The Green Chemistry Centre of Excellence (GCCE) at the Department of Chemistry, University of York, is a world leading research centre with over 20 years experience in the area of green chemistry covering the development and implementation of green and sustainable chemical solutions and technologies into both commercial products and industrial processes.

The Centre has around 80 personnel including academic experts, specialist and support staff as well as postgraduate researchers. Modern research facilities include a range of specialist analytical instrumentation and specialist reactors based on clean technologies, which are available at demonstrator scale in the associated Biorenewables Development Centre (BDC).
RESEARCH

Renewable Materials: Utilising naturally abundant resources and in particular agricultural and food by-products, we have developed a range of materials which take full advantage of the chemical composition, rich functionality and structure in plant metabolites and other biomass.

Clean Synthesis and Platform Molecules: Our expertise in developing cleaner manufacturing technologies and processes makes the production of a range of chemicals possible in a manner which maximises efficiency and minimises waste.

Microwave Chemistry: We have been involved for a number of years in research on the effects of microwave radiation on chemical compounds. This has provided new insight and understanding on how microwaves can accelerate chemical reactions.

Alternative Solvents: We promote the use of new alternative solvents - supercritical/liquid CO₂, bio-based solvents and solvents from food waste - as sustainable and economically attractive alternatives to conventional organic solvents.

CO₂ Chemistry: Carbon dioxide is a readily available and sustainable carbon feedstock for a future chemicals industry. Research within GCCE is exploring the development of new routes to convert CO₂ into valuable chemicals including cyclic carbonates and polymers.

EDUCATION

MSc in Green Chemistry & Sustainable Industrial Technology: The first course of its kind to be accredited by the Royal Society of Chemistry; the course is highly recommended by both students and industry.

NETWORKING

Northern Sustainable Chemistry (NORSC): A network formed from top universities in the North of England.

COST EUBIS: A COST Action network led by York on food waste valorisation for sustainable chemicals, materials & fuels.

CO2Chem: An EPSRC Grand Challenge Network, which brings together academics, industrialists and policy makers to consider the utilisation of carbon dioxide as a single carbon chemical feedstock for the production of value added products.

G2C2: A Global Network of Green Chemistry Centres, created following a gathering of world leaders.

CURRENT PROJECTS

CHEM21 - Innovative Medicines Initiative: A major research project which aims to develop sustainable manufacturing routes to pharmaceuticals.

ALTEREGO: Alternative Energy Forms for Green Chemistry: Aims to develop a hierarchical methodology for targeted supply of three alternative forms of energy in novel reactors to precisely control chemical transformations and reaction pathways.

TSB Collaboration—Wet Waste: This multi-partner project focuses on the recovery and transformation of wet perishable process streams into higher value functional and textural ingredients for incorporation into food products.

Sustainable Chemical Feedstocks: Aims to develop the next generation of structured polymeric materials for the efficient production of platform chemicals and bio-surfactants from waste biomass.

Open-Bio: Aims at increasing the uptake speed of standards, labels and harmonized product information lists for bio-based products.

Materials Substitution: Aims to develop green routes from bio-based platform molecules to polymerisable monomers and then to develop a wide variety of polymers from these.

Production of Cyclic Carbonates from CO₂ Using Renewable Feedstocks (CyclicCO2R): Aims to create a process that removes the dependency on fossil fuel and increases the energy efficiency to create a net CO₂ uptake in the production of cyclic carbonates.

Sustainable Solvent Selection Service (S4): A combination of computational modelling and design, supported by laboratory testing in order to develop bespoke bio-based solvents.

IBCat: Integrated energy efficient microwave and unique fermentation processes for pilot scale production of high value chemicals from lignocellulosic waste.
Renewable feedstocks, one of the key areas of education and research at the Green Chemistry Centre of Excellence (GCCE), are becoming an increasing viable and important alternative resource. Research is directed at chemical aspects of biomaterials and bio-energy as well as bio-chemicals (see figure below). Based on a wide range of renewable feedstocks (including low value plants such as trees, grasses and heathers; energy crops and food crop by-products; marine resource wastes and food wastes) we are researching the application of green chemical technologies (including supercritical fluid extraction, microwave processing, catalytic and other clean synthesis methods) with the aim of developing new, genuinely sustainable, low environmental impact routes to important chemical products, materials and biofuels.

Examples of past and on-going projects in the group in this area are:

- Selective extraction and fractionation of secondary metabolites from wheat straw (Triticum aestivum), heather (Calluna vulgaris) and sitka spruce (Picea sitchensis) using environmentally-friendly supercritical carbon dioxide.
- Development of novel materials based on biopolymers including starch, cellulose, chitosan and lignin.
- Conversion of lignin to industrially useful products such as vanillin through methods including microwave treatment.
- Selective conversion of lignocellulosic biomass to chemicals and fuels using low temperature microwave processing.
- Conversion of biomass platform molecules including succinic acid and glycerol into valuable industrial products.
Polysaccharides have high inherent functionality, difficult to introduce in petroleum-based polymers. This presents a great opportunity for new materials, but access to this functionality is hindered by the low surface area of the raw materials.

Simple but controlled physical modifications enabled development of a range of novel porous materials with applications in nanotechnology, chromatography, acid catalysis, adsorption, chromatography and composites, where these materials offer superior performance characteristics. These include a new class of mesoporous materials “Starbons®” which have surface properties ranging from starch-like to carbon-like. Starbons® Ltd was formed in 2012 as the GCCE’s first commercialisation company, and is based near the BDC and the GCCE in the York Science Park.

**APPLICATIONS**
- Catalysis
- Separation media
- Absorbency
- Remediation
- Effluent treatment
- Water purification
- Fuel cells

**PROPERTIES**
- High mesoporosity (0.4 - 0.7 cm³/g)
- High surface areas (150 - 500 m²/g)
- Readily functionalisable
- Excellent solvent stability
- Good chemical and heat resistance
- Controllable electrical conductivity
- Formation of composites / blends
- Particulate/monolithic forms

Starbon application: Decolourisation of peat water
SWITCHABLE ADHESIVES FOR CARPET TILES

Disposal of post-consumer carpet tiles and waste from manufacture such as off-cuts produces large volumes of non-readily degradable waste, such as bitumen, SBR-latex and nylon with 90% of this ending up in landfill.

This represents an unacceptable level of waste and future legislation will force manufacturers to accept back used tiles for recycling. A number of means to recycle carpet tiles have been looked at, but none are satisfactory enough to allow full recycling due to adhesive contamination of the fabric layer. However, the novel modified expanded starch adhesive developed by Interface-York solves this problem by being able to “switch” adhesive properties under controlled conditions. This will lead to a reduction of 2160 tonnes of CO₂ and an equivalent 153,979 tonnes of CO₂ according to greenhouse gas potentials being released into the atmosphere during complete manufacture.

The switchable adhesive discovered at York has been developed in a TSB funded project in collaboration with InterfaceFlor, Contract Chemicals, Itac and the NNFCC.
The majority of structural panels, such as MDF and particle boards used in the furniture and construction industry are made of wood bound with organic resin. Availability of FSC certified wood for this application is limited due to competing needs in the energy and other sectors. The organic resins used as binders are typically formaldehyde/ isocynate-based. Both resins are petroleum-derived contributing to the product’s carbon footprint and they are toxic/harmful in production and/or use.

Bio-boards
We have developed new bio-boards with lower environmental footprint, whereby key product components, including aggregate, binder, hardener and additives are plant derived:

(1) Aggregate:
Agricultural/ other lignocellulosic by-products avoid the need for FSC virgin wood.

(2) Resin:
Inorganic silicates, derived from waste biomass combustion ashes, provide non-toxic, non-volatile, chemically and biologically resistant binders which also render the boards fire-retardant and can yield stiffer less materials intensive products.

(3) Hardener:
Suitable chemical functionalities can be naturally present / derived in situ in the aggregate or sourced from by-products of bio-fuels production.

Our production methodologies are applicable to a variety of raw materials to reduce dependence on any one feedstock and to minimise the impact of price, availability and geographical limitations. This approach will also minimise impact on biodiversity and will provide more secure income streams for farming communities.

The programme was sponsored by Defra through the Renewable Materials LINK Programme and by research grant from AHDB-HGCA.
Waxes are produced commercially in large amounts for use in cosmetics, polishes, surface coatings and many other applications. Many of these are of mineral origin but three in particular are derived from plant sources, these are Jojoba, carnauba and beeswax. The commercial applications and the natural function of the plant waxes are essentially the same in that both provide a hydrophobic coating that reduces water loss and protects the surface. Conventional extraction of waxes involves toxic solvents such as hexane, toluene, chloroform and dichloromethane.

A greener approach to obtaining plant waxes is to utilise by-products such as cereal straw as a raw material and to use benign extraction techniques such as supercritical CO₂ (scCO₂) to selectively remove these from the plant matrix. This has been demonstrated using wheat straw, maize stover, miscanthus and sugarcane, where a highly selective extraction of the lipid and wax fraction was obtained with no solvent residues.

A significant advantage of scCO₂ over conventional organic solvents is the possibility of carrying out fractional separation of crude waxes, whereby compounds are precipitated out in successive steps, at decreasing pressures and temperatures.

ScCO₂ extraction and fractionation of wax from maize stover gave rise to waxy fractions containing different compositions and melting points enabling their utilisation in different applications. One of the fractions was demonstrated as an effective de-foaming substance which can be implemented in detergents in place of non-renewable defoaming agents.

Foam ability and foam stability of washing powder hard water, maize wax 0.01 g and 0.02 g

A) Foam generation B) Control, run with maize stover wax.
Currently around 300 million tonnes of synthetic polymers are produced globally each year. After fuels, polymer production consumes more petroleum than any other industry, vastly outstripping solvents, pharmaceuticals and all other chemical products. Many of these materials are also produced using energy intensive processes and hazardous reagents. Clearly, therefore, the development of more sustainable and bio-derived alternatives to these materials has the potential to have a very significant impact on climate change and the depletion of petroleum reserves.

The materials substitution project aims to develop green routes from bio-based platform molecules to polymerisable monomers and then to develop a wide variety of polymers from these including polyalkenes, polyethers, polyesters, polycarbonates and polyurethanes. Several of these plastics are derived from the combination of carbon dioxide gas with the bio-based monomers and as such represent both carbon capture via plants from the original biomass but also the potential to capture waste carbon dioxide directly from power stations or industrial processes such as ammonia production or bioethanol fermentation.

The project is a collaboration across several institutions and includes Process Intensification engineers from Prof. Adam Harvey’s group at the university of Newcastle, leading polycarbonate and polyester chemists (Prof. Charlotte Williams’ group at Imperial College), lifecycle and technoeconomic analysts (Prof. Nilay Shah’s group at Imperial College) as well as a diverse industrial advisory board consisting of polymer manufacturers and users as well as companies interested in the production of platform molecules. As a platform grant the project aims to build collaboration and generate interesting leads which will attract further funding and become the basis of future research projects or commercial processes.
Oranges are grown year round on both sides of the equator and are highly processed and up to 50% of their weight is rejected under the form of peel. This fruit contains a large amount of marketable chemicals which are normally generated by separate industries, losing the chemical potential waste orange peel contains.

The Orange Peel Exploitation Company (OPEC) project plans to bring the new technology developed at the University of York wherever fuels and chemicals can be derived from orange peel waste. This has been carried out based on microwave technology as it is scalable and allows not only continuous processing but also the use of wet feedstock.

The process includes a series of low temperature (<150 °C) and acid free microwave hydrothermal extractions to successfully separate d-limonene containing citrus oil, pectin, four polymethoxy flavonoids, hesperidin and sugars from the cellulose based matrix of the peel - meeting, in every case, standard industrial specifications.

The OPEC Methodology
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With our collaborators in other universities the routes from biomass to polymer are subject to both lifecycle and technoeconomic analysis in order to determine the cost-effectiveness and environmental impact of the materials in order to guide the development work towards methods and materials that offer genuine sustainability improvements over conventional plastics and have the potential to be economically viable.
EUBIS - CHEMICALS FROM FOOD WASTE

Food Waste Valorisation for Sustainable Chemicals, Materials and Fuels (EUBIS)

EUBIS (COST Action TD1203) is a network of researchers and industrial partners working together to advance research on the valorisation of food supply chain waste (FSCW) for the production of sustainable chemicals, material and fuels. The GCCE initiated the Action due to our expertise in clean technology and using waste as a resource, and as the grantholder the Centre is responsible for the organisation of the network. The network is based around four interconnected Working Groups (WGs):

- WG1: Pre-treatment and extraction
- WG2: Bioprocessing
- WG3: Chemical processing
- WG4: Technical and sustainability assessment/policy analysis.

Main Objectives

- To provide an integrated alternative renewable source of carbon for the production of industrially relevant bio-derived chemicals, fuels and materials via the exploration of novel and advanced routes for food supply chain waste valorisation.
- To bring about a critical mass of researchers and stakeholders to harness the potential of food supply chain waste (FSCW) as an alternative carbon source to produce commercially viable chemical commodities.
- To interconnect technology hubs across Europe and beyond, overcome technological barriers, go beyond first generation organic waste reuse/recycling, and bridge gaps between academic disciplines and between academia and industry.
- To identify major value-added products (chemicals, materials and fuels) to be produced from FSCW (product-driven biorefining) and to demonstrate the most promising FW valorisation processes at larger scale.

Participation

- 235 WG members (108 Female, 127 Male)
- 124 Institutions
- 34 Countries

www.costeubis.org

www.york.ac.uk/greenchemistry
CHEM21- INNOVATIVE MEDICINES INITIATIVE

CHEM21 is Europe’s largest public-private partnership dedicated to the development of manufacturing sustainable pharmaceuticals. The aim of CHEM21 is to develop a broad based portfolio of sustainable technologies for green chemical intermediate manufacture aimed at the pharmaceutical industry. New, more efficient catalyst classes will be utilised in greening processes, generating novel molecules and producing alternative pathways/transformations with broad applications. Bio-derived platform molecules are to be incorporated into drug synthesis, with such building blocks coming from existing pathways and modified microorganisms. Training materials will be developed throughout the lifetime of the project for implementation in driving education and long term innovation in the sector and beyond.

The network is based around six interconnected Work Packages (WPs):

- WP1: Problem identification
- WP2: Green catalysis and flow / intensification
- WP3: Bio-catalysis
- WP4: Synthetic biology
- WP5: Medicinal and process chemist education
- WP6: Management

Main Objectives

- To produce a wide range of sustainable catalysts for application in batch and flow for both direct replacement of current technologies and to open up synthesis of novel compounds such as sp3 hybridised drugs.

- To more widely incorporate biocatalysis into drug manufacture and to introduce synthetic biology to synthesise platform molecules/drugs in one pot directly from biomass.

- To establish a European research hub to act as a source of up-to-date information on green chemistry.

- To significantly green the European pharmaceutical industry, collating and assessing the green credentials of the current state of the art and any new research through a dedicated database complete with metrics toolkit.

- To educate medicinal and process chemists within the pharma industry and the next generation of chemists within academia, promoting the uptake and application of green and sustainable methodologies.

CHEM21 has received funding from the Innovative Medicines Initiative Joint Undertaking under grant agreement n°115360, resources of which are composed of financial contribution from the European Union’s Seventh Framework Programme (FP7/2007-2013) and EFPIA companies’ in kind contribution.
CARBONATES AS ALTERNATIVE SOLVENTS

Recent estimates by the pharmaceutical and fine chemical industry have suggested solvents account for 80-90% of the total waste produced in a typical batch process. For this reason there has been a large amount of interest in the field of alternative solvents. As it presents the opportunity for the most significant gains, in terms of reducing environmental impact.

Many efforts have investigated the use of neoteric or “new” solvents and solvent technologies, common examples include ionic liquids (IL’s), supercritical CO2 or fluorous solvents. However, these have often been limited to small scale industrial applications or high value products.

There still exists substantial scope for the exchange of volatile organic compounds (VOC) for molecular solvents with favourable environmental, health and safety characteristics. In recent years, organic carbonates (both cyclic and acyclic) have been highlighted as highly promising alternatives to VOCs (Figure 1). Current projects within the GCCE are investigating the use of carbonates as alternative solvents in various synthetic transformations.

Cyclic carbonates have predominately seen use as solvents in electrochemical and extractive applications, with the biggest consumer usage being lithium-ion batteries. However, cyclic carbonates have many favourable characteristics that make them suitable for organic synthesis.

Properties of Cyclic Carbonates
- Excellent solvation properties
- Produced by the 100% atom-economical reactions between epoxides and CO2 (Figure 2)
- Non-toxic
- Biodegradable
- Low ecotoxicity
- Odourless
- Low vapour pressure

The North group have previously shown that propylene carbonate can be used as a replacement for dichloromethane in the vanadium or titanium catalysed asymmetric synthesis of cyanohydrins (Figure 3) and as replacements for DMF and DMSO in amino acid catalysed reactions.

Acyclic carbonates have already found utilisation in a several fields, including intermediates in pharmaceuticals, agrochemicals and lubricants. They are considered sustainable solvents due to their low toxicities, facile degradation to harmless by-products and green synthesis. It has been shown that diethyl carbonate is a suitable replacement for toluene in asymmetric Michael additions catalysed by quinine (Figure 4).
The Sustainable Solvent Selection Service, or ‘S4’, was developed by the Green Chemistry Centre of Excellence at the University of York to offer advice and scientific expertise regarding bio-based solvents and solvent use.

S4 is a combination of computational modelling and design, supported by laboratory testing in order to develop bespoke bio-based solvents according to the specific application required. ‘S4’ uses a combination of specialized software packages and our own research driven knowledge in biomass valorization to develop benign renewable solvents specific to our clients.

Find more information at www.york.ac.uk/res/s4
There has been a global shift towards the use of biomass as a source of fuels and chemicals necessitated by decreasing fossil reserves, increasing oil prices, security of supply and environmental issues. It has also become clear that the manufacturing industry is embracing this change and has clearly stated its aims to develop sustainable and efficient routes to manufacturing products.

Recent advances in biorefinery technologies have been based on feedstocks that compete with food or feed such as starch or vegetable oils. Large-scale implementation of these technologies can have disastrous consequences for food security worldwide. Therefore, it is paramount that new biorefinery technologies are based upon sources of biomass that do not compete with food production. Hence the aim of this project is to develop the next generation of structured polymeric materials that will enable to efficiently produce platform chemicals and bio-surfactants from waste biomass.

This project is built upon the expertise in the GCCE specifically in the areas of microwave biomass activation, catalysis and materials science from the partners in York and Liverpool and their strong engagement with industry. The state of the art facilities in high-throughput materials discovery and characterisation have been utilized, and advanced techniques used which include supercritical CO₂ (scCO₂) extraction, microwave pyrolysis and microwave hydrolysis in reactors up to scales of 100L will be used.

Main Objectives

- Development of supercritical carbon dioxide (scCO₂) and microwave (MW) techniques for the production of high-grade fractions of bio-oils, suitable for conversion to surfactants from waste biomass.

- Discovery of new functional materials for biomass transformation, and in particular for 1) separation of components of bio-oils 2) the depolymerisation of biomass components 3) the synthesis of sugar-derived platform chemicals and 4) for one pot synthesis of surfactants from cellulose.

- Integration of scCO₂ and MW technologies with catalytic transformation to products.
There is currently an increasing interest in carbon dioxide chemistry driven by the realization that carbon dioxide can provide a sustainable C1-building block for future chemical industry and being one of the most significant greenhouse gases.

The objective of CyclicCO$_2$R is to create a process that removes the dependency on fossil fuel and increases the energy efficiency to create a net carbon dioxide uptake in the production of cyclic carbonates, especially glycerol carbonate. As an inexpensive waste product from biodiesel production, glycerol will be the main raw material, along with carbon dioxide, ensuring cost effectiveness and, thereby, a maximum commercial potential.

Two production routes will be explored:

1. A direct route: converting glycerol directly to glycerol carbonate. Starting point will be the use of pure glycerol, but ultimately impure glycerol derived directly from biodiesel production will be used.

2. An indirect route: converting glycerol to glycerol carbonate through the formation of epoxides. The indirect route has the potential to create enantiomerically pure cyclic carbonates via kinetic resolution.

The research project will focus on:

- Catalyst development for both routes
- Immobilization and recoverability of catalysts
- Intensify the process in a continuous flow reactor
- Bring the production of glycerol carbonate to a mini-plant scale
- Provide techno-economic analysis of the process, showing the commercial and environmental feasibility of the process.
To meet key climate change targets, while providing sustainable economic growth, the UK must develop a robust bioeconomy. This requires the valorisation of UK-specific and abundant waste lignocellulosic streams. Currently, the expense and inefficiency of the multi-stage acid pre-treated depolymerisation and enzymatic process has limited the growth in this sector.

This cutting-edge translational research project aims to significantly enhance industrial production of high value chemicals using the combination of the GCCE’s microwave technology with the University of Bath’s novel yeast grown on sustainably-sourced waste feedstocks. In this way we can move bio-based chemical production away from more limited and environmentally debatable feedstocks like palm oil to widely available and genuinely sustainable lignocellulosics.

The GCCE has reported an innovative one-step microwave process for the depolymerisation of bio-wastes. This key enabling technology achieves high sugar yields despite low energy inputs. While the inhibitors formed in the process limit the growth of most yeasts, the robust yeast Metschnikowia pulcherrima (Mp) thrives on this feedstock to produce valuable 2-phenylethanol, arabinitol and lipids. This project aims to develop a pilot scale multi-product biorefinery by coupling these breakthroughs in low energy biomass treatment and unique fermentation to produce marketable compounds.

The project is supporting an industrial supply chain covering feedstock to engineering to products and applications.
Carbon dioxide is emitted into the atmosphere on a gigatonne scale every year. As a greenhouse gas, the accumulation of carbon dioxide in the atmosphere has a negative effect on the environment. For example, we have seen an increase in global mean temperature and a rise in sea levels over the last few decades. Reducing our carbon dioxide emissions via carbon dioxide capture, utilisation and storage are therefore vital areas of research. Carbon dioxide storage can be performed in numerous ways including injection into deep underground rock formations. This can lead to carbon dioxide mineralisation, hence trapping the carbon dioxide as a solid mineral. This natural process however occurs over a long time scale, hence research in GCCE is currently being conducted to replicate this process more quickly in the laboratory.

Using efficient and “green” methods for carbon dioxide sequestration is extremely important, so that these methods do not emit more carbon dioxide than is ultimately captured. One option being developed in GCCE is to use electrochemistry, as electrochemical methods often require mild conditions, i.e. low pressures and temperatures, and can remove the need for toxic chemicals and flammable solvents. GCCE researchers from the North group in collaboration with Dr. Alison Parkin (University of York, Chemistry Department) have shown that electrochemistry can promote the capture and mineralisation of carbon dioxide using an aqueous electrolyte at room temperature. This technology is currently being developed to utilise entirely waste based materials and renewable energy for carbon dioxide capture and sequestration.

Another aspect of GCCE research on carbon capture is the development of novel solid absorbents for carbon dioxide to provide an alternative to amine based carbon dioxide capture agents. GCCE researchers have shown that the mesoporous Starbon materials developed within the GCCE make excellent carbon dioxide adsorbents which can capture and release carbon dioxide under mild pressure swing conditions and show excellent selectivity for carbon dioxide over other gases. The optimal Starbon based materials were found to be superior to activated charcoal in terms of both amount of carbon dioxide absorbed per gram of material and the selectivity for carbon dioxide adsorption. Ongoing work is aimed at optimising the Starbon structure for carbon dioxide capture and release and understanding the mechanism of absorption and why a mesoporous carbon is superior to microporous activated charcoal.