Green Chemistry
Centre of Excellence

THE UNIVERSITY of York

The Role of Green Chemistry in Sustainable Formulations

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Green Chemistry Centre of Excellence

University of York

10th November 2010

Research

Industry

Networking

Education

Introduction

- Introduction
  - Sustainability
  - York and Green Chemistry Centre of Excellence
  - Green Chemistry Centre of Excellence
    - Technology Platforms
- Case Studies
  - Starch to ‘Switchable Adhesives’ (whole formulation)
  - Starch to Starbons® (drop-in replacement)
  - Bio boards (whole formulation)
- Enabling Technologies
- Summary

Green Chemistry Centre of Excellence

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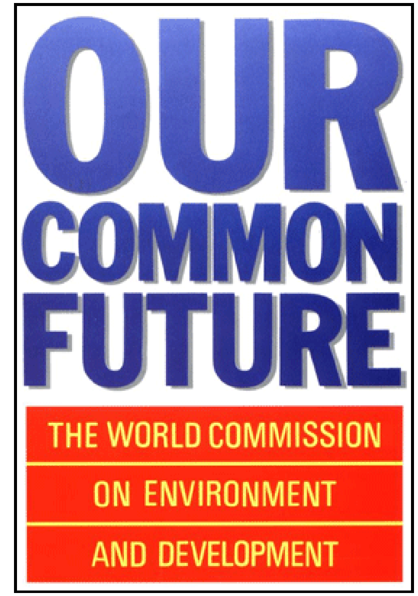
Introduction

York and Green Chemistry

- Top 100 World- and Top 10 UK-ranked University
  - THES 2010
- Top 5 UK-ranked Chemistry Dept
  - Guardian/Independent 2010
- Internationally-leading Green Chemistry research centre dedicated to creating genuinely sustainable supply chains for chemical and related products

Introduction

Sustainability

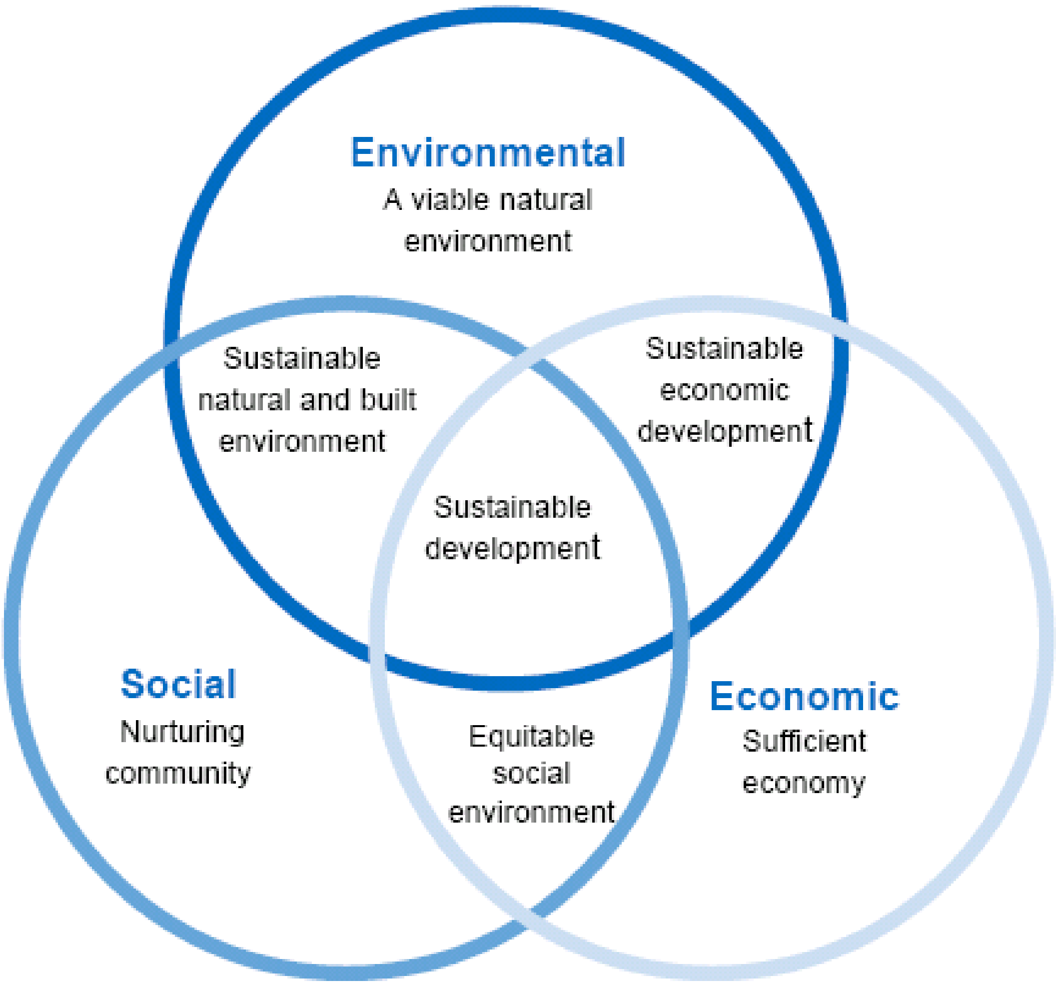


BRUNDTLAND REPORT (1987)

“*sustainable development should meet the needs of the present without compromising the ability of future generations to meet their own needs*”

Introduction

Sustainability



Introduction

Sustainable Chemistry

Chemical procedures and intermediates that have minimal environment impact through the use of highly eco-efficient, scalable and adaptive processes that have smaller physical and ecological footprint.

Responsible Care®

Introduction

• 12 Principles of Green Chemistry

1. Prevention
It is better to prevent waste than to treat or clean up waste after it has been created.

2. Atom Economy
Synthetic methods should be designed to maximise the incorporation of all materials used in the process into the final product.

3. Less Hazardous Chemical Syntheses
Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

4. Designing Safer Chemicals
Chemical products should be designed to effect their desired function while minimizing their toxicity.

5. Safer Solvents and Auxiliaries
The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

6. Design for Energy Efficiency
Energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimised. If possible, synthetic methods should be conducted at ambient temperature and pressure.

7. Use of Renewable Feedstocks
A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

8. Reduce Derivatives
Unnecessary derivatisation (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimised or avoided if possible, because such steps require additional reagents and can generate waste.

9. Catalysis
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

10. Design for Degradation
Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

11. Real-time analysis for Pollution Prevention
Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

12. Inherently Safer Chemistry for Accident Prevention
Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

P. T. Anastas, J. C. Warner, Green Chemistry: Theory and Practice, Oxford University Press, New York, 1998.

Introduction

Sustainable through Green Chemistry

- Green Chemistry
  - focuses on the design, manufacture, and use of chemicals and chemical processes that have little or no pollution potential or environmental risk and are both economically and technologically feasible.

Prevent wastes
Renewable materials
Omit derivatization steps
Degradable chemical products
Use safe synthetic methods
Catalytic reagents
Temperature, pressure ambient
In-process monitoring
Very few auxiliary substances
E-factor, maximize feed in product
Low toxicity of chemical products
Yes, it is safe

S. L. Y. Tang, R. L. Smith and M. Poliakoff *Green Chem.* **7,** 761–762; 2005

Green Chemistry Drivers

- Legislation - product, process & environmental
- Cost - manufacturing & waste disposal
- Consumer and retailer pressure
- Sustainability
- Process efficiency
- Unique routes to natural molecules
- Formulation Strategies
  - Deconstruction of formulations
    - Complex, for example >35 components in sunscreen
  - Drop in like for like replacement
  - Interdependence
  - Whole Formulation

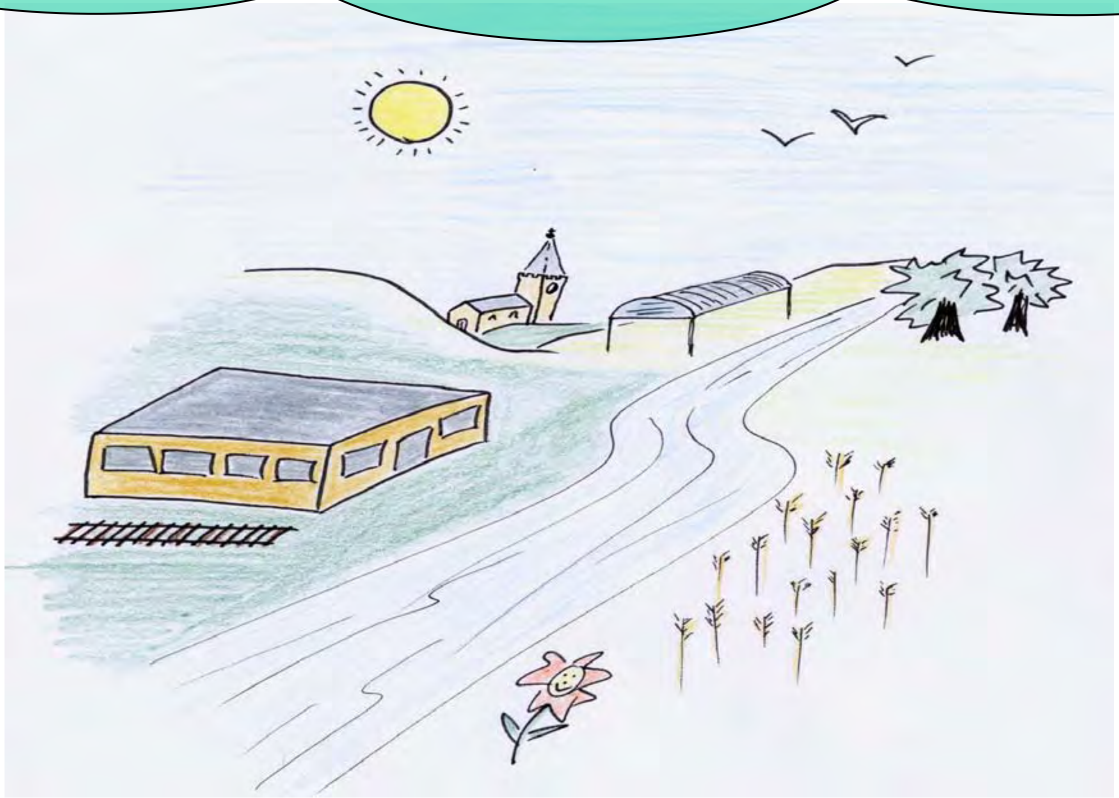
Introduction

Sustainable through Green Chemistry

Green Principles

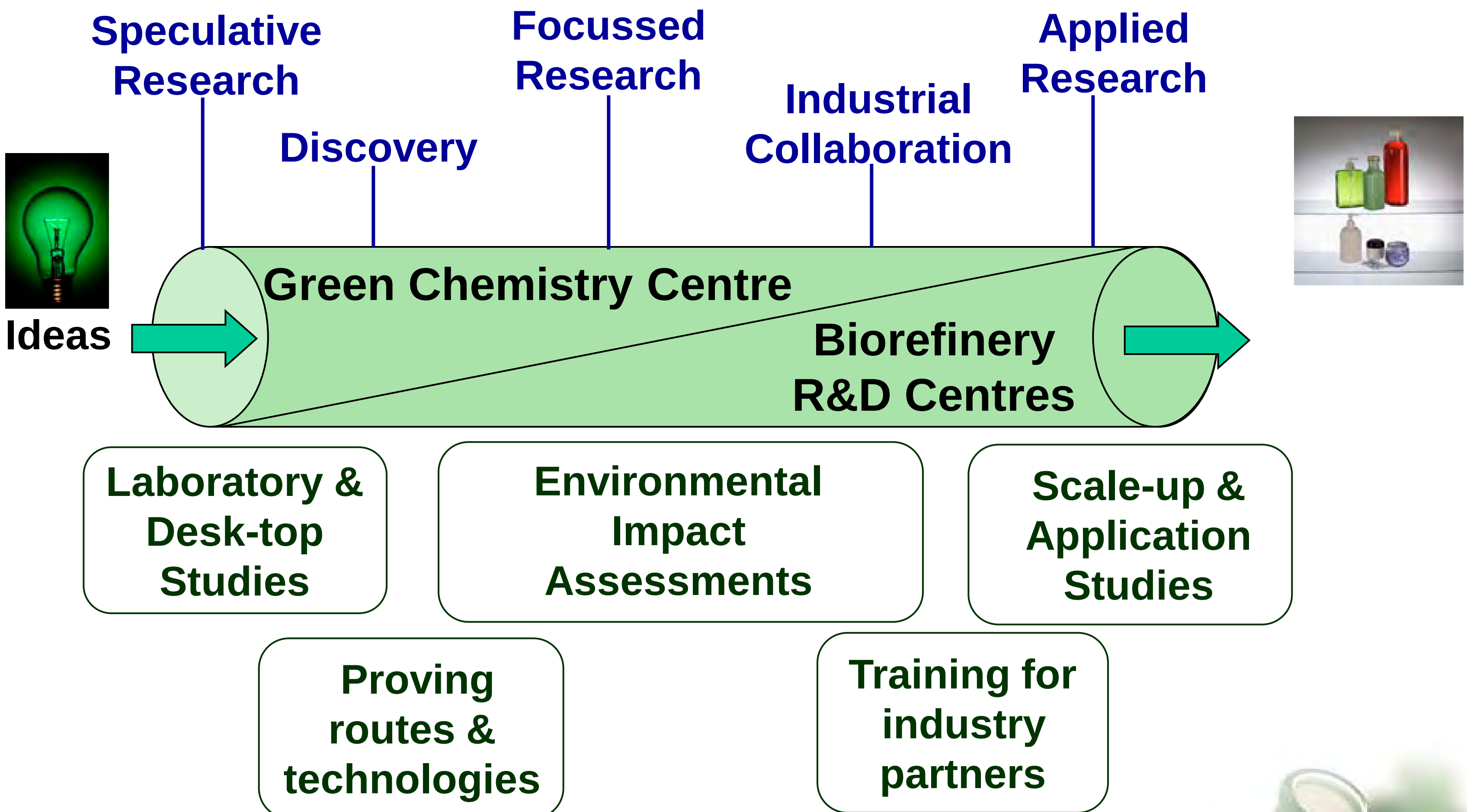
INNOVATION

Sustainable chemistry



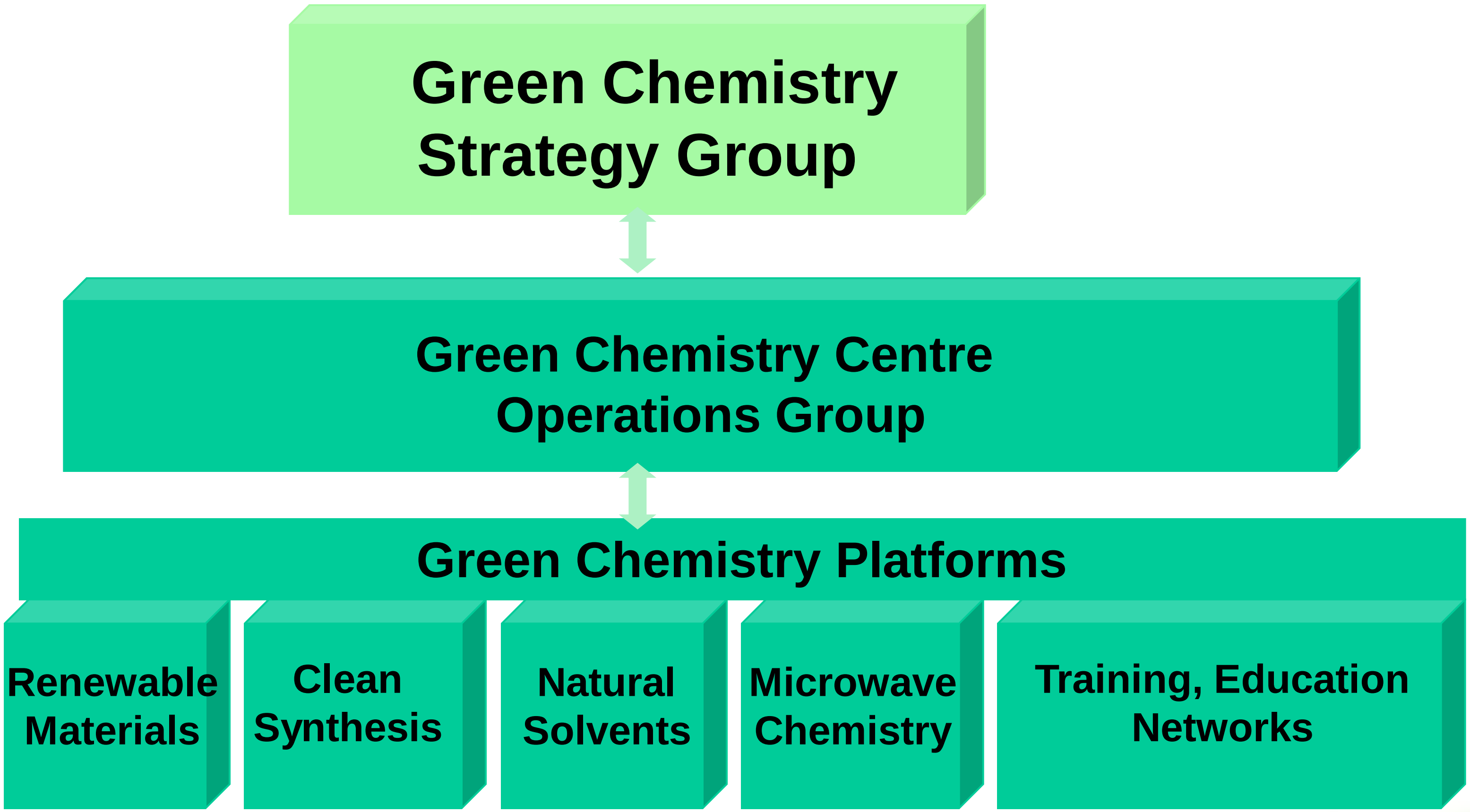
Introduction

York and GC



Introduction

York and GC



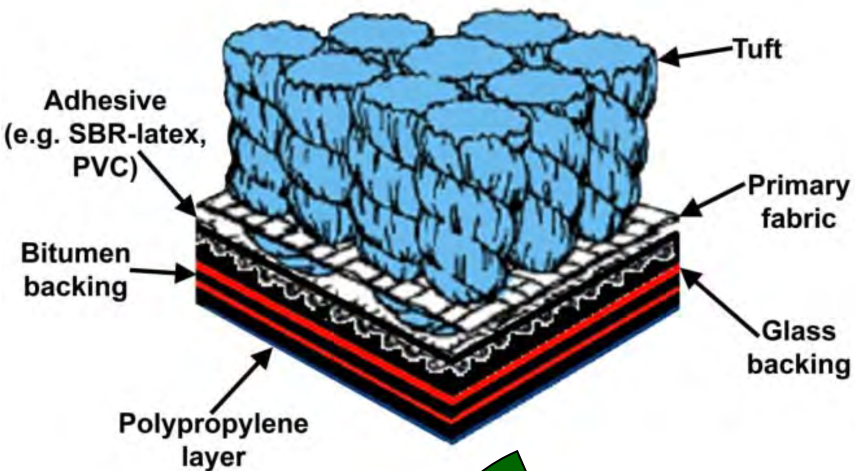
Case Study 1

From starch to switchable adhesives

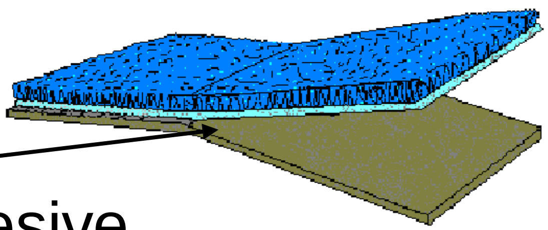
Whole Formulation

Case Study 1

From starch to switchable adhesives



~45M m^2 pa
(10M kg nylon,
50M kg bitumen)



~90% landfill
Waste costs!

Switchable adhesive layer

Case Study 1

From starch to switchable adhesives

Year	2003 – 2006	2007	2008-9	2009-10	2010-11
Project year	**I - III**	**IV**	**1**	**2**	**3**
Activities	PhD project	Feasibility study	Scale up & reduce costs	Pilot scale: 100k m^2 $year^{-1}$	Industrial scale: 4 M m^2 $year^{-1}$
Funding	Industry	DTI & Industry	TSB & Industry		
Commercial benefit	• Reduce use & need for virgin material – lower cost long term • Enhanced company reputation				
Sustainability benefit	• Reduce non-renewable resources • Reduce impact of adhesive application – hot-melt • Nylon recycling – eliminate a large source of NO_x very high GWP. • Towards zero waste during project				

Case Study 1

From starch to switchable adhesives

- Why polysaccharides (starch)?

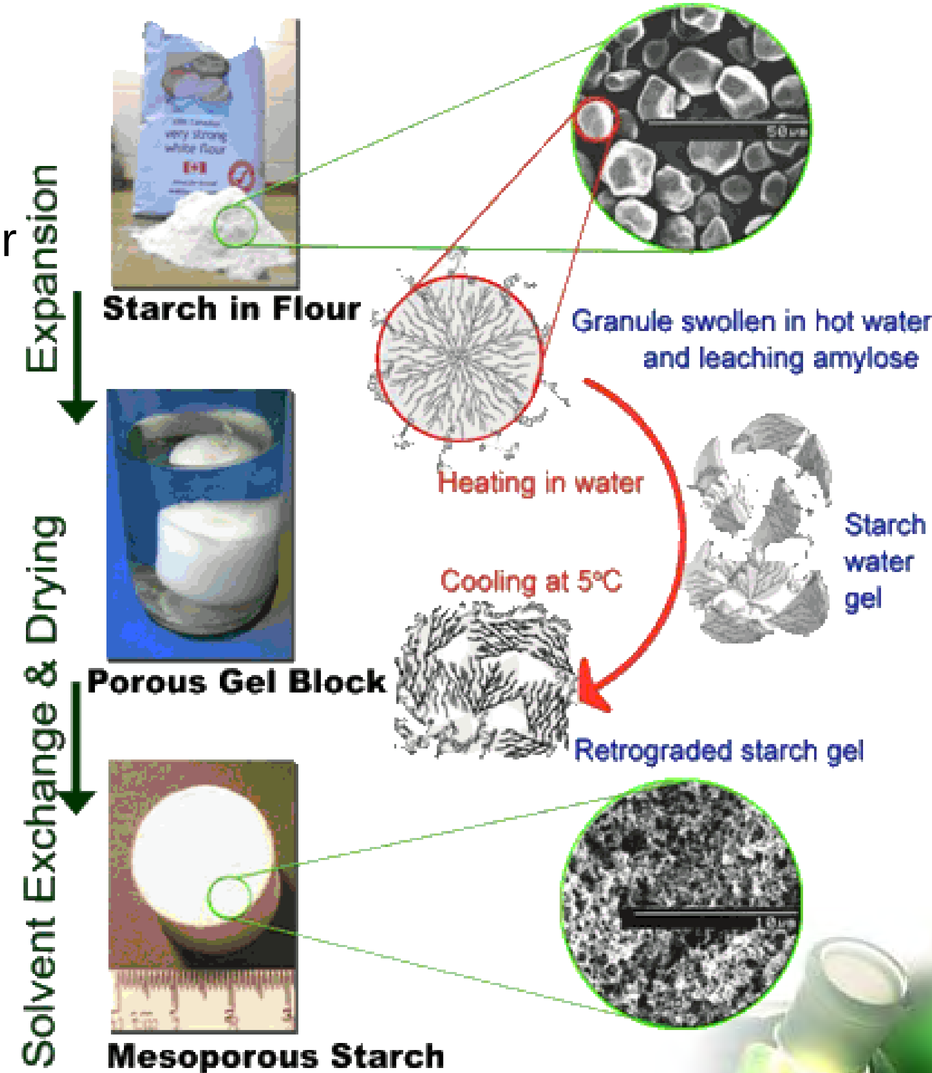
- Advantages
  - Renewable material with assured supply
  - Biodegradable
  - Inexpensive
  - It's white!
  - Organised structured polymer

- Disadvantages
  - Properties affected by water
  - Biodegradable
  - Mechanically unstable with time
  - Difficult to process/ modify

Case Study 1

From starch to switchable adhesives

- Expanded starch
  - Slow release media for drugs
  - Encapsulation media for metals etc.
  - Cooking
  - Chromatography
  - Plastics/ Adhesives



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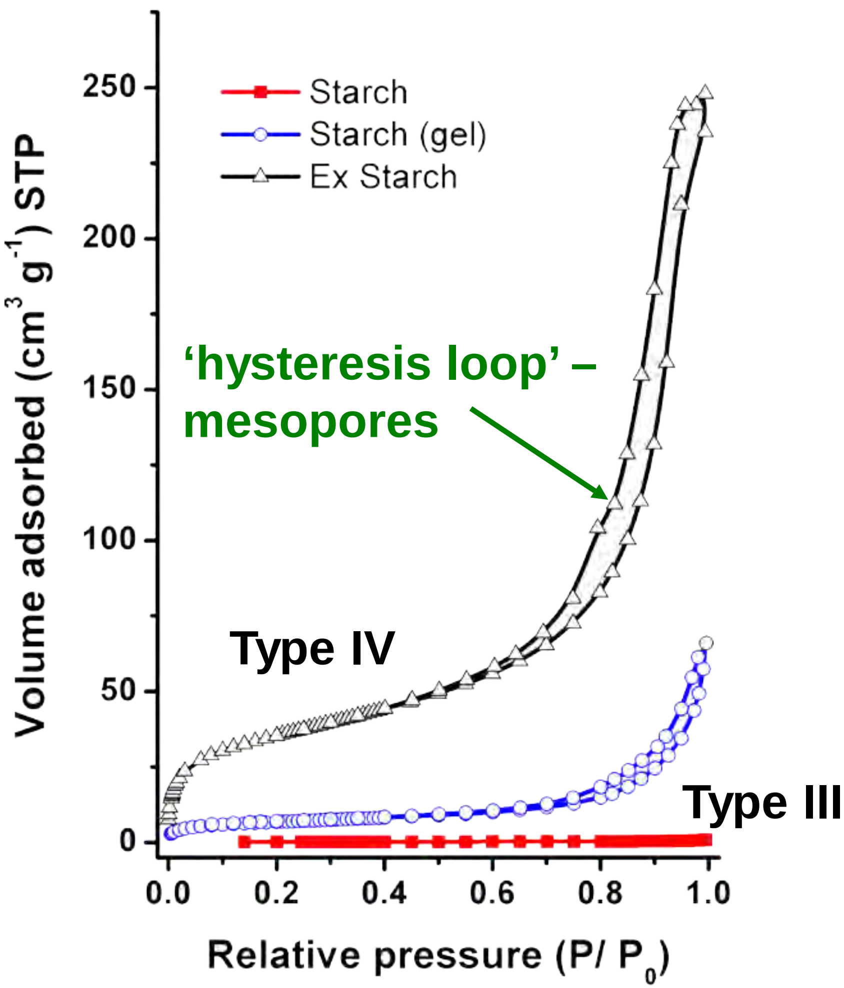
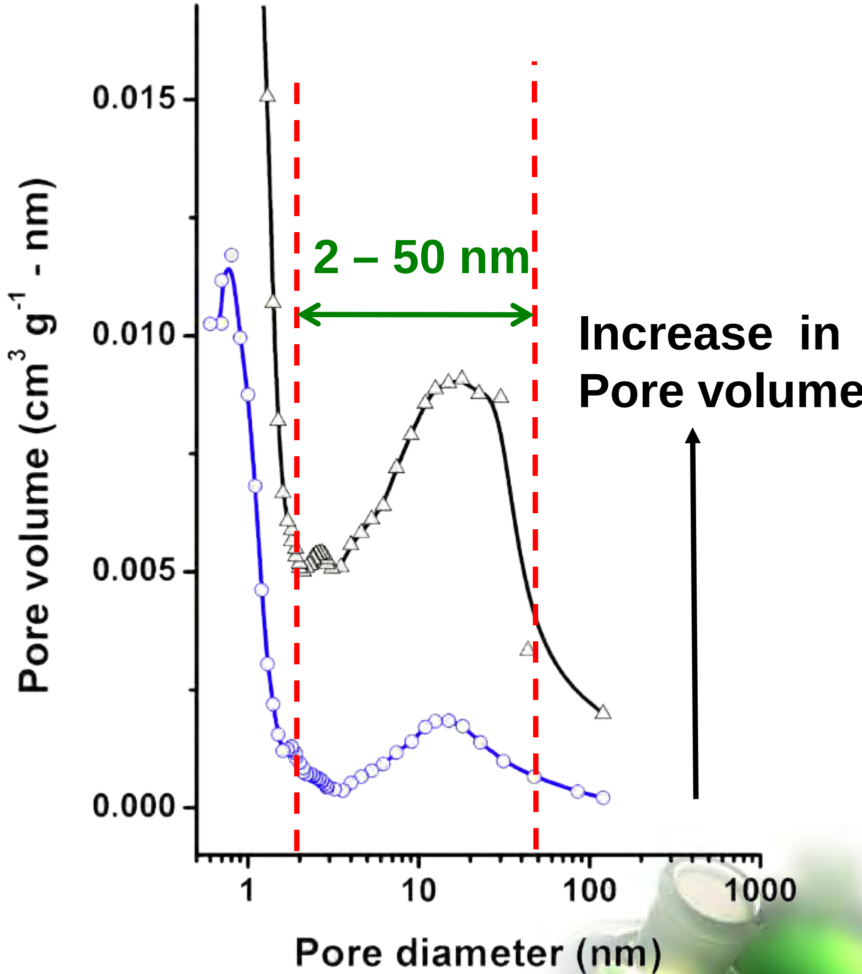
Case Study 1

From starch to switchable adhesives

- Nitrogen isotherm



- Pore size distribution



Research

Industry

Networking

Education

Case Study 1

From starch to switchable adhesives

- Modification of starch surface

20 L scale

Product for prototype carpet tile

Case Study 1

From starch to switchable adhesives

- Adhesive formulation

Homogeniser

Final product

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Case Study 1

From starch to switchable adhesives

Test	Grade (Pass ✓ fail ✗)	Comment
Loop withdrawal	✓	Similar to commercial adhesives – suitable for commercial use
Martindale	✓	
Castor chair	✓	
Dimensional stability	✓	
Flammability	✓	Excellent – no need for added flame retardants
Switchability	✓	Strength reduced – no adhesive contamination

Research

Industry

Networking

Education

Case Study 1

From starch to switchable adhesives

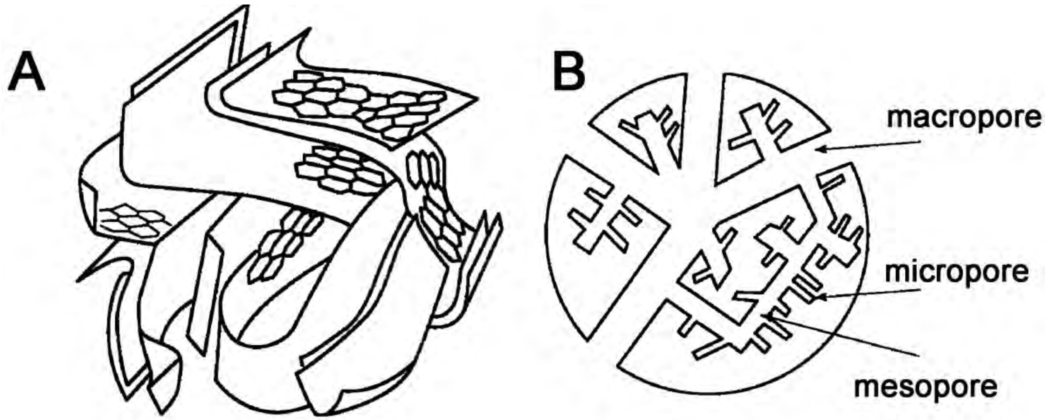
Case Study 2

From starch to porous materials

Drop in replacement

Case Study 2

From starch to porous materials



Pore type	Pore Size	Condensation mechanism	Type of Adsorption
Micropore	< *2 nm*	Three-dimensional	Non-specific
Mesopore	≥ *2* ≤ *50 nm*	Capillary	Specific
Macropore	> *50 nm*	No condensation	-

Case Study 2

From starch to porous materials

- Potential applications of mesoporous materials

Low microporous volume
High mesoporous volume
Good macroporous characteristics

Adsorption

Chromatography

Nanotechnology

Electrochemistry

Catalysis

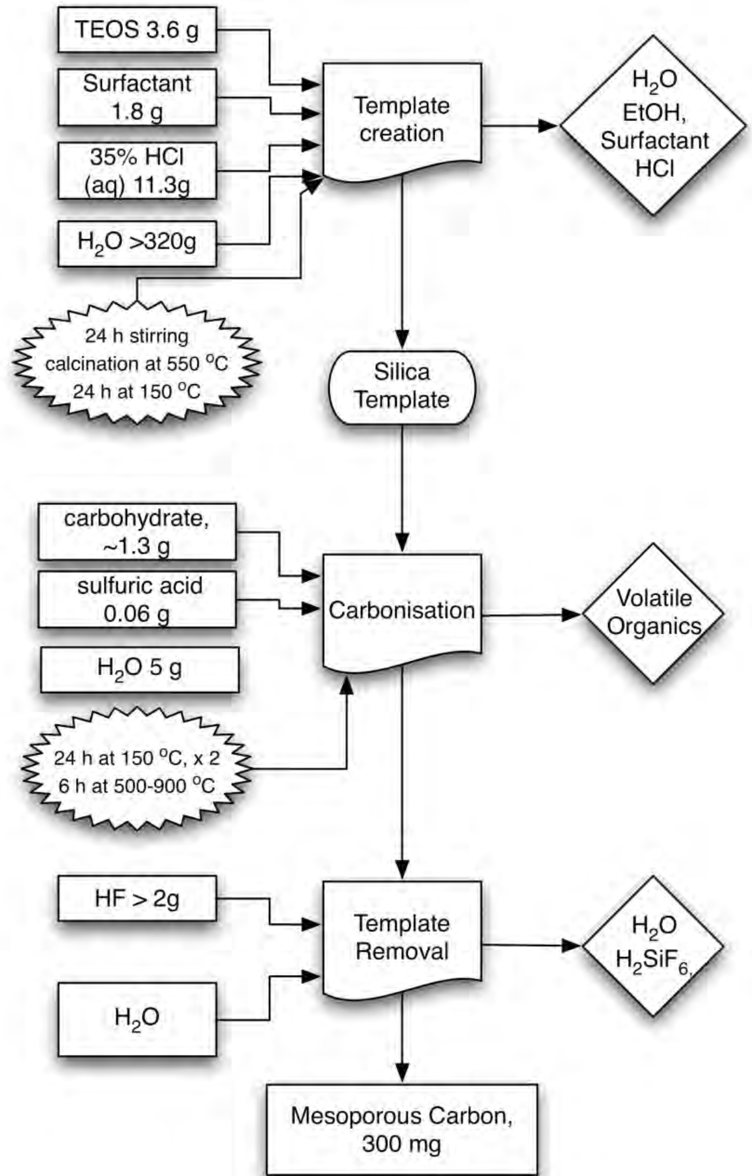
Filtration

Sensors

Case Study 2

From starch to porous materials

- Current preparation
- Resource intensive
- Energy intensive
- Significant waste



Research
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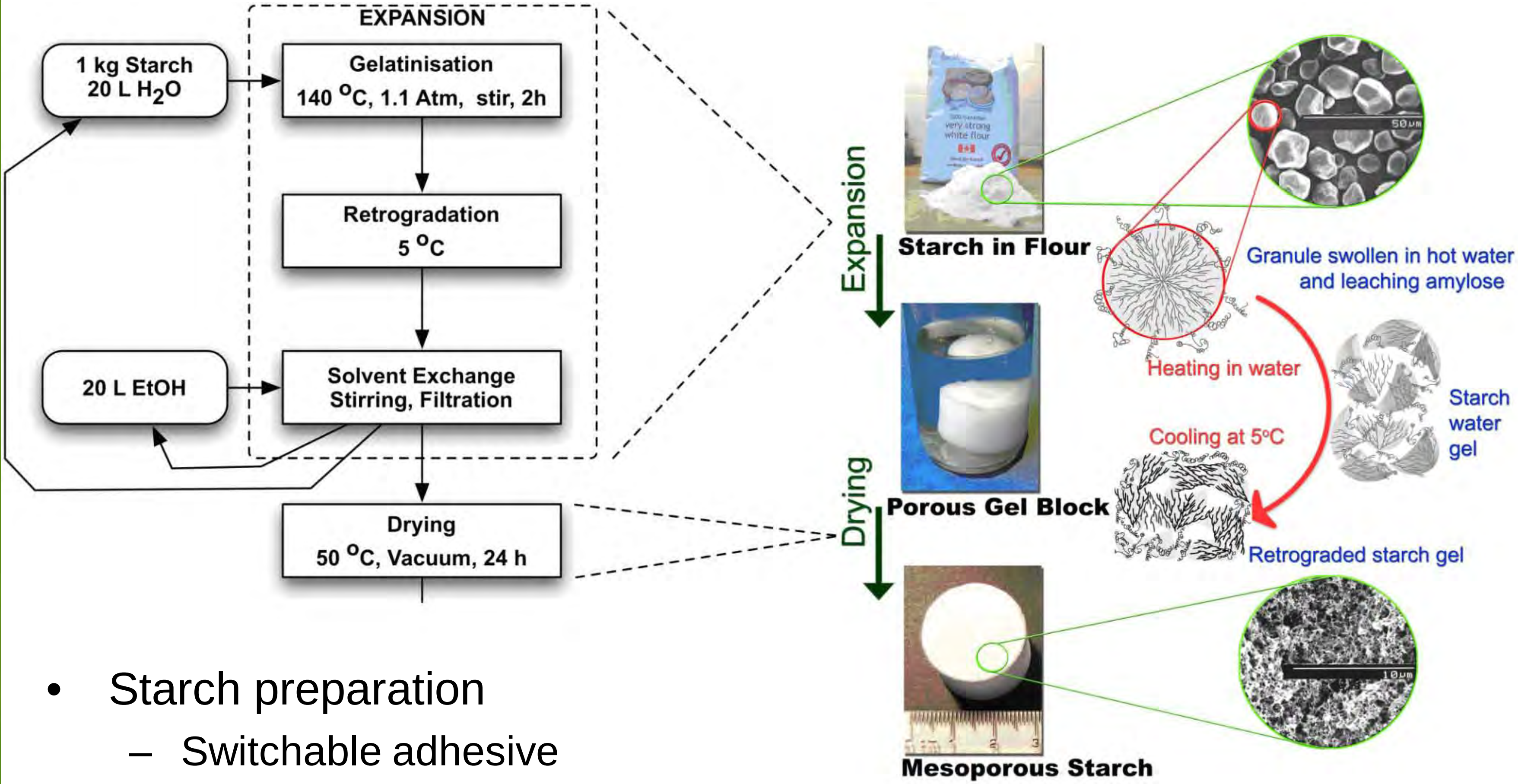
Education

Case Study 2

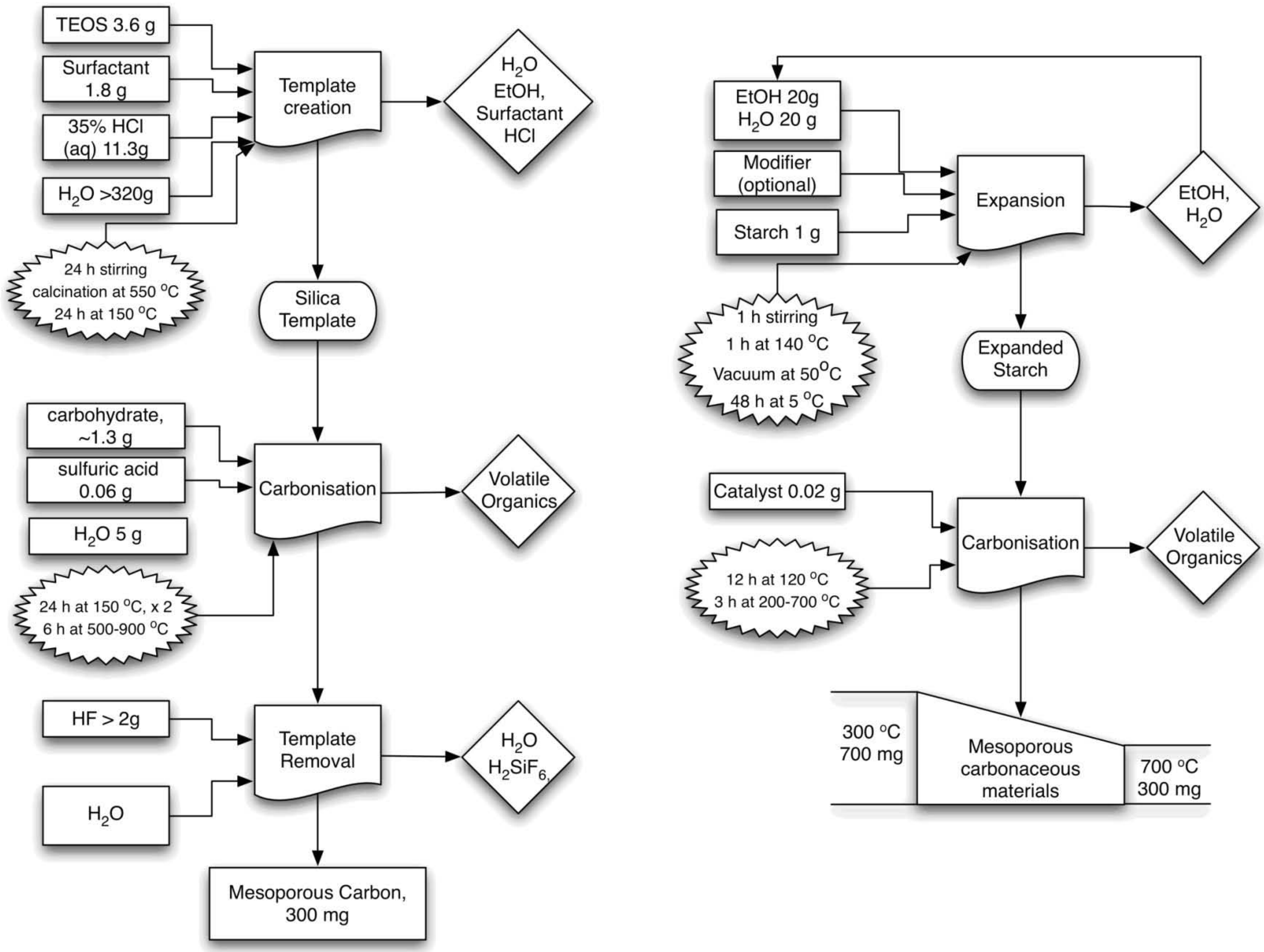
From starch to porous materials



- Starch preparation
  - Switchable adhesive

Case Study 2

From starch to porous materials



Case Study 2

From starch to porous materials

- Properties:
  - Tuneable surface functionality
  - High mesoporosity (up to 2.0 cm^3/g)
  - High surface areas (up to 500 m^2/g)
  - Controllable electrical conductivity
  - Particulate / monolithic forms

Starch

"Starbons"

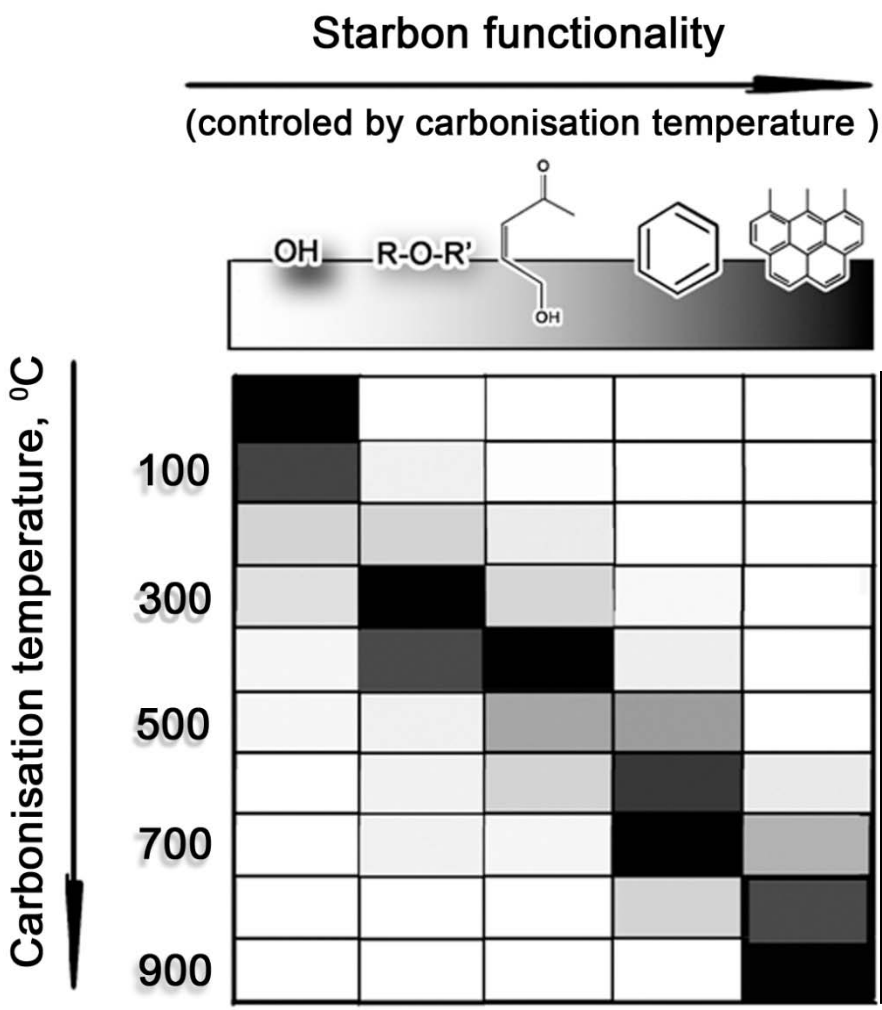
100^0C

600^0C

Mesoporous Carbon

Case Study 2

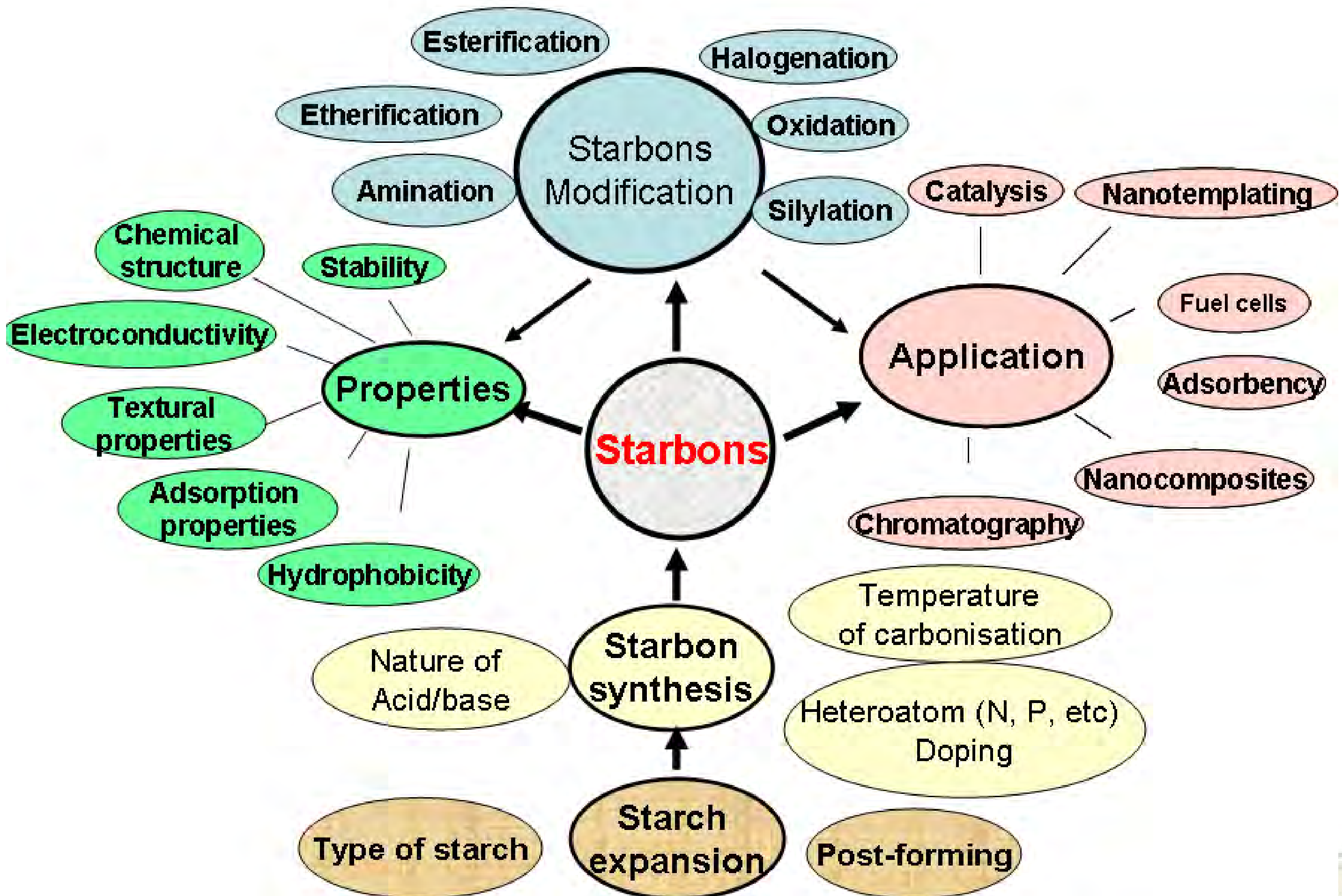
From starch to porous materials



Nanotechnology	Chromatography	Acid catalysis	Organic adsorption	Metal adsorption
✓✓				
✓✓				
✓✓				
✓		✓	✓	
✓		✓	✓	
✓	✓	✓✓	✓✓	✓
✓	✓	✓✓	✓	✓
	✓	✓	✓	✓
	✓✓		✓	✓✓
	✓✓		✓	✓✓

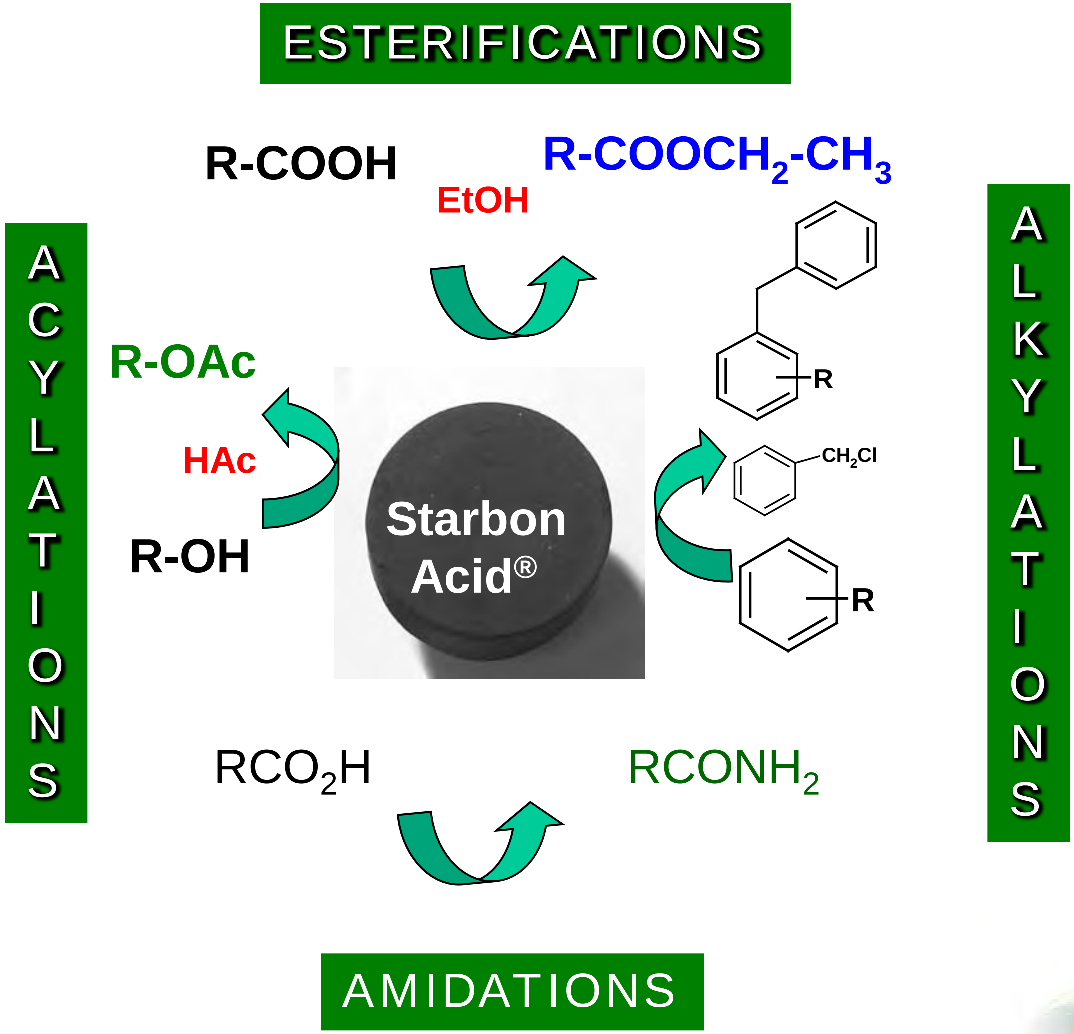
Case Study 2

From starch to porous materials



Case Study 2

From starch to porous materials

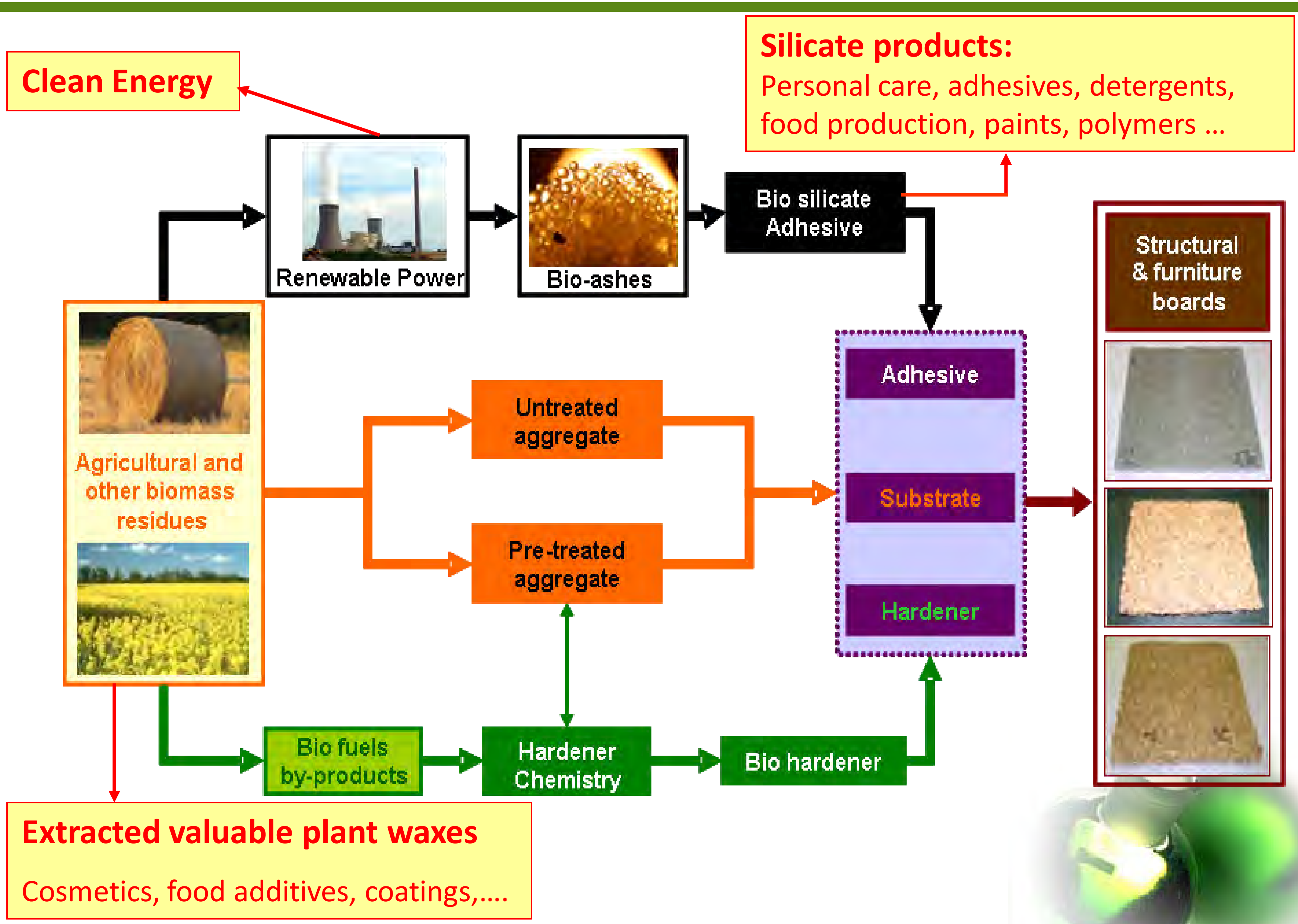


Case Study 3

Bio-Boards
Whole Formulation

Case Study 3

Bio-Boards



How do we deliver these green formulations?

Enabling Technologies

Introduction

York and GC

Green Chemistry Strategy Group

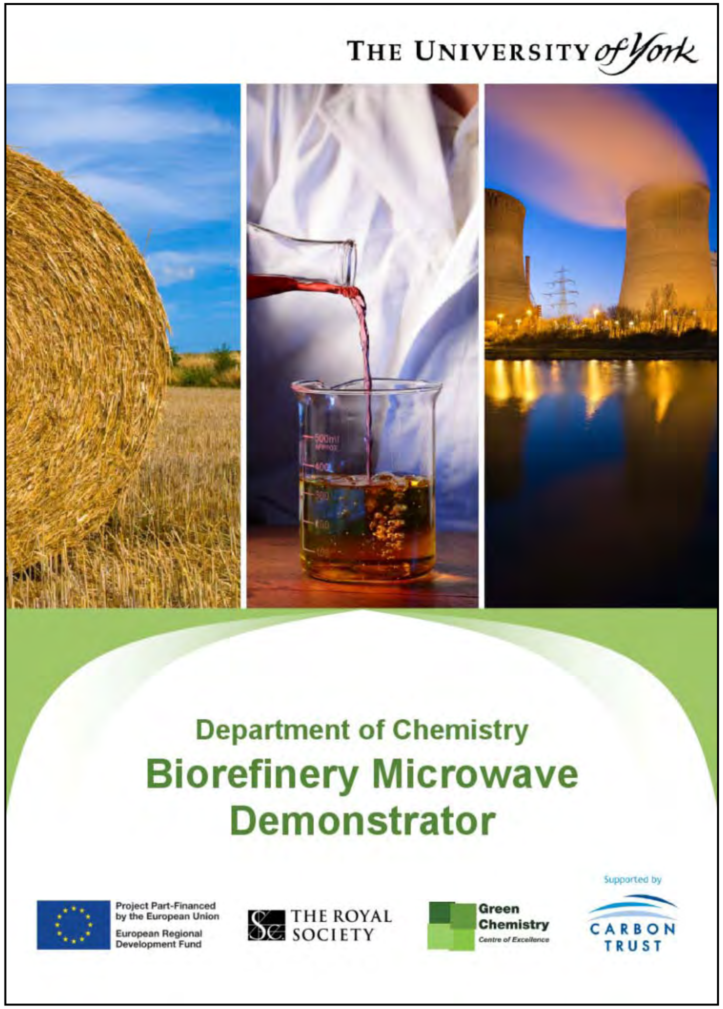
Green Chemistry Centre Operations Group

Green Chemistry Platforms

- **Renewable Materials**
- **Clean Synthesis**
- **Natural Solvents**
- **Microwave Chemistry**
- **Training, Education Networks**

Enabling Technologies

Microwave



- Microwave assisted chemistry
- Biomass pyrolysis
- Biorefinery demonstrator

Enabling Technologies

Microwave

Research
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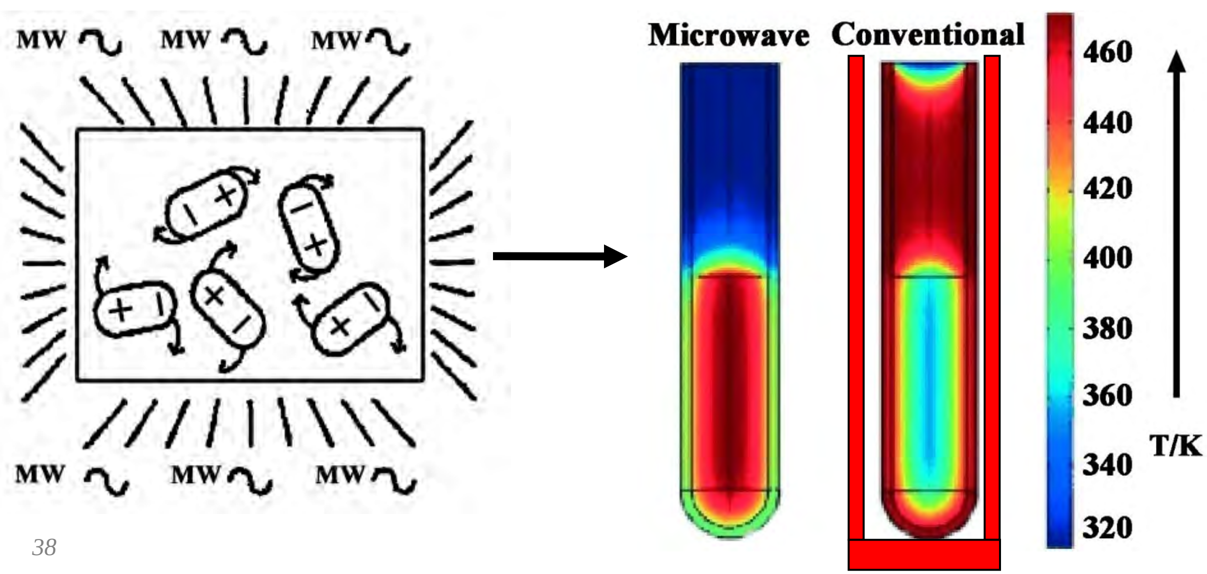
Networking
Education

- Advantages
  - Rapid internal heating
  - Uniform heating
  - Instant control
  - Acceleration of reaction rate
  - Selective interaction with active groups

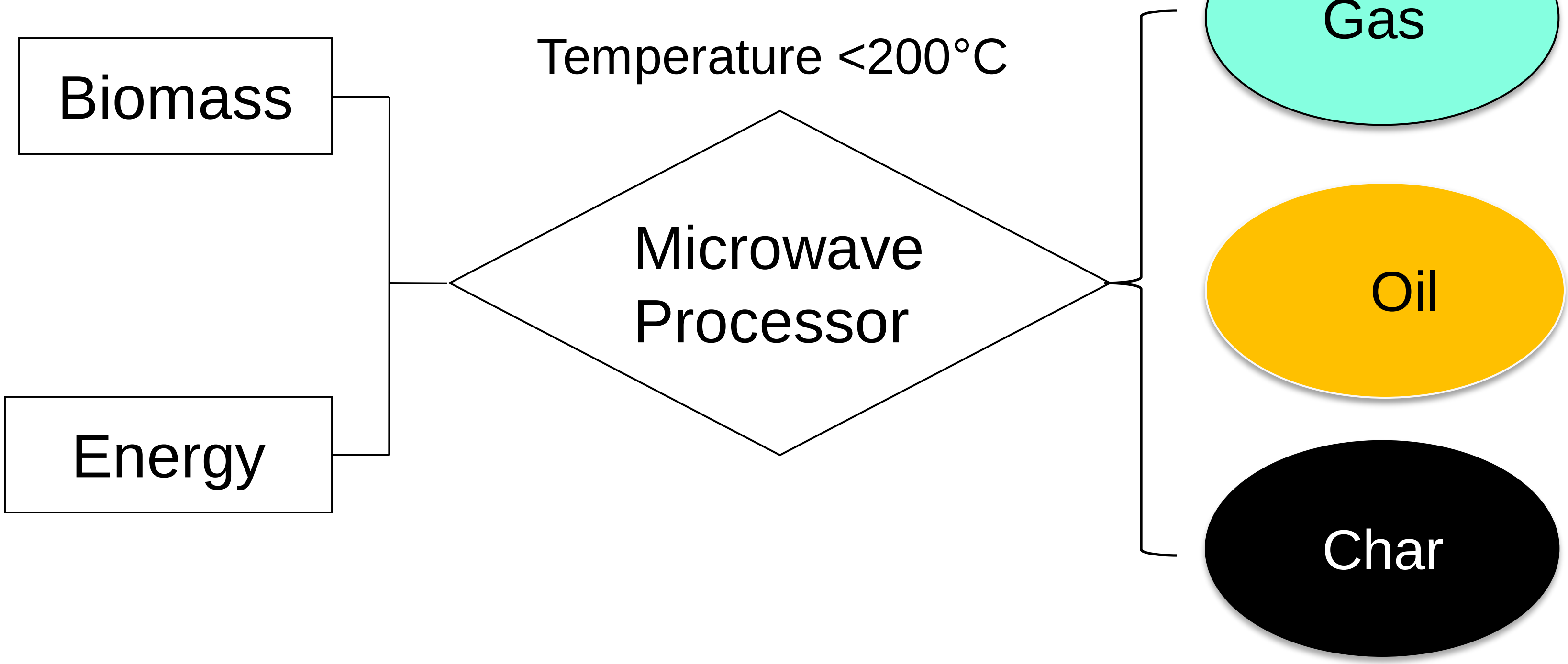
- Disadvantages
  - Polar environment required
  - Instrument variability
  - Scale-Up
    - (food industry)
  - Microwave activation still not fully understood



Enabling Technologies

Microwave

- Microwave processing of biomass



Wide range of feedstock + Flexibility of Microwave Parameters (time, temperature, power) = Products

Enabling Technologies

Microwave

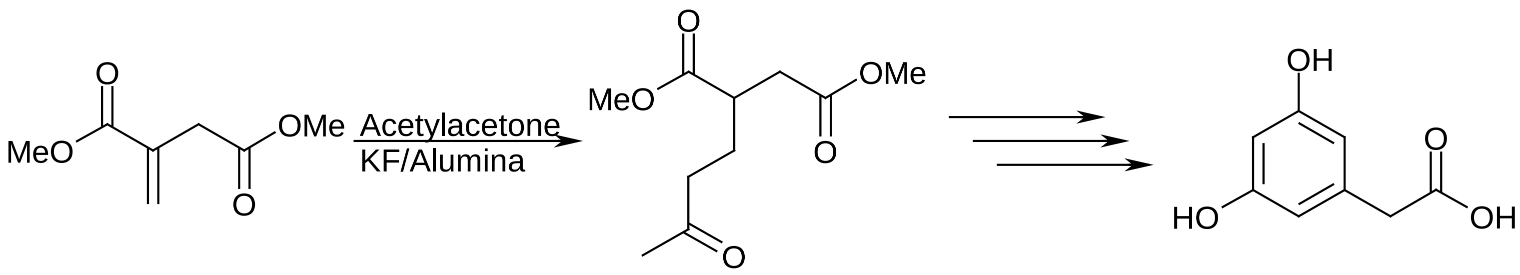
- Large scale continuous processing (30Kg/h)

18 Kg of wheat straw =	6.7 Kg of char +	5.7 Kg of oil
16-17MJ/g	25-30 MJ/g	22-26MJ/g

Enabling Technologies

Microwave

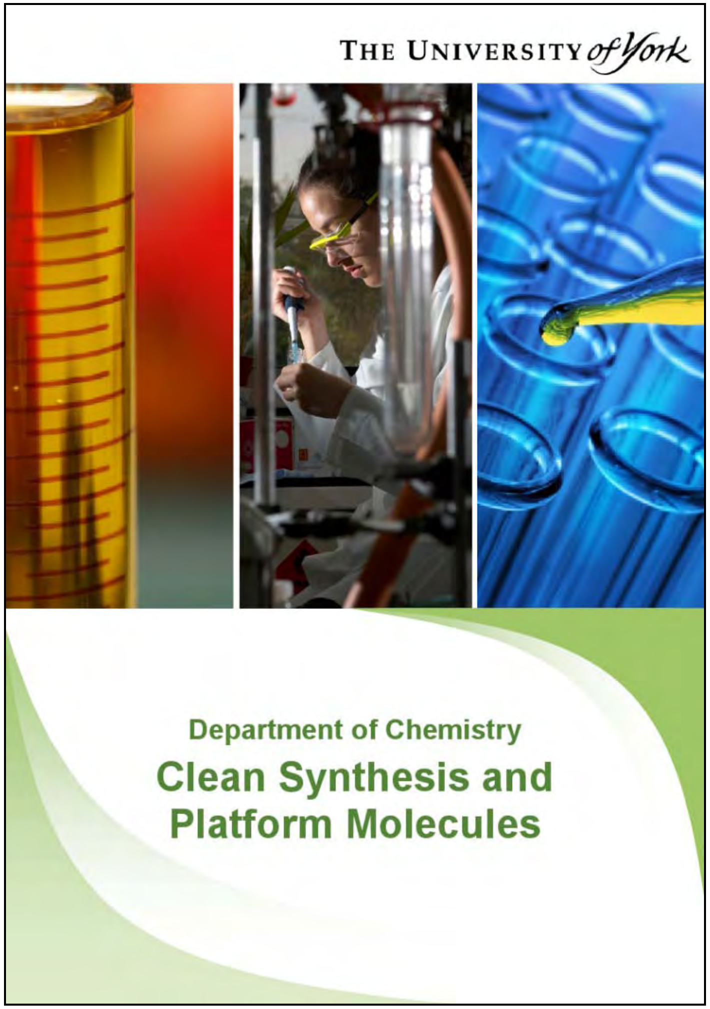
- Microwaves in Synthesis
  - Useful for carrying out “proper” reactions
  - Rate enhancements typically significant
  - Better selectivity / alternative pathways possible
  - Quick and easy to carry out trials on small scale



  - Conventional
    - Yield: 79%, selectivity 93% (65 hours at reflux)
  - Microwave
    - Yield: 73%, selectivity 81% (10 minutes, 120°C)

Enabling Technologies

Clean Synthesis and Platform Molecules



- Platform molecules
  - Derivable from high volume biomass
  - Use clean preparation methods
- Clean synthesis
  - Simple methodology
    - low/no waste
  - Low energy
    - ambient temperature or microwave
  - Catalysis
    - hetero and bio
  - Green solvents

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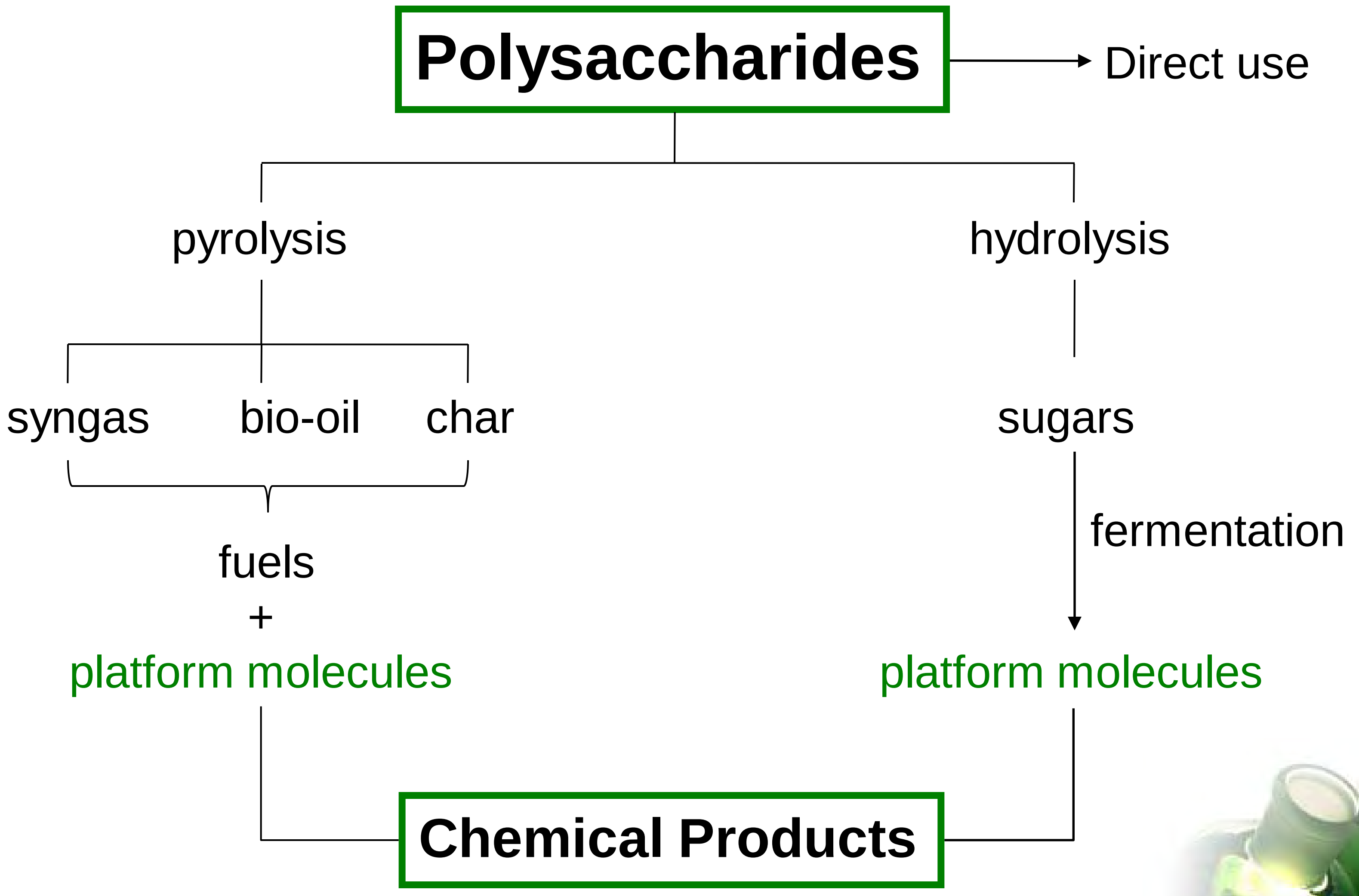
Enabling Technologies

Clean Synthesis and Platform Molecules



Research

Industry

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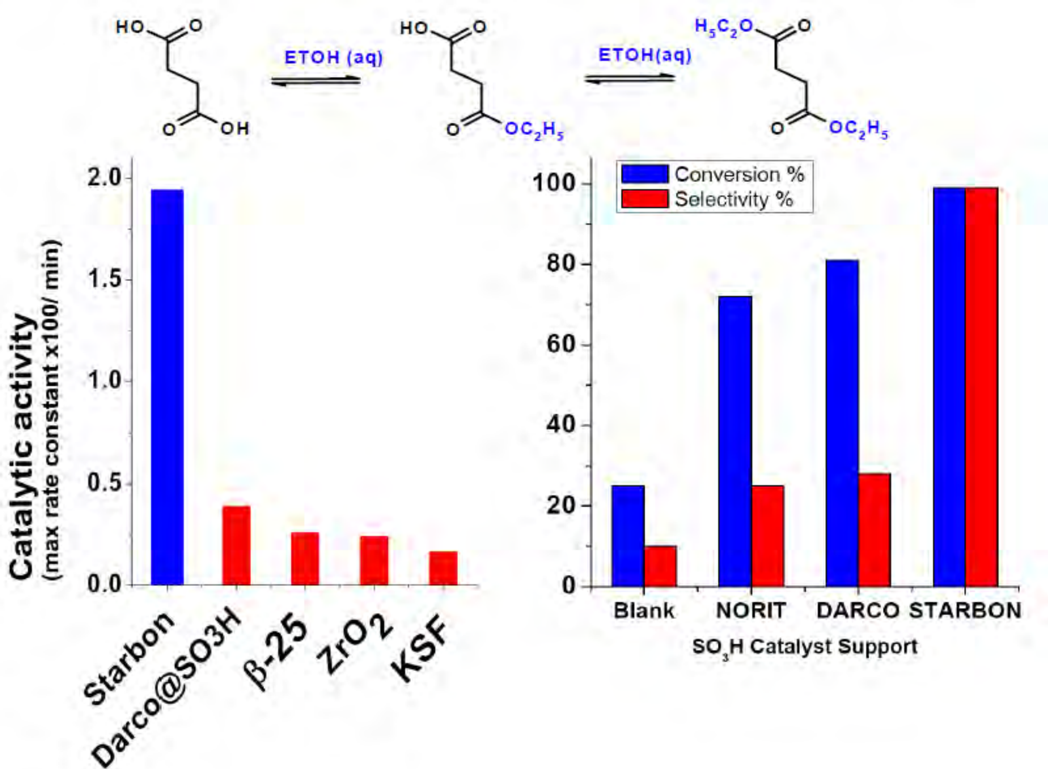
Education

Enabling Technologies

Clean Synthesis and Platform Molecules

- Clean synthesis: catalysis
- Starbon
  - Case Study 2
  - Acid catalyst directly on fermentation broth

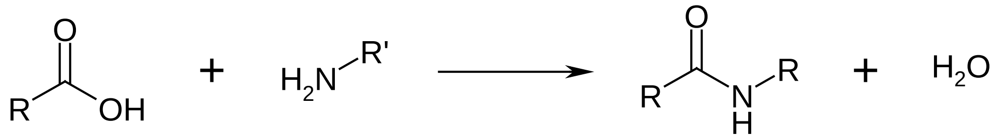
Catalytic activity, conversion and selectivity of STARBON® acids in comparison to other solid acids (and supports) in aqueous ethanol esterification of succinic acid



Enabling Technologies

Clean Synthesis and Platform Molecules

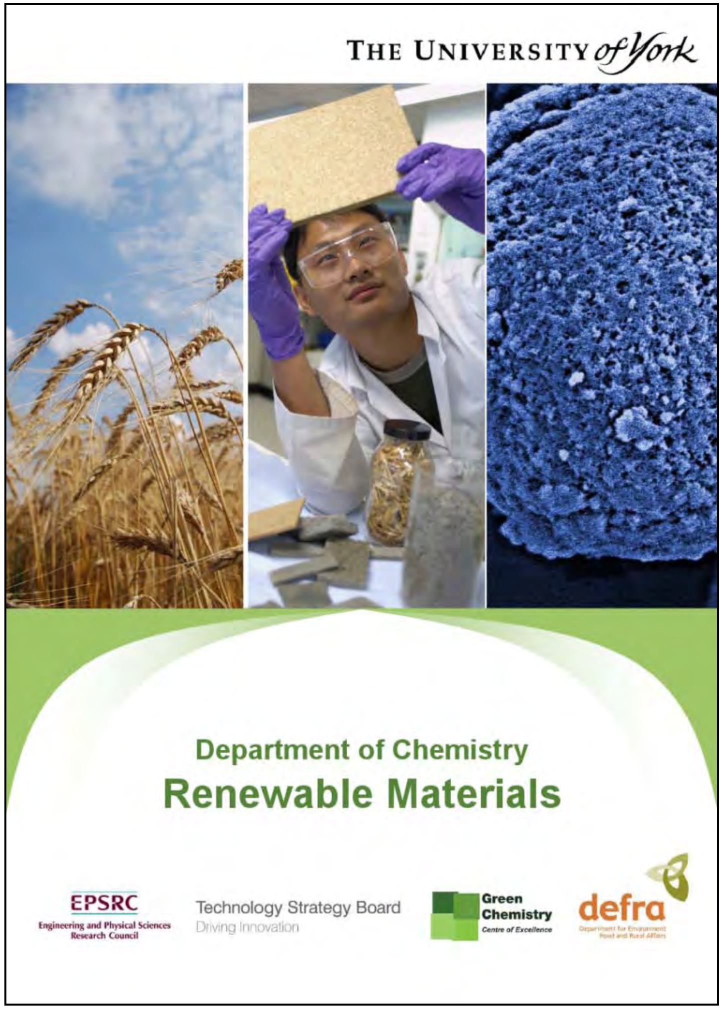
- Clean synthesis: catalysis
- Silica
- Chromatographic silica (with a trick!)
  - Simple catalyst for simple transformation



  - Aliphatic/aromatic 50-98% (110°C, 12h, toluene)
  - Product crystallises directly
  - Catalyst completely reusable several times
  - Catalyst not a dehydrating agent
  - Can be used in a flow reactor
  - Combining technologies: microwaves?

Enabling Technologies

Renewable materials

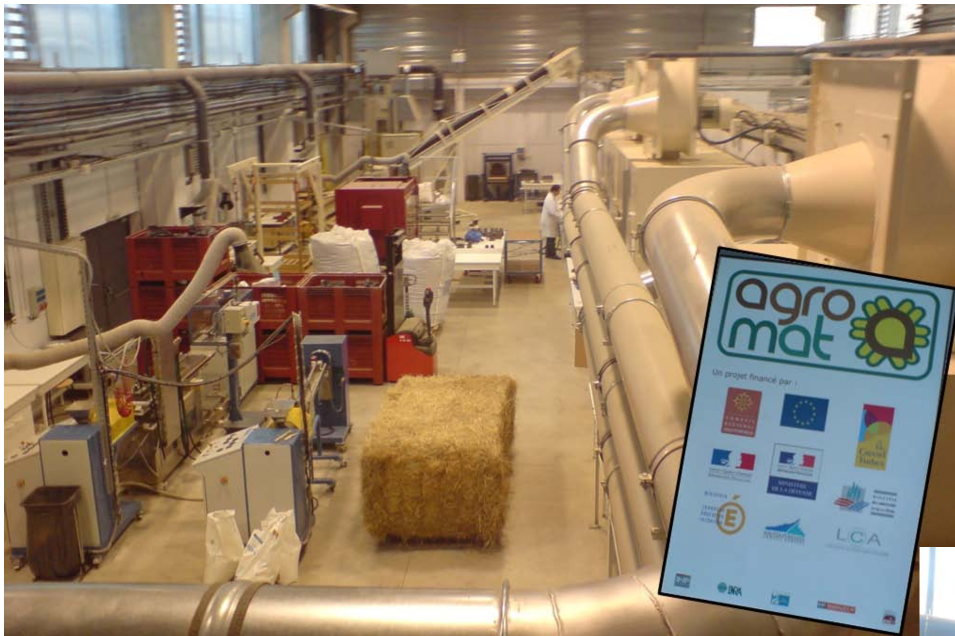


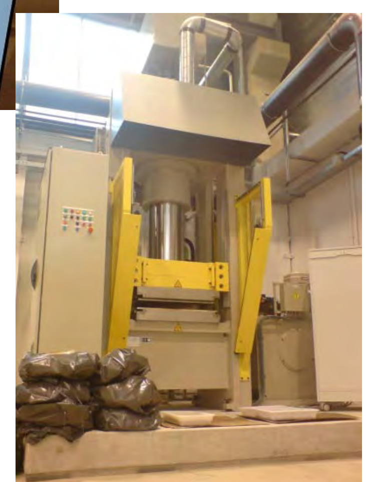
- Physical and chemical modification
  - Natural materials
- Starbons®
- Bio-boards
- Switchable adhesives
- PVC replacements

Enabling Technologies

Renewable materials

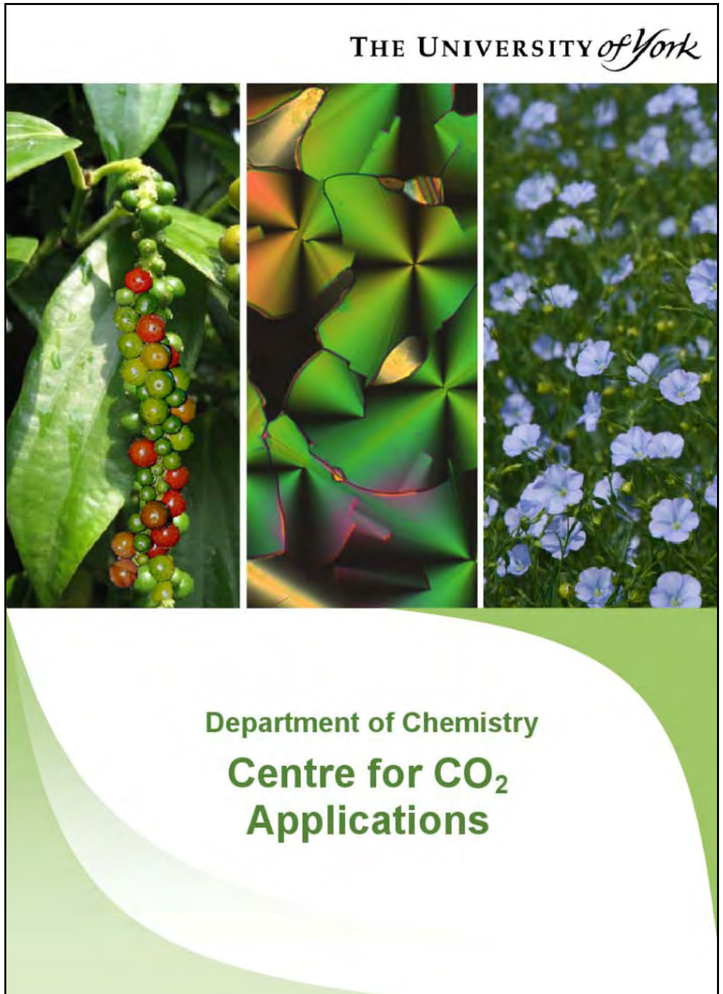
- Biodegradable materials





Enabling Technologies

Natural solvents

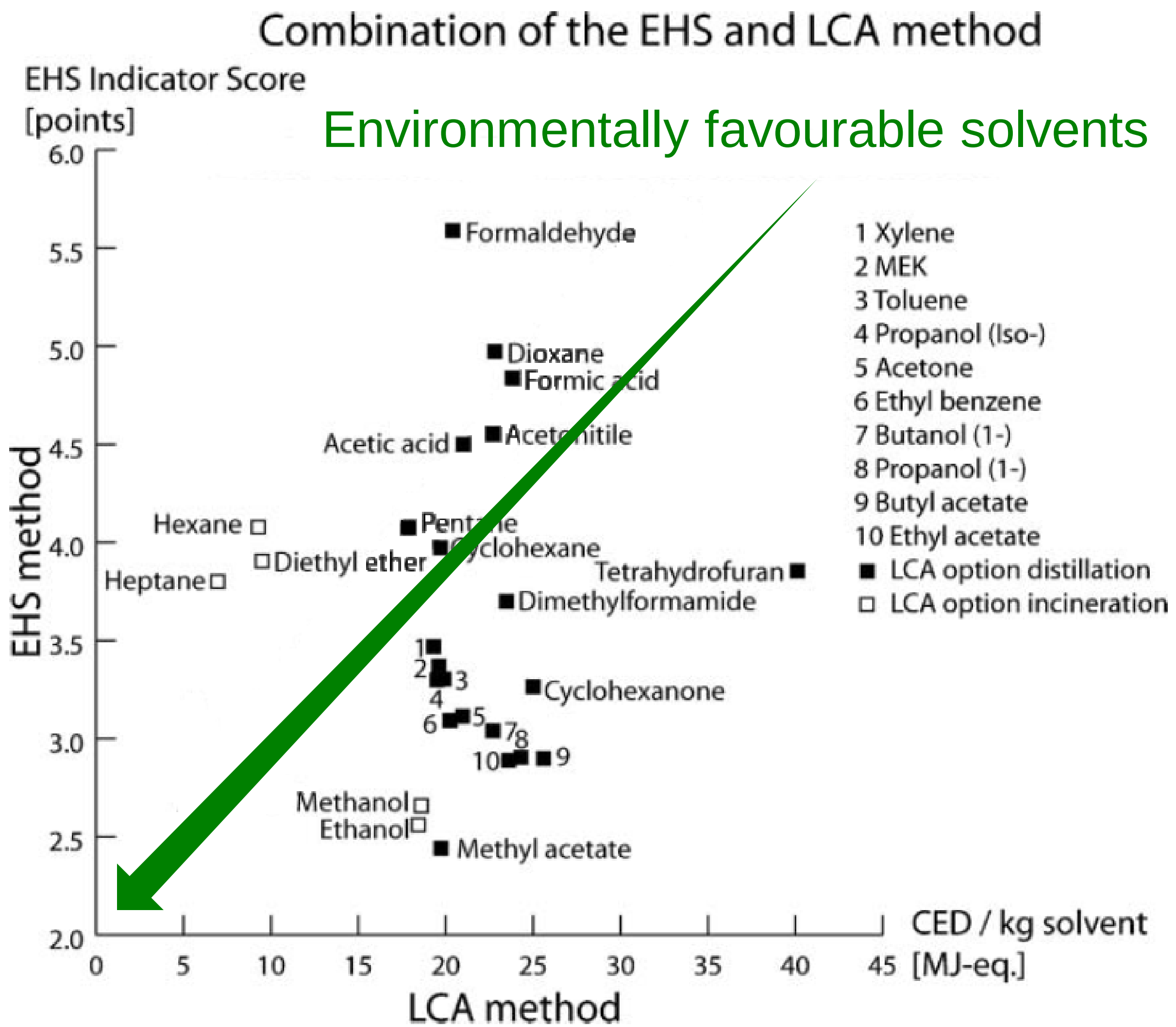


- Supercritical and liquid CO_2
  - Scale up
  - SFC
- Subcritical water
- Ethanol
- New green solvents

Enabling Technologies

Natural solvents

- How green is my solvent?



Capello, C., Fischer, U. and Hungerbuhler, K., Green Chemistry, 2007, **9**, 927-934

Enabling Technologies

Natural solvents

- Traffic lights

Solvent selection guide for pharmaceutical chemistry		
Undesirable	**Usable**	**Preferred**
Pentane	Cyclohexane	Water
Hexane(s)	Heptane	Acetone
Di-isopropyl ether	Toluene	Ethanol
Diethyl Ether	Methylcyclohexane	Propan-1-ol
Dichloromethane	Methyl t-butyl ether	Propan-2-ol
Dichloroethane	isooctane	Ethyl acetate
Chloroform	Acetonitrile	isopropyl acetate
Dimethyl formamide	2-methyl THF	Methanol
N-Methylpyrrolidinone	Tetrahydrofuran	Methyl ethyl ketone
Pyridine	Xylenes	Butan-1-ol
Dimethyl acetate	Dimethyl sulfoxide	t-Butanol
Dioxane	Acetic acid	
Dimethoxyethane	Ethylene glycol	
Benzene		
Carbon tetrachloride		

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Alfonsi,K. et al., Green Chemistry, 2008, 10, 31-36

Enabling Technologies

Natural solvents

- Food ingredients

Permitted extraction solvents		
Restricted by MRL	**Unrestricted**	**Organic**
Diethyl ether	Propane	Water
Hexane	Butane	Carbon dioxide
Cyclohexane	Ethyl acetate	Ethanol
Methyl acetate	Ethanol	
Butan-1-ol	Carbon dioxide	
Butan-2-ol	Acetone	
Butan-2-one	Water	
Dichloromethane		
Methanol		
Propan-2-ol		
Propan-1-ol		
1,1,1,2-tetrafluoroethane		

- Personal care products?
  - Cosmetics?
- Home care products?

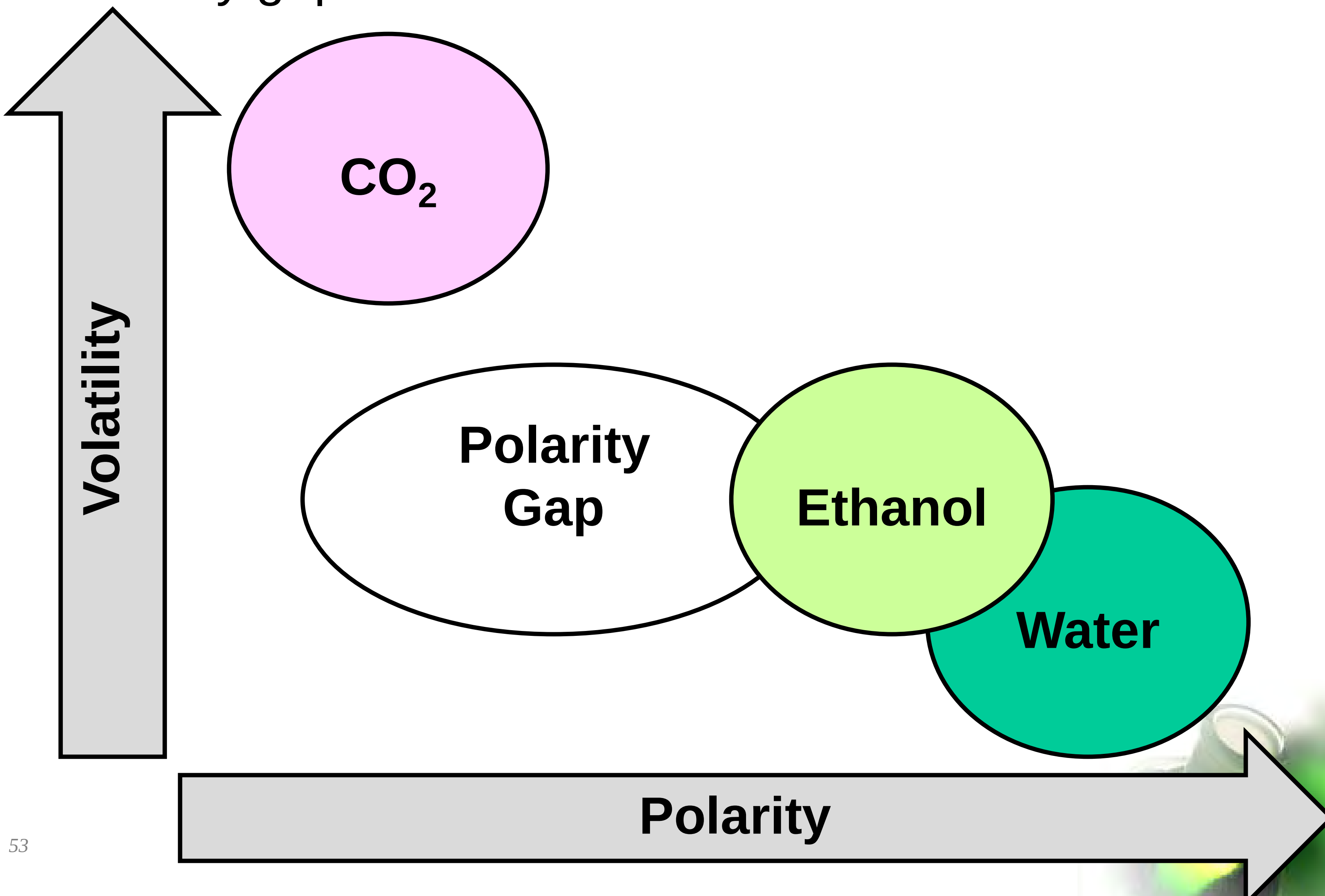
Directive 88/344/EEC + amendments
Soil Association SA Certs - clause 8.03.07a

Enabling Technologies

Natural solvents

- Liquid and supercritical CO_2
  - Extraction and fractionation
  - Lipids, waxes and secondary metabolites
  - Valuable molecules from waste streams
  - Ethanol used as co-solvent
- Reactions in supercritical CO_2
  - Biocatalysis
- Fractionation using SCF chromatography
- Analytical and preparative chromatography
- Superheated/subcritical water
  - Extraction
  - Complimentary to CO_2

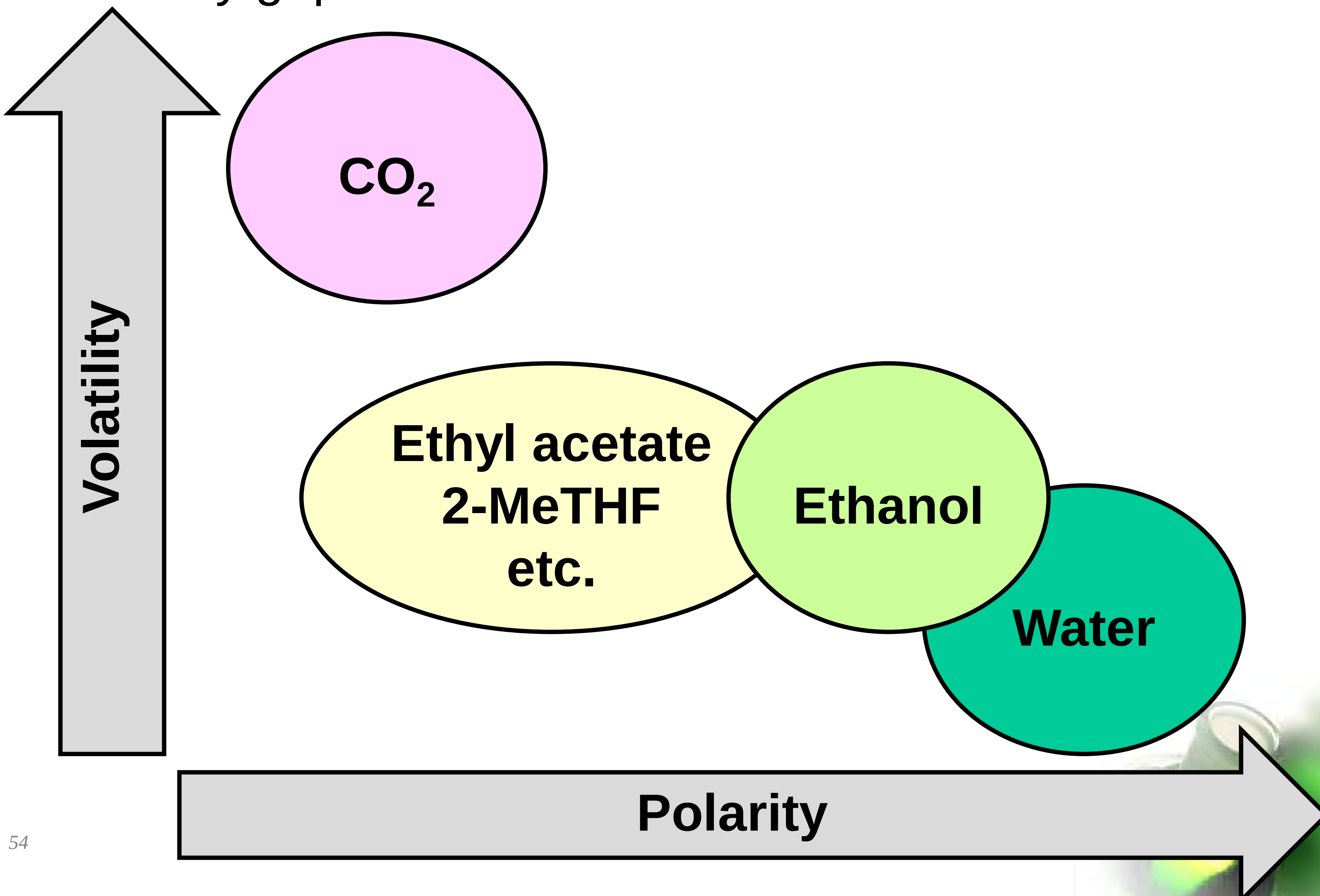
- Polarity gap of solvents



Enabling Technologies

Natural solvents

- Polarity gap of solvents



Enabling Technologies

Natural solvents

- Formulation challenge
  - Product with defined characteristics: petroleum based
  - Thermal behaviour crucial
- Isolate using green technology from natural source?
  - Identified a natural source
  - CO_2 Extraction: good yield
  - Measurable parameters (DSC/GC) acceptable
  - Formulation (aerosol); failed *(currently)*
- Collaboration and communication essential
  - Both ingredient and product formulators
- Drop-in replacement
  - Rarely the best option

Enabling Technologies

Natural solvents

- Pilot scale equipment

Extraction

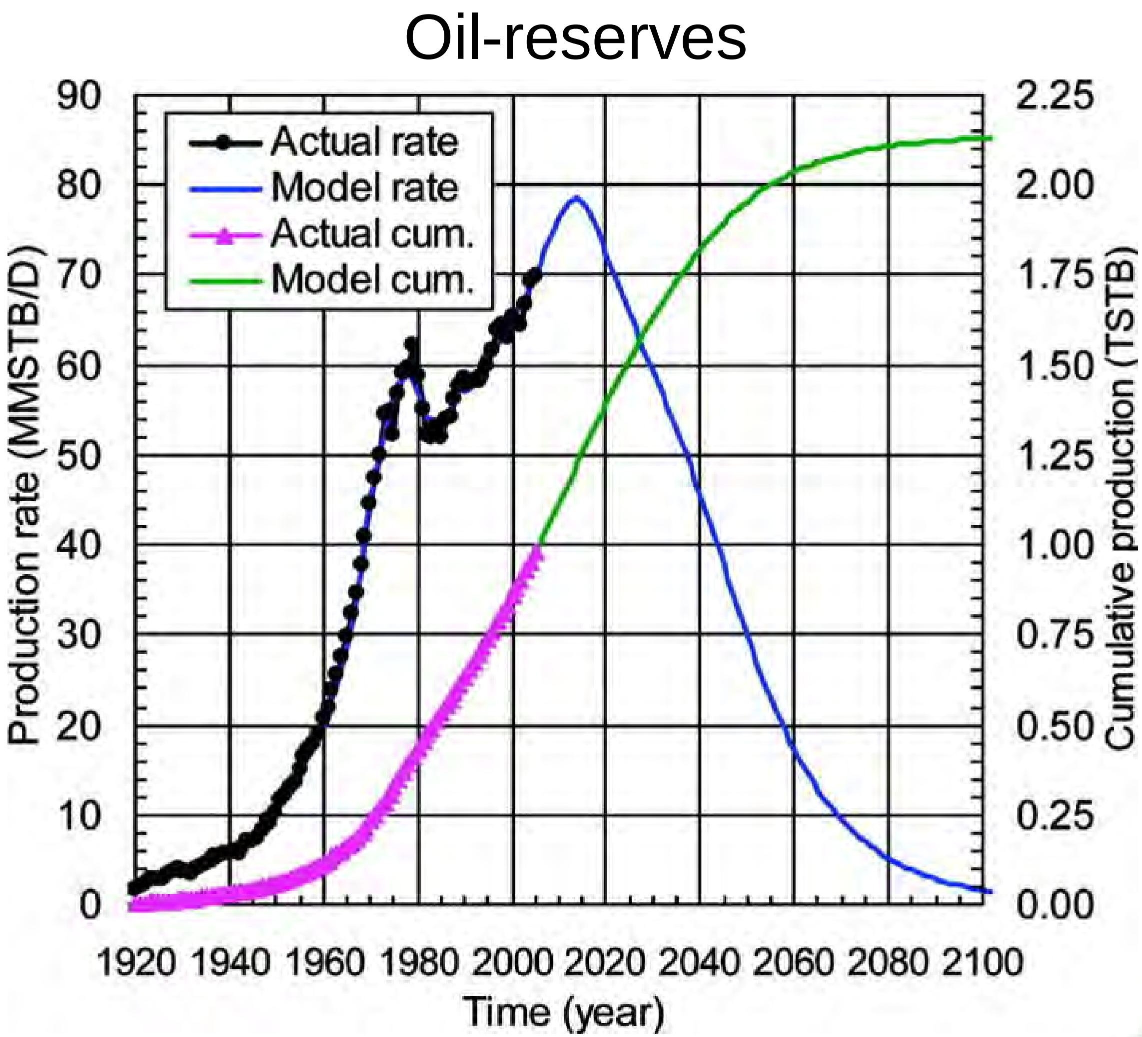
Fractionation

Reactions

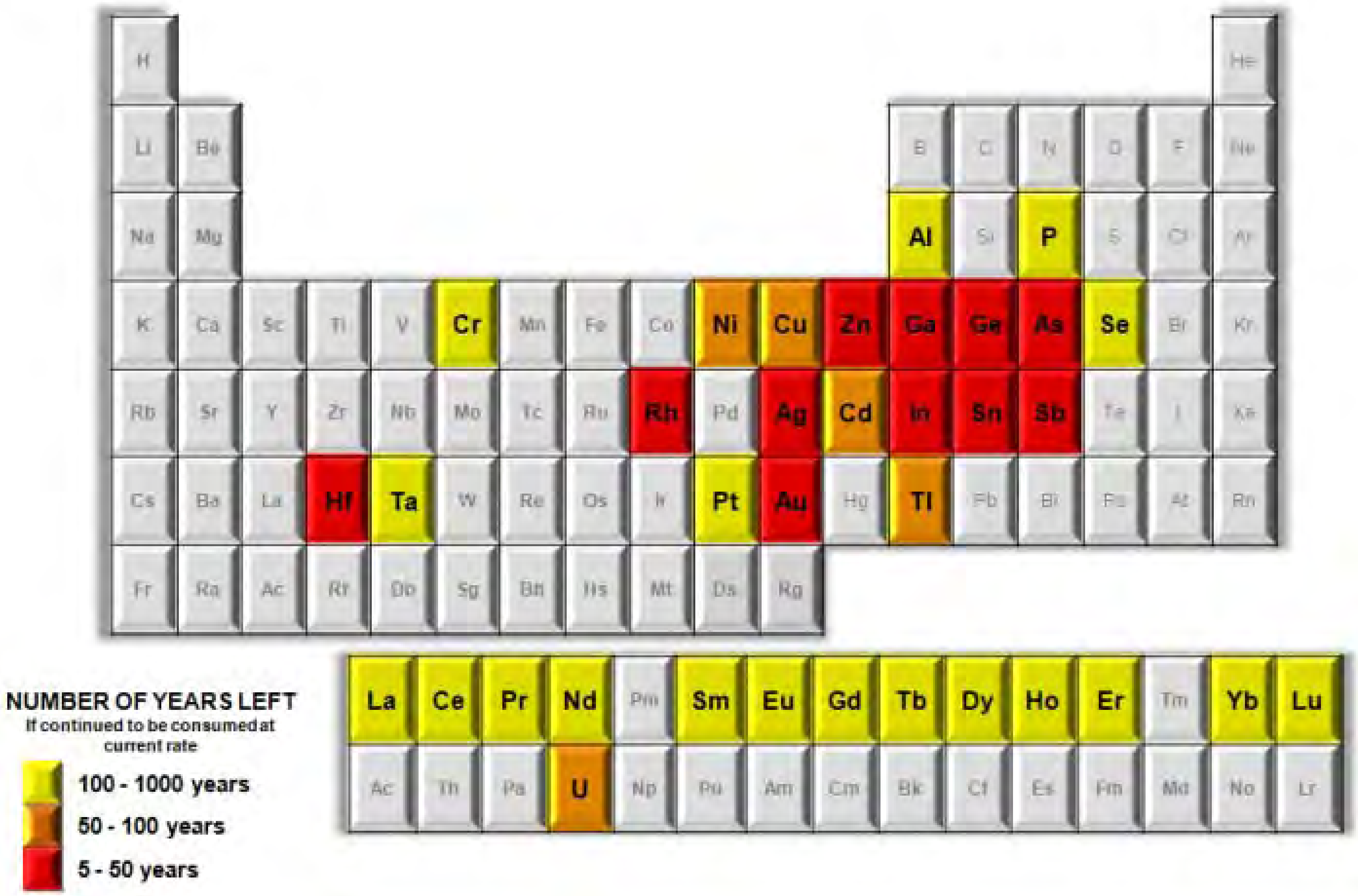
Summary

and the future?

The Global Challenge



Elemental Sustainability



The Drivers?

"We must work together to advance responsible investment and corporate sustainability"

UN Secretary-General Ban Ki-moon,
The Second World Investment Forum (WIF)
September, 2010

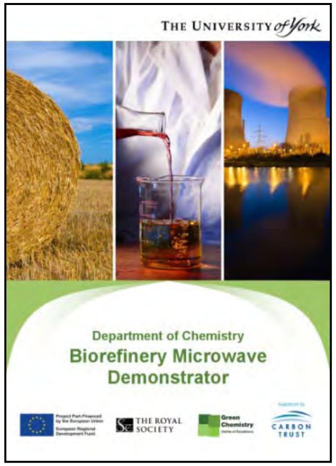
"The Annual Meeting of the New Champions will highlight how the sustainability imperative is transforming companies and reshaping industries"

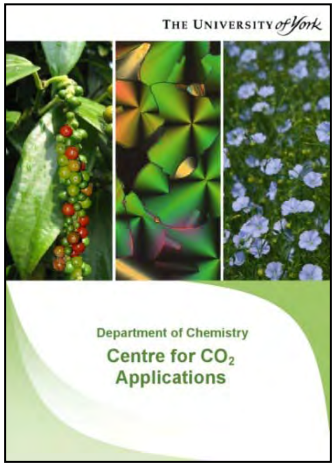
Jeremy Jurgens, Senior Director at the World Economic Forum and Head of the Annual Meeting of the New Champions and Community of Global Growth Companies
September 2010

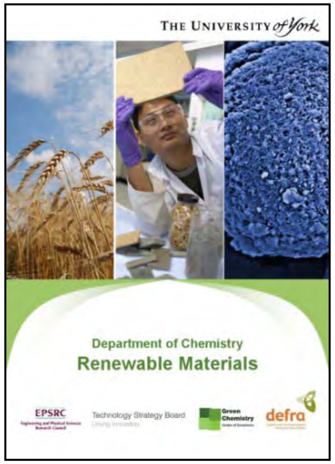
Summary

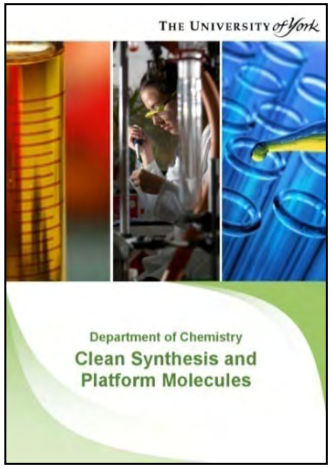
- Green Chemistry offers solutions to a wide range of topical issues
  - Waste reduction and recycling
  - Production of solid and liquid biofuels
  - Greener synthesis of a wide range of molecules
  - Green solvents to replace tradition petrochemicals solvents
  - Greater use of renewable materials and waste
- Formulation
  - Based on control of molecular structure
    - Solvents are crucial
  - Green supply chain
  - Whole formulation
  - Not drop in replacements

Thank you for your attention









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