



**Possibilities for Waste valorisation: the
concept of modular biorefineries**

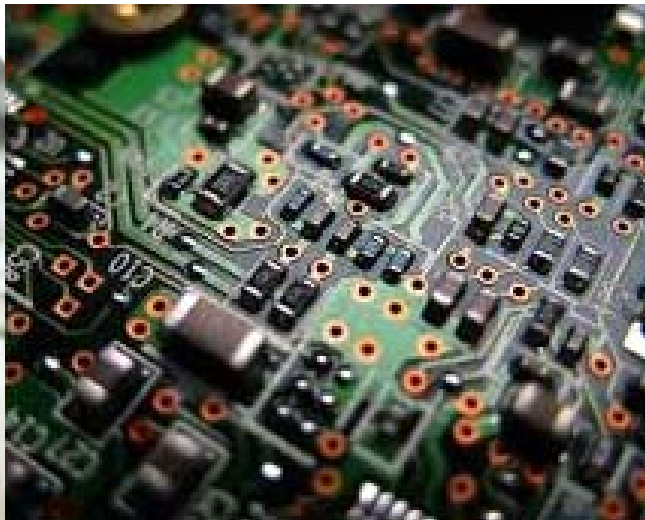
<http://www.uco.es/~q62alsor/>

Prof. Rafael Luque

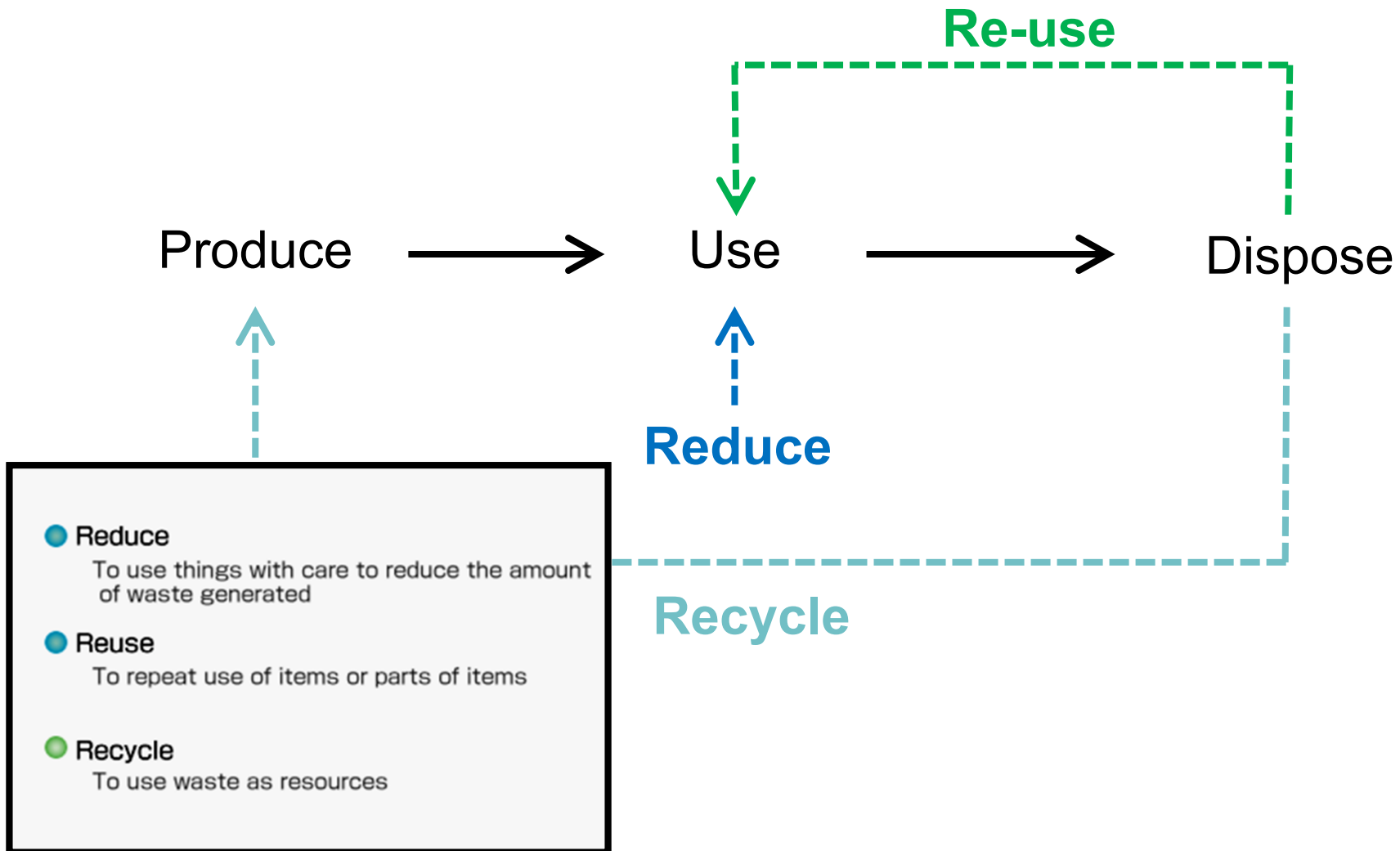
**DEPARTAMENTO DE QUÍMICA ORGÁNICA,
UNIVERSIDAD DE CÓRDOBA**

ITS ALWAYS THE SAME THING.....

Produce → Use → Dispose

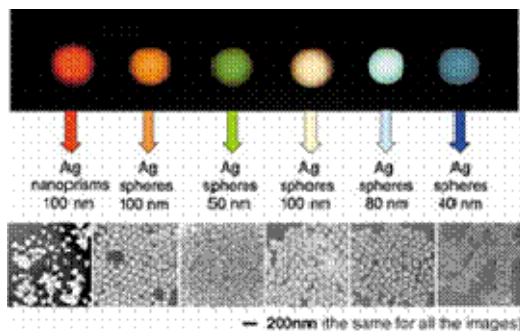


Something wrong with this?



What do we do?

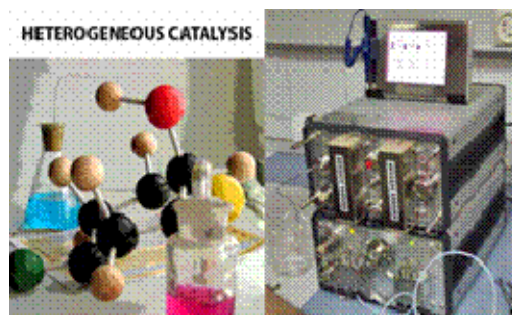
NANOSCALE CHEMISTRY



Supramolecular gels
Nanomaterials
Supported nanoparticles
Microwave nanocatalysis
Mechanochemistry (milling)

Group leader:
Alina M. Balu

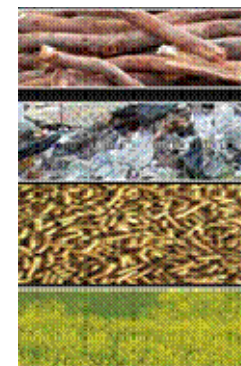
HETEROGENEOUS CATALYSIS & FLOW CHEMISTRY



Heterogeneous catalysis (acid-base, redox, C-C and C-heteroatom couplings)
Microwave assisted catalysis
Flow Chemistry

Group Leader:
Weiyi Ouyang

BIOMASS & WASTE VALORISATION

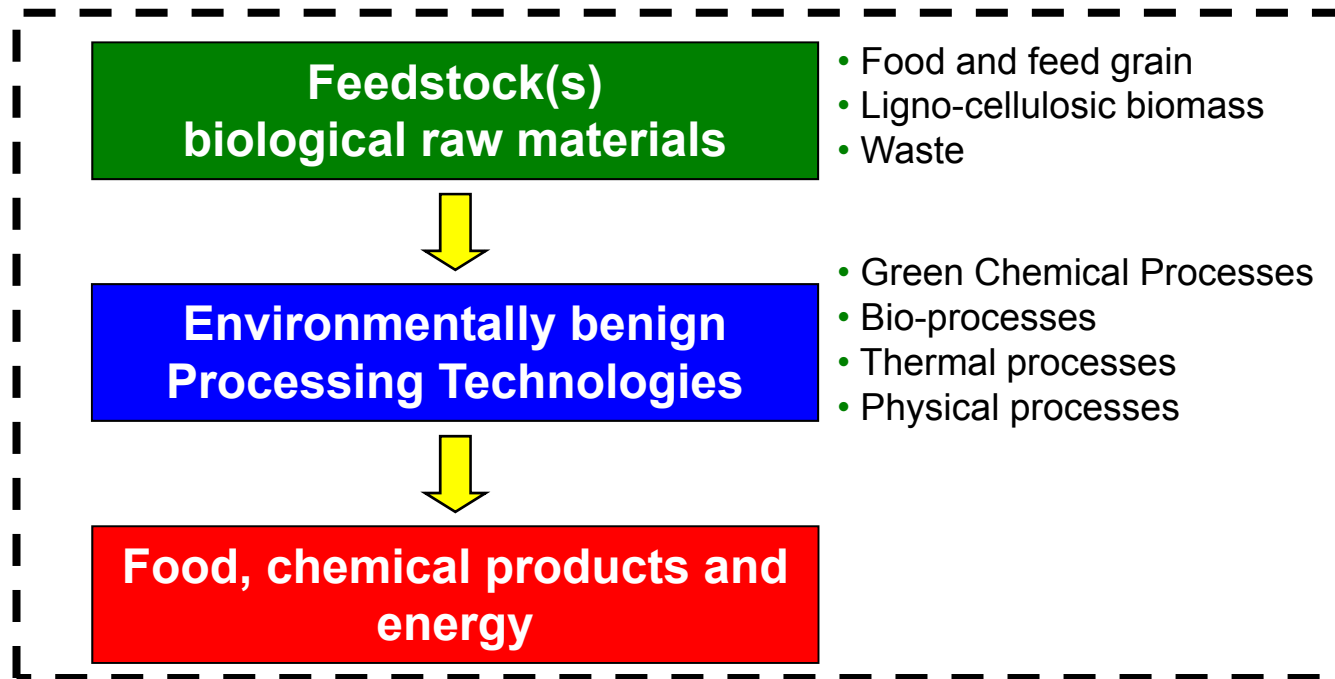


Transformations of platform molecules
Biomass valorisation
Biofuels production
Waste valorisation (biorefineries)

Group Leader:
Sudipta De

BIOREFINERIES

Integrated facilities that can convert a variety of bio-feedstocks into energy, chemicals and other valuable materials **cleanly** and **efficiently** maximising the value of the biomass and minimizing waste





<http://www.cbme.ust.hk/rafaluque.html>

WASTE TO WEALTH: FROM RESIDUES TO MARKETABLE PRODUCTS



Green technologies

(e.g. microwaves, extraction, fractionation)



Personal care products

Coatings and unguents



Paint additives



Biodegradable plastics



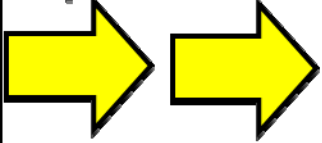
Other derivatives (chemicals, fuels, etc.)

Biorefinery: The big picture

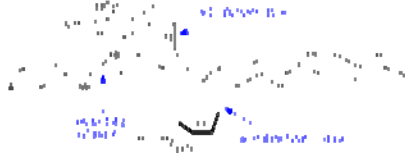


Forestry waste

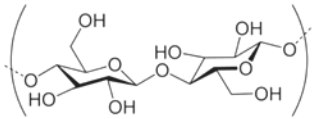
Separation



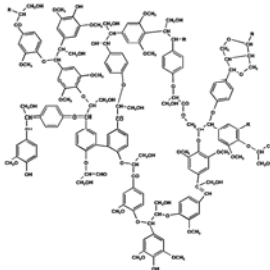
Fractionation



hemicellulose

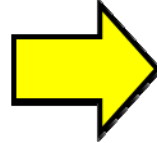


cellulose



lignin

Processing



Chemicals



Fuels



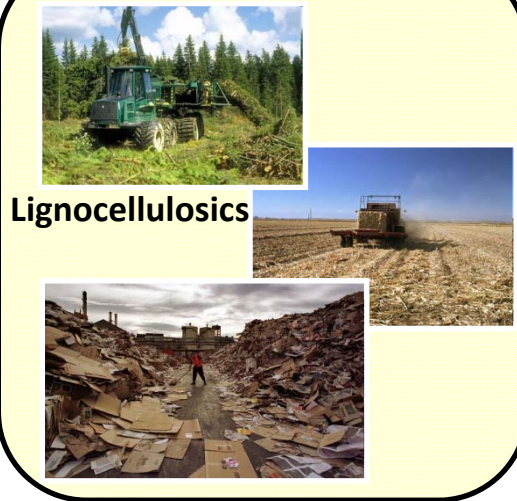
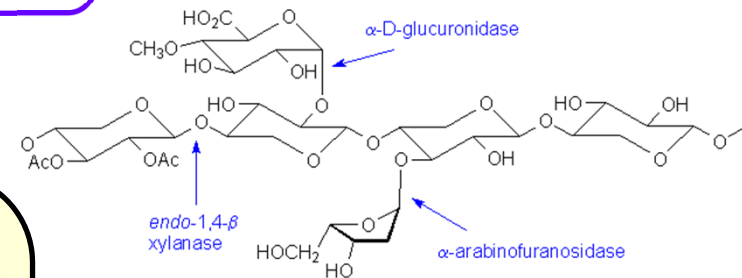
Materials



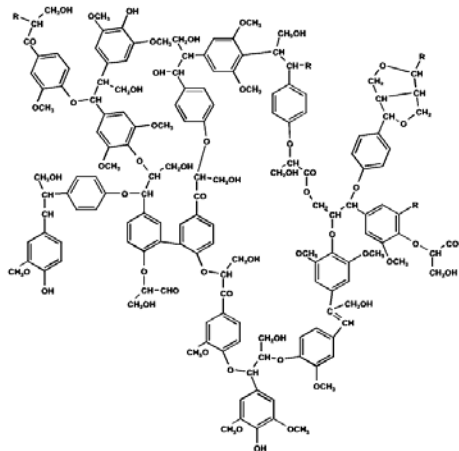
Polyesters

Knowing chemical composition is the key to success!!!

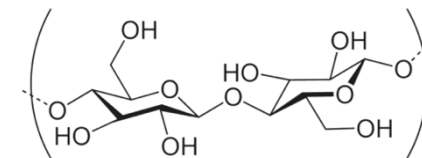
HEMICELLULOSE



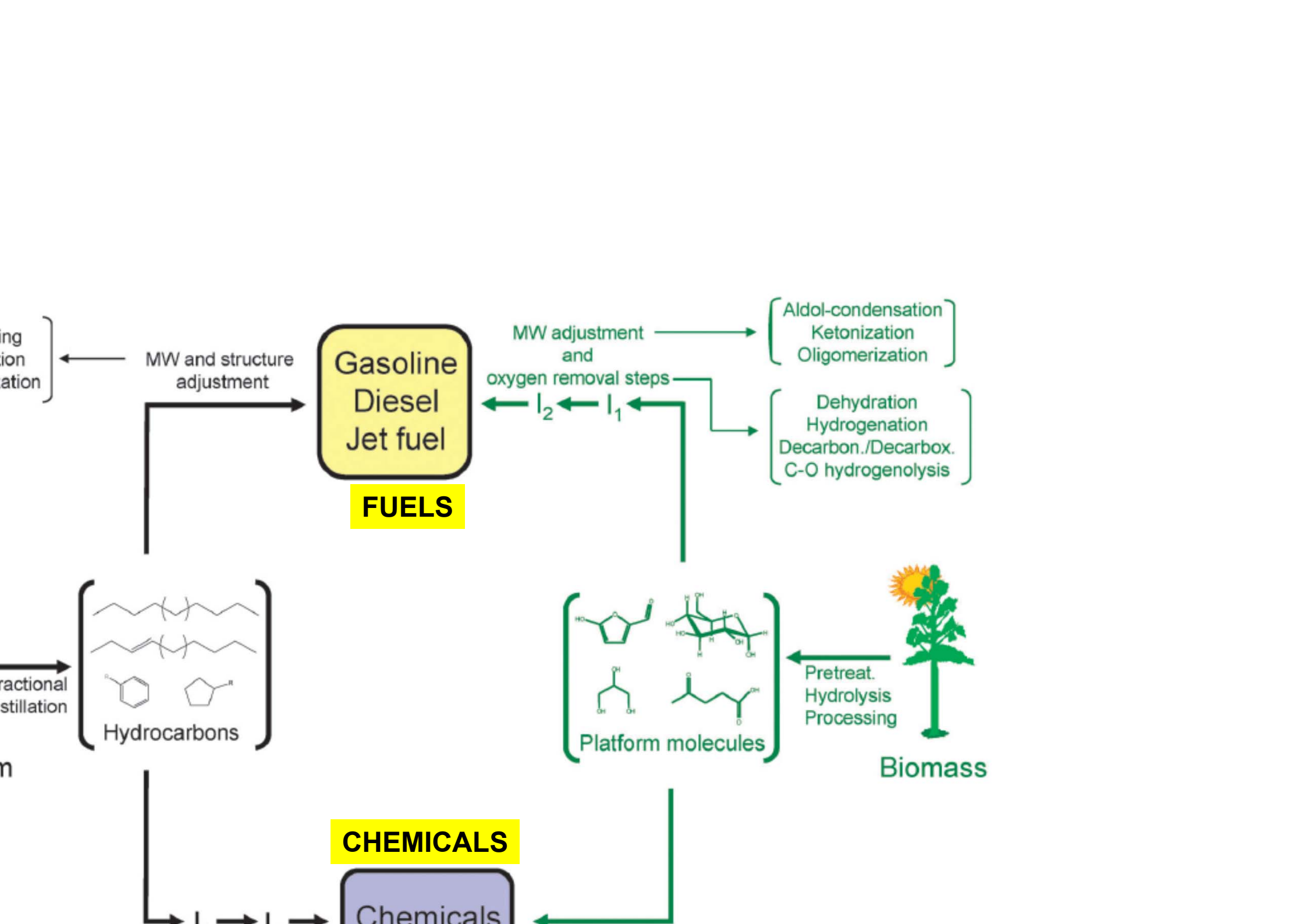
LIGNIN



CELLULOSE

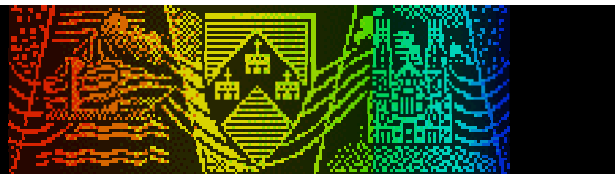


MINOR CONSTITUENTS





UNIVERSITY of York



**Green
Chemistry**
Centre of Excellence
MANCHESTER
1824
The University of Manchester

Wheat



Upstream
processing



Bioreaction



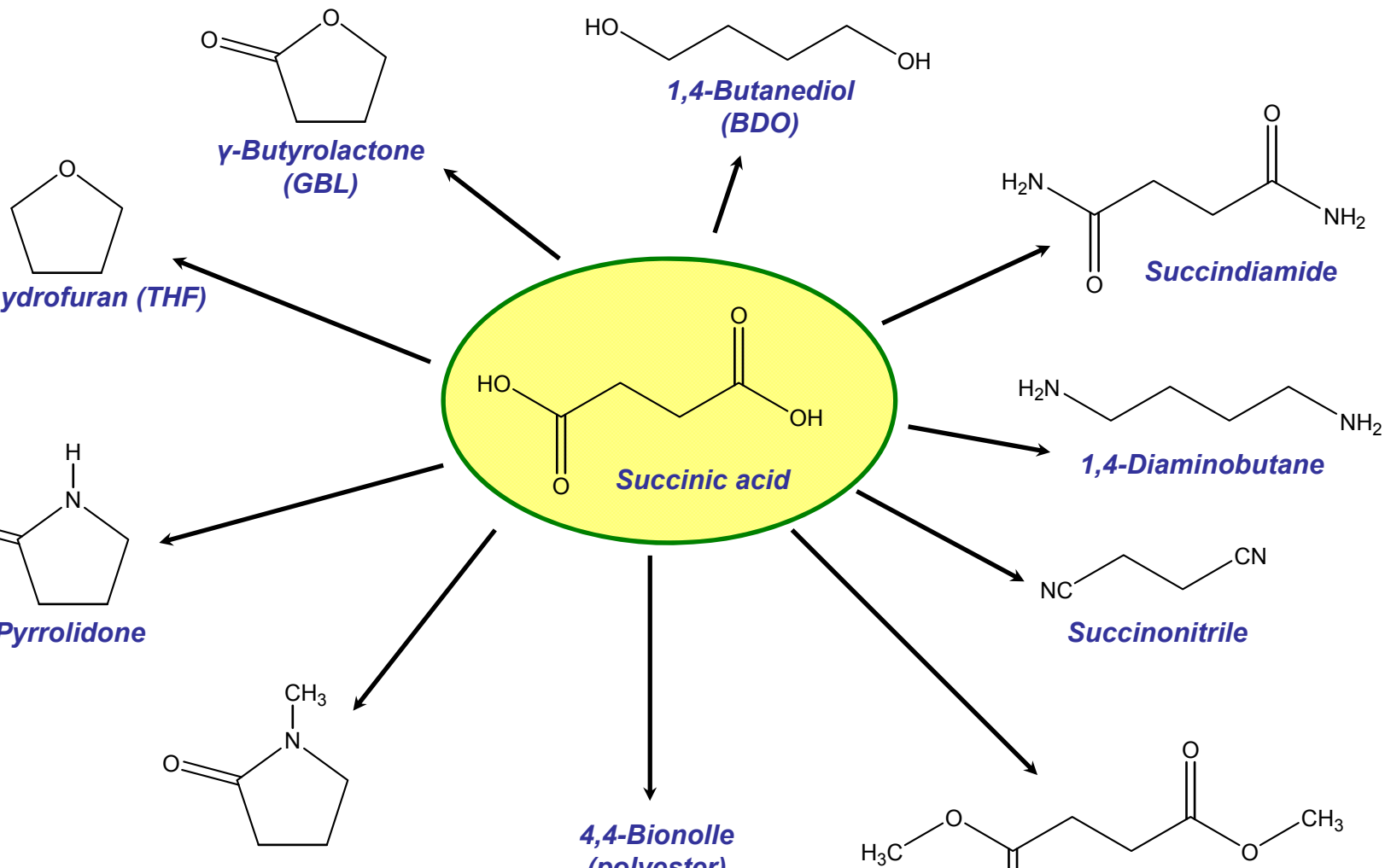
Downstream
processing



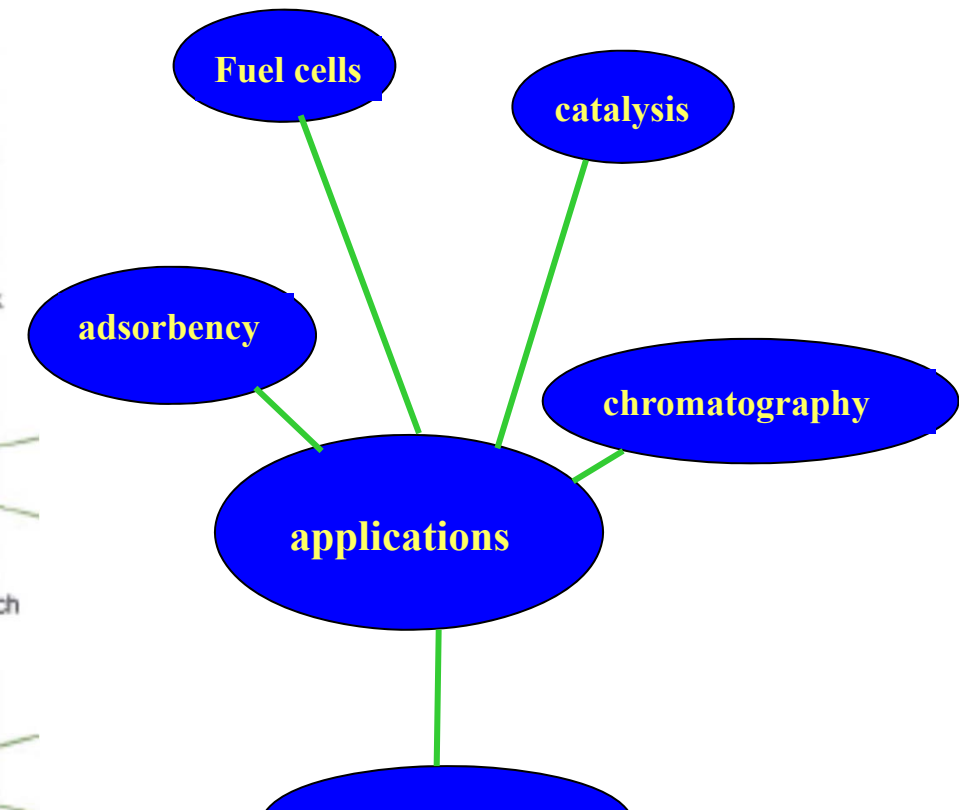
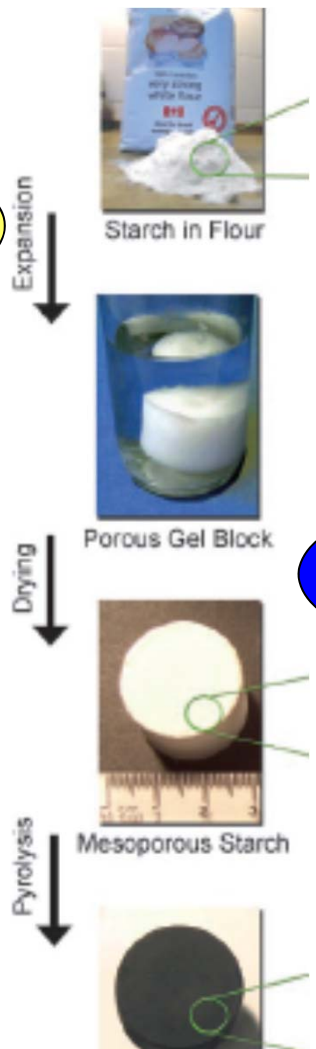
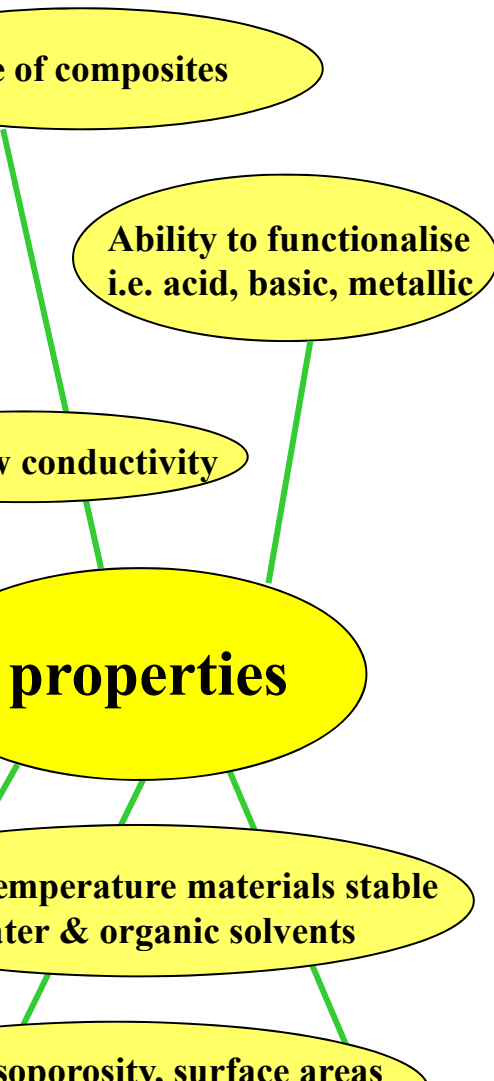
Succinic
acid



Succinic acid as a C4 building block



From Starch to Starbon[®]



With the mighty team at York (UK)



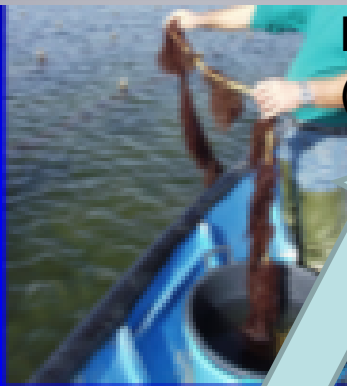
ALGAE VALORISATION: FROM HEALTH PRODUCTS TO BIOPOLYMERS



Algae plants



Longline



Gracilaria vermiculata (cv)

Extraction of Phytosterols
(cholesterol-reducing agents)



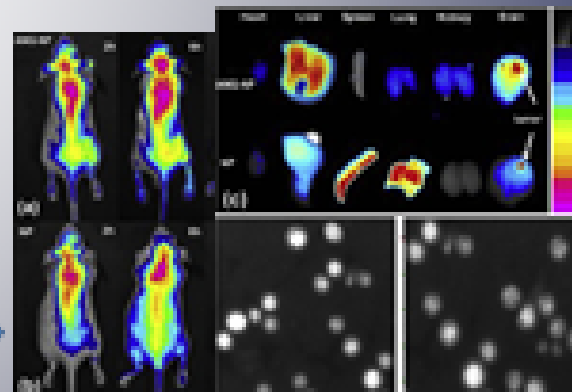
Highly porous and consistent
Antimicrobial foams (Ag NPs)

NP accumulation/migration

ALGAE GROWING
LAGOON IN ITALY



ZnO



Nanocrystals of

<http://www.cbme.ust.hk/rafaluque.html>

BIOMASS VALORISATION (II)... with INCAR (Oviedo)

MIP concept (EES 2012)



Gracillaria gracilis

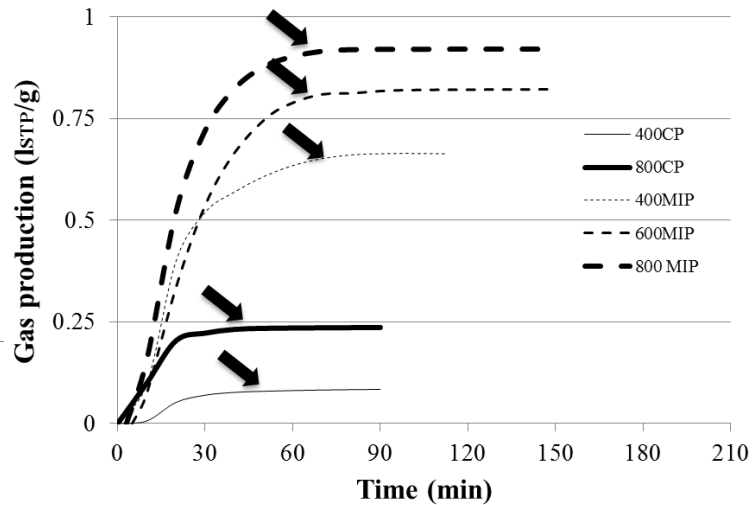
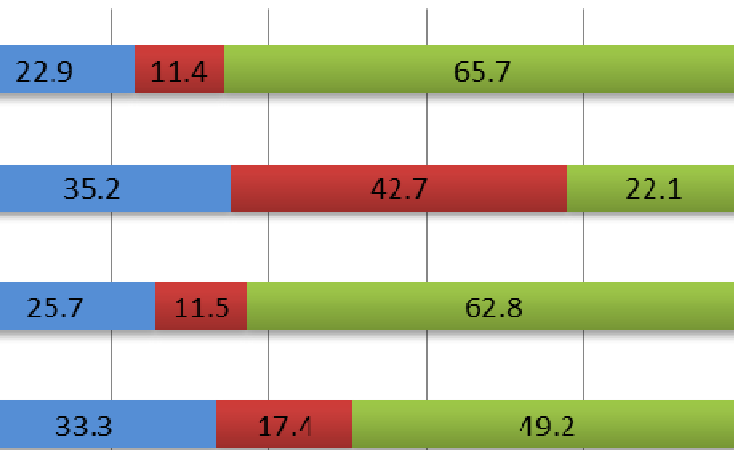


Table 1. Biochemical composition (% d.w.) of *Gracillaria gracilis* sampled in the Lesina lagoon (Italy).

Total Lipids	1.98
Fatty Acids Methyl Esters	0.47
Proteins	30.93

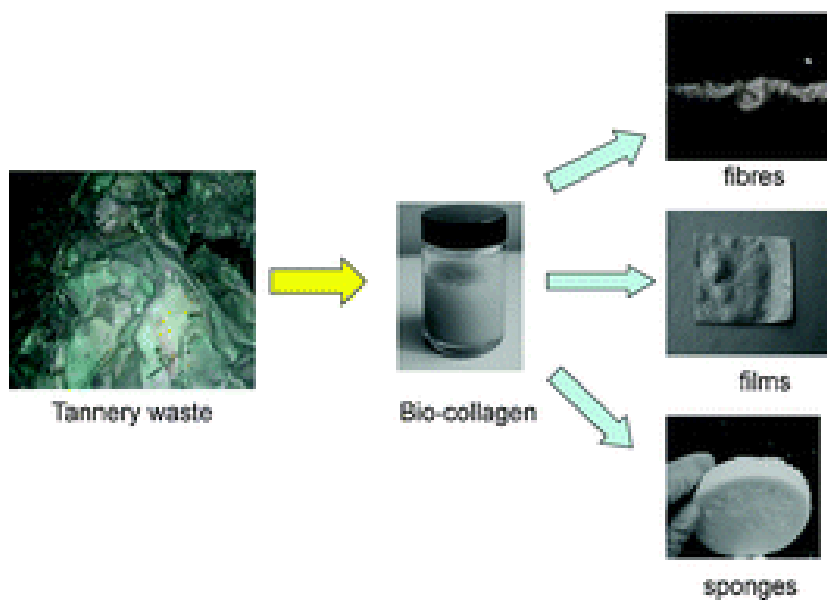


<http://www.uco.es/~q62alsor/>

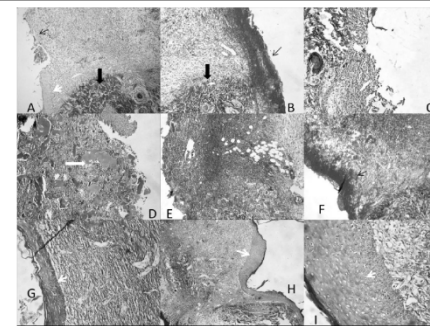
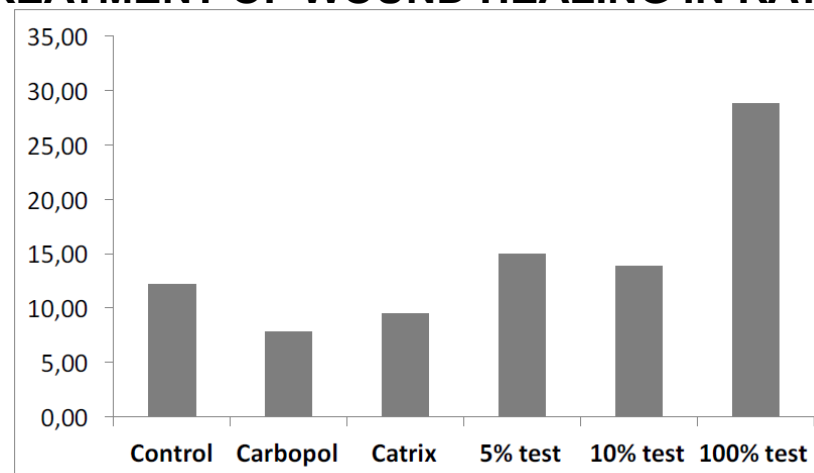


FOOD WASTE VALORISATION (II)... with Jaume Cot (IQAC)

FROM SLAUGHTER WASTE TO BIO-HEALING NATURAL POLYMERS (BIO-COLLAGEN)



TREATMENT OF WOUND HEALING IN RATS



Green Chem. 2012, 14, 308

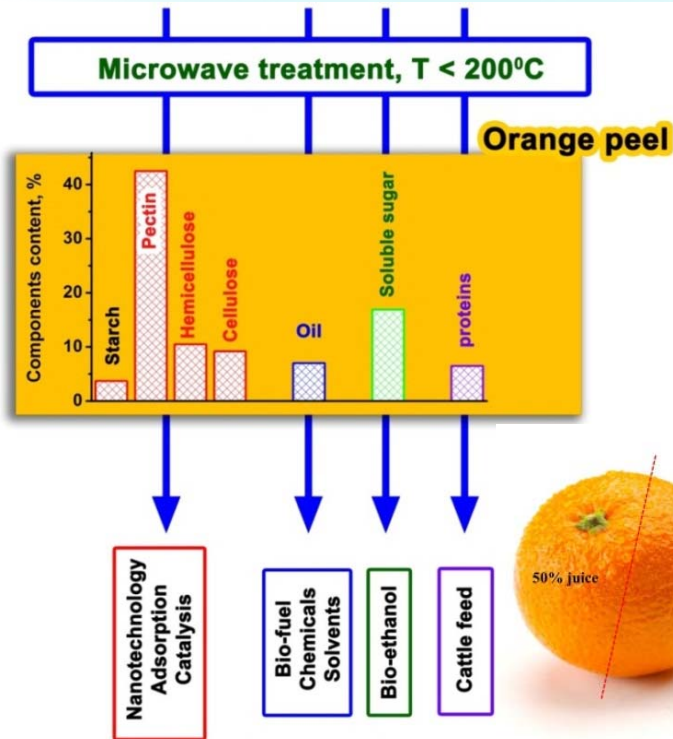
PCT Patent 2013

Materials 2013, 6, 1599
Materials 2013, 6, 4641



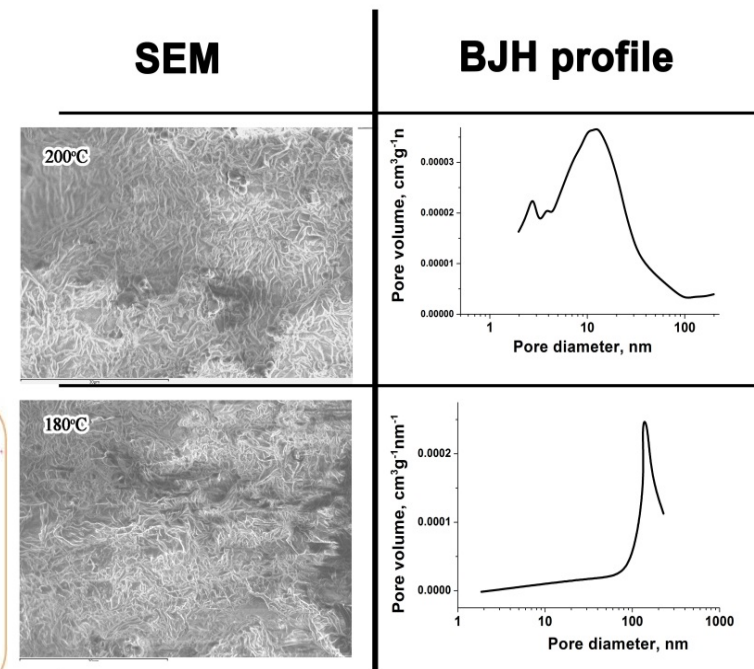
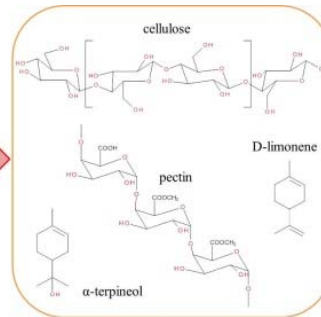
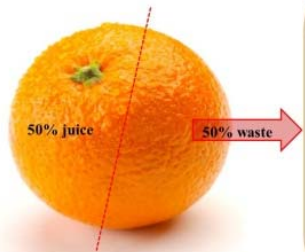
FOOD WASTE VALORISATION (III) :

ChemSusChem, 2012; *Energy Env. Sci.* 2013

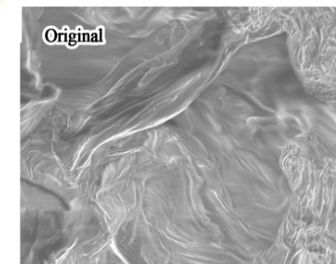
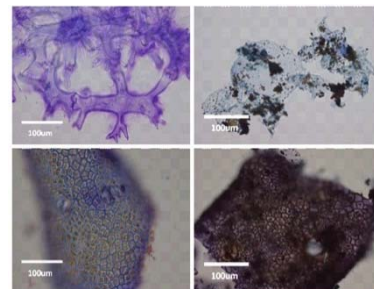


Microwave-assisted extraction:

- simple
- rapid (5-10 min)
- efficient

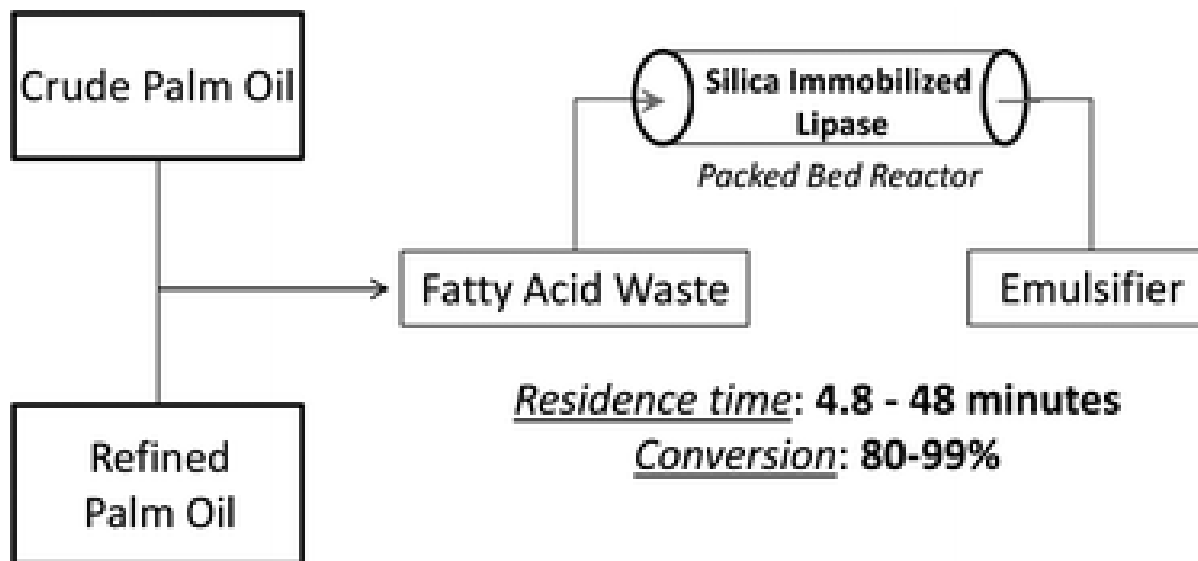


Unique form of mesoporous cellulose



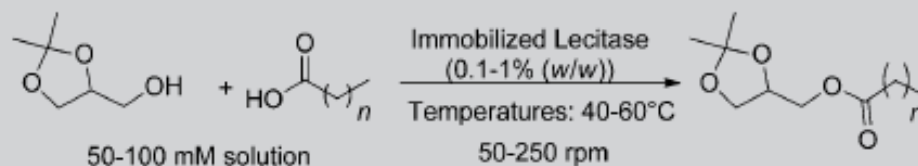
Sample	Surface area (m^2g^{-1})	Pore volume (ml g^{-1})	Pore size (nm)
MW-150°C	2	0.01	35
MW-180°C	6	0.68	88
MW-200°C	26	0.38	19

Porous materials



Green Chem. 2013
ChemSusChem 2013

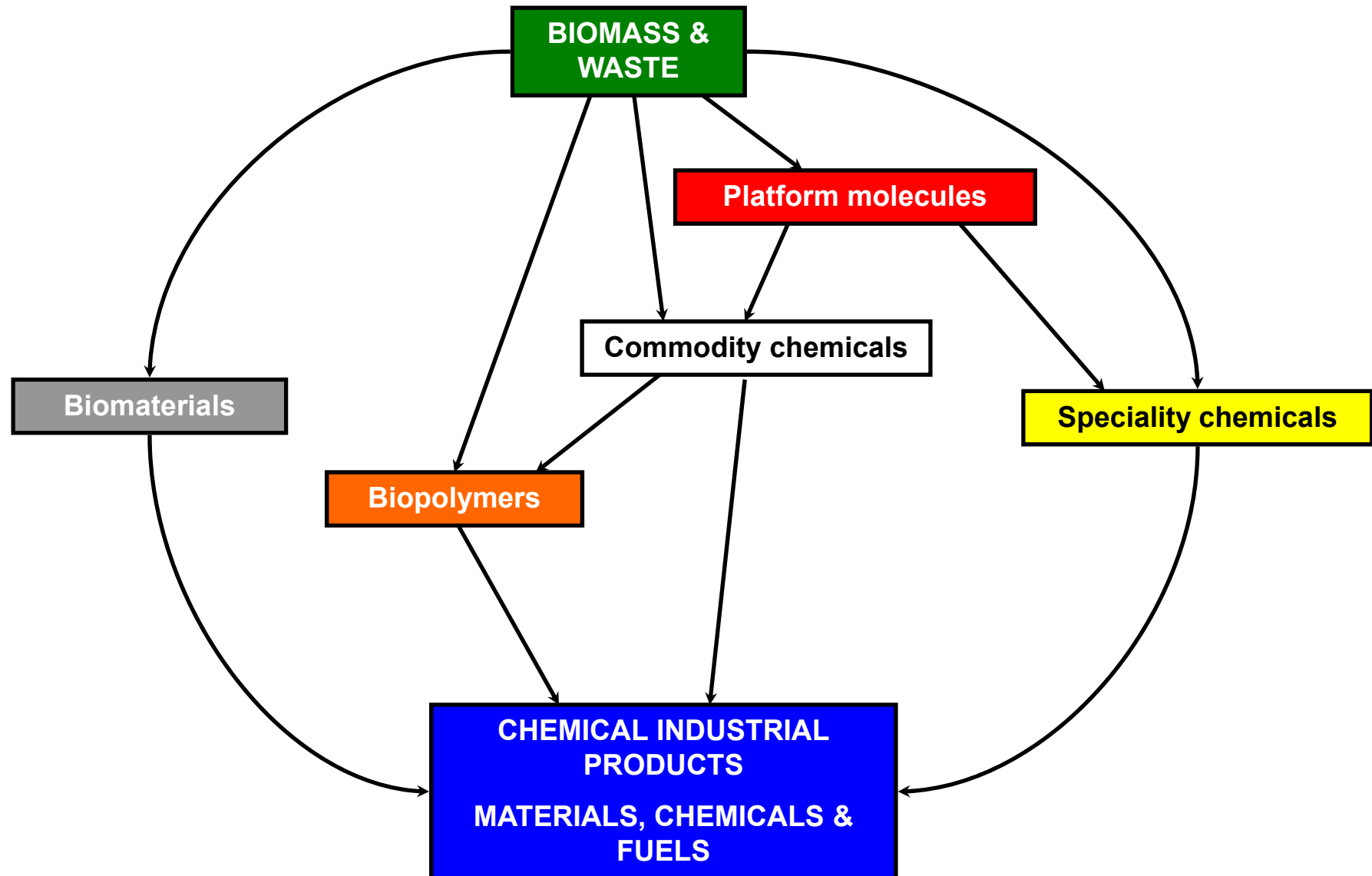
Table 4. Optimum reaction conditions obtained for immobilized derivatives from Lecitase Ultra.^[a]



Entry	T [°C]	[E] [%]	[S] [mM]	Stirring [rpm]	Conversion [%]			
					CMXAD2	USXAD2	CMXAD4	USXAD4
1	60(+)	1(+)	100(+)	50(-)	53.6	58.3	28.0	14.9
2	40(-)	0.1(-)	100(+)	250(+)	29.2	11.7	44.5	53.1

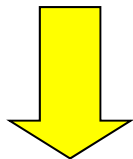
[a] Higher (+), middle (0), and lower (-) amounts of enzyme ([E]) by total weight of the system.

Conclusions



Some food for thought....

- The synthesis of 1 kg of **polystyrene** requires a total of **2.26 kg of fossil oil** (1 kg to generate electricity and 1.26 kg to serve as feedstocks for polymer production).
- The production of 1 kg of **PHAs** requires **2.39 kg of fossil resources**.



Simply deriving chemical products from renewable resources is NOT ENOUGH!

**Real environmental benefit?
Biodegradability?
Toxicity?
SAFETY!!!**

Can biotechnology move us toward a sustainable society?

A case study of biodegradable polymer production from agricultural feedstocks casts doubt on the premise that alternative biological processes always offer environmental benefits over conventional manufacturing processes.

Tillman U. Gerngross

The sustainability of a society based on finite fossil resources is the subject of ongoing scientific and political debate. One aspect of this debate, besides exploring alternative energy sources, is the challenge to provide chemical commodities (fuels, lubricants, adhesives, solvents, paints, materials, etc.) to an advanced consumer society, without depleting nonrenewable resources. An approach that has recently gained popularity advocates the use of biological (fermentation) processes to produce chemical commodities from agricultural feedstocks. Fueled by advances in the area of metabolic engineering, an array of products, ranging from polymers to polymer intermediates and industrial dyes, can now be produced by fermentation. With numerous such biological approaches currently under consideration, it is pertinent to analyze whether the proposed processes have the intended effect of sparing nonrenewable resources and benefiting the environment.

Fermentation-based processes offer intuitive advantages, such as aqueous processing environments, nontoxic waste, and most importantly the use of renewable, nonfossil feedstocks. In most cases, however, these benefits have not been critically weighed against an overall inventory of materials and energy required to generate a given product. This article offers a side-by-side comparison of a biological versus a conventional petrochemical plastic manufacturing process to illustrate the complexity of choices confronting society and the commodity biotechnology industry in the coming years.

Weighing the alternatives

Much has been made of the environmental shortcomings of conventional, fossil oil-based polymers, such as polyethylene, polypropylene, and polystyrene. While these polymers offer good material properties at a low price, their environmental impact and manufacture

has traditionally been viewed in a negative light. As a result, much effort has been dedicated to developing alternative plastic materials that are both biodegradable and produced from renewable resources, preferably of agricultural origin.

Of the various alternative polymers developed to date, polyhydroxyalkanoates (PHAs), a class of aliphatic microbial polyesters, have been considered among the leading candidates to replace conventional plastics on a large industrial scale¹. Like their petrochemical counterparts, PHAs are moldable, water insoluble, thermoplastic polymers. The most common PHA, poly-3-hydroxybutyrate (PHB), is a stiff, high melting point aliphatic polyester similar to many industrial polyolefins. Unlike polyolefins, however, PHAs can be synthesized by microorganisms, which can produce and store the polymer in the form of intracellular inclusions at levels exceeding 80% of the cell dry mass (see Fig. 1). These microbial polymers can be made entirely from glucose in a fermentation process and, in addition to offering favorable material properties, are completely biodegradable. Thus, the replacement of conventional plastics with PHAs has been promulgated as a desirable approach to solid-waste management and sustainable polymer production^{2,3}.

A cradle-to-grave analysis

Several factors contribute to the environmental impact and the degree of sustainability of a given product or material. In many instances, however, environmental impact is the result, not of the product per se, but rather of the consumption of raw materials and the release of waste products generated during manufacture. Thus, a "cradle to grave" analysis, which incorporates manufacturing practices, energy input/output, and overall material flows, is a good benchmark for assessing environmental impact and sustainability^{4,5}.

Contrary to the widespread belief that PHAs are a sustainable alternative to polymer production, a surprisingly high latent energy content is associated with their fermentative production. By considering the utilities required to make glucose from corn, it is possible to estimate that a PHA fermentation process consumes 22% more steam, 19-fold more electricity, and 7-fold more water than a conventional process for producing polystyrene. While only polystyrene is directly derived from fossil oil, both polystyrene and PHAs require energy in their manufacture. As

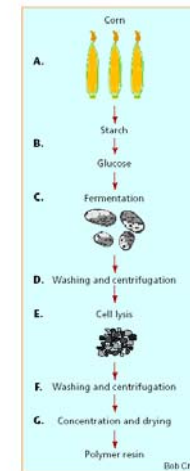
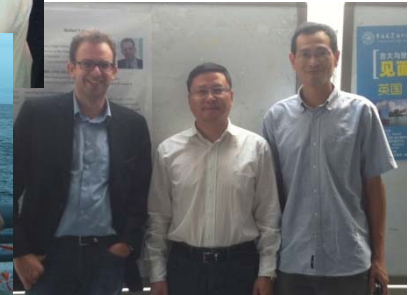
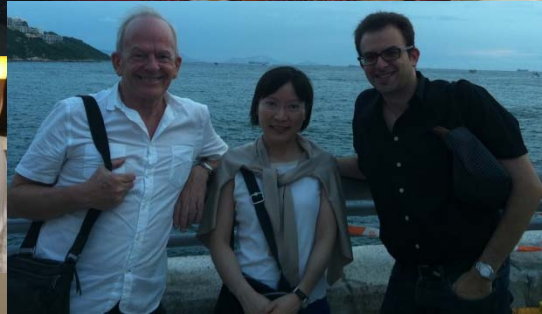


Figure 1. The analyzed multistep PHA production process. (A) Growing and harvesting corn. (B) Processing of corn to yield glucose. (C) Sterilizing the medium and conducting a fermentation process by which glucose is converted to PHA (note cells containing PHA polymer in the form of intracellular inclusions). (D) Recovering the biomass containing the polymer and washing it by centrifugation. (E) Disrupting the cell wall and releasing the polymer from the cells. (F) Washing the polymer by centrifugation. (G) Drying the polymer slurry to a powder that can be processed to a final consumer product.

Tillman U. Gerngross is assistant professor of biochemical engineering, Thayer School of Engineering, Dartmouth College, Hanover, NH 03755 (tillman@dartmouth.edu)



Many thanks for your attention!!

