Conversion of Wet Waste to Fuel and Value-Added Products using Hydrothermal Carbonization

Introduction to Hydrothermal carbonisation

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Part 1- Introduction

Session 1: Introduction to Hydrothermal conversion

Session 2: Introduction to Hydrothermal carbonisation

Session 3: Application of products

Session 1- Introduction to hydrothermal conversion

This session will cover:

- What is hydrothermal conversion
- Types and yields of products
- Properties of water
- Types of feedstocks

Session 2- Introduction to hydrothermal carbonisation

This session will cover:

- What is hydrothermal carbonisation
- Types of feedstocks
- Properties of products

Session 1- Application of products

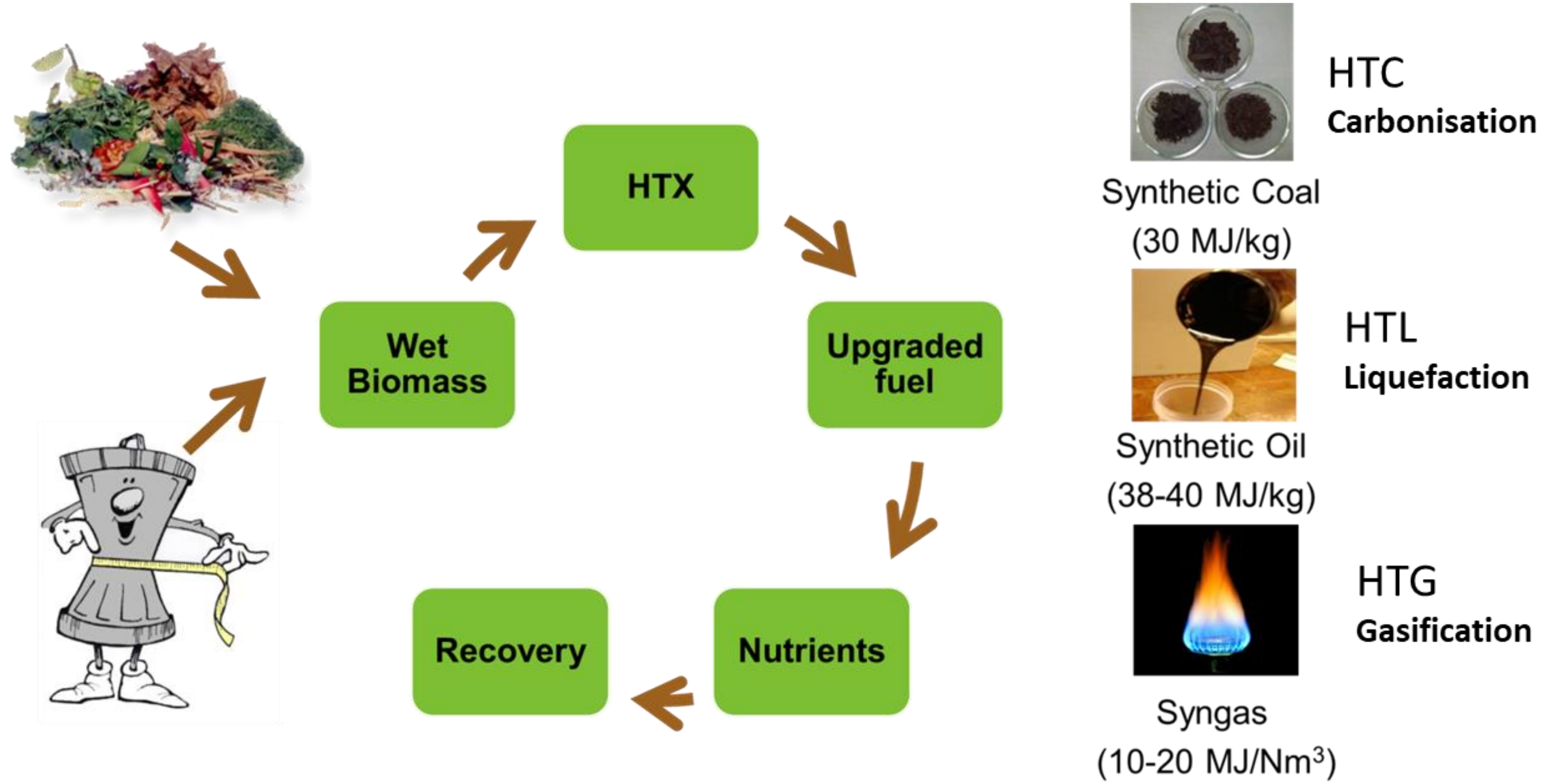
This session will cover:

- Application of the solid and liquid products
- Energy Applications
- Agronomic applications
- Resource recovery

Session 1

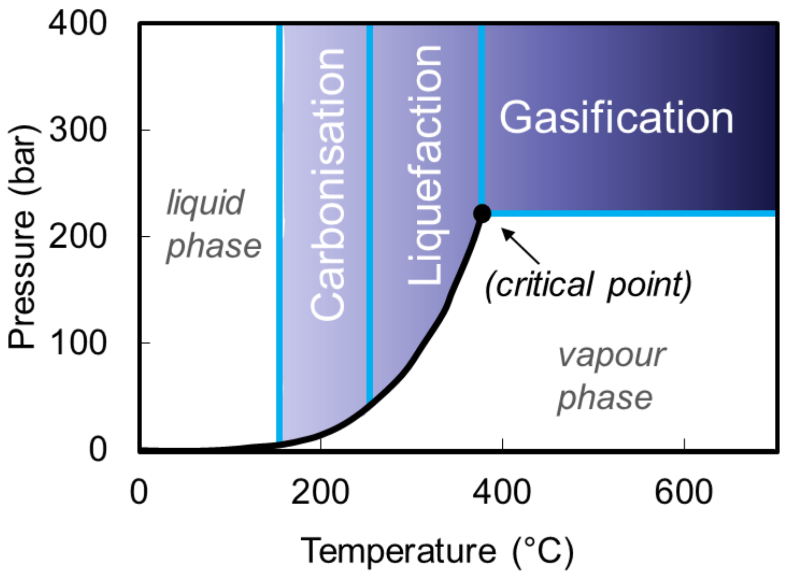
Introduction to Hydrothermal conversion

Hydrothermal conversion



Hydrothermal conversion

- Hydrothermal conversion involves the processing of organic material in hot compressed liquid water
- Products depend upon severity of conditions

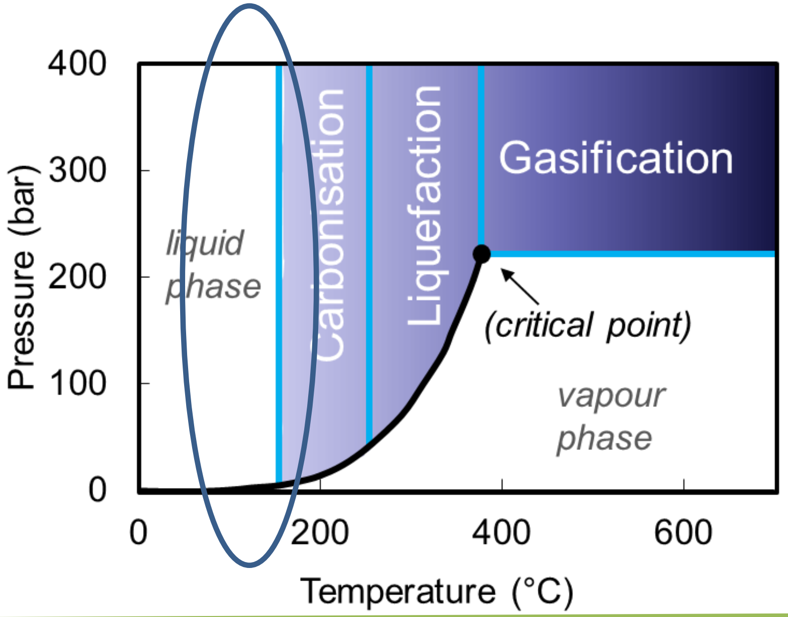


Conversion of water/biomass slurry at high pressure

Sometimes in the presence of catalysts

Thermal hydrolysis

- **Hydrolysis** performed at temperatures ~ 120-160°C
- Promotes the breakdown of complex molecules into smaller molecules



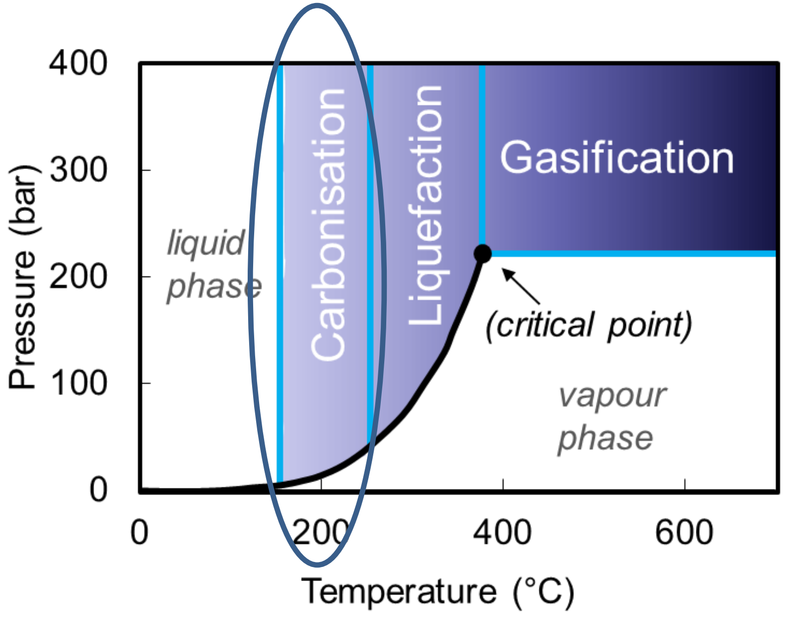
Thermal Hydrolysis

Products: Slurry made up of suspended solids in water. increased solubilisation of smaller molecules as temperature increases

e.g. carbohydrate to sugars

Hydrothermal Carbonisation

- **Hydrothermal carbonisation** is performed at 180°C - 260°C
- Promotes the hydrolysis, condensation and polymerisation of smaller molecules to produce a carbonaceous char



Hydrothermal carbonisation

Products: Hydrochar & water solubles

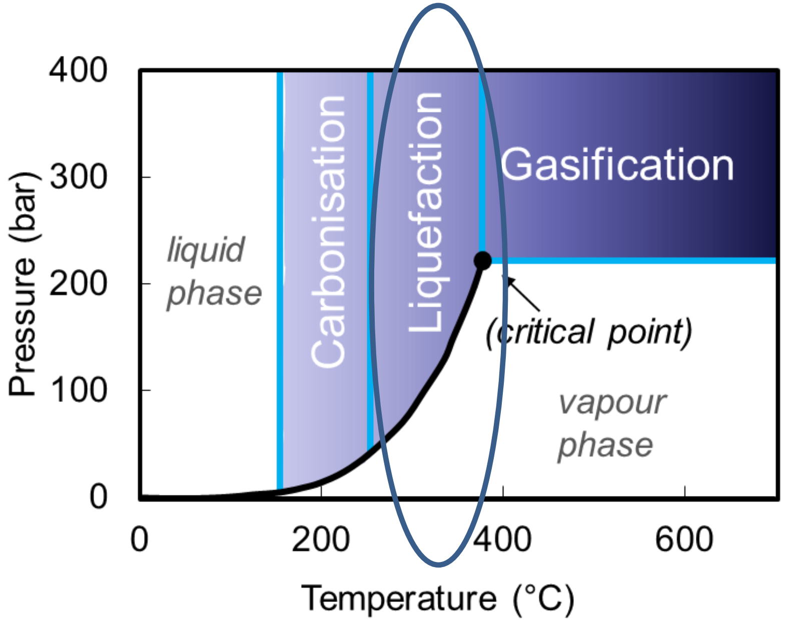
Influence of inorganics, solid fuels

Processing of Aqueous phase

Range of feedstocks

Hydrothermal liquefaction

- **Hydrothermal liquefaction** is performed at 280°C to 375°C
- Promotes the liquefaction of biomass into an oily bio-crude intermediate



Hydrothermal Liquefaction

Products: Biocrude & water solubles

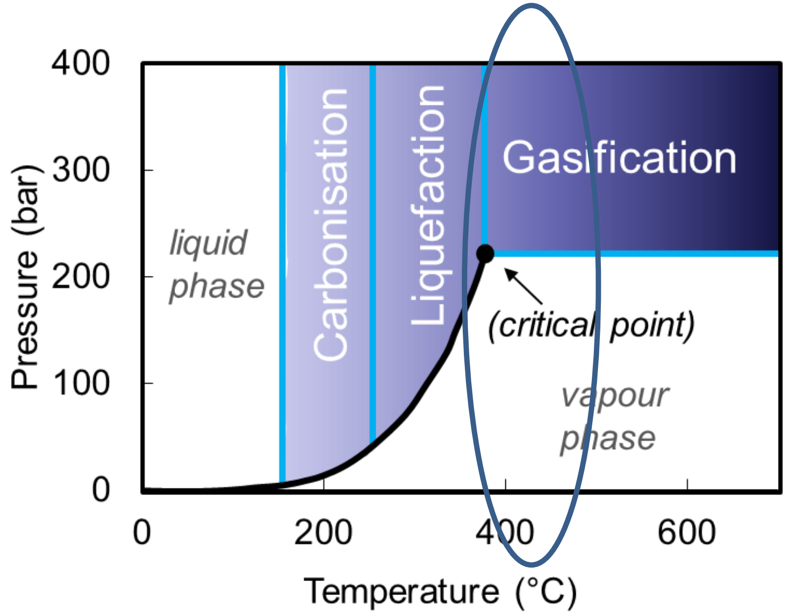
Catalysis, hydrogen donors

Upgrading and combustion of Oils

Algal and sewage sludge feedstocks

Hydrothermal gasification

- **Hydrothermal gasification** is performed >350°C-500°C
- Promotes the production of a gaseous product containing CH_4, CO and H_2.



Hydrothermal Gasification

Products: Syngas & small amount of residual solid (Char& Inorganics)

Catalysis, hydrogen and methane production

Solid and liquid feedstocks

Hydrothermal conversion

Bio-coal (30 MJ/kg)

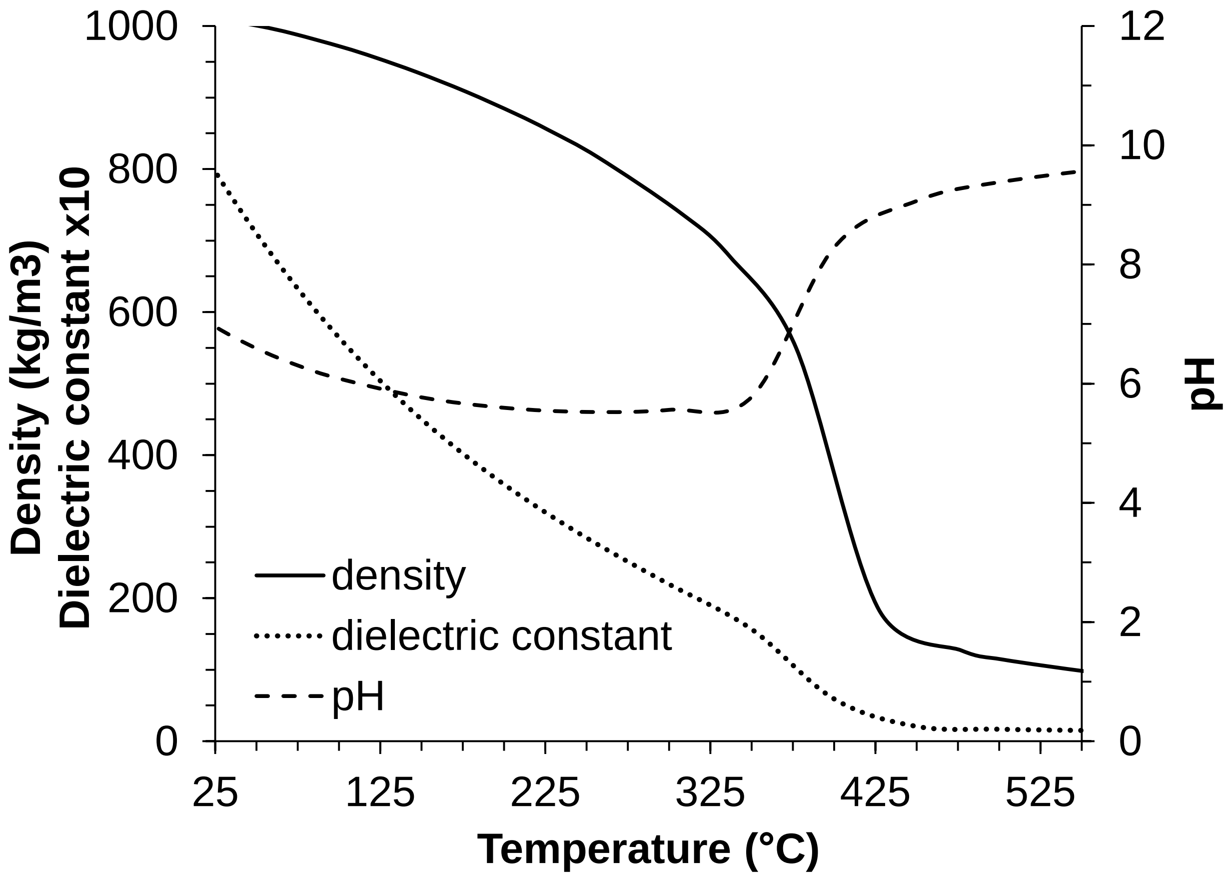
Biocrude (38-40MJ/kg)

Accelerating Nature !!

Acceleration of humification, coalification, kerogen formation (diagenesis), oil formation (catagenesis) and gas fomation.

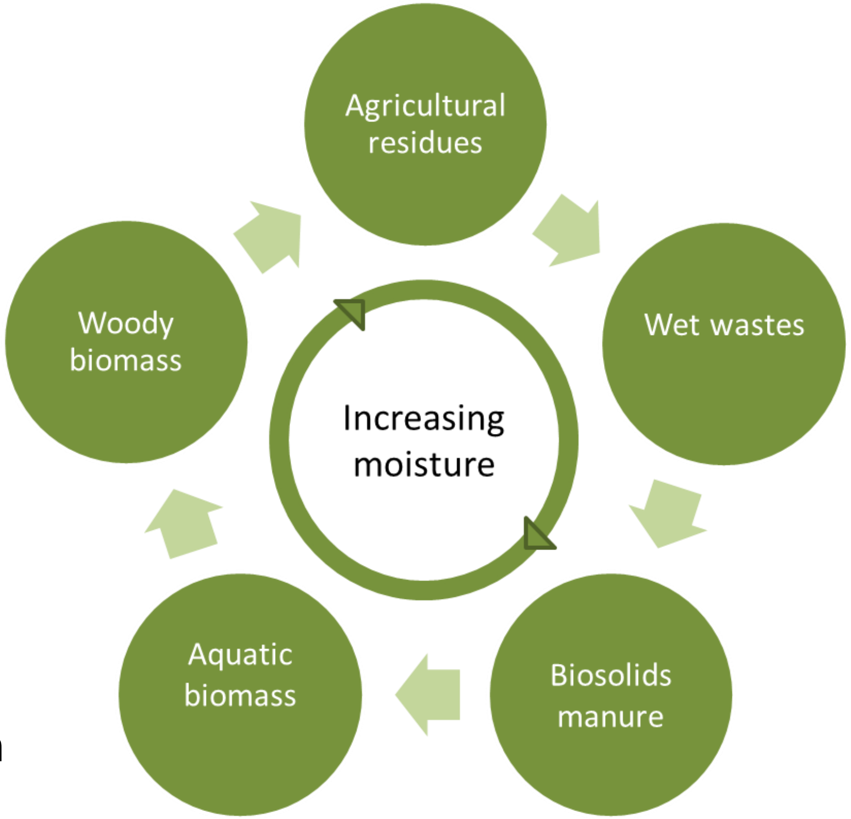
Syngas (10-20MJ/Nm^{3})

Properties of water



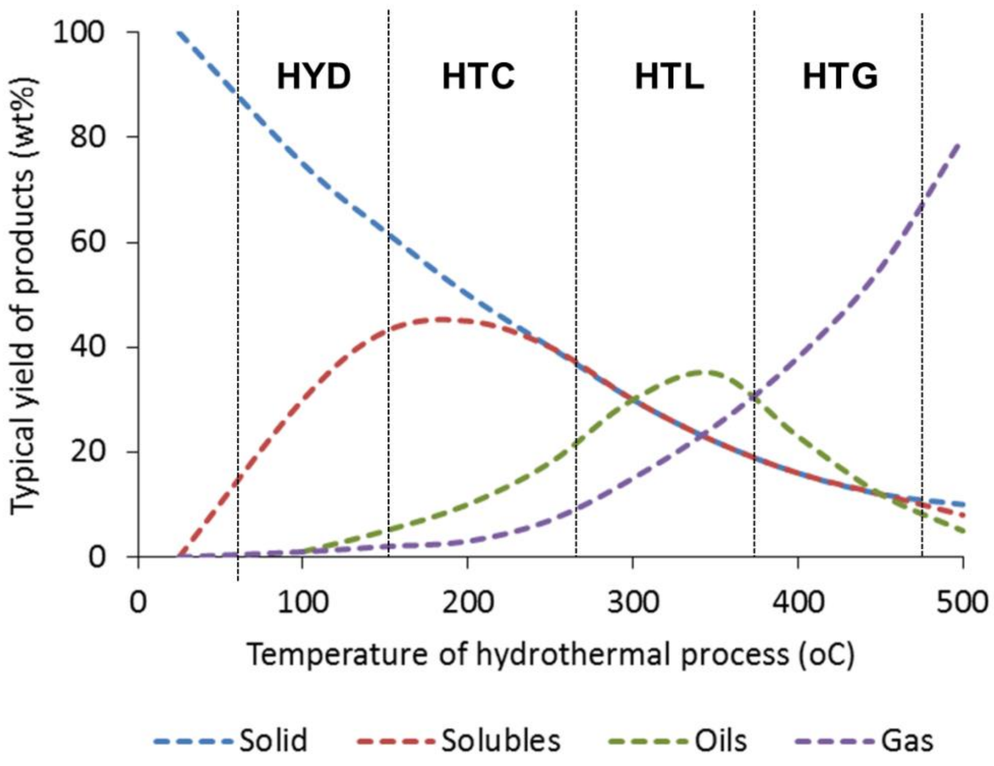
Suitable feedstocks

- Any feedstock can be processed by hydrothermal conversion
- Well suited for wet feedstocks, removing the need for drying
- Pumping and feeding an important consideration
- Biochemical composition effects the behaviour during hydrothermal conversion



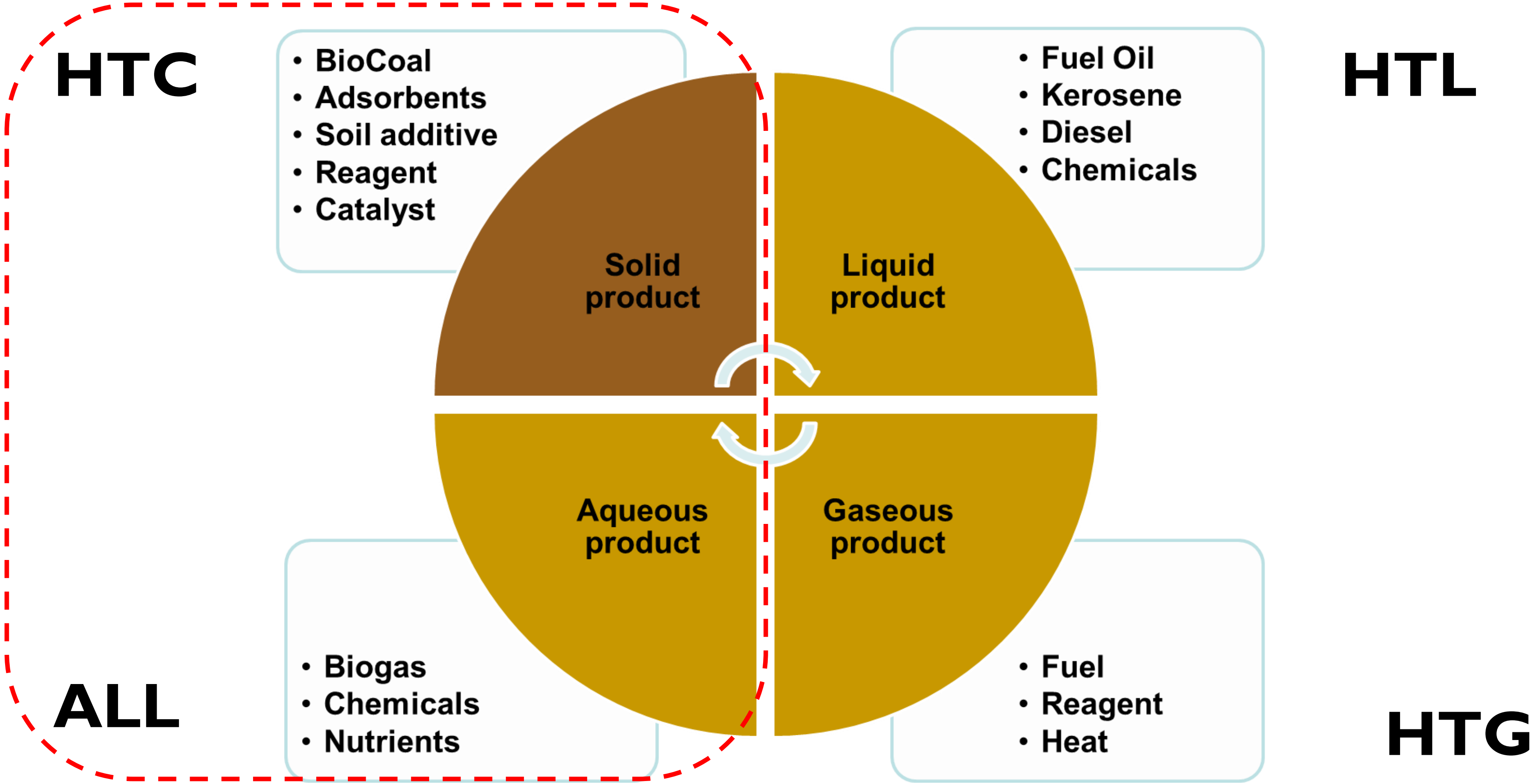
Hydrothermal conversion is highly feedstock dependent

Product yields



- Composition of biomass effects yield and quality of products
- High starch/protein content good for hydrolysis
- High cellulose & lignin content good for HTC
- High Lipid content good for HTL

Types of products



Question and answer session

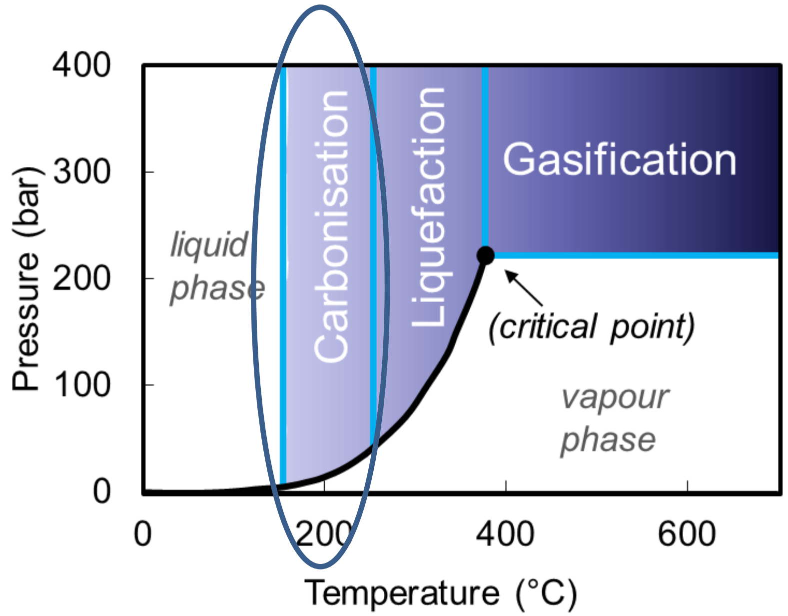
- Thank you for listening,
- Any Questions?

Session 2

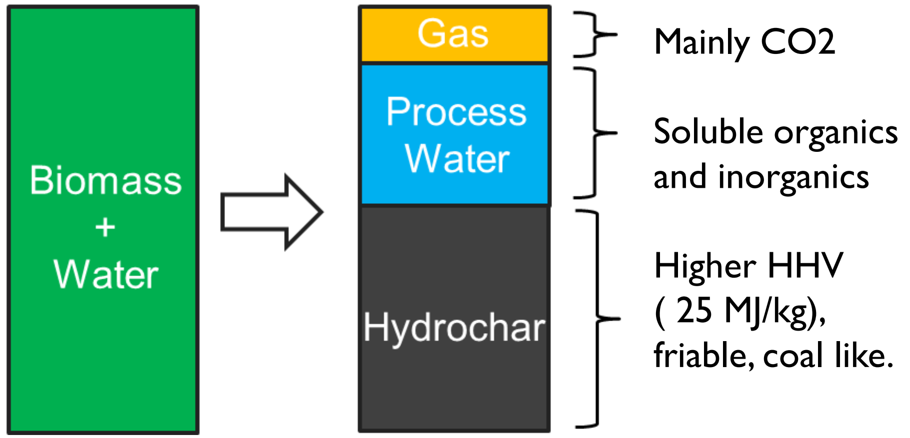
Introduction to Hydrothermal Carbonisation

Hydrothermal carbonisation

- HTC converts organic material in hot compressed liquid water into 3 main products (hydrochar, water solubles & gas).
- Increasing interest in treatment of waste streams such as biosolids and MSW by hydrothermal carbonisation;

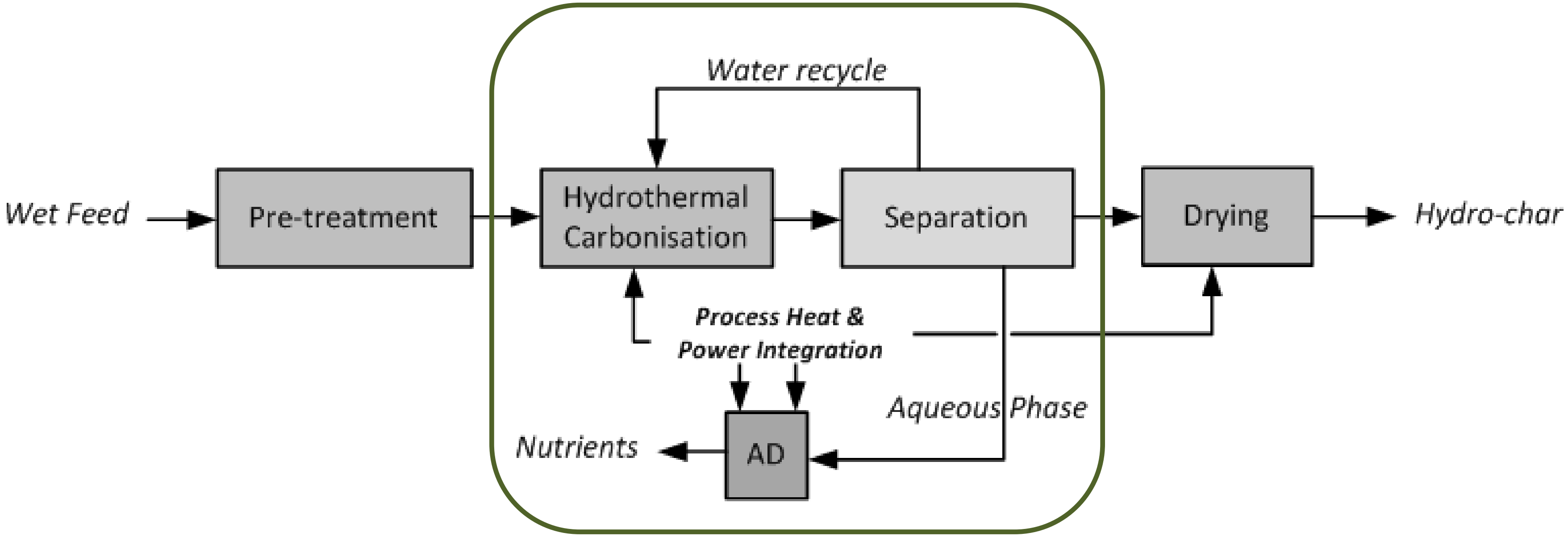


Hydrothermal carbonisation (HTC)



180-250°C, 10-40 bar

Process layout



- Hydrothermal carbonisation can be integrated with anaerobic digestion enhancing biogas yields.
- Process water recycle influence product yields.
- Product quality, distribution and energetics feedstock dependent.
- Pilot scale using batch and continuous designs

Technology status

- Technology Readiness Level (TRL 6-7)

- Notable European technology developers

Terra Nova Energy (Germany)

treatment of sewage sludge

demonstration plant operated in China

Terra nova Ultra – Jining/China

Ingelia (Spain)

treatment of waste (agricultural, green, forestry, agro-industrial, fruit and garden waste

New UK Venture with CPL/Nottingham University

- Solid Fuels, Soil additives, nutrient extraction

CPL plans UK's first commercial-scale hydrothermal carbonisation (HTC) plant

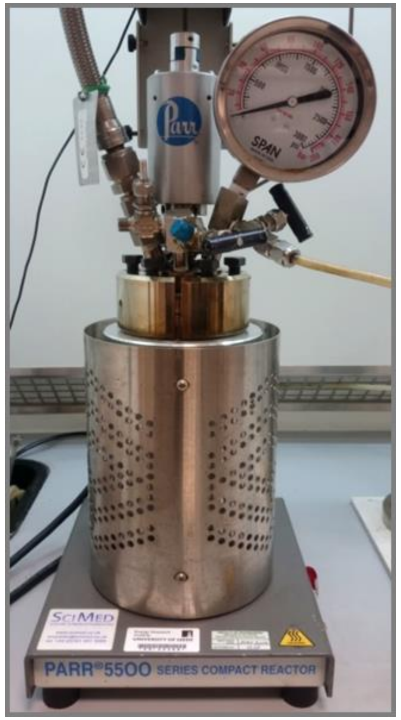
Bioenergy International · Pellets & Solid Fuels · November 22, 2017

CPL Industries Ltd, a UK-headed developer, producer and distributor of solid fuels has announced plans to install a commercial-scale hydrothermal carbonisation (HTC) facility at its production site in Immingham. This facility, scheduled to begin production in mid-2018, will be the first commercial-scale example of this technology, developed by CPL's Spanish partner Ingelia, anywhere in the UK.

Artist rendering of the hydrothermal carbonisation (HTC) plant to be built in Immingham (image courtesy CPL Industries).

Laboratory studies

2L reactor



500 ml reactor

Processing

- High pressure batch reactors (80ml to 2 L)
- Process variables (temp, time, loading)
- Conventional vs microwave heating

Characterisation of products

- BioCoal/Hydrochar characterisation
- Fuel properties, agronomic, environmental
- Analysis and treatment of process water

Feedstocks

- Variable levels of lignin, protein, lipid, ash

Feedstocks for HTC

Energy densification & demineralisation to high quality bio-coal

Grasses
AGR

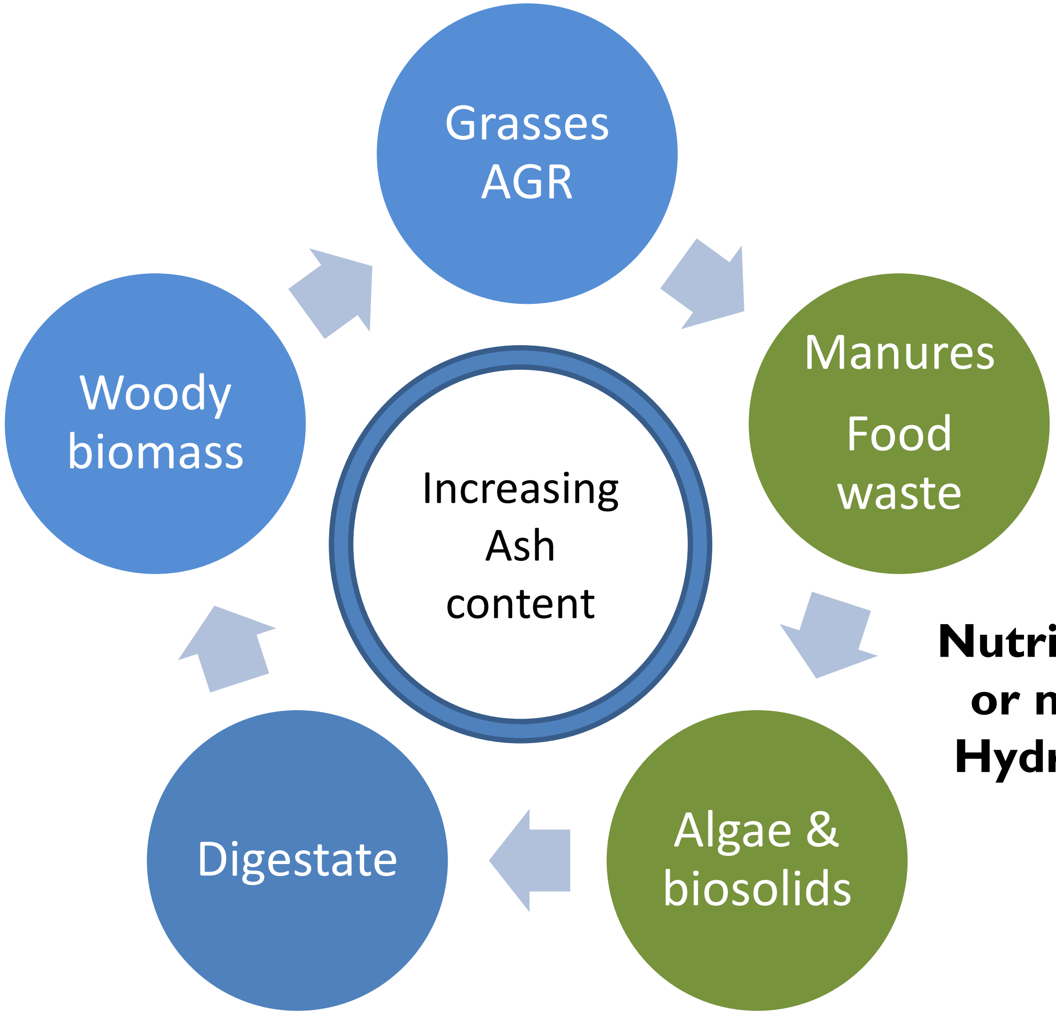
Manures
Food waste

Algae
biowastes

Digestate

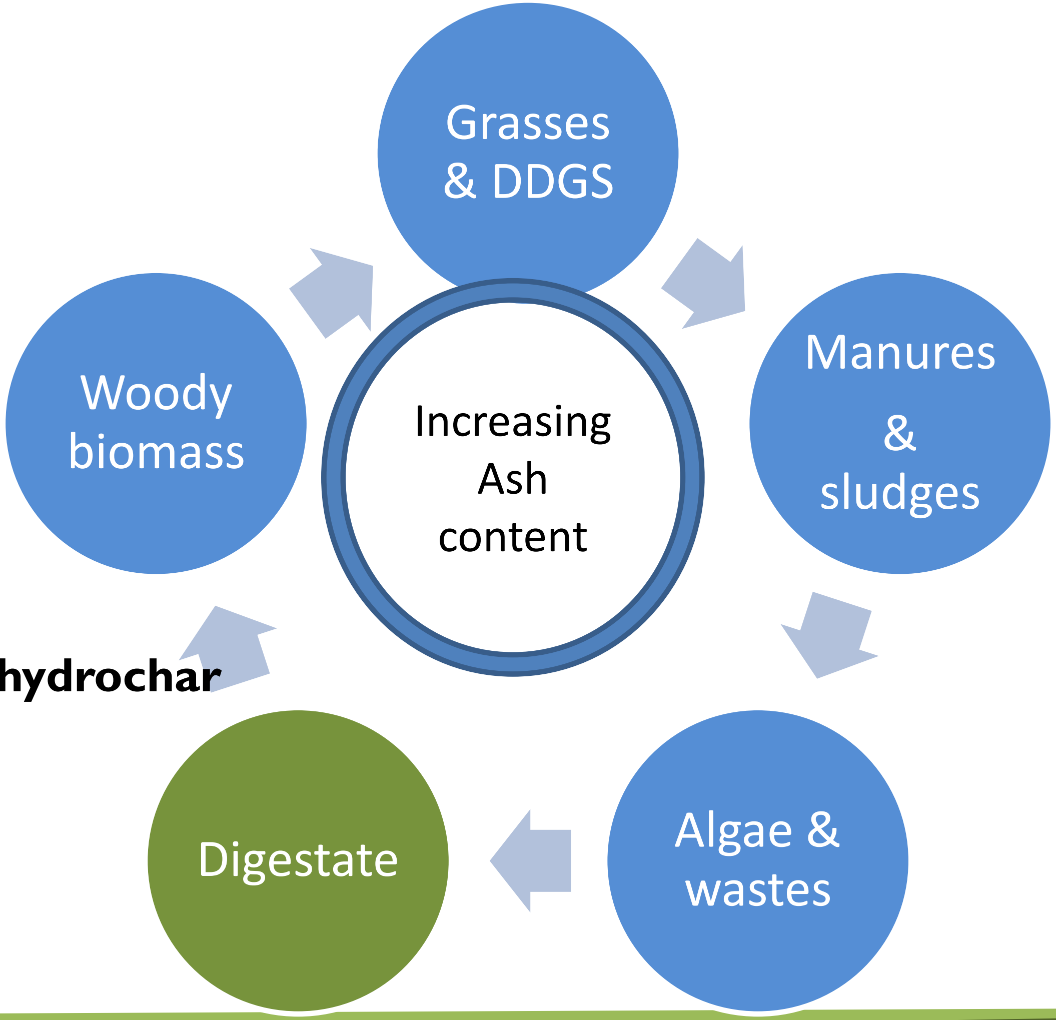
Woody biomass

Feedstocks for HTC



Nutrient immobilisation or nutrient extraction
Hydrochar or bio-coal ?

Feedstocks for HTC



High ash containing hydrochar

Factors effecting hydrochar properties

Composition of feedstock (biochemical & ash content)

Reaction conditions (Temp, time, solid loading)

Reactor considerations (heating rate, recycle, salt removal)

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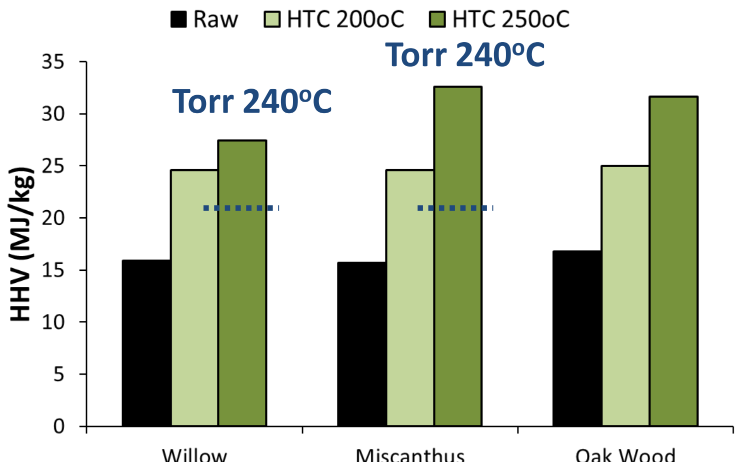
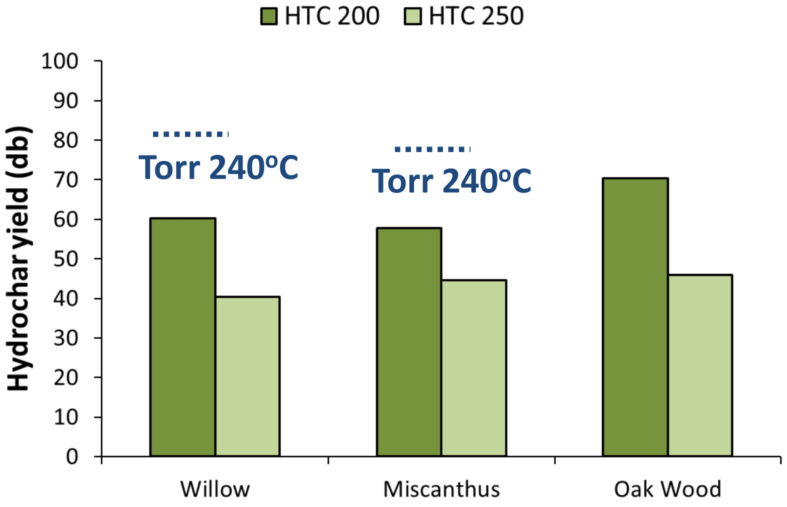
Energy densification





A.M. Smith et al./Fuel 169 (2016) 135–145

- Woody biomass show a high energy densification
- Typical yields at 200°C ~60-70 wt% bio-coal 25 MJ/kg (db)
- Typical yields at 250°C ~40-50 wt% bio-coal 30 MJ/kg (db)
- Bio-coal more hydrophobic and easier to grind (more friable)

Energy densification due to de-oxygenation due to removal of hydroxyl (-OH), carboxyl (C=O) and carbon-oxygen bonds (C-O)

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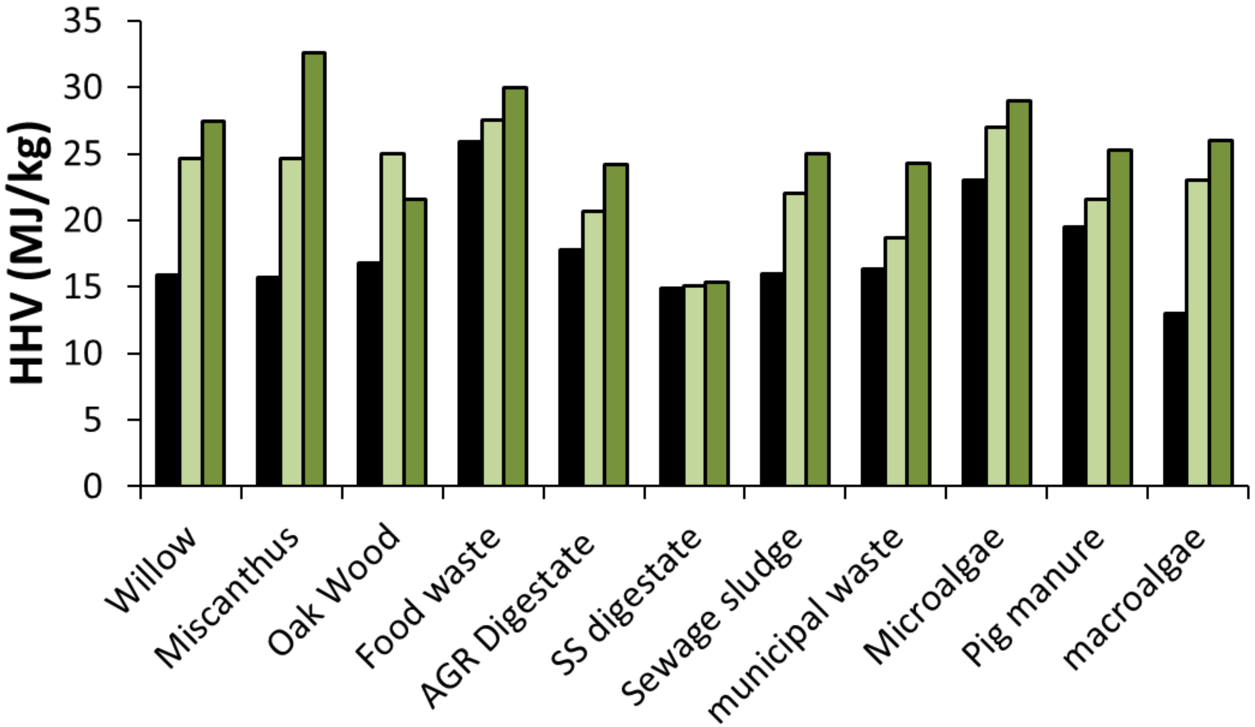
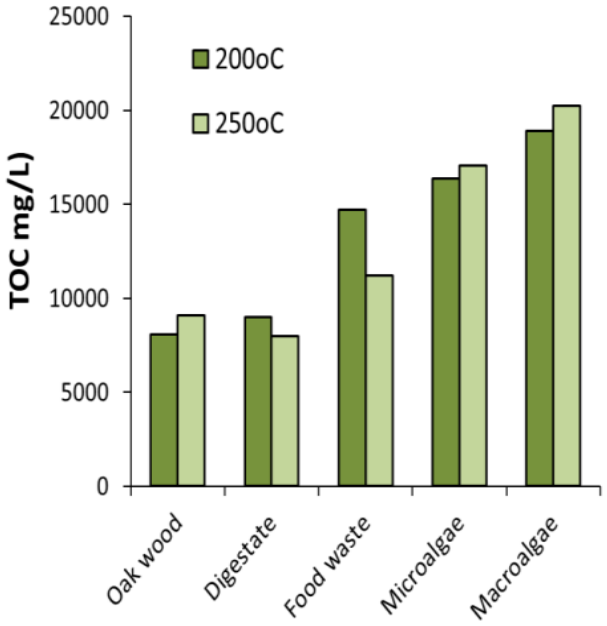
Feedstock dependency

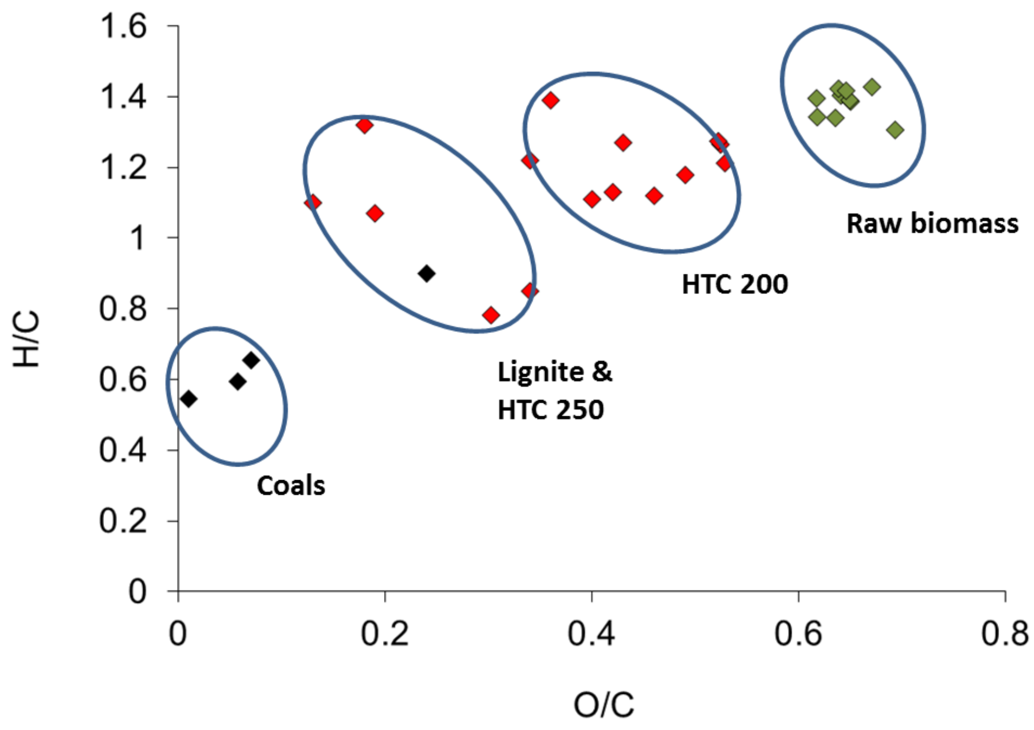




- HTC results in significant energy densification but behaviour feedstock dependent
- Typically significant levels of soluble COD in process waters

Deoxygenation during HTC

Van-Krevelen Diagram



- **Deoxygenation results in:**
  - Increased Energy Density
  - More 'coal like' fuel
- **Influence of Temperature:**
  - Higher HHV
  - Reduced O/C
  - Effects demineralisation

High ash feedstocks

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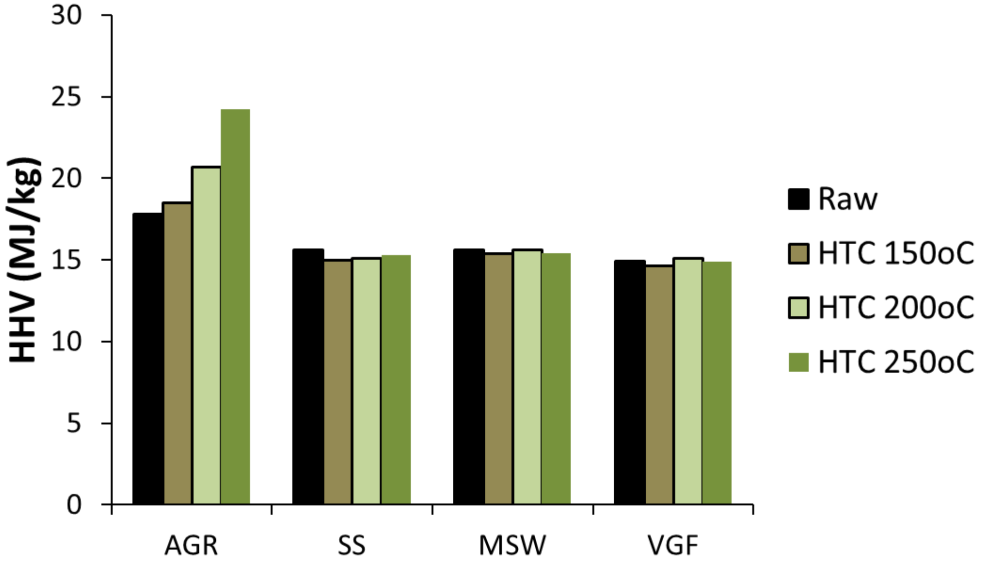
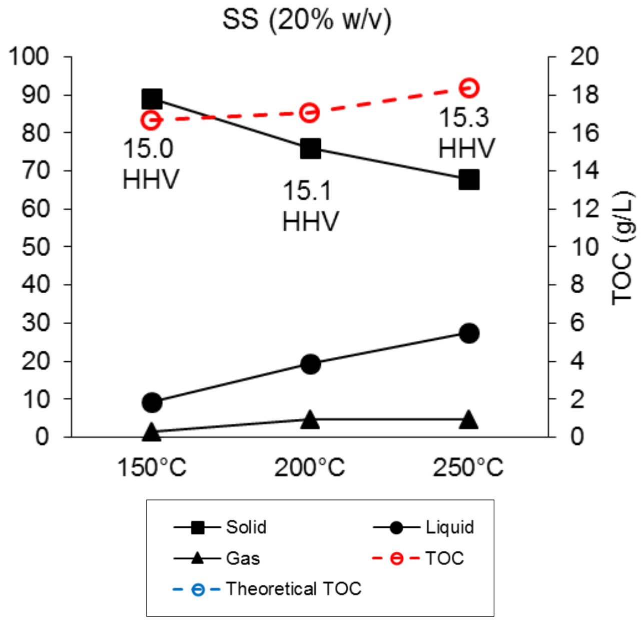
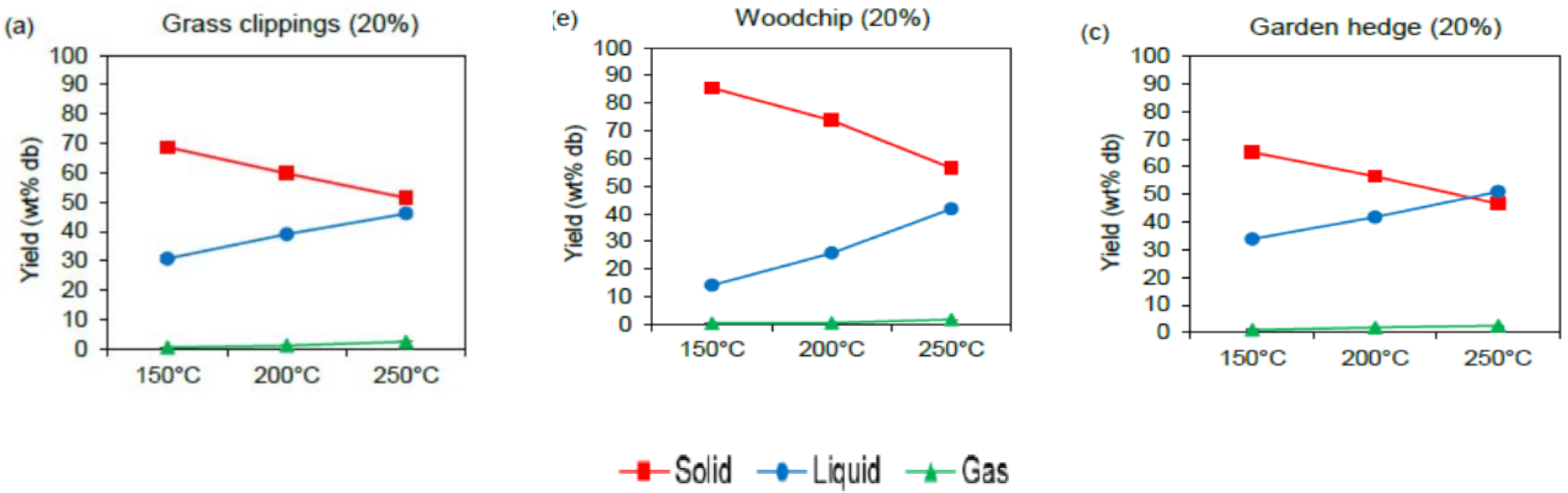
Digestate less attractive for production of 'Bio-coal'.





Products yields



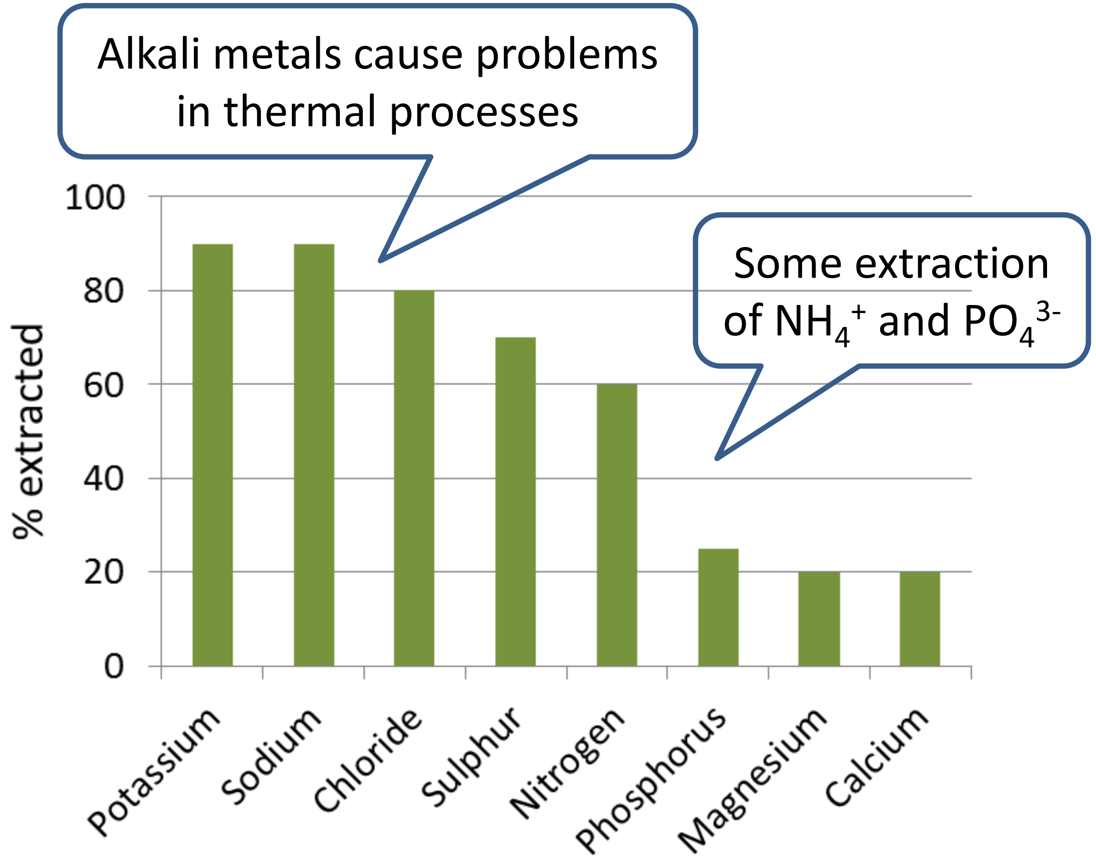
Demineralisation

HTC leads to significant demineralisation

Reduces ash related problems

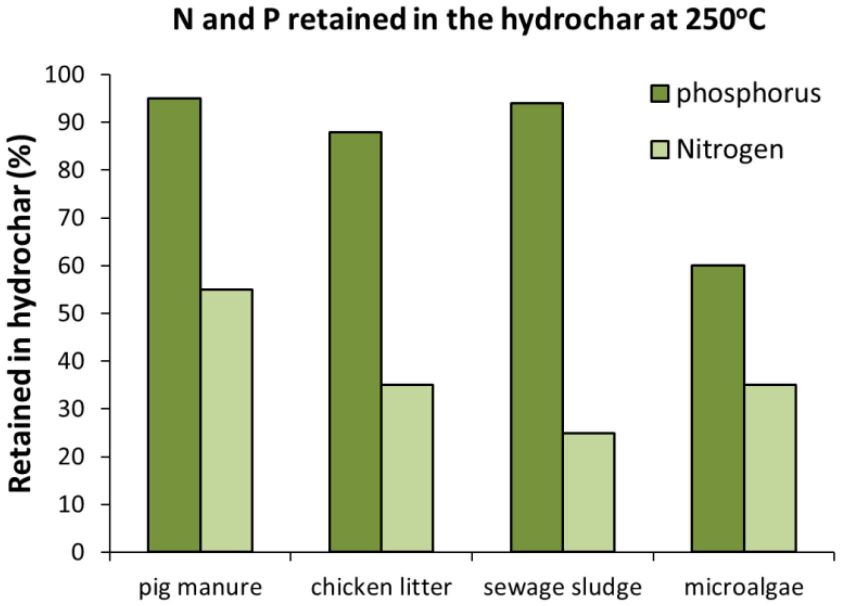
Improved properties for combustion and gasification

Potential for recovery of extracted minerals from water



Extraction is highly feedstock dependent!

Fate of N and P



- Fate of N&P and many other micronutrients vary and influenced by ‘matrix effects’.
- Limited amounts of P extracted into water for some feedstocks (e.g. manure and sewage sludge) although others behave differently (e.g. microalgae).
- Significant fraction of N extracted into process waters (NH_4^+, NO_3^- and Org-N) although N in hydrochar can still be high.

Composition of process waters

- pH range from 3 - 6.0
- TOC range from 10,000 – 20,000 mg/L
- C/N ratio from 8-14
- Ammonium 100-400 mg/L
- Phosphate 100-600 mg/L

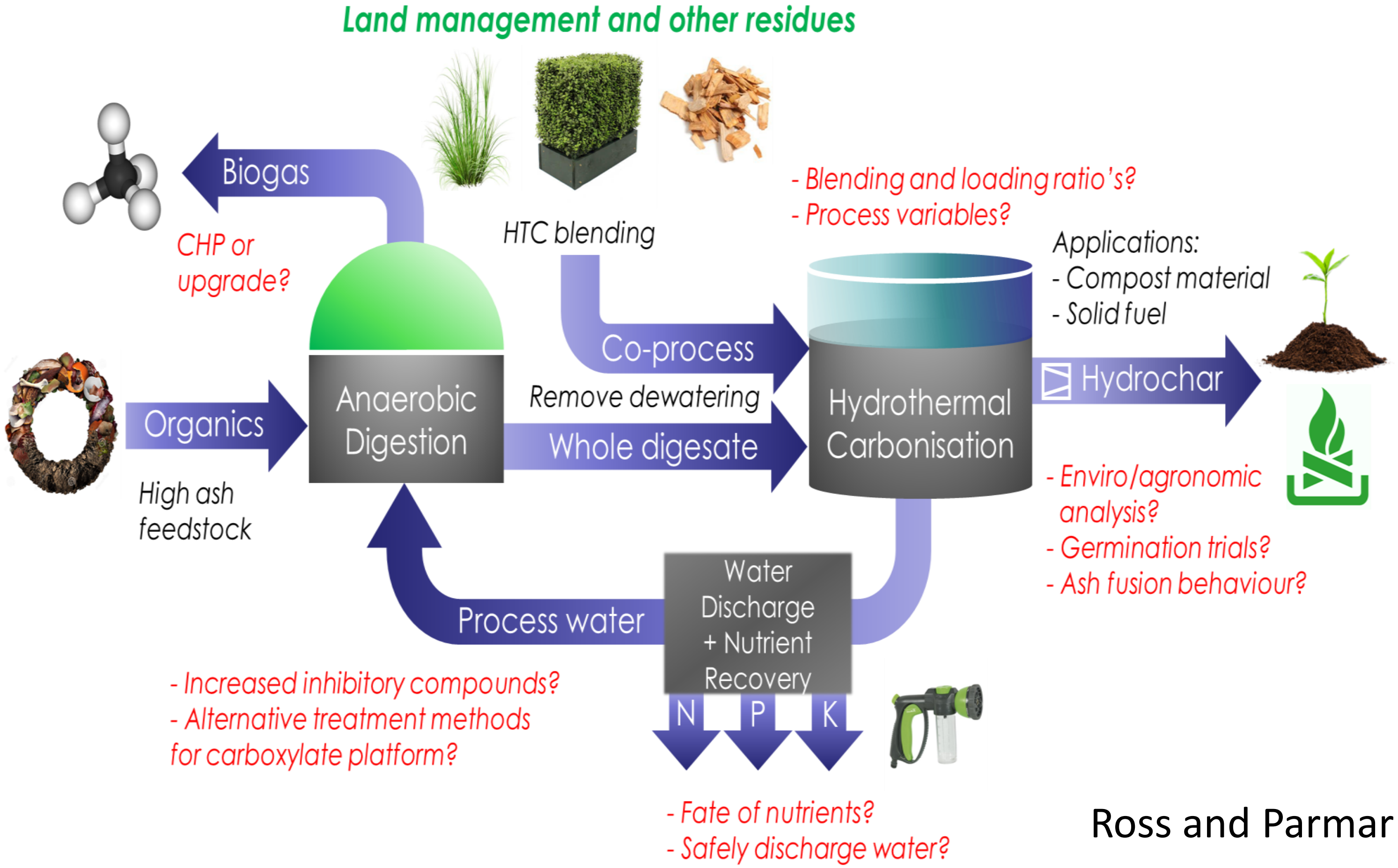
- Process water typically contains around 15% mineral matter and 85% VM

Typical components in process water

Sugars	VFA	Other
Glucose	Acetic acid	Furfural
xylose	Formic acid	4-HMF
Org-N	Lactic acid	phenols
PO_4^{3-}	Citric acid	NH_4^+

Increasing temperature →

Integration options



Ross and Parmar 2019

Question and answer session

- Thank you for listening,
- Any Questions?

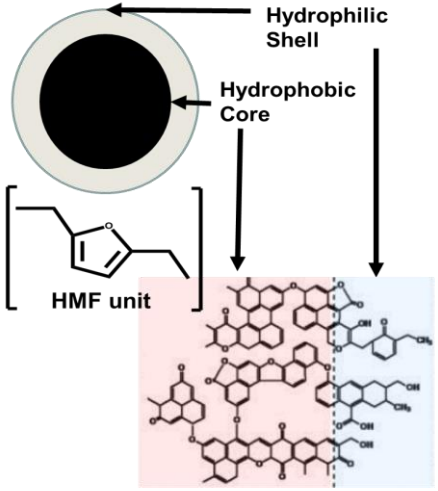
Session 3
Application of the products

Application of products

Solid product

Hydrochar or Biocoal

Energy carrier
Functionalised carbons
Adsorbents
Catalyst supports
Soil additive



Aqueous product

Sugars, VFA and inorganics.

Energy via AD (CH_4, biohythane)
Fermentation (ethanol)
Extraction of nutrients (PO_4^{3-})
Source of chemicals (HMF, VFA)

Opportunities for Hydrochar

HTC = potential pre-treatment for biomass and waste

- Producing a homogeneous product from a heterogeneous feedstock
- Significant improvement in Combustion and gasification behaviour
- Coal can **'replace'** coal or can be **'co-fired'** with coal
- Opportunities in the domestic sector as a blend or as a binder
- Process is largely driven by Waste management

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Benefits of HTC

Biomass/biowaste

- Low bulk density ☹
- High moisture ☹
- Low calorific value ☹
- Hydrophilic ☹
- Difficult to mill ☹
- Slagging and Fouling propensity ☹

Bio-Coal

- Higher bulk density? ☺
- low moisture ☺
- High calorific value☺
- Hydrophobic ☺
- Easily friable ☺
- Reduces Slagging and Fouling propensity ☺

HTC = potential pre-treatment for biomass

- Combustion and gasification
- Integration with AD

Bio-coal properties

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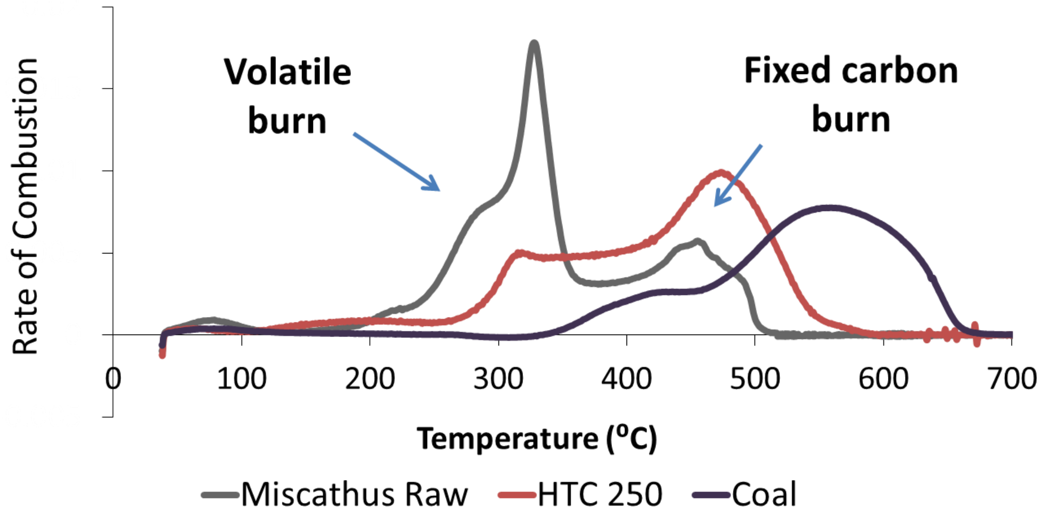


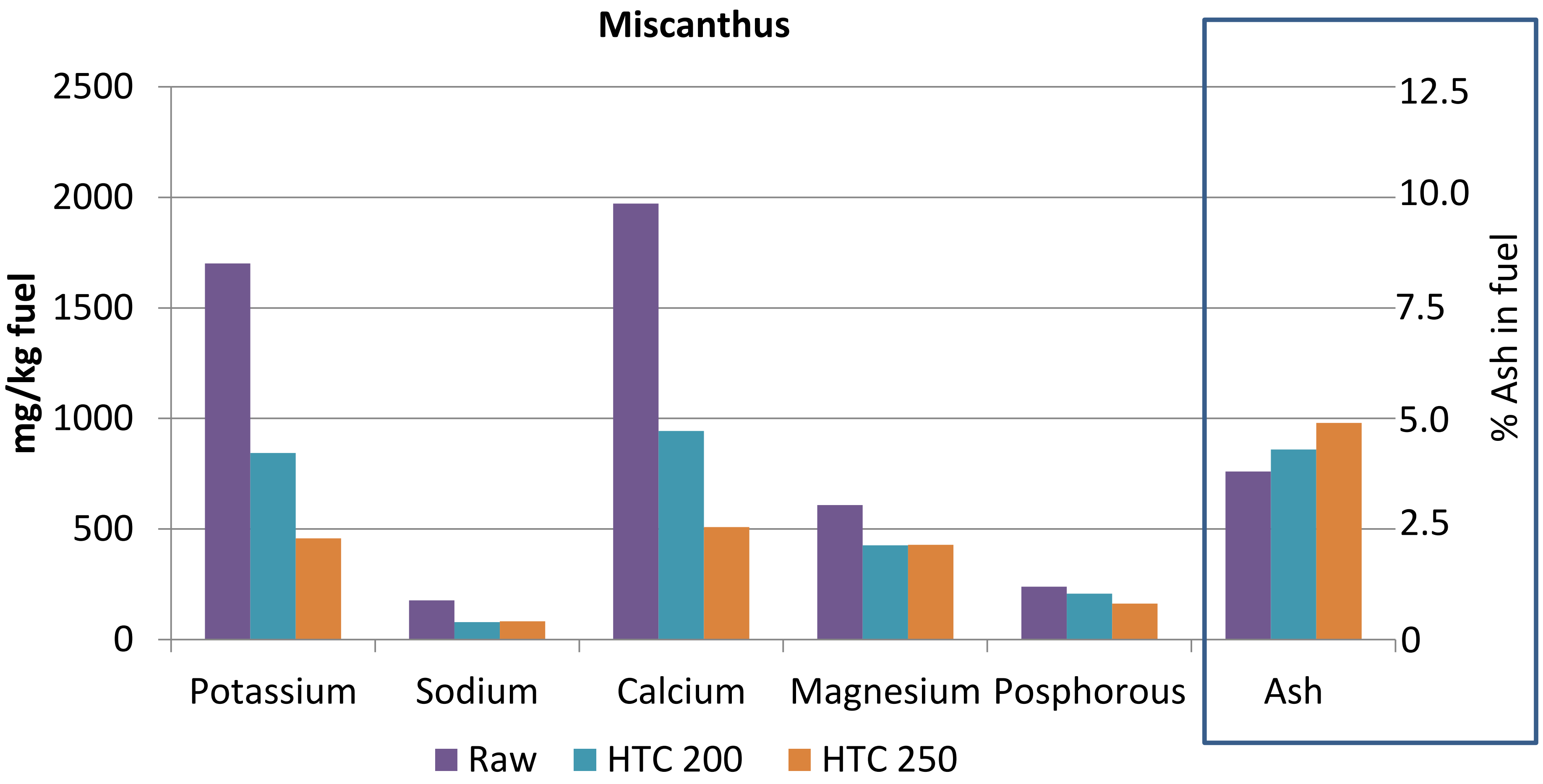
Burning profile of HTC bio-coal vs biomass and coal

- Increased energy density
- Hydrophobic (<4% moisture)
- Grindability improves (HGI - 177)
- Improved handling and storage

More like coal!

Improved combustion AND gasification performance

Demineralisation



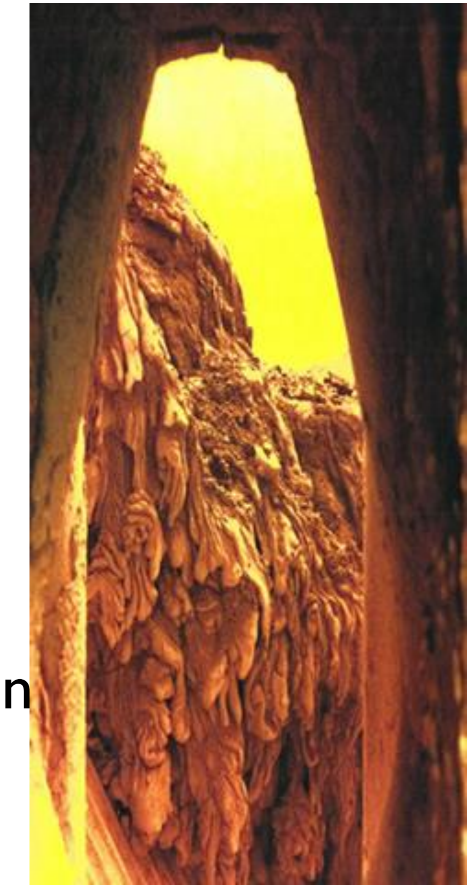
Slagging, fouling and corrosion

Ash = metal oxides in fuel

- Can be problematic
- Slagging = melting and fusion of ash in furnace

  low temp = ☹

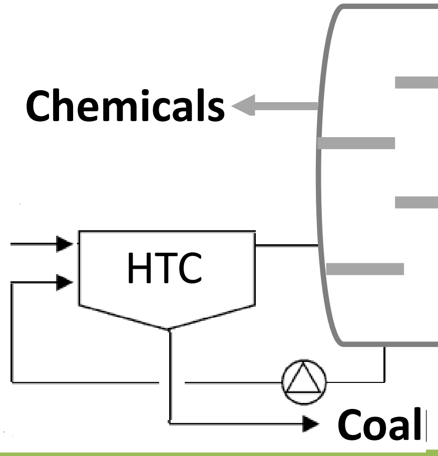
  high temp (1500°) = ☺
  - K + Na lower melting temperature
  - Ca + Mg increase melting temperature
- Fouling = formation of corrosive alkali chlorides on heat exchangers
  - K + Na + Cl + S problematic



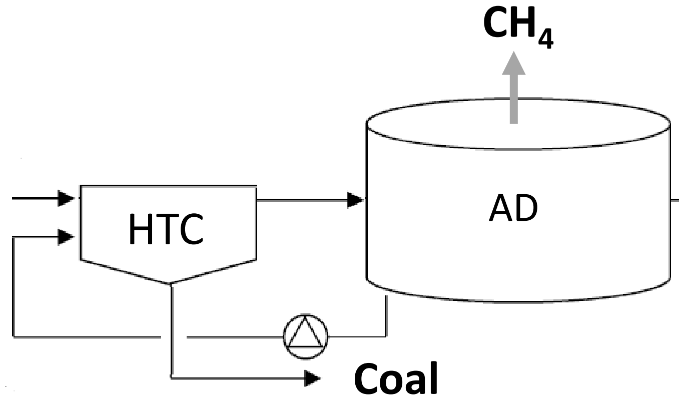
Application of process waters

- 10-15 % original organic matter
- Complex mixture of sugars, organic acids, phenols and inorganic salts
- Recovery of C essential
    - Efficiency
    - Waste disposal

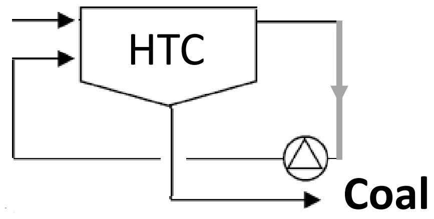
a) Extract chemicals?



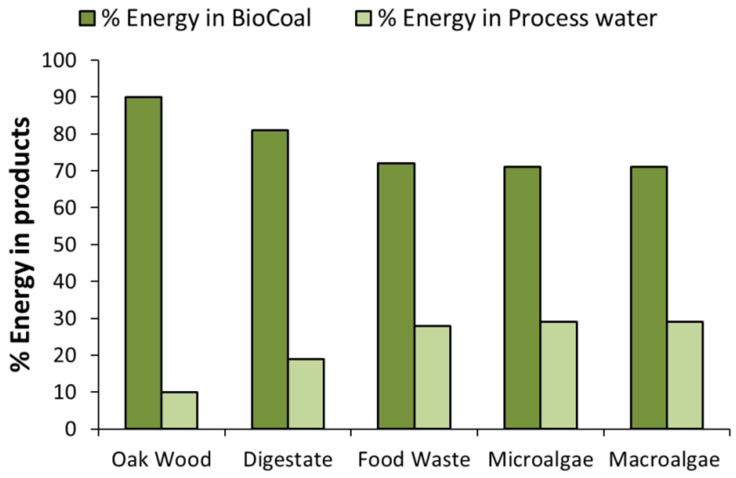
b) Anaerobically digest?

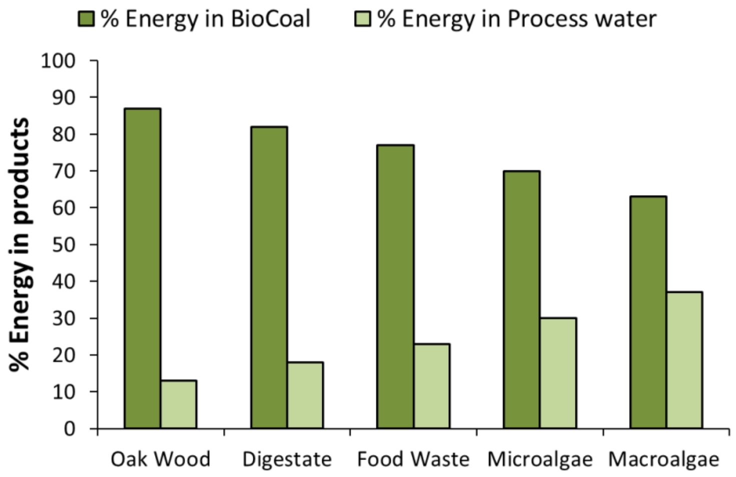


c) Recycle waters?

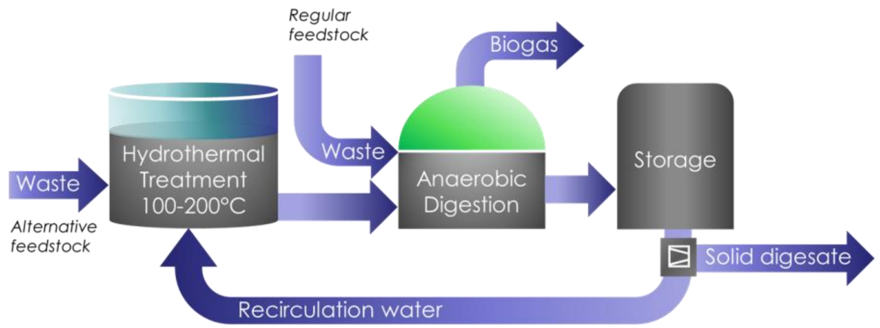


Integration with AD



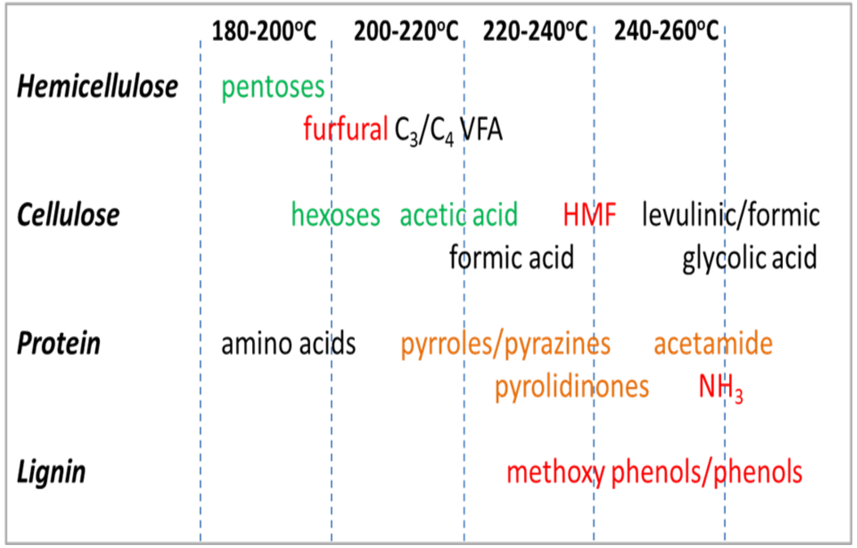


- Considerable potential for enhanced energy recovery from process water by AD
- Inhibition and biodegradability is being investigated by multiple groups.



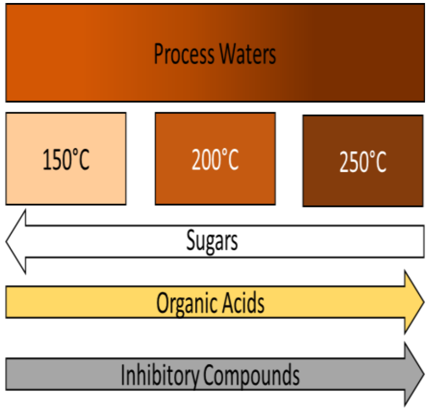
- Inhibition is highly feedstock and temperature dependent.

Formation of inhibitory compounds



Overcoming inhibition
Is a challenge:

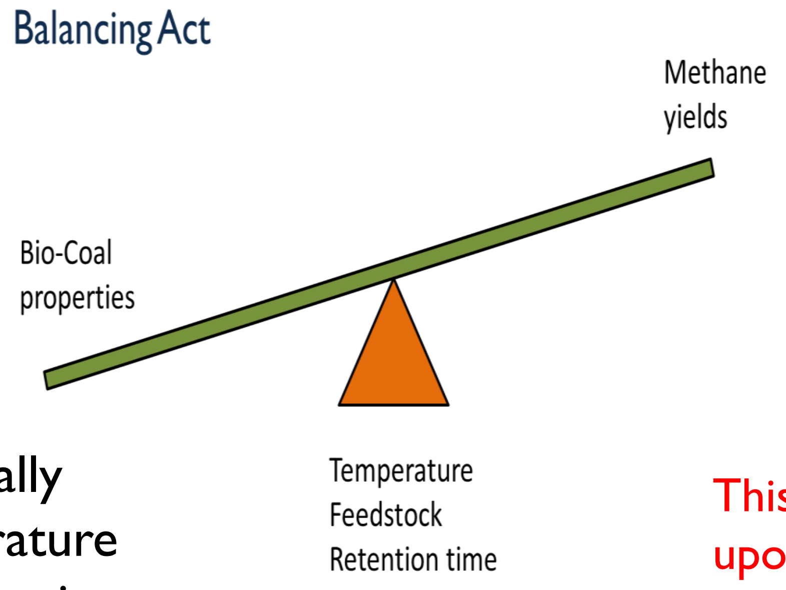
- minimise production by controlling conditions
- **Remove or suppress the effects of inhibition**



Difficult to predict BMP of process waters as the generation of furanic compounds, phenols and sugars are different depending upon feedstock and reactor configuration

BUT Generally
Lower temperature/lower residence times appear best!

Choice of conditions



BMP generally decreases with temperature

- Inhibition
- biodegradability

Bio-coal quality generally increases with temperature

- Energy densification
- Ash chemistry
- Handling properties

This balance is dependent upon your favoured end use and energy considerations

Bio-coal or Soil additive

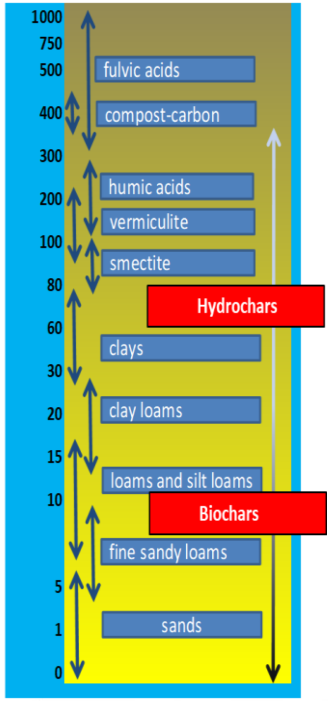
HIGH energy density → Bio-Coal

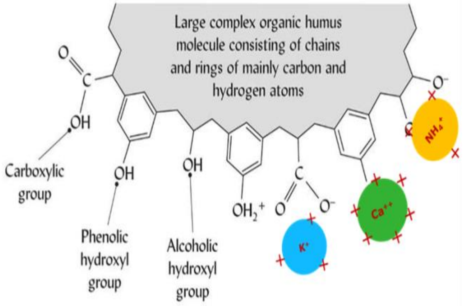
LOW energy density → Soil Additive

Hydrochars exhibit:

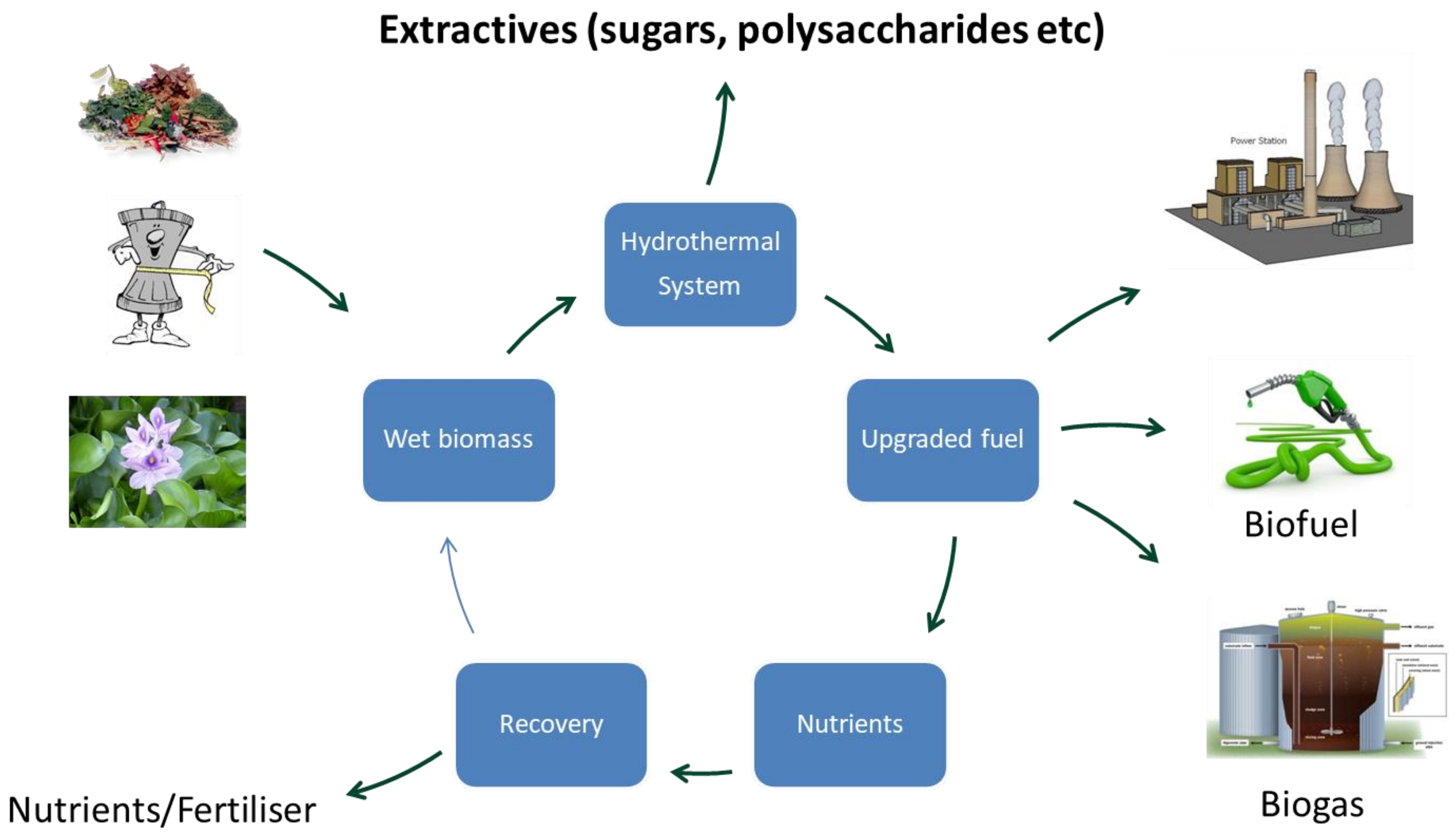
- High functionality– retain nutrients, high CEC, AEC
- Enrichment of P in the hydrochar
- Recalcitrant carbon –sequestration potential
- Labile carbon – high TEOC, WEOC, WEON.
- Safety – PAH low

CHAR TYPE	TEOC (µg/g)	Total PAH (µg/g)	WEOC (µg/g)	VM (%)
SS Biochar 600ºC	2900	8.1	109	6.9
SS Hydrochar 250ºC	21400	3.18	2752	20.2

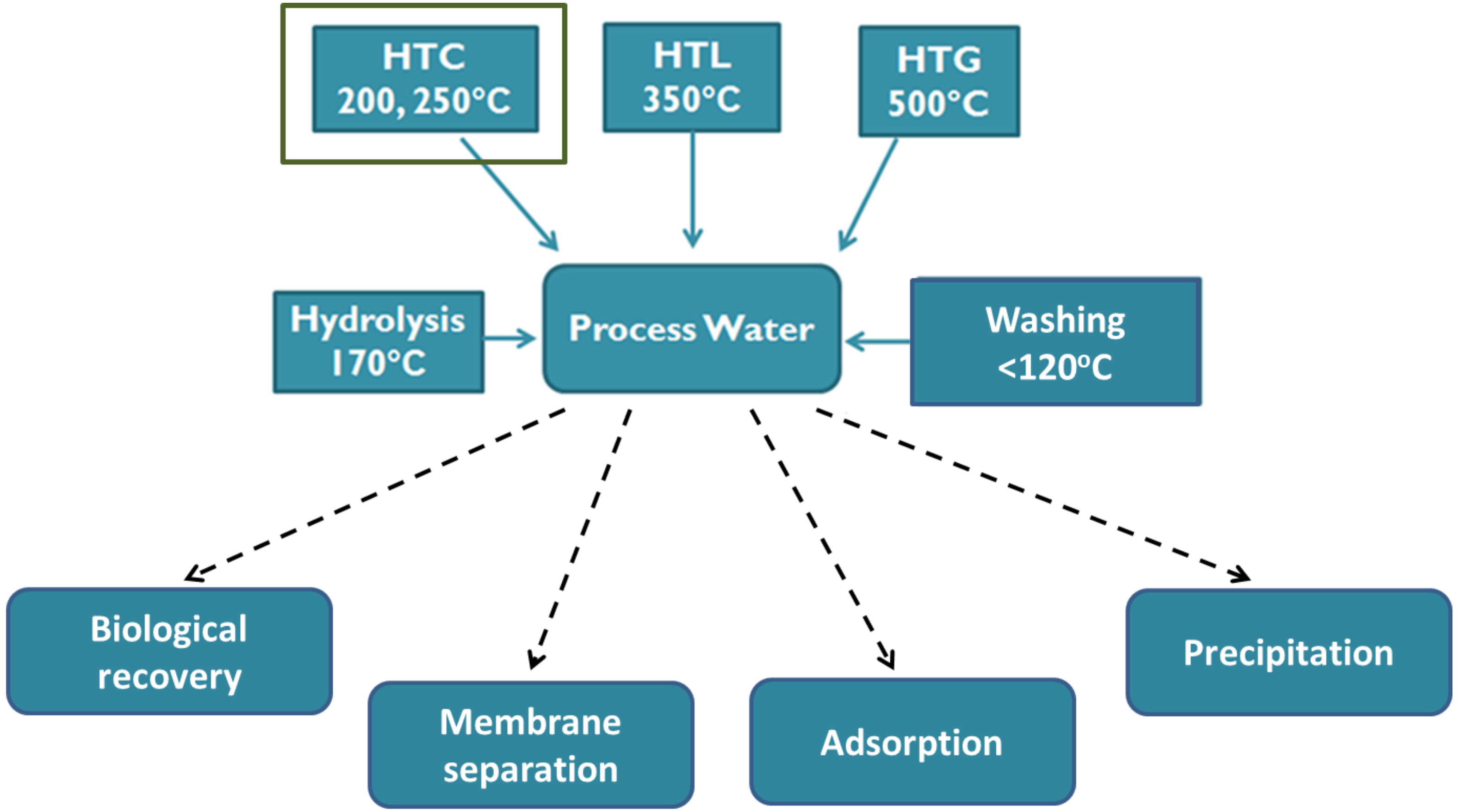




Energy and nutrient cycling



Nutrient recovery



Recovery of Nutrients

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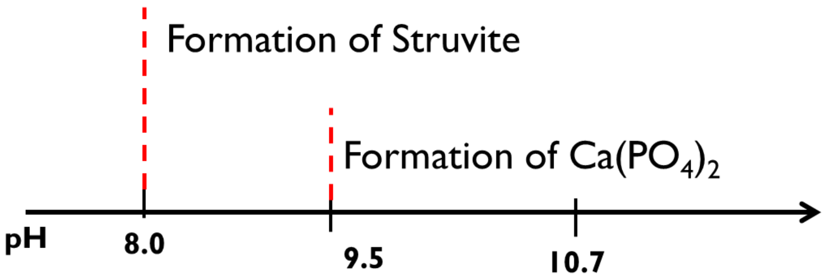
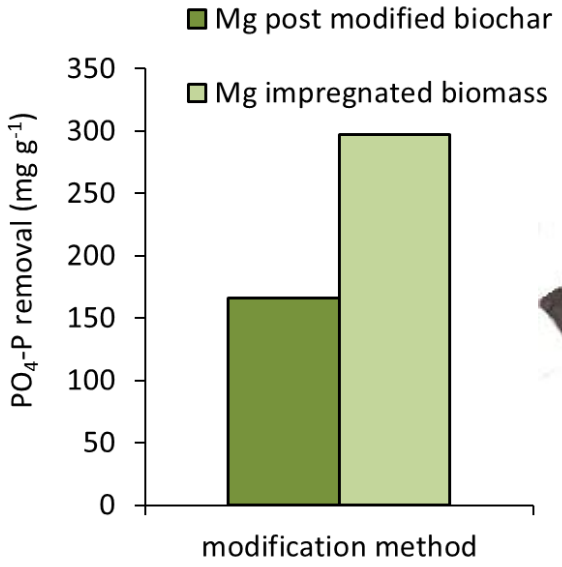
Potential for removal of nutrients by precipitation (*Kruse*)

pH dependent -

Struvite (MAP) $NH_4MgPO_4.6H_2O$

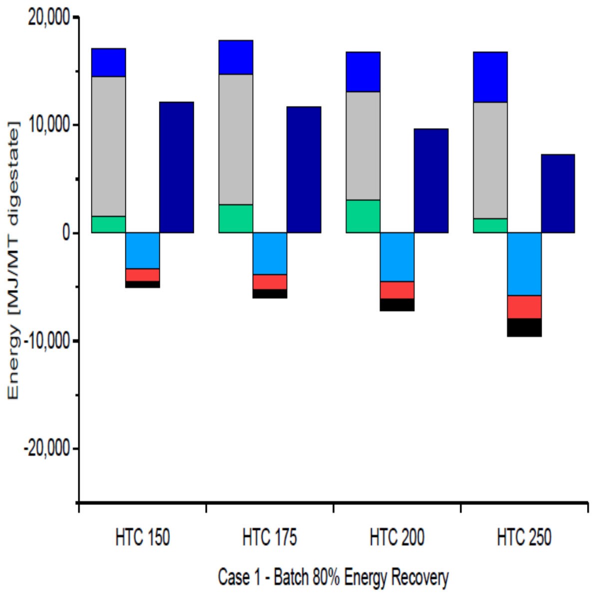




- Magnesium impregnated biochar has high propensity for phosphate removal.

Modified from: Takaya et al, Journal of Environmental Chemical Engineering,2016

Energy considerations



- The energy balance appears better at lower temperatures, however the composition of the hydrochars needs to be taken into account.
- Temperature, solid loading and residence time main variables.

E_{BG} Potential energy from combustion of biogas from AD of process waters
E_{HC} Energy released from combustion of hydrochar
E_{ER} Energy recovery from the process waters
E_{W} Energy required to heat the water to the HTC processing temperature
E_{HTC} Energy lost from vessel during 1 hour processing time
E_{h} Energy loss from vessel as it heats up to HTC processing temp
E_{NET} Net energy taking into account above energies

Reaction	Overall energy produced per Kg of feedstock (MJ)	Energy consumed per Kg of feedstock (MJ)	Net Energy Balance (MJ)
2.5% Solids	13.2	40.7	-27.5
5% Solids	13.1	19.8	-6.8
10% Solids	13.7	9.4	4.3
15% Solids	11.6	5.9	5.6
17.5% Solids	11.4	4.9	6.5
20% Solids	13.2	4.2	9.0
25% Solids	13.1	3.1	10.0
30% Solids	13.4	2.4	11.0

Energy in char 10.4-12.3MJ, Energy in water from 2.18 -1.1MJ

Choice of conditions

There are multiple opportunities for treating wet wastes by hydrothermal conversion.

Can provide multiple benefits

- Reducing waste and digestate enhancement
- Production of Bio-Coal
- Production of Soil additive
- Enhanced biogas yields by integration with AD

Opportunities potentially exist for new developments:

- Nutrient recovery
- Extraction of platform chemicals/humic materials

Challenges of MSW type wastes

- High levels of heavy metals can contaminate hydrochar and process waters
- Plastic essentially melts during HTC contaminating product and can result in processing problems
- Food waste is a promising feedstock with potential for resource recovery
- **The UKIERI/DST project on food waste will compare the HTC behavior of UK and Indian food waste and investigate the different applications of the products in the different regions**

Question and answer session

- Thank you for listening
- Any Questions?