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Possibilities and Limits for Feedstock, Processes and Applications

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Abstracts Booklet

Keynote lectures

Performance Enhancing Doping and Hydrothermal Carbons

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Catalysts will underpin sustainable circular energy and chemical economies based on renewable energy, CO_2 and biomass.[1] In this context, carbon supported catalysts have an important role to play provided there their properties can be subtly tailored at the nanoscale to address applications in these economies (e.g. challenging aqueous phase chemistry of the Biorefinery). In this context, the development of efficient methods to meet this need - i.e. the synthesis of tuneable functional materials with suitable porosity - would be of interest. Controlled nanostructuration is beneficial in terms of diffusion and mass transport, whilst control of bulk and surface chemistry may lead to application benefits (e.g. metal-support interactions, retention behaviour etc.), and in turn lead to the establishment of structure-activity relationships and further optimisation opportunities. This "tailoring" however has to be achieved based on scalable and sustainable technologies to be market competitive (e.g. vs. Activated Carbons). In this presentation, approaches based on hydrothermal carbonisation (HTC),[2] to produce nitrogen-doped carbons will be discussed, demonstrating the option to direct both functionality,[3] and porosity (e.g. micro- vs. mesoporosity)[4] with life cycle advantages over industrial equivalents. One particular approach of interest is the HTC of model (amino) sugars and globular proteins or amino acids to porous, functional, nitrogen-doped carbonaceous materials. Scope to tailor nitrogen incorporation (e.g. pyrrolic vs. pyridinic content) will be discussed. Inspired by this work, the nitrogen containing organic precursor can be exchanged for an inorganic-based precursor (e.g. 3-aminopropyl triethoxysilane), which opens access to a range of nitrogen-doped carbons, carbon/silica hybrids and carbide/nitride systems in the form of xero- and aerogels.[5] These synthesis are based on a Maillard-type reaction between reducing saccharides and amine groups (as the nitrogen source), and lay the basis for the development of a flexible, controllable synthesis platform, to materials suitable for a wide range of applications (e.g. as catalysts supports, electrodes, etc.). As an example of the potential application benefit, the demanding direct oxidation of CH_4 (e.g. as sourced from biogas) to CH_3OH will be presented.[6] Likewise, the use of these N-doped carbons as templates in the synthesis of meso-structured single crystal zeolites (e.g. H-ZSM-5 for CH_3OH upgrading),[7] will also be discussed, highlighting further the remit of these synthetic approaches.

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Opportunities for Energy and Nutrient cycling using Hydrothermal Carbonisation

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Hydrothermal carbonisation (HTC) is emerging as a promising technology for the conversion of biomass and bio-waste into high energy density bio-coal and bio-products. HTC is feedstock flexible but the yields and quality of its products are highly feedstock dependent. The fractionation of inorganics during processing results in significant improvement in the combustion quality of the resulting bio-coals. This is due in part to reductions in alkali metals and other contaminants which can reduce slagging and fouling propensity. Not all feedstocks however produce high energy density bio-coal and other applications maybe more feasible. Lignocellulosic biomass generally produces higher quality bio-coal whereas bio waste’s generally result in high mineral matter containing hydrochar and higher TOC containing process water owing to their initial composition. For some feedstocks, there is potential for recovery of energy and minerals from the process water. Integration of hydrothermal processing with anaerobic digestion (AD) has recently been proposed to have significant potential for treatment of process waters. The extraction of nutrients such as phosphorus into the process waters during hydrothermal processing is also gaining interest and is dependent upon process severity, pH and mineral content of the original feedstock. There is potential for enhancing nutrient extraction by operating at lower pH resulting in further improvement of the properties of the resulting bio-coal. The keynote will discuss the relationship between feedstock composition and HTC behaviour, the fate of inorganic content and the influence this has on bio-coal quality. Options for integration of HTC with anaerobic digestion will be discussed together with potential routes for nutrient recovery.

HYDROTHERMAL DERIVED CARBON DISCS AND THEIR APPLICATION IN ELECTROCATALYSIS

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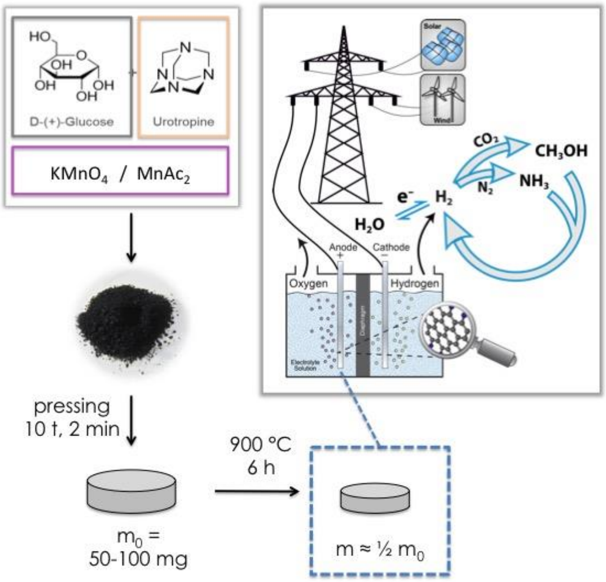
To overcome the today's energy challenge highly efficient, environmental friendly and inexpensive pathways are required. Electrochemical water splitting from renewable energy sources and the storage or conversion of the produced hydrogen, which is a chemical energy carrier with a high energy density, is one of the possible routes. Noble metals (Pt, Ir, Ru), transition metals or their oxides (Ni, Co) have been used as electrode materials, which have to be replaced by suitable alternatives to satisfy the global demand.

Carbon is attractive for electrochemical applications due to the tuneable physicochemical properties including conductivity and targeted surface modifications as well as abundance and low cost. The bottom-up approach of hydrothermal carbonisation allows systematic variations and the incorporation of heteroatoms in the carbon structure and is therefore eminently suitable for the synthesis. Methodical changes of the initial pH, the addition of nitrogen precursor and the use of manganese salts as catalytic active species are investigated.

Thorough characterization of the synthesized materials is essential to investigate relations between material properties and their electrochemical performance. As the long-term stability is a crucial point when carbon materials are applied in electrochemical processes our research focuses on thermal and electrochemical oxidation processes.



Carbonization in water: A contradiction?

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The formation of hydrochar is from the chemical view mainly an elimination of water from carbohydrates in water as solvent. This seems to be a contradiction itself and it has consequence for properties and applications. In fact, the structure of hydrochar is different from pyrochar, although both are carbonizations and e.g. the heating value of the products is similar. The different structure has consequences e.g. if it used as “biochar” in soils. The carbonization in water influences the partition of nitrogen and the precipitation of salts. As example, this enables the isolation of phosphate after hydrothermal carbonization of sewage sludge as commercial fertilizer. On the other hand, comparing the product after a chemical activation, the properties are very similar. It seems that heating-up transforms hydrochar to pyrochar. This presentation is an approximation on the question how a hydrothermal reaction pathway of a carbonization influences the properties, and as consequence, the possible application of product. As conclusion, we have to state that we still not have understood exactly, what hydrothermal carbonization is.

Catalytic conversions of humins using heterogeneous catalysts

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Lignocellulosic biomass is considered an attractive feedstock for biofuels and biobased chemicals. An example of a conversion is the acid-catalyzed dehydration of glucose to form the key platform molecule 5-hydroxymethylfurfural (HMF). Subsequent rehydration of HMF yields the valuable building blocks levulinic acid (LA) and formic acid. Unfortunately, these conversions with current catalytic technologies in water invariably lead to the formation of solid waste products known as humins. Humins are carbonaceous, heterogeneous, poly-disperse materials of which the molecular structure is largely unknown. Applications of such humins are limited, examples are the use as supports for heterogeneous catalysts and as soil improvers. We here report our studies on the characterisation of humins derived from glucose as well as our experimental findings related to the liquefaction of these humins using heterogeneous catalysts with the objective to obtain high liquid yields, preferably enriched in valuable bulk chemicals like phenolics and aromatics. The emphasis was on catalytic hydrotreatment reactions using hydrogen donor solvents in combination with noble metal catalysts Humin conversions of up to 80% were obtained. The liquid products were analysed using 2D-GC, GC-MS/FID, GPC, CHN and were shown to consist of mixtures of low molecular weight products including phenolics, aromatics, naphtenes and alkanes.

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HYDROCHAR AS PRECURSOR OF HIGHLY POROUS FUNCTIONAL MATERIALS FOR ENERGY APPLICATIONS

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One of the main challenges in the HTC technology is the development of porous products. Unfortunately, the hydrochar materials are non-porous, which severely limits their range of applications. In particular, for many energy-related applications (e.g. supercapacitors, Li-ion/Li-S/Li-air batteries, H_2 storage or CO_2 capture), a well-developed surface area is needed, besides a well-controlled pore size distribution (and also surface chemistry). My group has demonstrated, however, that hydrochar, on the other side, does constitute an excellent precursor of highly porous materials by means of chemical activation approaches. In this regard, KOH is the leading activating agent, being massively used in the scientific literature, yielding porous carbons with BET surface areas up to around 3000 m^2/g and a controlled PSD in the micro-supermicropore range. More recently, we have shown the possibility of enlarging the pore size into the mesopore range by the introduction of melamine into the activation mixture, which additionally leads to N-doping of the material. These advanced textural and chemical properties have led to excellent energy storage and power handling materials in supercapacitors with a variety of electrolytes,[1] besides large capacity adsorbents for H_2 storage[2] and CO_2 capture.[2a, 3] However, in spite of all its positive features, KOH activation still poses challenges from the industrial point of view owing to its toxicity and mainly its high corrosiveness. Thereby, greener activation approaches are in high demand for the widespread commercialization of porous hydrochar-based systems. In this regard, we have recently shown that certain less-corrosive chemical agents are capable of producing materials mimicking the properties of KOH-activated carbons.[4]

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Oral presentations

From Hydrothermal to Ionothermal Carbon Sol-Gel Chemistry

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Hydrothermal carbonization (HTC) can be regarded as a complex polymerization / condensation of carbohydrates leading to crosslinked carbon-rich matter that is referred to as hydrothermal carbon or hydrochar. The particle size of polymers derived from polycondensation depends on the reaction rate and so it is for HTC. By applying an effective and inexpensive catalyst, namely Borax, we could apply well-known principles of sol-gel chemistry to the HTC process to obtain hydrothermal carbon aerogels with controllable surface area and porosity.[1] When it comes to the conversion to conductive carbon aerogels the materials unfortunately undergo pore collapse due to high interfacial energy throughout the solvent removal and the pyrolysis. The presence of simple inorganic salts such as alkali chlorides and zinc chloride leads to a retained stable solid-liquid interface throughout thermal conversion towards carbon aerogels.[2] This way the pore collapse can be significantly reduced and carbons with high surface area and high porosity are obtained. An interesting side-effect is that the increased boiling point of the salt solution/melt allows the conversion of sugar solutions into carbon with high yields at atmospheric pressure. Recently we found that in-situ crystallization of alkaline earth halides throughout the polymerization / carbonization can be employed to obtain interesting anisotropic tubular porosity also resulting in very high surface area and porosity, however on the costs of lower yields.

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BINDER-FREE N-FUNCTIONALIZED CARBON DISC ELECTRODE MATERIALS FOR ELECTROCHEMICAL APPLICATIONS

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N-functionalized hydrothermal carbon materials (N-HTC) with spherical morphology were specifically synthesized by hydrothermal synthesis using glucose and urotropine as starting materials. Both, decomposition products of glucose and urotropine react together opening up a variety of possible reaction pathways. The pH has a pronounced effect on the reaction mechanisms of the corresponding reaction steps. Hence, widespread functional groups and structural motifs are reflected on the carbonaceous materials that were analyzed in detail. The molar ratio of glucose and urotropine has been varied in order to achieve a continuous increase of the N-content. The powder materials were pelletized, resulting in mechanically stable disc electrodes (Figure 1). By increasing the amount of nitrogen, N-contents from 5 wt% up to maximal 8 wt% were obtained after pyrolysis at 900 °C.

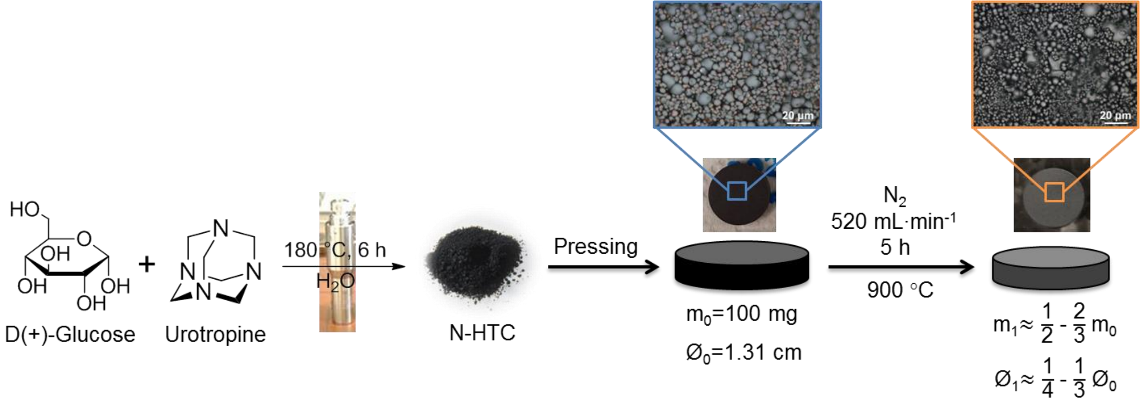

Figure 1: Schematic illustration of the preparation of disc electrodes and subsequent pyrolysis accompanied by a mass and diameter loss as well as by a shrinkage of the spherical particles.

The work is divided into three parts: a) intrinsic characterization of pristine and pyrolyzed N-HTC materials, b) the electrocatalytic performance including electron transfer characteristics and c) the electrochemical stability under basic and acidic conditions. Increasing N-incorporation leads to higher conductivities as well as to favourable electron transfer kinetics. In addition, electrochemical degradation measurements within OER conditions have been studied in acidic and basic environment for 24 h. Based on in-depth post-mortem analytics of disc electrodes and electrolyte, different degradation procedures were discussed.

Tunable heteroatom doped carbogels as sustainable electrocatalysts

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The most recent global agreement in Paris on limiting the climate change by a maximum of 2 °C in order to prevent making global warming catastrophic and irreversible, is a milestone in trying to save our planet. It is clear that major changes need to be carried out in order to reduce and on the long run completely avoid carbon dioxide emission. One solution could be the shift to a hydrogen based energy economy, where hydrogen could be won from renewable energy resources and used in fuel cells, to produce electricity and heat. With a high electrical efficiency, polymer electrolyte membrane (PEM) fuel cells are a promising opportunity for future automotive, stationary and portable power applications, already becoming more popular by the commercialisation of fuel cell cars.

Currently, electro-catalysts for the oxygen reduction reaction (ORR) at cathodes of PEM fuel cells involve platinum and Pt-alloys. Pt catalysts show a number of shortcomings, such as slow ORR kinetics, but most crucial low availability and high cost, which is why alternative catalytic materials are highly desirable.[1]

We use a new approach for an environmentally friendly and low cost production of heteroatom doped materials called hydrothermal carbonisation (HTC). Here, in a matter of hours any biowaste can be converted into useful carbon materials under moderate temperatures and self-generated pressure.[2] By using this process we are able to convert biowaste into different multifunctional nanoporous carbon materials containing nitrogen, sulphur and boron heteroatoms as well as inorganic nanoparticles, such as iron, with a high specific surface area, large pore volume and tuneable pore sizes. Our aim is to understand how these parameters can influence the catalytic activity towards the ORR in order to synthesise true novel materials that can compete with commercially used platinum catalysts to make fuel cells more affordable and especially more sustainable. We will present the physical, chemical and electrochemical characterisation of the synthesised carbon materials and compare their ORR performance with the commercial platinum catalyst.

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CO_2 Sorbents from Biomass and Biomass Waste

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Hydrothermal carbonization was used as the first step to convert fibre-rich biomass to hydrothermal carbons that were activated in CO_2 to give activated carbons that were tested for their ability to adsorb CO_2. The common Swedish biomass, flax fibre, as well as the biomass waste product cornhusk, were tested. In some cases milk, an aqueous suspension containing both organic matter and other elements such as Ca and P, was used in place of water for the hydrothermal carbonization; however, activated carbons produced using this procedural modification adsorbed less CO_2. In general, more CO_2 could be adsorbed on activated carbons that had been activated for long times (up to 20 h) and under a stream of undiluted CO_2 (1 bar). Although the highest capacities for CO_2 sorption (>3.8 $\mathrm{mmol_{CO2}/g_{sorbent}}$ at 0 °C; >2.6 $\mathrm{mmol_{CO2}/g_{sorbent}}$ at 30 °C) were obtained on activated carbons derived from the more processed flax fibre material, adsorption capacities above 3 $\mathrm{mmol_{CO2}/g_{sorbent}}$ at 0 °C and 2.2 $\mathrm{mmol_{CO2}/g_{sorbent}}$ at 30 °C could be obtained over activated carbons derived from the waste material, cornhusk. Spectroscopic techniques such as solid-state ^{13}C NMR spectroscopy were used to relate features of the hydrothermal carbons to the properties of the corresponding activated carbons.

Results from rapid hydrothermal torrefaction of sawdust samples

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A rapid torrefaction-type hydrothermal pre-processing of a sawdust sample was carried in subcritical water (neutral) and with added Na2CO3 (alkaline compound) and Nb2O5 (solid acid). The gas products (≈ 1.5 wt% of biomass), consisted mainly of carbon dioxide. The solid products were recovered via vacuum filtration, dried at 105 °C for 2 h and characterized for their elemental and proximate compositions. The dried recovered solids were friable and easily pulverized into dust, and were denoted as SN (neutral subcritical water), SA (Na_2CO_3 added) and SB (Nb_2O_5 added).

Characterization results indicated that SN had a 55% reduction in the ash content compared to the original biomass, while Nb_2O_5 was mostly retained in the solid product, giving SB a 28 wt% of ash. The calorific value of the recovered solid were respectively, 13.5%, 31.8% and 29.0% higher for SA, SB and SN than the original biomass. The alkaline additive led to increased solubilization of the sawdust so that it retained only 51 wt% of carbon, while losing more than half its original mass. On the other hand, neutral subcritical water and the presence of Nb_2O_5 gave solid products that retained slightly above 50% of the mass of the original sawdust, while retaining nearly 80 wt% of its carbon. In addition, the recovered solids gave much higher coal-like fixed carbon contents than the original sawdust.

Rapid hydrothermal torrefaction could be used to increase the energy density of biomass, its grindability and carbon/oxygen ratio for application in different bioenergy technologies, particularly in biomass combustion and entrained-flow gasification. Results showed that subcritical water alone was capable of biomass torrefaction to produce an energy-dense solid with lower ash contents compared to the original sawdust, which may be a solution to the problems of ash in direct co-fired combustion systems in power plants. The soluble aqueous phase product could be also applied for bioenergy production via anaerobic digestion or supercritical water gasification.

Hydrothermal carbonization and wet oxidation of sewage sludge in the framework of the project CARBOWERT

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In the project CARBOWERT, hydrochars were produced by hydrothermal carbonization (HTC) of sewage sludge on industrial scale for application as soil amendment. In an economic assessment, treatment of the process water (PW) has to be considered. One solution for PW treatment could be a subsequent wet oxidation (WO). Chemical oxidation aims at the removal of bio-recalcitrant fractions and the partial oxidation of dissolved organic matter into readily biodegradable intermediates, such as short chain carboxylic acids.

WO was first optimized for reducing chemical oxygen demand (COD) and carbon content (DOC) in separated PWs. The optimized WO conditions (200°C, 4 h, 30 bar O_2-pressure) were applied to five PWs: mildly and strongly carbonized sewage sludge (170°C, 2 h or 210°C, 10 h), and sewage sludge, straw, as well as a mixture of sewage sludge and straw in a ratio of 70:30 (210°C, 4 h). WO was performed on separated PW and HTC slurries (hydrochars plus PW). The reduction of DOC and COD in separated PW was up to 60% and 67%, respectively. In HTC slurries, COD reduction in the PW was <10%. In some suspensions, the DOC increased due to release of low molecular weight compounds from the hydrochars. As hydrochars showed a mass loss and an increase in oxygen functional groups, our recommendation of combining HTC and WO for subsequent biological PW treatment in a WWTP is the following: 1. HTC plant, 2. hot-filtration unit, 3. WO reactor for PW, 4. optional filtration unit, 5. anaerobic digestion or aerobic biological treatment.

TOWARDS THE HYDROTHERMAL CARBONIZATION OF HUMINS: A PRELIMINARY INSIGHT INTO THE MECHANISM

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In recent years, hydrothermal carbons (HTC) have attracted attention due to their variable structure and their potential use in many applications. However, the formation of these HTC, in particular from complex biomass, is not often well understood.

Meanwhile, the advancement of sugar conversion to important platform chemicals often has a price: the inevitable production of the so-called humins. The remarkable similarities of the furanic-linked structure of humins and HTC carbons suggest the high potential of this biomass waste in the production of novel carbonaceous materials.

However, the low water solubility of humins (1.4 mg mL^{-1}) calls for a modification of the traditional hydrothermal carbonization treatment. For this reason, alternative solvents have been investigated for unravelling the first steps of the HTC mechanism, by comparing the influence of different operating conditions in the fragmentation of this biomass waste.

In particular, subcritical and supercritical catalytic continuous flow reactions of different humins solutions have been carried out at various operating conditions (180-240 °C; 5-86 bar), and the resulting samples were analysed by GC-MS. In only 43 seconds of residence time, a variety of oxygenated products were obtained, comprising of the most infamous 5-hydroxymethylfurfural (HMF) as the main product.

The hydrolysis potential of humins offers an indirect view of the building blocks the HTC carbon, and will thus give a better insight in their formation. In addition, the possibility of recycling this so-far considered waste by deconstruction in products of higher values will create additional value for the overall biomass conversion process.

THE INFLUENCE AND IMPLICATIONS OF RECYCLING HYDROTHERMAL PROCESS WATERS ON HYDROCHAR COMBUSTION CHEMISTRY

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HTC can produce a high quality coal-like fuel without the combustion limitations imposed by the starting feedstocks inorganic and heteroatom chemistry. In order to maximise resource efficiency and avoid waste waters, there is a requirement to utilise these process waters which contain about 10 to 15 % of the original organic matter in the form of sugars and organic acids. Recycling of these acids have been shown to catalyse the reaction and can improve the yields at little or no cost; however these process waters also contain alkaline metals, chlorides, sulphates and nitrogen based compounds initially extracted by the HTC process. While these inorganic and heteroatoms may bring about a catalytic effect, reincorporation within the solid fuel can bring about significant issues in terms of slagging, fouling, corrosion and airborne emissions during combustion. The effect and potential implications of recycling process waters on the fuels inorganic chemistry has, until now, been overlooked.

In this research miscanthus was carbonised at 200^{0}C and 250^{0}C, with a retention time of one hour. The process waters were recycled 10 times. The results show a modest increase in char yield, heating value and carbon content up to an equilibrium point. The results do however show reuptake of nitrogen, alkaline metals and chlorine back into the fuel, which increases with recycling runs and is detrimental to the fuels combustion properties. The results nevertheless suggest that optimal conditions are possible to both maximise yield while overcoming combustion limitations imposed by the starting feedstocks inorganic and heteroatom chemistry.

Hydrothermal treatment of insect rearing residues and whole insects – The use of experimental design for finding trends and correlations

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Insects are currently being discussed as an alternative source of protein, not only for livestock or fish feed, but also for human nutrition. The omnivorous insect species black soldier fly (*Hermetia illucens*) has been the subject of several recent studies, since it offers multiple benefits as a source of protein. It is not regarded as a pest or vector, has a promising protein and fat spectrum at larvae stage, and has limited requirements for growth.

In this ongoing study, rearing residues from *H. illucens* larvae grown on a mixture of rye coarse meal, wheat bran, and water as well as whole larvae were subjected to hydrothermal conditions. Both – rearing residues and insects – were obtained from a pet food production site located in Germany. A design of experiments response surface methodology was used to analyse the influence of temperature, holding time, and feedstock-to-water ratio, which were varied between 183-267 °C, 19-221 min, and 8-42 %, respectively. Analytical work was done with a focus on energetic use, production of chemicals (5-HMF), and nutrient recovery.

First results reveal clear trends and correlations between process parameters and product concentrations of certain chemical compounds in the liquid phase, whereas other product characteristics like the higher heating value of the solid were only slightly influenced. The development of statistical models to describe the influence of process parameters on product characteristics is promising as a tool for optimizing process conditions to achieve targeted values.

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Biomass derived carbon dots using hydrothermal carbonisation

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Semiconductor quantum dots (QDs) are nanocrystals with sizes around 10 nm (10^{-8} m) that have attracted much attention as a novel class of material with unique optical properties dictated by their size. Vast majority of QDs used today in the biomedical field as fluorescent labels are based on II-VI systems (CdTe, ZnS etc.). These QDs offer a number of advantages over fluorescent dyes and proteins as they resist photobleaching and exhibit size-tunable emission spectra. However not all the properties of QDs suit the stringent criteria of in vivo applications with their cytotoxicity and hydrophobicity being some of the key issues. Carbon quantum dots (CQDs) have the potential to replace the toxic metal-based QDs. Such carbon nanoparticles are biocompatible, chemically inert, strongly luminescent and well-dispersible in various solvents showing promising potential in human applications.

In our study, we have been investigating these CQDs to establish the relationship between their structure and optical properties. Bright CQDs were synthesized by one-step hydrothermal carbonization of different biomass precursors (glucose in this case) at 200°C. This low-cost and green chemistry method provides a feasible route for value-added and sustainable utilization of biomass. Their strong fluorescence is likely to be due to a complex mechanism related to both quantum confinements in the sp^2/sp^3 core as well as surface energy traps due to the polar functional groups. The optical properties depend on the starting precursor and can be correlated to their different chemical structure and different surface functionalities.

Our biomass-derived CQDs are easy to make, non-toxic, bright, use low cost and highly abundant precursors and produced with tuneable functional groups. Next step in our research will be the functionalization of the CQDs with various biomarkers in order to enable targeted biolabelling and bioimaging of cellular structures including those in cancer cells.

LIGHT-EMITTING CARBON NANOMATERIALS WITH TUNABLE OPTICAL RESPONSE AND THEIR APPLICATION IN ENVIRONMENTAL PHOTOCATALYSIS

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As newcomers to the world of nanomaterials and nanolights, luminescent carbon nanodots (CNDs) have recently attracted growing attention due to their great potential in biological labeling/imaging, photocatalysts and sensor design. In contrast to conventional quantum dots, which are based on relatively scarce, heavy elements, photoluminescent CNDs are superior in chemical inertness, low cytotoxicity and excellent biocompatibility. Furthermore, there is also a strong need to develop sustainable and cost-effective ways to maximize sunlight collection and especially to expand the photocatalytic performance of commonly used semiconductors beyond the UV region. One approach is the use of sensitizing elements that can introduce additional states into the semiconductors band gap and increase the absorbance of visible light. In this regard, CNDs can be considered as a good sensitizing alternative to other organic molecules with shorter emission lifetimes and more prone to photobleaching.

In this work, we present a green approach to obtain stable fluorescent CNDs with capabilities under NIR excitation wavelenths (up-converting photoluminescence capabilities). This property, coupled with water-stability and low-toxicity, enabled their application as nanosensitizers to expand the absorption of conventional photocatalysts towards the UV-visible-NIR range and dramatically enhanced the degradation rates of recalcitrant organic contaminants in wastewaters under visible light, through a mechanism of generation of reactive oxygen species (ROS).

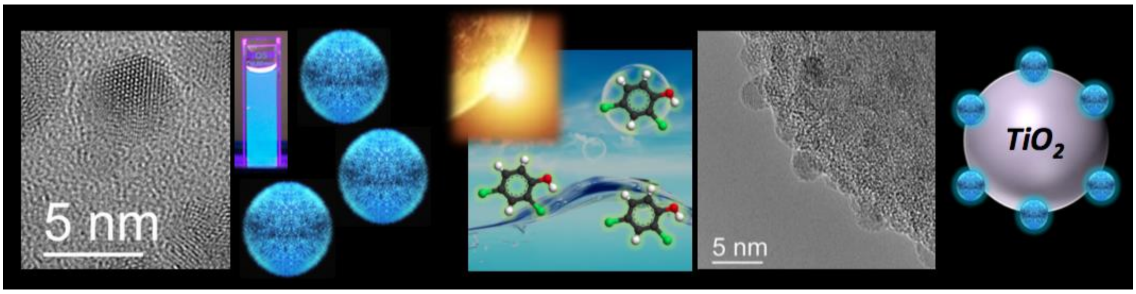

Figure 1. Schematic drawing highlighting the luminescent nature of the carbon nanodots and their subsequent assembly on TiO_2 supports for photocatalytic degradation applications.

Examination of the surface functionality of Nitrogen Doped Hydrothermal carbons from different Ammonium Salts through NEXAFS and XPS

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Synchrotron based Near Edge X-ray Adsoption Fine Structure has been shown to provide invaluable insight into the surface functionality of hydrothermal carbons. This is due to NEXAFS being able to adequately distinguish functionalities that are commonly overlapped in XPS or FTIR spectra of hydrothermal carbons. For instance, C-OH and C-O-C furan groups are easily discernible, as well as pyrolic and pyridinic nitrogen functionalities in nitrogen doped hydrothermal carbon [1].

In this study, we have investigated the effects of different ammonium containing anions ($(NH_4)_2SO_4$, $(NH_4)_2HPO_4$, NH_4Cl, $(NH_4)_2Fe(SO_4)_2$) on the surface composition of hydrothermally produced carbons to easily modify nitrogen functionality. To examine the benefits of NEXAFS, carbon, oxygen and nitrogen XPS and NEXAFS spectra from the forementioned nitrogen doped hydrothermal carbons are compared. Additionally, different methods for the analysis of NEXAFS spectra and its applicability in understanding how hydrothermal carbons function in supercapacitors is also examined.

[1] Latham KG, Simone MI, Dose WM, Allen JA, Donne SW. Synchrotron based NEXAFS study on nitrogen doped hydrothermal carbon: Insights into surface functionalities and formation mechanisms. Carbon. 2017;114:566-78.

IMPROVING POROUS TEXTURE AND ELECTROCHEMICAL PERFORMANCE OF GREEN-ACTIVATED CARBON PREPARED THROUGH H_3PO_4-ASSISTED HYDROTHERMAL CARBONIZATION BY HEAT TREATMENT AT HIGH TEMPERATURES

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Supercapacitors are highly interesting electrochemical energy storage devices since they combine high power density with a long cycle life and stability. Activated carbons (ACs), are the best suited materials for filling the cost, performance and environmental impact requirements of such devices. Recently, hydrothermal carbonization method (HTC) of lignocellulosic precursors has been proposed for the production of biochars that could be part of a new pathway for ACs production. The most limiting factor hindering the effective exploitation of HTC carbons is their low surface area and porosity. In order to introduce porosity in them, post-activation methods are required.

In this work, H_3PO_4-assisted HTC using two biomasses as the raw materials is proposed for the production of low-cost ACs. Following this procedure, ACs with a well-developed porosity and surface areas above 1500 $m^2\ g^{-1}$ have been obtained by hydrothermal processing of the biomasses in the presence of H_3PO_4 followed by thermal treatment in an inert atmosphere at different temperatures. Interestingly, an increase in the carbonization temperature improves the development of porosity and the specific surface area because the polyphosphates produced during the thermal treatment serve as scaffolds of the porous structure and impede its collapse. In addition, it has been found that the electrochemical performance of the electrodes is greatly improved when the carbonization temperature is raised up, while the preparation yield is still higher than that achieved following conventional ACs production routes. These are promising results that can green the production and lower the costs of carbon electrodes for energy applications.

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MATERIALS RECOVERY FROM A COMPLEX MIXTURE OF PHARMACEUTICAL WASTES VIA HYDROTHERMAL CARBONIZATION

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Every year allover the world, tons of unwanted pharmaceuticals are either incinerated, pyrolysed or dumped into landfills as toxic or hazardous waste.

Herein, we report for the first time, results from laboratory-scale application of hydrothermal carbonization of a complex pharmaceutical waste mixture. For this study, a simulant feedstock of 14 distinct non-prescription and 10 prescription drugs in the form of tablets and capsules were blended to form a homogenous mixture. To understand the impact of HTC on such wastes, aliquots of 20 g of the simulant waste plus 20 g of deionized water were carbonized for 24 hours in batch experiments at temperatures of 180, 230 and 275 ^{o}C, respectively. Resultant materials were characterized by Fourier Transform Infrared (FT-IR) spectroscopy and X-ray powder diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy-dispersive x-ray Spectroscopy (EDX) to determine the corresponding physicochemical properties.

The FT-IR spectra did identify a correlation between the appearance and disappearance of multiple functional groups per carbonization temperature. The XRD pattern did show the formation of identical crystalline phases of calcite ($CaCO_3$) and chesterite ($((Mg,Fe)_{17}Si_{20}O_{54}(OH)_6)$) materials irrespective of the carbonization temperature.

With these results, we have provided some evidence that hydrothermal carbonation could serve as a sustainable alternative to the incineration, pyrolysis and landfilling of pharmaceutical waste. This approach could also lead to the recovery of useful carbonaceous and/or other derivative materials. It is evident that the exploration of HTC to recover, design and synthesize materials of interest from pharmaceutical wastes is worth pursuing.

Hydrothermal Carbonisation of Organic Fraction – Municipal Solid Waste

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Biowaste valorization through HTC process represents a valid solution for the recovery of this type of waste streams, while generating a solid fraction that can be used both for energy and for the generation of new bioproducts and soil ammelioration. HTC process allows a carbon recovery that forms the basis for other applications of the hydrochar in the bioeconomy. The biowaste is highly humid and and heterogeneous and therefore is not storable and difficult to use in its original state. Its natural decomposition or fermentation generates CO2 and CH4 emissions into the atmosphere. The high content of plastics is a disadvantage for the composting process, but for the HTC process neither moisture nor plastics (depending on the amount and its degradation in the process), are a disadvantage enabling the biowaste treatment.

As a pretreatment the biowaste is passed through a trommel to remove pieces larger than 4cm. It would also be convenient to install a metal separator to avoid large metal parts reaching the process. Another convenient pretreatment would be the separation of stones and other hard materials that can cause abrasion and equipment degradation.

By means of posttreatment, small pieces fo glass, stones, metals and other inerts that have passed through the process, are separated. The final ash content is around 12% according to the test, so that hydrochar is suitable for combustion in industrial boilers, based on tests carried out by Ingelia. Industrial boilers usually have ash extraction facilities and particle separation cyclones. Recent combustion tests with this type of biofuel have been carried out in industrial boilers with satisfactory results in terms of emissions, without slag formation and with high performance and combustion stability. This application allows the substitution of fossil fuels and the reduction of transport of residues, however, other applications for the use of hydrochar, such as gasification and manufacture of bioproducts, absorbents, soil ammenders.

The organic content of the excess liquid phase can be easily valuated as biogas by anaerobic digestion, before being discharged. In case of heavy metals in the residues, they remain mainly in the ashes of the solid fraction. The option of recovering fertilizers from process water, especially potassium and nitrogen, can also be studied. Phosphorus remains mainly in the ashes of the hydrochar.

A key advantage of the application of the HTC process is the significant decrease in odors and the amount of air to be treated. Once the biomass has entered in the pumping system, the emissions are minimal and easy to manage. The separation of inerts in the post-treatment is done in liquid phase. Only the thermal drying implies an air flow that requires a particle removal treatment.

The economical feasibility of the HTC process with organic fraction is obtained by a combination between the biowaste gate fee and the sale of the solid bioproduct obtained.

Industrial Scale HTC Plant for Sewage Sludge Treatment in Jining/China and Phosphate Recovery by TerraNova® Ultra HTC Process

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In the City of Jining/China 14.000 tons of dewatered sewage sludge are annually treated by the TerraNova® Ultra HTC technology to generate a solid fuel for energy production. The attractive economics of such application are based on the considerable mass reduction due to the loss of dry matter (DM) during HTC and mechanical dewatering to 70% DM after the HTC treatment. The TerraNova® Ultra Technology, the energy- and mass-balance as well as typical project economics for an installation in Europe are presented.

Furthermore, TerraNova® Ultra offers the recovery of Phosphorous from sewage sludge. By adjusting the pH level during the HTC process Phosphorous is leached into the liquid phase and extracted through the filtrate path during dewatering. By addition of CSH minerals to the filtrate >80% of the Phosphorous is recovered as fertilizer product. The moderate use of reagents and the one-step process allow for low specific cost. The process and the fertilizer specifications are presented.

COMMERCIAL-SCALE DEMONSTRATION OF HIGH QUALITY SOLID FUEL PRODUCTION FROM BIOMASS AND WASTES EMPLOYING HTC

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Pre-treatment of wastes requires crushing, drying and deodorizing, which are normally different processes. But we have developed innovative hydrothermal carbonization technology (HTC) which can perform these three pre-treatment functions in one process utilizing high pressure saturated steam. We have been developing this technology for 15 years, and successfully commercialized this technology for the treatment of hospital wastes (Japan), sewage sludge (China) and municipal solid wastes (Indonesia). Also we are planning to commercialize this technology for agricultural residue treatment focusing on the empty fruit bunch (palm oil extraction residue). These feedstocks are fed into the high pressure reactor, and then, 200-220℃, 2-2.5MPa saturated steam is supplied into the reactor for about 30 minutes and the blades installed inside the reactor rotates to mix the feedstocks and steam for about 10 minutes. Then the product is discharged after extracting steam. The product is powder-like substance and the moisture content is almost the same as the raw material, but is easily dried by natural drying. The inert material such as metal, glass and stones can be easily sieved out after drying. There is almost no bad smell in the solid products, and the products can be used as solid fuels which can be easily mixed with coal for power generation or cement production. Only 10-15% of the product is enough for steam production in a boiler. Up to 100tons/day commercial-scale operational experience of this technology will be presented.

VALORIZATION OF OLIVE OIL RESIDUES BY HYDROTHERMAL CARBONIZATION

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The energetic valorisation of solid residues from olive oil production is a method to contribute to the management of this waste and also to improve the economic and agronomical benefits in this sector in Mediterranean Europe and Africa. Depending on the extraction process, olive oil production residues have moisture content up to 70%. In this work, we investigate the feasibility of hydrothermal carbonization (HTC) process to this waste material to obtain a stable carbonaceous solid lignite-like material called "hydrochar". Compared to previous work, the originality of the present one is to focus on the total residue of the olive-oil production process and not only on olive-stone.

The hydrochar is an energy dense product that can potentially be used as a substitute for fossil fuels. We have conducted HTC experiments at temperatures ranging from 180 to 250°C using biomass to water weight ratios between 1:10 and 1:2. The influence of treatment duration on the mass and energy yields is also investigated. Proximate and ultimate analyses of the raw material and the hydrochars, higher heating value (HHV) determination by calorimetry, TGA/DTG and FTIR analyses have also been performed to analyse the results.

The results show that higher HTC temperatures and longer treatment durations decrease the hydrochar yields because of increased gasification and aqueous carbon solubilisation. The obtained hydrochar is obvioulsly more carbonaceous than the untreated material (61.2-67.8% vs. 53.5%). It is also found that HTC treatment increased by 23% the HHV of hydrochar compared to raw olive-oil waste, under optimal conditions. Based on solid yield and densification ratio we demonstrate that a 30 min HTC treatment at 215°C (with biomass to water weight ratio of 1:6) can be an attractive alternative and energy efficient treatment of olive-oil waste to produce hydrochars with thermal characteristics close to lignite-like fossil fuels.

PROBING THE REACTION MECHANISMS OF HYDROTHERMAL CARBONIZATION THROUGH MOLECULAR DYNAMICS SIMULATIONS

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Hydrothermal carbonization (HTC) reaction mechanisms postulated in the literature are from well-established dry pyrolysis processes. These mechanisms include hydrolysis, dehydration, decarboxylation, aromatization, and recondensation. In situ experimental observation of these mechanisms is difficult because of the high temperatures and pressures associated with the HTC process. This study seeks to elucidate and verify reaction mechanisms during HTC through molecular dynamics (MD) simulations. Constant pressure MD simulations with conventional forcefields at 13.8 MPa and 523 K showed an average density of 854 kg/m^3 for a 20% glucose feedstock. Spatial and temporal variations in the density observed during a 50 ns production run in a 9x10^5 nm^3 domain showed densities as high as 1340 kg/m^3 with an 86% glucose concentration. The propensity of glucose to form molecular clusters is conducive to reactions that ultimately lead to carbonization. Accelerated ab initio MD and MD simulations with reactive forcefields of a 10 molecule glucose cluster with and without associated waters showed the formation of low molecular weight products such as H_2, H_2O, CO_2, COH, CH_3COOH, and HCOOH. This is consistent with experimental observations of gas and process water products. Product distributions and reaction pathways identified through the MD trajectories show direct evidence of initial dehydration followed by decarboxylation. This is also consistent with reports in the literature showing van Krevelen diagrams with similar evolution of solids characteristics. Pentagonal ring structures were also observed, as well as long chain carbon structures with oxygen to carbon ratios lower than the initial feedstock.

LIFE CYCLE ASSESSMENT OF HYDROTHERMAL CARBONIZATION AND OTHER MANAGEMENT TECHNIQUES APPROACHES: CASE STUDY OF OLIVE MILL WASTE

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Olive mill waste (OMW) is currently managed through technologies that pose several operational challenges due to its high polyphenols and water content. Hydrothermal carbonization (HTC) is a promising technology that is capable of overcoming those limitations, being also expected to be more energy beneficial and, therefore, more environmental friendly.

The goal of this study is to perform a life cycle analysis (LCA) to compare the environmental implications of HTC coupled with subsequent energy production with those associated with current biological and thermal treatment technologies, including anaerobic digestion, composting and direct incineration. LCA modelling was performed using the EASETECH software. Inventory data were either calculated from experimental results or collected from previously published data sources and/or Ecoinvent databases.

Results indicate that HTC coupled with energy production results in net environmental benefits and highlighted that the energy offsets derived from electricity production are critical to achieving these savings. However, HTC-liquor discharge is the component that most contribute to create environmental impacts. In comparison with current technologies, scenario using HTC is more environmental advantageous than biological treatments and equal or slightly more beneficial than direct incineration when the electricity recovery efficiency (η_e) is greater than 30%. However, the energy lost during HTC process (35-45%) leads to less environmental benefits than direct incineration when the η_e is lower than 30%. Accordingly, it is recommended that future research efforts focus on methods to improve the energetic retention efficiencies of the hydrochar and the development of environmentally beneficial HTC process water treatment approaches.

HYDROTHERMAL CARBONIZATION OF DIGESTATE – PROCESS INTEGRATION IN BIOGAS PLANTS

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Suitable business cases for the use of hydrothermal carbonization (HTC) to produce energy carriers need to be set up in the area of waste management because the current market value of the obtained product is low. One suitable source may be digestate which is a by-product of anaerobic digestion to produce biogas. It is a valuable fertilizer but can only be applied locally to avoid high transportation cost. Especially for larger biogas production units, digestate may represent a waste stream if the fertilizer cannot be applied locally in the required quantity. There are already some existing results that have shown the feasibility to apply HTC for the conversion of digestate. But little has been studied on the integration of HTC with an existing plant for anaerobic digestion despite the fact that there are important open questions that require further attention, e.g. internal reuse of HTC process water to yield additional biogas, heat integration with on-site combined heat and power units, fate of relevant nutrients along the conversion chain, and need for digestate dewatering. This study focuses on the energy part of these issues and investigates the integration of HTC in a representative plant for anaerobic digestion. The data basis is supplied by experiments conducted with digestate obtained from such an installation to supply the required mass balances and properties of the products. The energetic efficiency of the conversion chain is evaluated with respect to heat integration, dewatering of digestate, and the biogas potential in the HTC process water.

Environmental and economic assessment of different hydrothermal carbonization concepts producing coal from sewage sludge for energetic and agricultural use

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The CARBOWERT project aims at contributing to resource and climate protection by developing innovative and sustainable concepts of hydrothermal carbonization (HTC) of municipal sewage sludge producing HTC coal. Within CARBOWERT, two applications have been investigated in detail. Firstly, HTC coal can be used in the energy sector where it contributes to the substitution of electricity and heat based on fossil fuels. Secondly, HTC coal can be applied in agricultural systems potentially leading to improved soil fertility and increased yields.

The different HTC concepts including both applications are assessed and compared to conventional agricultural and energy production systems by means of life cycle assessment (LCA) and economic assessment. The scientific innovation is to compare two completely different applications of HTC coal and to solve the methodical challenges behind. The assessments are based on mass and energy balances considering actual data from the project consortium including agricultural field experiments.

After the environmental and economic assessments of the HTC concepts including the different applications of the HTC coal are conducted, the concept with the highest greenhouse gas (GHG) savings and the concept with the minimum costs compared to the conventional systems are identified. Furthermore, optimisation potentials for reducing GHG emissions and costs are shown. Finally, the GHG mitigation costs are calculated to indicate the economic efficiency of the concepts avoiding GHG emissions. This is done in order to increase the contribution of the concepts to climate protection and to increase their chances for an implementation in the market.

SOME STEPS IN MODELLING THE HTC PROCESS OF BIOMASS. KINETICS OF THE SOLID PHASE

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The numerous mechanisms and phenomena taking place during hydrothermal carbonization (HTC) are complex, and make really difficult the analysis of the process. Despite the bibliography provides some studies aimed to analyse the process, the most of them were carried out considering temperature as a constant parameter, without taking into account the initial heating period, and considering the raw matter as pure substances. Moreover, these models, to the best of the authors known do not consider important reaction features such as the reactor geometry or materials, which definitely affect heat transfer processes and in consequence condition the actual reaction conditions.

This work joined both experimental and theoretical studies, with the aim of providing insight in the field of HTC modelling and the comprehensive knowledge on the processes taking place. Kinetics of several biomasses hydrothermal carbonization was investigated over different reaction times and temperatures, as a function of their composition on hemicellulose, cellulose and lignin, developing a first-order reaction model by finite elements, where chemical and heat transfers processes were connected. This allows us to considerer the reaction temperature as a function of time, T(t), in the kinetic equations. The output parameter from the model was the solid yield (SY). It is interesting to remark that SY was found to be correlated with several hydrochar characteristics such as high-heating value, H/C, and O/C, allowing the chemical composition and energy densification to be predicted.

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Impact of Bentonite clay on *in situ* upgrading of hydrothermal carbonization and pyrolysis biofuels and biochars for renewable fuel and sustainable material production

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The future success of the integrated biorefinery for carbonaceous waste management depends on a number of factors, including available biomass and valorization of waste, potential for upgrading and transforming bio-products, and identification of value-added products, among other factors. In this work, we determine the feasibility of simultaneously upgrading biofuels from hydrothermal carbonization and pyrolysis, while co-producing heterogeneous adsorbents for environmental applications. Avocado pits were used as a raw biomass source, to which 20 wt% of bentonite clay was added without additional pretreatment. The raw and impregnated materials were hydrothermally carbonized at 200°C for 1 hour using 15 grams of sample and 100 mL of water in a 150 mL HTC reactor. To compare the hydrochars to pyrolysis biochars, the raw and impregnated samples were pyrolyzed in a fixed bed reactor at 600°C for 1 hour under nitrogen. The BET surface area of the untreated hydrochar was less 15 m^2/g, increasing to 60 m^2/g for the impregnated sample. Likewise, the biochar obtained from pyrolysis had a surface area of 35 m^2/g, which increased to over 160 m^2/g for the heterogeneous sample. The bentonite clay treated samples had markedly higher adsorption capacities and adsorption rates for methylene blue, a model organic compound. Moreover, though the hybrid hydrochars show lower surface areas than their pyrolyzed counterparts, their adsorption capacities are surprisingly higher. Extracted organics from the raw and impregnated hydrothermally carbonized show similar compositions, however the pyrolyzed bio-oils are higher in 5-hydroxymethyl furfural and lower in polycyclic aromatic hydrocarbons.

AGRO-WASTE TO SOLID BIOFUEL TRHOUGHT HTC: THE ROLE OF PROCESS VARIABLES ON SECONDARY CHAR FORMATION AND HYDROCHAR ENERGY PROPERTIES

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Several research studies have appeared recently where HTC is used to upgrade fuels from agro-industrial wastes. Since the interest in HTC increased, scientists have focused on the influence of process parameters on mass yields and energy properties of hydrochars.

In the present work, we evaluate the influence of HTC reaction temperature, reaction time, and solid load on hydrochars obtained from three agro-industrial wastes: olive tree trimmings, olive pulp, and *Opuntia ficus-indica* cladodes.

The following ranges of the HTC process variables were tested: reaction temperature: 120-250 °C; reaction time: 0.5-3 h; dry biomass to water ratio (by weight) B/W: 0.07-0-30. Hydrochars were characterized in terms of mass yield, ultimate and proximate analyses, HHV, thermal stability, and morphological features (SEM analysis coupled with EDS microanalysis).

In the reported set of experiments, solid load proved to be a crucial parameter in determining the energy properties of hydrochars. The lower B/W, the lower was the degree of carbonisation (in terms of total carbon and fixed carbon content), and hence the energy properties of hydrochars. Temperature and solid load proved to be crucial in promoting "secondary char" (or "coke") formation, which was found in large amount only at high solid load and reaction temperature. Secondary char showed a sphere-like structure formed by overlapping layers. EDS microanalysis showed that secondary char is characterised by a significantly higher carbon content than parent "primary char", thus confirming its contribution towards enhancing the energy properties of hydrochars.

AGGREGATING LITERATURE-REPORTED CARBONIZATION DATA: INVESTIGATING THE ROLE OF FEEDSTOCK PROPERTIES ON CARBONIZATION PRODUCTS

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The number of published papers reporting on various aspects of HTC has increased significantly over the past ten years. A survey of this existing HTC-related literature was conducted. Process related data (e.g., reaction time, reaction temperature, solids concentration) and experimentally collected carbonization product information from each study were tabulated. A total of 415 papers associated with hydrothermal carbonization were collected, resulting in a total of 1,664 data points. The most commonly reported carbonization product parameter was hydrochar yield. The recovered solids carbon content was the second most reported carbonization product. Process related parameters were also reported, with the most common being reaction time and temperature. The least reported process parameters were heating rate and heating time. All collected data was used to build linear and non-linear models (e.g., regression tree, random forest). Critical feedstock properties and carbonization process conditions associated with each model were identified using Sobol indices and one-at-a-time sensitivity analysis. Results from these analyses indicate that both linear and non-linear models fit the data well. Sobol indices based on linear models indicate that hydrochar yield is highly sensitive to feedstock polarity and oxygen content. Sobol indices based on non-linear models suggest hydrochar yield is sensitive to individual and/or parameter interactions associated with temperature, initial solids content, and feedstock polarity, ash, volatile matter, hydrogen, and oxygen contents. The most influential range of each parameter on hydrochar yield was also identified using one-at-a-time sensitivity analysis.

Hydrothermal carbonization of sewage sludge for soil amelioration: Key-results from the joint research project CARBOWERT

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Significant amounts of carbon and plant nutrient rich sewage sludge are waiting for sustainable treatment and recycling options. These materials can be included in strategies that rely upon the biochar concept.

The joint research project CARBOWERT aims at the development of strategies for the hydrothermal carbonization (HTC) of municipal sewage sludge and the agricultural reuse of HTC sewchars. Based on material, energetic and economic balances, HTC systems are analysed with respect to their contribution to climate protection and agricultural productivity.

Within HTC based sewchar systems, the conservation or transfer of nutrient elements into plant available speciation is of major importance. To study this aspect sewchars were produced in a pilot plant under different temperature (170–210 °C) and time (1–8 h) regimes. The effects (i) on the overall mass balances and elemental distribution into core and adsorbed sewchar fractions, process waters and HTC gases, (ii) on the chemical speciation of phosphorus and heavy metals (HM) and (iii) on plant yields during a three-year field trial will be presented.

Overall, the results show that phosphorus and HM are primarily accumulated in the sewchars. Intensifying the HTC process conditions increases the share of sparingly soluble phosphorus and HM fractions. The field trial reveals that sewchars applied in amounts even fivefold higher than allowed by the German Ordinance for the agricultural reuse of sewage sludge do not inhibit plant growth. Positive effects on biomass production are dominant during the first year after application and are based mainly on their fertilization effects.

HYDROTHERMAL CARBONIZATION OF ANIMAL MANURES AND SOIL APPLICATION OF SWINE MANURE-BASED HYDROCHARS

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The increase in concentrated animal feeding operations (CAFOs) calls for alternative manure management options with minimal environmental impacts. Alternatives to direct manure application are composting and thermochemical conversion which can destroy pathogens and improve handling and storage. The effect of four forms of swine manure-based soil amendments (raw, compost, hydrochar, and pyrochar) on soil fertility and leachate water quality characteristics of a sandy soil were investigated in soil incubation experiments. The effects of various hydrothermal carbonization (HTC) process conditions on hydrochar yields and properties were studied along with the fate of carbon and nitrogen. All four amendments significantly increased soil carbon, cation exchange capacity and available nutrient contents of the soil. However, hydrochar amended soil leached lower amounts of N, P, and K compared to the other amendments including the control. On the other hand, pyrochar amended soil leached higher concentrations of P and K. Subsequent tests on the hydrochar for K and N adsorption isotherms and surface analysis via XPS suggested that these nutrients were not sorbed directly to the hydrochar surface. Although it is still not clear how these nutrients were retained in the soil amended with hydrochar, it suggests a potential for hydrochar as an alternative manure management option as the hydrochar can be soil applied while minimizing potential environmental issues from the leaching of high nutrient concentrations to water bodies.

Designing the HTC-process and hydrochar characteristics to match the demands of the application: improve agricultural nutrient use efficiency

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In order to reverse the unsustainable movement of nutrients from our soils to the atmosphere or aquatic environments, current practices in agriculture must be redesigned to recycle nutrients. This presentation will discuss the potential for intervention in the nutrient cycle via the hydrothermal carbonization process. Potential points for intervention are 1) at the farm level, redirecting the nutrients flows from animal and plant production processes back to the soil using the HTC-process to treat agricultural residues, and 2) at the field level, using the solid product, hydrochar, to influence nutrient movement in soils.

At the farm level, an evaluation of literature and own results to determine how process conditions influence the partitioning of nutrients between product phases revealed there is still much to be learned. Similarly, our recent field trials in Germany and Malaysia have shown that char addition to soil can have significant effects on soil nitrogen use efficiency, but many questions still remain open. Complex interactions between microorganisms, soil components and char induce changes in nitrogen flows. The recent studies showed different mechanisms are most likely at work in soils in temperate zones and the tropics. To lay the foundation, overviews will be given on the mass flows and mechanisms involved in interventions via the HTC-process as well as through the application of char as a soil improver. Both aspects and their interlinking will be discussed to highlight how further research on product characteristics and process operation need to be matched.

Poster Presentations

HYDROTHERMAL CARBONIZATION A PROMISING ALTERNATIVE FOR SLUDGE TREATMENT WITHIN THE PULP AND PAPER INDUSTRY

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Sludge treatment and disposal represents a significant challenge for the pulp and paper industry. In Sweden alone the industry generates ca. 550,000 dry tonnes of sludge residues every year, 75% of which are incinerated in the solid fuel or recovery boilers at the mills. However, current means of sludge dewatering can only reach a sludge solids content of 10-50%, which decreases energy recovery and creates capacity problems at the mills. In addition, current trends in European waste regulation are increasingly hindering the deposition of organic material and the difficulty in acquiring new sites for waste disposal.

Hydrothermal carbonization shows promise for sludge treatment within the pulp and paper industry. Hydrothermal processes are robust and thus insensitive towards potential shutdowns, fluctuations or biological disruptors. Biological sludge residues can be decomposed and sterilized in a matter hours, producing solid fuels that are easier to dry and can potentially be used as auxiliary fuels in existing boilers. The pulp and paper industry also offers good opportunities for hydrothermal carbonization. The steam required for industrial hydrothermal processes is readily available and the decomposed solids can potentially be treated on-site at the wastewater treatment plants of the mills. This contribution provides an overview of our research efforts within hydrothermal carbonization of pulp and paper industry sludge residues for solid fuel applications and identifies boundary conditions for future implementation.

Effect of thermal biochar and hydrothermal biochar application as soil amendments in tomato cultivation

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Recently, both thermal biochars and hydrothermal biochars (HTC) have been extensively studied as soil amendments in schemes for the improvement of soil fertility for plant growth and for soil restoration. Thermal biochar or biochar, produced through incomplete burning in partial or total absence of oxygen, enhances nutrient retention due to its high cation exchange capacity (CEC) and high surface area. The application of biochars to the soil have been shown to increase productivity, crop yield, soil microbial biomass, and reduction in nutrient leaching. Hydrothermal biochars (HTC) are the product of wet hydrothermal carbonization, and are being increasingly discussed as an alternative or an addition to improve chemical and physical properties for plant growth. This study aims to assess the effects of thermal biochar and HTC application to tomato growing media as soil amendments. In potting experiments at the greenhouse, nutrient leaching and plant growth were observed over eight weeks where thermal biochar and HTC had been added to the potting soil in the rate of 2.5%, 5%, and a combination of 2.5% each. The measured leachate parameters were nitrate, total Kjeldahl nitrogen (TKN), soluble reactive phosphorus (SRP), and total phosphorus (TP) from the randomized four replication. .We found a significantly higher leaching reduction from HTC treated pots, and even more effective when used in combination with thermal biochar. Plant growth and biomass of tomato by the effect of char type will be presented.

HTC Filtrates: Potential Use as Fertilizer Amendments

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Hydrothermal carbonization (HTC) produces a large quantity of residual liquid or HTC filtrate. Considerable research has been focused on the solid product (hydrochar). However, the liquid fraction (filtrate), which is the larger mass fraction, must be valorized to improve HTC's economics. Because HTC filtrates are enriched with plant nutrients it has the potential to provide a renewable source of nutrients for crop growth. However, some studies have observed suppression in germination and plant growth following application. Herein, we evaluated HTC filtrates derived from animal manures and a slurry digestate (corn fermentation by-product from ethanol production). These filtrates were added to 4 different soil types and compared to a null control (no fertilizer or amendments) for impact on corn growth and soil nutrient properties. Compared to the control there was significant increase in plant height (1.66 times) across all filtrates and soils when applied at low application rates (0.25 mL/100 g soil). The greatest improvement in plant performance was for the sandy soil (2x above ground biomass). These results highlight the importance of proper application rates to avoid the negative consequences of filtrate soil application.

PRODUCTION OF BIO-COAL, BIO-METHANE AND FERTILIZER FROM SEAWEED VIA HYDROTHERMAL CARBONISATION

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Macroalgae has emerged as a potential future source of feedstock for the production of chemicals and biofuels. The main drawback of macroalgae in terms of a biofuel feedstock is its low heating value (HHV), high halogen content, high ash content and high slagging and fouling propensity. In this investigation, three species of kelps; (i) *Laminaria digitata* (ii) *Laminaria hyperborea* and (iii) *Alaria esculenta* have been processed by HTC at 200 °C and 250 °C. The yields and properties of the resulting hydrochars including their HHV, CHNS, mineral content and ash fusibility properties have been determined and compared to the starting material. Significant improvement in fuel quality is observed resulting in an increase in energy density from 10 MJ/kg to typically 25 MJ/kg, which is comparable to that of a low rank coal. The results indicate significant demineralisation of the fuel, in particular a significant removal of alkali salts and chlorine. This results in improved combustion properties due to a reduction in the slagging and fouling properties of the fuel. Analysis of the HTC water phase indicates the presence of high levels of soluble organic carbon consisting of sugars and organic acids, and high levels of potassium, magnesium and phosphorous. The potential for production of bio-methane and recovery of nutrients following anaerobic treatment of the water phase is assessed. A prediction of the bio-methane yields for the different seaweeds has been calculated. Processing of biomass collected throughout the growth season indicates the influence of seasonal variation on energy and nutrient recovery.

FATE OF INORGANIC MATERIAL DURING HYDROTHERMAL CARBONISATION OF BIOMASS: INFLUENCE OF FEEDSTOCK ON COMBUSTION

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A range of biomass have been processed by HTC at 200 °C and 250 °C, with feedstocks including food waste, secondary sewage sludge, AD press cake, microalgae, macroalgae, fibre derived from municipal derived wastes and three lignocellulosic biomasses. The yields and properties of the resulting hydrochars including their HHV, CHNS, mineral content and ash fusibility properties have been determined and compared with their starting biomass. Typical char yields for lingocellulosic material range between 58-70 wt% at 200 °C and reduce to 40-46 wt% at 250 °C. The behaviour and mass balance is however very feedstock dependent and the higher lignin biomass produce higher yields of hydrochar. There is a significant upgrading of the energy density of the hydrochars with calculated HHV ranging from typically 24 MJkg^{-1} at 200 °C to 28-31 MJkg^{-1} at 250 °C for lignocellulosic material. The exception is for sewage sludge and AD press cake which result in a significant solubilisation of organic matter. A significant removal of alkali metals is observed and this in turn changes the ash chemistry. This change in ash chemistry has been shown to change the ash melting behaviour and the hemisphere temperatures (oxidizing conditions) were seen to increase substantially. A number of predictive slagging and fouling indices have been used to evaluate the influence of the ash chemistry on the fuel combustion behaviour and this combined with the ash fusion testing has shown that HTC reduces the potential fouling and slagging in some of the resulting hydochars if combusted.

HYDROTHERMAL CARBONIZATION OF MIXED FOOD WASTE FOR NUTRIENT RECOVERY AND REUSE

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Food waste represents a rather large and currently underutilized source of potentially available and reusable nutrients. Laboratory-scale experiments evaluating the hydrothermal carbonization of food wastes collected from restaurants located in Columbia, SC were conducted to understand how changes in feedstock composition (e.g., food waste with and without packaging materials) and carbonization process conditions (e.g., reaction time and temperature) influence primary and secondary nutrient fate. Results from this work indicate that at all evaluated reaction times and temperatures, the majority of nitrogen, calcium, and magnesium remain integrated within the solid-phase, while the majority of potassium and sodium reside in the liquid-phase. The fate of phosphorus is dependent on reaction times and temperatures, with solid-phase integration increasing with higher reaction temperature and longer time. A series of leaching experiments to determine potential solid-phase nutrient availability were also conducted. Results from the leaching experiments suggest that, at least in the short term, tightly bound nitrogen within the solid matrix is unlikely to be released, while almost all of the phosphorus present in the solids generated when carbonizing at 225 and 250 ^{o}C is released. At a reaction temperature of 275 ^{o}C, smaller fractions of the solid-phase total phosphorus are released as reaction times increase, likely due to increased solids incorporation. Using these data, it is estimated that up to 0.61% and 1.82% of nitrogen and phosphorus-based fertilizers, respectively, in the US can be replaced by nutrients integrated within hydrohcar generated from currently landfilled food wastes.

REDUCTION OF PATHOGENTS AND MICROBIALLY-DERIVED DNA FROM LIVESTOCK MORTALITY USING HYDROTHERMAL CARBONIZATION

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Livestock mortality from animal production facilities may pose a potential threat to public health and to surrounding environments with emissions of nutrients, malodour, and pathogens. A treatment method that can adequately eliminate infection potential from livestock mortality is critical for developing sustainable animal production systems. Hydrothermal carbonization (HTC), utilizing relatively low temperature and pressure, has the potential to treat livestock mortality by inactivating pathogens and antibiotic resistance genes (ARG) in an environmentally safe and economically effective manner. While several methods are utilized to treat livestock mortality, there remains a paucity of data on the elimination of microbially-derived DNA in these treatment practices. This DNA, most notably ARGs, if it survives treatment, can be reintroduced in agricultural environments where it could potentially be passed to pathogens, posing a risk to animal and human populations. This study evaluated the survivability of microbially-derived DNA in the treatment of livestock mortality by HTC. We examined three treatment temperatures (100 °C, 150 °C, and 200 °C) at autogenic pressures at three treatment times (30, 60, and 240 min). We examined the amplification of a plasmid-borne reporter gene carried by *Escherichia coli* DH10B introduced to both beef bone and tissue. Results indicate that while all three temperatures, at all treatment times, were suitable for complete pathogen kill, only temperatures of 150 °C and 200 °C were sufficient for eliminating microbial DNA. These results serve as the basis for future potential HTC treatment recommendations for livestock mortality when considering the elimination of pathogens and ARGs.

Incorporation of manganese oxides into HTC during the hydrothermal process

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The water splitting process is a key reaction in the field of energy research to store energy in form of hydrogen, whereupon not the hydrogen evolution reaction (HER), but the simultaneous occurring oxygen evolution reaction (OER) with its highly oxidizing conditions and overpotential is the main challenge. Due to its appearance in the oxygen evolving center of the photosystem II, manganese oxide is becoming the focus of attention as possible, cheap alternative for the currently used OER catalysts ruthenium and iridium oxide. In fact, manganese oxides exhibit the promising activity, but suffer from low conductivity. A possible method to overcome this issue is the combination of manganese oxides with a conductive support, e.g. carbon.

In the presented research, hydrothermal carbon (HTC) is used as carbon support for manganese oxides. Manganese oxides are incorporated into HTC during the hydrothermal process, in which a manganese oxide precursor is added to the precursor solution. This is not accomplishable without an additional nitrogen precursor like urea. Systematic investigations, how the final structural product properties like morphology and porosity as well as the elemental composition influence the electrochemical performance, are in the focus of our research.

Engineered Organo-Mineral Particles for long-term Carbon Sequestration in Soil

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When it comes to carbon capture and storage, many technologies are still expensive and not yet sophisticated. Biochar as well as hydrochar application on soils could be a cheap alternative but their long-term stability is still under debate. The approach of this work was to establish a stabilization mechanism that is naturally occurring in soils during hydrothermal carbonization (HTC): organo-mineral interactions between organic matter and clay minerals. Clay minerals are hydrous alumo-silicates that increase the stability of soil organic matter by adsorption and formation of organo-mineral associations. During HTC, the reduced dielectric constant of subcritical water could lead to higher coagulation of organo-clay particles. Additionally, mineral surfaces could influence the carbonization process giving rise to deeper conversion of intermediates.

Within this work it was determined how the addition of clay minerals and the variation of process conditions (temperature, time, pH) affected the properties of the hydrochars. Anaerobic digestate from biogas production was used as feedstock and different clay minerals (montimorillonite, goethite, illite and a mixed clay fraction separated from soil) were added before hydrothermal carbonization. Elemental ratios of H/C and O/C were used to describe the degree of carbonization. The stability of the different hydrochars was determined by the fixed matter content and thermogravimetric analysis. Additionally, a short-term incubation experiment (Respicond) was conducted to determine the bioavailability of the hydrochar carbon.

Hydrothermal carbonization of waste biomass: Process design, modeling, energy efficiency and cost analysis

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An industrial scale, 2.5 ton/h, continuous hydrothermal carbonisation (HTC) plant is designed and modelled on the basis of experimental data previously obtained for two organic residues: off-specification compost and grape marc. The HTC process layout with all the auxiliary equipment is reported. By means of an *ad hoc* developed software code (written in the programming language C#), the energy performances of the HTC plant proposed are evaluated, considering different HTC process conditions (reaction temperature T: 180, 220, 250 °C; reaction time ө: 1, 3, 8 h). The model accurately estimates the mass and energy demands at all equipment present in the path to transform raw biomass to dry pelletized hydrochar for sale. Thermal and electric energy consumption and plant energy efficiencies are estimated at the different process conditions. In the most favourable operating condition (T = 220 °C; ө =1 h; dry biomass to water ratio b/w = 0.19), the thermal energy and power consumption are equal to 1,170 kWh and 160 kWh per ton of hydrochar produced, respectively, and the corresponding plant efficiency is 78%. In addition, the techno-economical aspects of the HTC process are analysed in detail, considering both investment and production costs. The production cost and the break-even point of hydrochar pellets are determined to be 157 €/ton and 200 €/ton, respectively. Such values make the waste biomass hydrochar pellets competitive with wood pellets. The results are very promising for large-scale utilisation of hydrochar as a carbon neutral fuel.

High-energy biofuels production via hydrothermal carbonisation of wet waste biomasses and bioenergy crops

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The need of replacing fossil fuels with more environmentally friendly energy sources has boosted in recent years the search for alternative energy feedstock. Thermochemical conversion of wet, low valuable, residual biomasses (i.e. agricultural and agro-industrial residues, bioenergy crops that can be efficiently grown into semi-arid marginal lands, as well as the organic fraction of municipal solid waste) into high energy biofuels, can result in a circular-driven economy. Exploitation of such biomasses could lead to models for sustainable production. In this study, we report the influence of HTC operating conditions (temperature, residence time and dry mass solid to water ratio, b/w) on energy, thermal and morphology properties of four different feedstocks. The agricultural and agro-industrial residues: olive tree trimmings (OT) and olive mill pulp (OP) were carbonised at 120-250 °C, at fixed residence time of 0.5 h and b/w 0.25. The influence of the b/w (0.07-0.25) is examined for samples carbonised at 250 °C. The use of *opuntia ficus indica* as a bioenergy crop is also studied by HTC at 180-250 °C, 0.5-3 h and b/w 0.07-0.30. HTC of OFMSW is carried out at 120-260 °C, 3 h and b/w 0.15. The energy, thermal, chemical and morphology properties of raw materials and hydrochars were assessed by calorimetric, thermogravimetric, proximate and ultimate analyses, ATR-FTIR spectroscopy, SEM and EDS. Results show that both temperature and solid loads have a strong effect on energy and morphology features of hydrochars.

EMISSIONS ASSOCIATED WITH THE HYDROCHAR COMBUSTION: ANALYSIS OF VOLATILES AND PAHs COMPOUNDS

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When considering the use of hydrochar as a renewable fuel, the emissions associated with its combustion must be assessed to provide information regarding their toxicity.

The objectives of this work are: to assess the emissions associated with the combustion of hydrochar, wood, anthracite and blends; and to discuss the applicability of hydrochar as a fuel in domestic and/or industrial heating systems.

Combustion and pyrolysis experiments were carried out in a laboratory furnace (AOX). The exit of the furnace was coupled with a resin to retain the condensable compounds. Non-condensable compounds were collected and analyzed through GC-TCD/GC-FID. Condensable compounds in the resin were subsequently extracted and analyzed through GC-MS. Experiments were also carried out in a commercial domestic pellet stove, in which non condensable gases were continuously measure by using a portable gas meter. Accordingly to the US EPA, the sixteen more toxic PAHs compounds were assessed, as well as the major volatile compounds.

Results indicate that hydrochar leads to the highest PAHs formation when the combustion does not occur properly. Total Toxic Equivalency factor associated with hydrochar emissions was 270 vs. 170 and 70 of wood and anthracite). No significant differences are found when comparing the volatile compound emissions. It could be conclude that it is mandatory to ensure good combustion conditions to avoid the formation of toxic PAHs compounds when using the hydrochar as a renewable fuel, and/or is recommended to couple the combustion system with a suitable gas cleaning system to avoid their release to the environment.

Life cycle assessment of activated carbon versus biochar for mercury adsorption from water

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The main goal of this study is to compare the environmental impacts associated with the use of AC or biochar for mercury adsorption from water. Such information will be relevant to identify the "environmental weaknesses" through the process steps. This helps researchers to modify and optimize the process and furthermore helps decision makers, scientists, authorities, and industries to choose between different process/material alternatives.

Mercury is one of the most well-known heavy metal environmental pollutants because of its toxicity and its ability to bioaccumulate in the food chain. The LCA of the environmental impacts associated with the use of AC or biochar for the treatment of 1000 m^3 of water contaminated with 5 mg Hg^{2+} L^{-1} was evaluated. With the help of Umberto NXT software it was found that in most cases AC has a higher environmental impact than biochar, that can be linked to additional steps of activation causing emission of additional products to the environment.

Changing the source for biochar production in the Umberto model did not significantly influence the impact if the other parameters of the model remained the same. However, in real life, each of the source materials will cause emission of different pollutants or will require changes in operational conditions. That will reflect on the environmental impact of the whole process.

Changes in sorption capacity influence the impact of the model for both AC and biochar. This relationship presumably has an exponential character. Therefore, using of sorbents with high sorption capacity can significantly decrease the environmental impact of the process.

THE EFFECT OF HTC TEMPERATURE ON SURFACE PROPERTIES OF SLUDGE AND MANURE CHARS

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Waste based carbon materials could become cost-effective and environmentally feasible alternatives to conventional activated carbons that are commonly used as adsorbent materials in wastewater treatment. A wide variety of low-cost biochars have been increasingly studied during recent years and they have shown promising adsorption properties.

In this study, we have studied the effect of the HTC temperature and feedstock on surface characteristics in order to gain knowledge on how adsorbent surfaces may be altered by selection of these variables. Horse manure, digested sewage sludge, fibre sludge from paper mill and digested paper mill sludge were carbonized at three different temperatures, 180, 220 and 260 °C for 2 h, giving twelve carbon materials. Surface characteristics of these biochars were studied by X-ray photoelectron spectroscopy (XPS), attenuated total reflectance – Fourier transformation spectroscopy (ATR-FTIR) and N_2-adsorption.

XPS and FTIR analyses revealed that two lowest temperatures gave nearly identical products in case of fibre sludge and horse manure, while at the highest temperature they underwent most substantial change. The proportion of carbon increased while oxygen-containing functional groups and the yield dropped drastically at the highest temperature, which may be due to the breakdown of cellulose. Digested sludge chars were not as clearly influenced by the temperature, and the proportions of C, O and N were varying only slightly with the temperature. Specific surface areas were clearly highest for digested sludge chars and the highest surface areas in each temperature series were found at 220 °C.

VALORIZATION OF SEWAGE SLUDGE BY HYDROTHERMAL CARBONIZATION AND AIR-ACTIVATION

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The hydrothermal carbonization of dehydrated sewage sludge (DSS) was optimized by a central composite rotatable design to study the effect of carbonization temperature (140-220 ºC) and holding time (0.5-4 h) on yield, fixed carbon, ash, volatile matter (VM), heating heat value (HHV) and BET area. Yield and VM decrease as time and temperature increased, with values in the range of 35.3-62.3 % and 61.3-75.5 % (w/w), respectively. Also, the hydrochars showed ash, fixed carbon and HHV contents in the range 15-23 % and 8-16 % (w/w) and 19.1-22.3 MJ/kg, respectively. BET areas were relatively low and increased up to 24 m^2/g for the DSS carbonized at 220 ºC for 2.3 h. The liquid fraction from HTC revealed a fairly complex composition with the presence of several product as phenol, benzene, ketones and nitrogen compounds (pyrazines and pyrazole). Soluble COD, TOC and TN concentrations were within 10-81 g O_2/L, 35-51 g C/L and 1.6-2.7 g N/L, respectively. With the aim to obtain activated carbon for adsorption applications in liquid phase, the effect of air activation temperature on BET area development of hydrochars was study between 300-500 ºC for 2 h. BET area dropped sharply for temperatures higher than 325 ºC probably due to porous collapse. Finally, hydrochars were air activated at 325 ºC for 2 h, which allowed obtaining an activated carbon with a BET area 5-fold times higher for the hydrochar obtained at 220 ºC for 2.3 h and increasing 3-fold times the mesoporous contribution.

ACTIVATED CARBON FROM SEWAGE SLUDGE BY HYDROTHERMAL CARBONIZATION AND CHEMICAL ACTIVATION

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Different ways of treatment of sewage sludge (SS), such as pyrolysis, activation or gasification, are being investigated in the last two decades. As an alternative to these methods, hydrothermal carbonization (HTC) followed by chemical activation are proposed for the valorization of the SS, with the aim to achieve a carbonaceous material with high mesoporous area likely for adsorption applications in aqueous phase. HTC was performed in a pressure vessel (208ºC - 1 h) using dewatered SS at 85 % of moisture content. The solid fraction was recovered by centrifugation (3500 rpm - 1 h), dried at 105 °C for 24 h, grounded and sieved in the range from 0.1 to 0.25 mm. The hydrochar was activated with $FeCl_3$, $ZnCl_2$, KOH and K_2CO_3 at different temperatures (650, 750 and 850 ºC) for 1 h in a continuous flow of N_2 (30 NmL/min). The ratio of activating agent /dried SS used was of 1:1 wt.

HTC process allowed obtaining a mesoporous material with a BET area (21 m^2/g) 7-fold times higher than dried SS. All the activated materials developed high BET areas within 400 - 1030 m^2/g. Materials prepared with $FeCl_3$ showed the lowest values (around 410 m^2/g) in the range of temperature studied. It could not establish a relationship between the activating agent and the activation temperature according to the obtained BET areas in the resulting materials, reaching the following optimum values: 1030 m^2/g with $ZnCl_2$ at 650 ºC; 968 m^2/g with NaOH at 850 ºC; 987 m^2/g with K_2CO_3 at 750 ºC.

Catalyst Supported on Hydrothermal Carbons & their Derivatives

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Hydrothermal carbonisation (HTC) is a sustainable synthetic technique to produce nanostructured porous functional materials based on natural abundant precursors (*i.e.* biomass and associated derivatives)[1] in H_2O under autoclave conditions at relatively low temperatures (*e.g.* 180 °C) and autogenous pressures (< 10 bar)[2]. It was previously demonstrated the conversion of glucose in the presence of structure directing additives (*e.g.* egg protein[3], sodium borate[4]), which is generating the opportunity to control the material porosity in tandem with surface functionality.

The use of the protein in the synthesis also has the additional benefit of acting as a "nitrogen" doping source and the introduction of this heteroatom into the base "*carbonaceous*" material structure. The mild processing conditions of the HTC platform in turn allows the application of secondary thermal carbonisation step to enable further influence over carbon chemical structure and as such offers a basis to manipulate and optimise surface chemistry (*e.g.* C aromatisation / N condensation). With respect to catalysis, this is a very exciting concept as a variety of factors can be controlled (*e.g*. hydrophobicity, basicity, *etc*.), generating the opportunity to moderate and develop structure/activity relationships for a given catalytic conversion[5]. This poster will highlight the exciting potential of these tuneable materials in heterogeneous and solid catalyst design and development, offering potentially improved performance (*e.g*. cost and activity) in relation to the market state of the art comparison (*e.g*. Activated Carbon). As an example, HTC carbon supports produced via tailoring of both chemical functionality and porosity, importantly based on simple control vectors (*e.g*. carbonisation temperature) will be presented.

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Influence of hydrothermal pre-treatment on biofuel production from microalgae

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There is an increasing interest in the hydrothermal processing of microalgae for the production of high energy density biofuels, such as bio-coal and bio-crude. There are however, certain drawbacks to hydrothermal processing, which include problems with recovery of valuable nutrients, contamination of intermediates with inorganics, high amounts of phosphorous and nitrogen along with high levels of corrosion. Hydrothermal carbonisation as a means of pre-treatment has the ability to reduce these issues. Therefore the main aim of the research is to investigate the potential of hydrothermal carbonisation as a means of pre-treatment to improve the quality of products from hydrothermal processing of microalgae. The main objectives are to recover and recycle nutrients in the process waters and to understand the influence of nutrient removal on product quality and its impact on process operations such as grinding and pumping.

The process waters produced from the hydrothermal carbonisation of microalgae have been investigated. The potential for nutrient recovery and recycling has also been demonstrated. The methods of separation and recovery of the nutrients include physical and chemical separation along with in-situ and regenerative adsorption. Further work will investigate the use of the formulated process waters from sequential treatment, which contain soluble hydrocarbons and inorganic compounds, for the cultivation of microalgae in the recycled process waters.

This approach also has the potential for application to other high nutrient and high ash containing feedstocks such as macroalgae, sewage sludge, manure and other biomass materials.

Non-oxidizing thermal treatments of contaminated soils

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Contaminated soils from saw mills contain not only contaminants such as heavy metals, but some also have a high organic content, such as saw dust, bark and other organic materials. The high organic content makes this waste difficult to treat in the Swedish waste management system, since the organic content is too high for landfilling, and too low for incineration without support fuel. Therefore, this project aims at developing new methods for removing organic materials from these types of soils and other types of materials with similar organic content. Two different thermal treatments are being evaluated, one dry: pyrolysis, and one wet: hydrothermal carbonization. Initial results for pyrolysis show decreased mobility of most heavy metals, however, arsenic, molybdenum and antimony becomes more mobile after pyrolysis, likely due to the increase in pH. During pyrolysis the water in the soil have to be evaporated, which requires energy. Hydrothermal carbonization (HTC) is tested as an alternative. By being a wet method, no energy is required to evaporate water during treatment. Organic acids may form in the HTC process, which may influence mobilization of heavy metals differently compared to pyrolysis. In our ongoing work, biological, chemical and physical characterization assays are used to compare the methods and their suitability to treat these kinds of soils

HTC-plant :metabolon

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In the recent years HTC-characteristics of several biomass and model substances have been tested under different conditions, mostly in laboratories. However, experience in commercial scale is rare. Missing know-how in handling of educts and products and carbonisation in large scale constrains the implementation of HTC as a common technology. The “Bergischer Abfallwirtschaftsverband (BAV)”, a public waste management association and the Technische Hochschule Köln (TH-Köln) installed a steam carbonisation plant at the :metabolon research and competence centre in Lindlar. The aim of :metabolon is the demonstration of multiple processes for bio waste treatment in pilot plant scale. The HTC pilot plant is part of the :metabolon research and teaching program. This demonstration plan enables carbonisation of up to one cubic metre of biomass, with temperature up to 228 °C and pressure up to 30 bar. The plant is operated by TH Köln. The main aims are testing of several types of biomass and improvement of the technology and operation. The focus of investigation is on the specification of the produced coal and process water. A flexible paddle stirring system, high reaction temperatures and a novel steam injection system are outstanding features of this plant.

First results show a similar behavior to laboratory HTC experiments. As it was expected, the higher amount of masses leads to a longer batch process. Coals from dry educts show similar moisture contents than raw materials. Different biomasses from agriculture, waste industry and sewage sludge were carbonised under different conditions.

RESEARCH ACTIVITY ON HYDROTHERMAL PROCESSING OF AGRICULTURAL RESIDUES FOR BIOMATERIALS IN "WASTE AND BIOMASS CONVERSION LABORATORY – KASETSART UNIVERSITY, THAILAND"

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Waste and Biomass Conversion Laboratory (WBCL) focuses on conversion of waste and biomass materials into biofuels and biomaterials using subcritical water treatment technology. Thailand is abundant in biomass owing to its agro-industry based economics and currently, it aims to create sustainable bioeconomy. Thus, the production of biomaterials through sustainable processes became crucial. WBCL has been working on conversion of biomass such as empty fruit bunch (EFB), frond of palm, and trunk of palm into high value-added products. By utilizing low temperature hydrothermal liquefaction in range of 250-300 ˚C for 10 to 60 min with the pressure of 40-90 bar, phenolic-rich bio-oil, which could be used as a precursor to many useful materials, was obtained. Moreover, a relatively low temperature treatment, i.e. hydrothermal carbonization (HTC), of EFB has been studied in term of financial feasibility of the technology for commercialization in the near future. In Thailand, sugar industry has a major role in economic sector; therefore, WBCL has been started applying HTC at 180-240 ˚C for several holding time with subsequent steam activation to convert bagasse into activated carbon for decolourization process used within the sugar factory. Lastly, as microalgae is one of the promising biomass resources for production of biofuels and biomaterials, our laboratory has been working on process optimization of microalgae utilization. A two-stage extraction has been proposed as protein solution would be extracted by mechanical processes prior to a low temperature HTL (275-330 ˚C) and soxhlet extraction for bio-oil production. This would optimize value-chain of microalgae valorization.

Life Cycle Assessment (LCA) for HTC of sewage sludge

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For a sustainable development and the establishment of a circular economy for nutrients, hydrothermal carbonization of sewage sludge was investigated. Currently the environmental life cycle analyses hydrothermal carbonization of sewage sludge compared to those of general process chains of incineration and landfilling. With carbonization and application of hydrochar in agriculture, a sustainable nutrient recycling can be achieved, especially for phosphate. Different investigations including char incinerating, use as soil conditioner in agriculture and peat substitution in horticulture. Energy and material balances were observed for an economic assessment. Beside the monetary aspects of integrating an additional stage into wastewater treatment, concentration and accumulation of pollutants such as PCDD/PCDF, PCB and heavy metals were taken into account to quantify the environmental impacts and underline possible utilizations of hydrochar. The system boundary covers the production of the dewatered sewage sludge, production of the hydrochar, possible transportation, power and heat production and char application. LCA calculations were performed with the professional software tool GaBi based on lifecycle inventory (LCI) datasets from GaBi and ecoinvent (v3.3). Environmental impacts were analyzed by using the life cycle impact assessment (LCIA) after ReCiPe midpoint-methodology.

Integration of hydrothermal carbonisation in waste water treatment

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In recent years sewage sludge management has been considered one of the biggest concerns for the environment for its high content of pollutants. Hydrothermal Treatments are a good option for converting wet biomass such as sewage sludge into higher value products. The digestate following anaerobic treatment of sewage has high organic matter content despite initial conversion and is normally spread on land or composted, however this does not fully harness its properties. The digestate is therefore a potential feedstock for hydrothermal processing and this route may produce higher value products. In this study, the potential of hydrothermal processing as a novel alternative to treat the digestate has been be evaluated. The effect of temperatures is evaluated with respect to product yields, biomethane potential and solubilisation of organic carbon. Three different temperatures were evaluated, 160, 220 and 250°C at 30 minutes reaction time. The biochar yields obtained were 73.42% at 220°C, followed by 68.79% at 250 °C and 56.75% at 160°C treatment. The solubilisation of carbon was increased from 4.62% in the raw feedstock to 31.68%, 32.56% and 30.48% after thermal treatments of 160, 220 and 250°C respectively. The thermal treatment enhanced the methane production in all products after the thermal treatments up to 283% for the whole fraction (hydrochar+ processed water) and up to 302.9% for the processed waters alone. The Boyle's and Buswell's equation were used to compare the theoretical BMP yields with the experimental biomethane potential of the thermal products and indicated that the Boyle's equation had closer agreement to the experimental values.

Integration of Hydrothermal Carbonisation with Anaerobic Digestion; Opportunities for Valorisation of Digestate.

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Anaerobic digestion (AD) is an established technology in the UK for treatment of waste and opportunities exist for integration of AD with hydrothermal technology for enhanced biofuel production. Digestate, a by-product from AD, is typically disposed to land, however environmental legalisation limits these disposal options. Therefore, the research aim is to investigate the potential for valorisation of digestate by hydrothermal carbonisation (HTC) and subsequent integration with AD to treat process waters. The objectives are to understand the influence of feedstock compositions and process conditions on the product yields and properties of hydrochar and process water following HTC.

Feedstocks investigated include digestate from anaerobic digestion of agricultural waste, secondary sludge, residual municipal solid waste and vegetable, garden and fruit waste. The influence of AD feedstock and digestate composition on the chemical make-up of hydrochar and process water have been assessed. The potential for increased biogas yields from process water recirculation have been predicted and the prospective applications for the hydrochar as a fuel, adsorbent or soil additive are evaluated. Potential integration strategies to maximise energy recovery are proposed including co-processing of digestate with additional lignocellulosic wastes.

This integration approach delivers a promising method to convert digestate into a safer, higher quality product with multiple uses, while improving AD efficiency and operator revenue by increasing biogas yields. This approach also helps to meet renewable energy targets and creates significant economic gain to the bioenergy and bio-economy sector. Benefits to the environment are also made by mitigating fugitive methane emissions (by reducing disposal of digestate to land) and provides additional supply chains for solid fuel.

Insights into the origin of the catalytic activity of biomass-derived carbon

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The threat of climate change and ever-depleting natural resources are driving a move towards reduced use of fossil reserves and rare metals. The aims of the present work are to demonstrate that biochar, a by-product of biomass pyrolysis, can act as heterogeneous catalyst and to gain insights into the origins of this activity. The reactions investigated are important in a future, sustainable, chemical industry; namely (1) the reaction of glycerol and CO_2 to form to form glycerol carbonate (GlyC), a useful precursor for the formation of polymers and plastics; and (2) the synthesis of dimethoxymethane (DMM) from methanol (MeOH), as a precursor to dimethylcarbonate, a green solvent. Three biochars from different source materials have been extensively characterized by a variety of methods with several physiochemical aspects of the biochars being investigated, i.e. structural, surface chemistry and compositional factors. In addition to being of interest in their own right as catalysts, insights into the origin of their catalytic activity can lead to a greater understanding of beneficial carbon deposition on other heterogeneous catalysts and open up new classes of catalytic material.

The performances of the biochars in the two reactions varied; for instance whilst oil seed rape biochar (OSB) and rice husks biochar (RHB) showed no activity for the formation of DMM from MeOH, they were the most effective catalysts for the conversion of glycerol to GlyC. Similarly, soft wood biochar (SWB) and commercial activated charcoal (AC) were the most effective catalysts for DMM formation, but SWB was the least effective catalyst in the formation of GlyC. Extensive characterisation work has shown that the catalytic activity of the biochars is not simply correlated by BET surface area or CO2 adsorption capacity. Thermogravimetric analysis (TGA) and XPS analysis have shown differences in composition between the biochars; SWB contains almost no ash, whilst OSB and RHB have a much higher ash content. It is therefore possible that mineral content in the ash may be contributing to catalytic activity in the glycerol upgrading reaction - this will be tested by producing demineralised biochars from the same feedstocks and testing their subsequent catalytic activity. XPS analysis shows that SWB is composed of 90% C and 10% O, with no metals detected within the detection limit of the instrument. Comparison with AC suggests that the active sites for the conversion of methanol may therefore be carbonaceous in character.

This work has demonstrated that carbonaceous materials derived from biomass, including waste sources, can act as effective heterogeneous catalysts. A comparison of different biochars shows that different factors can impart activity for different processes. This presents a new class of catalytic material to open up new reaction routes, with both catalyst and reaction leading to improved sustainability in chemical processing. The insights gained are also applicable to the understanding of carbon deposits formed in situ on the surface of catalysts during reactions, and can hence be applied to broad range of catalytic systems.

BIOMASS-DERIVED LOW COST NEGATIVE ELECTRODES IN Na-ION BATTERIES

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Sodium-ion batteries (NiBs) are primary candidates for an alternative to lithium ion batteries (LiB) for large-scale and low cost electrical energy storage applications. NiBs have attracted a great interest as NiBs have similar chemistry to LiBs and additionally Na is cheaper and more abundant; therefore, they could be used a promising commercial product for rechargeable batteries. Optimization of negative electrodes is a key aspect for the development of NiBs and the absence of a suitable negative electrode material hinders their development. The optimisation here corresponds to the good stability and recyclability on charge/discharge tests along with its cost effective production. Carbon based materials are among the most promising anode materials that have been reported for use in NiBs. Here we report the synthesis of various hard carbon materials from biomass or biomasss derivatives including glucose and chitin by a hydrothermal method whereby we investigated the influence of the carbonisation temperature. Hard carbons produced from glucose showed the best performance with a specific capacity of ~ 90mAh/g when carbonised at 1300^{o}C. The samples also showed a good cycling performance with a capacity retention of 80% after 50 cycles. An initial columbic efficiency of 60% was reported. Additonally, the doping of nitrogen heteroatoms and porosity effect on the microstructure and electrochemical performance were further investigated. The promising results show the material's potential use as negatives electrodes in Na-ion batteries and are believed to be close to the level required for practical applications.

Oxygenophilic Ionic Liquids Promote Oxygen Reduction Reaction Catalysis in Nanocarbons

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Oxygen reduction reaction (ORR) is key reaction in fuel cell device where clean electricity can be generated. So far, the 'practical' catalysts known for the ORR are platinum-group metals. However, the use of scarce metals is a huge problem, hindering the commercialization of fuel cells.

Recently we have produced efficient Pt-free catalysts bases on nitrogen and iron-nitrogen doped carbons or the ORR reaction in PEMFCs operating with similar performance to Pt in both acid and alkaline media and we have also demonstrated their scalability and effectiveness in full anion exchange membrane fuel cells.

Here we want to present a revolutionary concept used to further improve fuel cell performance. This new concept is based on addition of ionic liquids to manipulate the catalyst-electrolyte-gas triple phase microenvironment where the ORR take place. The ionic liquid layers at nanocarbon surface forms a water-equilibrated secondary medium with a higher O2 solubility to promotes oxygen adsorption onto the catalytic active site, meanwhile the hydrophobic nature prevented water from building-up locally, and the protic character provided sufficient H+/H3O+/OH- conductivity.

We have demonstrated this concept on two types of Pt-free nanocarbon catalyst, and this modification strategy exhibits a remarkable improvement for ORR in both alkaline and acid electrolyte, in regards to the catalytic activity and long-term stability. This work offers a new direction for the improvement of nanocarbon-based electrocatalysts, and provides some fresh insights in the design principles to improve nanocarbon materials in different fields.

GRAPHENE QUANTUM DOTS SYNTHESIS FROM MOLECULAR PRECURSORS

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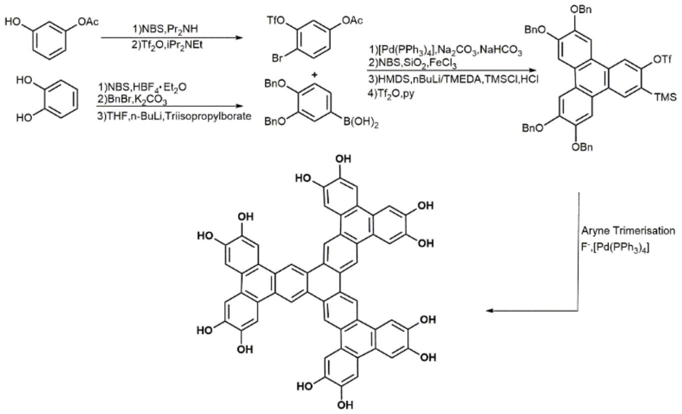
We would like to present a revolutionary new class of optical materials as an alternative to the traditional semiconductor quantum dots for the next generation of transparent coloured displays in flexible electronics. These materials are based on small graphic domains at nanoscale (2-4 nm) containing an aromatic core with sp^2 hybridised carbon atoms and potential for functionalisation around the perimeter with both sp^2 and sp^3 hybridised atoms using selected functional groups such as hydroxyl, amines or carboxylic acids.

Our new generation of graphene quantum materials are produced using bottom up chemical approaches. Arynes are perfect for our synthetic purposes because they enable the rapid generation of molecular complexity from simple aromatic building blocks in the controlled manner that we are looking for. Using aryne chemistry, two aryne precursors can be obtained from simple, low cost and readily available starting materials-catechol and resorcinol monoacetate. Followed by synthesis of polycyclic aromatic compounds with specific edge groups using trimerisation reaction (Scheme. 1).



Scheme. 1 Reaction scheme for the bottom up production of graphene quantum dots

This synthetic methodology allows us to tailor the size (number of aromatic rings) as well as introduce tailored functionality onto these new class of materials. Hence we are able to make clear correlations between their chemical structure and optical properties and tune their absorption and emission properties to cover a wide range of wavelengths. Absorption wavelengths vary from UV to visible while they emit from blue to red as well as exhibit up conversion properties. These new class of materials presents clear advantages to the existing technologies such as high stability under atmospheric conditions, resistance to photo bleaching, low cost and increased processability. They can be easily incorporated into various conductive transparent displays based on conductive polymers, metal oxides or other materials as well as formulated into inks and printed or deposited onto various substrates. Our poster will present few types of such materials along with their synthesis, characterisation and optical properties.