The Role of Green Chemistry in Sustainable Formulations

Simon Breeden
Green Chemistry Centre of Excellence
University of York
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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
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
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

Environmental
A viable natural environment

Sustainable development
- Sustainable natural and built environment
- Sustainable economic development

Social
Nurturing community

Economic
- Equitable social environment
- Sufficient economy
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
Sustainable through Green Chemistry

• 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.

• 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.

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

Speculative Research
Discovery

Focussed Research
Industrial Collaboration

Applied Research
Scale-up & Application Studies

Green Chemistry Centre

Laboratory & Desk-top Studies

Proving routes & technologies

Environmental Impact Assessments

Training for industry partners
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
Case Study 1
From starch to switchable adhesives
Whole Formulation
Case Study 1
From starch to switchable adhesives

~45M m² pa (10M kg nylon, 50M kg bitumen)

Switchable adhesive layer

~90% landfill Waste costs!
# Case Study 1

## From starch to switchable adhesives

<table>
<thead>
<tr>
<th></th>
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<tbody>
<tr>
<td>Project year</td>
<td>I - III</td>
<td>IV</td>
<td>1</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Activities</td>
<td>PhD project</td>
<td>Feasibility study</td>
<td>Scale up &amp; reduce costs</td>
<td>Pilot scale: 100k m² year⁻¹</td>
<td>Industrial scale: 4 M m² year⁻¹</td>
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<tr>
<td>Funding</td>
<td>Industry</td>
<td>DTI &amp; Industry</td>
<td>TSB &amp; Industry</td>
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</tbody>
</table>

### 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 NOₓ 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
Case Study 1
From starch to switchable adhesives

- Nitrogen isotherm

- Pore size distribution

'hydresis loop' – mesopores

Type III

Type IV

Starch
Starch (gel)
Ex Starch

Volume adsorbed (cm$^3$ g$^{-1}$ STP)

Relative pressure ($P/P_0$)

Pore volume (cm$^3$ g$^{-1}$ - nm)

Pore diameter (nm)

Increase in Pore volume

2 – 50 nm
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
# Case Study 1
From starch to switchable adhesives

<table>
<thead>
<tr>
<th>Test</th>
<th>Grade (Pass ✓ fail ×)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Loop withdrawal</td>
<td>✓</td>
<td>Similar to commercial adhesives – suitable for commercial use</td>
</tr>
<tr>
<td>Martindale</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Castor chair</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Dimensional stability</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>Flammability</td>
<td>✓</td>
<td>Excellent – no need for added flame retardants</td>
</tr>
<tr>
<td>Switchability</td>
<td>✓</td>
<td>Strength reduced – no adhesive contamination</td>
</tr>
</tbody>
</table>
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

<table>
<thead>
<tr>
<th>Pore type</th>
<th>Pore Size</th>
<th>Condensation mechanism</th>
<th>Type of Adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micropore</td>
<td>&lt; 2 nm</td>
<td>Three-dimensional</td>
<td>Non-specific</td>
</tr>
<tr>
<td>Mesopore</td>
<td>≥ 2 ≤ 50 nm</td>
<td>Capillary</td>
<td>Specific</td>
</tr>
<tr>
<td>Macropore</td>
<td>&gt; 50 nm</td>
<td>No condensation</td>
<td>-</td>
</tr>
</tbody>
</table>
Case Study 2
From starch to porous materials

- Potential applications of mesoporous materials

Low microporous volume
High mesoporous volume
Good macroporous characteristics

Adsorption
Nanotechnology
Catalysis
Sensors
Chromatography
Electrochemistry
Filtration
Case Study 2
From starch to porous materials

- Current preparation
- Resource intensive
- Energy intensive
- Significant waste
Case Study 2
From starch to porous materials

- Starch preparation
  - Switchable adhesive
Case Study 2
From starch to porous materials

**Materials and Processes**

- **Template Creation**
  - TEOS 3.6 g
  - Surfactant 1.8 g
  - 35% HCl (aq) 11.3 g
  - H₂O >320 g
  - 24 h stirring
  - Calcination at 550 °C
  - 24 h at 150 °C

- **Silica Template**
  - Carbohydrate, ~1.3 g
  - Sulfuric acid 0.06 g
  - H₂O 5 g
  - 24 h at 150 °C, x 2
  - 6 h at 500-900 °C

- **Carbonisation**
  - HF > 2 g

- **Template Removal**
  - H₂O

- **H₂O, H₂SiF₆**

- **Volatile Organics**

- **Expanded Starch**
  - EtOH 20 g
  - H₂O 20 g
  - Modifier (optional)
  - Starch 1 g
  - 1 h stirring
  - 1 h at 140 °C
  - Vacuum at 50 °C
  - 48 h at 5 °C

- **Expansion**
  - EtOH, H₂O

- **Expanded Carbonaceous Materials**
  - 300 °C 700 mg
  - Mesoporous carbonaceous materials
  - 300 °C 700 mg

- **Mesoporous Carbon, 300 mg**
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
Case Study 2
From starch to porous materials

<table>
<thead>
<tr>
<th>Carbonisation temperature, °C</th>
<th>Nanotechnology</th>
<th>Chromatography</th>
<th>Acid catalysis</th>
<th>Organic adsorption</th>
<th>Metal adsorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>✔ ✗</td>
<td>✔ ✗</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>300</td>
<td>✔ ✗</td>
<td>✔ ✔ ✔</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>✔ ✗</td>
<td>✔ ✔ ✔</td>
<td>✔ ✔ ✔</td>
<td></td>
<td></td>
</tr>
<tr>
<td>700</td>
<td>✔ ✗</td>
<td>✔ ✔ ✔</td>
<td>✔ ✔ ✔</td>
<td>✔ ✔ ✔ ✔ ✔</td>
<td></td>
</tr>
<tr>
<td>900</td>
<td>✔ ✔ ✔</td>
<td>✔ ✔ ✔</td>
<td>✔ ✔ ✔</td>
<td>✔ ✔ ✔ ✔ ✔</td>
<td>✔ ✔ ✔ ✔</td>
</tr>
</tbody>
</table>
Case Study 2
From starch to porous materials
Case Study 2
From starch to porous materials

ESTERIFICATIONS

R-COOH → R-COOCH₂-CH₃ (EtOH)

ACYLATIONS

R-OH → R-OAc (HAc)

ALKYLATIONS

RCONH₂ → RCO₂H

AMIDATIONS
Case Study 3
Bio-Boards
Whole Formulation
Case Study 3
Bio-Boards

Clean Energy

Renewable Power

Bio-ashes

Bio silicate Adhesive

Silicate products:
Personal care, adhesives, detergents, food production, paints, polymers ...

Agricultural and other biomass residues

Extracted valuable plant waxes
Cosmetics, food additives, coatings, ...

Structural & furniture boards

Untreated aggregate

Pre-treated aggregate

Adhesive
Substrate
Hardener

Hardener Chemistry

Bio hardener

Bio fuels by-products

Research
Industry
Networking
Education
How do we deliver these green formulations?

Enabling Technologies
Enabling Technologies

Microwave

- Microwave assisted chemistry
- Biomass pyrolysis
- Biorefinery demonstrator
Enabling Technologies

Microwave

• 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

Biomass

Energy

Temperature <200°C

Microwave Processor

Gas

Oil

Char

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
Enabling Technologies
Clean Synthesis and Platform Molecules

Polysaccharides

- pyrolysis
  - syngas
  - bio-oil
  - char
  - fuels
    - + platform molecules

- hydrolysis
  - sugars
    - fermentation
    - platform molecules

Direct use

Chemical Products
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
    \[
    \text{RCOOH} + \text{H}_2\text{NR'} \rightarrow \text{RCONH}_2\text{R} + \text{H}_2\text{O}
    \]
  - 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 CO₂
  - Scale up
  - SFC
- Subcritical water
- Ethanol
- New green solvents
**Enabling Technologies**

Natural solvents

- How green is my solvent?

---

*Combination of the EHS and LCA method*

- **Environmentally favourable solvents**

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

**Natural solvents**

- **Traffic lights**

<table>
<thead>
<tr>
<th>Undesirable</th>
<th>Usable</th>
<th>Preferred</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pentane</td>
<td>Cyclohexane</td>
<td>Water</td>
</tr>
<tr>
<td>Hexane(s)</td>
<td>Heptane</td>
<td>Acetone</td>
</tr>
<tr>
<td>Di-isopropyl ether</td>
<td>Toluene</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>Methylcyclohexane</td>
<td>Propan-1-ol</td>
</tr>
<tr>
<td>Dichloromethane</td>
<td>Methyl t-butyl ether</td>
<td>Propan-2-ol</td>
</tr>
<tr>
<td>Dichloroethane</td>
<td>iso-octane</td>
<td>Ethyl acetate</td>
</tr>
<tr>
<td>Chloroform</td>
<td>Acetonitrile</td>
<td>isopropyl acetate</td>
</tr>
<tr>
<td>Dimethyl formamide</td>
<td>2-methyl THF</td>
<td>Methanol</td>
</tr>
<tr>
<td>N-Methylpyrrolidinone</td>
<td>Tetrahydrofuran</td>
<td>Methyl ethyl ketone</td>
</tr>
<tr>
<td>Pyridine</td>
<td>Xylenes</td>
<td>Butan-1-ol</td>
</tr>
<tr>
<td>Dimethyl acetate</td>
<td>Dimethyl sulfoxide</td>
<td>t-Butanol</td>
</tr>
<tr>
<td>Dioxane</td>
<td>Acetic acid</td>
<td></td>
</tr>
<tr>
<td>Dimethoxyethane</td>
<td>Ethylene glycol</td>
<td></td>
</tr>
<tr>
<td>Benzene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
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</tbody>
</table>
### Enabling Technologies

**Natural solvents**

- **Food ingredients**

<table>
<thead>
<tr>
<th>Restricted by MRL</th>
<th>Unrestricted</th>
<th>Organic</th>
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<tbody>
<tr>
<td>Diethyl ether</td>
<td>Propane</td>
<td>Water</td>
</tr>
<tr>
<td>Hexane</td>
<td>Butane</td>
<td>Carbon dioxide</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>Ethyl acetate</td>
<td>Ethanol</td>
</tr>
<tr>
<td>Methyl acetate</td>
<td>Ethanol</td>
<td></td>
</tr>
<tr>
<td>Butan-1-ol</td>
<td>Carbon dioxide</td>
<td></td>
</tr>
<tr>
<td>Butan-2-ol</td>
<td>Acetone</td>
<td></td>
</tr>
<tr>
<td>Butan-2-one</td>
<td>Water</td>
<td></td>
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<tr>
<td>Dichloromethane</td>
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<td></td>
</tr>
<tr>
<td>Methanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propan-2-ol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propan-1-ol</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,1,1,2-tetrafluoroethane</td>
<td></td>
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</tr>
</tbody>
</table>

- **Personal care products?**
  - Cosmetics?

- **Home care products?**

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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$_2$
Enabling Technologies
Natural solvents

• Polarity gap of solvents

Polarity Gap

CO₂

Ethanol

Water

Volatility

Polarity
Enabling Technologies
Natural solvents

- Polarity gap of solvents

- Volatility
  - CO₂

- Polarity
  - Ethyl acetate
  - 2-MeTHF etc.
  - Ethanol
  - Water
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
  – CO₂ Extraction: good yield
  – Measurable parameters (DSC/GC) acceptable
  – Formulation (aerosol); failed \textit{(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

Oil-reserves

- Actual rate
- Model rate
- Actual cum.
- Model cum.

Production rate (MMSTB/D)

Cumulative production (TSTB)

Time (year)
Elemental Sustainability
"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