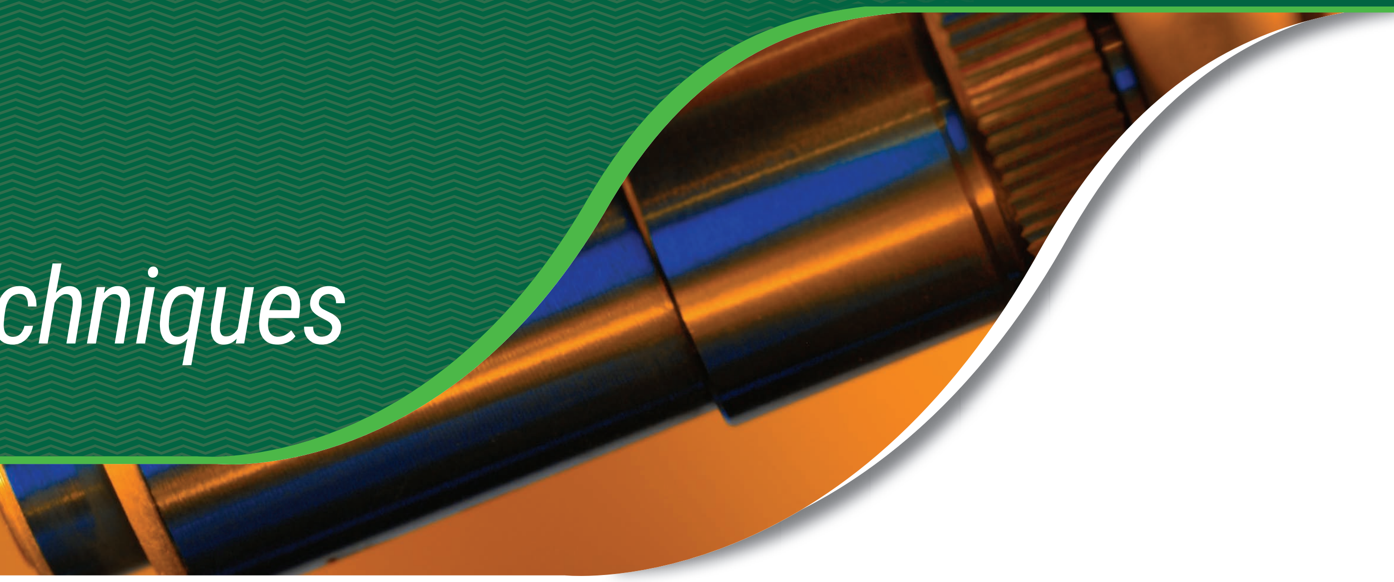

Customising Biochar Morphology Could Herald Great Breakthrough for Environmental Applications

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Work to overcome existing knowledge gaps in the thermochemical decomposition of biomass could enable production of tailor-made bio-chars for high priority environmental applications. This is why the work of Dr Roberto Volpe and his team at Queen Mary University of London, UK is attracting so much interest. He believes that he and his team are the first to get to the bottom of the porosity of biochars. They achieved this in conjunction with colleagues at UCL and in collaboration with Diamond Light Source (Harwell Campus Oxford, UK) who enabled them to image for the first time the porosity of biochars via unprecedented operando experiments at Diamond.

The carbonisation of biomass is a technique that dates back to the beginning of mankind by turning wood into charcoal. However, the full thermo-chemical aspects of this process is still largely unknown. A charcoal-like product known as 'biochar' can be produced from agricultural waste. Dr Volpe's team are working to overcome existing knowledge gaps in the kinetics of pyrolysis and physical activation of biomass. This is because a lack of understanding of how biomass morphology changes during biochar production makes it difficult to produce tailor-made bio-chars for specific environmental applications.

One conversion method is pyrolysis, a process that involves heating the waste in the absence of oxygen. During pyrolysis, changes in the size and shape (morphology) of particles increase the surface area of the biomass. This surface area controls how biochar binds to (adsorbs) pollutants, speeds up chemical reactions and stores energy.

Dr Roberto Volpe in Experimental Hall and Dr Christoph Rau - Principal Beamline Scientist I13 (Images Copyright of Diamond Light Source 2023)

Biochars created from raw biomass of almond and walnut shells

Dr Roberto Volpe's group, have used Photon and Neutron facilities over the years to work on the development of biochars from agricultural waste. Their current research at Diamond involves examining and identifying the chars created from raw biomass of almond and walnut shells as their porosity during thermo-chemical breakdown is key to unlocking significant technological development.

The ability to customise the morphology of these chars could herald a great breakthrough to help address global challenges by creating inexpensive and renewable solutions for a whole range of applications including: energy storage, catalysis, removing pollutants from water, desalination of water as well as improving quality; soil remediation and reduction of soil emissions of greenhouse gases, reducing nutrient leaching and soil acidity as well as reducing irrigation and fertilizer requirements. Tracking the morphology of biomass during biochar production is the first step towards achieving this.

"What we do is simple. We take almond and walnut shells and we put them through pyrolysis to create a char biomass – the study of carbonisation of biomass essentially reflects techniques dating back to the beginning of mankind by turning wood into charcoal. However, in our study, the process is monitored every step of the way and what we are interested in, is the porosity that is being created. By accurately heating, we can form up to more than a thousand square metres of accessible surface area in the intricate network of pores inside a single gram of formed biochars," explained Dr Volpe.

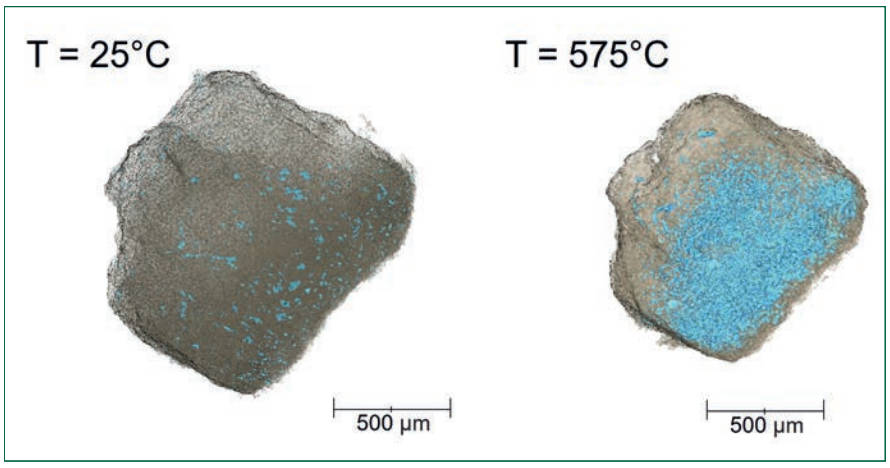


Figure 1. 3D renderings of a single walnut shell particle (in grey) and the pore network (in light blue), before and after pyrolysis - Credit Queen Mary University of London, University College London and Diamond Light Source - I-13

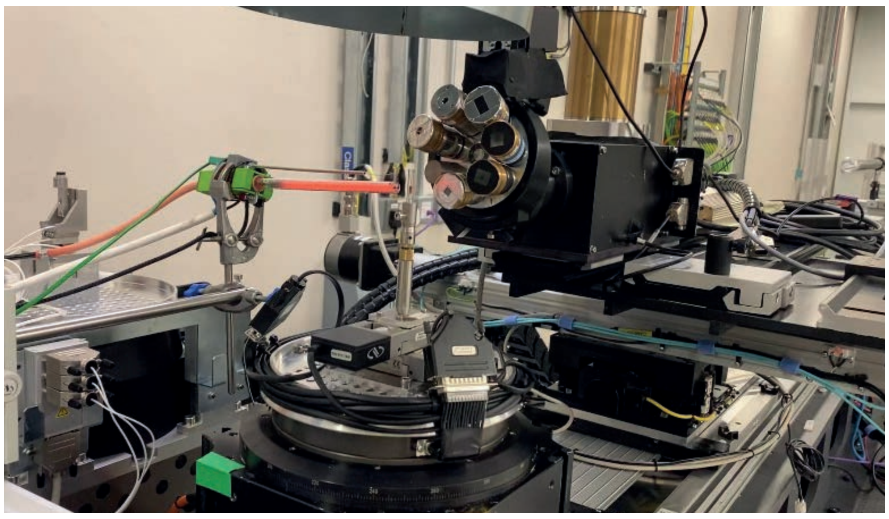
"Applications for this work are many, as contaminants (bacteria, metals, polluting molecules) or ions (in the case of energy storage) can be carried by water (or by an electrolyte) into the intra-particle pore network and they can be trapped there. Tracking the evolution of this pore network as we heat the biomass particles is key and the real novelty of this work."

The team chose to use almond and walnut shells as they are more homogeneous compared to other biomasses, so the particles resemble more to each other and are more consistent in their thermal behaviour (hence easier to find robust correlations). Also the lignin content is high, so during heating process they can preserve both the structure and the chemical functionality of lignin which would be more difficult to do with 'softer' samples. It also allows them a range of tunability that softer biomass does not allow.

Many potential applications including reducing bacterial contamination in water

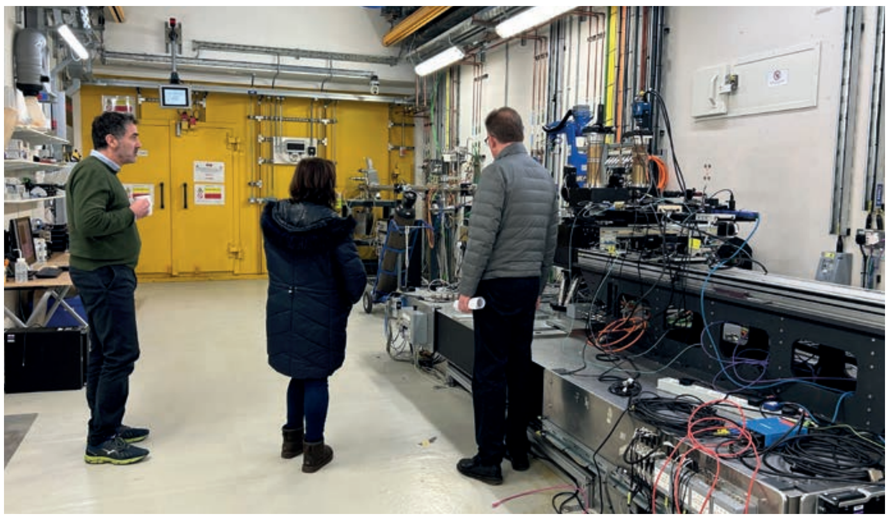
In terms of applications, the team have already successfully tested bacteria or E-coli adsorption, thereby reducing the bacteria contamination in water by 96% using biochars produced above 500C. Dr Volpe commented; "In general the material can be used for cleaning water from contaminants such as heavy metals, or pharmaceuticals such as anti-biotics or antiseptics. This situation is typical of hospital wastewater and presents a large problem for today's hospital environment especially in Low and Middle income countries where water sanity is less possible. For instance in Uganda 60% of households' tap water and communal drinking water supply is heavily contaminated by E.coli."

Diamond's Manchester Imaging Branchline team (I13-2) collaborated with the researchers to conduct rapid high-resolution X-ray imaging of biomass. Diamond worked with them from the experiment feasibility, the complex measurements, to experimental setup of the furnace to create the correct environment and optimal X-ray imaging conditions, to mining the wealth of data generated.



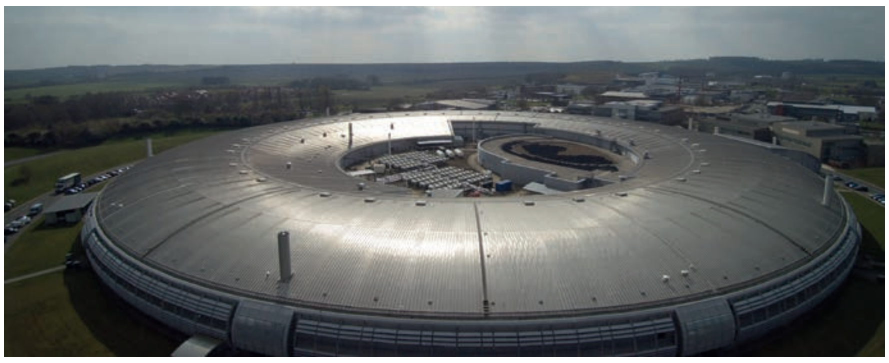
Quartz tube reactor and imaging cell on stage with heating furnace.
Credit - Queen Mary University of London and Diamond Light Source I-13

This allowed real-time tracking of particle morphology and porosity during pyrolysis. The results showed that the morphology and porosity of different nutshells evolved differently during pyrolysis. However, these differences were less pronounced in biomass pre-soaked with an alkaline solution. Almond shells shrank more but gained less porosity than walnut shells, which have thicker walled cells on average. The results suggest that the difference is related to how heat penetrates particles of biomass during pyrolysis. Porosity was found to accumulate towards the centre of particles during pyrolysis for the same reason.



International Labmate I13 Beamline Visit - Copyright of Diamond Light Source 2023

The difference is related to how different chemical reactions occur in the confined space of evolving pores of biomass and how fast or how slow – the produced vapours are progressively released out of the particle through that evolving network of pores during pyrolysis. As such, as temperature is increased up to approximately 500°C, pores develop more towards the surface, while beyond 500°C, porosity starts to develop more towards the centre of particles. These heat and mass transport limitations are what make pyrolysis so challenging to resolve and control.



Diamond Light Source Aerial Image - Copyright Diamond Light Source Ltd

How heat and duration applied affects porosity and morphology of the nut shells:

In function of the slow heating ramp applied the team distinguished four different regimes:

1. 100-225 degrees: no significant changes
2. 225-350 degrees: swelling due to a phase transition, presumably by the lignin,
3. 350-500 degrees: moderate speed size reduction due to evaporation of constituents of the particle, pore development, more prominent at the particle surface
4. 500–650 degrees: faster reduction in size and pore development faster towards the centre of the particle

Holding at 650 degrees: constant size no reduction, progressive stabilisation of the carbon

Designing a reactor that also serves as an imaging cell

Principal Beamline Scientist, Professor Christoph Rau explained; "The data is recorded with the very brilliant rapid and high resolution X-ray beam at I13-2. The very intense radiation permits short exposure times in the range of milliseconds. A complete 3-D tomographic data set with several thousands of projections is recorded within several minutes. To fulfil the data acquisition strategy we had to first scan with the sample under static conditions. This involved, starting the heating ramp, levelling to a given target temperature, tomographic scan, continuing heating ramp and so on. The tricky bit is to scan the sample under stable conditions. The trick to solve this issue was to design a reactor which also serves as an imaging cell. A quartz capillary tube that holds the sample particle which is heated by a flow of hot inert or reactive gas (Argon, CO_2). The sample has to remain thermally stable and also the radiation should not have an impact on the sample stability (radiation damage). The challenge is to avoid much movement between one tomography and the other one meaning that each tomography (which takes around one minute) should not involve too much change in temperature as this reduces the exposure time and therefore the contrast of the image."

Dr Roberto Volpe holding Sample at I13 2 - Copyright of Diamond Light Source 2023

Dr Paul Quinn, Science Group Leader for Diamond explained; "Imaging techniques at Diamond allow the team to visualise the structure of the solid particle with enough detail to examine small gaps or pores and track any changes over time and with variations in temperature. This means that we can extract a great deal of detail about the evolution of these pores and their intricate geometry. This result sheds light on the fundamental behaviour of thermally treated biomass and at the same time allows Dr Volpe and his team to uniquely correlate the particle and pores geometry to temperature."

The group is consciously developing an environmental cost-benefit analysis for the use of biochar because of the energy needed to turn the biomass into it before it can then be used to adsorb pollutants. Dr Volpe commented: "This is very important. We are aiming at a fully circular approach where the char that is saturated with pollutants can be used as solid fuel to prepare new bio char from raw biomass. This will certainly favour the environmental benefits versus the cost when compared to using a traditional fossil-based activated carbon, yet a fully comprehensive analysis to quantify the benefits is to be done perhaps using a life cycle assessment method."

One of Dr Volpe's next moves will be to visit MIT and its 'combustion group' at the Department of Mechanical Engineering, on a Royal Society grant to combine his images with their mathematical models in an example two of the world's leading groups on biomass conversion working together. He is also coming back to conduct further work at Diamond in April, as the group's next step to increase the 'tunability' of biochar will be to resolve porosity at smaller resolution aiming at below the 100 nanometers.