

# Green Chemistry And Sustainability

**James Clark**

Green Chemistry Centre of Excellence  
Chemistry Department  
University of York, UK

*[www.greenchemistry.net](http://www.greenchemistry.net)*



**Chemicals are everywhere  
and vital for a growing  
population seeking higher  
living standards**

Research

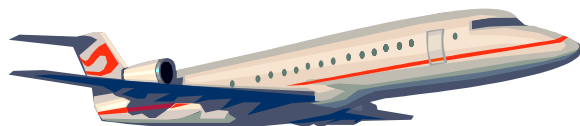
Industry

Networking

Education



# Benefits of the Chemical Industry



But chemicals are unpopular with the public and government pressure through legislation is growing - especially in the EU.....

Research

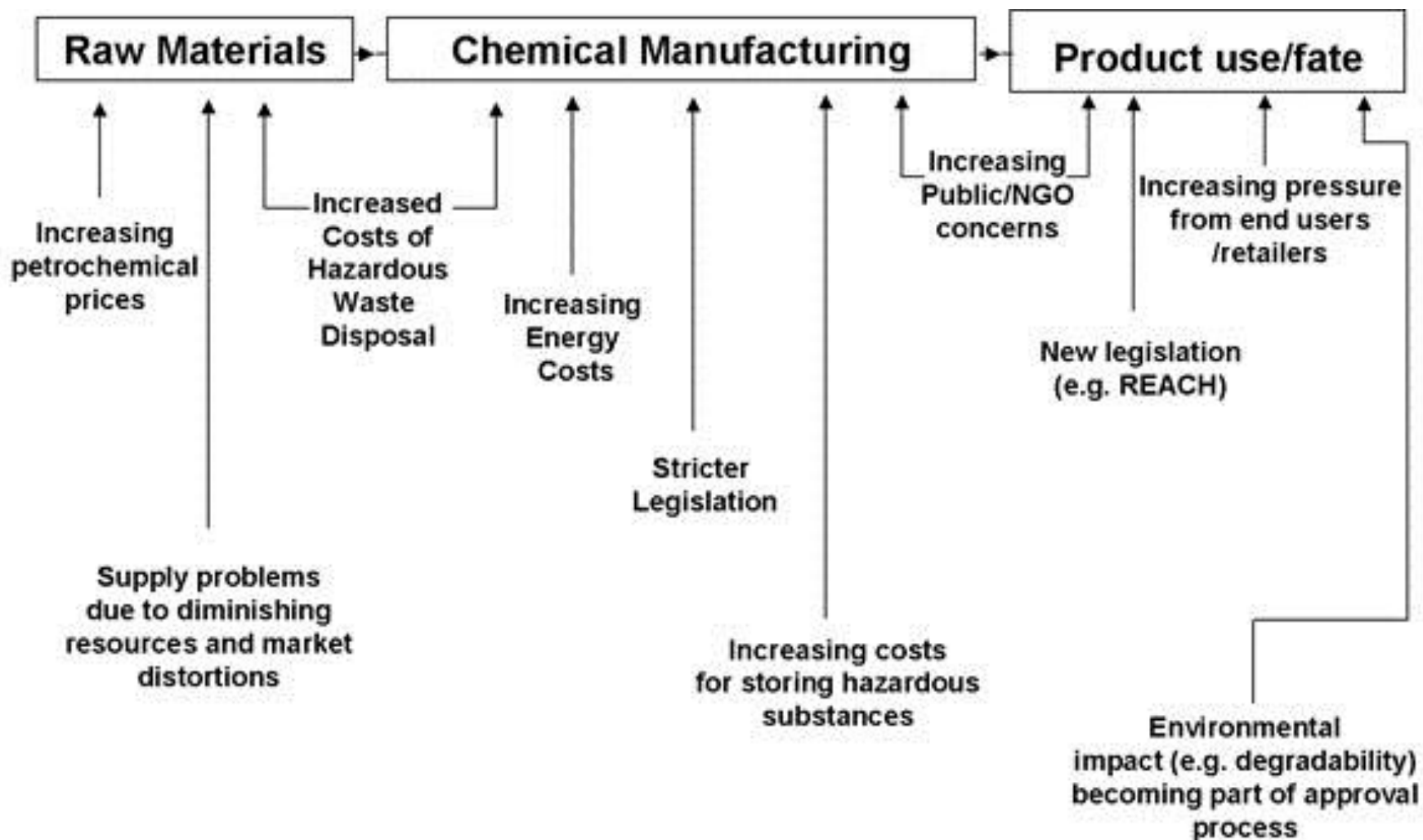
Industry

Networking

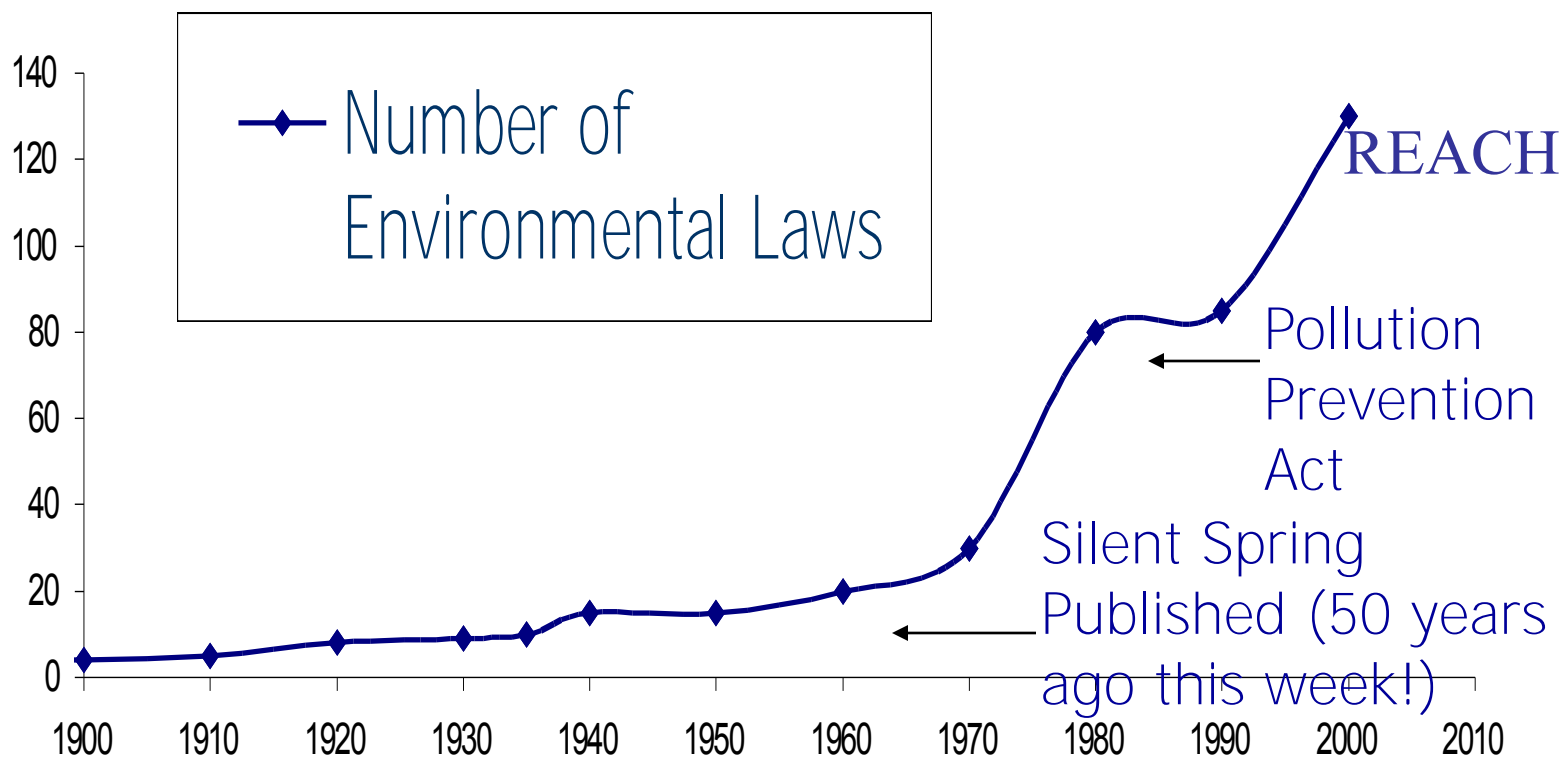
Education



# Pressures on Chemicals across the Lifecycle



# Background to Green Chemistry



**We need Green Chemistry  
to make safe products using  
cleaner manufacturing  
based on *renewable  
resources***

Research

Industry

Networking

Education





# Making your raw material *more sustainable*

*The chemical industry is too dependent on traditional virgin sources of raw materials - sources that are becoming scarce, expensive and unreliable, and often from regions with uncertain social and political conditions*

Research

Industry

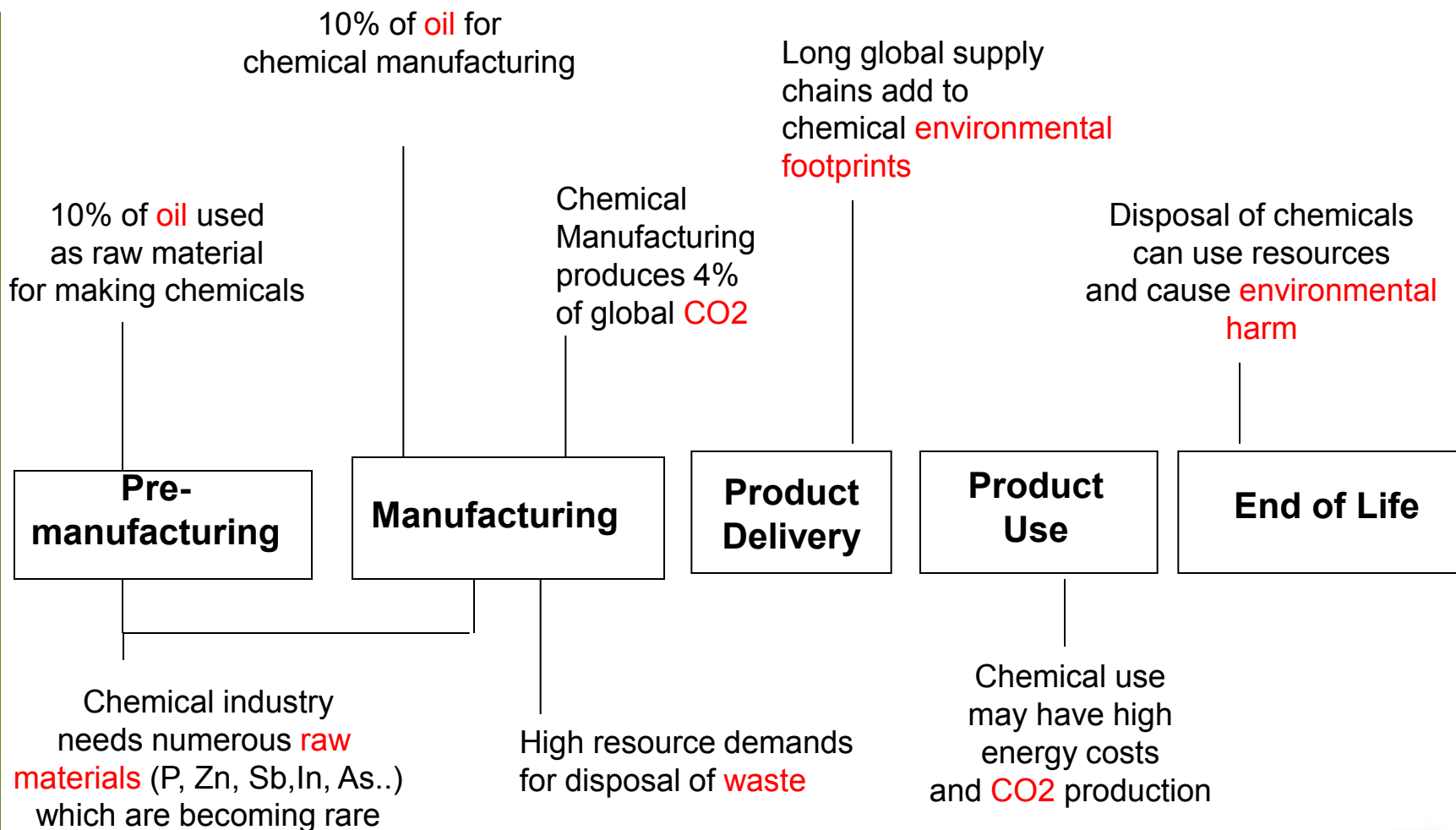
Networking

Education





# Resource demands of chemical manufacturing



Research

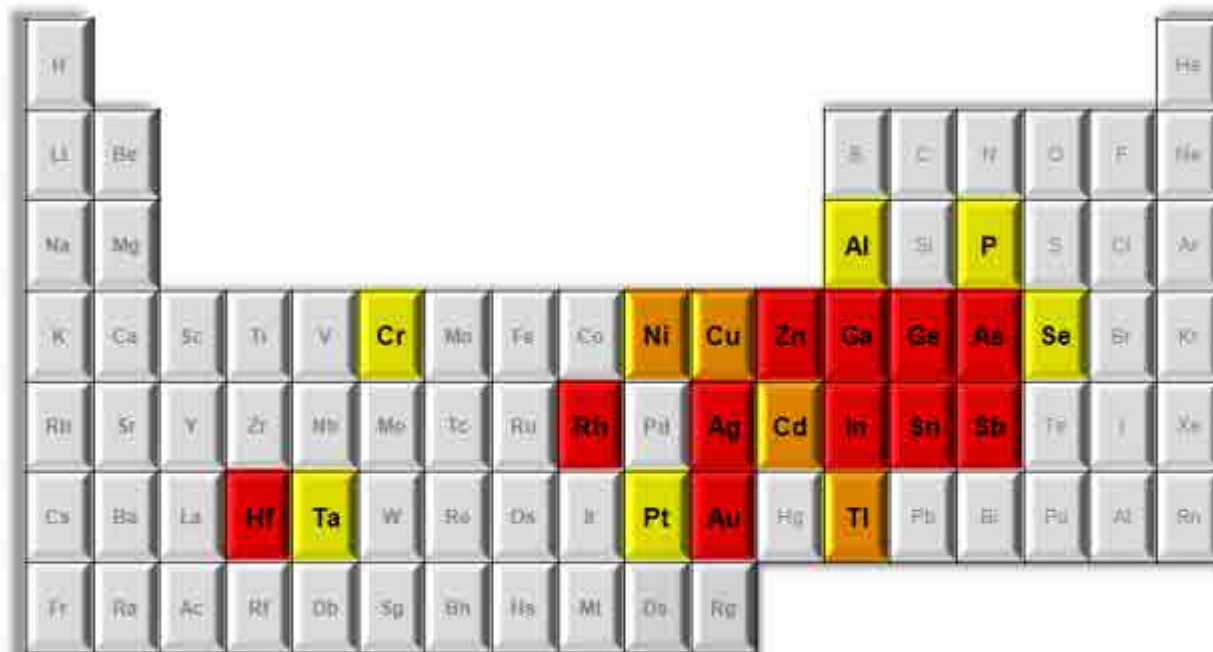
Industry

Networking

Education

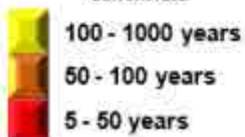


# Elemental unsustainability



## NUMBER OF YEARS LEFT

If continued to be consumed at current rate



...and this is not up-to-date.....



**We turn carbon and other elements  
from a resource to a product  
and then to a waste....**

**We have to remove waste from  
our elemental cycles.....  
and move towards closed-loop manufacturing**

Research

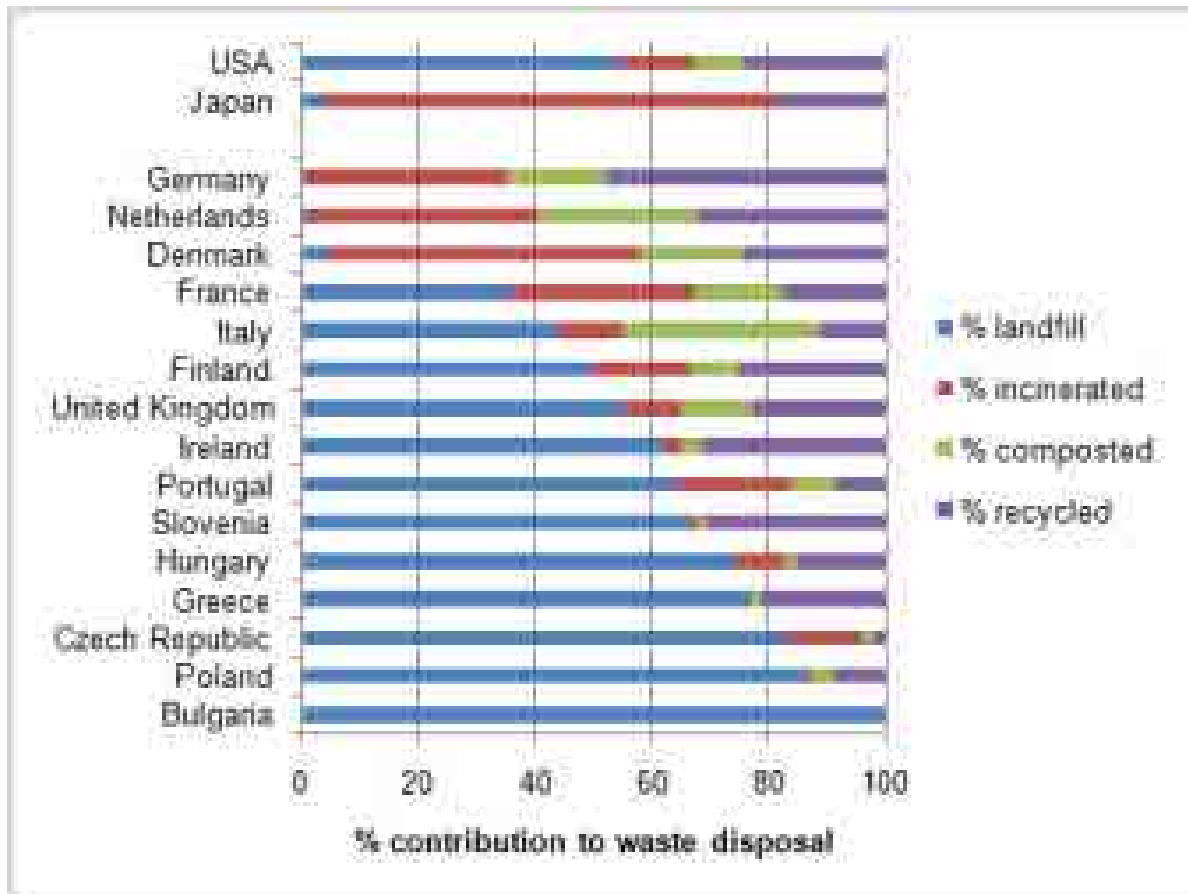
Industry

Networking

Education



# What do we do with our waste?



*We treat our waste....like a waste....what a waste!!!*



# Waste is tomorrows resource



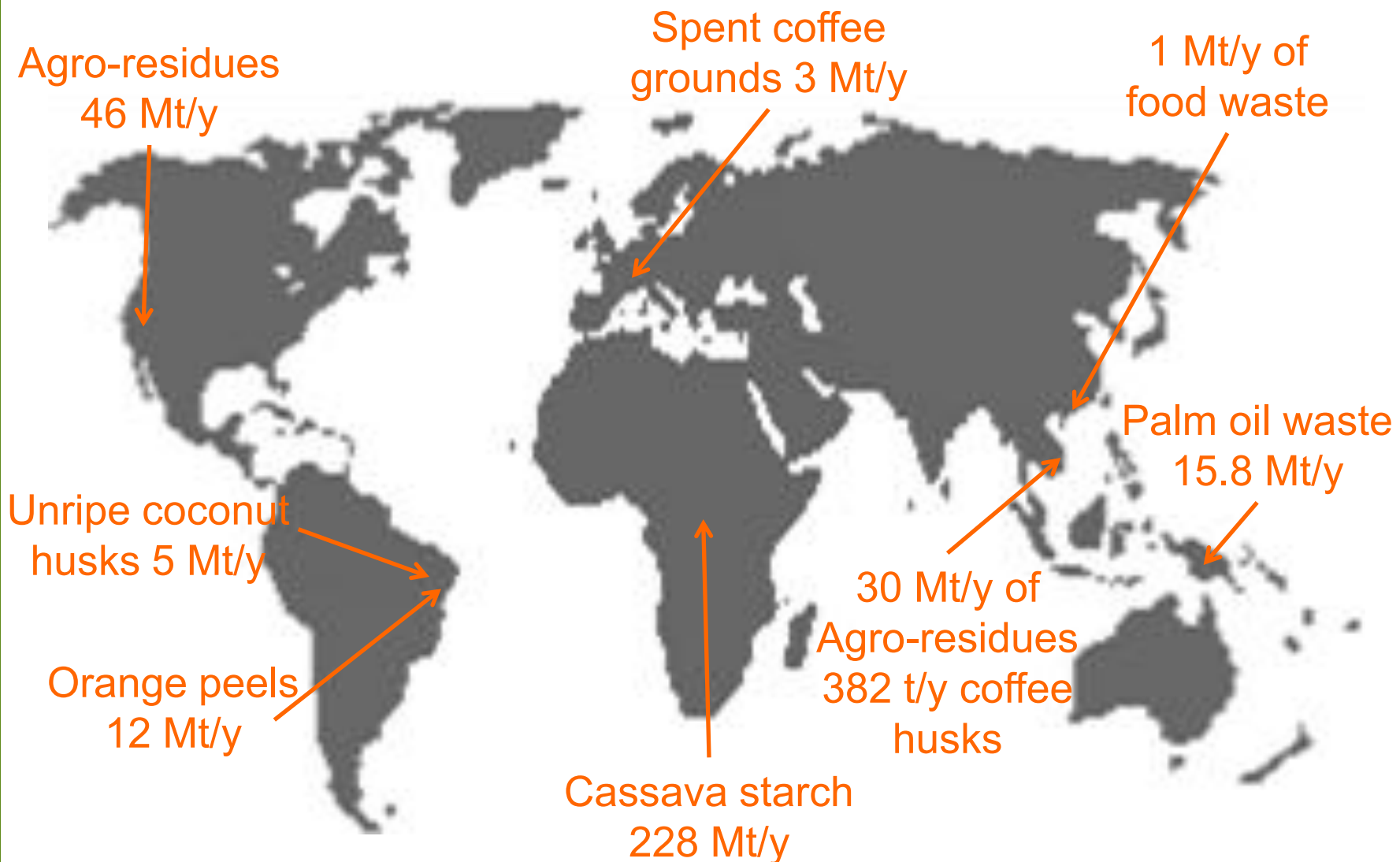
*We need to encourage the greater use of chemically rich waste as a resource*





## Food supply chain waste:

## A world of possibilities...



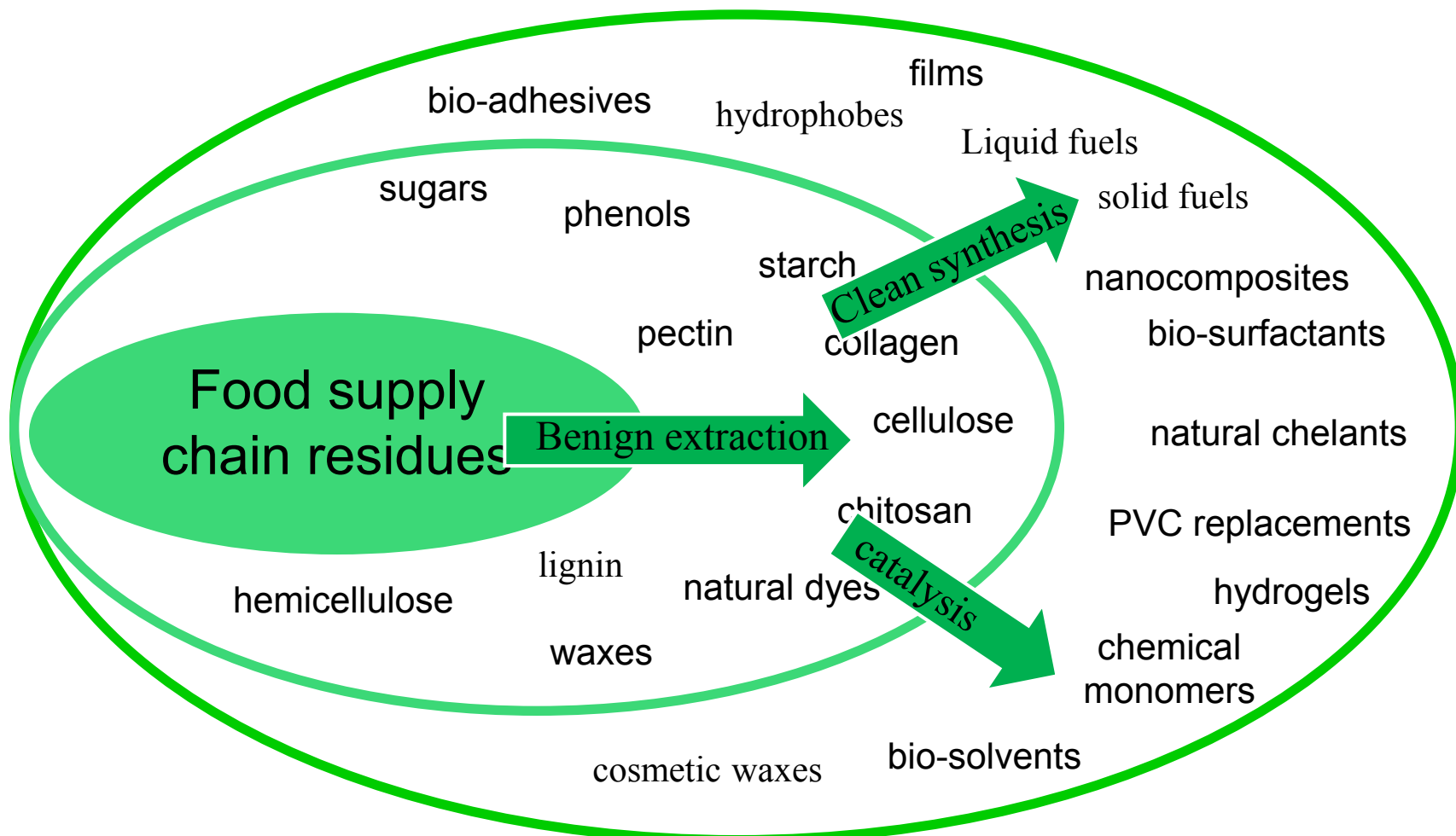
Research

Industry

Networking

Education

# Chemicals from food waste



Research

Industry

Networking

Education



# *Sustainable sources of Carbon*

*Over 90% of organic chemicals are based on petroleum feedstocks  
- this is not sustainable*

Research

Industry

Networking

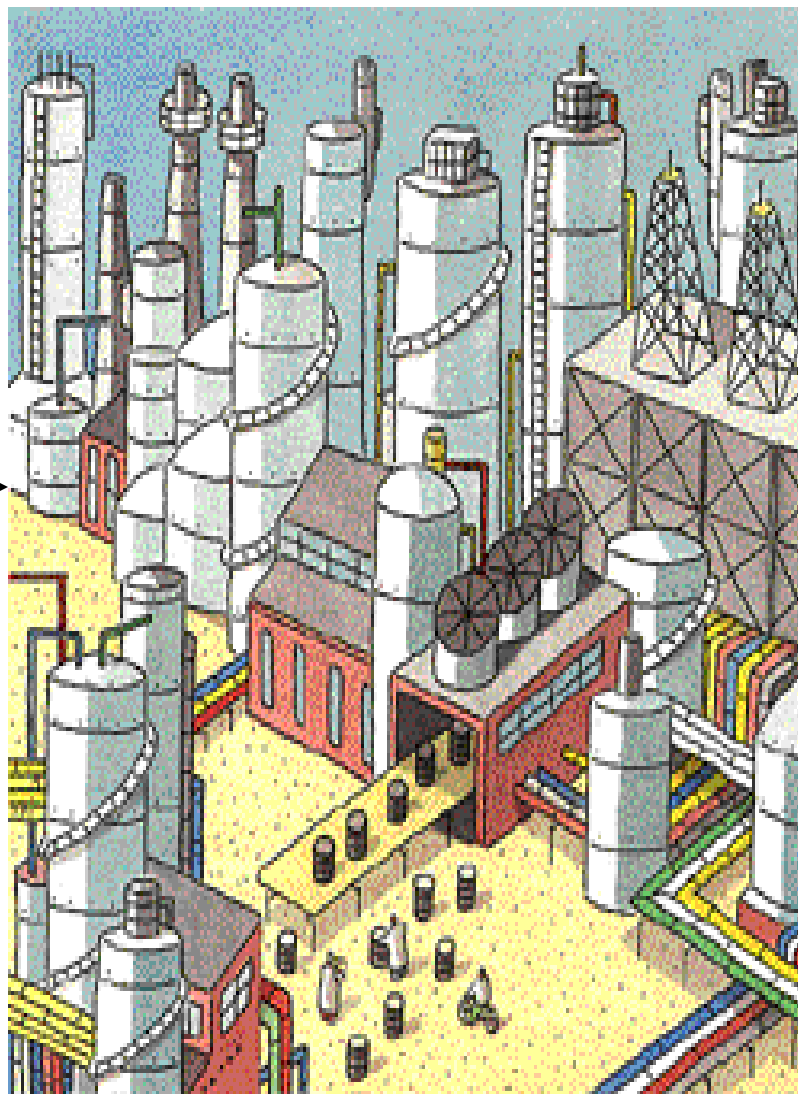
Education



# Petroleum Refinery



Petroleum  
feedstock



- Fuels
- Solvent
- Bulk chemicals
- Plastics
- Fibres
- Fine chemicals
- Oils

# Bio-refinery

Biomass  
→



→ Fuels



→ Solvent



→ Plastics



→ Bulk chemicals

→ Fine chemicals



→ Fibres

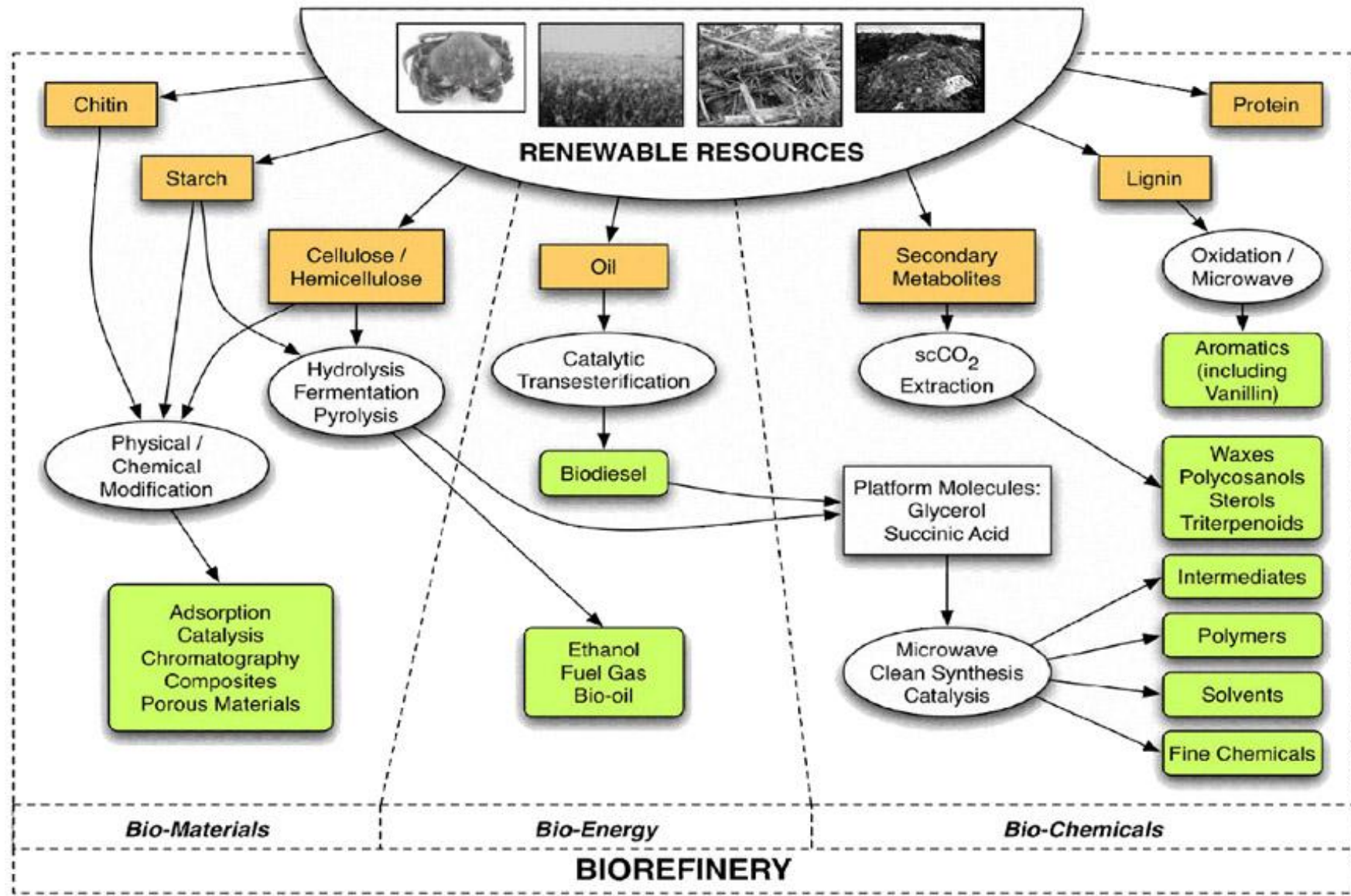


→ Oils



**Don't use food quality feedstocks!!**

# Renewable Resources & Biorefineries



Research

Industry

Networking

Education

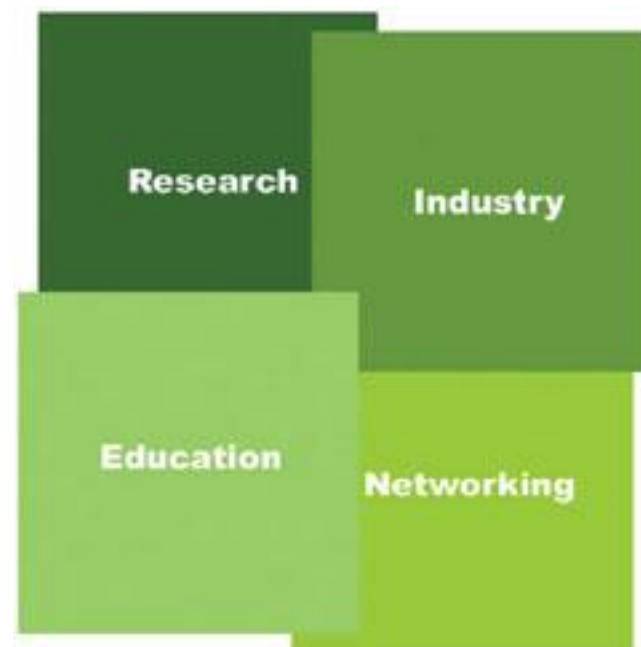


# Green Chemistry at York

## Activity Areas

The Centre's Activities can be grouped into 4 areas:

- **Research**
- **Industry** collaboration
- **Education**, including development of teaching and promotional materials
- **Networking** with all chemical stakeholders



# GREEN CHEMISTRY CENTRE OF EXCELLENCE

**Renewable  
Materials**

**Clean Synthesis  
&  
Platform  
Molecules**

**Training,  
Education  
and  
Networks**

**Natural Solvents  
&  
Biolubricants**

**Microwave  
Processing**

Research

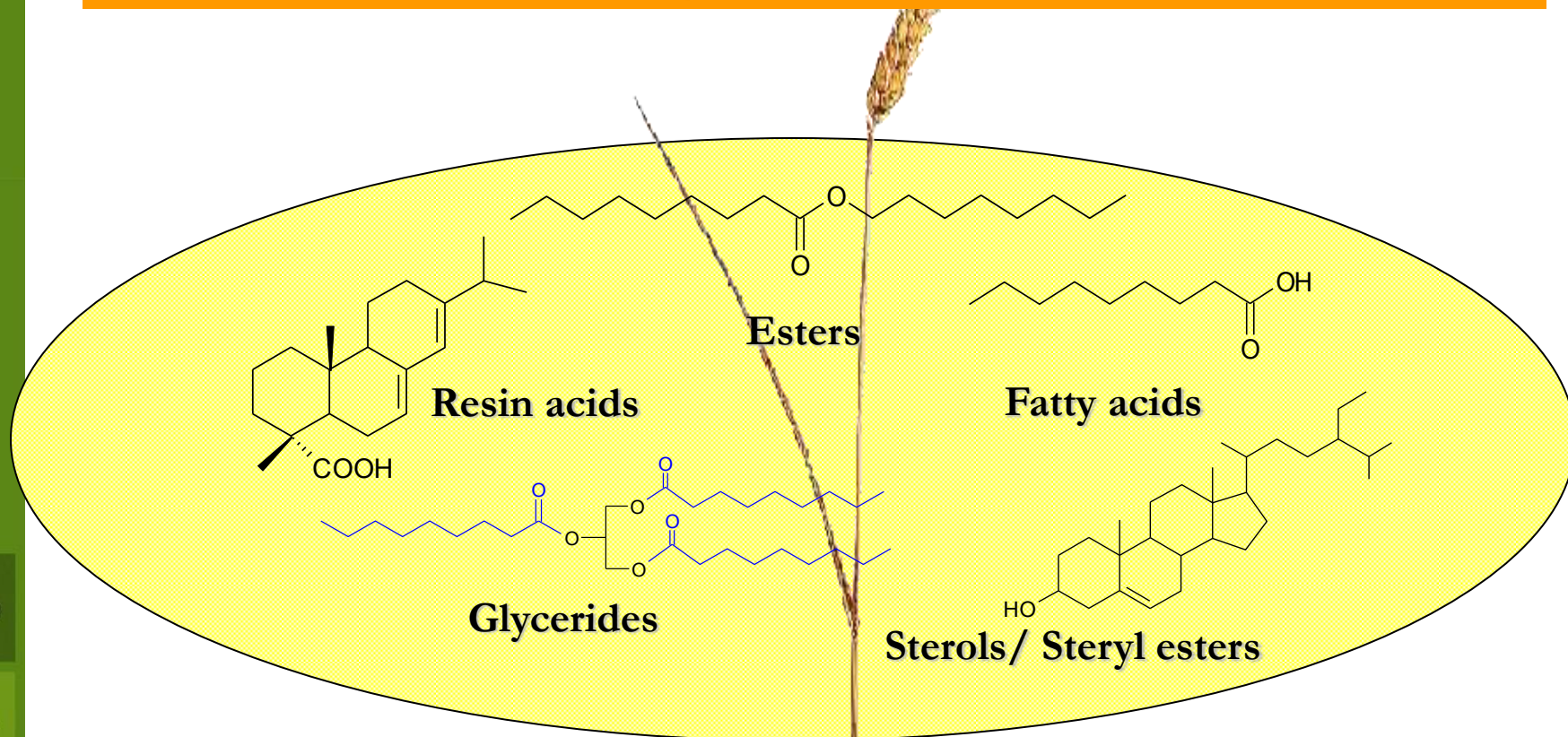
Industry

Networking

Education



# Plant waxes (surface chemicals)

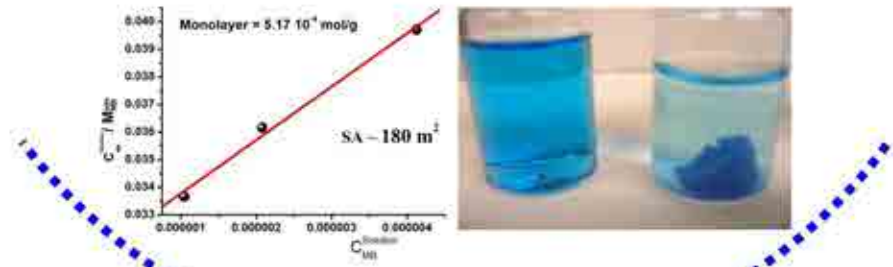


*They need to be extracted using green solvents...*



# Food waste....

## Porous polysaccharide-derived materials



### Native Starch

### Expanded Starch

**Retrogradation**

**Gelatinisation**

**Solvent Exchange**

The diagram illustrates the structural changes in starch granules. On the left, native starch granules are shown with a crystalline core (8 nm) and an amorphous shell (9 nm). An arrow labeled 'Gelatinisation' points to a central representation of gelatinized starch chains. A second arrow labeled 'Solvent Exchange' points to an expanded starch structure on the right, which has a highly porous, disordered structure with a pore size of 7-9 nm. A blue dotted arc labeled 'Retrogradation' connects the expanded starch back to the native starch.

10  $\mu\text{m}$

Surface Area  $< 1 \text{ m}^2\text{g}^{-1}$   
Pore Volume  $< 0.002 \text{ cm}^3\text{g}^{-1}$

2  $\mu\text{m}$

Surface Area  $> 180 \text{ m}^2\text{g}^{-1}$   
Pore Volume  $> 0.5 \text{ cm}^3\text{g}^{-1}$

# STARBONS®

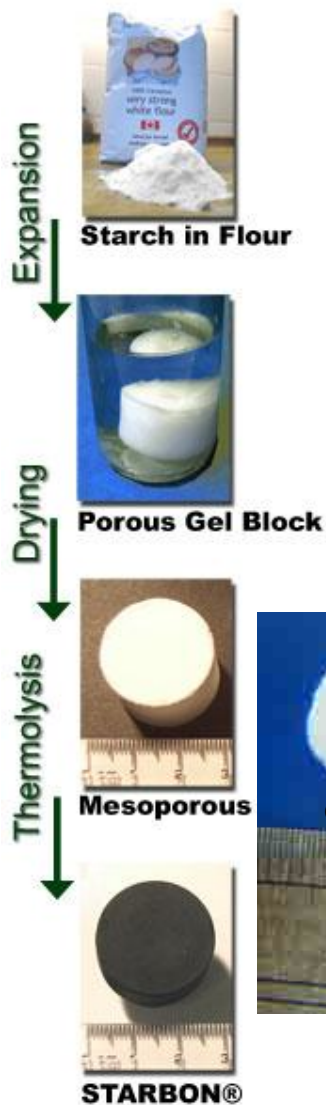
*An exciting new class of carbonaceous materials*

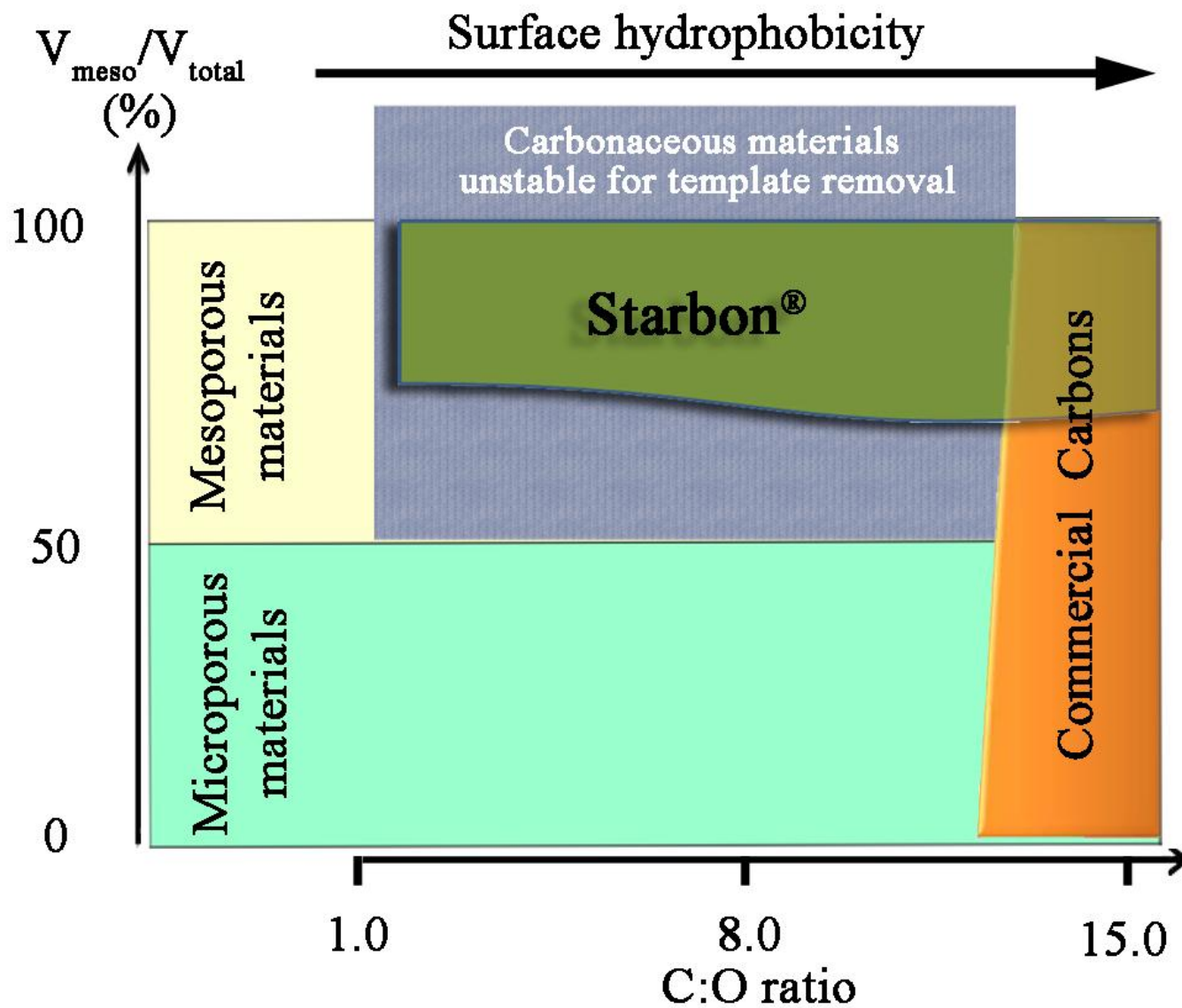
## Properties

- Adjustable surface energies and polarities
- High mesoporosity and surface areas
- Readily functionalisable with acid/base/metal functionality
- Excellent solvent stability
- Good chemical and heat resistance
- Controllable electrical conductivity
- Formation of composites and blends
- Particulate/ monolithic forms

## Applications

- Separation media
- Catalysis
- Absorbency
- Water purification
- Fuel cells





# Making your process *greener*

*Chemical manufacturing is largely based on chemistry that is complex, energy-, solvent-, and water-intensive and produces a lot of CO<sub>2</sub> and considerably more (often hazardous) waste than product*

Research

Industry

Networking

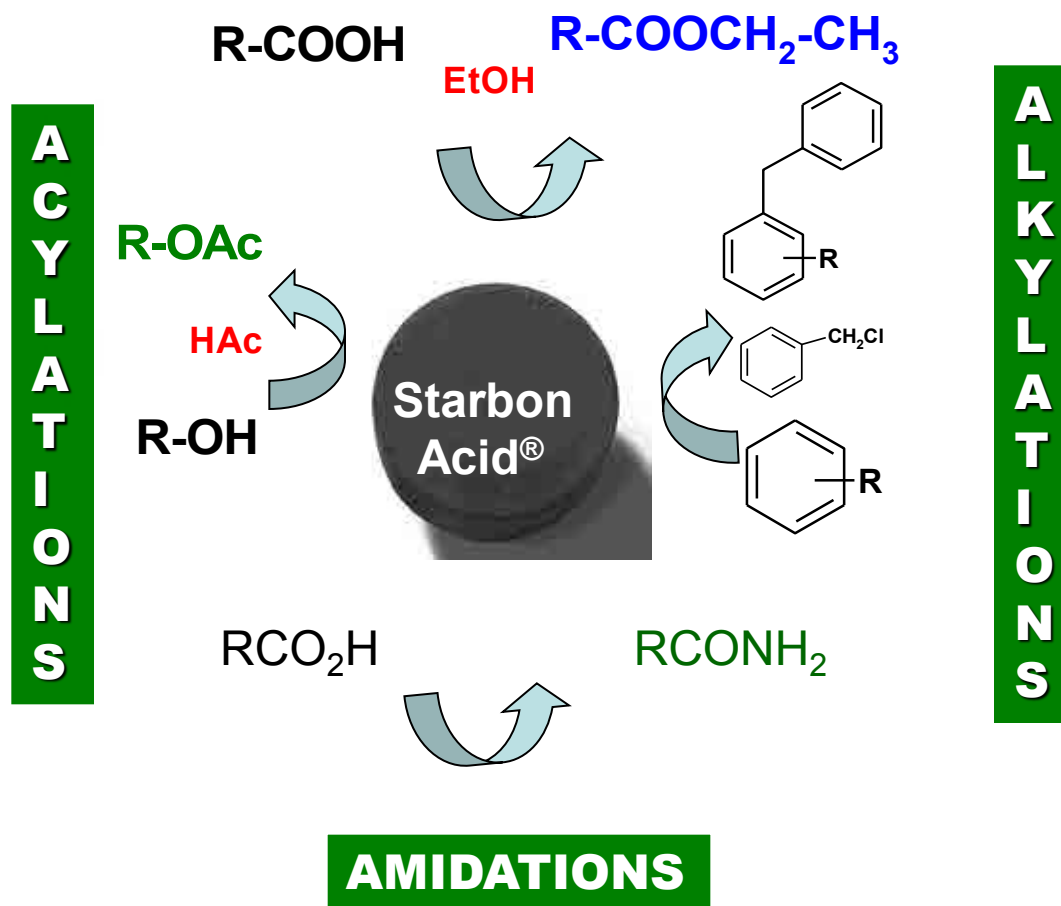
Education



# STARBON<sup>®</sup> ACIDS as catalysts

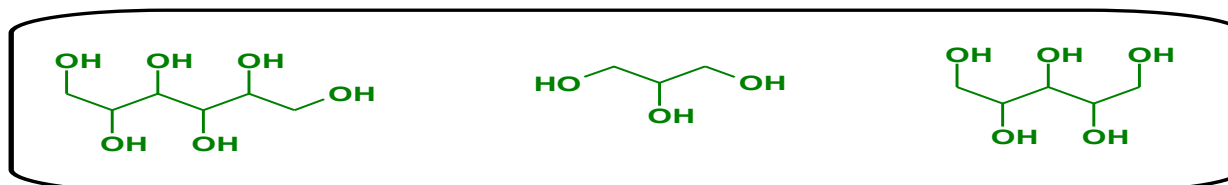
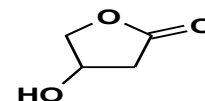
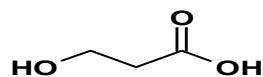
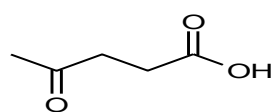
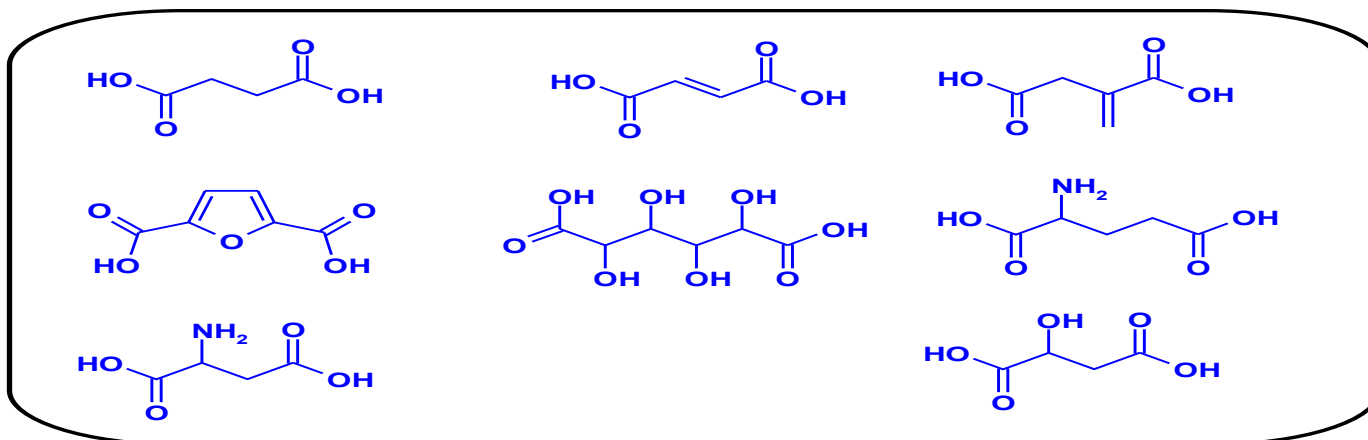
## *direct downstream chemistry on fermentation broths*

### ESTERIFICATIONS





## Major platform molecules via fermentation



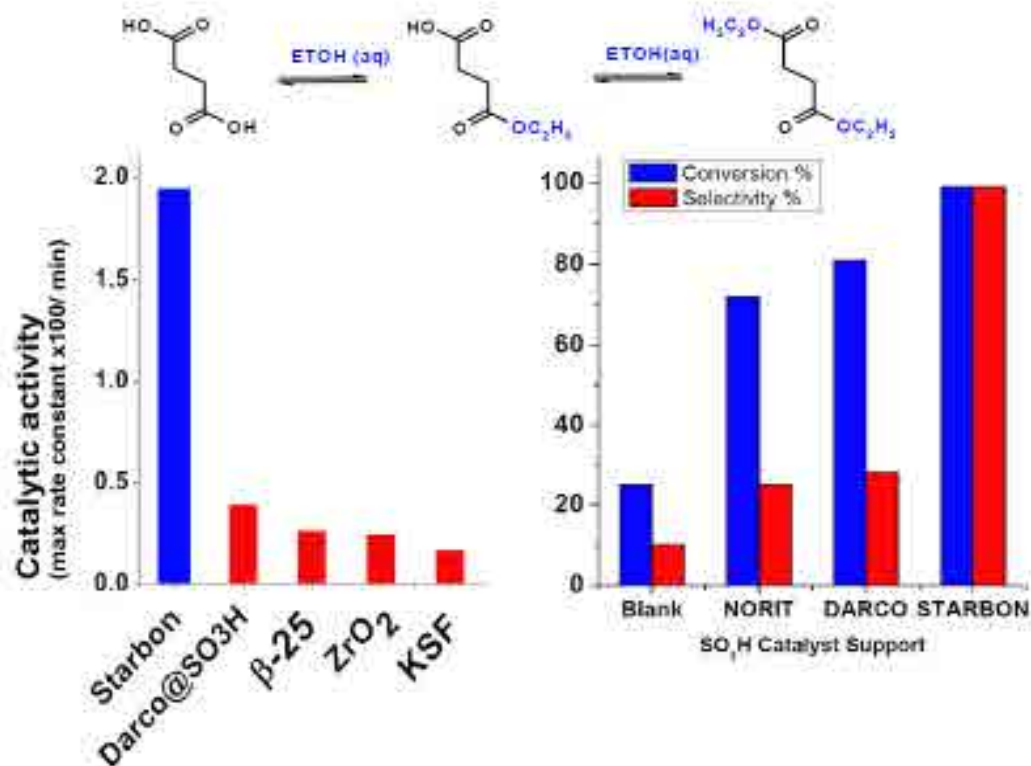
Clean  
Synthesis  
methods

A very wide range of useful products

# Starbons- a new generation of water-tolerant catalysts

## -Acid catalysis directly on fermentation broths

Catalytic activity, conversion and selectivity of STARBON® acids in comparison to other solid acids (and supports) in aqueous ethanol esterification of succinic acid



Esterification of succinic acid.







# Starbon® Technologies Ltd

The bio-based mesoporous material company



**Starbon® is sustainable, reusable and environmentally benign.**

Visit us at the CIA Stand at ChemSpec

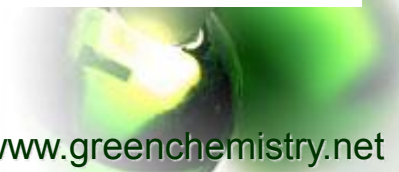




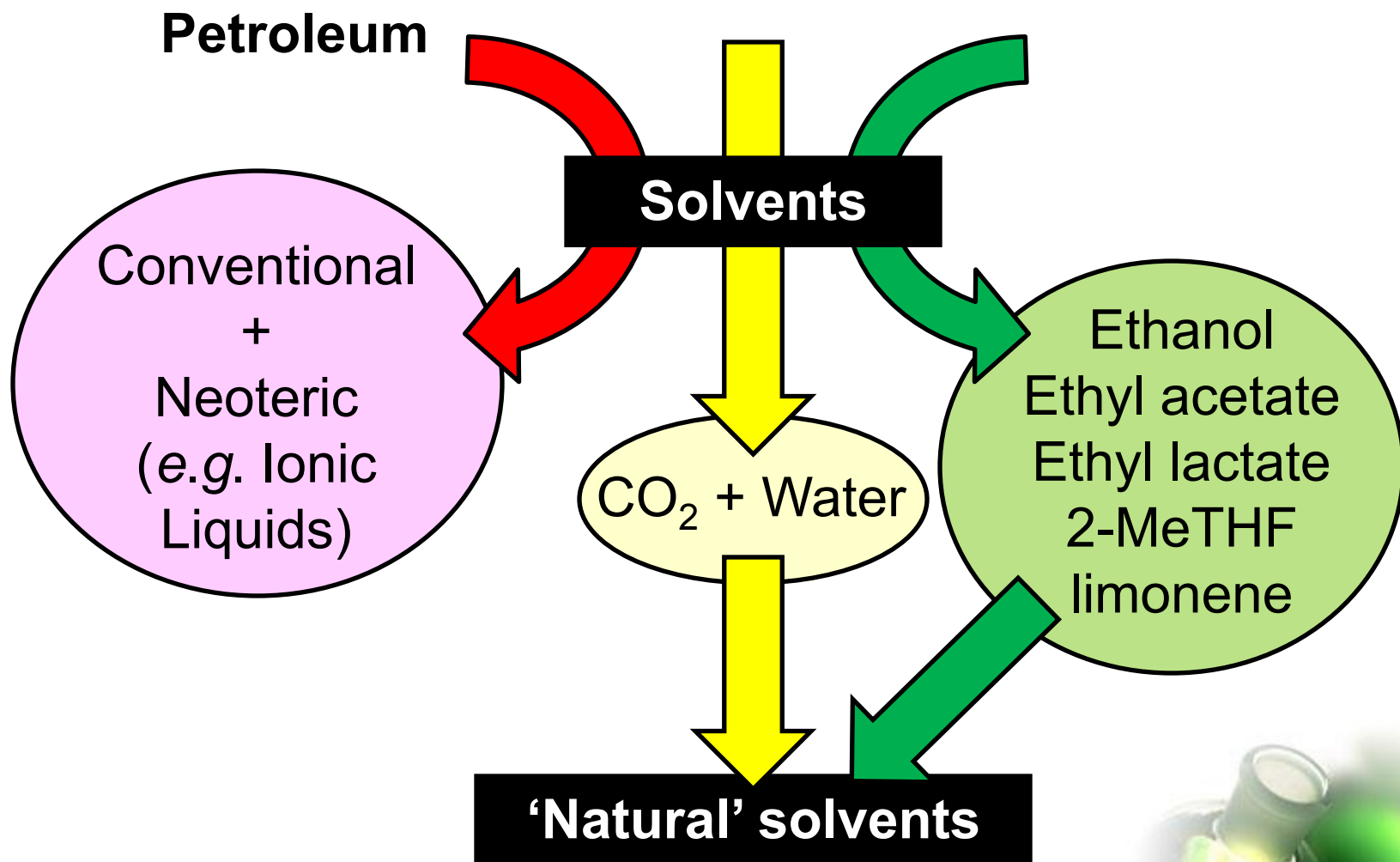
# Starbon® Technologies Ltd

## Starbon® product Series

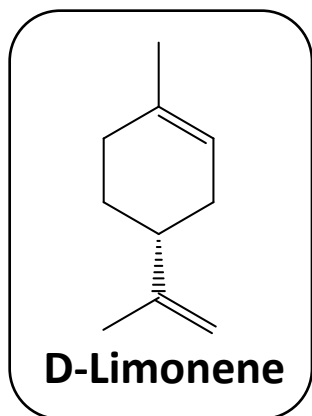
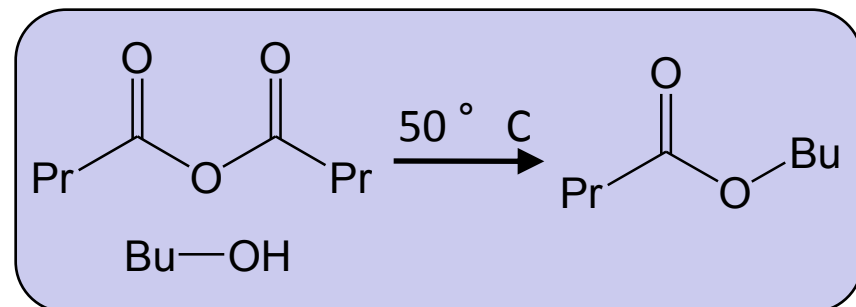
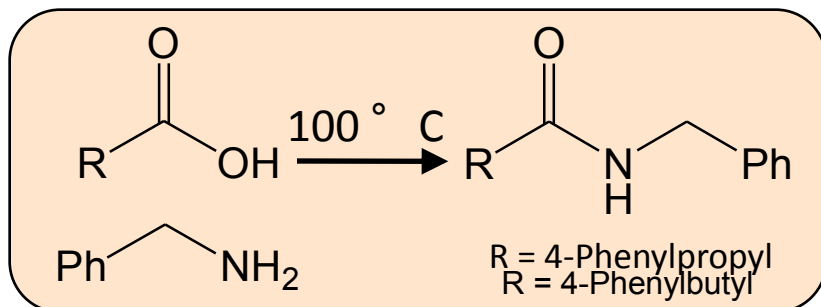
	Application areas	Key advantages	Benefits
<b>Starbon® C SERIES</b>	Catalysis particularly esterification in aqueous media	Aqueous systems Recoverable and reusable Improved selectivity (v. Acid Resins)	Active in aqueous systems Ease of product isolation Reduced catalyst use
<b>Starbon® S SERIES</b>	Separation by chromatography of complex mixtures with Starbon® as the stationary phase	Better separation Greener technology (v. PGC)	Higher productivity Separations effected that are difficult or impossible by other methods
<b>Starbon® P SERIES</b>	Purification of water and clean up of waste streams	Captures larger molecules Faster adsorption rate Recoverable and reusable (v. Activated Carbons)	Removal of harmful organics Transferable Global availability of starch
<b>Starbon® R SERIES</b>	Recovery of precious metals	Reductive adsorption of noble metals (v. Activated Carbons)	More efficient and effective recovery of precious metals



# Greener Solvents

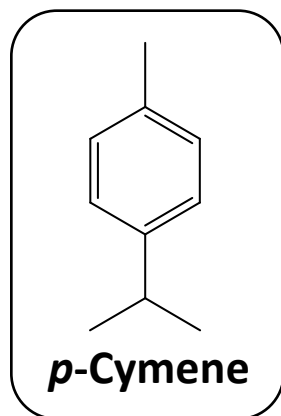


# Amidation and Esterification in Bio-Solvents



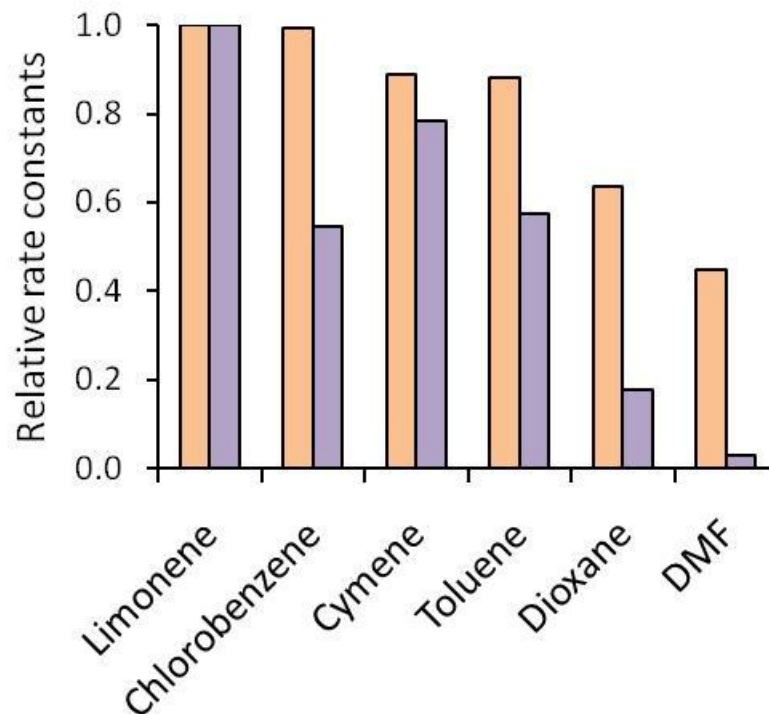
scCO<sub>2</sub> extraction

Orange peel

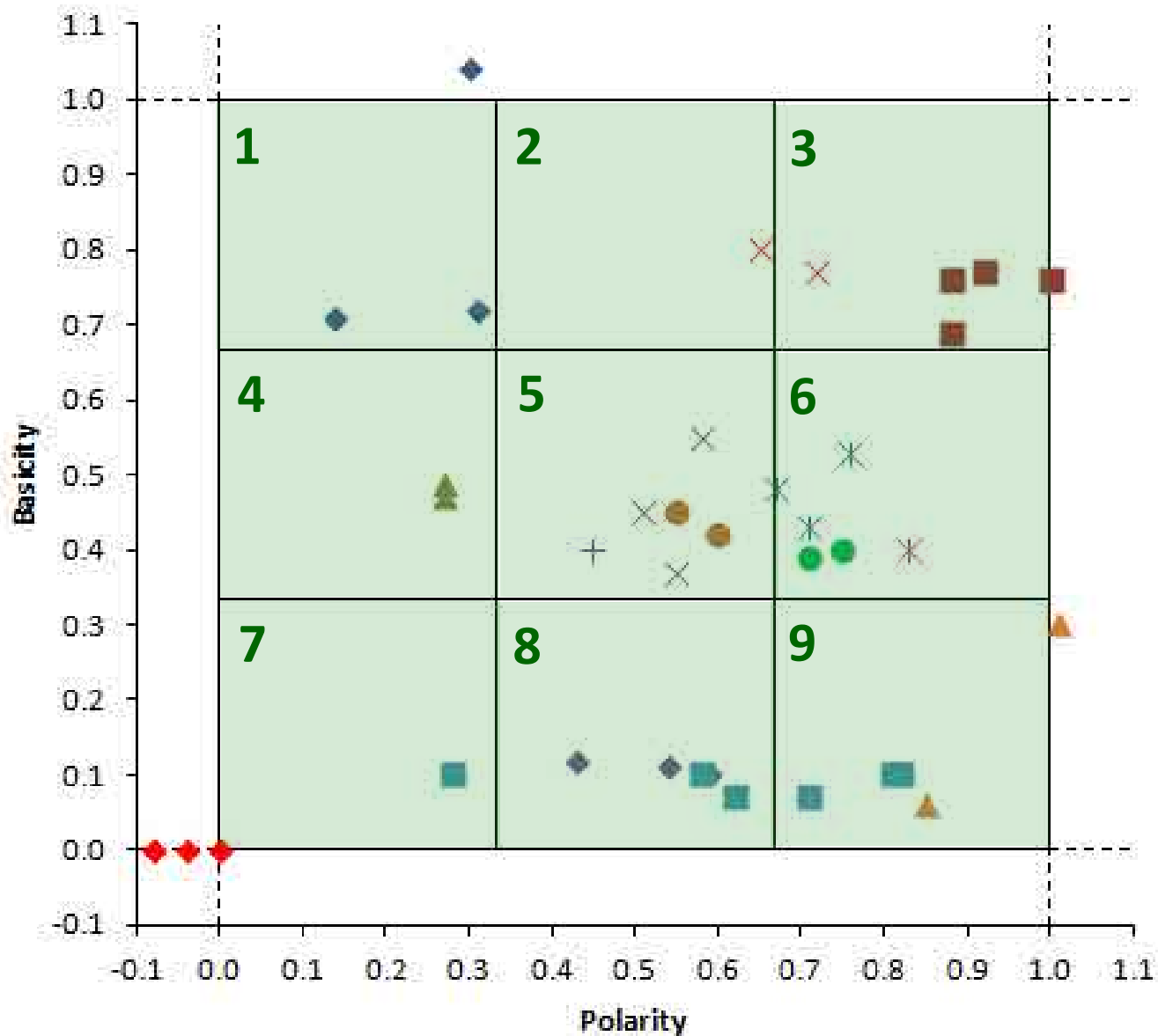


O<sub>2</sub> + Pd-γ-Al<sub>2</sub>O<sub>3</sub>

Eucalyptus oil



# Solvent Polarity Map (Aprotic)



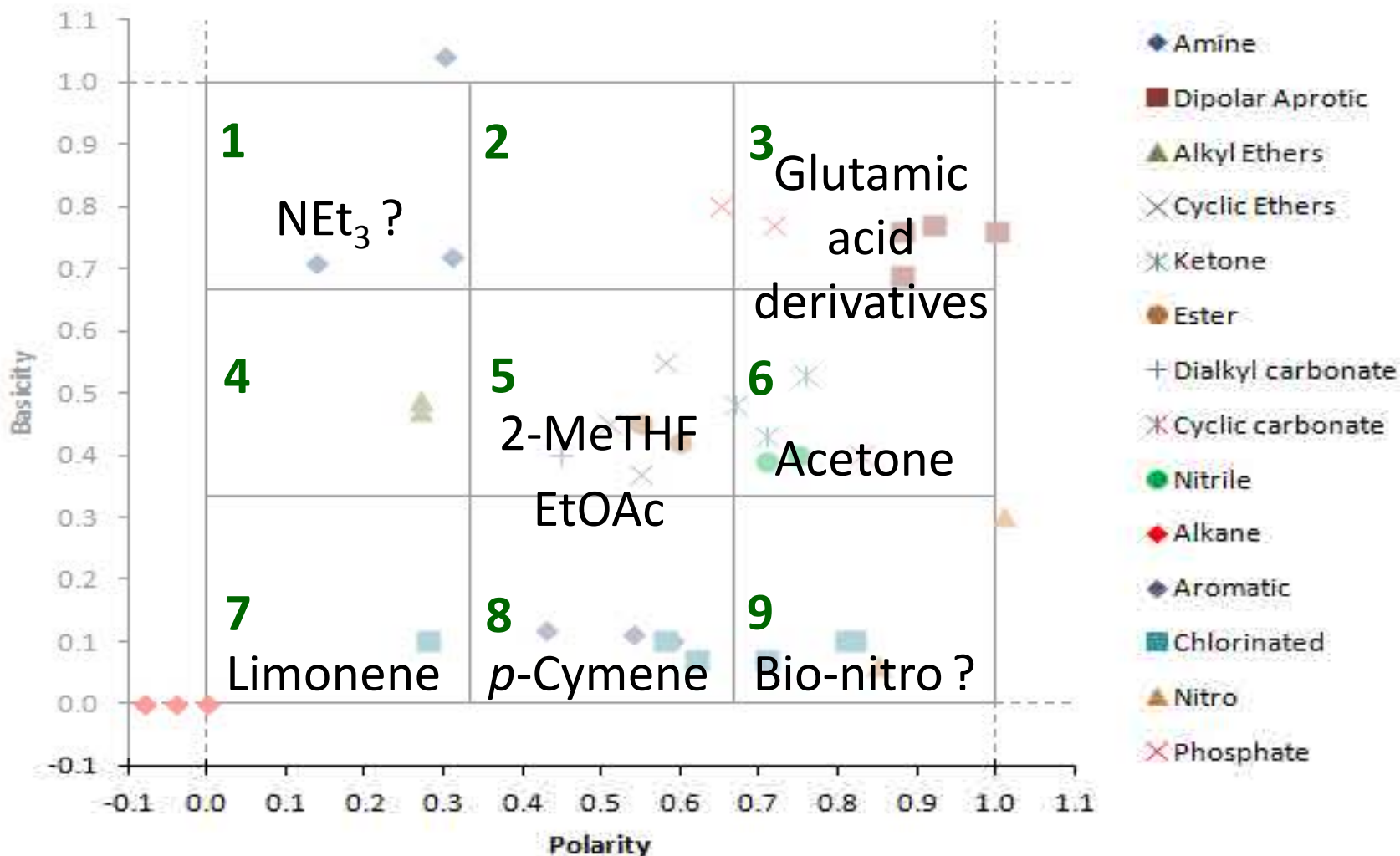
Research

Industry

Networking

Education

## Sustainable Solvent Polarity Map (Aprotic)



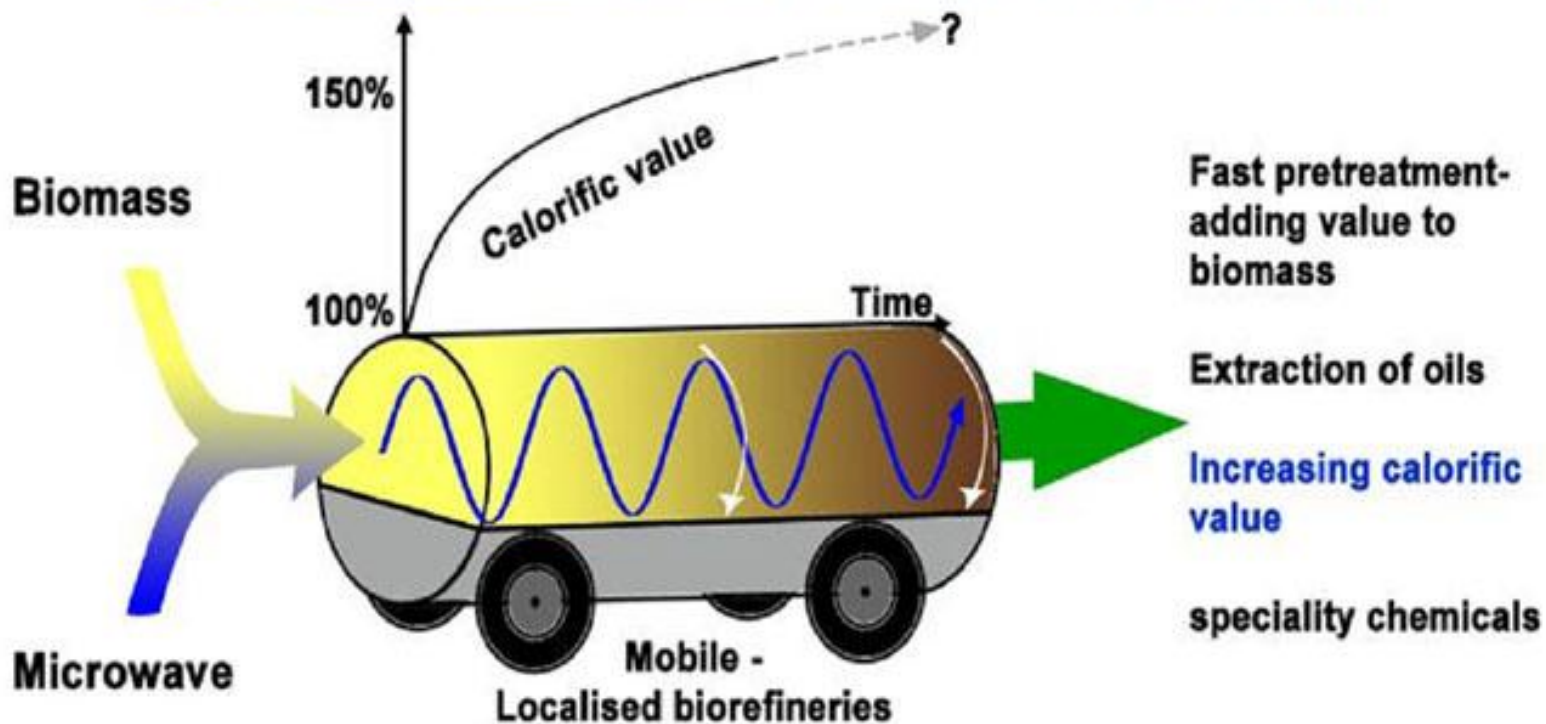
New from the GCCE:

*Sustainable Solvents Selection Service- S4*



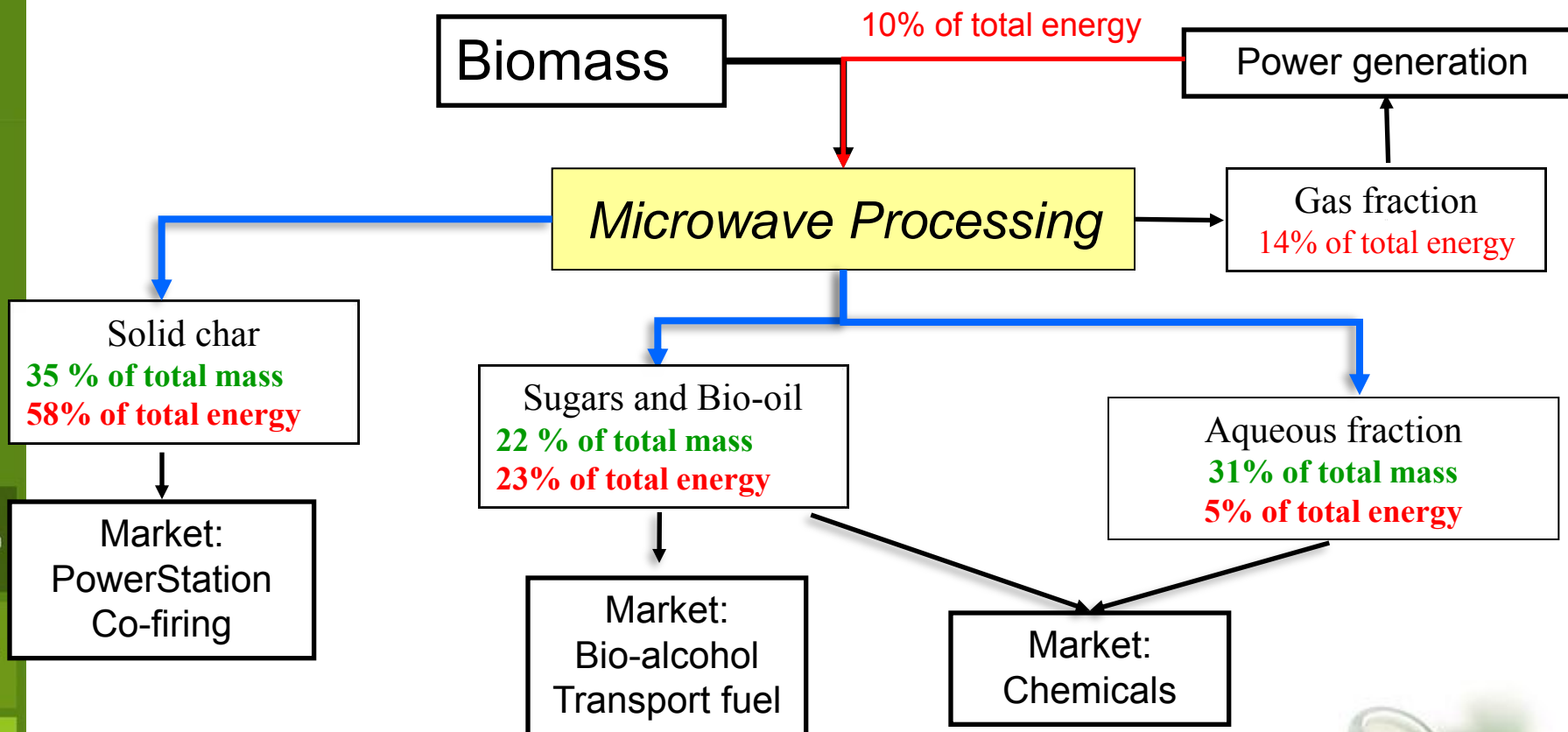
# Microwave activation of biomass

## *development of an alternative method of decomposing biomass*





# Microwave Biorefinery Flow Chart



# Making your product *greener*

*Social, environmental, legislative, supply chain and worldwide political pressures make the introduction of greener products imperative*

Research

Industry

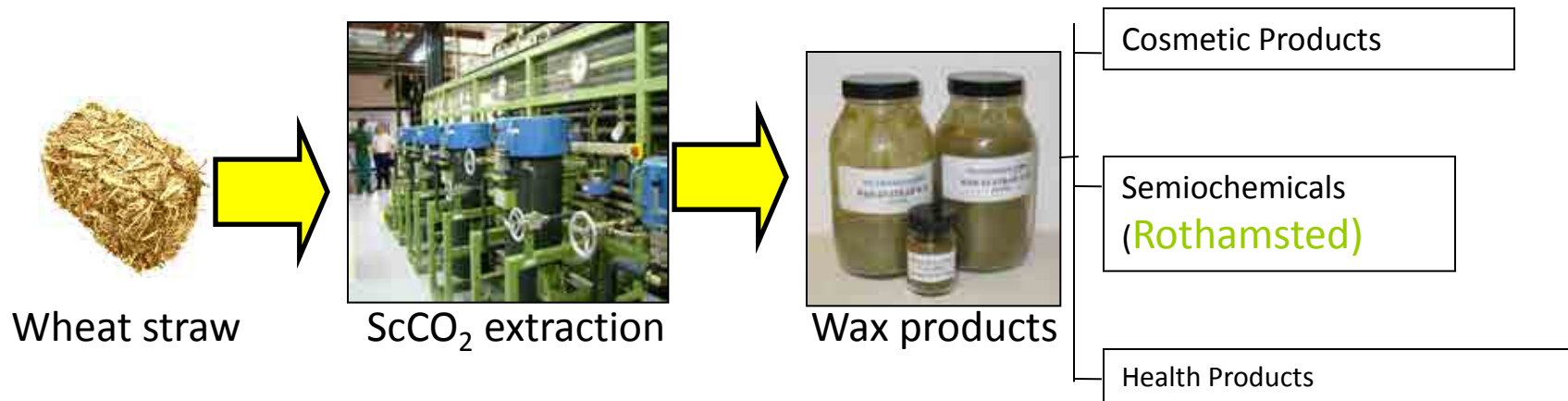
Networking

Education



## Eco-waxes

Charles Jackson Farms - Botanix - Croda - L'Oreal - Processum



“Natural” products are very desirable...they need to be:

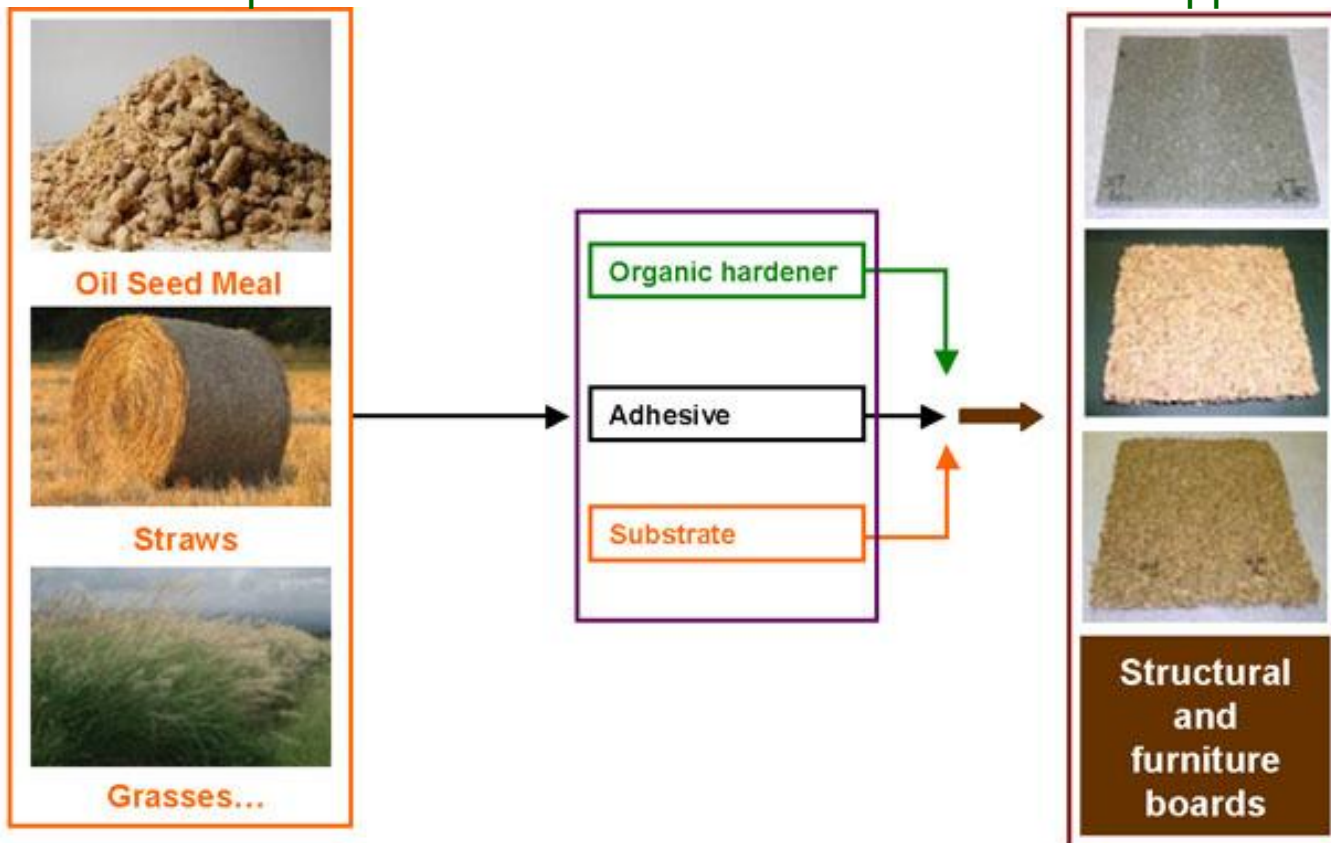
- *derived from natural resources*
- *extracted using “natural” solvents (H<sub>2</sub>O, EtOH, CO<sub>2</sub>)*
- *modified only by “natural” methods (biocatalysis)*

and for the residues.....

# Green Office

## Velcourt-Bical-BCC-PQ-B&Q-Compak

Bio-based composite materials for structural and furniture applications

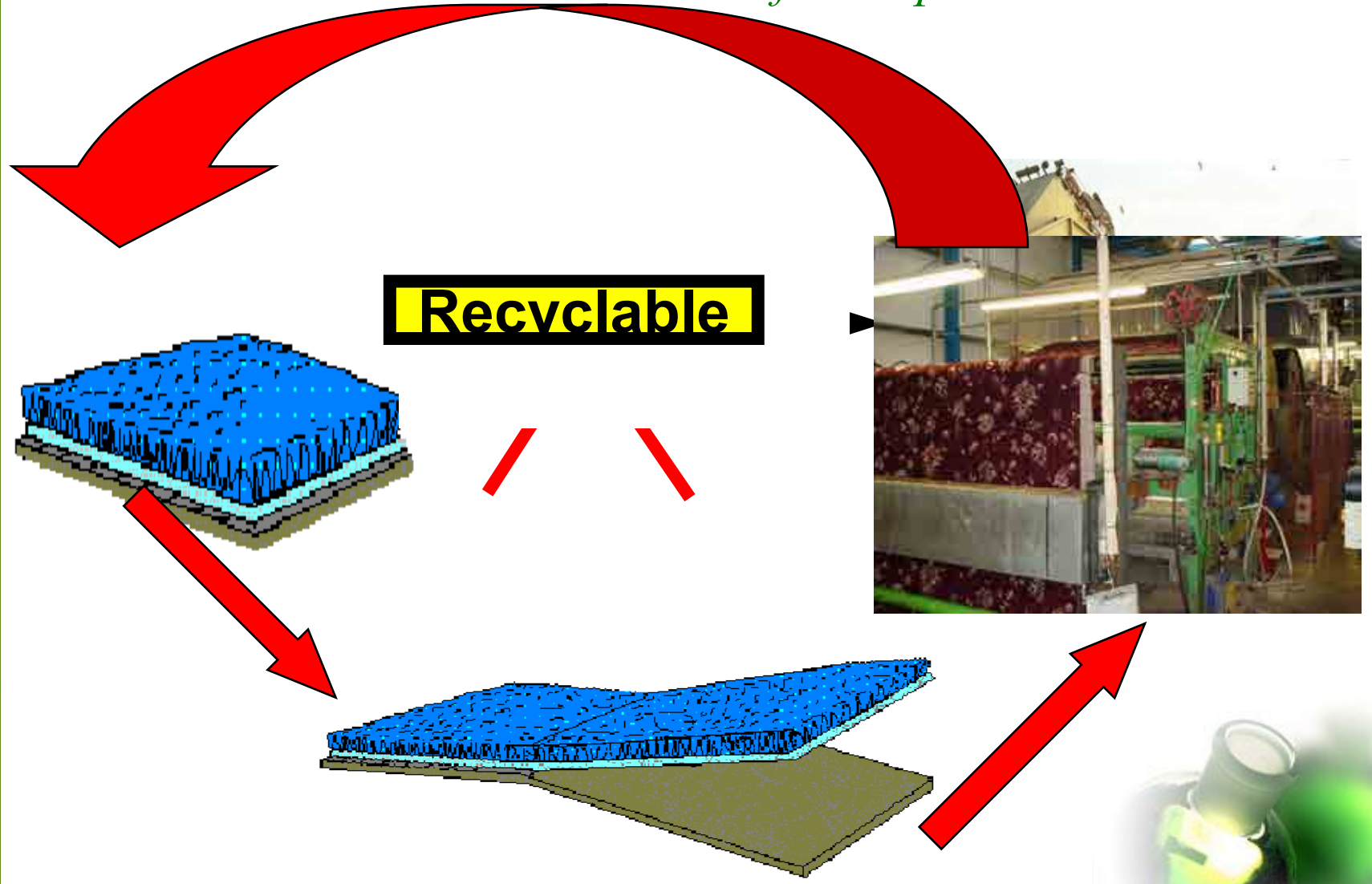


Agricultural and related residues

Overall good metrics for sustainability, greener products, waste avoidance and low environmental impact manufacturing

# York-Interface-Itac-Contract Chemicals

*Fire-resistant switchable adhesives for carpet tiles...and more...*



**Recyclable**



- Research
- Industry
- Networking
- Education

*One type of future biorefinery  
based on single large volume feedstock  
and using green chemical technologies  
to make a range of products*

Research

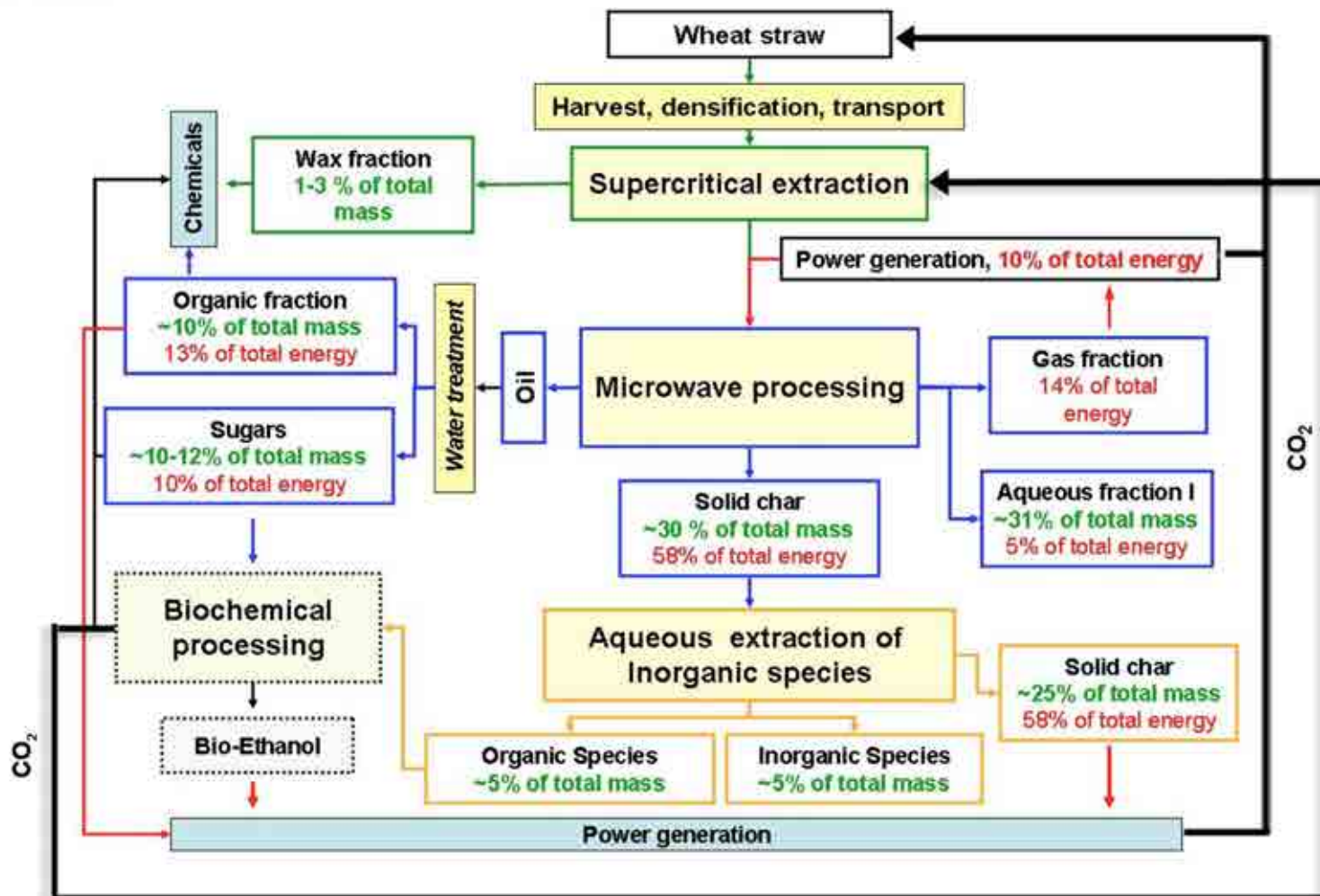
Industry

Networking

Education





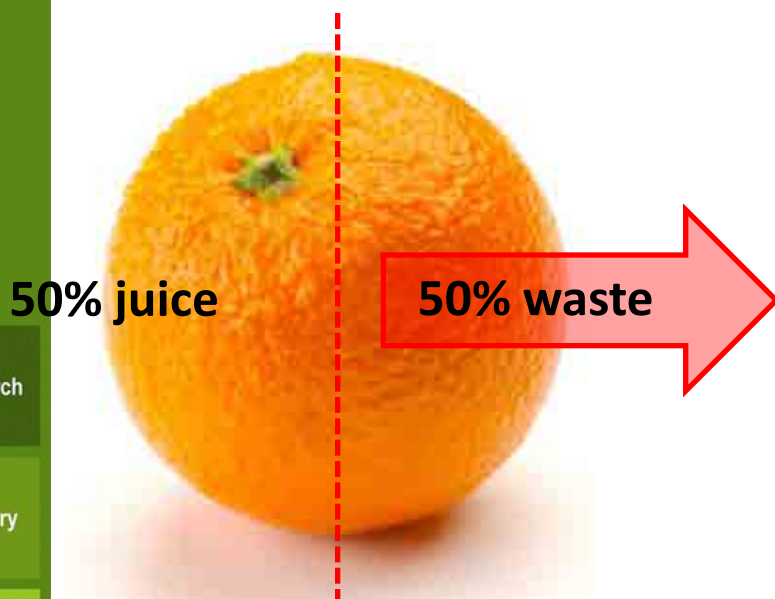


## *Integrated wheatstraw biorefinery*



# A new OPEC- Orange Peel Exploitation Company

Valorisation of a million ton scale pre-consumer waste to bio-chemicals, bio-materials and bio-fuels.



## BIO-CHEMICALS

Bio-solvents  
Natural fragrance chemicals  
Chemical intermediates  
acid catalysts

## BIO-FUELS

bio-ethanol      chars  
sugars              liquid fuels

## BIO-MATERIALS

catalysis  
separations      water purification

*100 million MT oranges  
(Brazil, USA, China, India,  
Africa, Mexico, Spain....)*



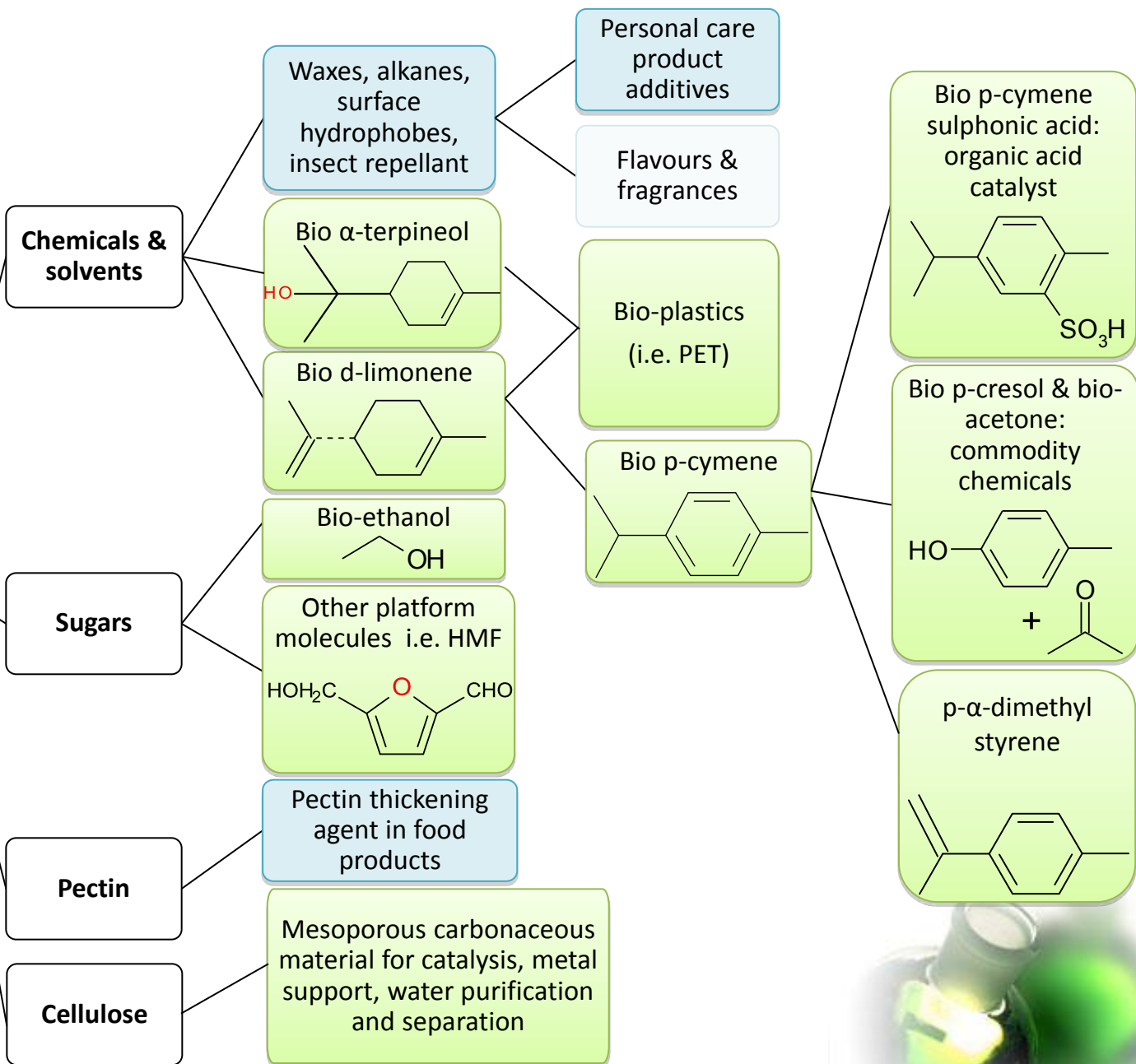
Oranges



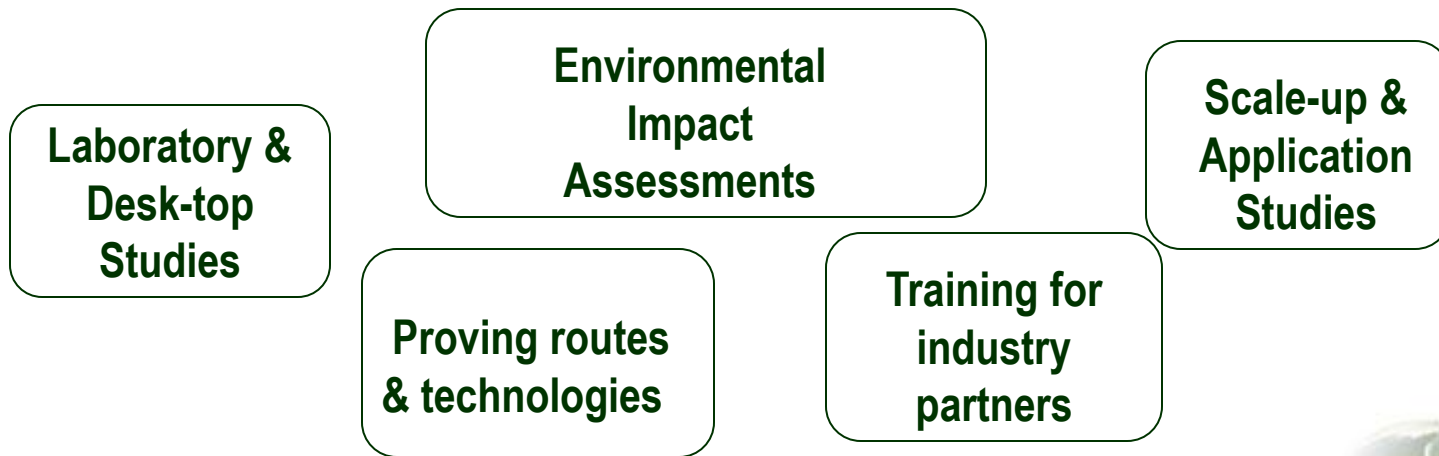
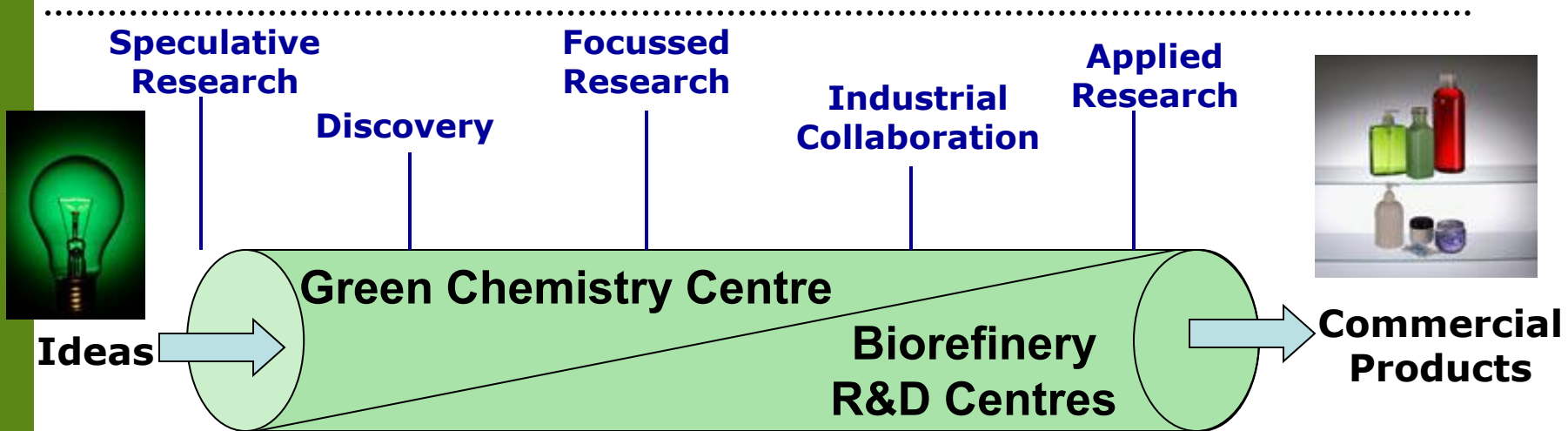
Juicing process



**8,069,705 T/y**  
*of waste orange peels available in Brazil for example*



# Green Chemistry at York: from research bench to semi-scale



# BDC **Biorenewables** Development Centre

*[www.biorenewables.org](http://www.biorenewables.org)*

Project Part-Financed  
by the European Union



European Regional  
Development Fund

Project Sponsor



Science City York

*A collaboration between the Green Chemistry Centre  
CNAP, FERA and Science City York*







## Facilities

- A range of pre-treatment equipment including a granulator, hammer mill, pelletizer and macerator all scaled to handle up to 100kg batches of biomass.
  - A 30kg/h continuous flow, low temperature, microwave pyrolysis system.
  - A 10 litre sub- and super-critical CO<sub>2</sub> extraction and fractionation capability.
    - A 100 litre high pressure and temperature fibre explosion system.
  - A microbiological suite including fermentation capacity up to 42 litres.



# BDC Biorenewables

## Development Centre



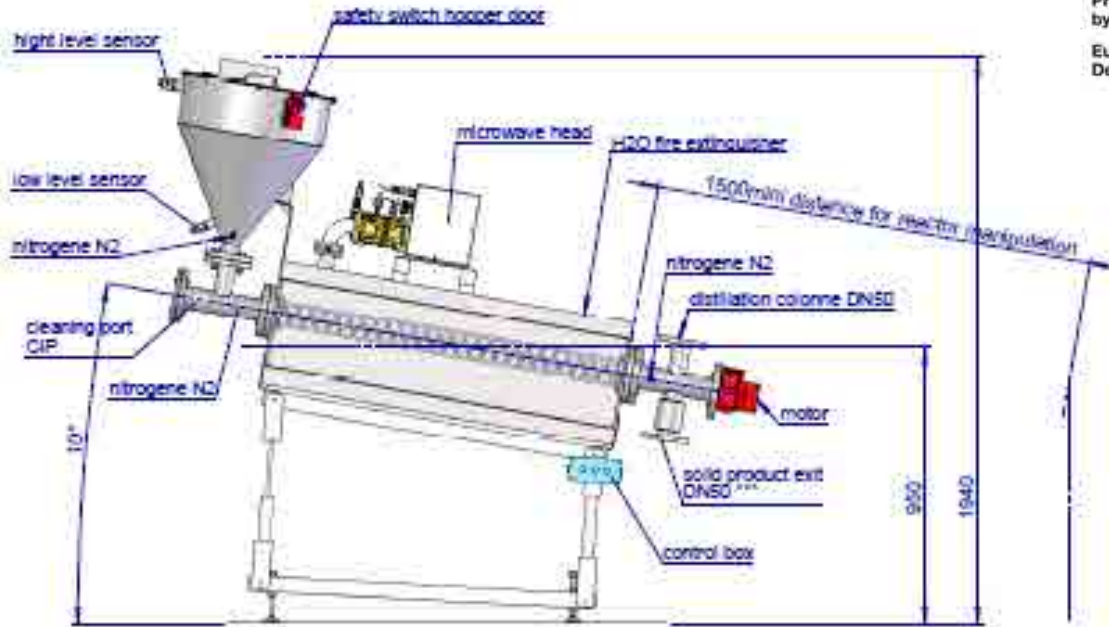
- **Biorenewables Feedstock Development Unit** will source, evaluate and develop plants, algae and fungi as production systems for high value chemicals and materials.
- **Biorenewables Process Development Unit** will allow pre-treatment, extraction, processing and separation of biorenewable feedstocks on an industrial scale.
- **Biorenewables Business Development Unit** will engage with relevant industrial organisations to identify business opportunities and help companies develop new economically viable products and processes.

*Official launch by UK Government Minister  
July 5, York*

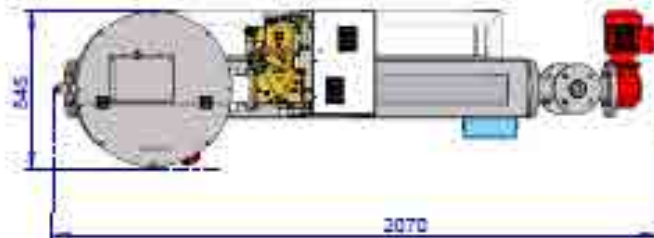
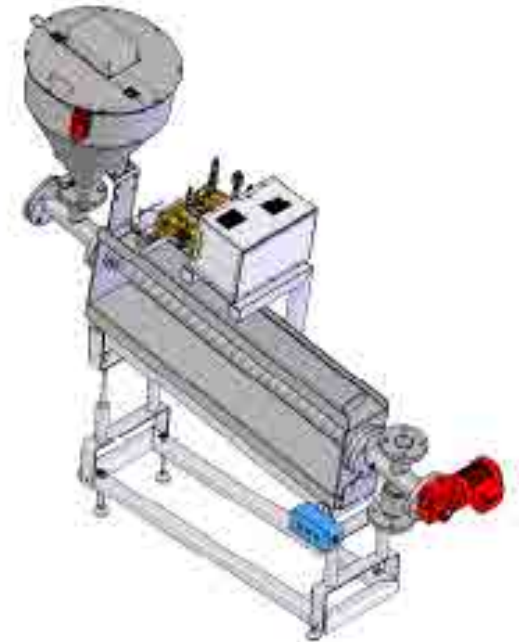
# BDC Biorenewables Development Centre

Project Sponsor

Project Part-Financed  
by the European Union  
European Regional  
Development Fund



WITHOUT MW DOOR obs<sup>TM</sup> represented without thermal insulation



Research

Industry

Networking

Education





The Biorenewables Development Centre is a major new initiative focusing upon the identification, development and processing of biorenewable materials including bio-wastes. BDC facilities include demonstrator scale continuous microwave, supercritical and fermentation processes. The BDC has dedicated management, scientific, technical and business development staff.

Starbons® Ltd was formed in 2012 as a spin-out originating from research conducted at the University of York. It is the GCCE's first commercialisation company focusing on the Starbons® technology, which converts waste polysaccharide into high value mesoporous materials. Starbons® Ltd is based near the BDC and the GCCE in the York Science Park.

The latest Green Chemistry Centre network initiative, Biowaste Industrial Symbiosis (BIS), launched in 2012 and will reach across the globe to help create a multidisciplinary community with common interests in valorising food supply chain waste.



2012

## Green Chemistry Centre Developments



2013

### New Building



### Industrial Engagement Facility



The Industrial Engagement Facility will be integrated within the new Green Chemistry Centre building. It will provide a flexible meeting space for visiting industrialists to have discussions with Centre scientific staff. The IEF will have a dedicated manager and support staff.

### New Chair in Green Chemistry



In late 2012, the Green Chemistry Centre of Excellence will appoint a new Chair in Green Chemistry, expanding the senior academic staff to 5 and broadening its knowledge base and research expertise.

Email: [info@greenchemistry.net](mailto:info@greenchemistry.net)

More Information: <http://www.york.ac.uk/greenchemistry>



**NORSC**  
*Combining the expertise of the leading Northern England Universities to provide sustainable chemistry solutions to industry*

**MUSC**  
*The Chemical Industries Association and the Green Chemistry Centre working together to create new green and sustainable supply chains for chemical products*



*Promoting awareness and facilitating, education, training and practice of green chemistry worldwide*



**Green Chemistry**  
 Centre of Excellence

*Anglo-French collaboration chemicals from biomass using green chemistry and white biotechnology*

**SUSTOIL**  
*The international Network for alternatives to petroleum*

**Green Chemistry and the Consumer**  
*Green chemistry solutions for the retailer and producer*

**The BIS**  
*Biowaste Industrial Symbiosis*  
[www.sustoil.org/bis.html](http://www.sustoil.org/bis.html)

**Green Chemistry networks worldwide**  
*Greece, Portugal, Cyprus, Japan, USA, Mexico, India Korea, Brazil.....*





**BIS**  
Bio-waste Industrial Symbiosis

*We need the BIS to help us better valorize bio-wastes into chemicals, fuels and materials*

- ✓ *because we need to cross traditional disciplinary boundaries*
- ✓ *because we need to employ better technologies*
  - ✓ *because we need to work across national boundaries*
- ✓ *because we need to overcome legal obstacles and other barriers*

## NOW A NEW EUROPEAN COST ACTION

Join us at [www.sustoil.org/bis.html](http://www.sustoil.org/bis.html)

And at the launch in Santa Clara (June 21)

We work at all stages from young children to professional (re)training...

## Early Education and Outreach



### Aims

- To **excite** young people about **chemistry** and the **positive** impact it can have.
- To **enable** young people to **critically engage** with ideas and solutions

### Impacts/areas of work

- lots of projects and funding at key stage 2
  - Discovery Days, Countryside Days, Science Days in Primary Schools
  - High awareness about environment at young age, interest and enthusiasm
- opportunities at GCSE/A level stage



Training the next generation.....

# MSc in Green Chemistry & Sustainable Industrial Technology

## Principles & Technologies

Principles, Environmental Impact, Chemical Engineering,  
Catalysis for Green Chemistry,  
Alternative Reaction Media, Energy,  
Clean Synthesis, Renewable Resources,  
Greener Products

## Supporting Courses

IP, Business Opportunities, Green Chemistry Presentations,  
Legislation Presentations and Literature Research

## Research Project & Oral Presentation

In collaboration with Industry

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Research

Industry

Networking

Education



**Industry**

**Education**



**Green  
Chemistry**

*Centre of Excellence*

[www.greenchemistry.net](http://www.greenchemistry.net)

**Research**

**Networking**

# RSC Green Chemistry Book Series

**Series Editor in chief** : James Clark (UK),

Associate editors: George Kraus (USA), Andrzej Stankiewicz (EU);

Peter Seidl (Brazil); Yuan Kou (China)

Concise digest of the latest research and thinking in Green Chemistry

Accessible handbooks to both those entering and established in the field

Latest titles:

