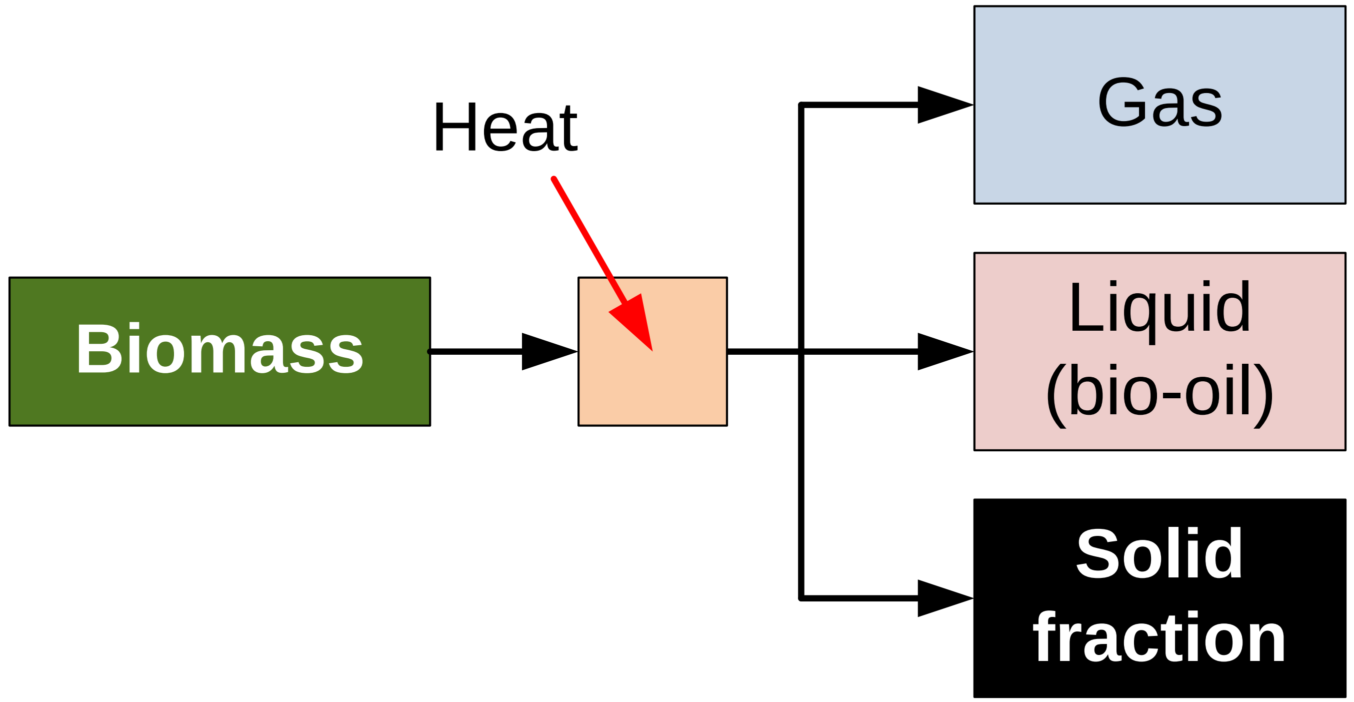
FAST PYROLYSIS: INTRODUCTION

Principle of fast pyrolysis

- The decomposition of biomass by heating in an oxygen-free or oxygen-limited environment
- Results in the production of three phases: gas, condensable vapours (leading up to bio-oil) and char (biochar)
- Gases and volatiles driven out of the biomass particles due to pressure built up in the particle
- Fast reactions, but in practice heat and mass transfer limitations occur affecting product distribution



FAST PYROLYSIS: INTRODUCTION

Based on the process condition (temperature, heating rate and atmosphere) the following conversion processes can be distinguished:

Type	Temp (°C)	Vapor residence time	Heat source	Char yield (*wt.*%)	Liquid yield (*wt.*%)	Gas yield (*wt.*%)
Slow pyrolysis	300-500	5-30 min	external/ internal (oxygen addition)	35 %	30 %	35 %
Intermediate pyrolysis	500	10-20 s	external	20 %	50 %	30 %
Fast pyrolysis	500-600	1 s	external	12 %	75 %	13 %
Torrefaction (partial pyrolysis)	< 300	minutes	external	80 %	5 %	15 %
Gasification	> 750	10-20 s	internal (oxygen addition)	10 %	5 %	85 %

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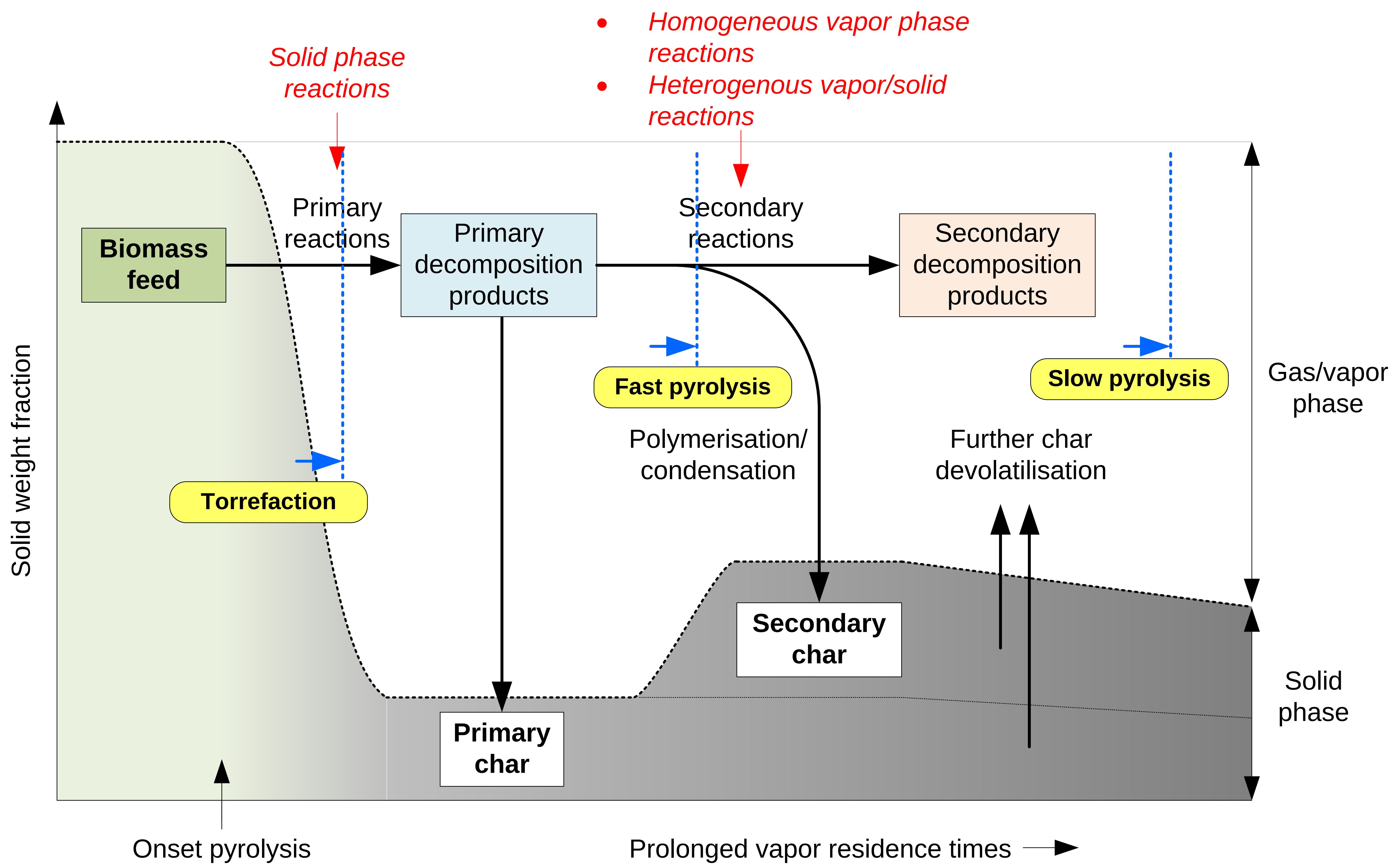
FAST PYROLYSIS: REACTIONS

Principle of fast pyrolysis

- Simplified reaction scheme
- Discern between primary and secondary decomposition reactions
  - **Primary reactions**
    - The decomposition of polymers (cellulose, hemicellulose and lignin) within the solid cell wall
    - Depolymerisation, fragmentation and rearrangement reactions
    - Highly endothermic
  - **Secondary reactions**
    - Primary decomposition products are not stable and could further undergo transformation
    - Cracking and condensation reactions
    - Increase the share of non-condensable gases and char at the expense of condensable organic compounds
    - Homogeneous and heterogeneous reactions (catalyzed by char and mineral compounds
    - Exothermic reactions

FAST PYROLYSIS: REACTIONS AND REACTION CONDITIONS



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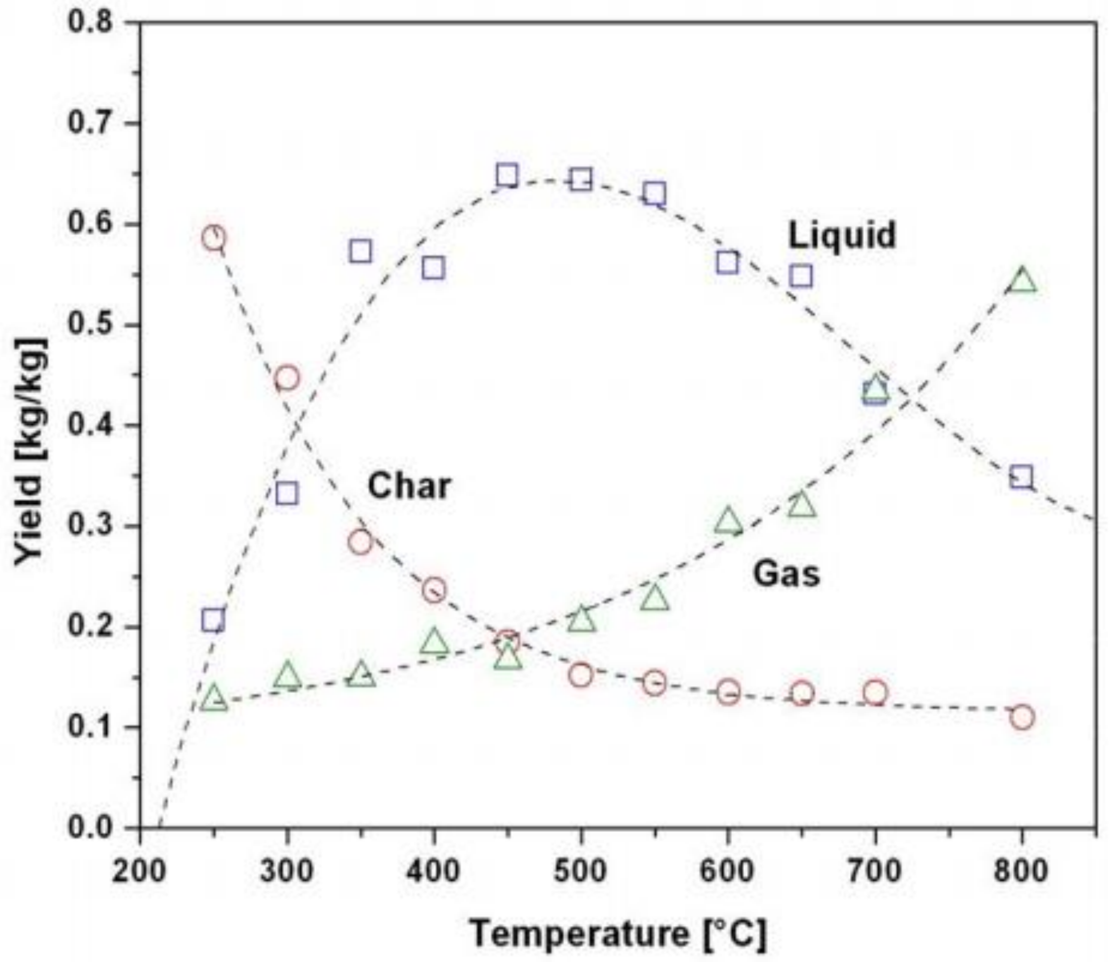
FAST PYROLYSIS: REACTIONS AND REACTION CONDITIONS

In fast pyrolysis, we want to maximize the yield in volatiles (minimize char/gas)

Hence, suppressing secondary pyrolysis reactions:

- Temperature ~ 500°C
- Fast heating of particles (up to 100°C/s)
- So small particles are only suitable (max. 3 mm → need to grind biomass)
- Pressure = 1 atm.
- Short vapor residence time (<2 s)
- Short but sufficient biomass residence time (>10 s)



Effect of pyrolysis temperature on gas/liquid/char yield (fluidized bed, 3 mm pine wood as feedstock)

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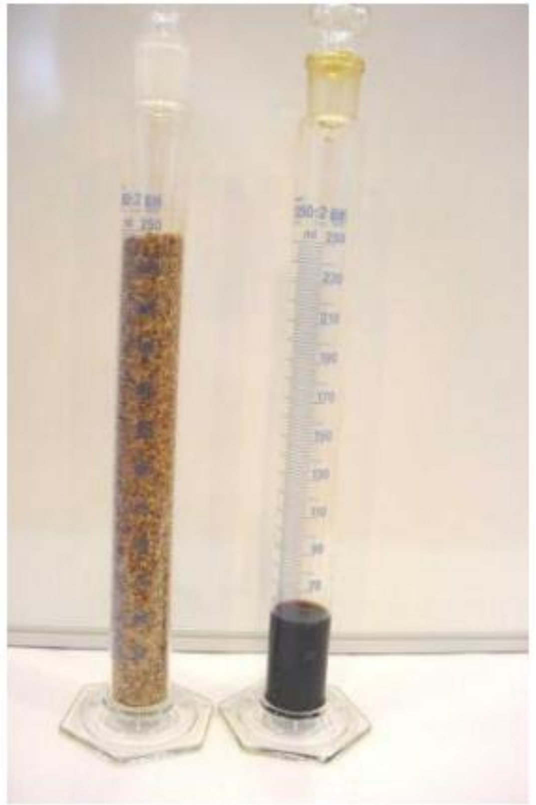
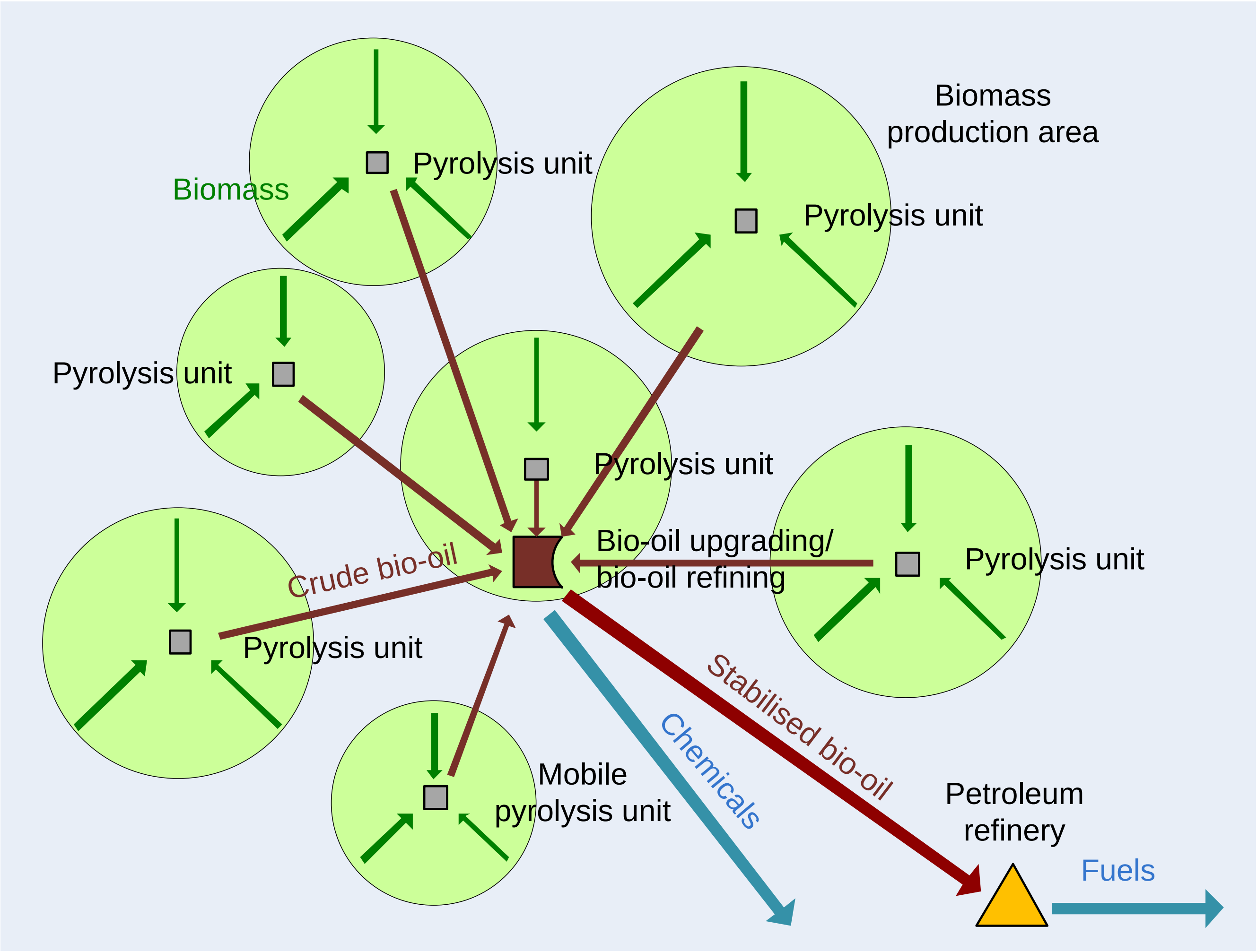
FAST PYROLYSIS: WHY ?

- **Energy densification**: Bio-oil, on a mass basis, has a HHV (higher heating value) equal to its parent biomass (18 ~ 20 MJ/kg for wood and wood bio-oil). However, density of bio-oil is ~ 1.1 kg/L – as such HHV on a volume basis can increase
- A **liquid** (bio-oil) is easier and more cheap to handle (transport, storage) than a bulk solid (parent biomass): local processing of biomass into liquid and central collection of liquid: cheaper logistics
- The bio-oil is virtually **free from mineral** compounds
- **Decoupling** of the conversion of biomass and the application of the bio-oil, both in time and space
- **Flexibility in applications** (see later)

Source: BTG





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FAST PYROLYSIS: WHY ?

Fast pyrolysis oil properties

- Combustible, HHV ~ 18 MJ/kg (half of that of petroleum)
- Rich in oxygenated organic compounds (same amount of O as the original biomass)
- 10 to 15 wt% water
- Highly corrosive, pH ~ 2
- Non distillable
- Unstable ('ageing' = polymerization bio-oil constituents during storage, deteriorating quality of the oil)
- Immiscible with hydrocarbons (unless use of surfanctans)
- Low cetane number (10 ~ 25)

Source: Piskorz, J., et al. In Pyrolysis Oils from Biomass, Soltes, E. J., Milne, T. A., Eds., ACS Symposium Series 376, 1988.	**White Spruce**	**Poplar**
Moisture content, wt%	7.0	3.3
Particle size, µm (max)	1000	590
Temperature	500	497
Apparent residence time	0.65	0.48
Product Yields, wt %, m.f.		
Water	11.6	12.2
Gas	7.8	10.8
Bio-char	12.2	7.7
Bio-oil	66.5	65.7
Bio-oil composition, wt %, m.f.		
Saccharides	3.3	2.4
Anhydrosugars	6.5	6.8
Aldehydes	10.1	14.0
Furans	0.35	--
Ketones	1.24	1.4
Alcohols	2.0	1.2
Carboxylic acids	11.0	8.5
Water-Soluble – Total Above	34.5	34.3
Pyrolytic Lignin	20.6	16.2
Unaccounted fraction	11.4	15.2

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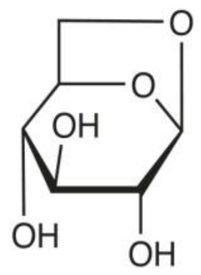
FAST PYROLYSIS: WHY ?

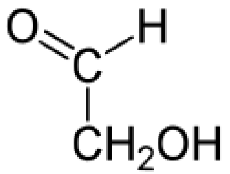
Compared to heavy fuel oil

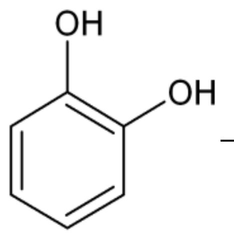
	bio-oil	heavy fuel oil	
vol. energy density	21	39	GJ/m^3
density	1220	963	kg/m^3
viscosity at 50 °C	13	351	mm^2/s
acidity	3	7	pH
water content	20	0.1	wt.%
ash content	0.02	0.03	wt.%
C	52	86	wt.%
H	7	10	wt.%
O	40	0.5	wt.%
N	0.1	0.6	wt.%
S	< 0.1	2	wt.%

FAST PYROLYSIS: WHY ?

Chemical composition (maximally reported concentrations)

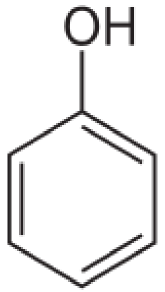


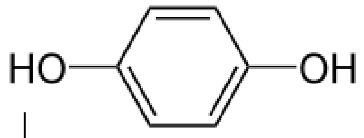


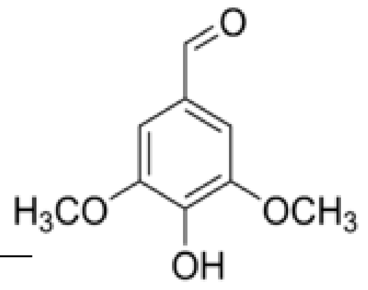


Compound		*wt.%*	Compound		*wt.%*
Levoglucosan	🔵	30.4	Formaldehyde	🔵	2.4
Hydroxyacetaldehyde	🔵	15.4	Phenol	🔴	2.1
Acetic acid	🔵 🔴	10.1	Propionic acid	🔵 🔴	2.0
Formic acid	🔵	9.1	Acetone	🔵	2.0
Acetaldehyde	🔵	8.5	Methylcyclopenten-2-one	🔵	1.9
Furfurylalcohol	🔵	5.2	Methyl formiate	🔵	1.9
Catechol	🔴	5.0	Hydroquinone	🔴	1.9
Methylglyoxal	🔵	4.0	Acetol	🔵	1.7
Ethanol	🔵	3.6	Angelica lactone	🔵	1.6
Cellobiosan	🔵	3.2	Syringaldehyde	🔴	1.5
1,6-anhydroglucofuranose	🔵	3.1	Methanol	🔵 🔴	1.4

🔵 Cellulose/hemicellulose derived 🔴 Lignin derived







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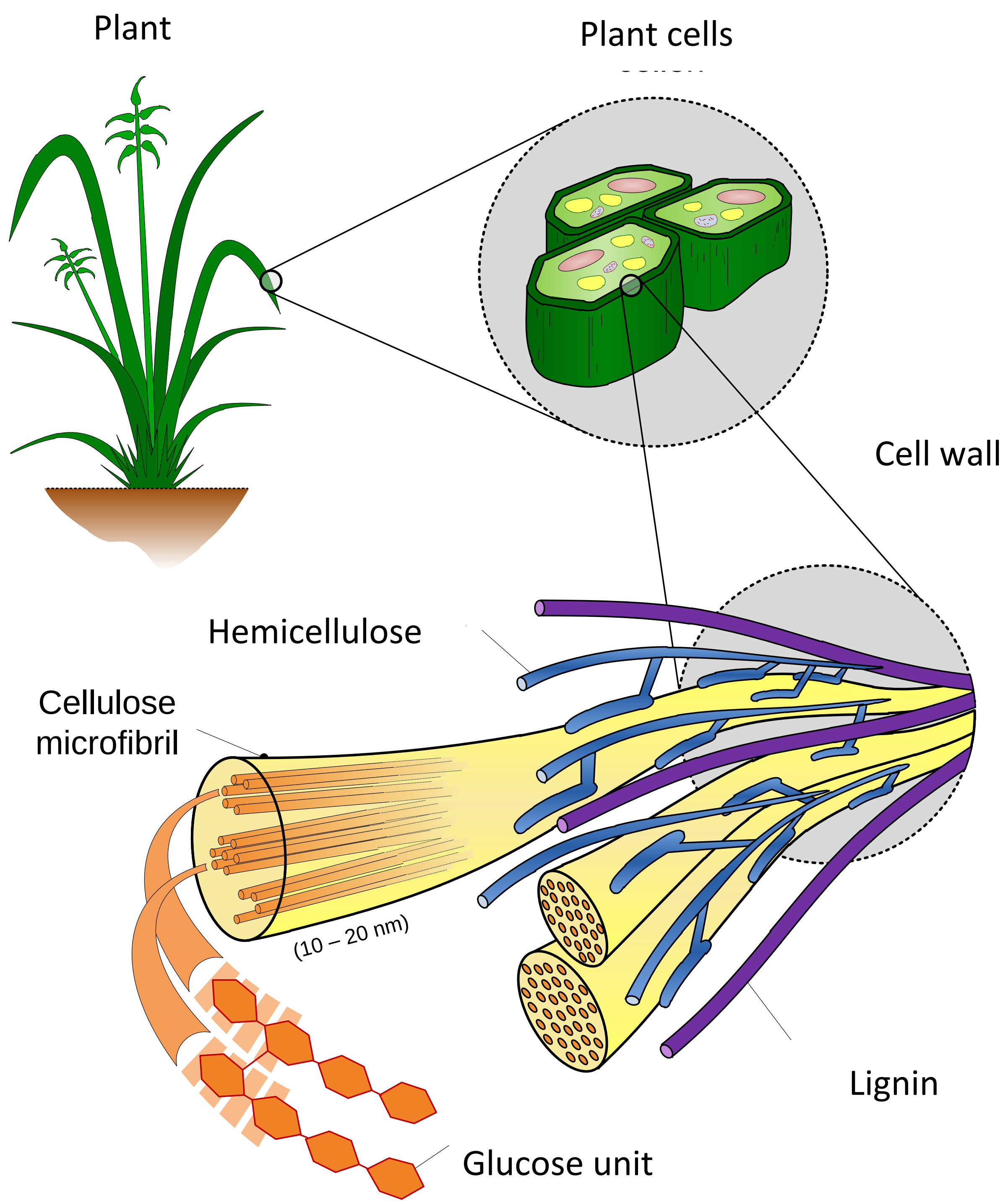
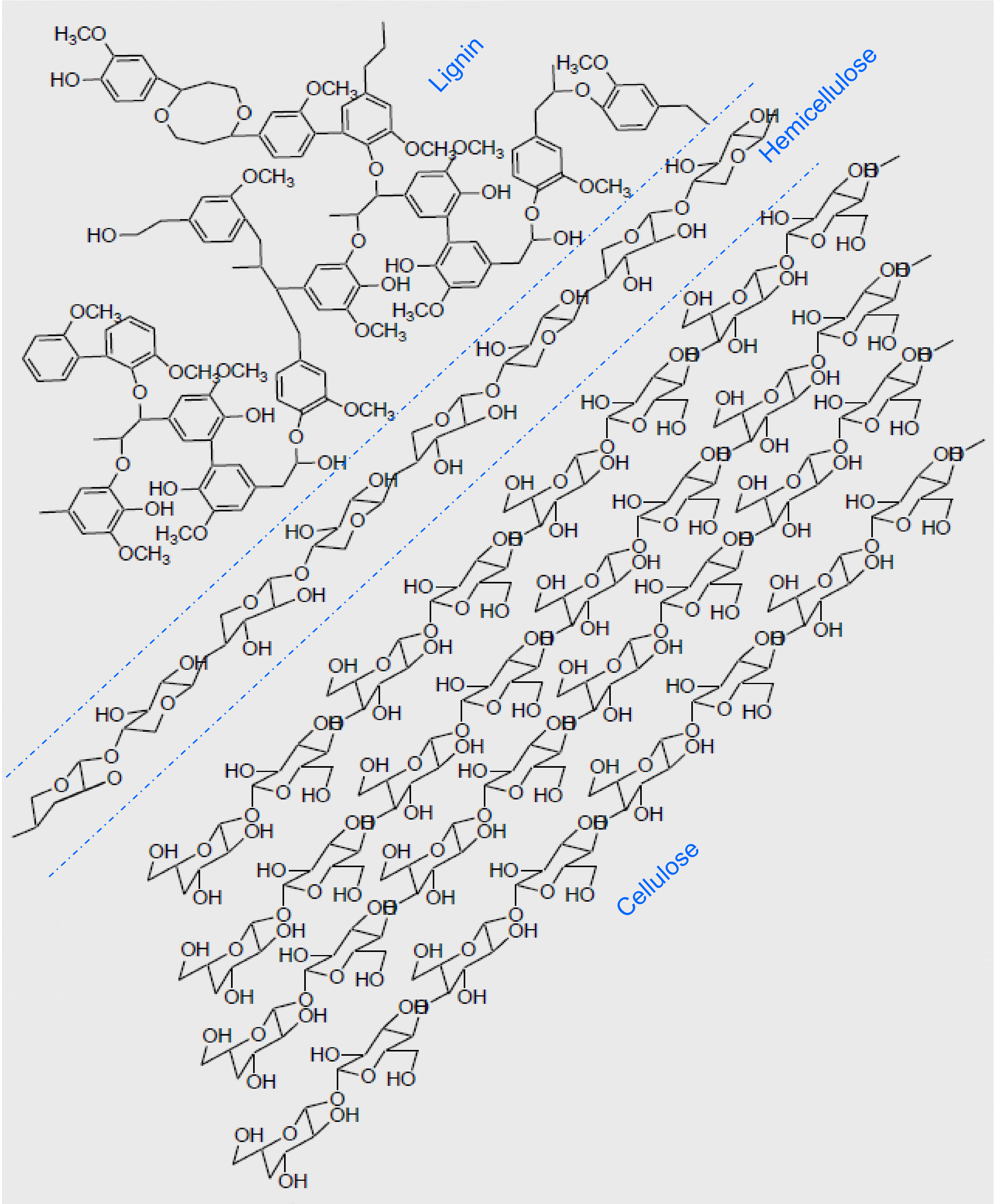
FAST PYROLYSIS: WHY ?

- Link biomass composition <> pyrolysis reactions





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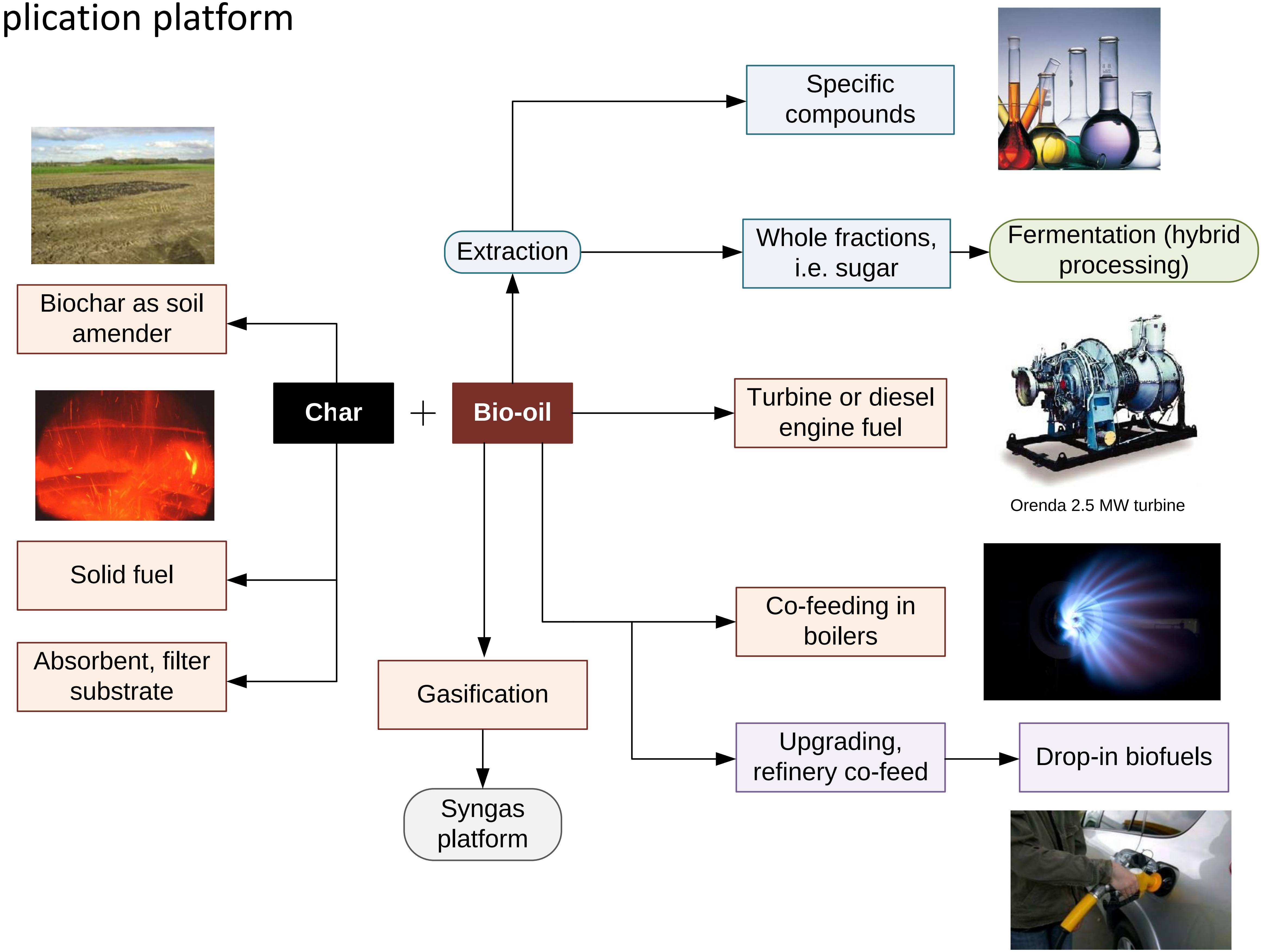
FAST PYROLYSIS: WHY ?

A versatile application platform



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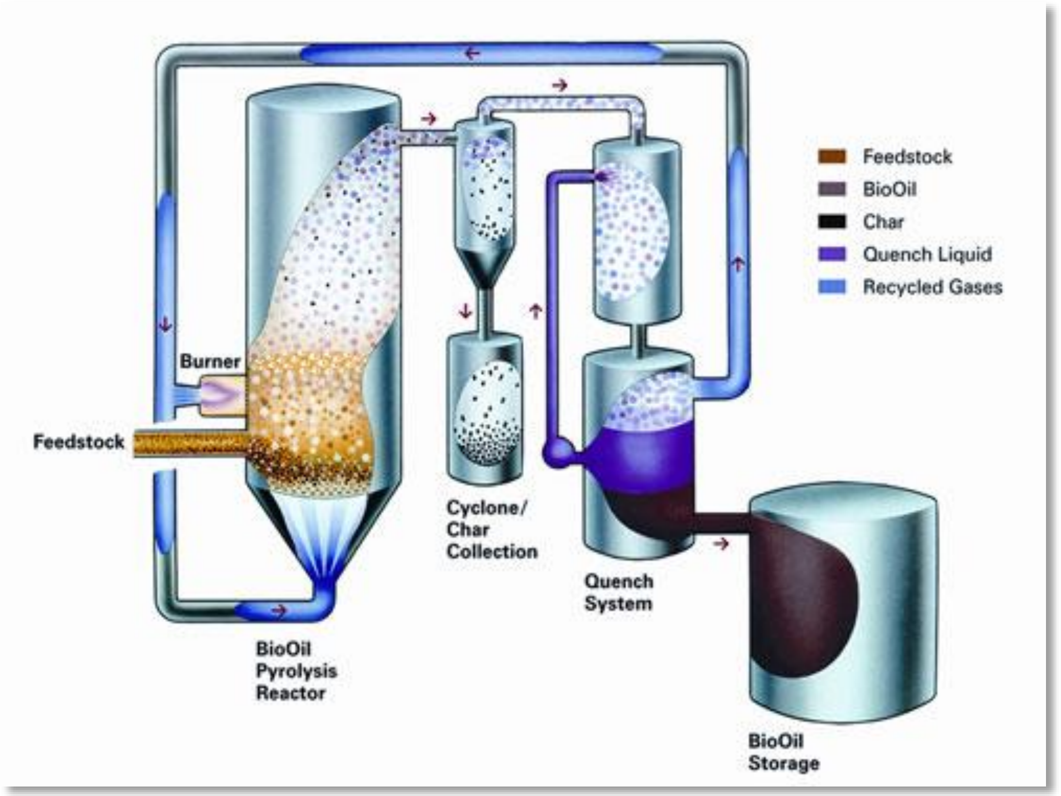
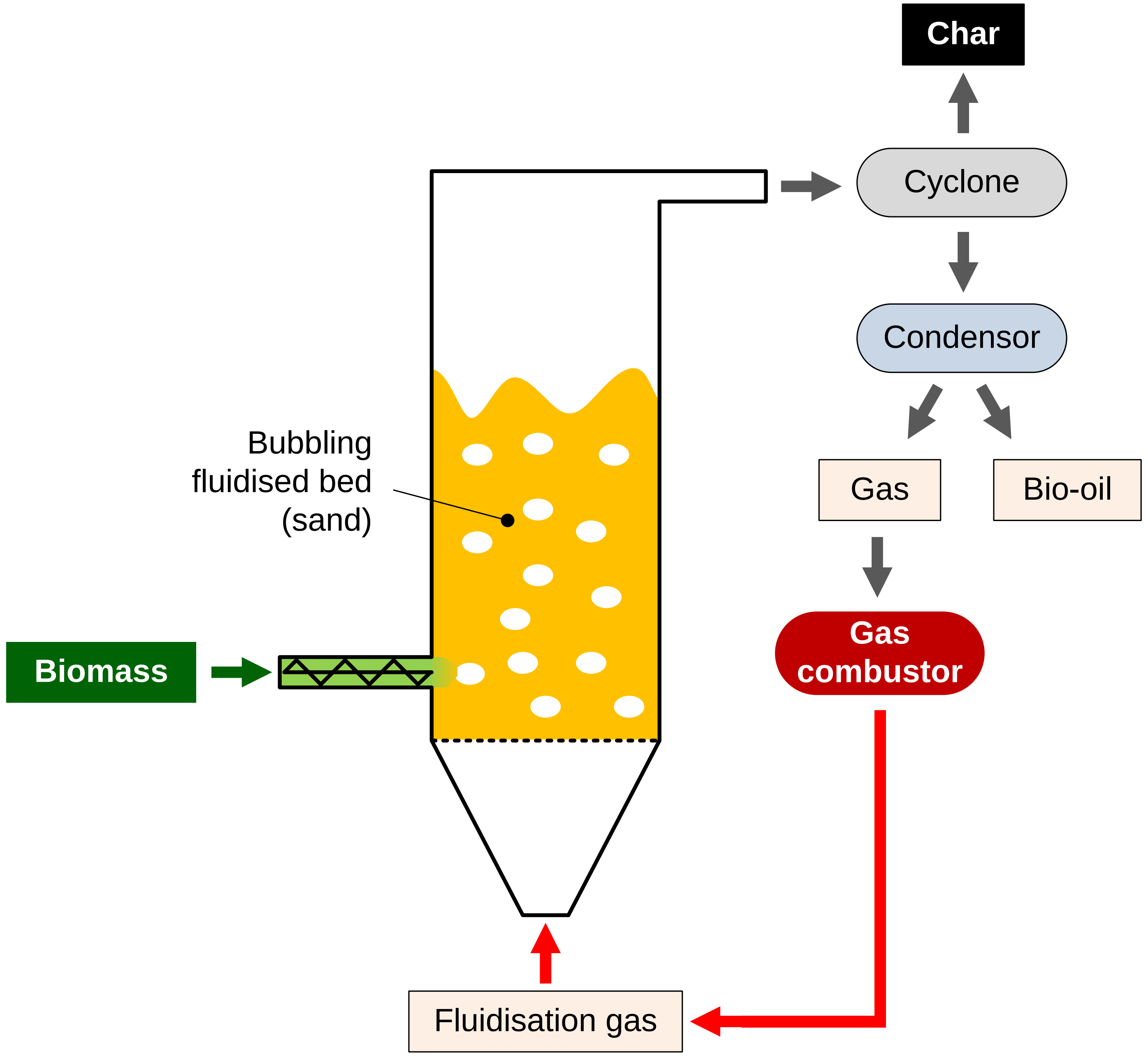
FAST PYROLYSIS: REACTOR TYPES

How ? Typical reactor systems, tried and proven on large scale

1. ***Bubbling* fluid bed**

- Fluidized bed of heat carrier (e.g. sand)
- Heat carrier ensures required heat transfer rates
- Char separation using cyclones or hot vapor filtration
- Reheating of heat carrier through gas or char combustion
- Typical commercial example Dynamotive (defunct)



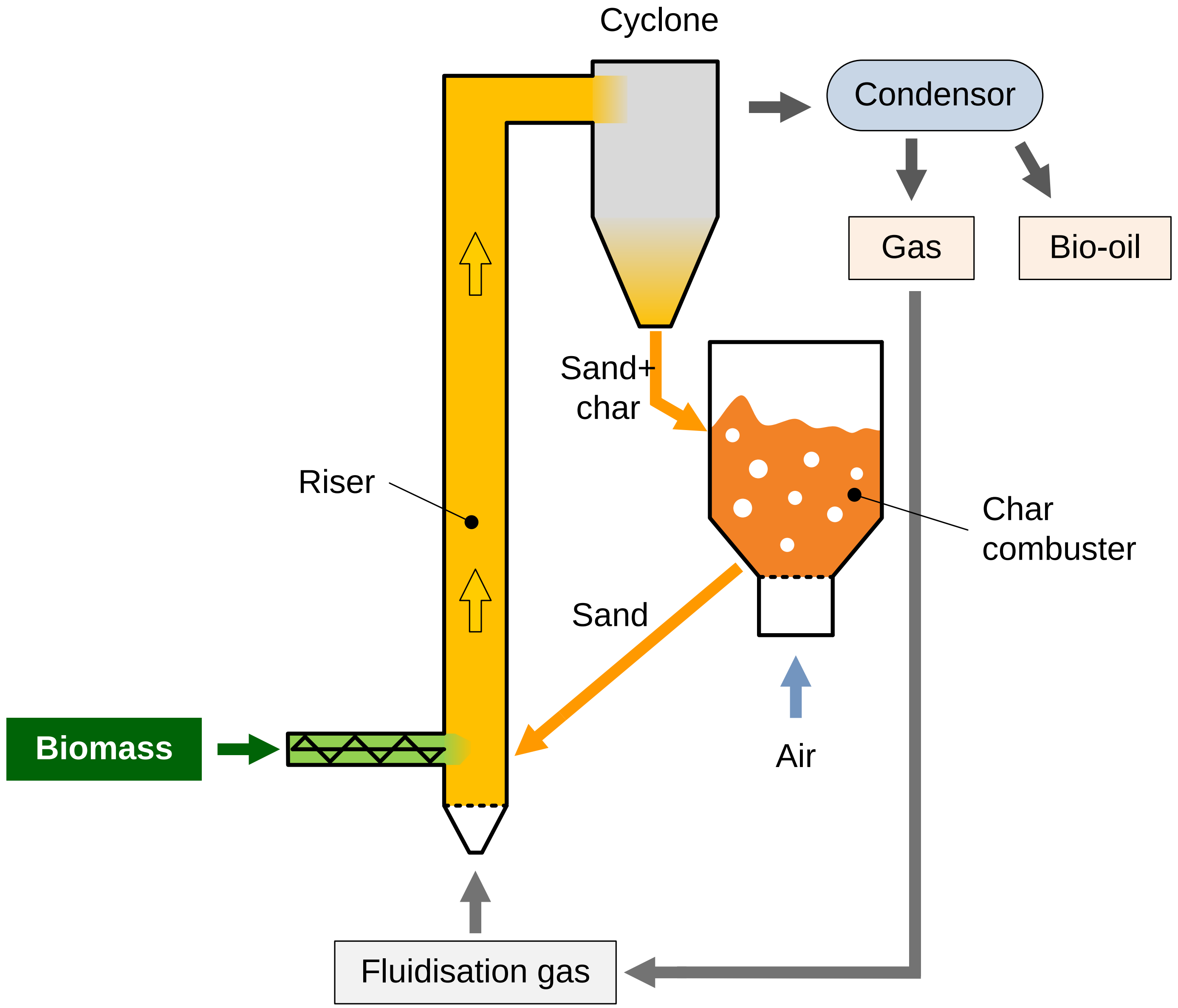


FAST PYROLYSIS: REACTOR TYPES

How ? Typical reactor systems, tried and proven on large scale

2. *Circulating* fluid bed

- Circulating fluidized bed of heat carrier (e.g. sand)
- Cyclone separates sand + char from vapor + gas
- Char burnt in a separate combustor
- Burning of char reheats the sand/heat carrier
- Typical commercial example: Ensyn and Metso-VTT



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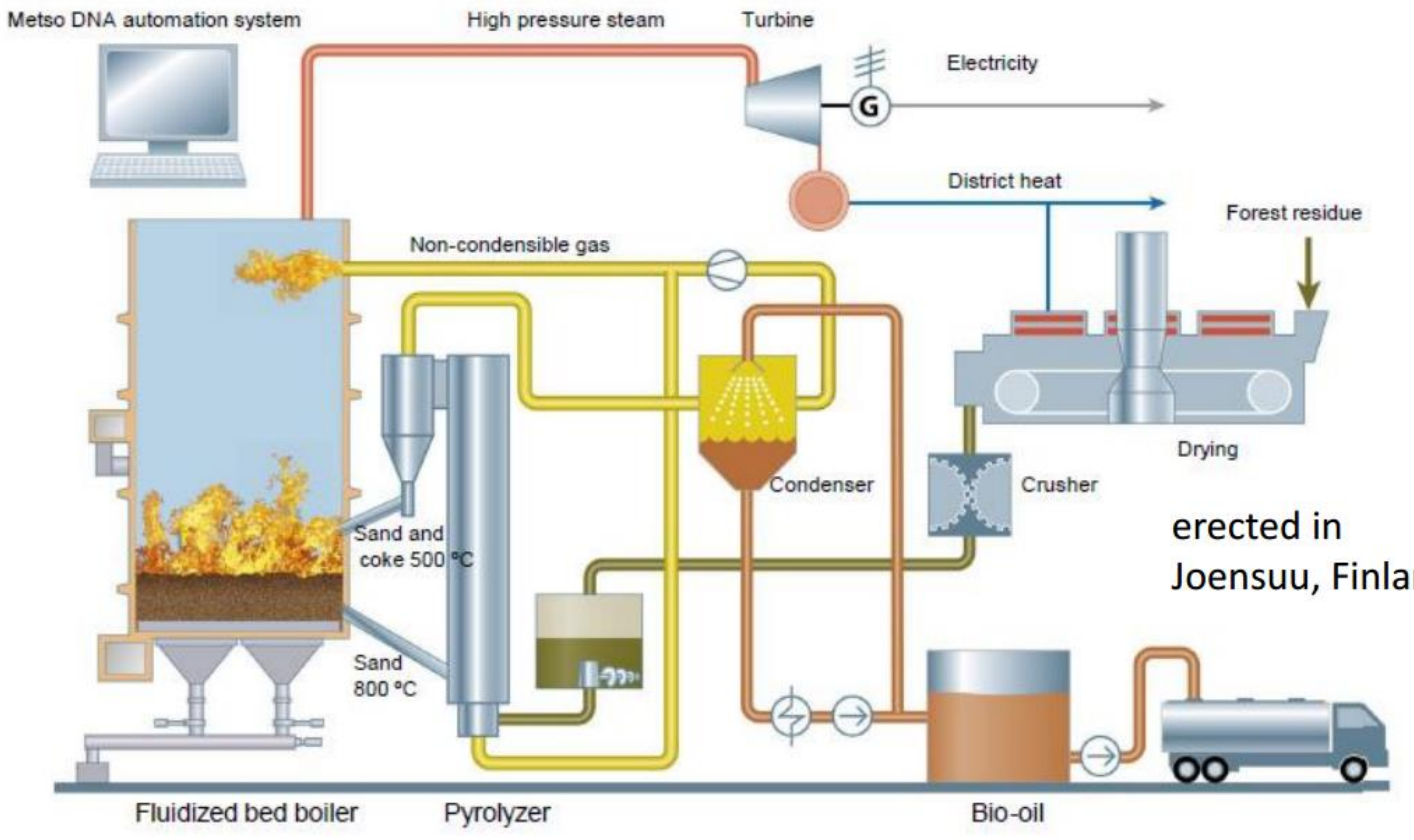
FAST PYROLYSIS: REACTOR TYPES

How ? Typical reactor systems, tried and proven on large scale

2. *Circulating* fluid bed

Metso-VTT system: integrated into a fluidized bed combustor (coal fired power plant) with sand as common heat carrier



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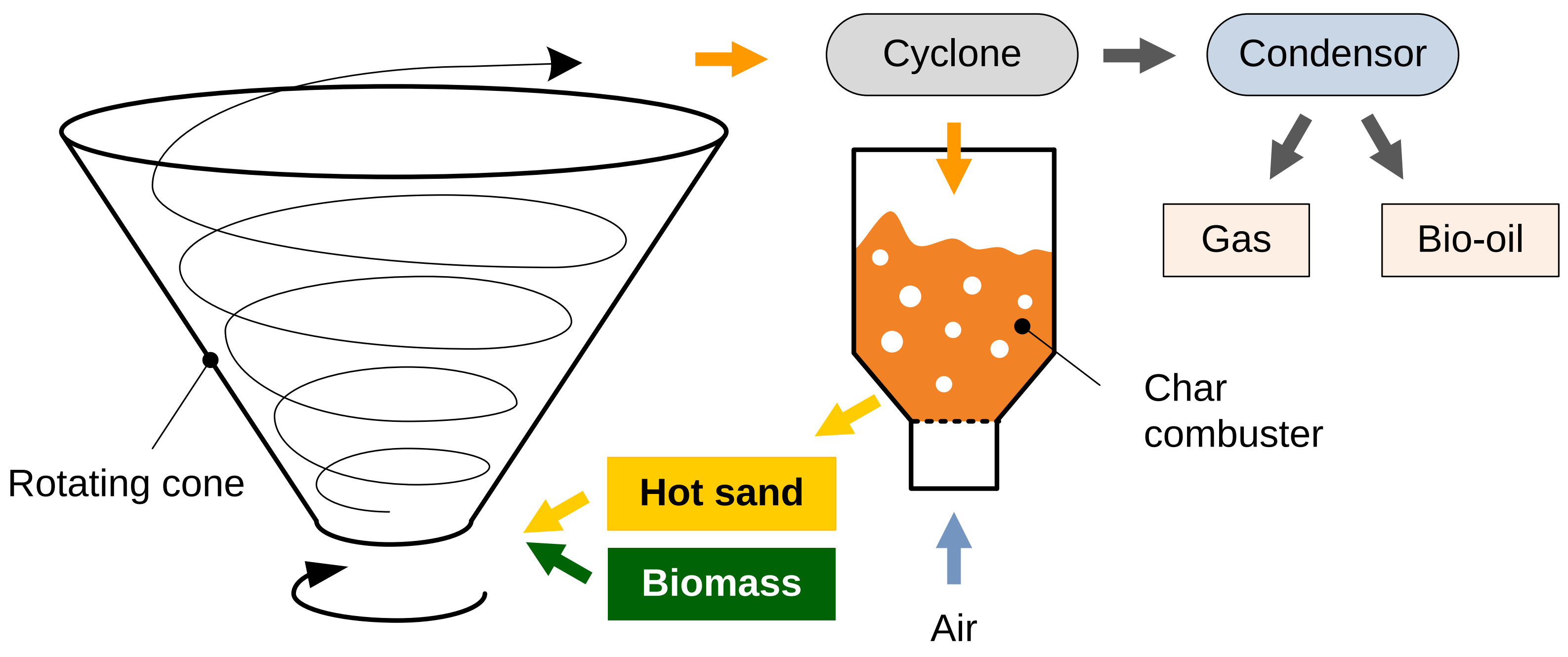
FAST PYROLYSIS: REACTOR TYPES

How ? Typical reactor systems, tried and proven on large scale

3. Rotating cone reactor

- Sand as heat carrier, mixed with biomass by means of centrifugal force
- Char burnt in a combuster (air fluidised *bubbling* fluidised bed)
- No need for fluidisation gas: vapors are less diluted then FB systems
- Technology commercialized by BTG (NL)
- Empyro plant (on-line 2015) in Hengelo: 120 tpd



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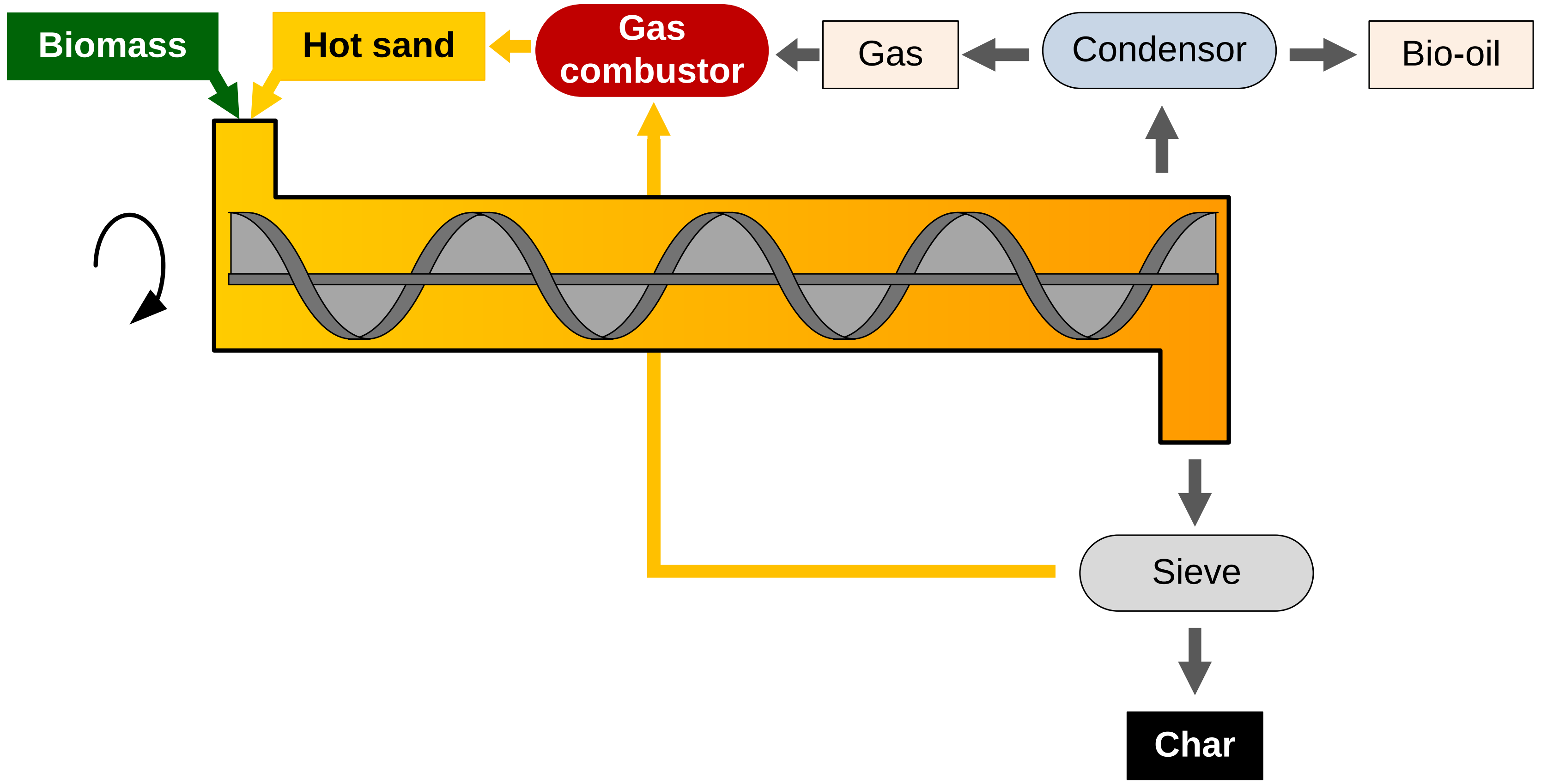
FAST PYROLYSIS: REACTOR TYPES

How ? Typical reactor systems, tried and proven on large scale

4. Auger or screw conveyor reactor

- Needs hot sand to achieve the required heating rate (without sand = slow pyrolysis)
- Mixing and transport controlled by screw
- Single and twin screw configurations
- More flexibility with respect to particle morphology
- e.g. KIT-bioliq



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GENERAL CONCLUSIONS

- Fast pyrolysis is a technique to turn solid biomass into a liquid
- Application thereof in fuels, chemicals and energy production
- The key lies in the control of process conditions as well as feedstock
- Fast pyrolysis has become mature, with large-scale implemted technologies available

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Questions ?

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