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Next in the ACS GCI Series June 19th @ 2pm ET

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From Waste to Wealth Using Green Chemistry

Dr. Joseph Fortunak
Howard University

Dr. Avtar Matharu

James Clark

Dr. Andrew Hunt

Lucie Pfaltzgraff

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All Speakers
Green Chemistry Centre of Excellence, University of York

From Waste to Wealth Using Green Chemistry

James Clark

Avtar Matharu

Andrew J. Hunt

Lucie A. Pfaltzgraff

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

www.york.ac.uk/greenchemistry
Who Are We?

James Clark is Professor of Chemistry and Director of the Green Chemistry Centre of Excellence at the University of York where he runs a large team researching bio-renewables, waste valorization and sustainable chemistry. He has distinctions including medals from the Royal Society of Chemistry, the Society of Chemical Industry and an honorary doctorate from the University of Gent. He has about 400 research articles and many edited books.

Who Are We?

Dr. Avtar Matharu is Deputy Director of the Green Chemistry Centre and Scientific Leader for Renewable Materials Technology Platform. His background is synthetic organic chemistry relevant to design, synthesis and characterisation of functional materials such as liquid crystals and ultra-high capacity optical data storage media. His research now focuses on technological innovations in green and sustainability chemistry.
Dr. Andrew J. Hunt is scientific leader of the natural solvent technology platform at the Green Chemistry Centre. His research interests include elemental sustainability, solvents and supercritical fluids. His work on the recovery of polyvinyl alcohol from waste LCD’s received significant attention including a press conference at the ASC green chemistry conference, Washington DC, June 2010. He has recently edited a book on “Elemental recovery and sustainability” as part of the RSC Green Chemistry book series.

Lucie A. Pfaltzgraff is a PhD student at the Green Chemistry Centre under the supervision of Professor James Clark. Her research interests include the valorisation of food supply chain waste as a valuable biorefinery feedstock, mapping the availability and studying the cost effectiveness of this resource. Her project focuses on the use of low temperature microwave processes for the combined extraction of citrus peel compounds.
Benefits of Chemicals - Everywhere!

But we are running out of key resources...

Elemental unsustainability

And it’s getting worse

Because we turn elements from a resource to a product and then to a waste....

What do we do with our waste?

And this does not include the waste we don’t “manage” that is destroying our environment...what a waste!

Instead of a problem, waste can become tomorrow’s resource

But we must use green technologies

2014 = European Year of Food Waste

U.S.A.
- Whey 43,091,275 T/yr
- Corn stover 80–100 million T/yr (dry basis)
  California:
- Vegetable crop residue 1 million T/yr (dry basis)
- Tomato pomace 60,000 T/yr (dry basis)
- Nut shells & pits 40,000 T/yr
- Meat processing waste 65,000 T/yr (dry basis)
- Food scraps in MSW 1.6-2 million T/yr (dry basis)

E.U.
- Starch 8 million T/yr
- Tomato pomace 4 million T/yr
- Post manufacturing food waste 34 million T/yr
- Used cooking oil 0.7-1 million T/yr
- Surplus whey 13,462 T/yr
- Surplus wheat straw 5.7 million T/yr (UK)
- Bread surplus 680,000 T/yr (UK)
- Citrus waste 0.6 million T/yr (Spain)

WORLD
- Rice husks 110 million T/yr
- Citrus peel residue 15.6 million T/yr
- Apple pomace 3-4.2 million T/yr
- Grape pomace 5-9 million T/yr
- Banana peels 9 million T/yr
- Kiwi residue 0.3 million T/yr
- Surplus whey 13,462 T/yr
- Surplus wheat straw 5.7 million T/yr (UK)
- Bread surplus 680,000 T/yr (UK)
- Citrus waste 0.6 million T/yr (Spain)

BRAZIL
- Sugar cane bagasse 376.5 million T/yr
- Corn residue 41.7 million T/yr
- Cassava residue 51.6 million T/yr
- Rice straw 4.5 million T/yr
- Wheat straw 5.4 million T/yr
- Citrus residues 9.4 million T/yr

AFRICA
- Citrus waste 139,724 T/yr (South Africa)
- Cocoa pods 20 million T/yr (Ivory Coast)
- Cashew Shell Nut Liquid 20,000 T/yr (Tanzania)

MEDITERRANEAN BASIN
- Olive mill residue 30 million T/yr

ASIA
- Palm oil 15.8 million T/yr (Indonesia)
- Food waste 1.2 million T/yr (Hong Kong)
- 25MMT rice straw burned in open fields (Vietnam)

Chemicals from Food Waste

Food supply chain residues

Benign extraction

Clean synthesis


Question for the Audience

Making Metals Sustainable

What is the best option to ensure the sustainability of key processes and products that depend on metals we are running out of?

• Improve recycling
• Find new virgin sources of the metals
• Develop replacements
• Another solution?
- Sales revenue >$100 billion (2011)
- >100 Mill. LCD TV’s sold 2011/12
- LCD TV largest growth area
- >220 million m² LCD glass sold (2012)
LCD E-WASTE

WEEE DIRECTIVE (2002/96/EC)
“LCD containing WEEE with a surface area greater than 100 cm² and those with Hg containing backlights must be isolated…”

LCD CONTAINING WEEE IS THE FASTEST GROWING WASTE SOURCE IN THE EU

LCs classified as non-hazardous (waste code number 16 02 16)

CURRENT PRACTICE: Remove Hg Lamp and shred the rest
Elemental Sustainability

• Elemental sustainability is a concept whereby the sustainability of each element in the periodic table is guaranteed.

• For an element to be sustainable, its use by this current generation should not impair or restrict future generations from also utilising that same element.

• Exciting new book now available!

AIM: Capture metals in plants via phytoremediation and utilise this trapped metal insitu for catalysis, focusing on the platinum group metals.

Waste (mine tailings)

Nanoparticle formation

Green chemistry applications

Metal uptake by plants

37


38


PHYTOCAT Project

Metal uptake:

*Arabidopsis thaliana* plants grown hydroponically until 3 weeks old...

Nanoparticle formation:

...plants were dosed with aqueous solution of K$_2$PdCl$_4$ & monitored over 24 hours...
PHYTOCAT Project

Pd leaching & mechanism of activity:
...an investigation into the catalyst mechanism was carried out by monitoring Pd leaching...

1. Pd dissociation from the support.

2. Coupling reaction proceeds quasi-homogeneously.

3. Pd redeposits onto support.


PHYTOCAT Project

Reuse of catalyst:
...catalyst was successfully reused...

### Suzuki-Miyaura Reactions

![Reaction Scheme]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aryl halide</th>
<th>Yield(^b) (%)</th>
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<tr>
<td>1</td>
<td>![Aryl Halide 1]</td>
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</tr>
<tr>
<td>2</td>
<td>![Aryl Halide 2]</td>
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<td>3</td>
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<tr>
<td>6</td>
<td>![Aryl Halide 6]</td>
<td>94</td>
</tr>
</tbody>
</table>

\(^b\) Yield isolated by column chromatography

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aryl halide</th>
<th>Yield(^b) (%)</th>
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</tr>
<tr>
<td>12</td>
<td>![Aryl Halide 12]</td>
<td>81, 41</td>
</tr>
</tbody>
</table>

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### Question for the Audience

**Food for Thought**

Food supply chain waste is available in very large quantities worldwide. How do you think it is best exploited?

- Traditional uses such as feed and animal bedding
- Anaerobic digestion
- Extraction of high value chemicals
- Conversion to commodity chemicals
- Other uses
The OPEC project

- D-limonene 3.8% w/w
- flavonoids 4.5%
- pectin 20-30%
- cellulose 37.08%
- hemicellulose 11.04%
- sugars 9.57%


Why microwave technology?

Desirables for the design of an integrated conversion process:

- volumetric heating
- scalable
- flexible
- allows continuous processing
- feedstock agnostic
- allows the use of wet feedstocks
**Integrated process used**

- **Wet orange peel**
  - Orange peel residue 1.
  - MW treatment 100-130 °C
  - MW assisted steam distillation 800-1200 W

- **Work-up**
  - D-limonene 1.08%
    - Flavour & fragrance
    - Electronics
    - Platform molecule
  - Flavonoids 2.22%
    - Broad spectrum of biological activity
  - Pectin 8.74%
    - Food applications
    - Cosmetics
    - Pharmaceutical

**Product range obtained**

- 94.83% D-limonene
- 2.18% α-myrcene
Summary of Food Waste Valorisation

✓ A low temperature hydrothermal microwave process separating pectin from cellulose in the cell wall without any acid or other additive has been developed.

✓ The process releases pectin, D-limonene, flavonoids, sugars, furans & cellulose.

✓ Product work-up done with food grade accepted solvents only.

✓ D-limonene and pectin meet standard quality requirements.

✓ The process potentially could be run in one step.

✓ Techno-economic evaluation currently underway.

Conclusion

• We cannot afford to continue to throw away such large amounts of valuable chemicals especially as many traditional resources are liable to run out in a matter of years

• What we currently consider to be waste streams are actually a rich source of chemicals

• Valorising current process wastes or by-products can give new business opportunities to companies and strengthen the overall business model for the process

• Food supply chain wastes are available worldwide and are a rich source of valuable chemicals and materials

• Citrus is a good example of a high volume widely distributed food waste that can be converted to chemicals and materials using green chemical technologies

• E-waste is an increasingly large volume waste that is a good source of waste organics and waste metals

• Phytomining is a green technology that can be used to capture valuable metals from mining and other waste streams
Further Info...

Find us on the web at www.york.ac.uk/greenchemistry

Green Chemistry at York Youtube Channel www.youtube.com/user/greenchemistryyork

Follow us on Twitter @GreenChemYork

Green Gown Award Video Case Study https://www.youtube.com/watch?v=iCZwsoSv63Q

www.biorenewables.org  www.costeubis.org  www.phytocat.org

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