HYDROTHERMAL CARBONIZATION

A Simple Process for Producing Advanced Materials

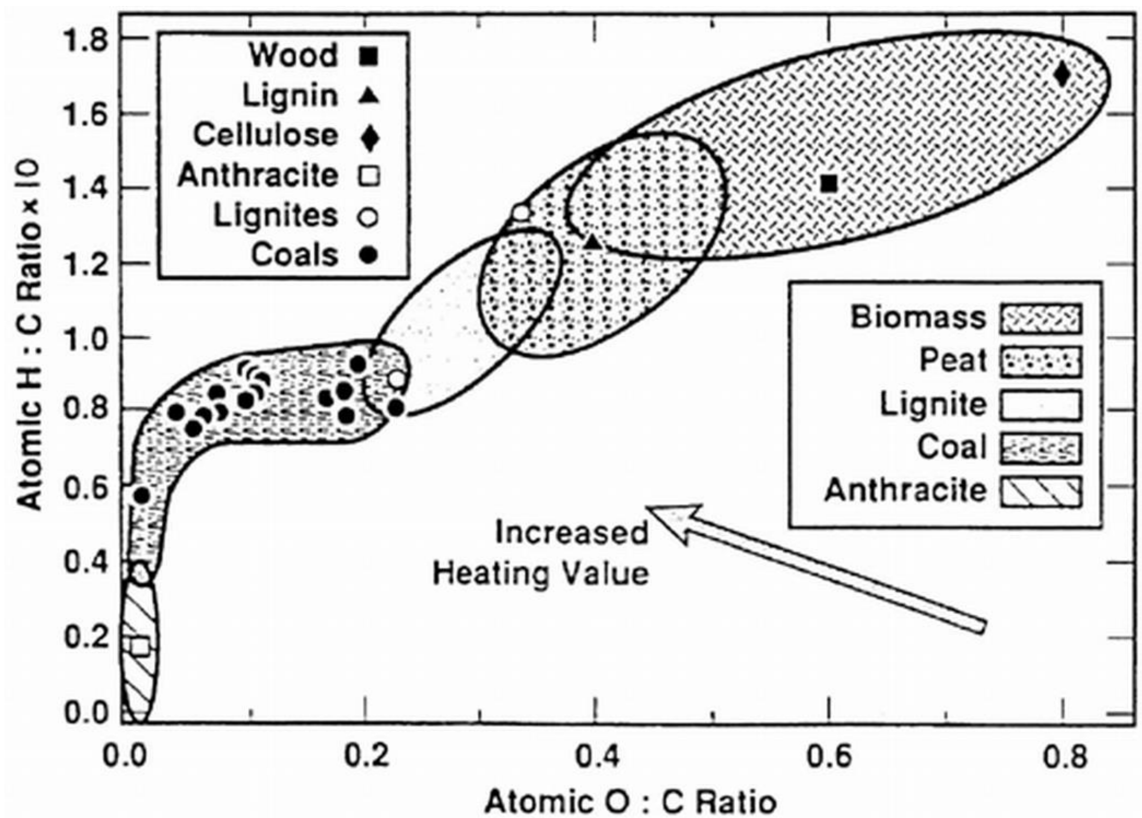
Dr. Kenneth Latham

UMEÅ UNIVERSITY

CARBONIZATION

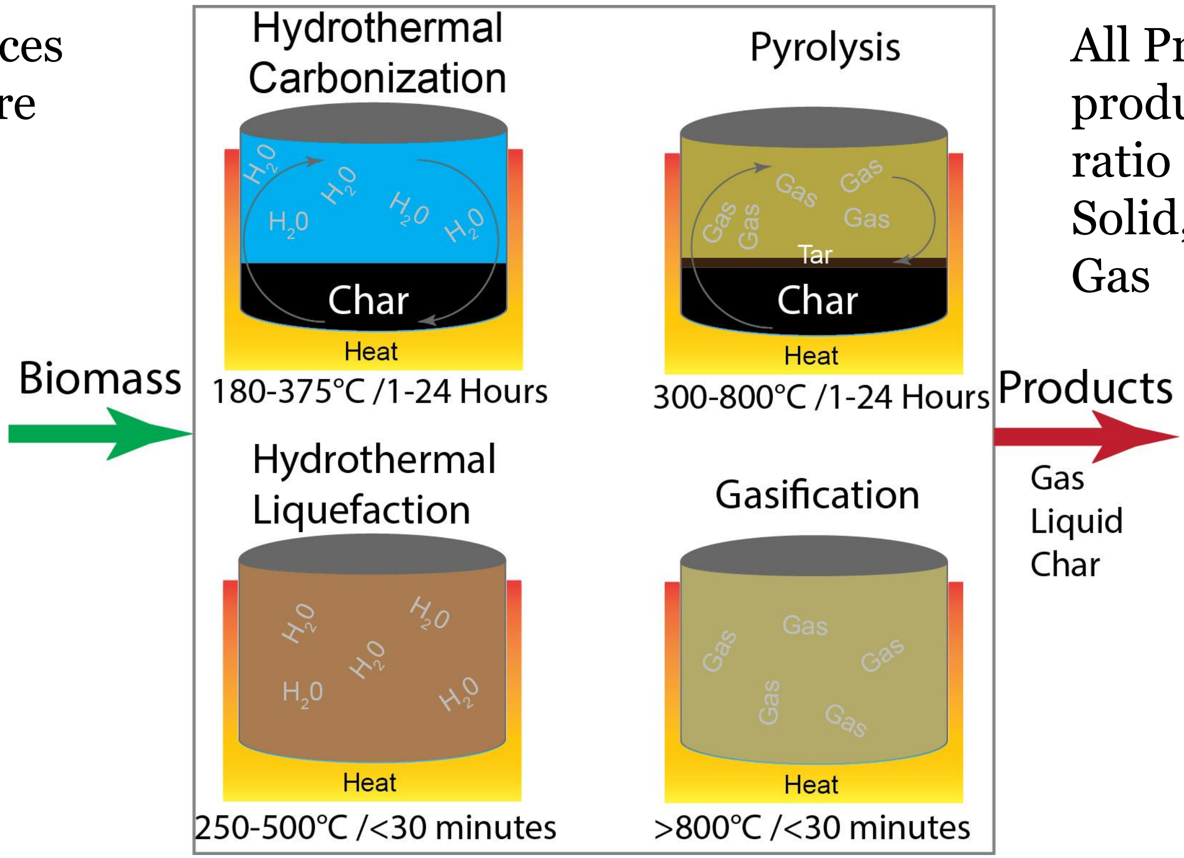
- Any process that increases the carbon content of the parent material
    - Physical – Pyrolysis
    - Chemical – Hydrothermal
    - Biological – Enzymolysis
- Carbon content increases through the removal of oxygen, hydrogen and other organic/inorganic elements

VAN KREVELAN DIAGRAM



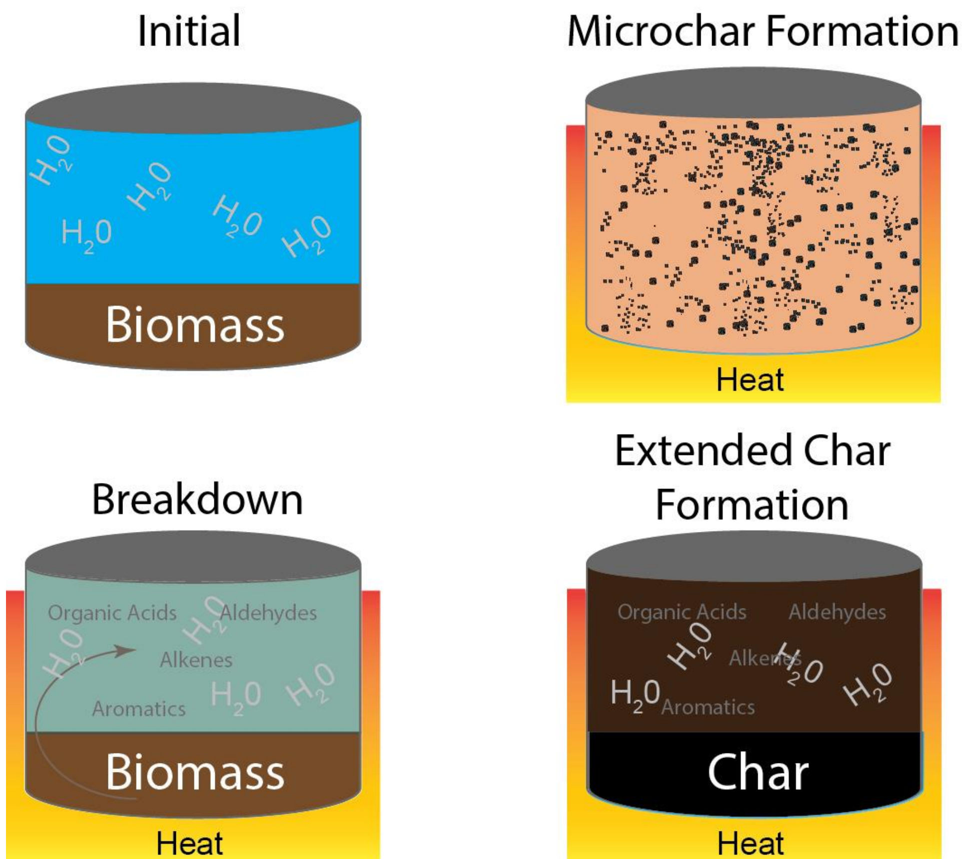
TYPICAL METHODS FOR CARBONIZATION

Main Differences
- Temperature
- Residence Time



All Processes produce a different ratio of products, Solid, Liquid, and Gas

HYDROTHERMAL CARBONIZATION



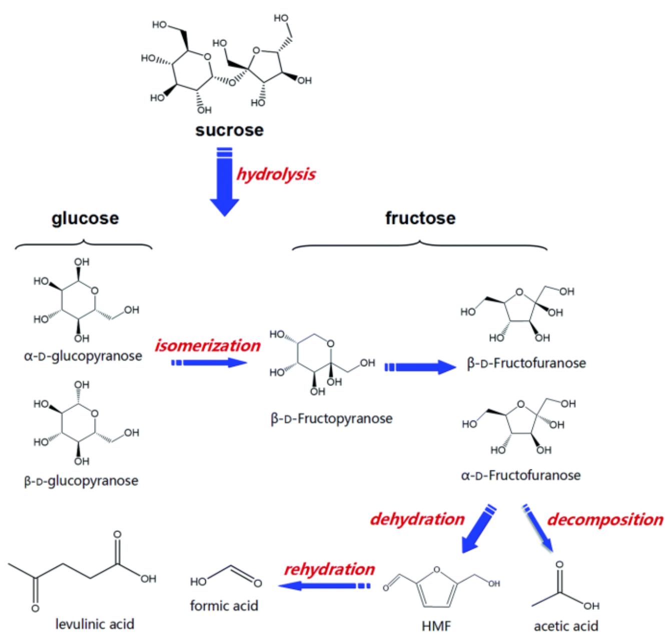
UMEÅ UNIVERSITY

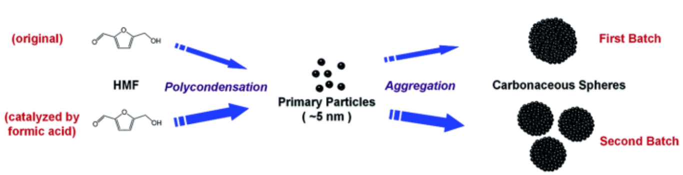
THE BREAKDOWN

- The bonds between chemical structures in the precursor (i.e., biomass, sludge, glucose) are broken. This is usually through dehydration reactions, breaking oxygen linkages.
- Solubility of the precursor is a major factor that is often overlooked
- If the precursor is insoluble in water, it requires sufficient temperature and interaction with the water to break down via hydrothermal reactions
- If these conditions are not met, then the reaction is mixed
    - Bulk – Low temperature pyrolysis reactions
    - Surface – Hydrothermal Reactions

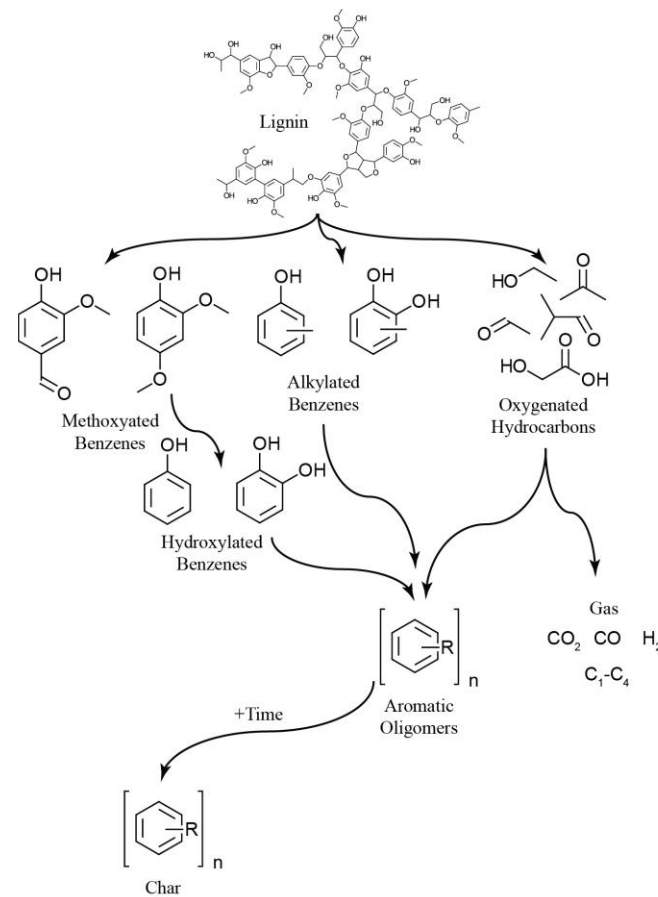
MICROCHAR FORMATION

- The char product is formed through a series of reactions that differ depending on precursor.

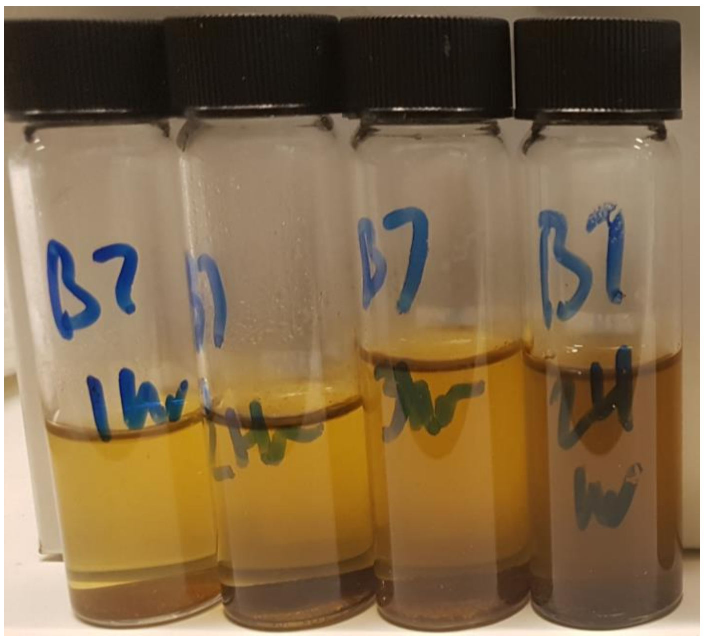


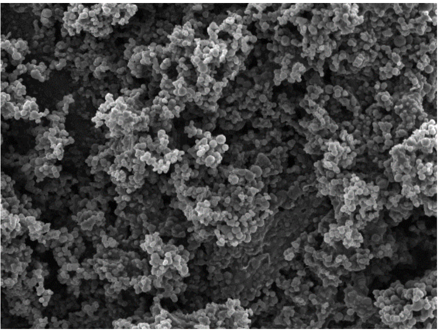


UMEÅ UNIVERSITY

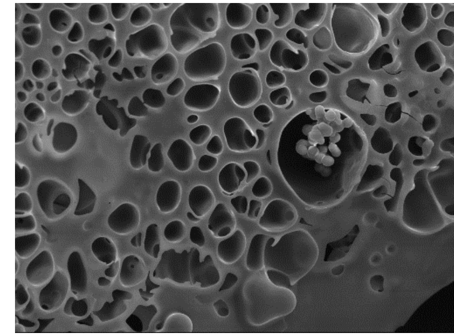


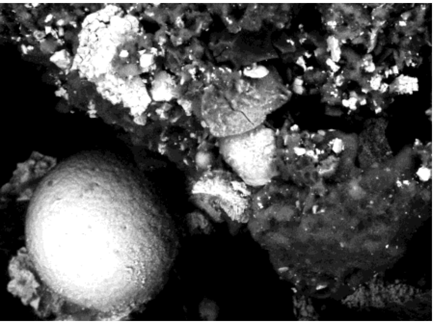
THE END PRODUCT

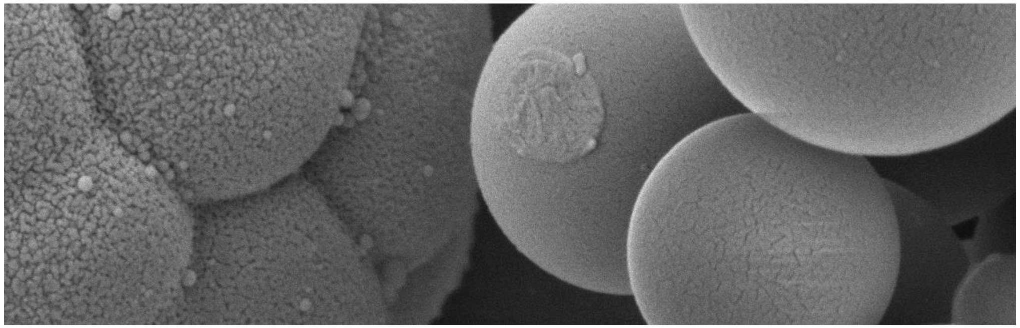


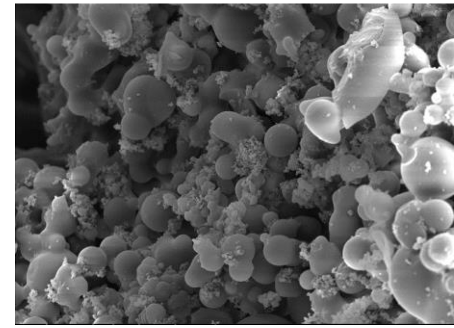


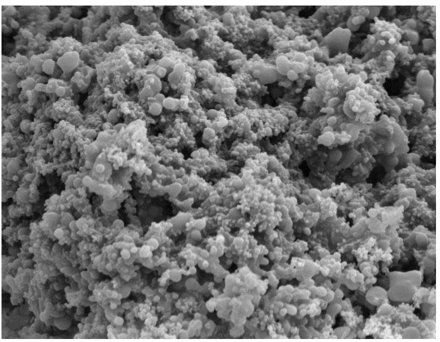
LOOKING A BIT CLOSER

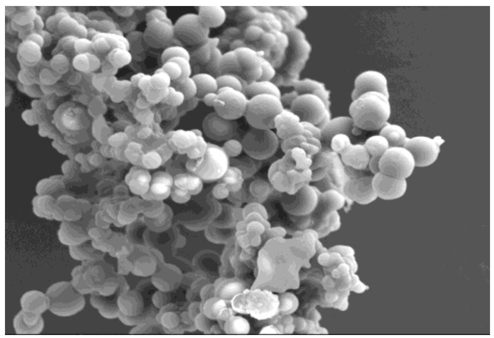


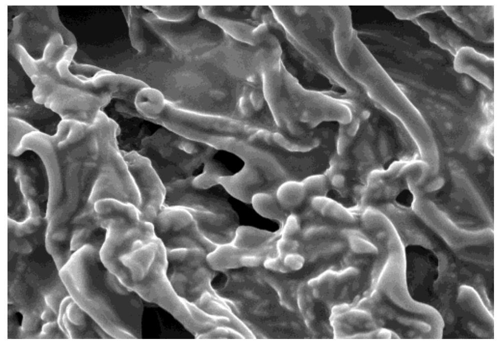


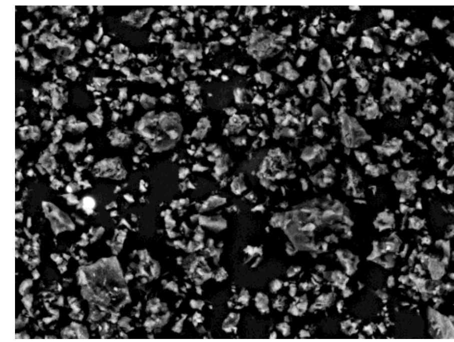


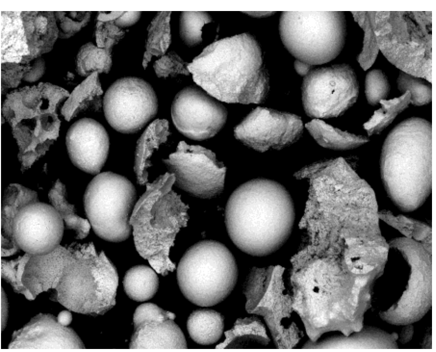


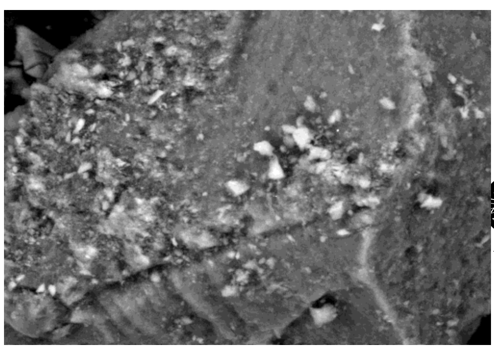


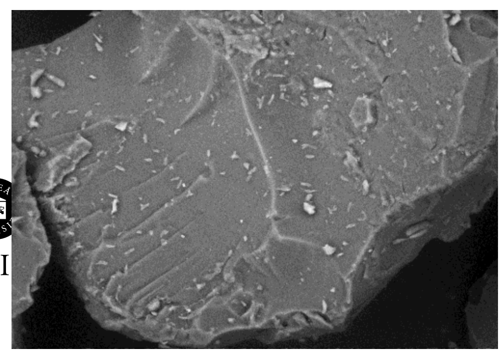


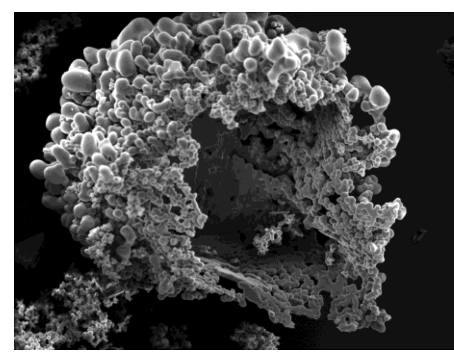












WHAT CAN BE HYDROTHERMALLY CARBONIZED?

From the literature:

- Raw Lignocellulosic Biomass – Tree's, leaves, branches, grasses, shells, skins, pits, seeds
- Animal Materials – Crustaceans shells (prawns and lobsters)
- Waste Materials – Sewage and biosludges, waste liquors, brewers waste
- Pure Materials – Glucose, fructose, sucrose, lignin, cellulose
- Other – Human hair, soft drink

If it contains a carbon structure, it can potentially be hydrothermally carbonized

ADVANTAGES OF HTC

Compared to other thermochemical methods

- Lower temperature (180-350°C)
- Limited gas production
- Wet biomass can be utilized directly
- Liquid contains a range of useful chemicals that can be extracted
- Properties of the char/liquid can be tuned through altering reaction conditions (temperature, residence time, pH)
- Dopants, such as nitrogen, can be easily incorporated

DISADVANTAGES OF HTC

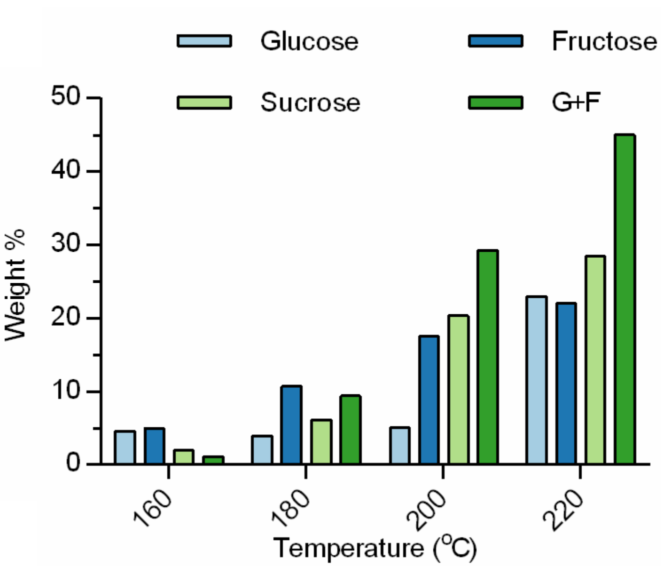
Compared to other thermochemical methods

- Cost – Pressurised reactors are required
- Continuous flow is difficult
- Energy requirement – can be negated with efficient heat exchanges
- Char needs to be separated from liquid

APPLICATIONS OF HYDROTHERMAL CARBON

- Hydrothermal carbon can be applied to a wide range of applications, such as
    - Water/air treatment (adsorbent)
    - Catalyst (oxygen-reduction fuel cell)
    - Energy Storage (electrode)
    - Drug delivery (slow release carrier)
    - Vivo imaging and cellular labelling (quantum dots)
    - Light-emitting diodes (quantum dots)
- It is possible to make the base carbon product for all of these applications off the same precursor from hydrothermal carbonization
- This is due to the process being highly tuneable

TUNING THE REACTION - TEMPERATURE



- Maximum yield is ~50%
- Yield increases with temperature in water soluble precursors
- Yield decrease with temperature in water insoluble precursors
- Sufficient temperature is required to break the bonds in the precursor (decomposition)

For lignocellulosic biomass

- Glucose – 160-180°C
- Cellulose – 200-220°C
- Lignin – >240°C

Lignin

Decomposition temperature is dependent on the precursor material

UMEÅ UNIVERSITY

Latham, K. G., Ferguson, A., & Donne, S. W. (2019). Influence of ammonium salts and temperature on the yield, morphology and chemical structure of hydrothermally carbonized saccharides. *SN Applied Sciences*. https://doi.org/10.1007/s42452-018-0055-2

TUNING THE REACTION - TEMPERATURE

Lignin

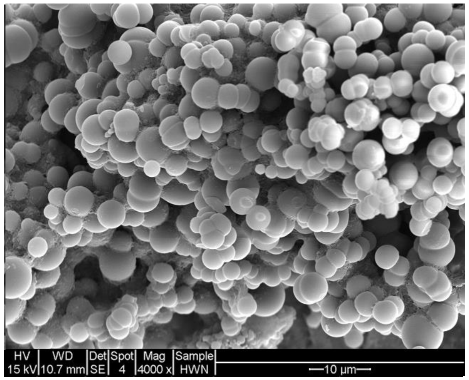
- Degree of carbon increases with increasing temperature
- Oxygen functionality is lost as a result of increasing temperature
- Thus, surface functionality can be tuned by simply changing the temperature

TUNING THE REACTION – RESIDENCE TIME

Lignin

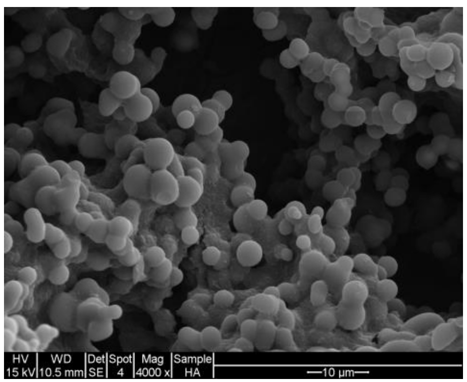
- Residence time has a similar impact to temperature, although a minimum temperature needs to be reached in order to have the reaction proceed

TUNING THE REACTION - PH



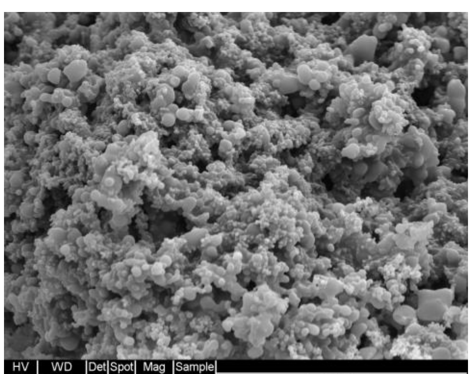
H_2O

Yield – 48 wt%
C- 66%
O- 29%
H- 5%



H_2SO_4

Yield – 11 wt%
C- 66%
O- 29%
H- 5%



NaOH

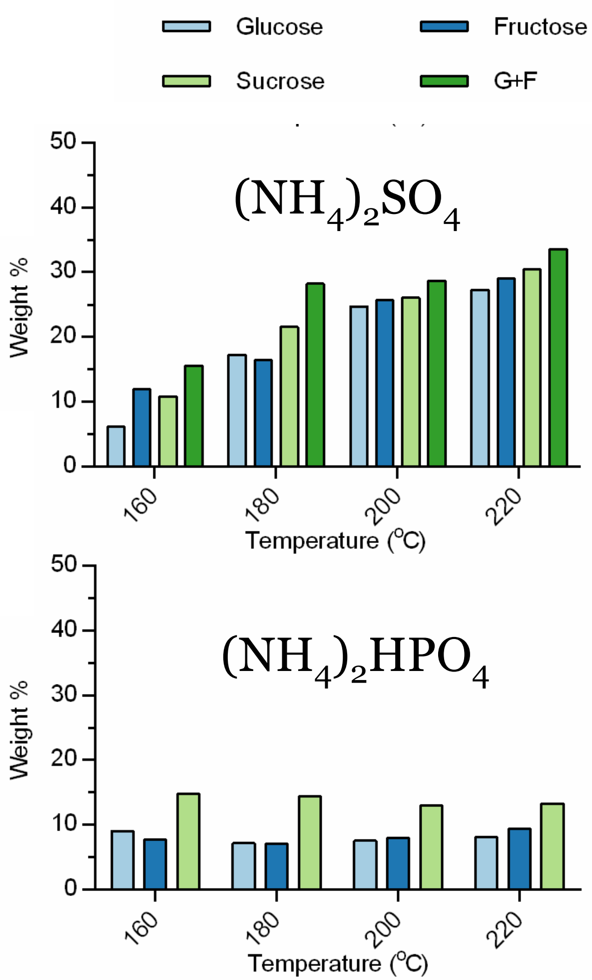
Yield – 3.5 wt%
C- 70%
O- 23%
H- 7%

- Sucrose – 200C, 4 hours
- Changing the water solution to 0.1M NaOH or 0.1M H_2SO_4 impacts the:
  - Yield
  - Morphology
  - Chemical Composition
- Provides a very simple way to create changes in the material

UMEÅ UNIVERSITY

Latham, K. G., Jambu, G., Joseph, S. D., & Donne, S. W. (2014). Nitrogen Doping of Hydrochars Produced Hydrothermal Treatment of Sucrose in H_2O, H_2SO_4, and NaOH. *ACS Sustainable Chemistry & Engineering*, *2*(4), 755–764. https://doi.org/10.1021/sc4004339

TUNING THE REACTION - NITROGEN



- Nitrogen, or other heteroatoms, can easily be introduced into the carbon structure by adding them to the hydrothermal solution prior to carbonization
- The degree that nitrogen is incorporated, and its form (aromatic vs amine), is dependent on the nitrogen form, biomass and conditions.
- Nitrogen sources include, ammonia salts, chitosan, amino acids, melamine, urea
- Despite having the same nitrogen group, ammonia salts interact very differently under hydrothermal carbonization

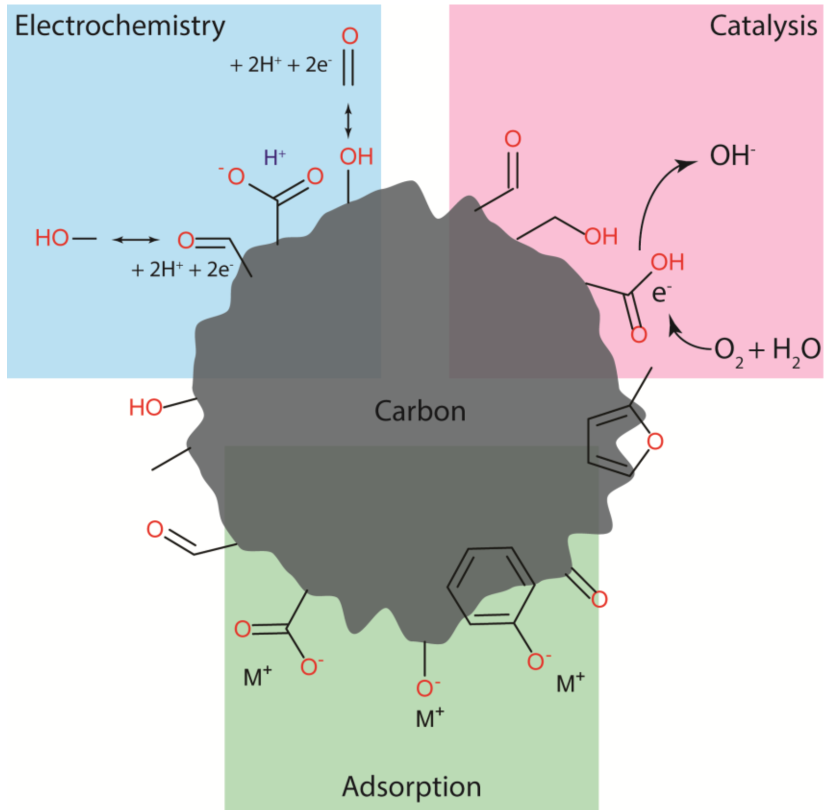
UMEÅ UNIVERSITY

Latham, K. G., Ferguson, A., & Donne, S. W. (2019). Influence of ammonium salts and temperature on the yield, morphology and chemical structure of hydrothermally carbonized saccharides. *SN Applied Sciences*. https://doi.org/10.1007/s42452-018-0055-2

INCORPORATING OTHER ELEMENTS

- Iron from an iron sand waste materials was added to lignin prior to hydrothermal carbonization
- The spherical structure is a single iron ball, which is representative of the iron structure prior to HTC.
- The lighter sections are iron fragments incorporated into the structure

UNDERSTANDING SURFACE INTERACTIONS USING HTC MATERIALS



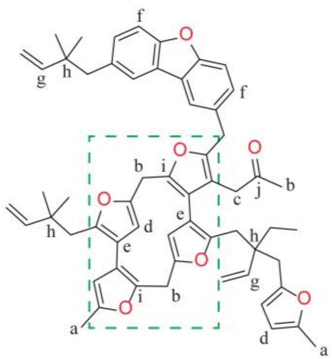
UMEÅ UNIVERSITY

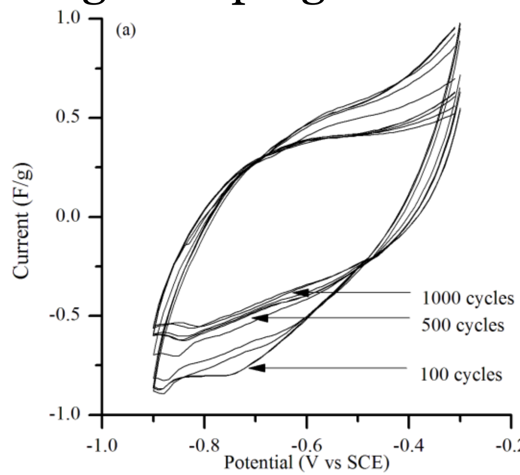
HYDROTHERMAL CARBON – AMAZING MATERIALS FOR DETERMINING SURFACE INTERACTIONS

- The low surface area exhibited by hydrothermal carbons is a major drawback in applications that are dependent on surface area (i.e., supercapacitors, water adsorption).
- These applications work through a series of surface interaction with the carbon surface and functional group
- Typically, functional groups play a lesser roll in the performance of these materials, but are critical in achieving higher levels of performance after surface area has been maximised
- Observing the interactions from different functional groups is very difficult in high surface area materials. Thus, the low surface area in hydrothermal carbons is highly beneficial for these studies

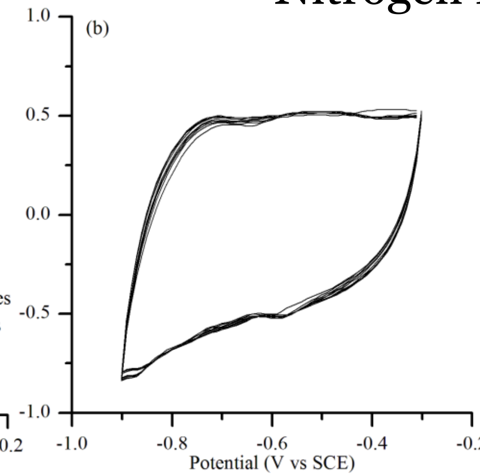
ELECTROCHEMICAL INTERACTIONS – NITROGEN DOPING

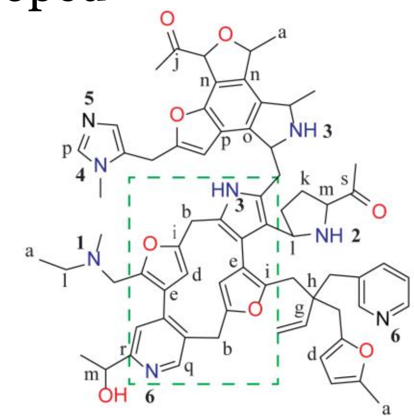
No Nitrogen Doping





Nitrogen Doped





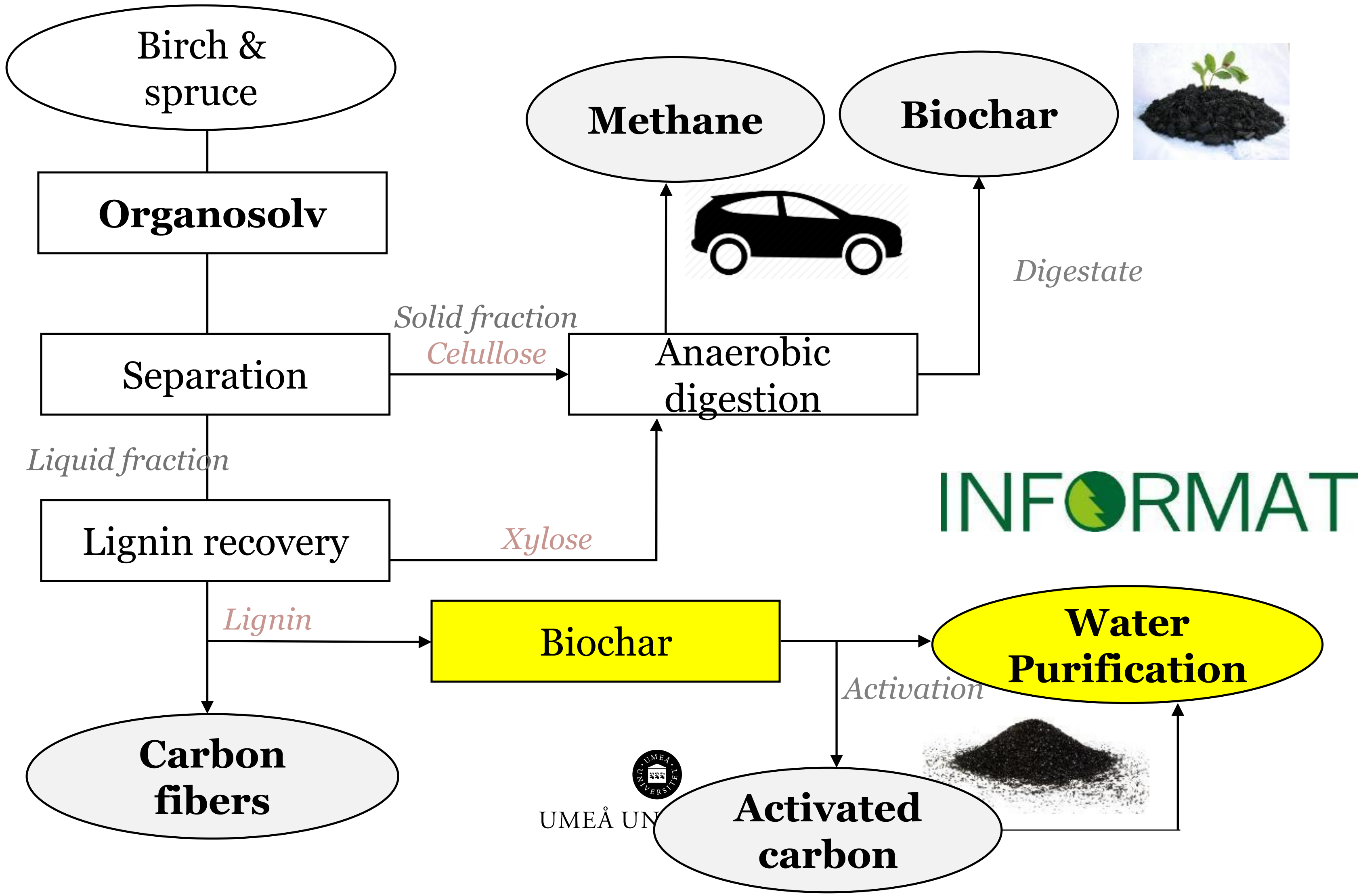
Nitrogen was seen to have a dramatic impact on capacitance (charge stored, larger window) and stability (shrinkage of window with cycle).

These are non-activated raw HTC materials, thus the effect was due to nitrogen incorporation into the structure

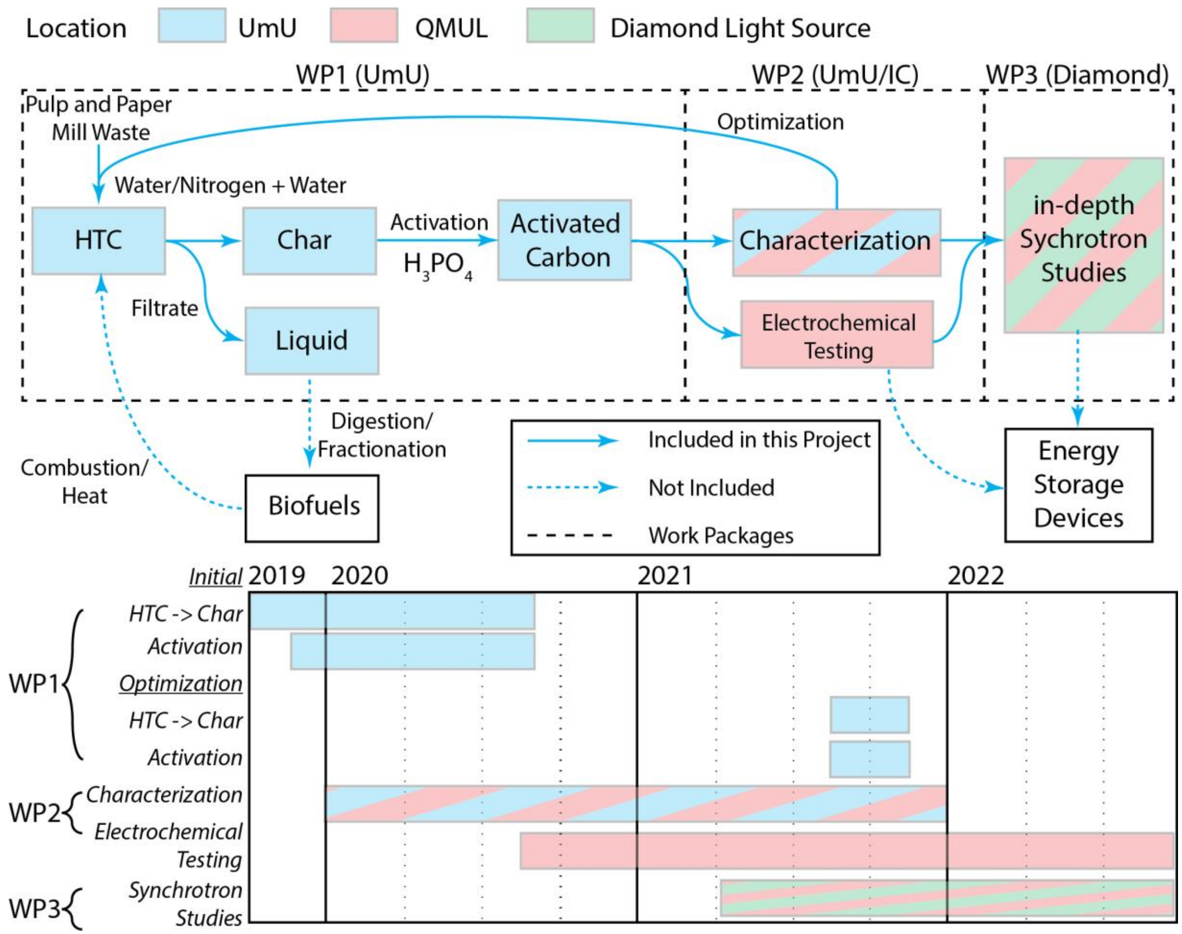
UMEÅ UNIVERSITY

Latham, K. G., Rawal, A., Hook, J. M., & Donne, S. W. (2016). RSC Advances Molecular structures driving pseudo-capacitance in hydrothermal nanostructured carbons. *RSC Advances*, *6*, 12964–12976. https://doi.org/10.1039/C5RA26136H

INFORMAT – ULTRAPURE LIGNIN FOR WATER TREATMENT



SUPERCAPACITORS FROM PULP AND PAPER MILL WASTE



Waste investigated
- Black liquor and various sludges

Energy Storage Devices
- Supercapacitors
- Na ion batteries

Synchrotron Studies
- Examining the movement of contaminates from the waste
- Examining the performance of the energy storage devices

UMEÅ UNIVERSITY

SUMMARY

- Hydrothermal carbonization can be applied to almost any carbon containing precursor
- Reaction conditions can be modified by
    - Precursor/solubility
    - Temperature
    - Residence time
    - pH
    - Dopants
- A wide range of advanced materials can be produced from hydrothermal carbonization

ACKNOWLEDGEMENTS

- Assoc. Prof. Stina Jansson (Umeå University, Sweden)
- Prof. Scott Donne (University of Newcastle, Australia)
- Dr. Aditya Rawal (University of New South Wales, Australia)
- Prof. Magda Titirici (Imperial College, London)
- FORMAS – INFORMAT Project (2016-20022)
- FORMAS – Mobility Starting Grant (2018-01041)
- Bio4Energy
- Umeå Core Facility Electron Microscopy

BIO4ENERGY

THE UNIVERSITY OF NEWCASTLE AUSTRALIA

UNSW AUSTRALIA

UMEÅ UNIVERSITY

Imperial College London

FORMAS