



The University of  
**Nottingham**

# Can Chemistry be Green?

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[www.nottingham.ac.uk/supercritical](http://www.nottingham.ac.uk/supercritical)

# China Cup



# Paper Cup



# Polystyrene Cup



# Which is best for the Environment?



**Paper**



**China**



**Polystyrene**

# Coffee Cups - Manufacture

China – most energy to  
make

Polystyrene – made from oil

Paper – made from wood,  
messy process

**Cost of Energy varies**

# Coffee Cups- Use

Polystyrene – use once

Paper – use once

China – **multi-use**

**BUT needs washing**

(hot water, detergent)

# Coffee Cups- Verdict

You have to use a china cup  
**1000 times** before it is  
environmentally better than  
Polystyrene



# Coffee Cups - Disposal

China – landfill

Polystyrene – landfill

**(125 times better)**

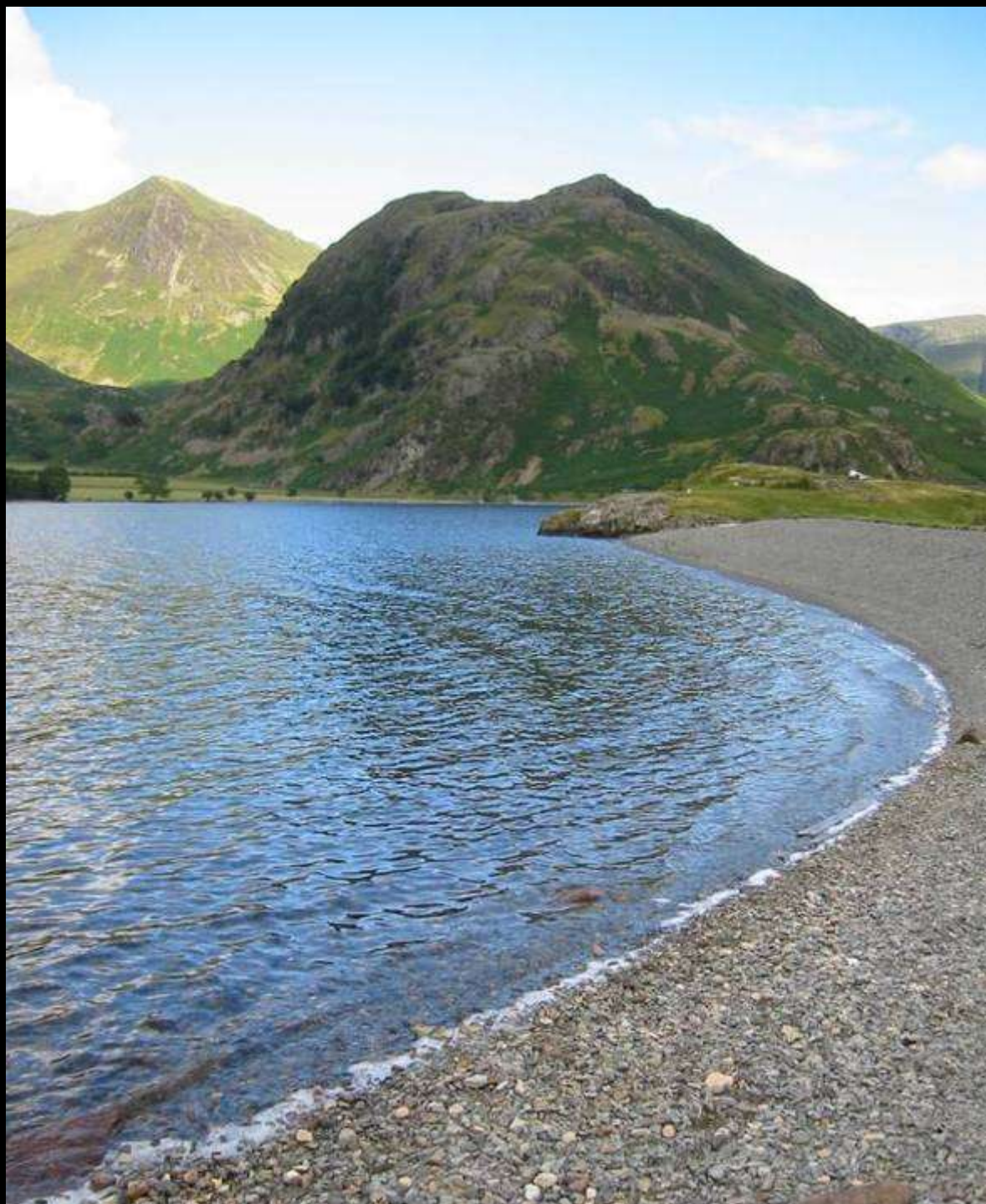
Paper – can be composted –  
generates CH<sub>4</sub>

**(greenhouse effect)**

**Life Cycle Assessment**







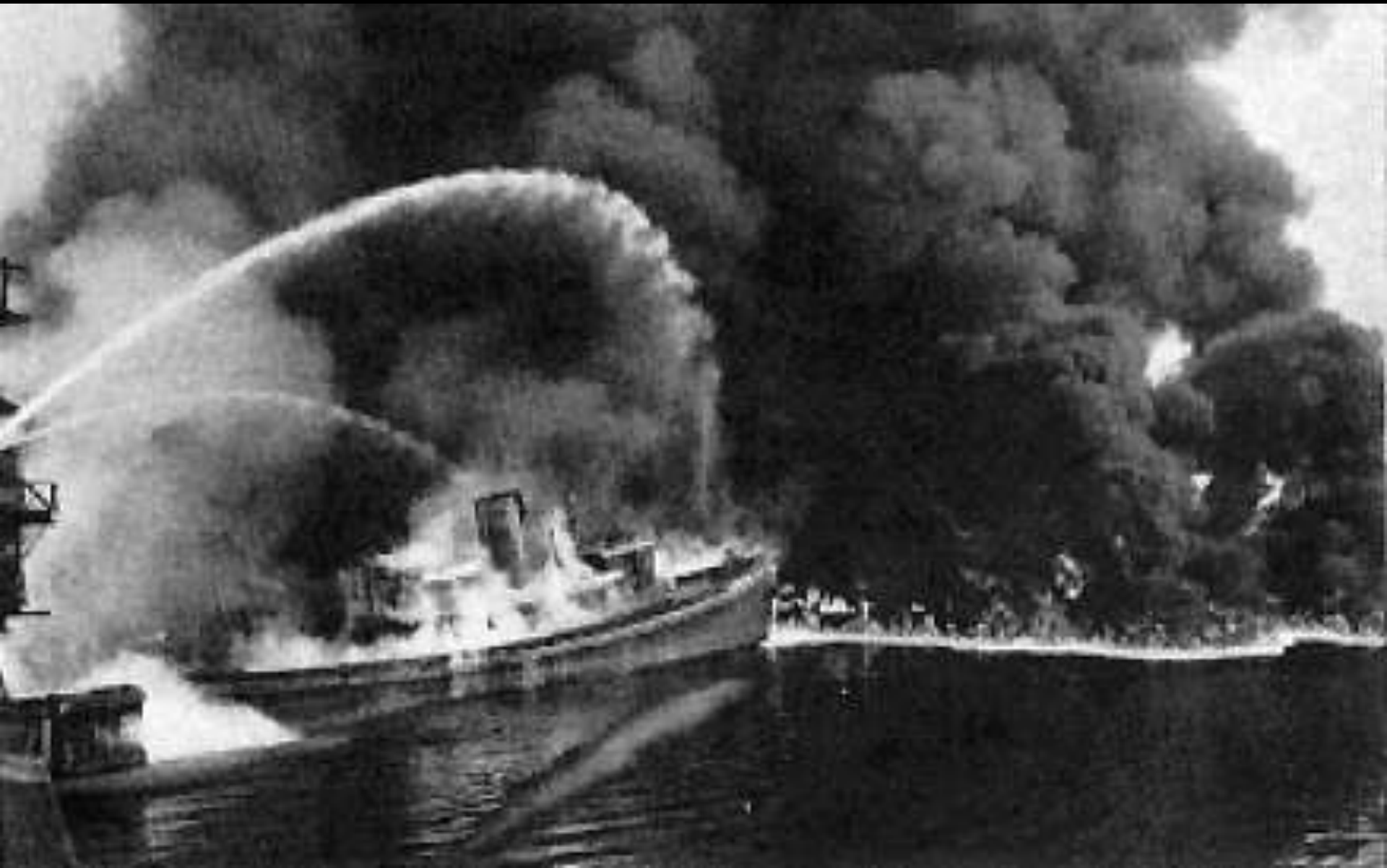


A photograph of a discarded coffee cup lying on a bed of dark, smooth river stones. The cup is a standard paper coffee cup with a white lid and a white base. The main body of the cup is brown with a decorative pattern of yellow and white swirls. The text "CAREFUL!" is printed in a bold, sans-serif font, with "It's very hot" written in a smaller font directly below it. The cup is positioned in the center-right of the frame, surrounded by numerous dark grey and black stones of various sizes. A single green leaf is visible on a stone to the right of the cup. The overall scene suggests environmental pollution in a natural setting.

CAREFUL!  
It's very hot

One of the main  
problems in chemical  
manufacture is the  
generation/disposal of  
**(toxic) waste**

# Cuyahoga River 1969







FLAMMABLE

CUYAHOGA  
RIVER

# Green Chemistry (early 1990s)

Cleaner approaches to  
making and using chemicals  
& materials



# Assessing Risk

$$\text{Risk} = \text{Hazard} \times \text{Exposure}$$

What we do now

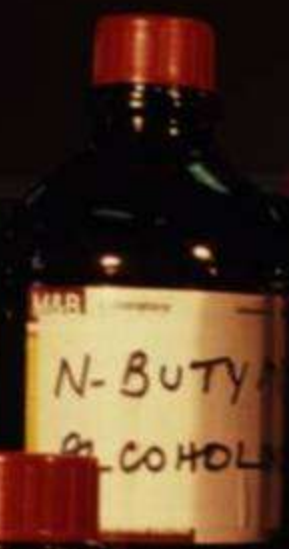
Limit Exposure  $\Rightarrow$  Acceptable Risk

Green Chemistry

if Hazard = 0  $\Rightarrow$  Risk = 0

# Areas of Green Chemistry

- New reactions
- New catalysts
- Alternative Feedstocks
- **Safer Solvents**



# Solvents: the problems

- Most solvents are Volatile Organic Compounds
- **Fire / explosion hazards**
- **VOC emissions** → atmospheric pollution
- **Disposal / recycle** → environmental pollution

# Fork Lift + Toluene → 'Big Bang'



# Solvents: Alternatives

- No solvent
- Water
- Ionic Liquids
- **Supercritical Fluids**

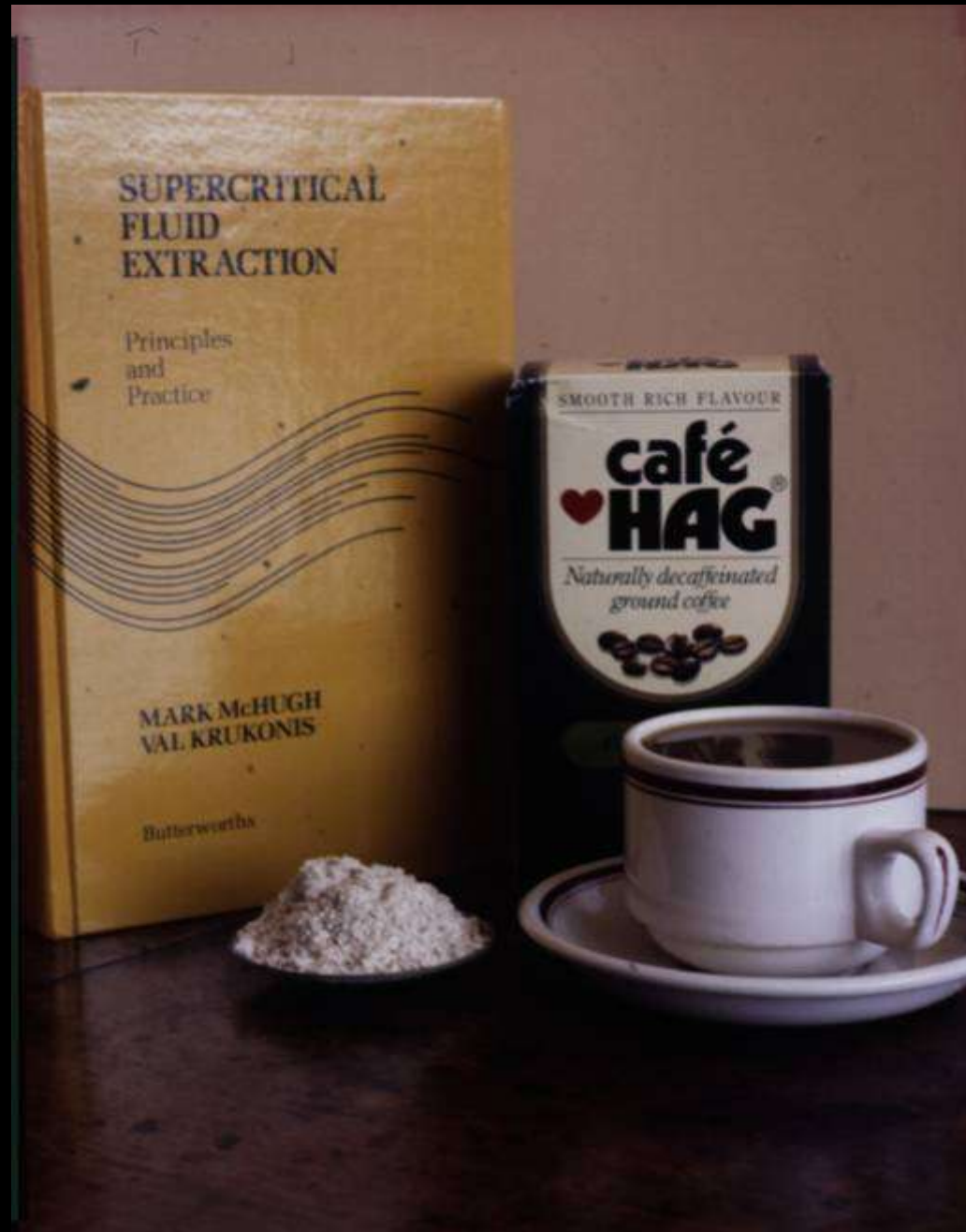


# Supercritical Fluids

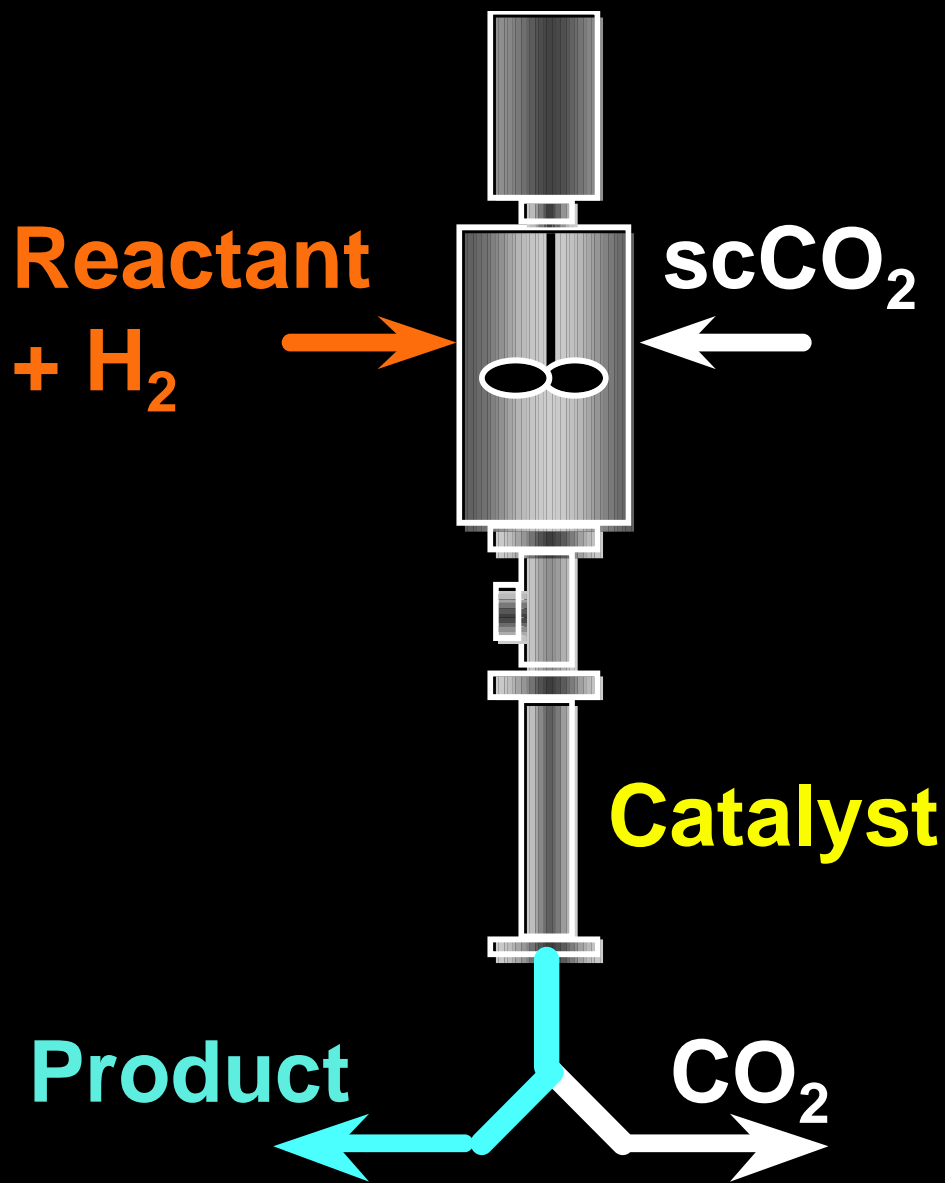
- Gases (e.g. CO<sub>2</sub>) compressed until they are nearly as dense as liquids
- **SCFs can dissolve solids**  
solubility increases with density (applied pressure)

# Decaffeination in $\text{scCO}_2$

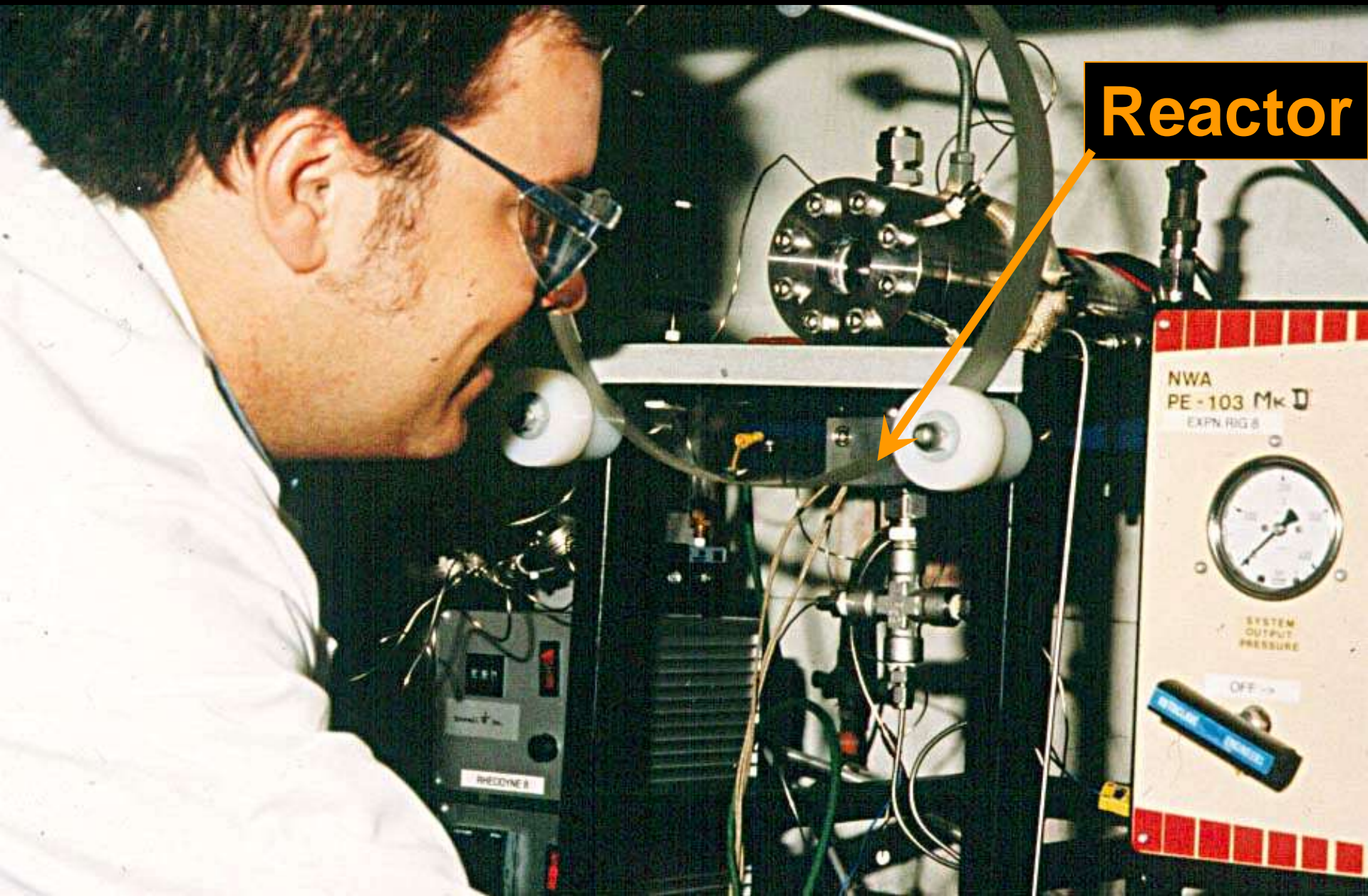
- Well established commercially



# Greener Hydrogenation in scCO<sub>2</sub>



# Lab Reactor



Reactor

NWA  
PE-103 Mk II  
EXPN RIG B



SYSTEM  
OUTPUT  
PRESSURE



RHODYNE B

# Greener Hydrogenation



**Use Supercritical  $CO_2$**

**sc $CO_2$  is completely miscible  
with  $H_2$  – more efficient reactions**



**DELOXAN®**  
Supported Precious Metal Catalyst

Type:	AP 2 / 8 % Pd
Support:	Aminoalkylsiloxane
Batch:	Pd 673.7
Particle size:	0.3 - 0.8 mm

**Degussa**   
Munich (AC-PE-C) · D-53175  
Germany, phone: +49 21 92 - 164 0760

# scCO<sub>2</sub> Chemical Plant

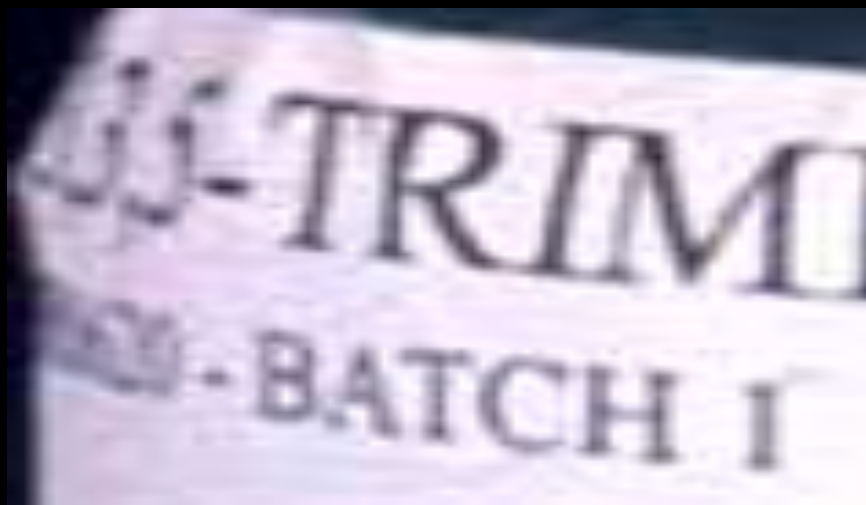
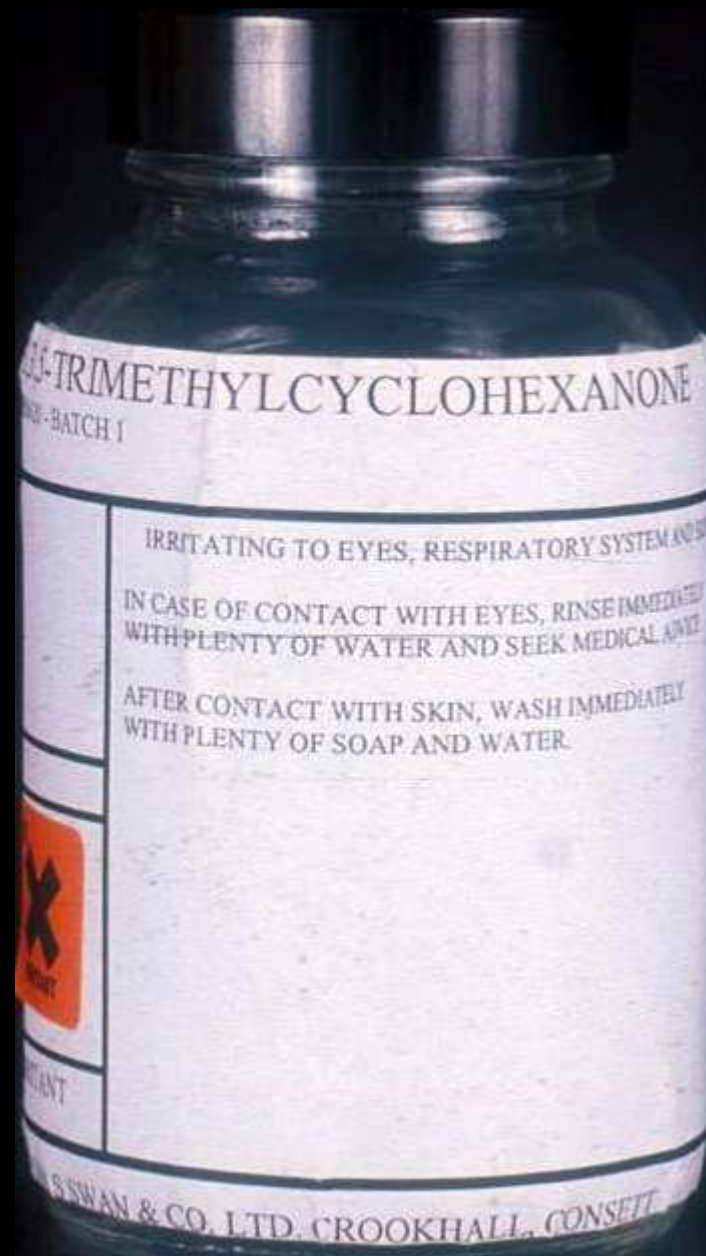
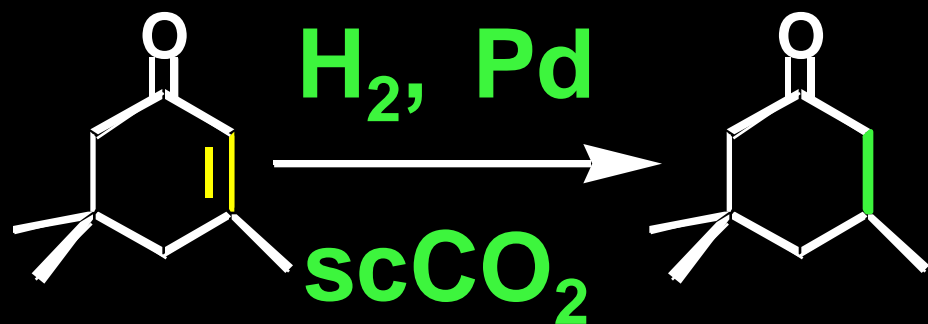
opened  
July, 2002

- continuous
- multipurpose
- 1000 ton p.a.

Thomas Swan & Co



# The First Product!





# Green Chemistry 12 Principles

P - Prevent wastes

R - Renewable materials

O - Omit derivatization steps

D - Degradable chemical products

U - Use safe synthetic methods

C - Catalytic reagents

T - Temperature, Pressure ambient

I - In-Process Monitoring

V - Very few auxiliary substances

E - E-factor, maximize feed in product

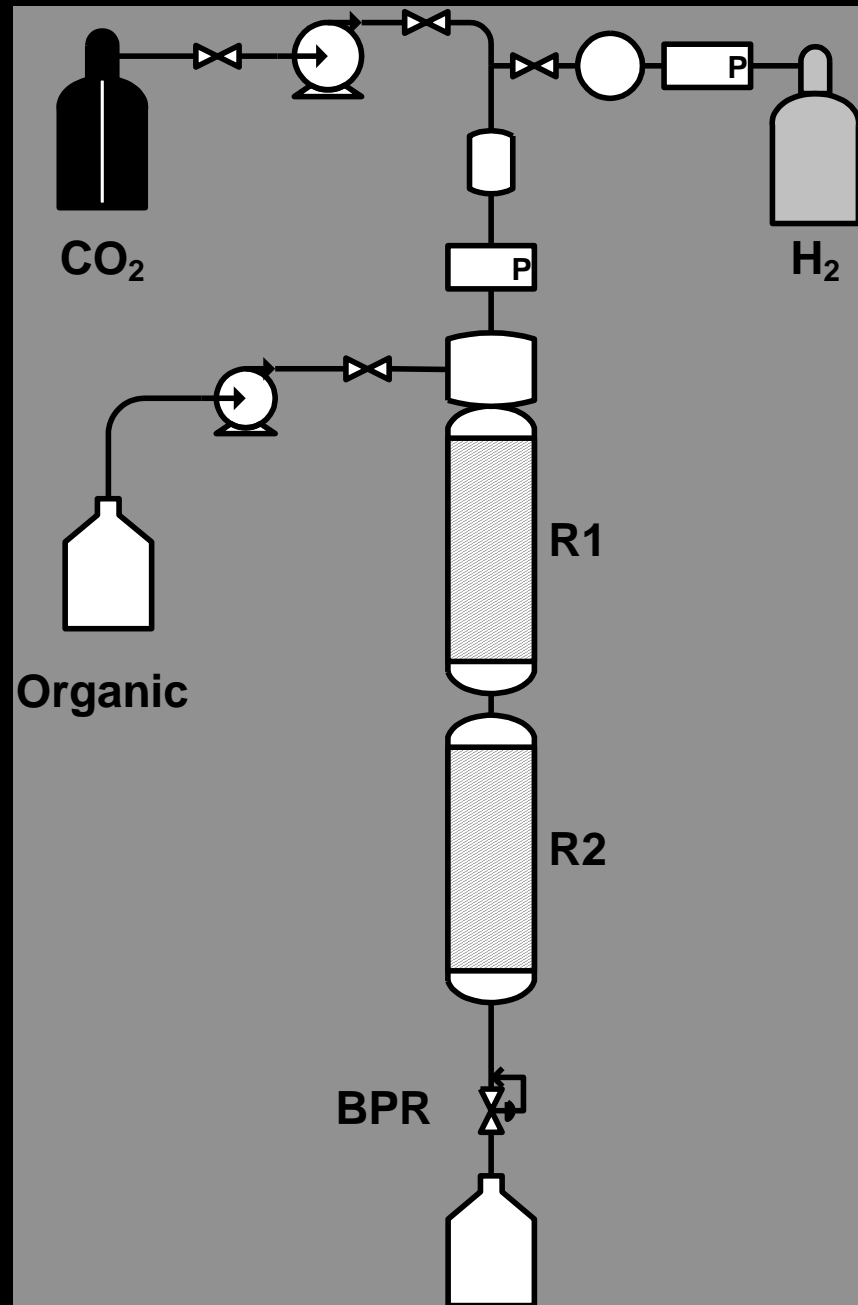
L - Low toxicity of chemical products

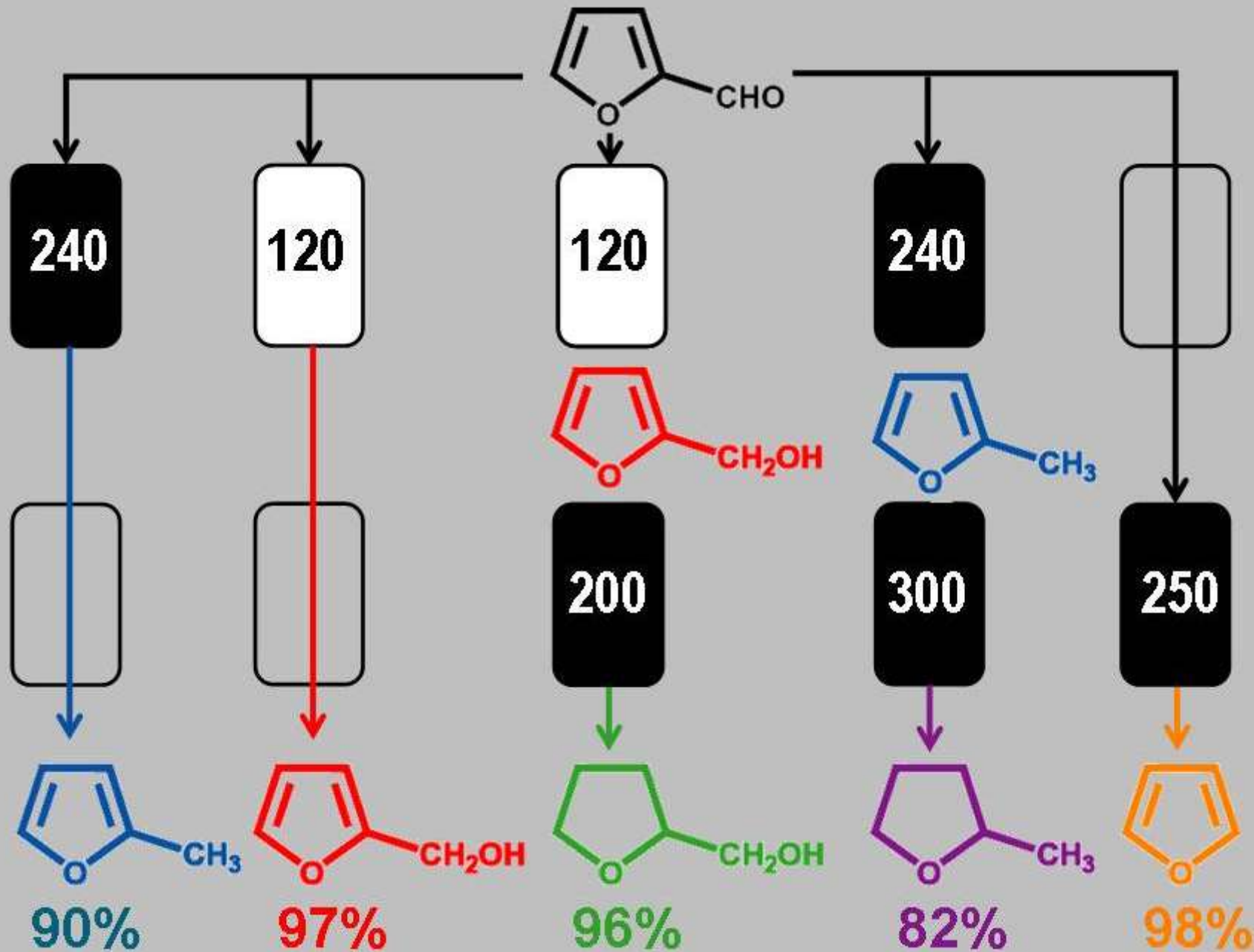
Y - Yes it's safe

# 'Chemical Vending Machine'

One precursor  
several different  
products?

**Two reactors:**  
different catalysts  
**Vary reactor  
temperatures**





# Supercritical Fluids: University Spin outs

- **Critical Pharmaceuticals:-**  
**Steve Howdle**, scCO<sub>2</sub> drug delivery  
[www.criticalpharmaceuticals.com](http://www.criticalpharmaceuticals.com)
- **Promethean Particles:-**  
**Ed Lester**, scH<sub>2</sub>O nanoparticles  
[www.prometheanparticles.co.uk/](http://www.prometheanparticles.co.uk/)

# Taking Green Chemistry to Developing Countries





**Hossana, Ethiopia**









# Sugar Cane





# Is it silly to make polymers out of sugar cane?

**No!!!**

- Sugar cane is grown in huge amounts
- It grows where there is little oil
- There is a surplus
- The farmers cannot sell all of it

# Sugar Cane



# How to do it?

**“To make a  
bag from  
sugar needs  
new**

**Chemistry”**

2<sup>nd</sup> July, 2003



# Polymers from Carbohydrate

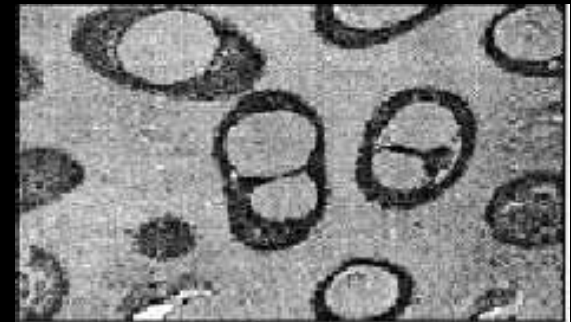
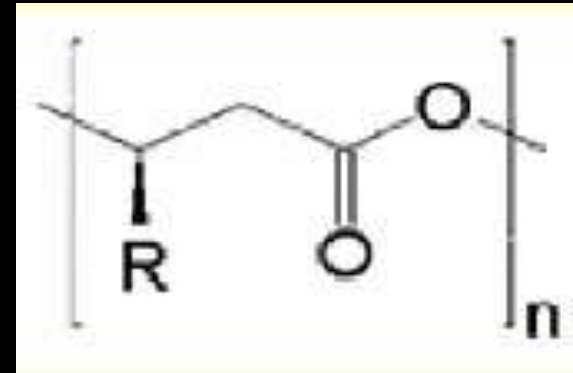
Dr Isao Noda, Procter & Gamble

Microorganisms eat  
carbohydrate

They store energy as a  
polymer

**Polymer is easily  
harvested**

Waste is recycled.



# P & G NODAX™



**Polymer from carbohydrate**



# Coffee Cups from Waste Carbohydrate

Cups for US Navy

Can be made on  
existing machines

**Composts in 2 days!**





**Dr Nigist in Washington 2005**

# Jimma, Ethiopia 2007



**Royal Society of Chemistry**  
**PanAfrican**  
**Chemistry Network**  
**1st Green Chemistry Congress**

15-17 November 2010  
Addis Ababa, Ethiopia







# **13 Principles of Green Chemistry for Africa**



- G** - Generate Wealth not Waste
- R** - Regard for All Life & Human Health
- E** - Energy from the Sun
- E** - Ensure Degradability & No Hazards
- N** - New Ideas & Different Thinking
- E** - Engineer for Simplicity & Practicality
- R** - Recycle Whenever Possible
- A** - Appropriate Materials for Function
- F** - Fewer Auxiliary Substances & Solvents
- R** - Reactions using Catalysts
- I** - Indigenous Renewable Feedstocks
- C** - Cleaner Air & Water
- A** - Avoid the Mistakes of Others



**Paul Anastas  
with the  
13 principles  
at the PACN  
Congress,  
Nov 2010**

# PACN Lecture, Addis, 2010

- ▶ SPME has been successfully used to sample and extract volatiles from Morama milk
- ▶ Its simple to operate
- ▶ Portable
- ▶ solvent free



SPME OFFERS POTENTIAL AS A 'GREEN' TOOL FOR SAMPLING AND EXTRACTION OF VOLATILE COMPOUNDS IN MORAMA MILK

Score on 13 principles of green chemistry =  $10/13=78\%$ )  
GENRAFRICA

# Influencing Policy Makers



**The Ethiopian  
Minister for  
Education  
in Nottingham  
Jan 13<sup>th</sup> 2011**



**The 13  
Principles**

**Green  
Chemistry:  
The Role of  
Government?**

TONY  
JUDT

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*Ill fares the land, to hastening ills a prey,  
Where wealth accumulates, and men decay*  
Oliver Goldsmith, *The Deserted Village*, 1770

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ILL FARES  
THE LAND

# Ill Fares the Land

- Some things are done better by the State

**running the railways**

# The Role of Government?

- **The success of Green Chemistry is vital for society**
- UK chemical manufacturing is going offshore
- **Huge opportunities for inventing new technologies**

# The Role of Government?

- Many of the key problems are long term
- **Government must support:**
  - Ambition in the research agenda**
  - Chemistry + Engineering + Business
  - Academia + Industry**



# What's our University doing?

- **Leading centre of Green Chemistry**
- £4M DICE project: **Driving Innovation in Chemistry & Engineering**
- **SM Howdle, S Kingman, M Binks:**  
development of Sustainable Processing/Chemistry in Nottingham
- **GSK £14 M investment in Green Chemistry at Nottingham**

***“We've invested in Nottingham because it's one of the best universities in Britain, in fact the world, from a chemistry point of view .....***

***There's a great record of excellence in that school and they absolutely deserve that investment.”***

**Andrew Witty,  
CEO GSK, BBC News**

**Mike George, Steve Howdle,  
Pete Licence, Sam Kingman  
Sam Tang**

**All our Students,  
Postdocs and Collaborators**

**P. Fields, R. Wilson, M. Guyler**

***INVISTA, Thomas Swan & Co, AstraZeneca  
EPSRC, Royal Society, EU Marie Curie***

# Green Chemistry: What Now?

- 19 years old – growing fast
- Spreading all over the world
- Increasing industrial interest
- **Is now part of A-Level!!**
- **Needs lots of new ideas**