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Pyrolysis of biomass

Tony Bridgwater

ETIP Webinar

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What is pyrolysis?

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- Biomass is heated in the absence of air or oxygen to decompose or devolatilise the biomass into:
  - **Solid char**
  - **Liquid as bio-oil, or tar and/or pyroligneous liquor**
  - **Gas**
- Three products are always produced
- Product yields depend on biomass, vapour and solids residence time, and temperature
- There are several modes of pyrolysis ....

Pyrolysis modes

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Mode	*Conditions Wt % products*	*Liquid*	*Solid*	*Gas*
Fast	~ 500ºC; very short hot vapour residence time (HVRT) <2s; short solids RT	75%	12%	13%
Slow	~ 400ºC; long HVRT; very long solids RT	35%	35%	30%
Torre-faction	~ 300ºC; long HVRT; long solids RT	Vapours	85% solid	15% gas + vapours
Gasif-ication	~ 800-900ºC; short HVRT; short solids RT	1-5% tars	<1% (all burned)	95-99%

Fast pyrolysis products

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- Fast pyrolysis aims to maximise liquids. This is achieved with very high heating rates usually requiring very small particle sizes of generally <3mm in size and <10% water
- Clean wood gives the highest liquid yield up to 75 wt.% on dry biomass feed. This is homogenous i.e. single phase, and low viscosity.
- The charcoal forms about 10-15 wt.% of the products. It retains virtually all the alkali metals.
- Bio-oil is defined by ASTM as the liquid from biomass fast pyrolysis

Fast pyrolysis liquid product

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The liquid is homogenous with some unusual properties

Water content	25 %
pH	2.5
Specific gravity	1.20
Elemental analysis	C:56.4 %, H: 6.2 %, O: 37.3 %
HHV as made	17 MJ/kg
Vacuum distillation	Max. 50%

Bio-oil yield

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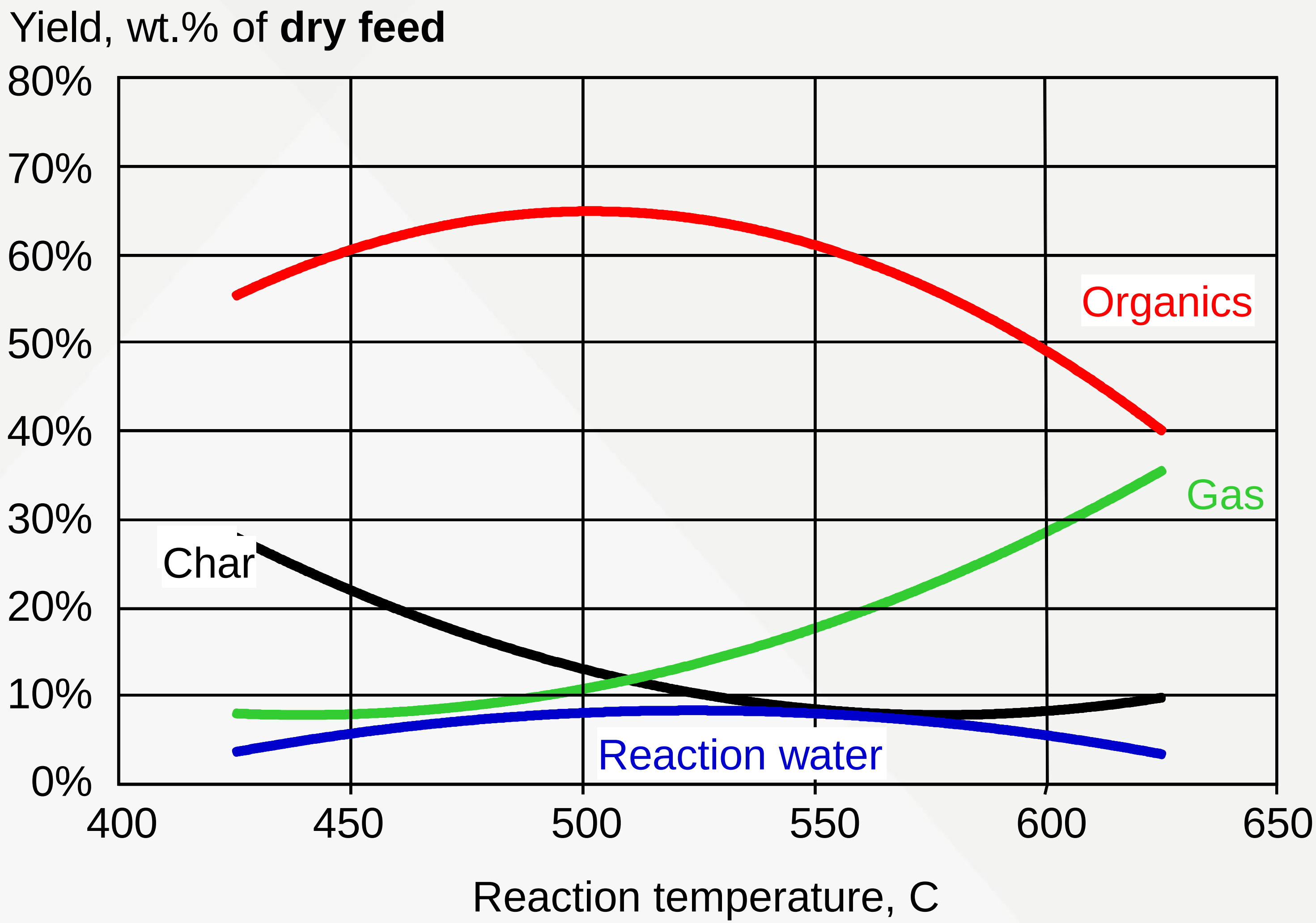

Bio-oil = Organics + Reaction water + Feed water

Fast pyrolysis requirements

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Organics provide the energy in the product and can be converted into chemicals and/or fuels. The organic yield is thus critical.

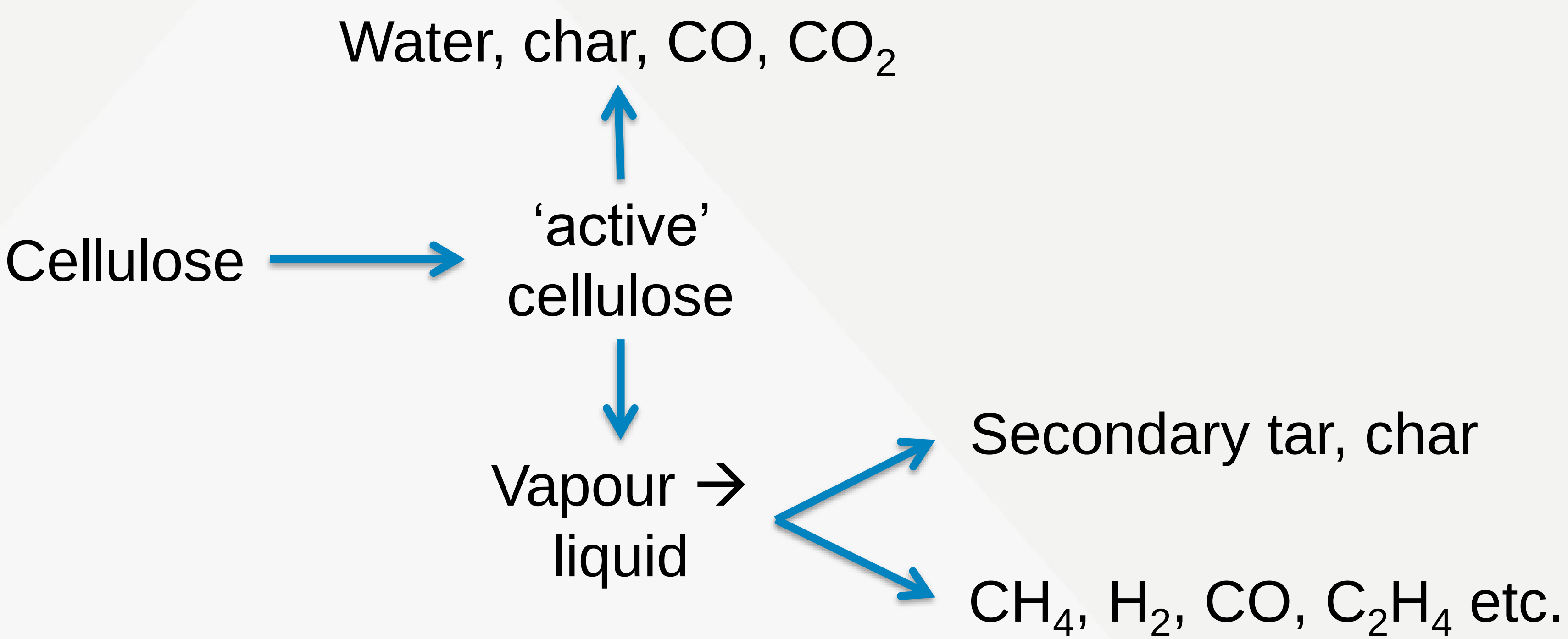
Fast pyrolysis requires:

- High heating rates: Small particle sizes needed as biomass has low thermal conductivity
- Dry biomass (<10wt.% water): Feed moisture goes into bio-oil product plus reaction water
- Carefully controlled temperature: ~500°C is optimum temperature for maximising liquid yield
- Rapid and effective char removal: Char and alkali metals are catalytic and reduce liquid yield and quality
- Short hot vapour residence time: Thermal cracking reduces liquid yield

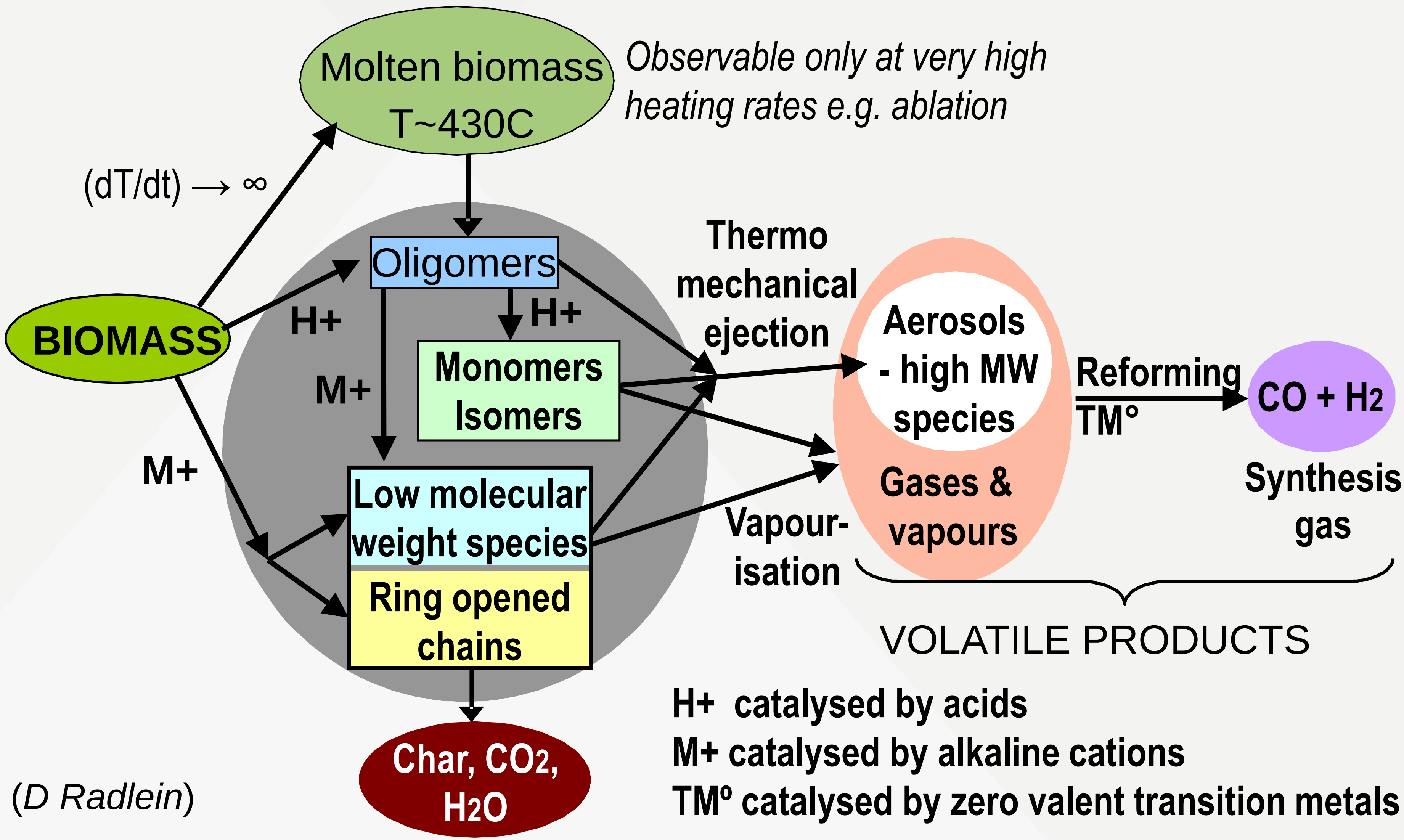
Fundamentals

Many pathways and mechanisms have been proposed

The Broido-Shafizadeh model for cellulose shows typical simplified pathways. This kind of model is widely used for modelling.



Pathways



H+ catalysed by acids
M+ catalysed by alkaline cations
TM° catalysed by zero valent transition metals

(*D Radlein*)

Particle pyrolysis

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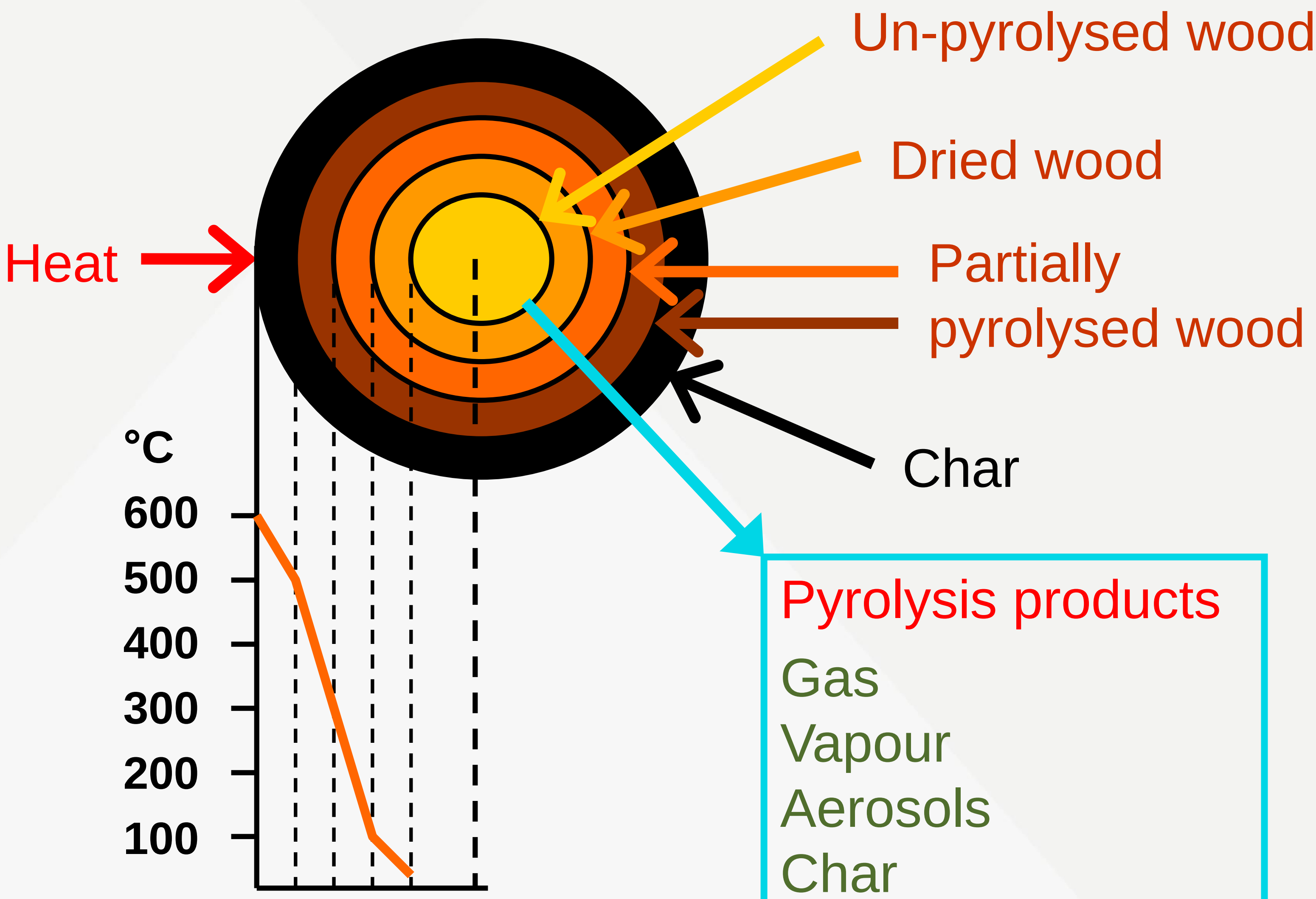

Pyrolysis products

- Gas
- Vapour
- Aerosols
- Char

Fast pyrolysis process

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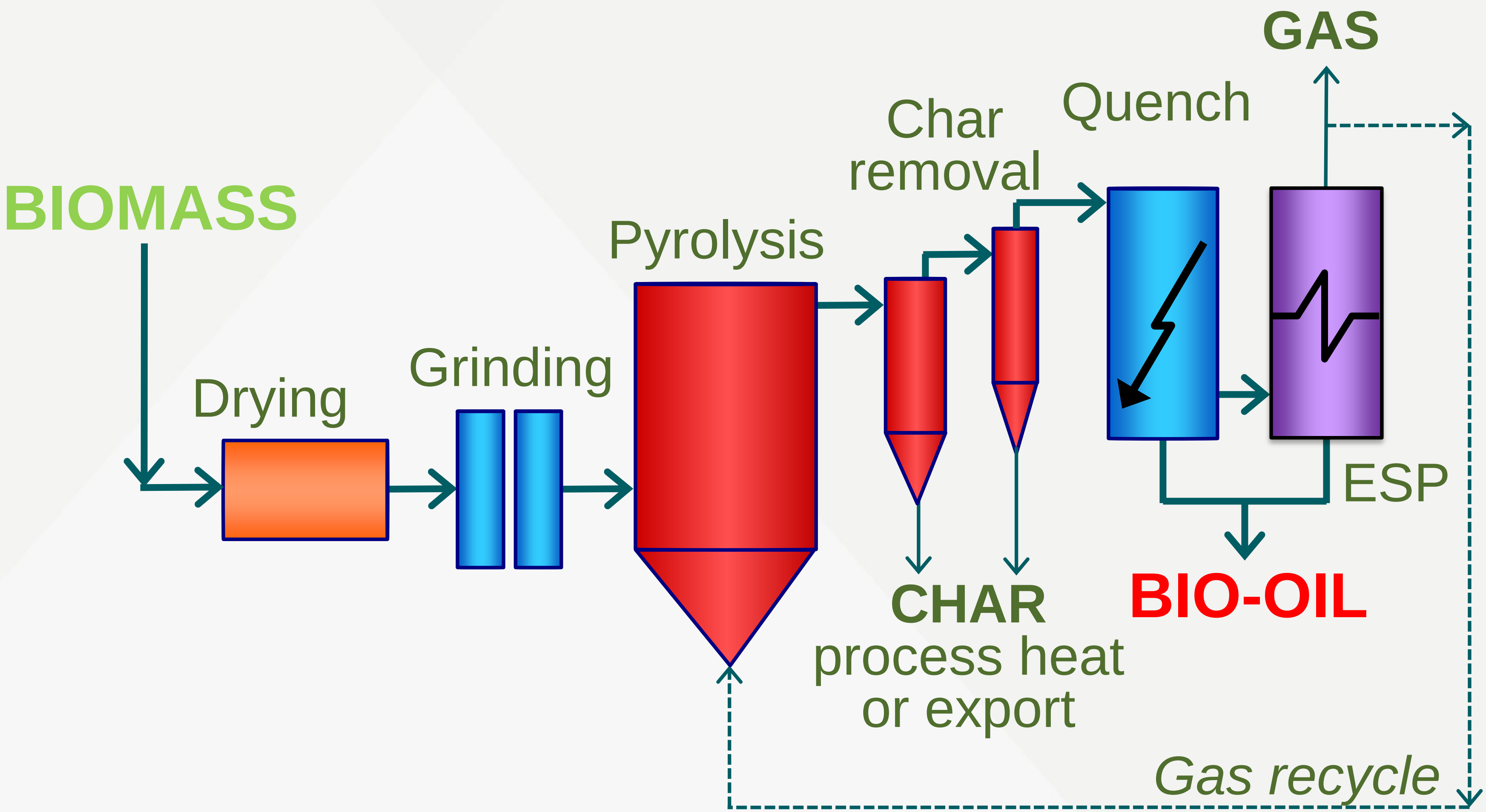
Drying	<10%. Feed moisture and reaction water report to bio-oil
Comminution	-2mm (fluid bed), -6 mm (CFB), +10 mm (ablative)
Fast pyrolysis	High heating rate, controlled T, short residence time, rapid cooling
Char separation	Efficient char separation needed
Liquid recovery	Condensation and coalescence.

Conceptual fast pyrolysis system



Fast pyrolysis reactors

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Circulating fluid bed
Spouted fluid bed
Transported bed

} **Commercial**

Ablative
Vortex
Centrifuge
Augur or Screw
Radiative-convective
Entrained flow
Microwave
Moving bed
Fixed bed
Ceramic ball downflow
Vacuum

} **Research**

Conceptual CFB/Transported bed reactor

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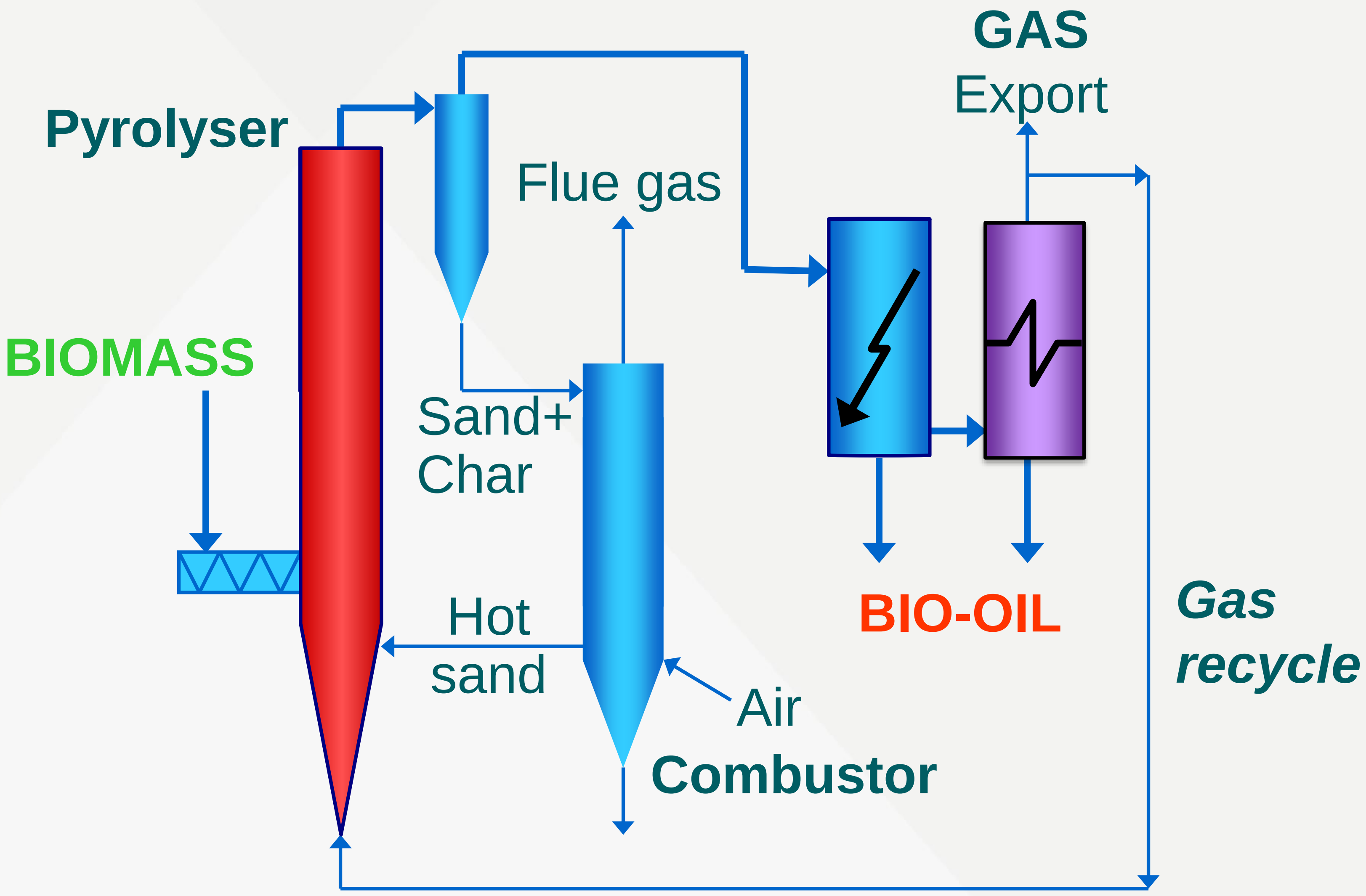

Pyrolysis routes to biofuels

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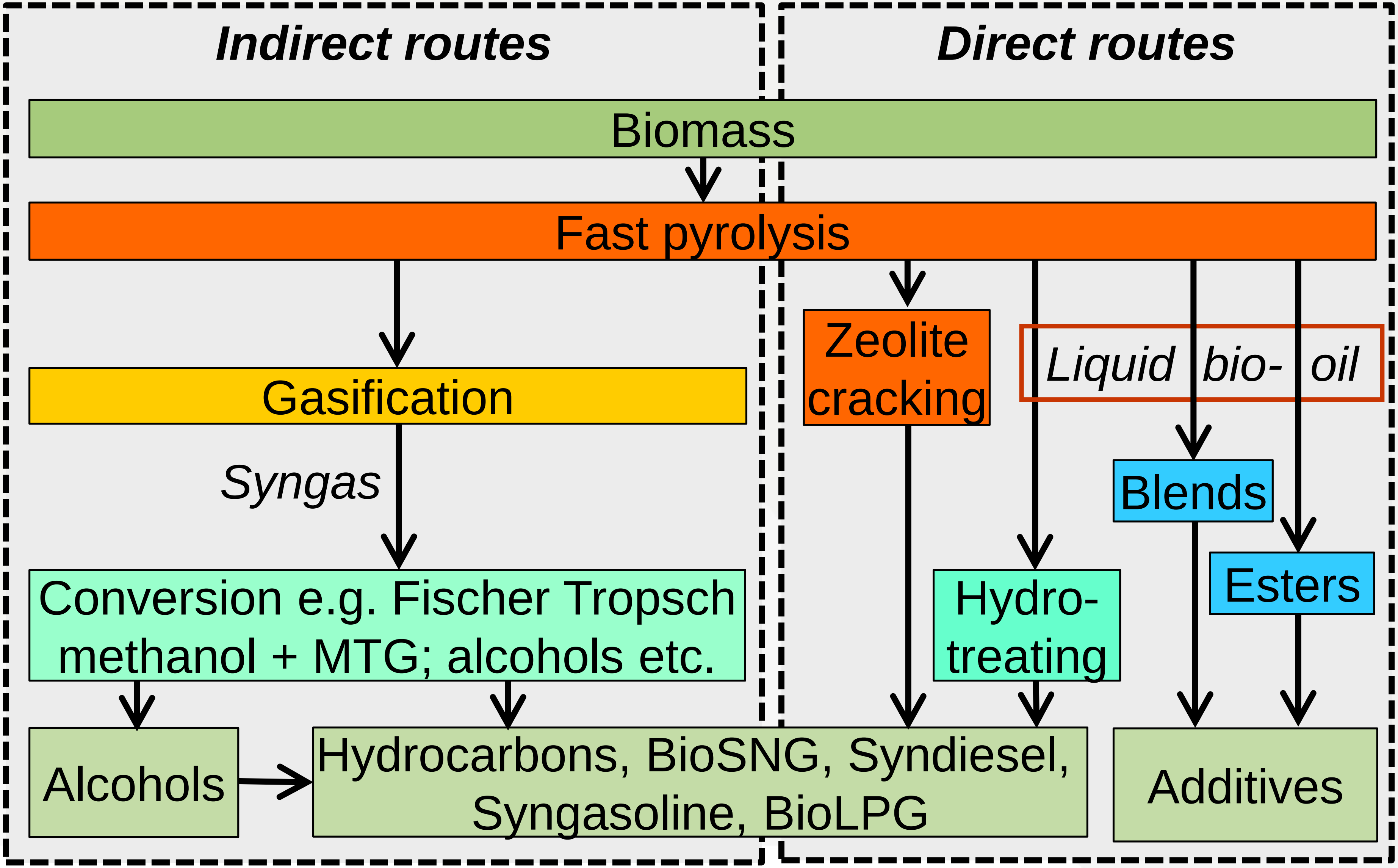

Catalysts

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All biomass contains inorganic materials which act as a catalyst as well as contaminant. Catalysts can also be added to the biomass prior to, during, or after fast pyrolysis.

Natural catalysts and contaminants

- Alkali metals (e.g. K, Ca, Na) as "ash" . K is the most active in cracking organics to CO_2 and H_2O and thus reducing liquid yield
- Heavy metals (e.g. Fe) from soil and wastes
- Non-metals (e.g. S, Cl, P) may also be present
- Char (which contains the biomass ash)

Synthetic catalysts for product enhancement

- In-situ
- Close coupled (ex-situ)
- Remote

Bio-oil upgrading to hydrocarbons

Bio-oil contains 35-40% oxygen which has to be rejected/removed for production of hydrocarbons

- **Hydro-treatment rejects oxygen as H_2O**
  - Liquid processing with hydrogen and high pressure
  - Projected yield of around 15% naphtha-like product for refining to diesel, using co-produced hydrogen
  - Product fractions can be upgraded
  - Although extensively researched, there is little work now.
- **Zeolite cracking rejects oxygen as CO_2**
  - Close coupled process for upgrading vapours requiring constant catalyst regeneration. No hydrogen, no pressure
  - Projected yield of around 18% aromatics for refining to gasoline or for use as chemicals

Upgrading considerations

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- There are a large number of catalysts and upgrading processes being researched and developed
- There are a large number of product quality criteria to be considered in defining upgrading requirements
- It is important to clearly understand and define which property or properties need to be changed and by how much
- The possibility of modifying the application to match the upgraded bio-oil characteristics should be considered. i.e. optimise the overall system.

Pyrolytic gasification

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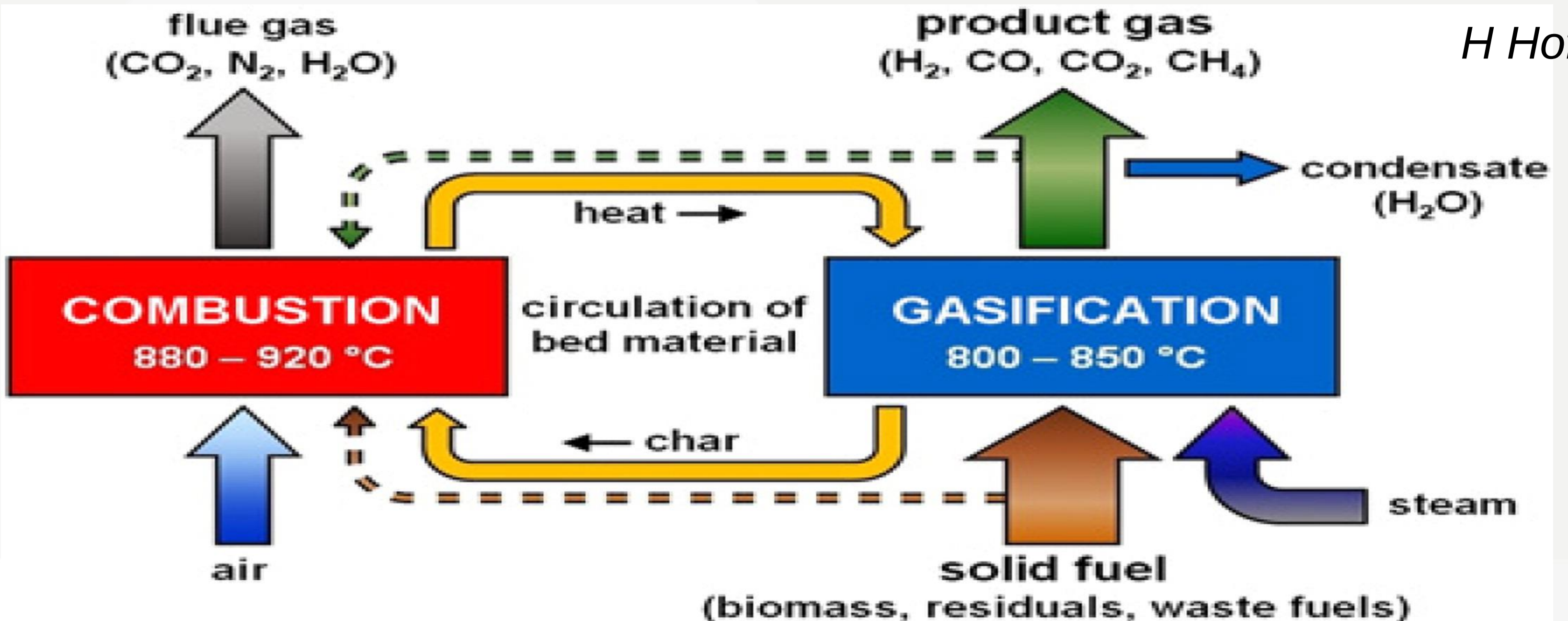
This is high temperature pyrolysis at up to 900ºC in the absence of air or oxygen to give a medium HV fuel gas. A dual fluid bed contacts biomass with recirculated hot sand heated by burning char (analogous to the CFB in fast pyrolysis for liquids). Capital cost is higher and carbon efficiency is lower than air blown gasifiers but the gas quality is much higher.



H Hofbauer

Slow pyrolysis or carbonisation

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- Charcoal has been manufactured for thousands of years and is still widely used for cooking and industrially for smelting and for activated charcoal applications.
- Moderate temperatures are required with long residence times.
- In less developed regions, local batch kilns are used, while in more industrialised areas, multiple continuous retorts are used.
- A key feature of slow pyrolysis is the co-production of liquids, both organic and aqueous, which phase separate and if not utilised require disposal.

Continuous retorts & chemical recovery

The Usine Lambiotte plant shown closed down in 2002. There were 2 retorts and a sophisticated chemicals recovery unit.

Primary distillation

Usine Lambiotte

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Outputs & revenues from ~95,000 t/y wet wood (2000-2001)

	t/year	€/t	k€/y	%
Charcoal	25,000	Est.100	2,500	31.5
Total pyroligneous liquid	40,000			
Water	30,000			
Organics	10,000			
Acids and alcohols	3,830	452	1,732	21.8
Oils	310	1,258	390	
Fine chemicals	56	49,732	2,785	35.1
Fuel	5,804	90	522	
Total organics	10,000	543	5,429	68.5
Total income			7,929	

Biochar

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- Biochar is charcoal made by slow pyrolysis. It is used as a soil amendment for soil health benefits and provides long term carbon sequestration.
- Biochar is a stable solid, with a very high carbon content, and can last in soil for thousands of years.
- The microstructure of the charcoal provides the features that provide biochar with its unique attributes, such as water retention, and microbial hosting.
- Extensive research has been carried out on attributing char characteristics to crop improvements, especially crop yield.

Torrefaction

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- This is low temperature pyrolysis at around 250-300C. It enhances the properties of the biomass by:
  - Removing water,
  - Reducing hemicellulose,
  - Improving heating value,
  - Improving the friability of the product for grinding in co-processing
- Vapours can either be:
  - Burned to provide some process heat or waste disposal
  - Collected to yield potentially valuable chemicals
- The role of torrefied biomass as a form of biochar is not well understood with unknown life in soil.
- Commercial interest has declined due to poor economics.

Fast pyrolysis: the promise

- Valuable and useful liquid product
- Valuable charcoal by-product where recovery is possible
- High yields – 75% wt. liquid
- High efficiency – 70% energy yield
- No external energy needed
- Minimal emissions
- Useful for
  - Energy carrier
  - Heat
  - Power
  - Chemicals and commodities
  - Transport fuels

Thank you!

a.v.bridgwater@aston.ac.uk