

Fast pyrolysis for bioenergy and biofuels

Pyrolysis Workshop, Shanghai, China,
7 November 2015

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What is pyrolysis?

- ▶ Biomass is heated in the absence of air or oxygen to decompose or devolatilise the biomass into:
 - ▶ Solid char
 - ▶ Liquid as bio-oil, tar 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

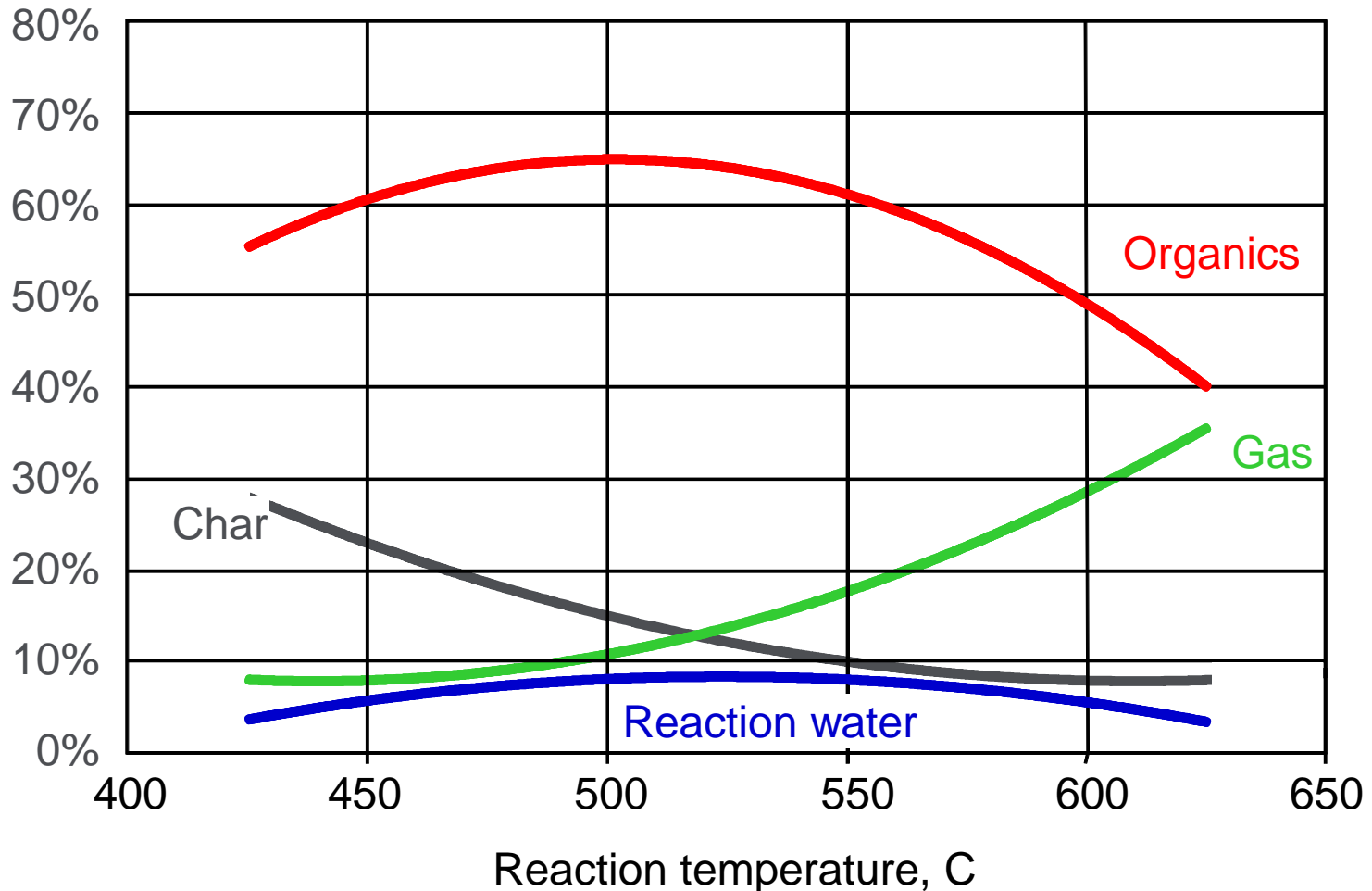
| Mode | Conditions <i>Wt % products</i> | Liquid | Char | Gas |
|---------------|--|-----------------|------------------|-------------|
| Fast | ~ 500°C; very short hot vapour residence time (HVRT) ~1 s; short solids RT | 75% | 12% | 13% |
| Inter-mediate | ~ 400°C; short HVRT ~10-30s; moderate solids RT | 40% in 2 phases | 40% | 20% |
| Slow | ~ 400°C; long HVRT; very long solids RT | 35% | 35% | 30% |
| Torre-faction | ~ 300°C; long HVRT; long solids RT | Vapours | 85% solid | 15% vapours |
| Gasif-ication | ~ 800-900°C; short HVRT; short solids RT | 1-5% | <1% (all burned) | 95-99% |

Fast pyrolysis products

- ▶ Fast pyrolysis aims to maximise **organics** as **liquids**. This comes from **very high heating rates** from small particle sizes of generally <3mm in **size** and < 10% **moisture**
- ▶ **Clean wood** gives highest liquid yield up to **75 wt.%** on dry biomass feed. This is single phase, low viscosity.
- ▶ **Ash** causes catalytic vapour cracking, hence lower organic yields, higher water and potential phase separation
- ▶ The **charcoal** forms about 10-15 wt.% of the products. It retains virtually all the **alkali metals**. It is usually consumed in the process to provide process heat.

Bio-oil yield from Aspen Poplar

Yield, wt.% of dry feed



Bio-oil = Homogenous mixture of organics + reaction water + feed water

Fast pyrolysis requirements

Organics provides 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
- ▶ **Short hot vapour residence time:** Thermal cracking reduces liquid yield

Catalysts

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

Natural catalysts

- ▶ Alkali metals (e.g. K, Ca, Na) as “ash”

Contaminants

- ▶ Heavy metals (e.g. Fe) from soil and wastes
- ▶ Non-metals (e.g. S, Cl, P) may also be present

Products

- ▶ Char (which contains the biomass ash)

Synthetic catalysts for product enhancement

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

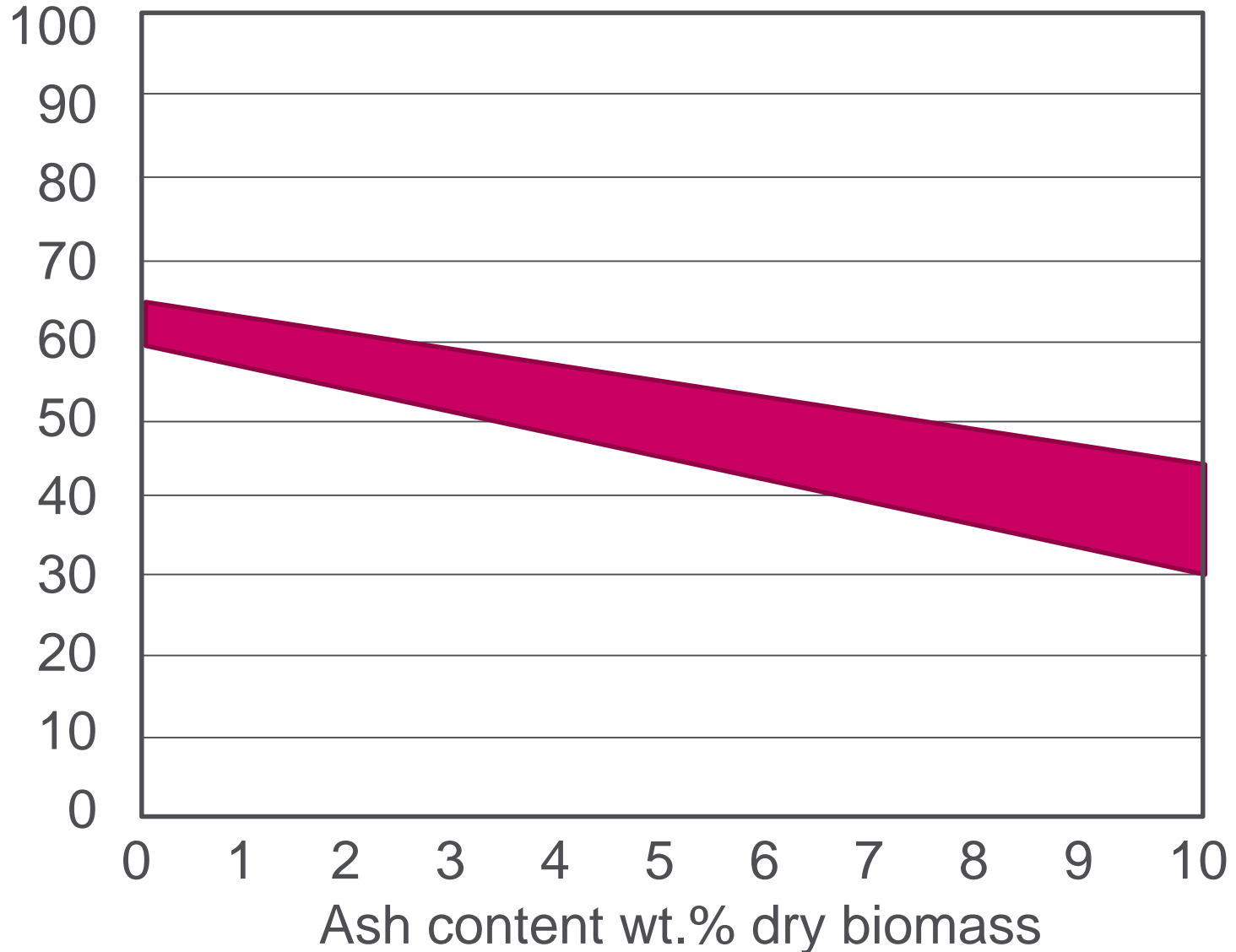
Effects of ash and contaminants

- ▶ Catalysts as ash and char **crack** organic products from pyrolysis into water and carbon dioxide leading to:
 - ▶ a **lower organic content** vapour and liquid with less energy
 - ▶ And potentially a **phase separated liquid** product
- ▶ **Potassium** is the most active alkali metal in cracking
- ▶ **Char** is also catalytic from the alkali metal content
- ▶ Ash contents of typically more than **3 wt.%** ash can cause **phase separation** in the liquid. Phase separation is non-reversible and can only be remedied by addition of high proportions of ethanol or similar solvents.



Effect of ash on organics

Organics yield

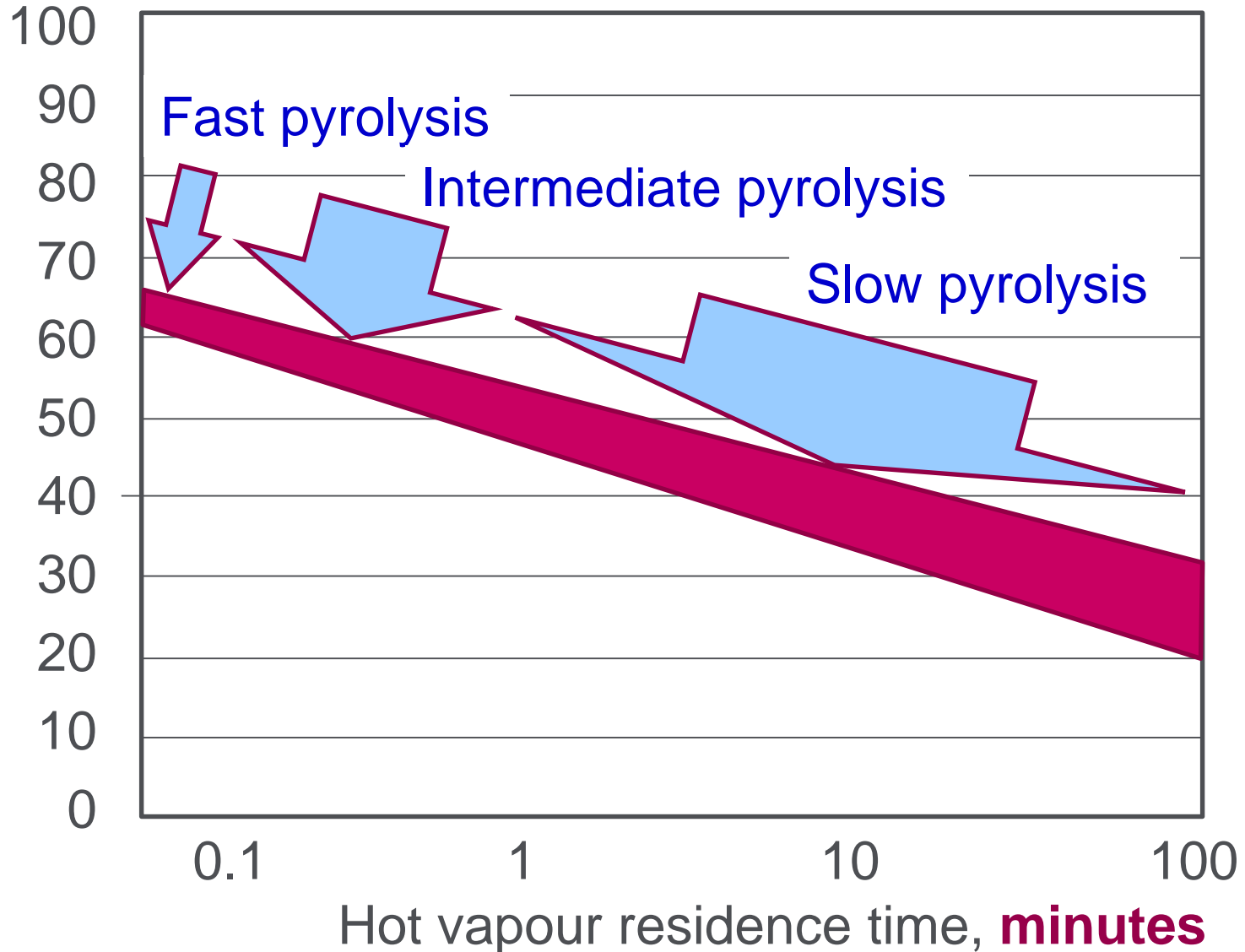


Control of ash

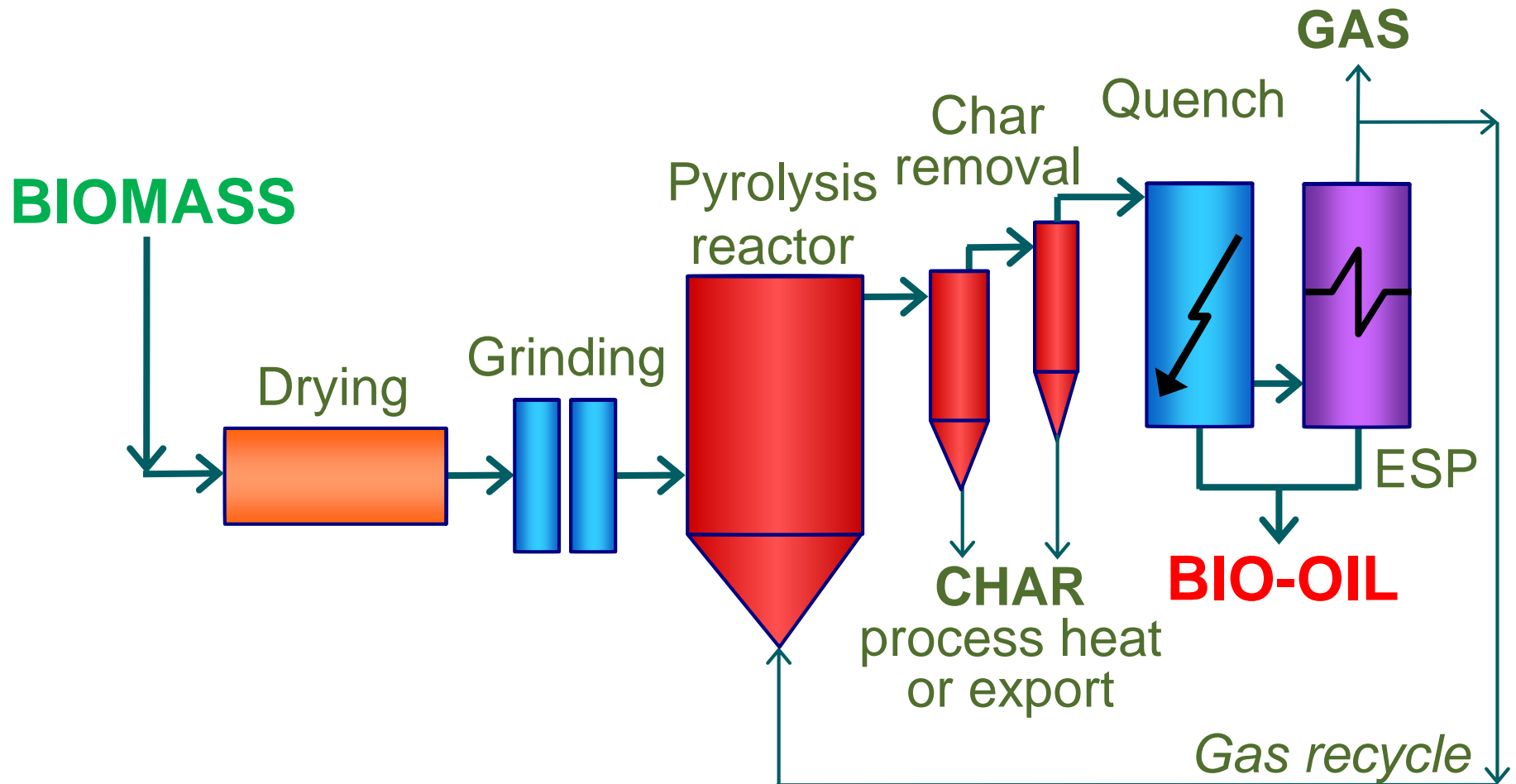
- ▶ As maximising the organic content of the pyrolysis vapour and liquid is paramount, ash control is very important
- ▶ Ash can be influenced by biomass **growing conditions**:
 - ▶ minimising **fertiliser** applications
 - ▶ managing **harvesting** times, e.g. miscanthus during senescence
 - ▶ managing harvest **practises** by minimising contamination with soil
- ▶ Ash content can be reduced by **washing**. This increases costs,
- ▶ Ash contents can be reduced by **blending** low ash and high ash biomass.

Effect of hot vapour residence time

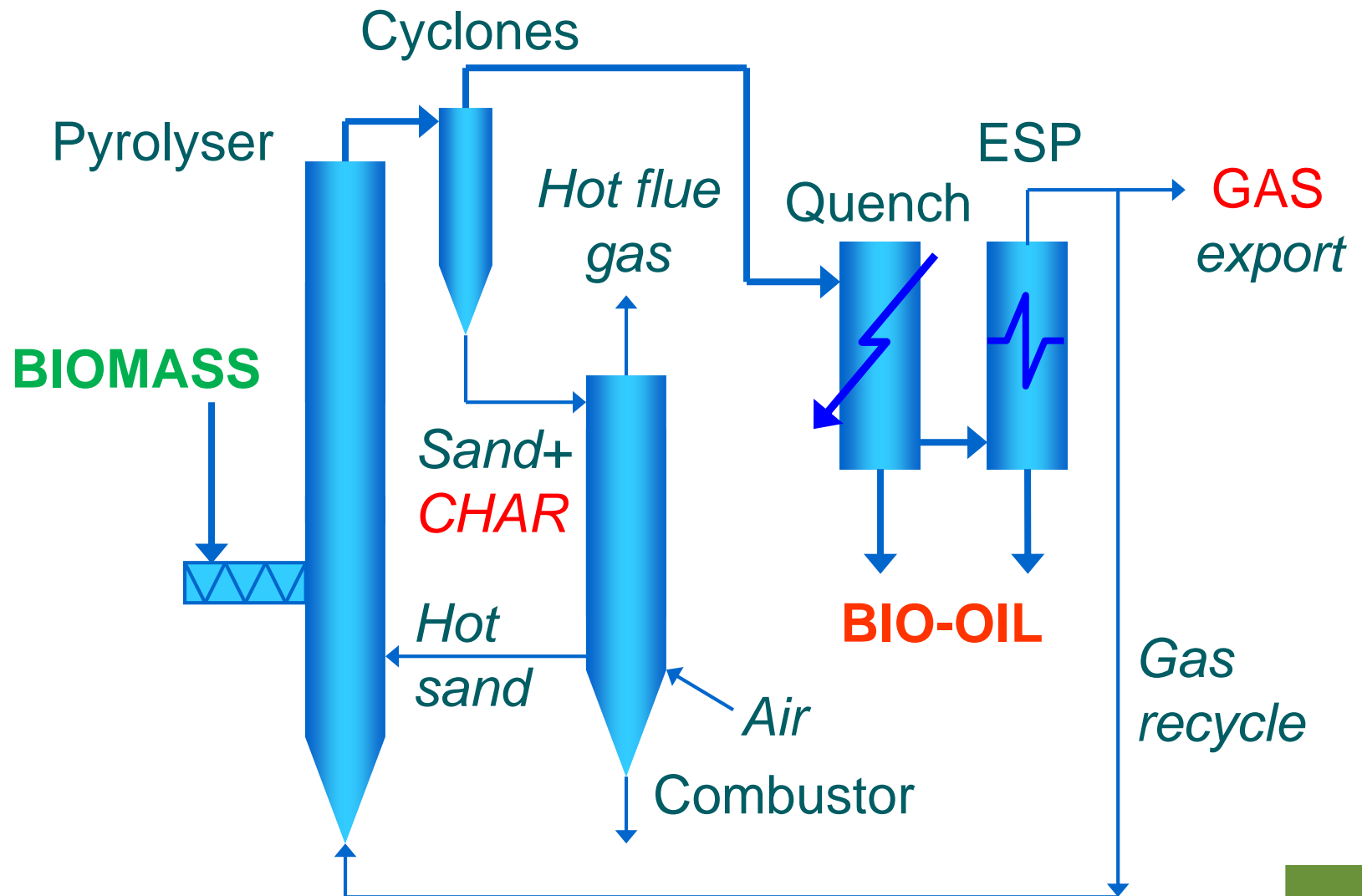
Organics yield




Typical fast pyrolysis reaction system



CFB or Transported bed reactor



Fast pyrolysis reactors

| | | |
|--------------------------|---|------------------------------|
| Fluid bed |  | Commercial activities |
| Spouted fluid bed | | |
| Transported bed | | |
| Rotating cone | | |
| Ablative | | |
| Circulating fluid bed | | |
| Vortex | | |
| Centrifuge reactor | | |
| Augur or Screw | | |
| Radiative-convective | | |
| Entrained flow | | |
| Microwave | | |
| Moving bed and fixed bed | | |
| Ceramic ball downflow | | |
| Vacuum | | |

Fast pyrolysis: commercialisation



BTG (NL) : 125 t/d transported bed - Empyro



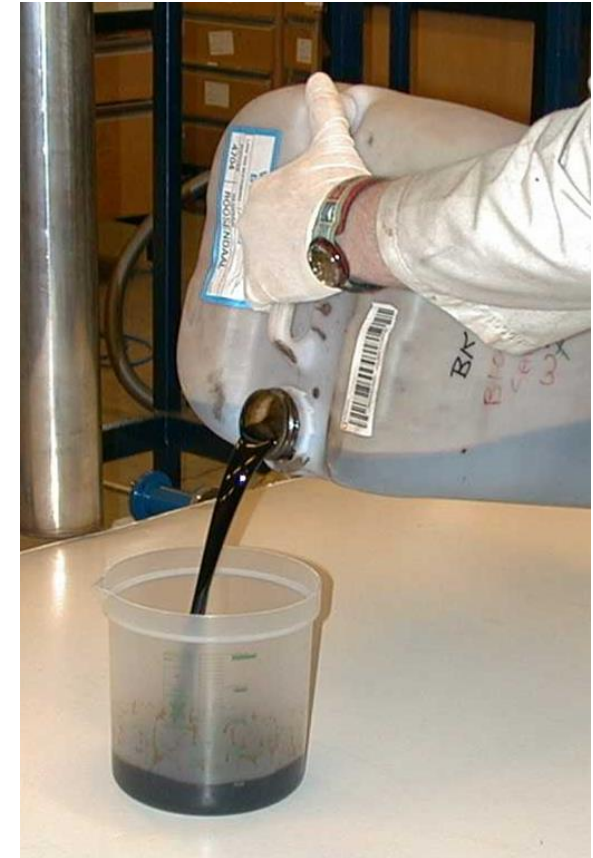
Fortum (FI) & Metso (FI):



Ensyn (CA): 100 t/d transported bed in Canada + 8 or 9 in USA

Fast pyrolysis liquid – bio-oil

| | |
|-----------------------------|-----------|
| Moisture content | 25 % |
| pH | 2.5 |
| Specific gravity | 1.20 |
| Elemental analysis | |
| C | 56.4 % |
| H | 6.2 % |
| O | 37.3 % |
| N | 0.1 % |
| Ash | 0.1 % |
| HHV as made | 17 MJ/kg |
| Viscosity (at 40°C) | 40-100 cp |
| Solids (char) | 0.05 % |
| Vacuum distillation residue | Max. 50% |



Characteristics

| | |
|---------------------------|-----------------------------------|
| Acidity - low pH | Low miscibility with hydrocarbons |
| Aging – phase separation | Nitrogen high |
| Alkali metals | Oxygen content very high |
| Char (solids) | Smell or odour |
| Chlorine | Solids content |
| Colour | Structure |
| Contamination of feed | Sulphur |
| Distillability is poor | Temperature sensitivity |
| High viscosity | Toxicity |
| Low H:C ratio | Viscosity |
| Materials incompatibility | Water content |

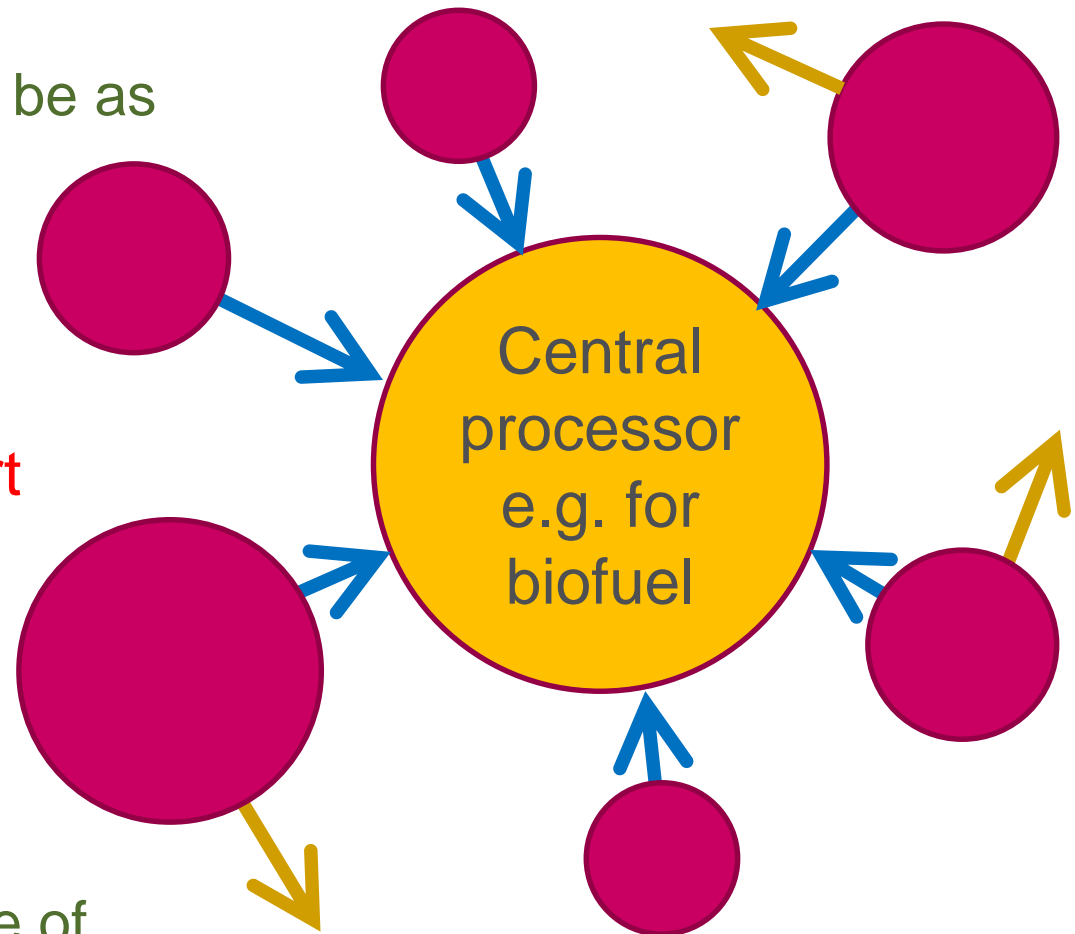
Decentralised fast pyrolysis

► Bulk density

- Biomass density can be as low as 100 kg/m^3
- Bio-oil density is 1200 kg/m^3

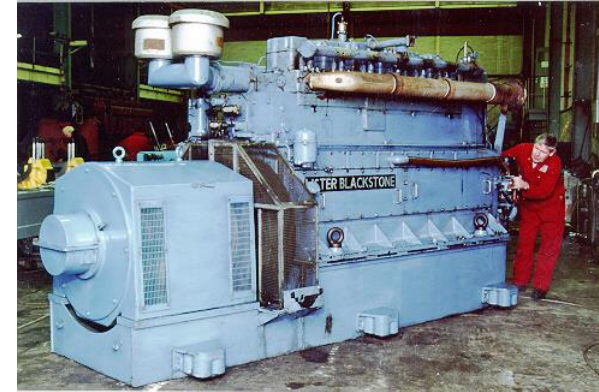
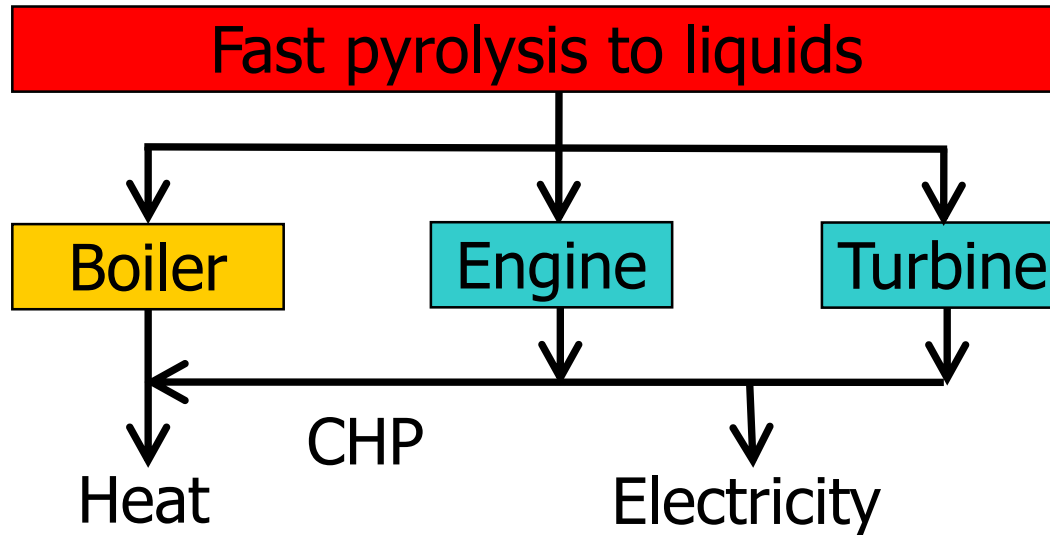
► Bio-oil liquid storage, handling and transport

- Tanks and pumps are used
- No windblown refuse, vermin, or mechanical handling
- Provides optimum use of loading weight restrictions



Direct use of whole bio-oil

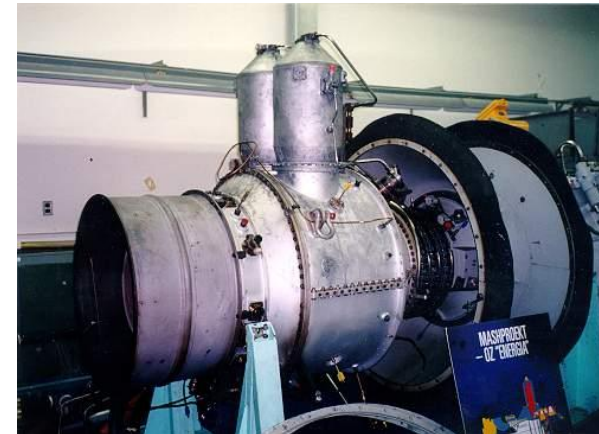
► Heat and power



► Chemical substitution

► Phenolics in wood resins

► Preservatives



Bio-oil for biofuels

▶ Indirect production

- ▶ Gasification of bio-oil followed by hydrocarbon or alcohol synthesis. There are many technical and economic advantages of gasification of liquid bio-oil rather than solid biomass

▶ Direct production

- ▶ Via catalytic upgrading of liquid or vapour
- ▶ Catalyst can be added to biomass; incorporated into the fluid bed material; use of a close coupled reactor; use of a remote reactor
- ▶ Ex-situ or secondary reaction offers independent control over process conditions;

Pyrolysis routes to biofuels

Indirect routes

Direct routes

Biomass

Fast pyrolysis

Gasification

Syngas

Conversion e.g. Fischer
Tropsch, Methanol etc.

Alcohols

Hydrocarbons, BioSNG, Syndiesel,
Syngasoline, BioLPG etc

Zeolite
cracking

FCC

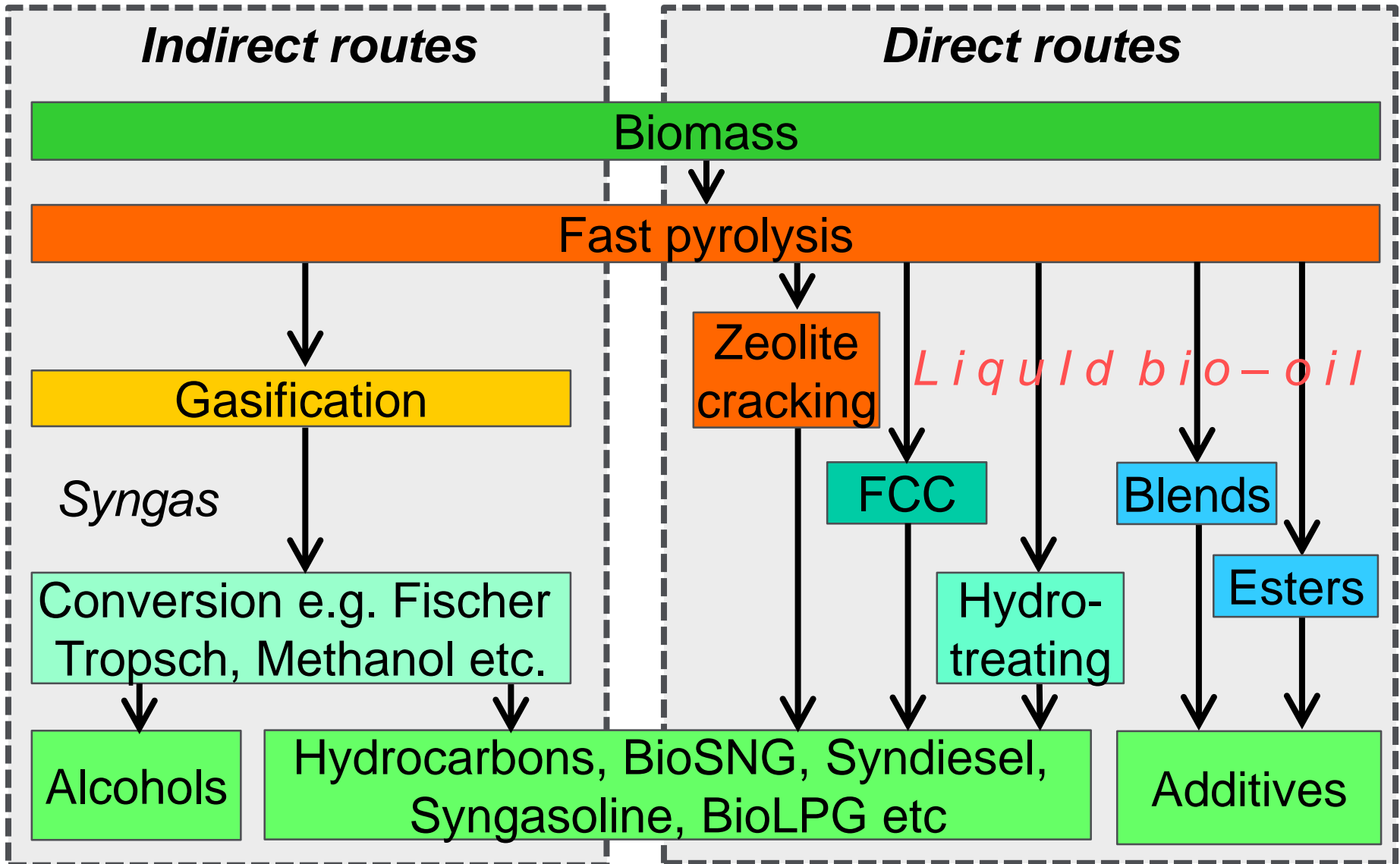
Hydro-
treating

Blends

Esters

Additives

Liquid bio-oil



Vapour cracking

- ▶ **Zeolite cracking** rejects oxygen as CO_2
 - ▶ Vapour processing in a close coupled process
 - ▶ No hydrogen requirement, no pressure
 - ▶ Projected yield of around 18wt.% aromatics
- ▶ This is now being developed by e.g. Kior and others
- ▶ **ZSM-5** has attracted most attention due to shape selectivity to **aromatics**, with promoters such as Ga or Ni.
- ▶ The catalyst rapidly **coke**s which requires frequent regeneration as in an FCC unit. Oxygen is thus removed as CO and CO_2 compared to H_2O in hydroprocessing.
- ▶ Production of **aromatics** is also likely to be of significant interest to the chemicals sector.

Hydrodeoxygenation (HDO)

- ▶ **Hydro-deoxygenation** rejects oxygen as H_2O
 - ▶ Liquid processing with **hydrogen** and **high pressure**
 - ▶ Projected yield of around 15wt.% for refining
- ▶ Original research used sulphided **CoMo** or **NiMo** catalysts on aluminosilicate which tended to hydrolyse due to water
- ▶ More recently, precious metal catalysts on inert supports have been developed with a preference for **Pd** and **Ru**
- ▶ High pressure (<200 bars) and temperature (<400C)
- ▶ Extent of deoxygenation depends on:
 - ▶ Severity of upgrading conditions
 - ▶ Bio-oil production process and feedstock
- ▶ It is likely that multiple upgrading steps will be needed
- ▶ Completion of upgrading in refineries is attractive

Hydrogen

- ▶ **Hydrogen** is a major challenge. Low conversion requires costly recycling with H_2 separation and compression.
- ▶ Since the hydrogen requirement is significant, it should be renewable and sustainable. Few refineries have a hydrogen surplus
- ▶ Hydrogen can be generated by **gasification** of biomass, shifting CO to H_2 followed by scrubbing CO_2
- ▶ The aqueous phase from bio-oil can be **steam reformed** to hydrogen.

Fluid Catalytic Cracking - FCC

- ▶ Increased interest in injecting bio-oil into a conventional FCC unit in a refinery
- ▶ Major petrochemical companies are testing and evaluating this approach.
- ▶ UOP and Petrobras have reported up to 5% addition successfully
- ▶ Other companies are exploring this route
- ▶ Utilises economy of scale and expertise.
- ▶ Can be explored with HDO

Other upgrading methods

A variety of methods and catalysts have been investigated in recent years as exemplified below:

- ▶ Acid cracking in supercritical ethanol
- ▶ Aqueous-phase reforming + dehydration + hydrogenation
- ▶ Blending
- ▶ Dicationic ionic liquid $C_6(\text{mim})_2\text{-HSO}_4$
- ▶ Esterification of pyrolysis vapours
- ▶ Esterification of liquid bio-oil
- ▶ Hydrogenation–esterification over bifunctional Pt catalysts
- ▶ Reactive distillation
- ▶ Solid acid catalysts $40\text{SiO}_2/\text{TiO}_2\text{-SO}_4^{2-}$
- ▶ Solid base catalysts $30\text{K}_2\text{CO}_3/\text{Al}_2\text{O}_3\text{-NaOH}$
- ▶ Steam reforming
- ▶ ZnO, MgO and Zn-Al and Mg-Al mixed oxides

Chemicals

Fractionated oil

- Liquid smoke (commercial)
- Anhydrosugars
- Asphalt
- De-icers
- Fuel additives
- Hydrogen
- Preservative
- Resin precursors
- Slow release fertiliser

Specific chemicals

- Acetic acid (commercial)
- Furfural
- Hydroxyacetaldehyde
- Levoglucosan
- Levoglucosenone
- Maltol
- Phenol and phenolics



Slow pyrolysis and chemical recovery

Usine Lambiotte carbonisers and liquid tar processing



Usine Lambiotte primary distillation column



Opportunity from ~100,000 t/y wood

| | t/year | €/t | k€/y | % |
|---------------------------|--------|--------|-------|------|
| Charcoal | 25,000 | *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 | |

Conclusions

- ▶ Pyrolysis is very **flexible** in the process and products.
- ▶ Fast pyrolysis provides a **liquid** as an energy carrier
- ▶ The liquid is **alkali metal free**
- ▶ **Decentralised** pyrolysis plants offer improvements
- ▶ Bio-oil can be used for fuel, chemicals and/or biofuels

- ▶ Fast pyrolysis technology needs to be **improved** to reduce costs and increase liquid yield and quality
- ▶ Fast pyrolysis liquid **upgrading** needs to be developed and demonstrated

Thank you

