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

Analytical Methods

UKIERI
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Part 3- Analytical Methods

Session 1: General methods of analysis

Session 2: Energy and Agronomic analysis

Session3: Surface functionality and surface area

Session 4: Analysis of process waters

Session I - General methods of analysis

This session will cover:

- Proximate and ultimate analysis
- Determination of calorific value
- Analysis of inorganics in hydrochar

Session 2- Energy and Agronomic analysis

This session will cover:

- Analysis of combustion properties of hydrochars
- Analysis of ash chemistry
- Agronomic analysis (CEC, humic acids, germination tests)
- Environmental analysis (PAH, leaching)

Session 3- Surface functionality and surface area

This session will cover:

- X-Ray photoelectron spectroscopy
- Infra Red analysis
- Gas adsorption analysis

Session 4- Analysis of process waters

This session will cover:

- Analysis of COD and TOC
- Analysis of pH, ammonia and phosphate
- Analysis of inorganics in process waters
- Analysis of dissolved organics

Session I

General methods of analysis

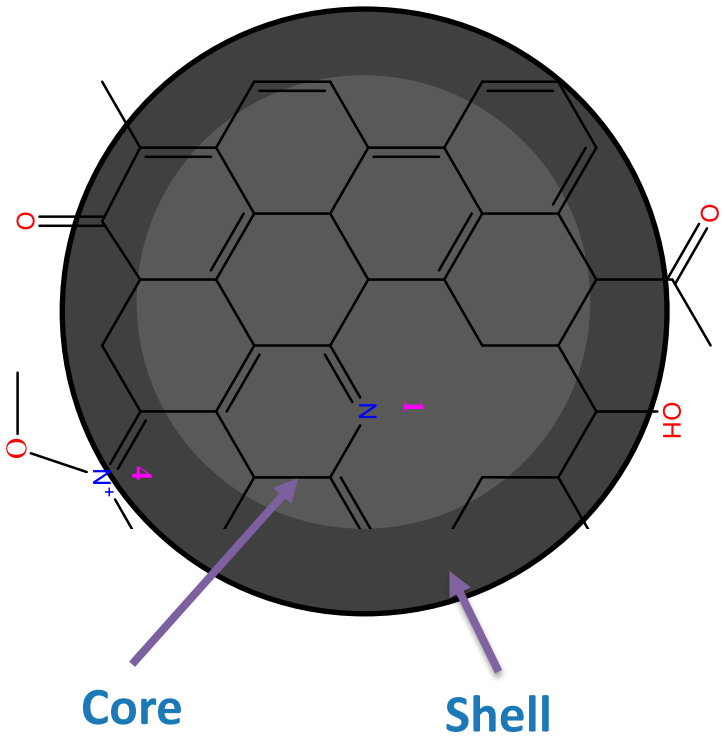
Introduction

- **Analytical methods for hydrochar composition**
  - Proximate, ultimate, metal analysis, surface area, agronomic and environmental properties, surface functionality
- **Methods for testing different applications**
  - Adsorption of nutrients and heavy metals, combustion properties, agronomic applications
- **Analytical methods for Process waters**
  - COD, TOC, analysis of hydrocarbons, analysis of nutrients,
- **Methods for testing different applications**
  - Biochemical methane potential (BMP), bio-hydrogen production

Hydrochar analysis

- Proximate analysis,
- Ultimate analysis,
- metal analysis (XRF, AAS, ICP-MS),
- Surface area,
- Cation exchange capacity,
- pH,
- Humic acid content,
- Py-GC-MS
- Solid state NMR
- Surface functionality by XPS

Session 1 Hydrochar properties



HTC parameter	Effect
Higher temperature	• Lower O/C and H/C ratios • OFG content decreased • The decrease of ion exchange capacity
Higher residence time	• OFG content decreased • Higher lactone (-C=O), and carboxyl (-COOH) content • Excessive polymerisation • Lower O/C and H/C ratios
Higher substrate concentration	• Poor hydrolysation • Less condensed products • Larger size microspheres • High O/C and H/C ratios

Session 1 Hydrochar characterisation

Bulk chemical analysis	Surface analysis	Physical analysis
Proximate composition ▪ TGA Ultimate composition ▪ CHNS Inorganics ▪ XRF	Surface functionality ▪ XPS	Surface area and porosity ▪ CO_2 at 273 K adsorption isotherm ▪ N_2 at 77 K adsorption isotherm

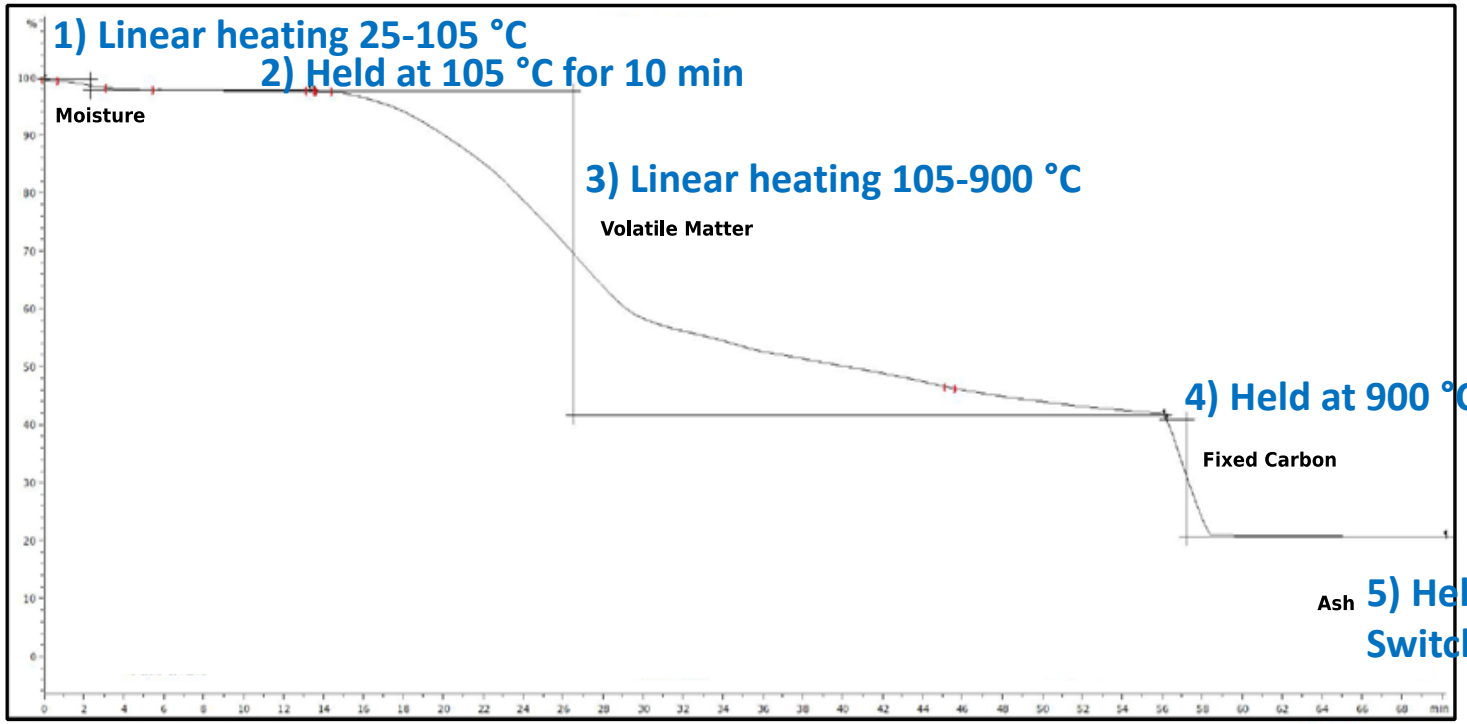
Proximate analysis (TGA)

Methodology for sample preparation

1. Samples may need size reduction prior to analysis (homogeneous and representative)
2. ~10 mg of the homogenised sample is placed into an Alumina 70 µL ceramic crucible.
3. The sample is compacted and flatted by carefully tapping on the worktop.
4. The weight is recorded, the sample is covered with metal lit, and then placed in the TGA.
5. The difference of mass loss during the heating stages allowed calculating the percentage for moisture, volatile matter, fixed carbon and finally ash.

Proximate analysis (TGA)

The analyser is set from 25 to 900 °C with a heating rate of 25 K/min and under a constant flow of nitrogen (50 mL/min). The program followed a temperature ramp.



Ultimate analysis

Determine **carbon, hydrogen, nitrogen and sulphur (CHNS).**
Uses the combustion method.
Accurate CHNS results rely on complete combustion of the sample.

Sample considerations:

Homogeneous and representative
Sample reduction but no less than 200µm
Low moisture content

Thermo Scientific Flash EA2000 elemental analyser

Ultimate analysis

Sample preparation
2.5-3.0 mg of sample were weighted inside tin foil capsules, crimped for removing the presence of air.

Analysis
Combustion at 1000 °C in He atmosphere, and known amount of O_2.

Conversion

$C \rightarrow CO_2$
$N \rightarrow NO_X$
$H \rightarrow H_2O$
$S \rightarrow SO_2$

Quantification
Gas chromatography (GC) coupled to a thermal conductivity detector (TCD)

Tin foil capsules

EA2000 elemental analyser

GC-TCD

Ultimate analysis

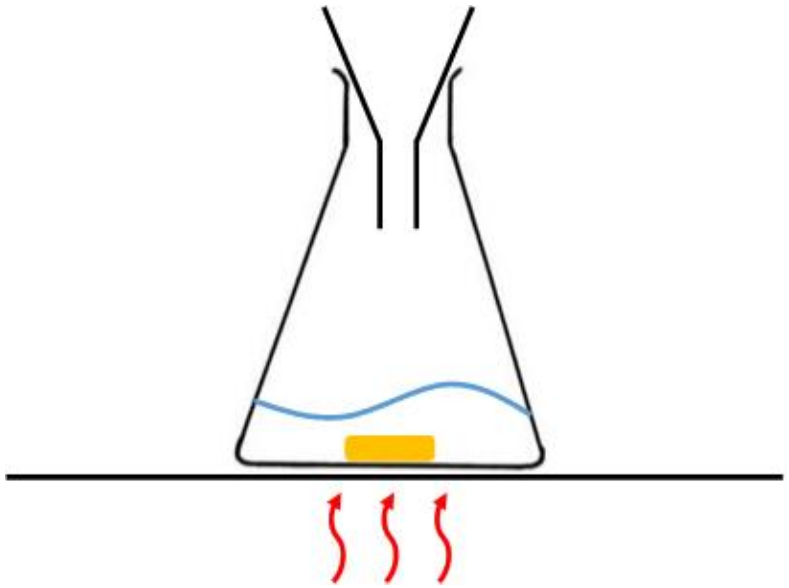
The values for CHNS are expressed as the percentage of total dry weight, with total oxygen (O) determined by difference as follows:

$$O\ (\%) = 100 - C(\%) - H(\%) - N(\%) - S(\%) - ash\ (\%)$$

Known composition of the standards used for ultimate analysis

Standard	Ultimate (% wt, db)				
	C	H	N	S	O
B2044 BBOT	72.53	6.09	6.51	7.44	7.43
B2276 Oat meal	47.76	5.72	2.09	0.16	-
B2306 Coal	-	-	-	2.03	-

Analysis of Inorganics



0.2±0.05g of sample is digested in 10ml of concentrated nitric acid using either microwave (Aston Parr, USA) enhanced digestion or on a hot plate.

Samples are digested for approximately 1 hour at 200°C, after which the temperature is increased to 250°C and the samples evaporated to dryness.

A further 5ml of concentrated nitric acid is added and warmed to dissolve the metals and samples are diluted to x500 for analysis.

Schematic for the apparatus set-up for hot plate acid digestion for metal analysis.

Energy Terms

Calculation of the energy densification of hydrochars.

$$\mathrm{ED} = \frac{\text{HHV of feedstock}}{\text{HHV of hydrochar}}$$

Calculation of the energy yield obtained from hydrochars.

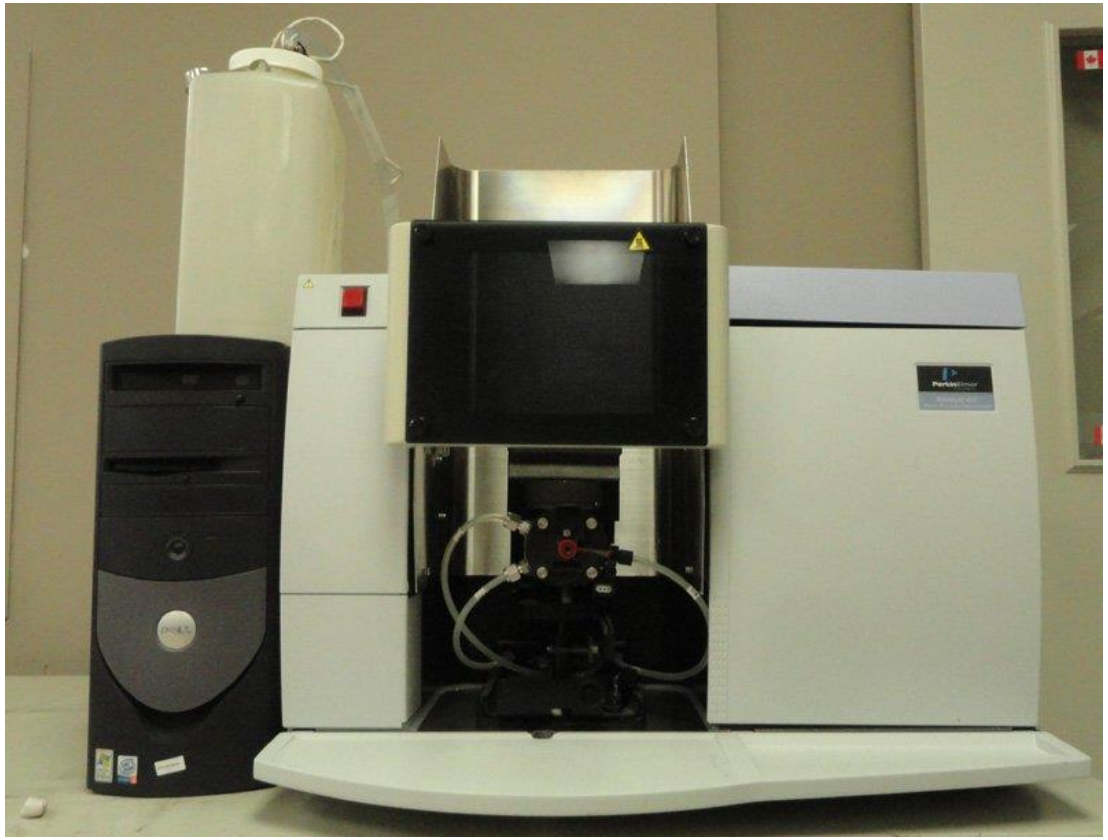
$$\mathrm{EY} = \mathrm{ED} \times \mathrm{HY}\ (\%)$$

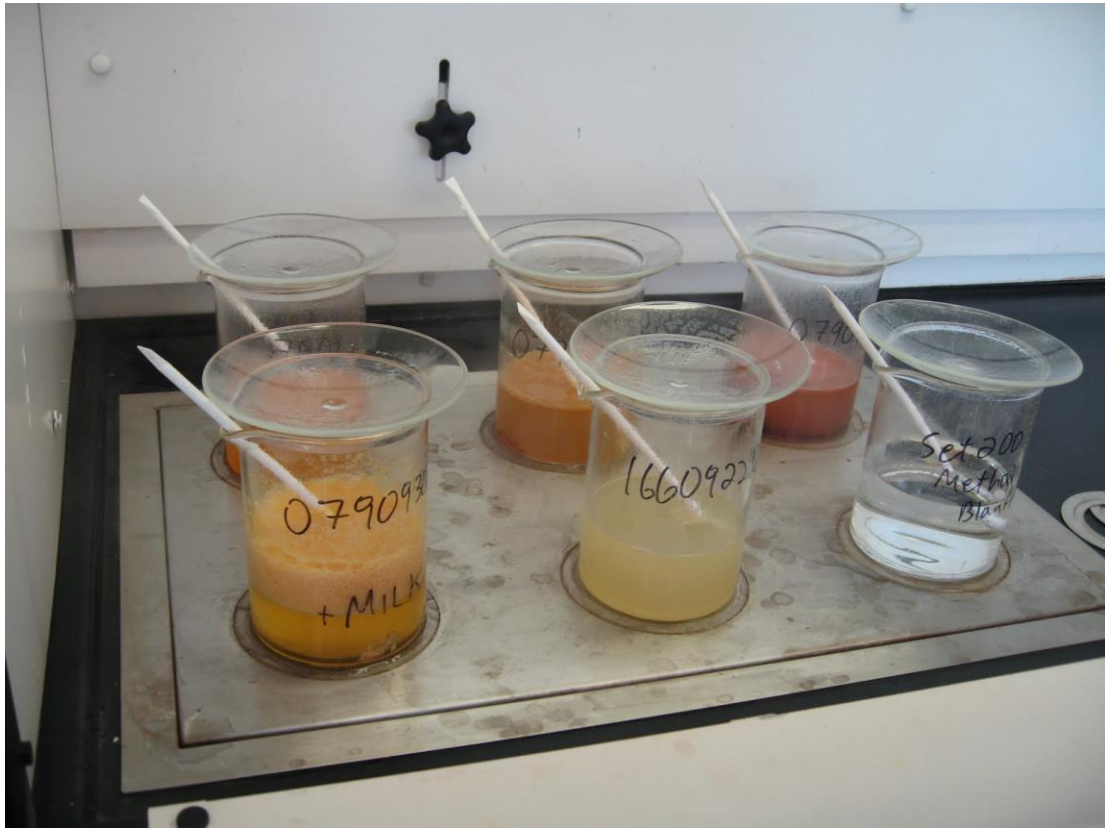
Calculating HHV

The higher heating value (HHV) of feedstocks and solid residues was calculated according to Dulong's equation

$$HHV(MJ/kg) = \left(0.3383 \times Carbon(\%)\right) + \left(1.422 \times Hydrogen(\%)\right) - \left(\frac{Oxygen(\%)}{8}\right)$$

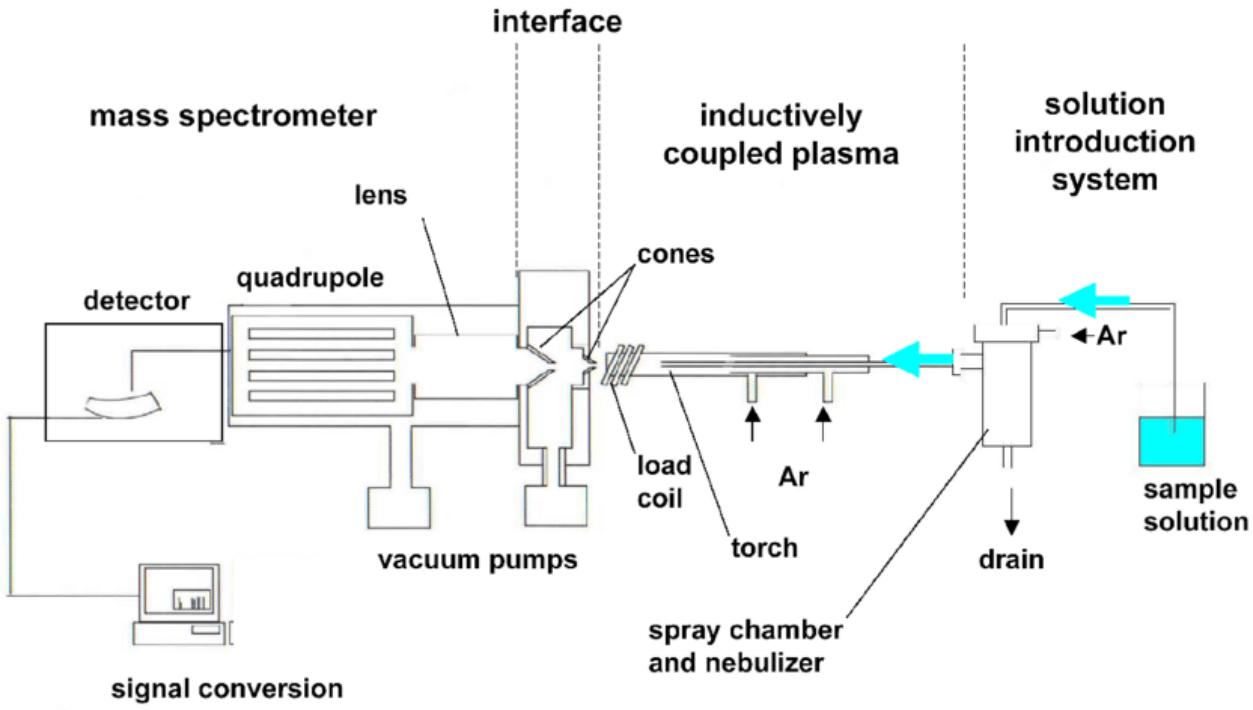
AAS





ICP-MS


VARIAN
ICP-MS
VARIAN


interface
mass spectrometer
inductively coupled plasma
solution introduction system
lens
cones
detector
quadrupole
Ar
load coil
Ar
sample solution
torch
drain
vacuum pumps
spray chamber and nebulizer
signal conversion

XRF

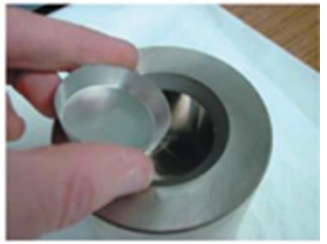

Grinding of the whole sample


Weigh 4g sample


Add 1g binder


2 minutes mixing


Use pelletfilm or


Aluminium cup


Pour the mix into the die


And press:


Perfect pressed pellet

Fibre Analysis

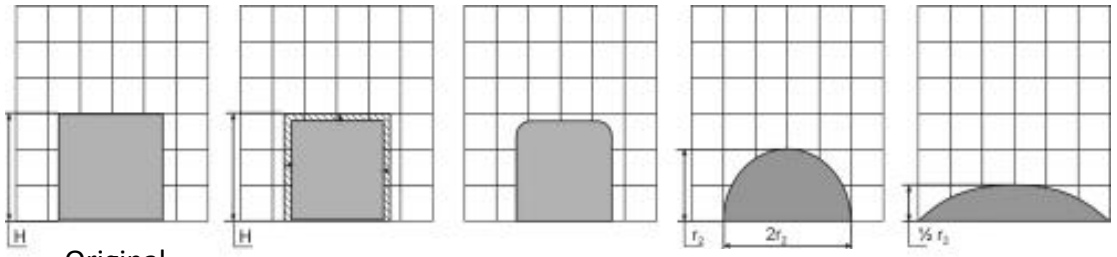
Question and answer session

- Thank you for listening
- Any Questions?

Session 2

Energy and Agronomic analysis

Ash fusion testing of bio-coal



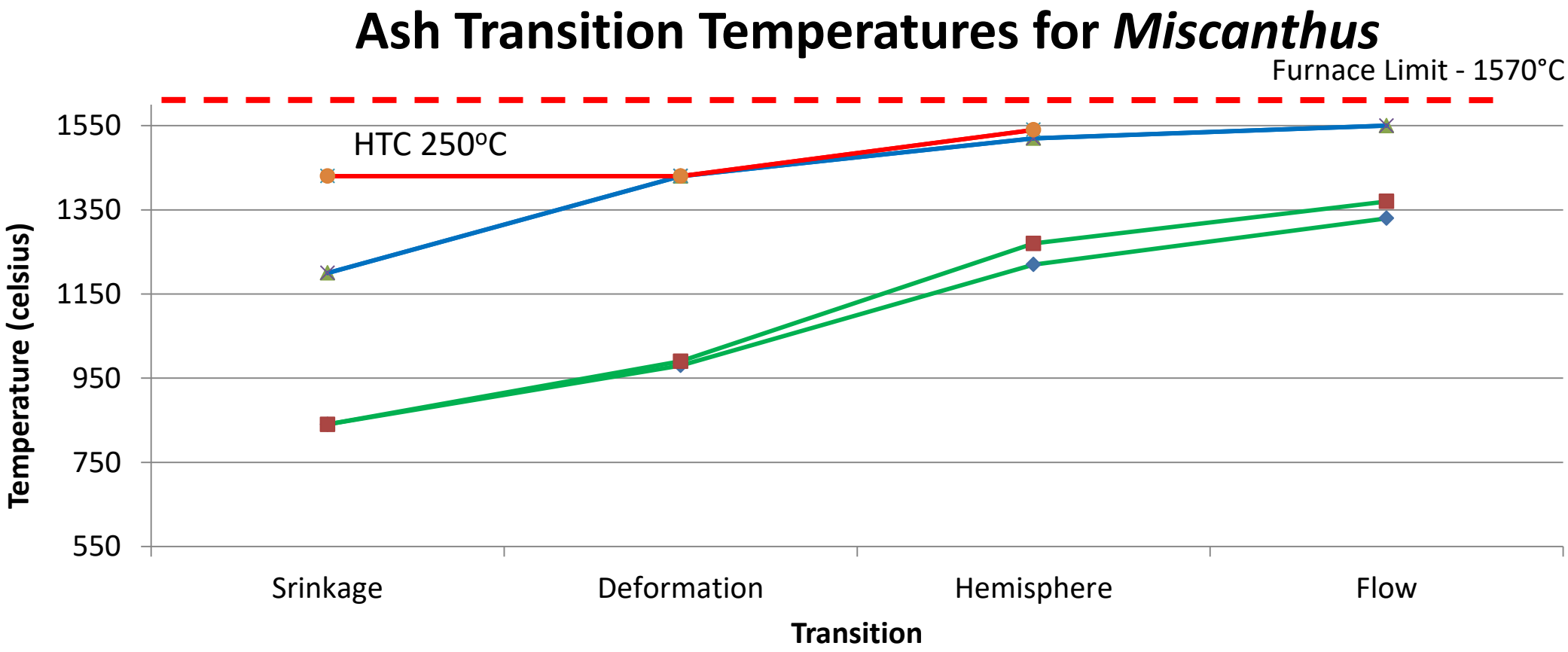
Original sample | Shrinkage | Deformation | Hemisphere | Flow

Alkali Index	$AI = \frac{Kg\ (K_2O + Na_2O)}{GJ}$	AI>0.34 almost certain slagging and fouling
Bed Agglomeration Index	$BAI = \frac{\%(Fe_2O_3)}{\%(K_2O + Na_2O)}$	BAI<0.15 bed agglomeration likely
Acid Base Ratio	$R_a^b = \frac{\%(Fe_2O_3 + CaO + MgO + K_2O + Na_2O)}{\%(SiO_2 + TiO_2 + Al_2O_3)}$	R_a^b <0.5 low slagging risk

Ash fusion test using an ash fusion oven

Other indexes include Slagging index (SI), fouling index (FI) and slag viscosity index SVI)

Ash fusion behaviour after HTC



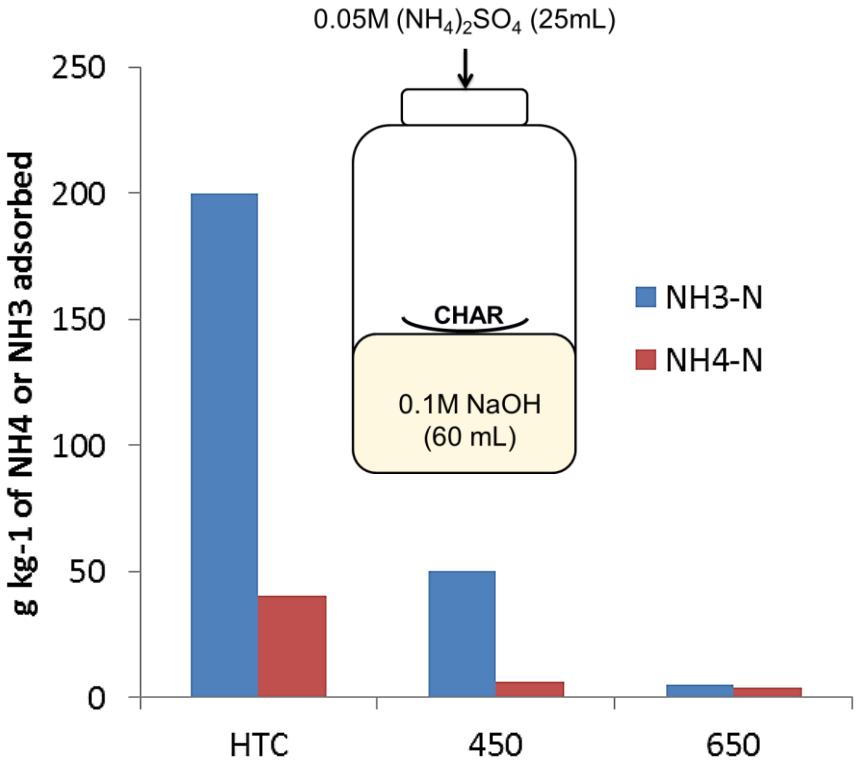
Predictive indices

Slagging/fouling Indices	Indices Initials	Equation	Analysis
Alkali index	AI	$\frac{kg\ (K_2O + Na_2O)}{GJ}$	AI < 0.17 safe combustion AI > 0.17 <0.34 probable slagging and fouling AI > 0.34 almost certain slagging and fouling
Bed agglomeration index	BAI	$\frac{\%(Fe_2O_3)}{\%(K_2O + Na_2O)}$	BAI < 0.15 bed agglomeration likely
Acid base ratio	$R\frac{b}{a}$	$\frac{\%(Fe_2O_3 + CaO + MgO + K_2O + Na_2O)}{\%(SiO_2 + TiO_2 + Al_2O_3)}$	$R\frac{b}{a}$ < 0.5 low slagging risk

Predictive indices

Slagging/fouling Indices	Indices Initials	Equation	Analysis
Slagging index	SI	$\left(\frac{\%(Fe_2O_3+CaO+MgO+K_2O+Na_2O)}{\%(SiO_2+TiO_2+Al_2O_3)}\right)$ * %S (dry)	SI < 0.6 low slagging indication SI > 0.6 < 2.0 medium slagging indication SI > 2.0 high slagging indication
Fouling index	FI	$\left(\frac{\%(Fe_2O_3+CaO+MgO+K_2O+Na_2O)}{\%(SiO_2+TiO_2+Al_2O_3)}\right)$ * $\%(K_2O+Na_2O)$	FI < 0.6 low fouling FI > 0.6 < 40.0 medium fouling FI > 40.0 high fouling
Slag viscosity index	SVI	$\frac{(\%SiO_2 * 100)}{\%(SiO_2+MgO+CaO+Fe_2O_3)}$	SVI > 72 low slagging indication SVI > 65 < 72 medium slagging indication SVI < 65 high slagging indication

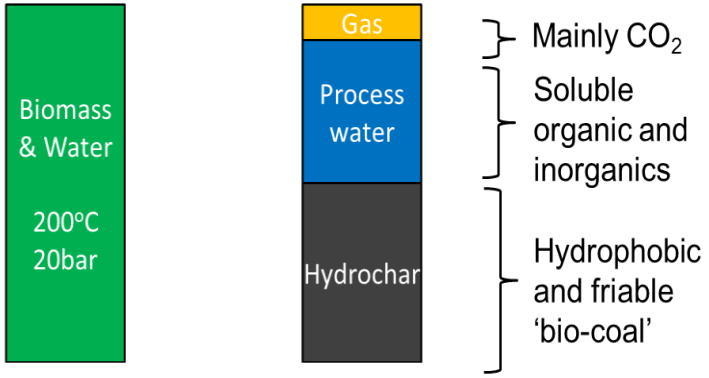
Ammonia/Ammonium Adsorption

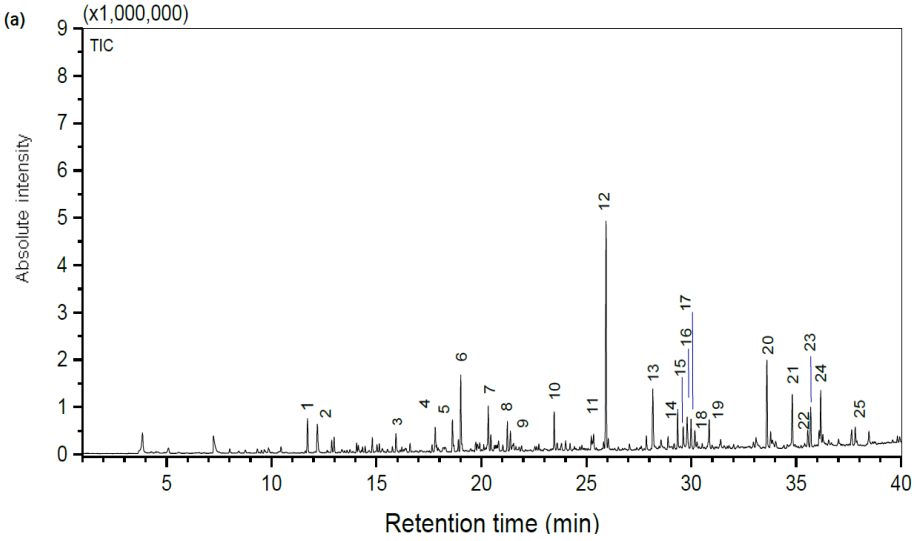


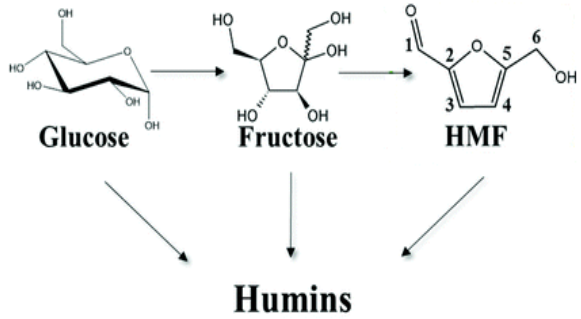
Parmer et al, 2018

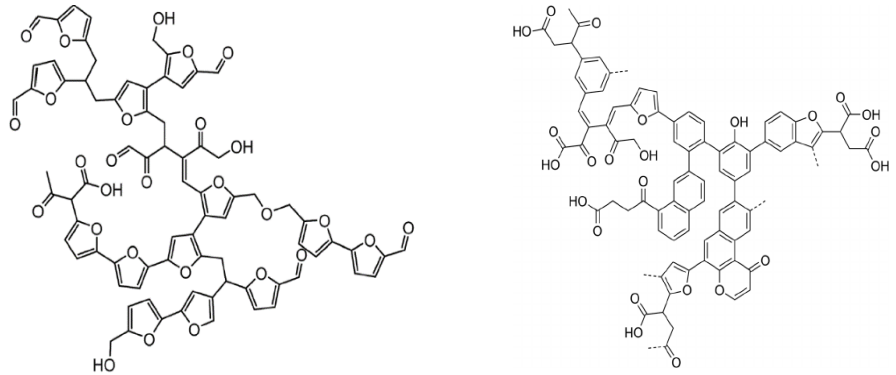
- Hydrochars have high propensity for removing NH4+ (compared to biochars)
- Hydrochars also have higher propensity for adsorption of ammonia gas.
- NH4/NH3 sorption: Chemical reactions with acidic 'humic like' functional groups.

Humic composition



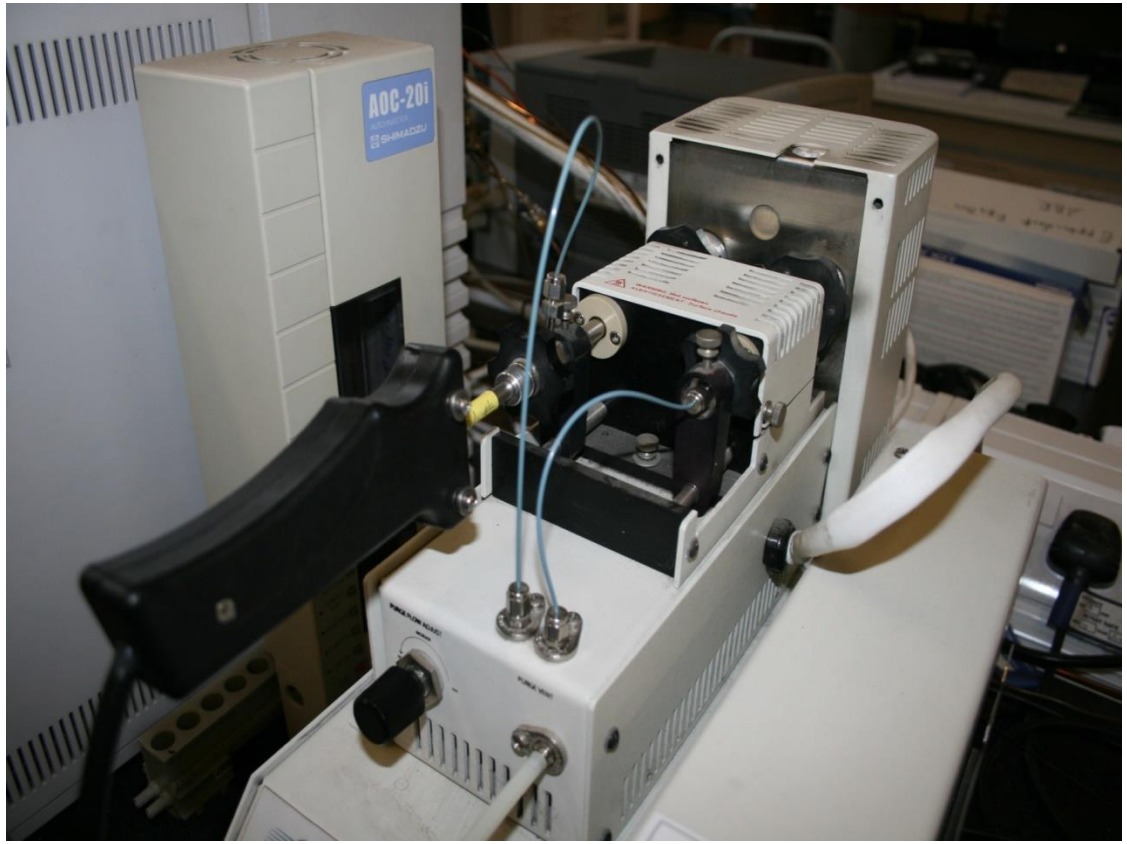




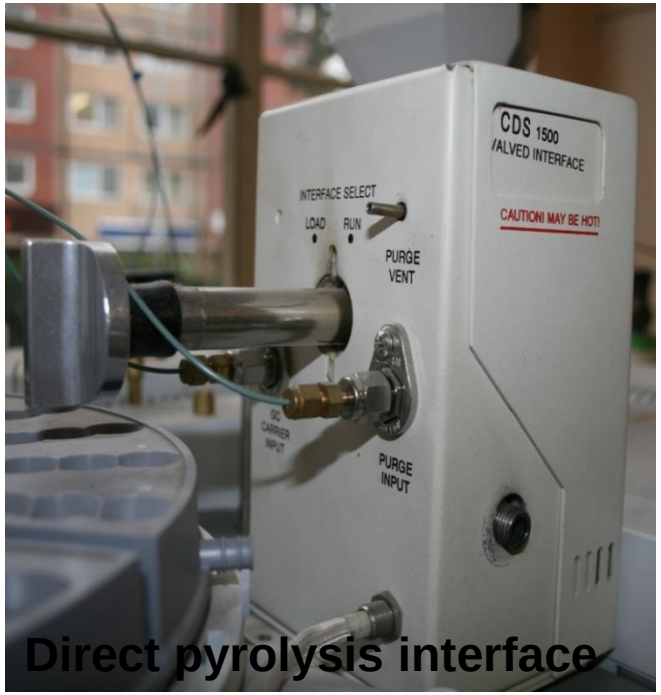


Source: Green Chem., 2015, 17, 4383

Instrumentation



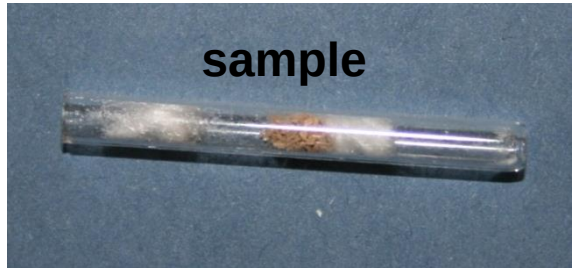
Integrated thermal desorption trap



Direct pyrolysis interface

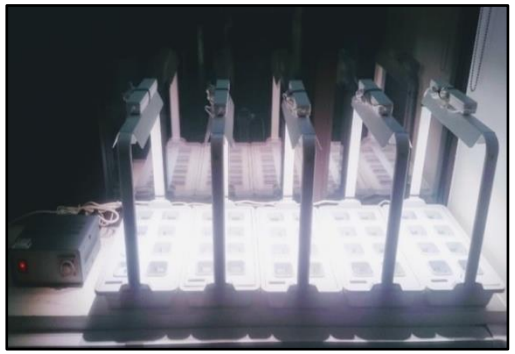
Pyrolysis GC MS

- Heating is achieved resistively by discharging a capacitor through a platinum ribbon or coil.
- A sample in solution can be placed directly onto a platinum ribbon followed by evaporation of the solvent.
- Solid samples are placed in a quartz tube in between quartz wool plugs housed inside the platinum coil.
- The pyrolysis assembly (probe) is inserted into a heated interface connected directly to the GC injector.



Hydrochar germination trials

- Seed germination trails (PAS110)
  - Phytotoxic effects
    - the need to stabilise hydrochar?



- Growing media: Irish sphagnum moss peat (10mm sieved) with 25% w/w hydrochar
- Fertiliser was not used in this study
- Tomato cultivar Shirley F1 hybrid seeds
- Lighting pattern of 16 hours on, 8 hours off.

- Low levels of heavy metals and PAH ✓
- HTC hydrochars are Pathogen free ✓

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

Question and answer session

- Thank you for listening,

Session 3

Surface functionality and surface area

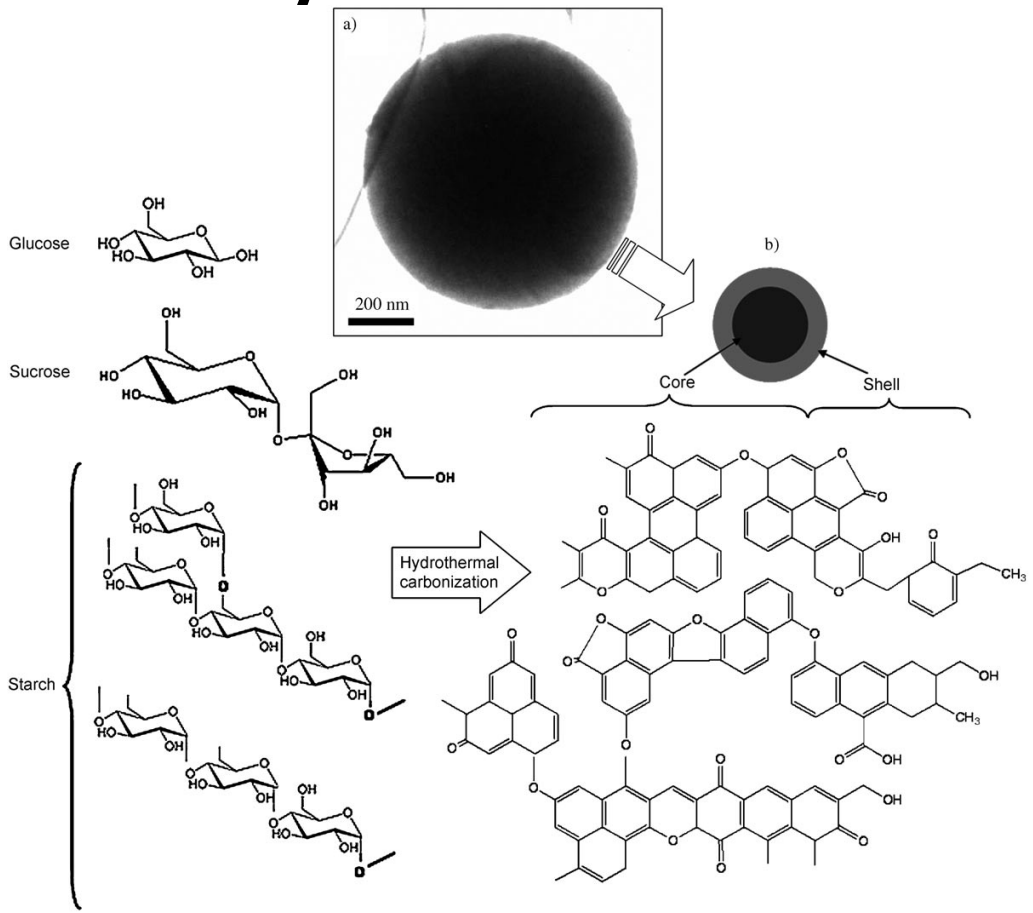
Question and answer session

- Thank you for listening,
- Any Questions?

Surface analysis

The surface chemistry of the chars exhibits hydrophilic, hydrophobic, acidic and basic properties directly related to their heterogeneous composition.

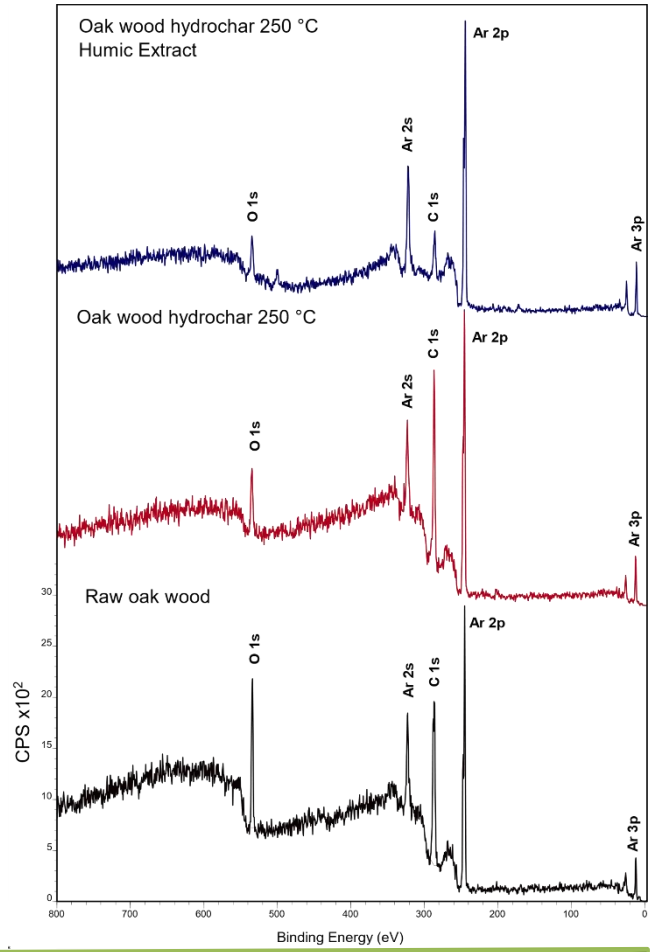
XPS is an analytical technique that identifies the elemental composition of a material by assessing the oxidation state of the surface elements and the dispersion of each element.



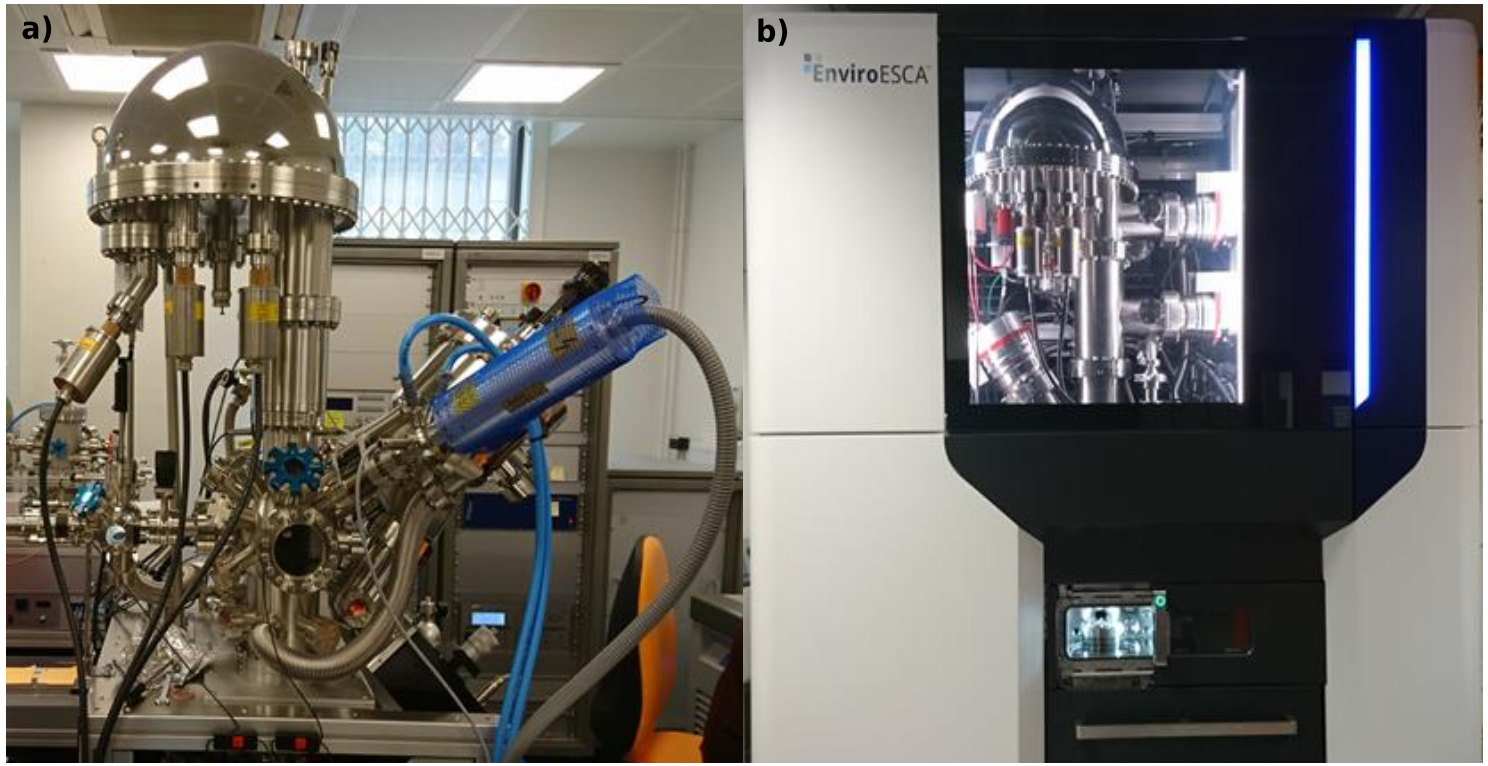
Core-shell chemical structure of hydrochar (Sevilla and Fuertes, 2009)

Surface functionality (XPS)

- The emission of photoelectrons leaves an energy spectrum that allows the identification of the surface atomic species
- Provide the semi-quantification of surface elements and elucidation of bonds between adjacent atoms
- XPS needs to be supported by other techniques, such as FTIR, EDX, NMR.



XPS

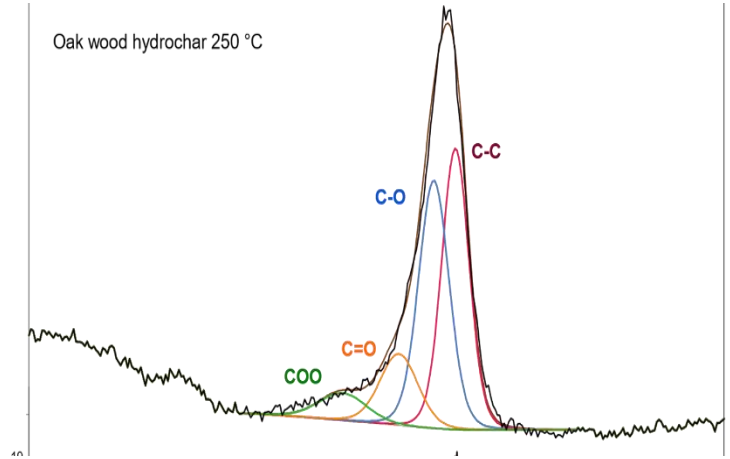


XPS equipment used for analysing the surface chemistry of the chars. a) ultra-high vacuum XPS Specs system; b) near ambient pressure EnviroESCA system.

Examples of XPS analysis

Semi-quantification of surface elements and groups

- Curve fitting and semi-quantification (CasaXPS)
- Examining the C 1s photoelectron line
- Assignment of XPS peaks to chemical elements
- Obtaining the ratio of each chemical element



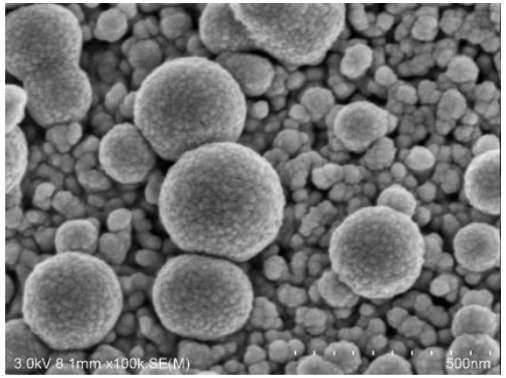
	C 1s			
Material	C-C (%)	C-O (%)	C=O (%)	COO (%)
Oak wood hydrochar 250 °C	40	39	14	7

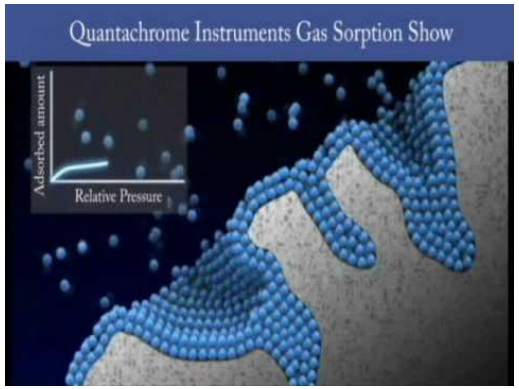
Physical analysis-Gas adsorption

Gas adsorption (physisorption) measurements are implemented for the analysis of the surface area (SA) and pore size distribution (PSD) of solid materials.

The mechanisms behind physisorption are dependent on the properties of the gas (adsorptive), and the material (adsorbent), particularly the shape of the pores.

The intermolecular forces involved in physisorption include attractive dispersion and short-range repulsive forces.



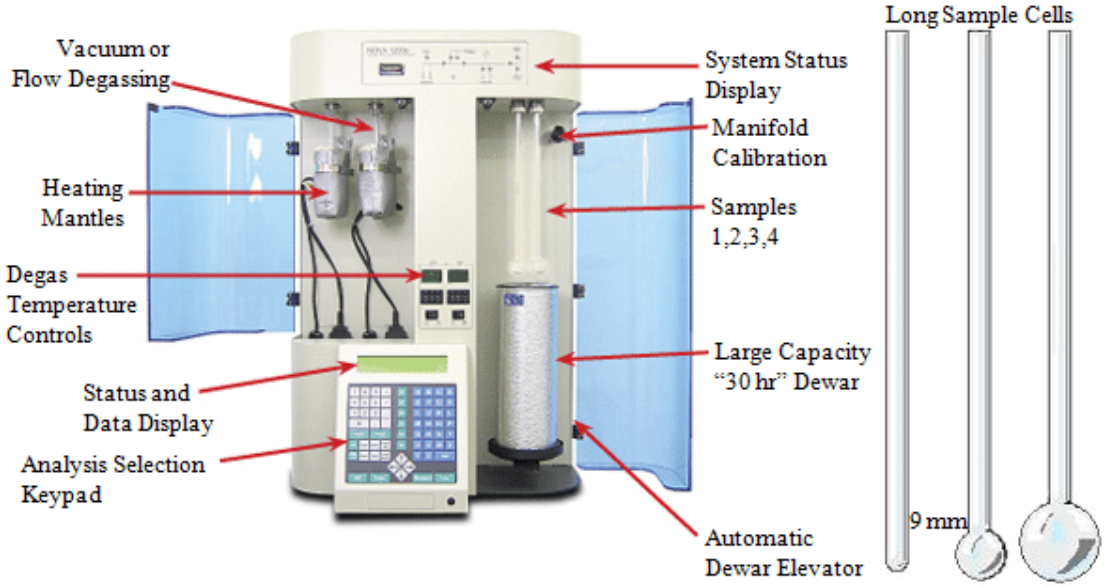


Selection of adsorptive

N_2 at 77 K	CO_2 at 273 K
Advantages ▪ Most used method ▪ Good for meso- and non-porous materials	**Advantages** ▪ Faster diffusion rate and ▪ Shorter adsorption equilibrium time ▪ Better than N_2 for carbon materials with large microporosity
Disadvantages ▪ Extremely long equilibrium time ▪ Diffusional problems in micro- and ultra pores ▪ Not always suitable for carbon porous materials	**Disadvantages** ▪ Pore size measurement is limited to 1.5 nm

Sample preparation and analysis

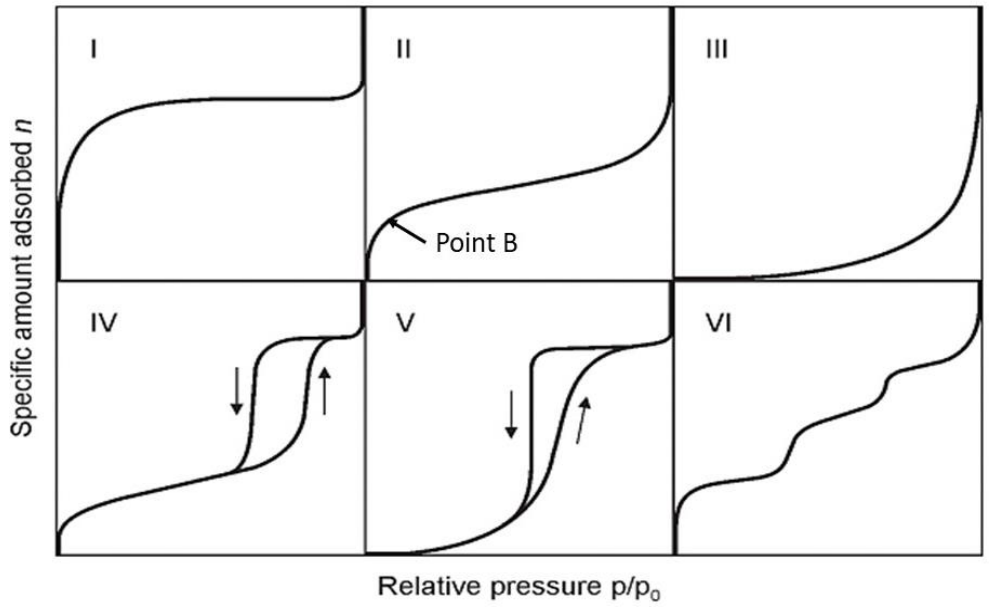
1. Tubes dried and weight
2. Add 0.2 g of sample
3. Vacuum outgassing with a controlled heating rate
4. Weigh after outgassing and prior to analysis
5. Place the tubes on the equipment
6. Fill the vessel with liquid N_2 or ice and water
7. Analyse



Physisorption isotherms

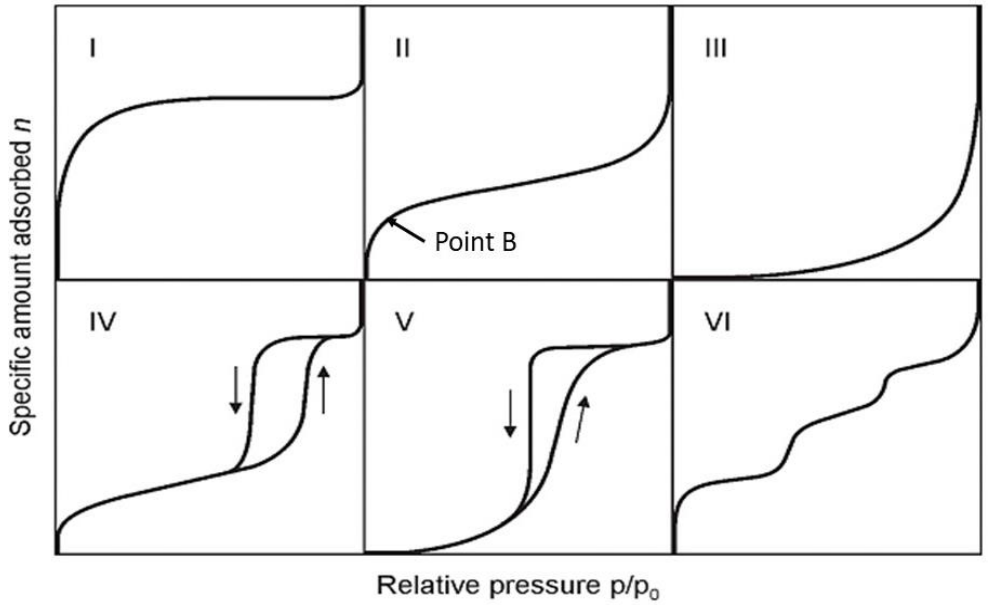
- The adsorption isotherms represent the relation between the amount of gas adsorbed and the equilibrium pressure of the gas at a constant temperature.

- At equilibrium pressure, the amount of gas admitted corresponds to the difference between the amount of gas adsorbed and the necessary amount of gas for filling the space that surrounds the hydrochar (i.e. dead space).



Physisorption isotherms

1) Type of isotherm
2) Adsorption process (monolayer-multilayer adsorption, capillary condensation or micropore filling).
3) Model for the quantification of the surface area and pore size distribution

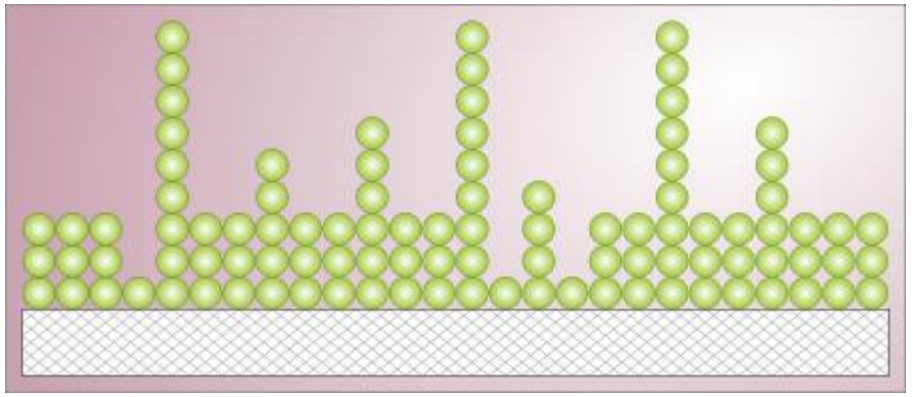


Physisorption isotherm types

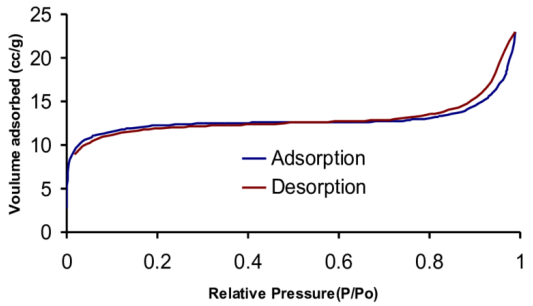
Models for analysing adsorption isotherms

Brunauer-Emmett-Teller (BET) model

- Most used for SA and PSD evaluation.
- The BET theory assumes that molecules are adsorbed on the material surface initially forming the first layer, which acts as a site for the adsorption of more molecules, and subsequent layers
- However, BET is not always suitable for heterogeneous char materials



$$\frac{p}{n^a(p^\circ - p)} = \frac{1}{n_m^a C} + \frac{(C-1)p}{n_m^a C p^\circ}$$

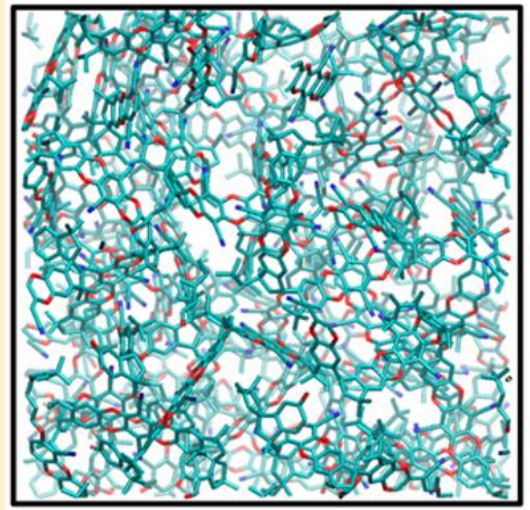


n^a is the amount of adsorbed gas at a relative pressure p/p°,
n^a_m is the monolayer capacity
C represents the enthalpy of adsorption for the first adsorbed layer.

Models for analysing isotherms

Nonlocal Density Functional Theory (NLDFT)

- Highly accurate for microporous materials
- Superior than BET model for the analysis of hydrochar
- Assumes pores to be infinite slits with graphene walls
- Measures equilibrium density profiles for the adsorption of a fluid on the surface and inside the pores of a material



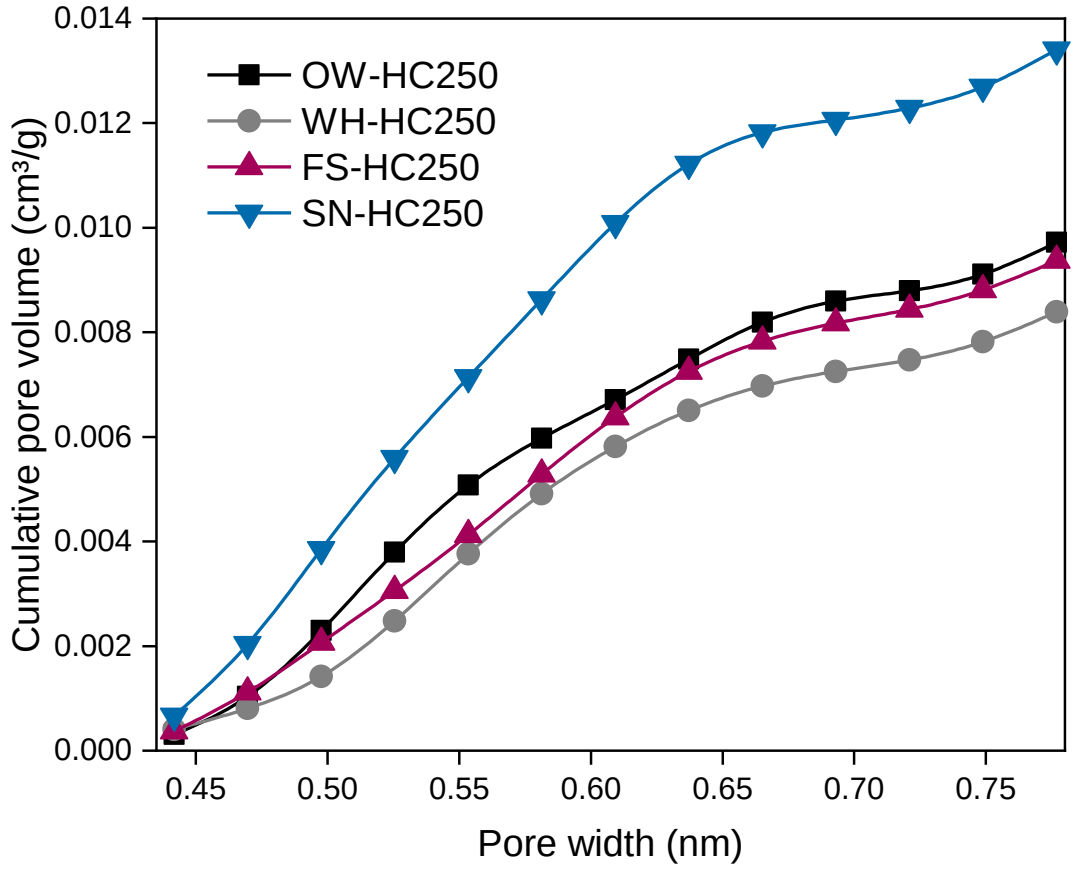
$$N\left(\frac{P}{P_0}\right) = \int_{W_{MIN}}^{W_{MAX}} N\left(\frac{P}{P_0, W}\right) f(W) dW$$

N(P/P0) adsorption isotherm data
N(P/P0,W) isotherm on a single pore of width (W)
f(W) is the PSD function

Physisorption isotherms

Methodology:
Adsorption isotherms
CO_2 at 77 K

Hydrochars
Low surface area and porosity
37-64 m^2/g



Conclusions

- Hydrochar properties indicate the changes taking place during HTC, and its possible further applications.
- Physical, chemical and functional characterisation complement each other towards the understanding of the hydrochars properties
- Given the microsphere structure of the hydrochars, the inner and outer layer differ. Hence the importance of characterise both the bulk and surface.
- Hydrochar surface is responsible for most of its interaction with organic matter
- OFGs on the carbon surface serves as anchoring and interaction sites for the biomolecules.

Question and answer session

- Thank you for listening,
- Any Questions?

Session 4

Analysis of process waters

COD analysis

COD- Chemical oxygen demand

Chemical oxygen demand (COD) is the amount of dissolved oxygen that must be present in water to oxidize chemical organic materials

Samples of process waters are regularly analysed for COD, in particular if samples are run using BMP tests.

As a rule of thumb, COD is typically 40% of the TOC values

TOC analysis

HACH IL 500 TOC-TN analyser

Figure 4 Front view of IL550 TOC-TN (Doors Open)

pH analysis

pH is regularly measured

Ammonium/ammonia analysis

TN analysis

Phosphate analysis

Total Phenol analysis

Analysis of inorganics (ICP-MS)

Analysis of inorganics (AAS)

Analysis of inorganics (XRF)

XRF
the

Analysis of inorganics (Ion Chromatography)

Analysis of organics (Aldehydes)

Column and programme

e.g. chromatogram of a sample or standard

Analysis of organics (VFA method)

Column and programme

e.g. chromatogram of a sample or standard

Analysis of organics (derivatisation)

Column and programme

Description of derivatisation

Analysis of sugars (HPLC)

Analysis of organics (NMR)