UNIVERSITY OF BIRMINGHAM
COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

Reducing critical materials through chemical catalysis

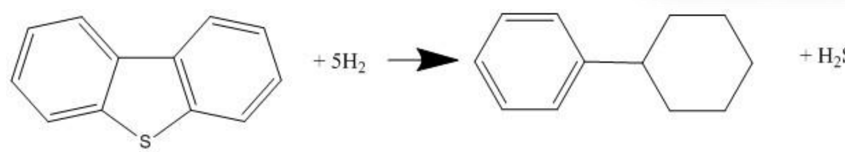
Professor Joe Wood

Catalysis and Reaction Engineering Group, Prof. Joe Wood

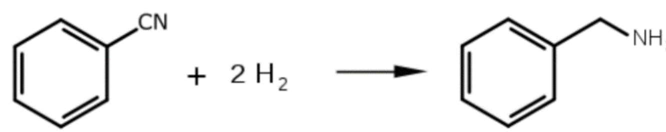
- 8 PhD students, 3 postdocs
- Research covers catalysis, upgrading of fossil and bio-oils, carbon capture
- Reaction-separation engineering via membranes EPSRC project (EP/P016405/1)
- Hydrodeoxygenation of pyrolysis and hydrothermal liquefaction (HTL) derived bio-oils
- Production of bio-based chemicals and fuel replacements such as 5-hydroxymethylfurfural (5-HMF) and 2,5-dimethylfuran (DMF)

Products from Catalysis

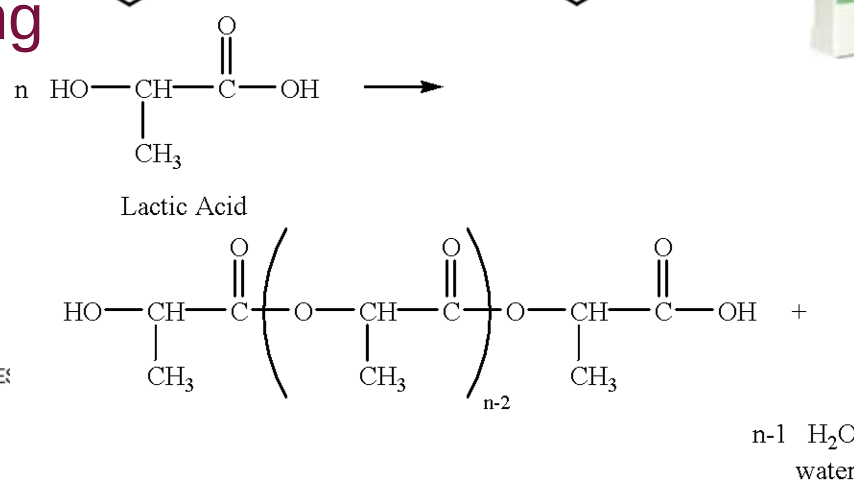
- Low sulphur petrol and diesel
  - Hydrodesulfurisation
  - $CoMo/Al_2O_3$



- Pharmaceuticals
  - Hydrogenation of benzonitrile
  - Ni/Al_2O_3

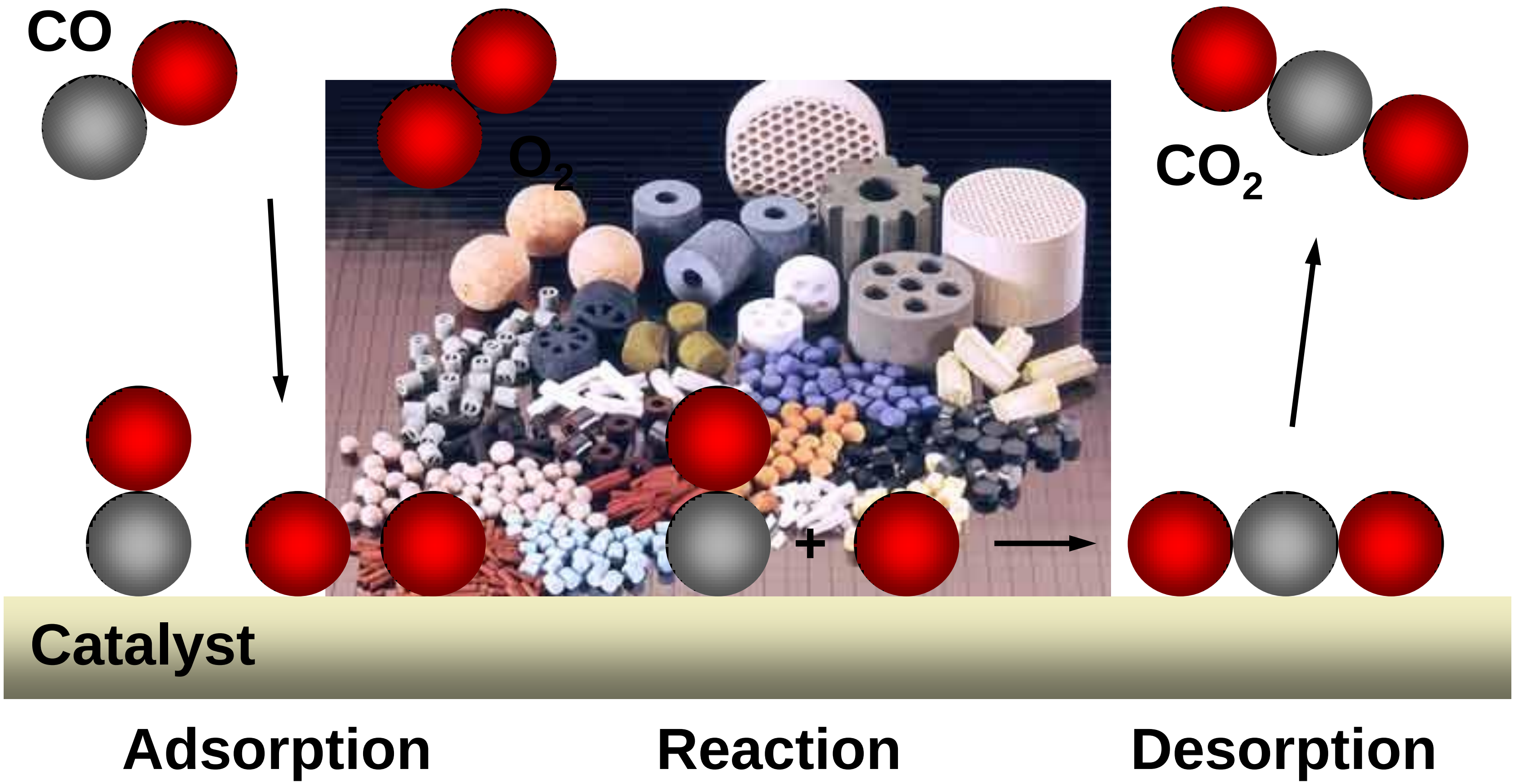


- Renewable packaging
  - Polylactic acid
  - H_3PW/C

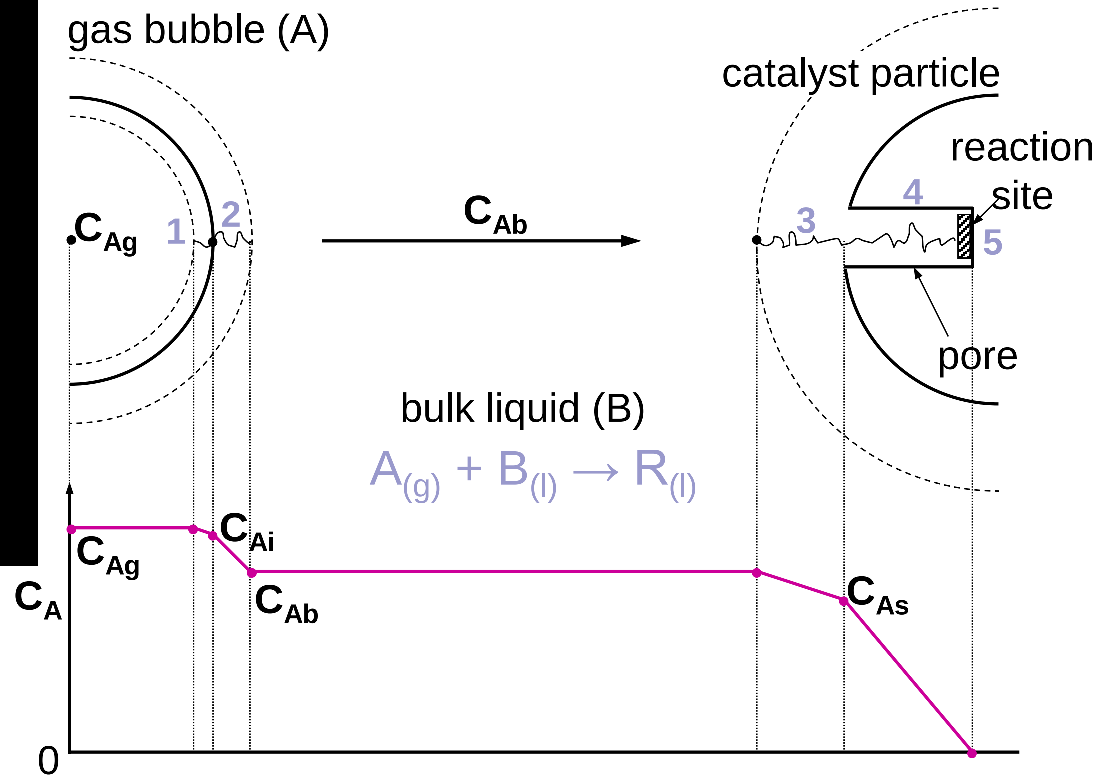


UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

Catalysis and Adsorption



Mass Transport Resistances

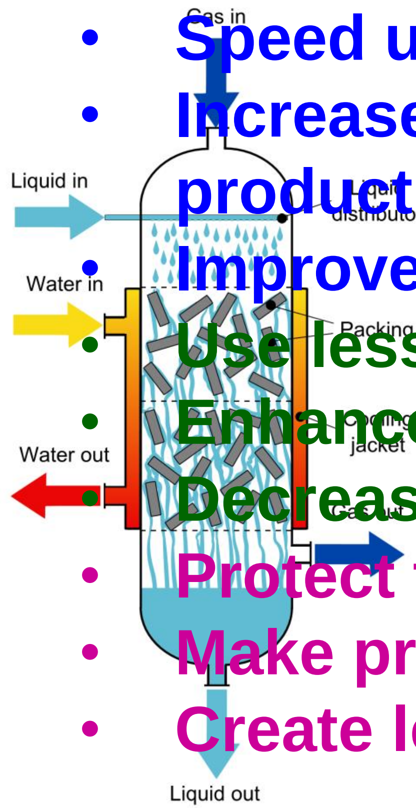


J.M. Winterbottom and M.B. King, Reactor Design for Chemical Engineers, Ch. 9, Stanley Thornes, 1999.

Reactor Design

- **Speed up reaction**
- **Increase selectivity to desired product**
- **Improve profitability**
- **Use less valuable metals**
- **Enhance catalyst lifetime**
- **Decrease use of solvents**
- **Protect the environment**
- **Make process safer**
- **Create less waste**

Continuous Stirred Tank Reactor



Trickle Bed

Monolith

UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

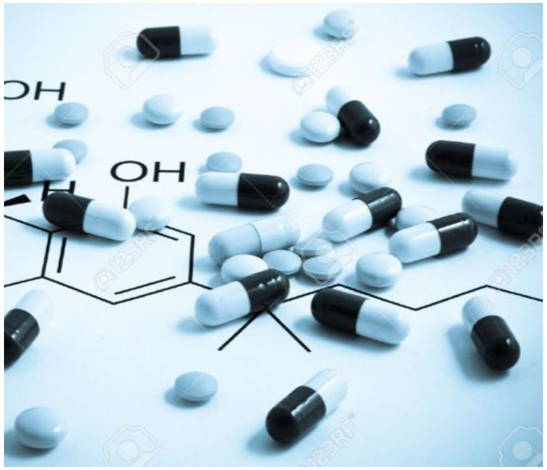
Monolith Reactors for Intensified Processing in Green Chemistry. J. Wood. In “Process Intensification Technologies for Green Chemistry”. Eds Kamelia Boodhoo and Adam Harvey 2013.

Three Phase Catalytic Reactors for Hydrogenation and Oxidation Reactions. J. Wood. In “Catalytic Reactors”. Ed. Prof. Basu Saha. De Gruyter Publishers. 2015.

Why are certain elements critical

- Large economic / environmental penalty for extraction
- Insufficient resource
- Geo-political factors, eg – quotas , taxes
- Difficult to recycle
- Concentration within one geographical area
- Rapidly expanding market for products containing critical materials
- Stockpiling

Examples of applications where critical / strategic elements have an impact



BIRMINGHAM ENERGY INSTITUTE

BIRMINGHAM CENTRE FOR STRATEGIC ELEMENTS AND CRITICAL MATERIALS

Companies where critical / strategic elements have an impact

Rolls-Royce

dyson

SIEMENS

SIMS RECYCLING SOLUTIONS

LAND ROVER

JAGUAR

TRW

Axionrecycling
Innovative resource recovery

Seagate

AstraZeneca

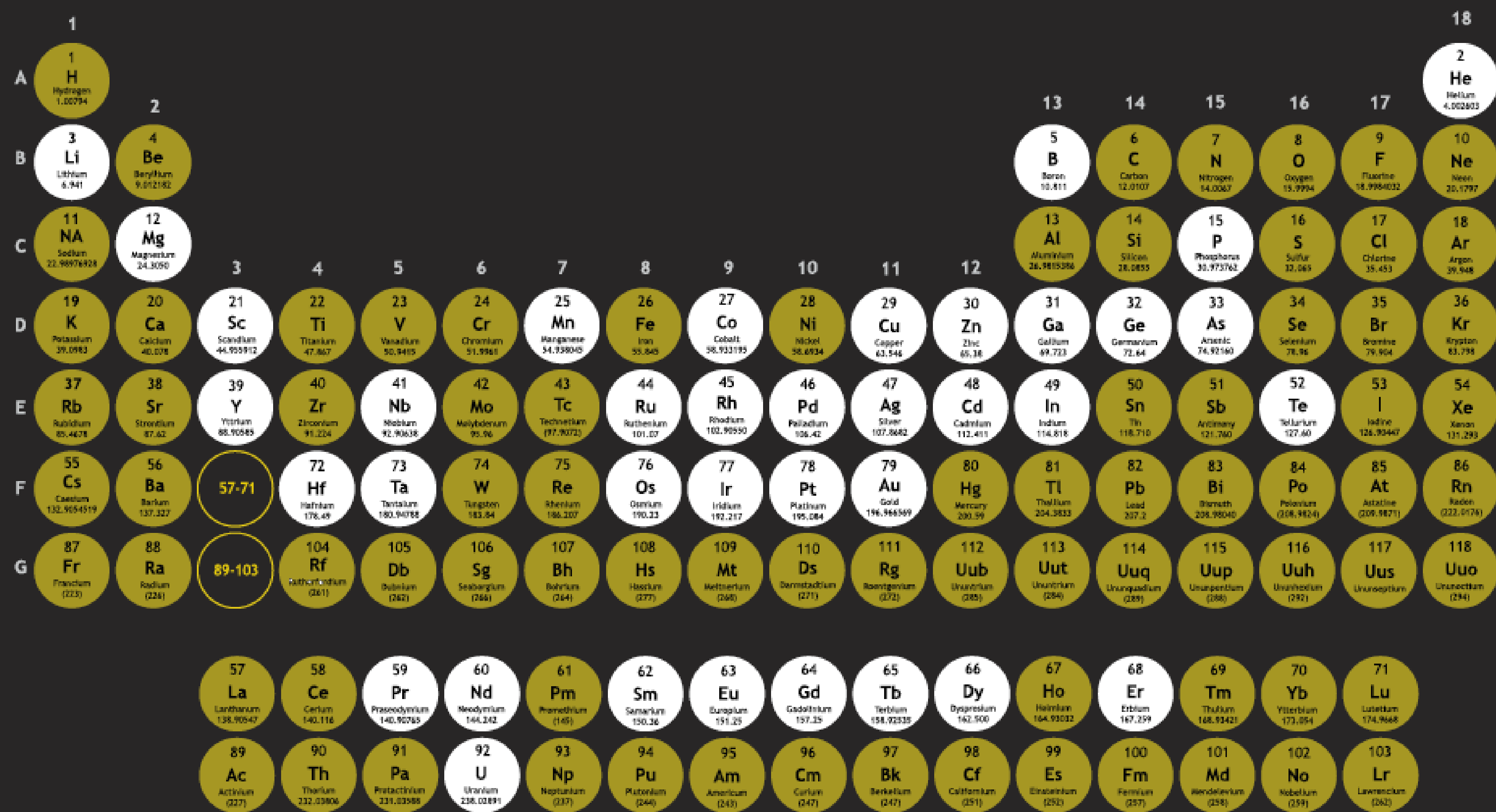
JM
Johnson Matthey

gsk

BIRMINGHAM ENERGY INSTITUTE

BIRMINGHAM CENTRE FOR STRATEGIC ELEMENTS AND CRITICAL MATERIALS

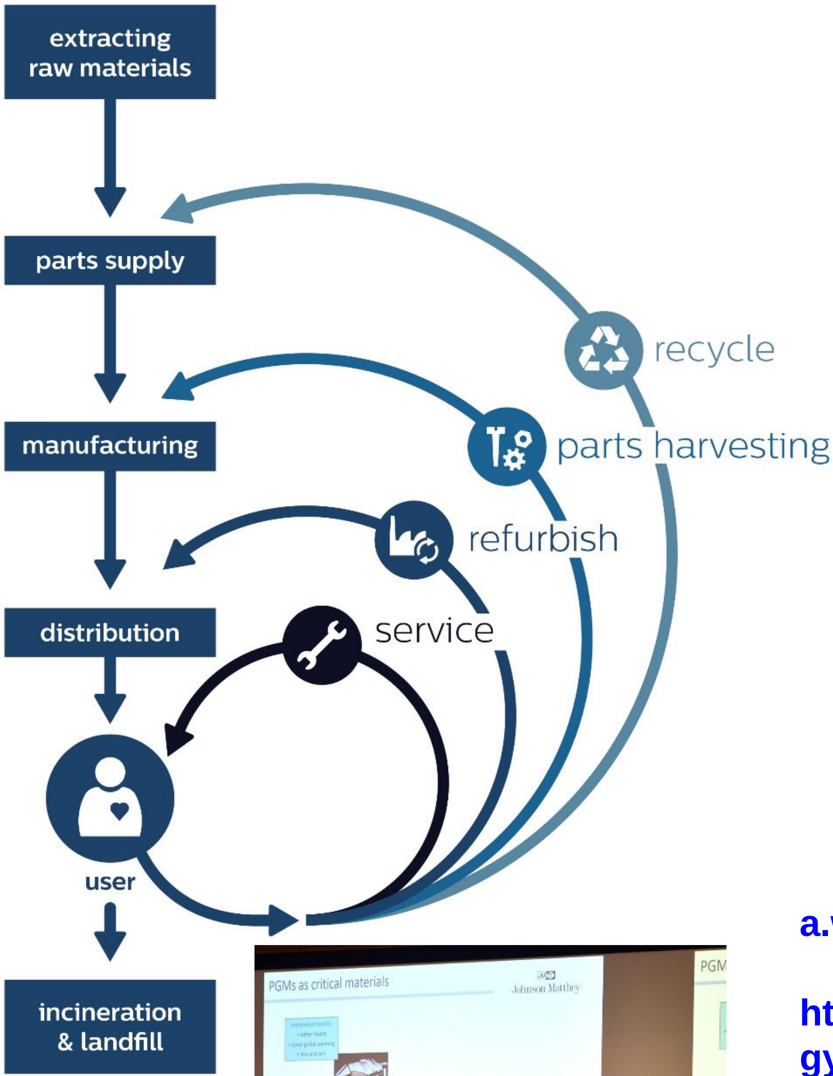
Periodic table of critical materials



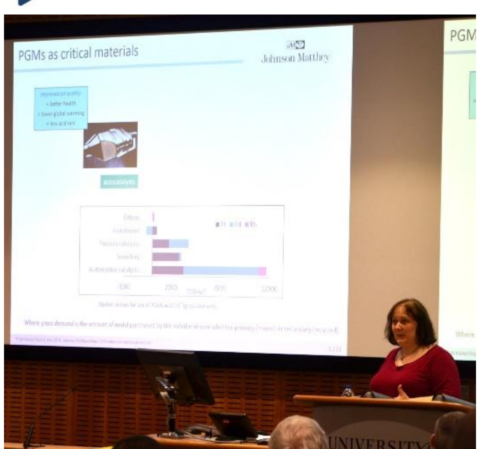
BIRMINGHAM ENERGY INSTITUTE

BIRMINGHAM CENTRE FOR STRATEGIC ELEMENTS AND CRITICAL MATERIALS

Solutions to the critical issue



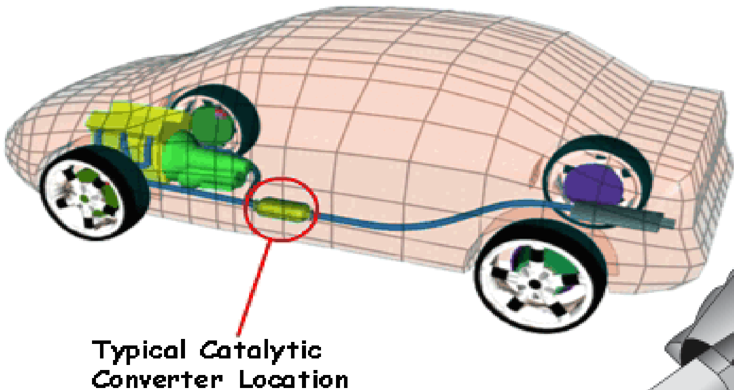
- New primary resources
- Recycling
- Re-use
- Substitution of application
- Substitution of material
- Efficient use of materials
- Change in policy

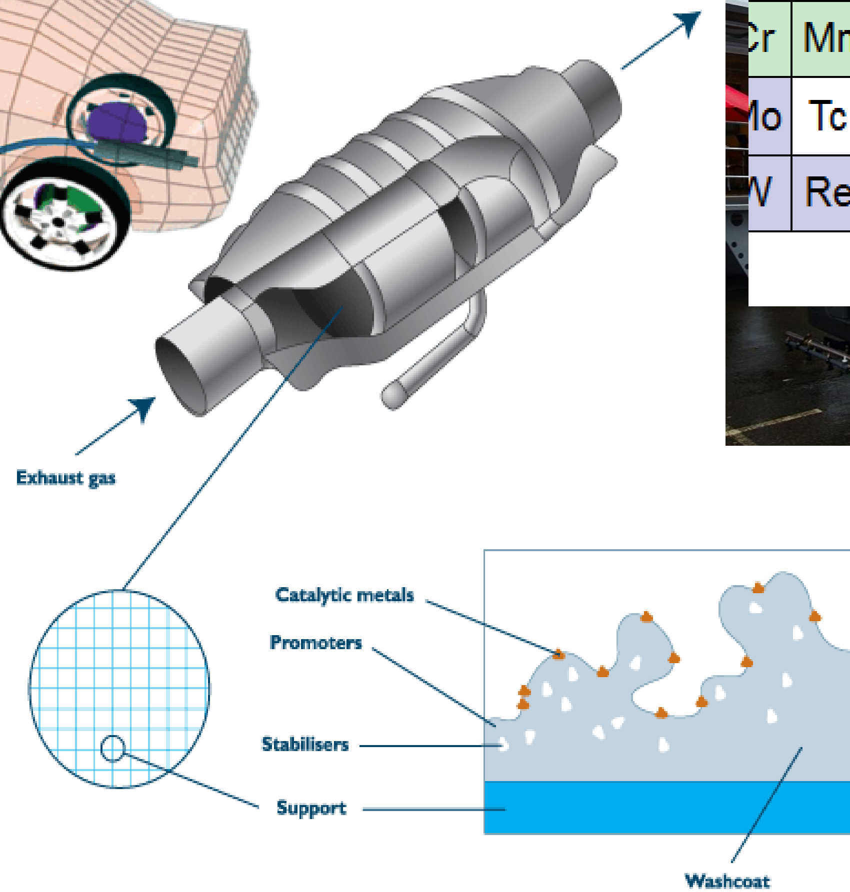


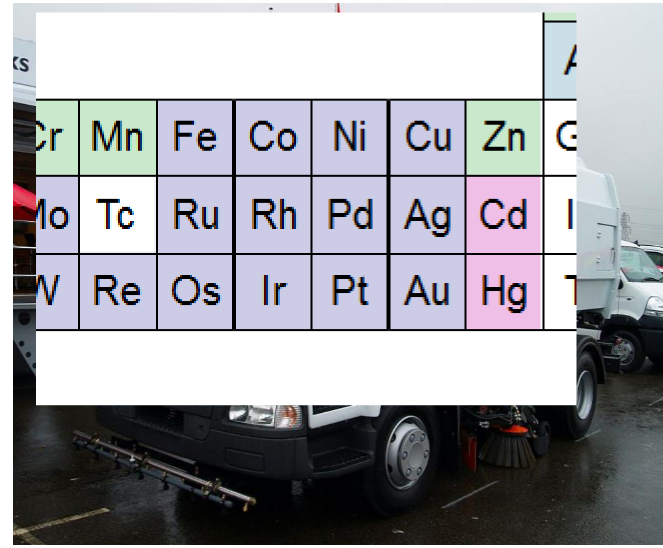
a.walton@bham.ac.uk, p.a.anderson@bham.ac.uk

http://www.birmingham.ac.uk/research/activity/energy/research/centre-strategic-elements-critical-materials/index.aspx

Recycling of Catalyst Metals





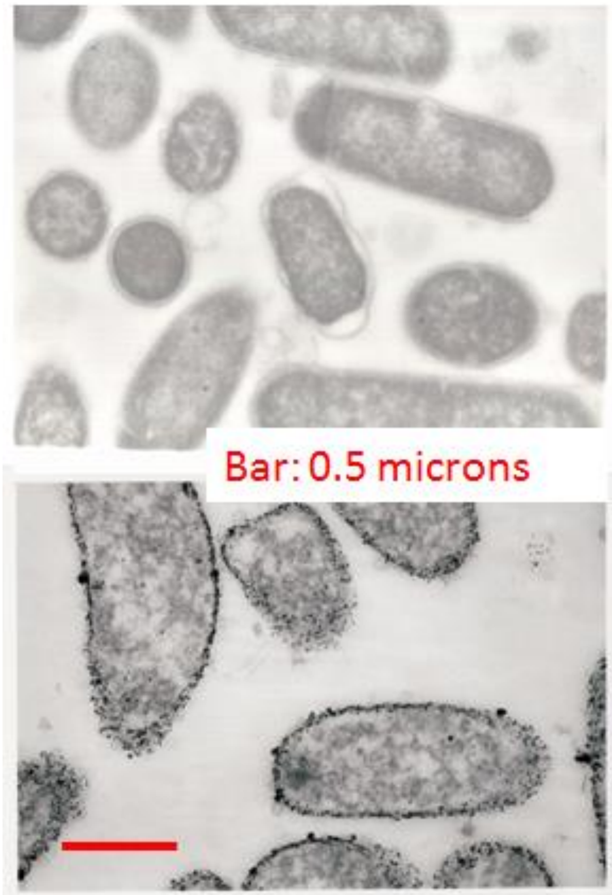


UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

Roads to Riches
Urban Platinum Recovery

L.E. Macaskie et al, Hydrometallurgy, 2010, 104, 483-487

Bio-NanoParticles



Desulfovibrio desulfuricans NCIMB 8307 grown in 2L medium

↓

Centrifuge, wash 3 times in 100 mL MOPS-NaOH buffer, resuspend in 50 mL same buffer, determine cell conc.

↓

Cell suspension combined with 2mM Pd (II) solution to give final 5 wt% Pd/biomass

↓

Sparging with H2 to reduce Pd(II) to Pd(0)

↓

Harvest, centrifuge, wash 3 times in distilled water

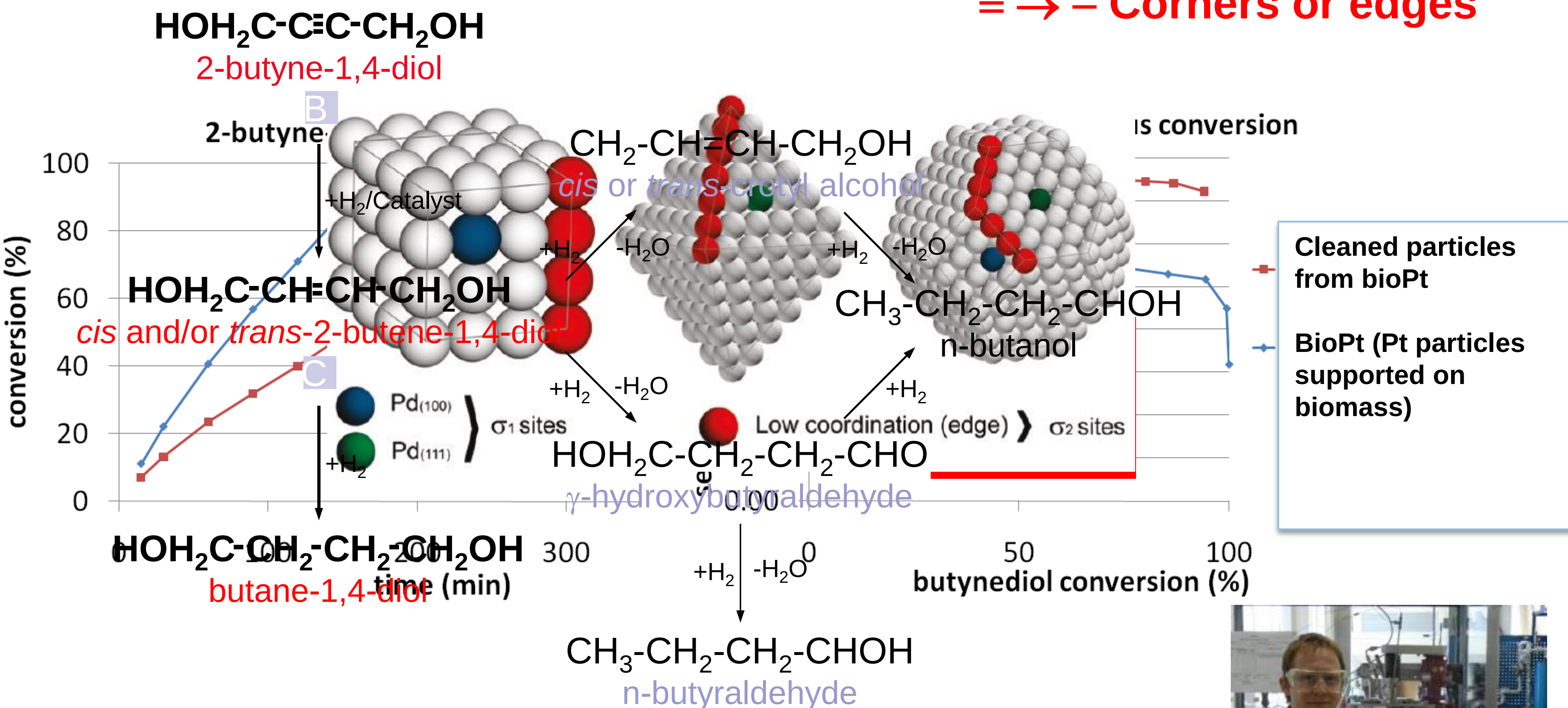
↓

Wash in acetone, dry, grind to give black powder

BioNPs developed by Prof. Lynne Macaskie's Group at Biosciences.

BioMetal Reactions

Alkyne hydrogenation
$\equiv \rightarrow =$ Terraces
Alkene hydrogenation
$= \rightarrow -$ Corners or edges

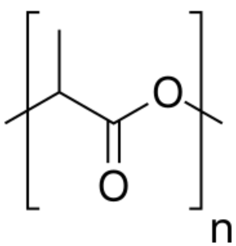


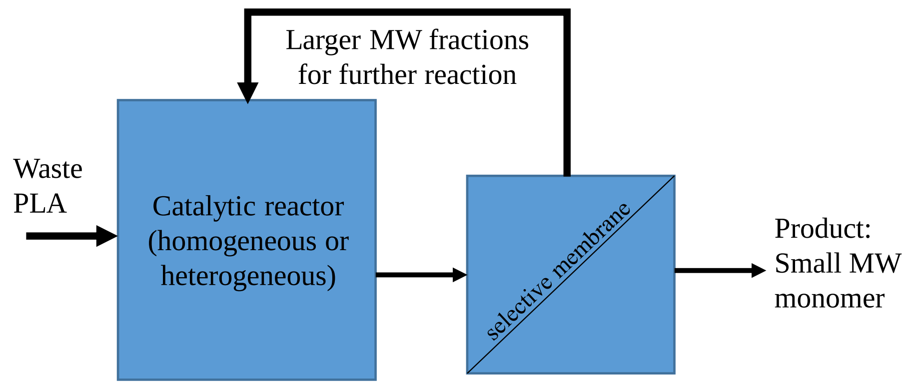
UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

Crespo-Quesada et al. J. Am. Chem. Soc. 2011, 133, 12787–12794
J. A. Bennett, G. Attard, S. Huxter, K. Deplanche, L. Macaskie, J. J. Shannon, J. Wood, 2012. ACS Catalysis, 2, 504 – 511.

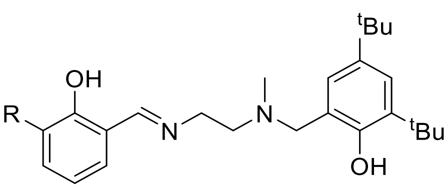
Novel Membrane Catalytic Reactor For Waste Polylactic Acid Recycling and Valorisation

- Reaction-Separation Engineering
- Recycling polylactic acid (PLA)



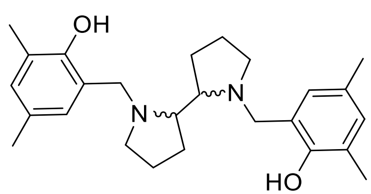


Homogeneous/heterogeneous catalytic reactor + membrane system

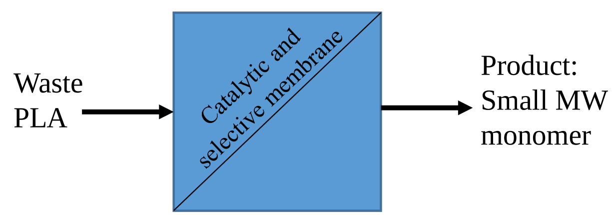


R = Me
R = H

SALALEN



SALAN



Catalytic membrane reactor system

UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

EPSRC Engineering and Physical Sciences Research Council

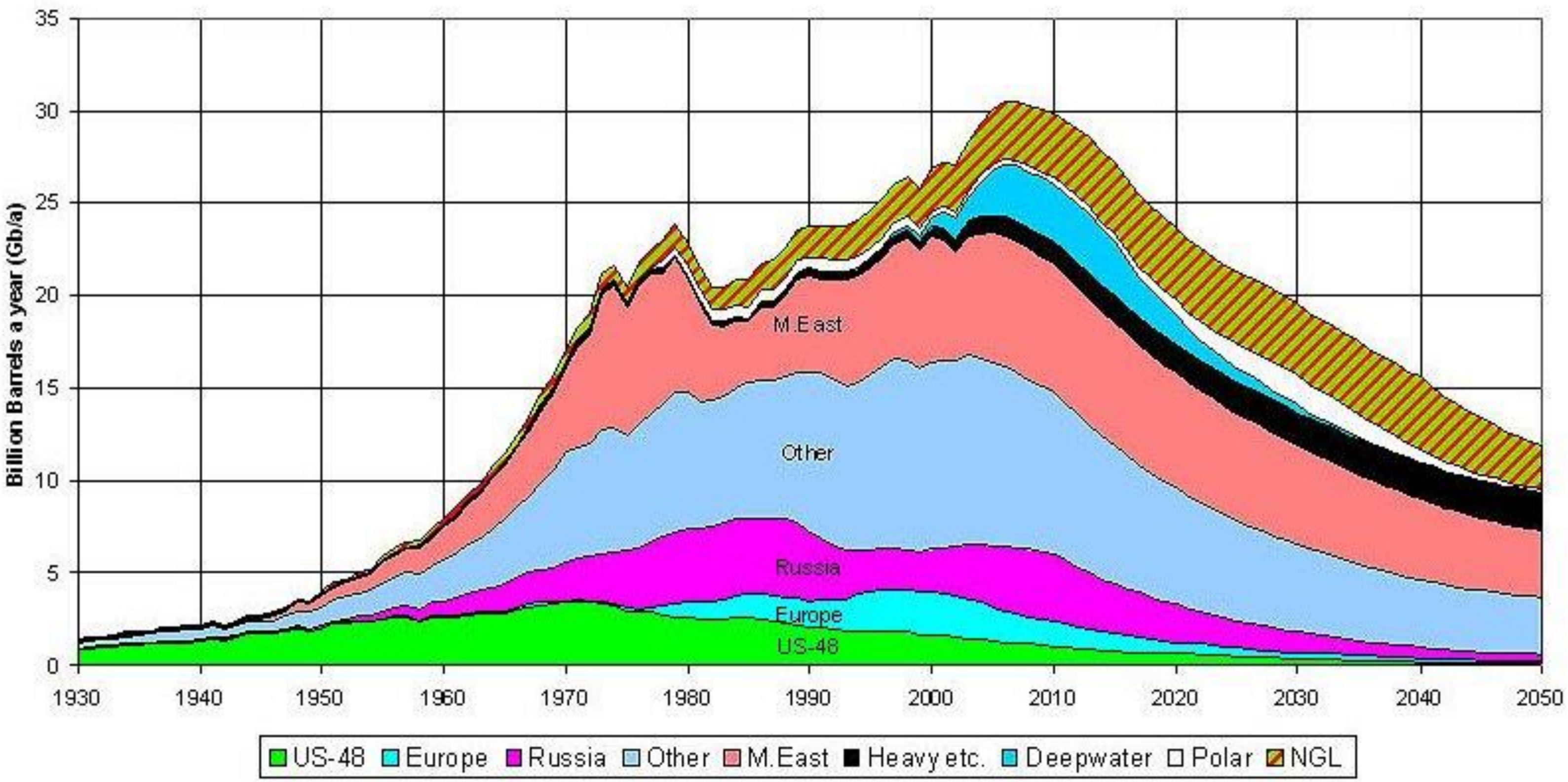
UNIVERSITY OF BATH

Oil Drilling at the University

UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

A.J. Biddlestone, History of the School of Chemical Engineering,
Keith Taylor Memorial Lecture, 2002.

Peak Oil and Transport Fuels



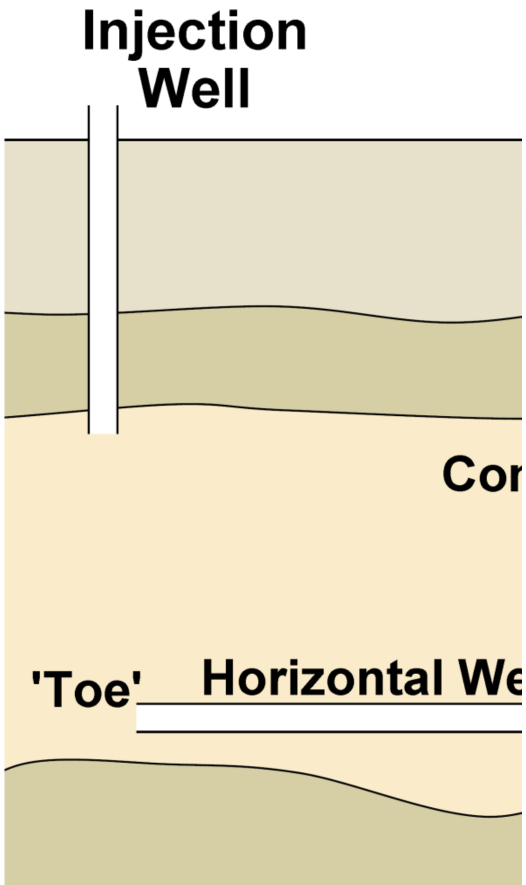
UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

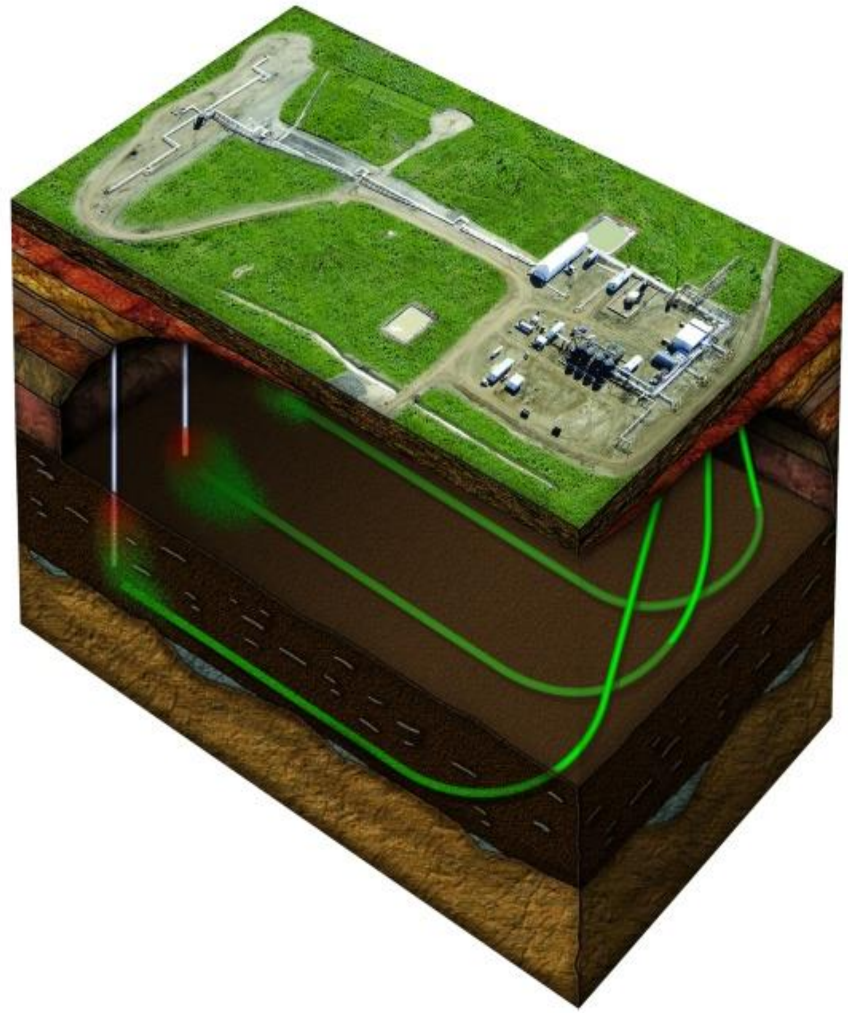
Association for the Study of Peak Oil, 2004

Heavy Oil Recovery

UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

Toe-to-Heel Air Injection (THAI)





UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

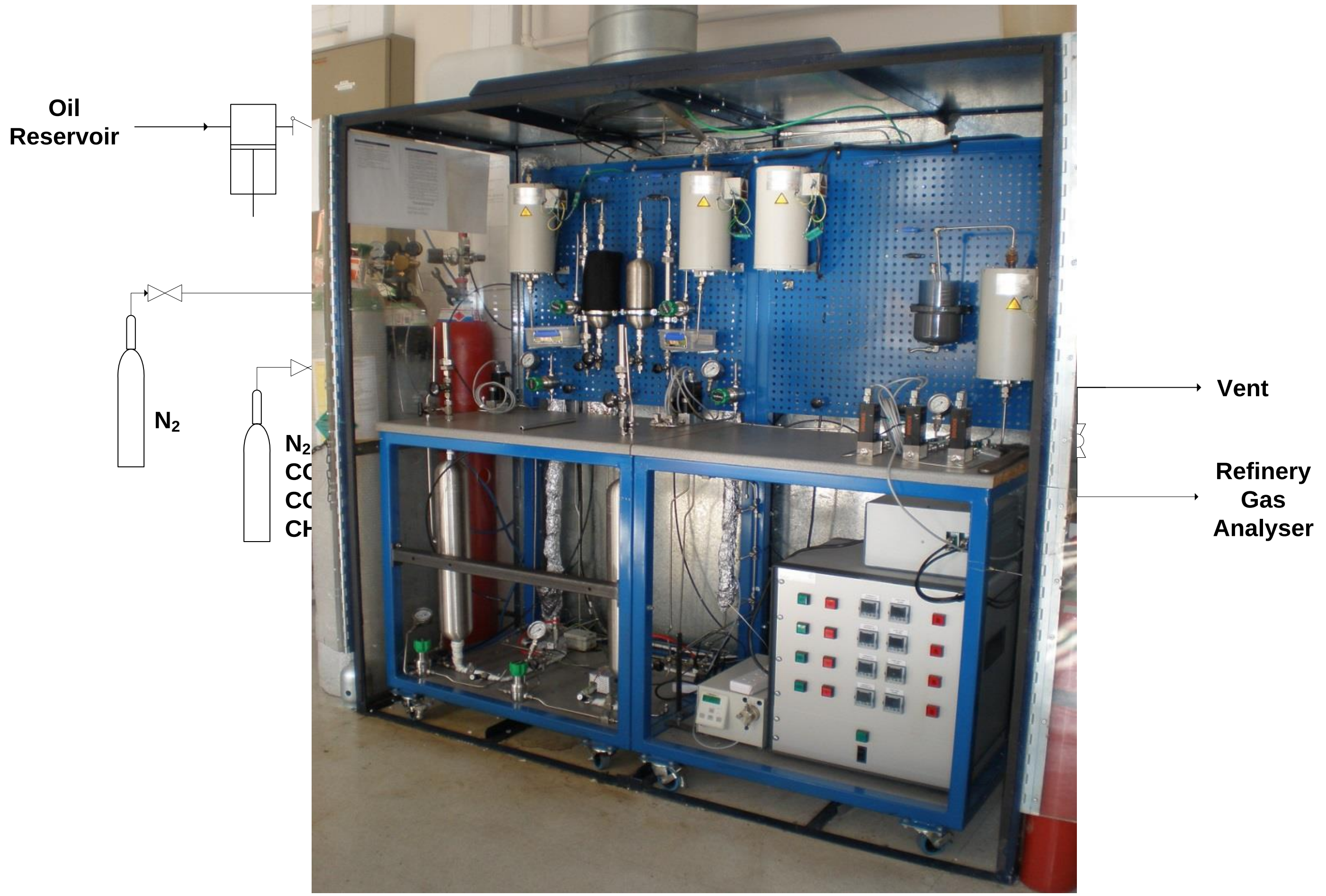
Greaves, El-Saghr, Xia, 2000, Abs. Papers. Am. Chem. Soc. 220, U145.

CAPRI

- High recovery of up to 85 % oil in place
- Requires low use of external heating, e.g. steam
- Thermal-catalytic effects cause significant upgrading

- Catalyst has to be packed in to the well
- Catalyst coking and lifetime may limit the process
- Difficult to regenerate catalyst in-situ

CAPRI Reactor Rig

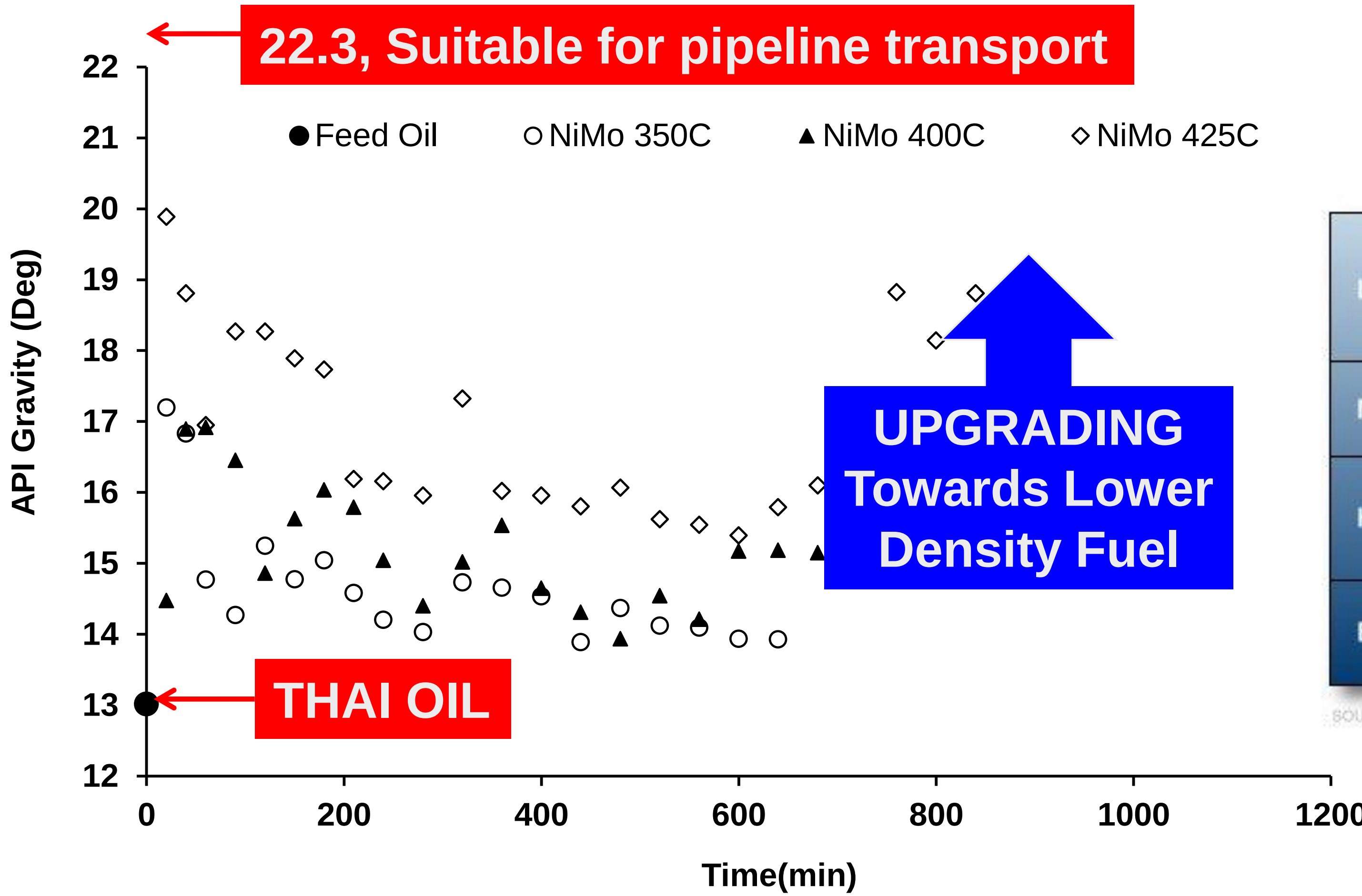


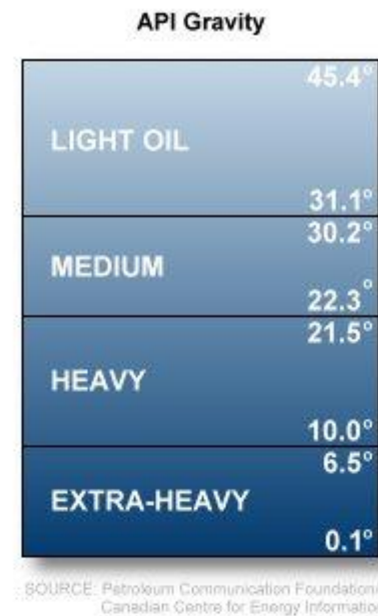
Experimental Conditions

- Effect of temperature: 350-425°C
- Pressure: 20 bar
- Catalyst:
  - CoMo, NiMo, ZnOCuO
- Reaction media:
  - Nitrogen, Hydrogen,
  - THAI gas – simulated combustion gas mixture
  - (N_2 80 %, CO_2 12-14 %, CO 2-3 %, CH_4 2-4 %)
  - THAI Oil (Whitesands) flow rate: 1 ml/min
  - Gas Flowrate: 0.5 l/min

UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

Effect of Temperature Upon API Gravity



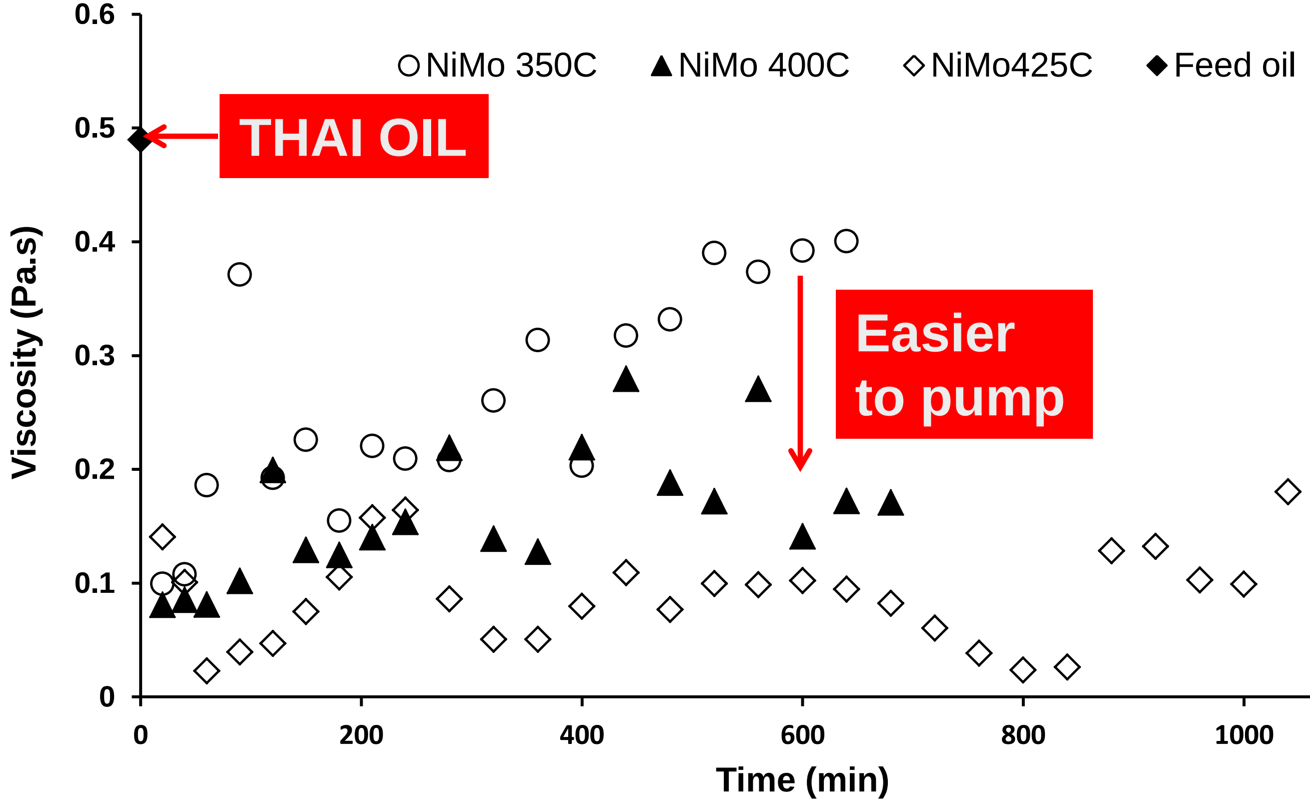


UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

(~17 hours on stream)

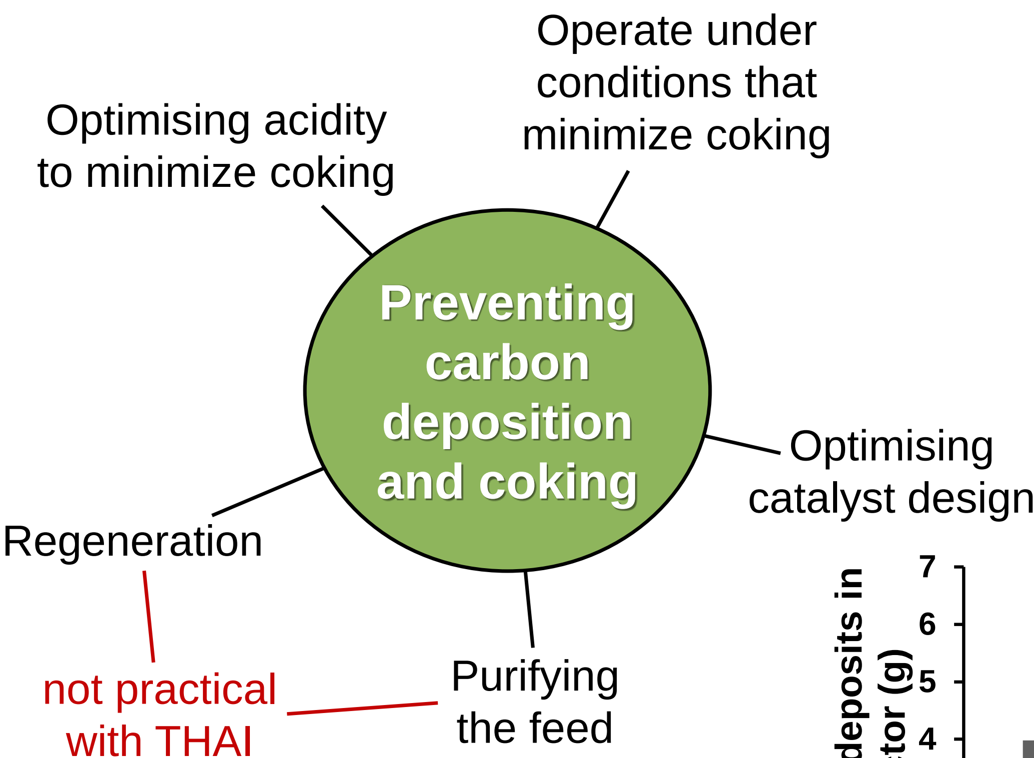
A. Hart, A. Shah, G. Leeke, M. Greaves, J. Wood, 2013. *Ind. Eng. Chem. Res.* 52, 15394-15406

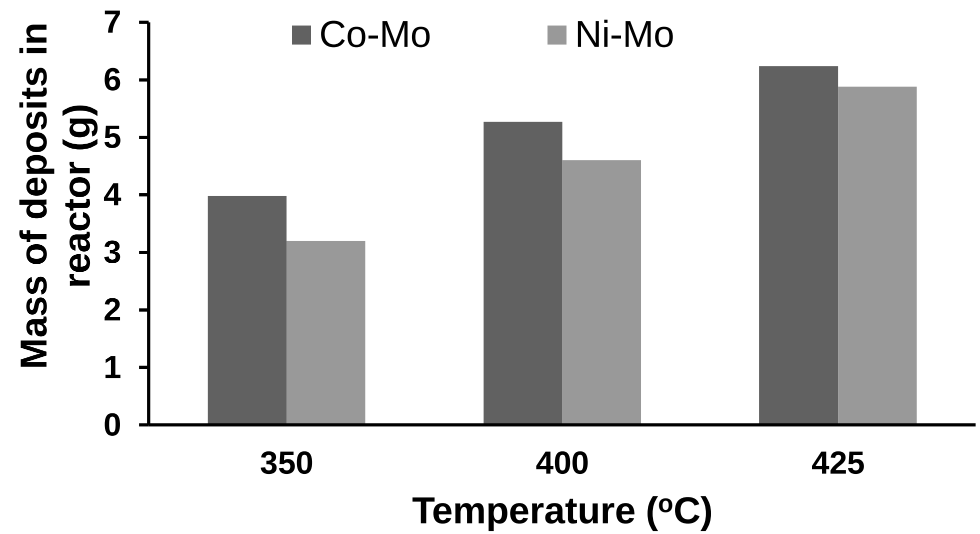
Effect of Temperature Upon Viscosity



(~17 hours on stream)

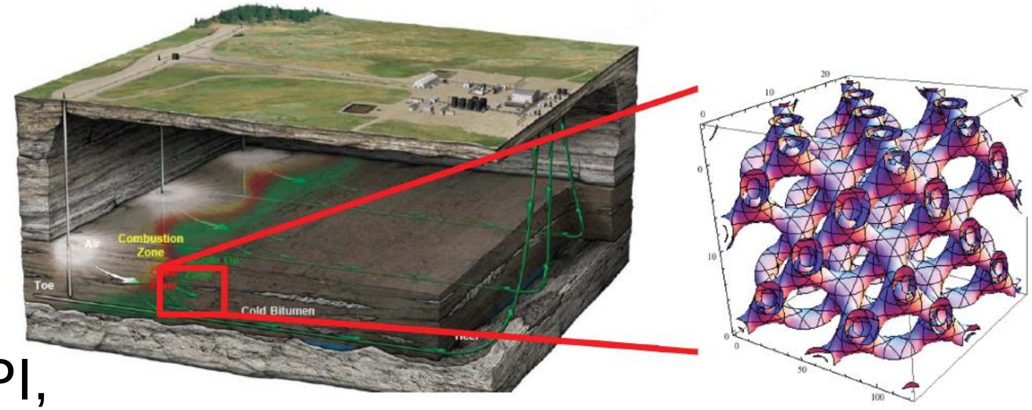
Coking of Catalyst

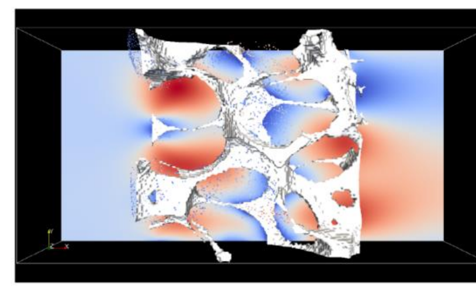


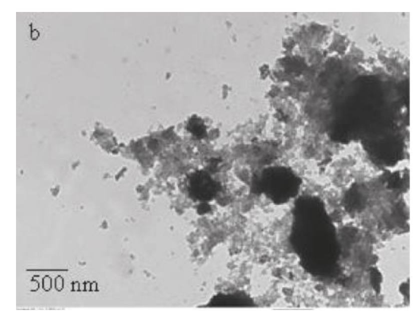


Dispersed Nanoparticles

- Ideal catalyst properties:
- A highly active catalyst
- Doesn't deactivate
- Upgrading beyond 4-8 °API,
- Towards a target of Δ 10 °API
- Examples of dispersed catalysts in surface upgrading
  - Nano Fe, red mud: VEBA Combi cracking
  - Submicronic NiWMo: Upgrading at near reservoir conditions
  - CoMo/TiO2: Hydrodesulphurisation







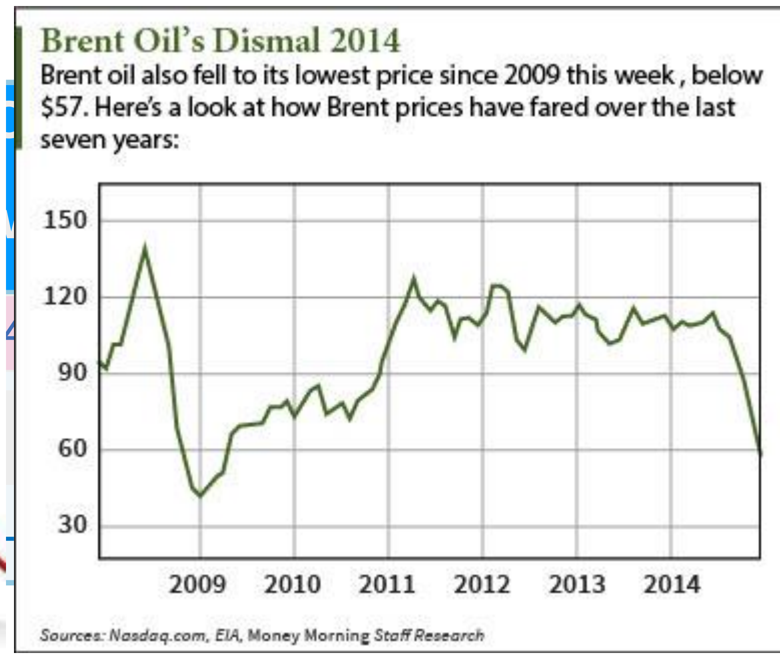
UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

C.E. Galarraga, P. Pereira-Almao, *Energy Fuels*, 2010, 24, 2383
N.N. Nassar, M.M. Husein, *Fuel Proc. Technol* 91, 164 , 2010.

Upgrading with Nanoparticles

- *425 ° C, 0.02 cat/oil, 20 bar, 500 rpm agitation, 10 min reaction time, N_2 atmosphere*

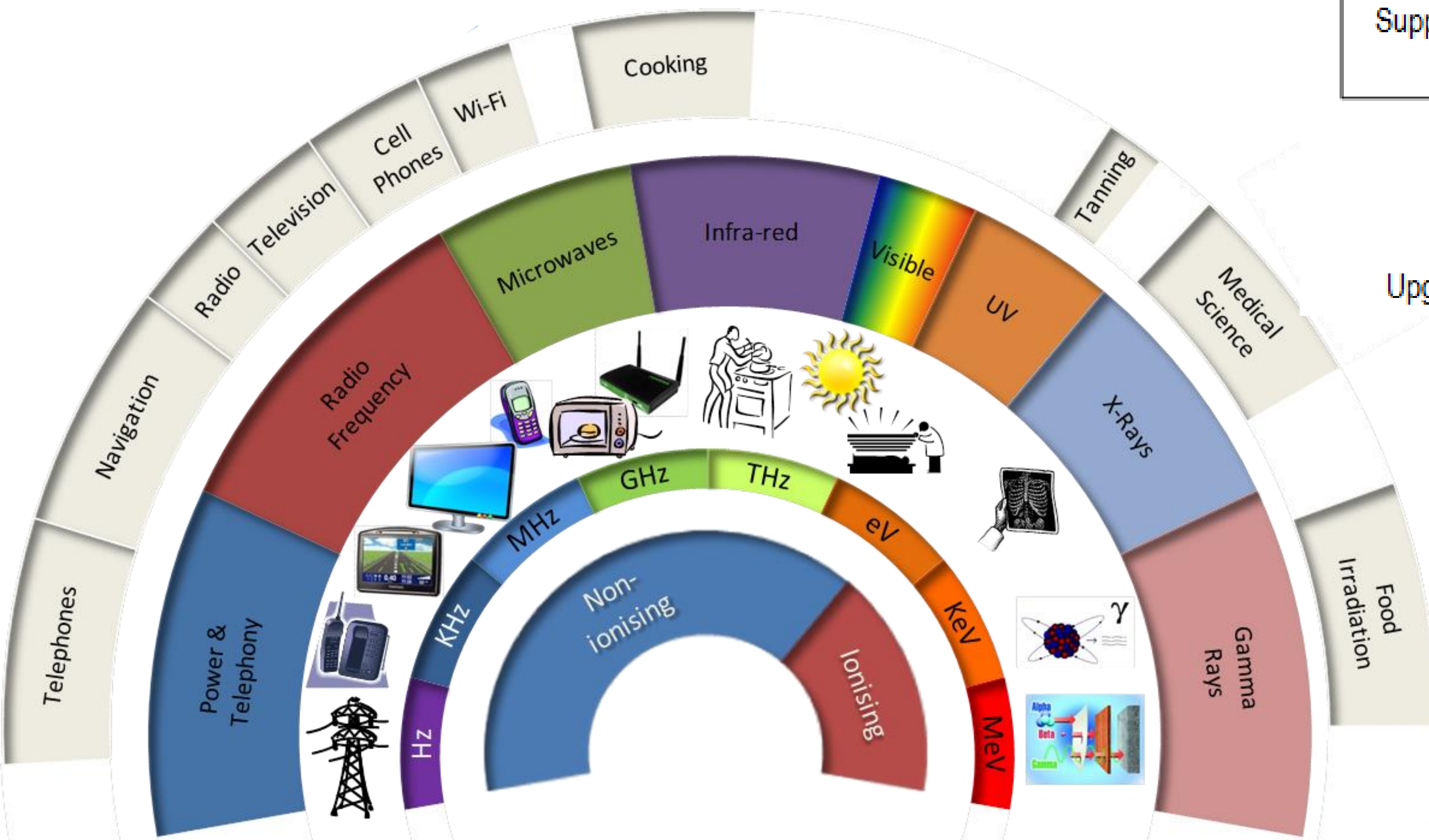
Lower coke

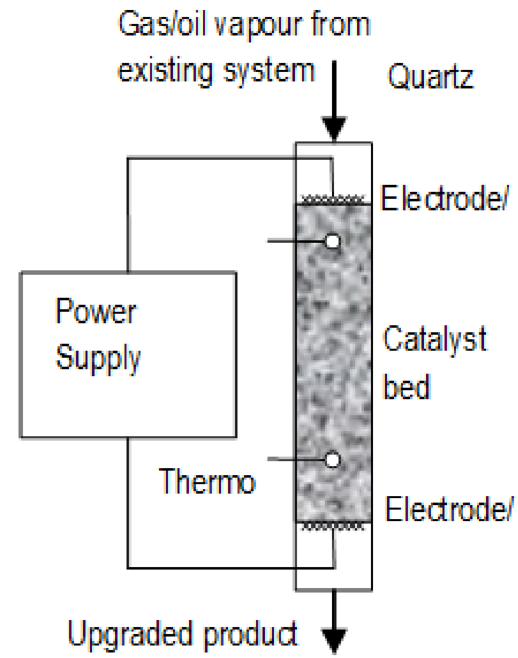


UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

A. Hart, M. Greaves and J. Wood, 2015. *Chemical Engineering Journal* 282, 213-223.

Electromagnetic Heating





UNIVERSITY OF BIRMINGHAM
COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

University of Nottingham
UK | CHINA | MALAYSIA

EPSRC
Engineering and Physical Sciences Research Council

Biofuels & Chemicals

Renewable packaging e.g. PLA, PEF
Biopharmaceuticals, e.g. Filicene
Chemicals from sugars HMF DMF

Provide a reliable source of drop-in fuels after peak oil (2020-50)

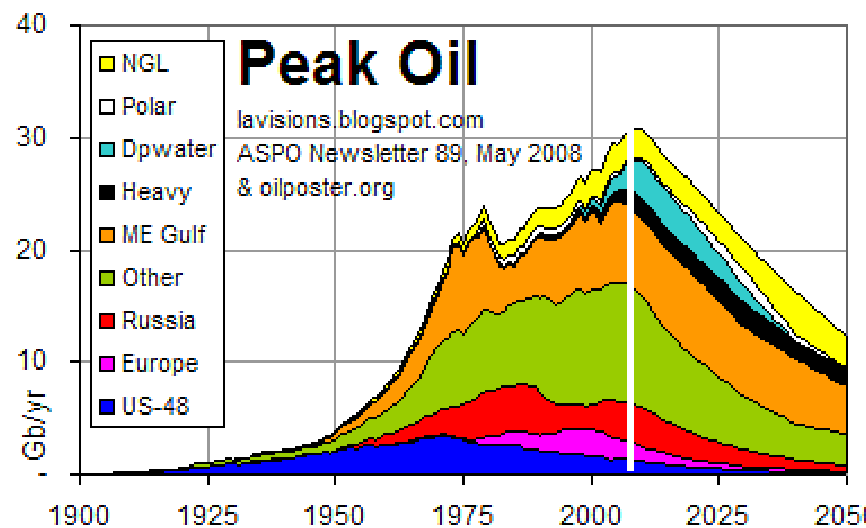
Help the UK to deliver commitments to GHG gas reduction (34 % 2020, 80 % 2050)[4]

Create new markets for bio-based chemicals (2020-)

£ **Economic value**

Biofuels will save 35-60 % CO_2 compared with fossil fuels (2016-18)[1]

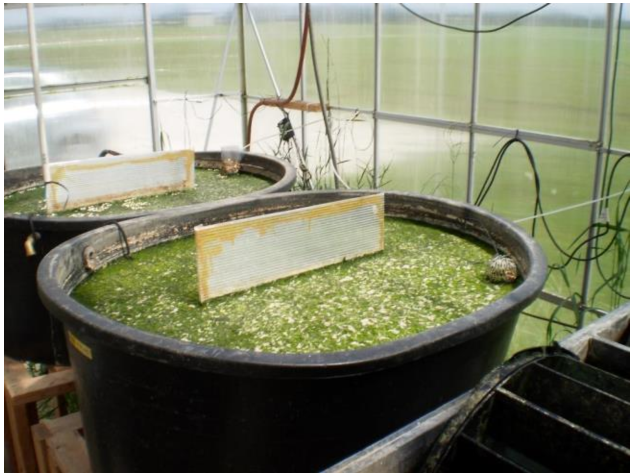
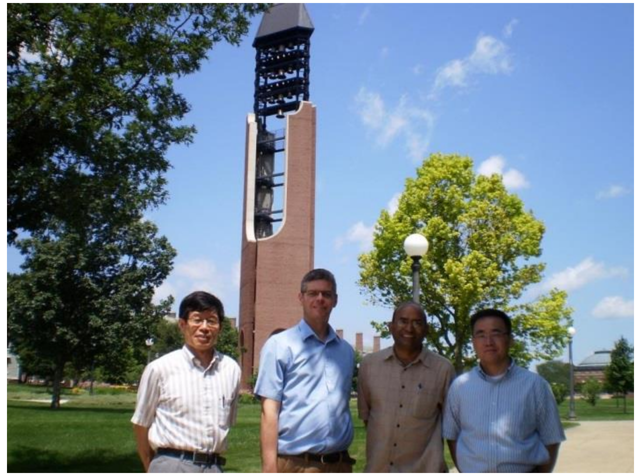
Biofuel will ensure we can deliver 15% renewables by 2020 UK[2]

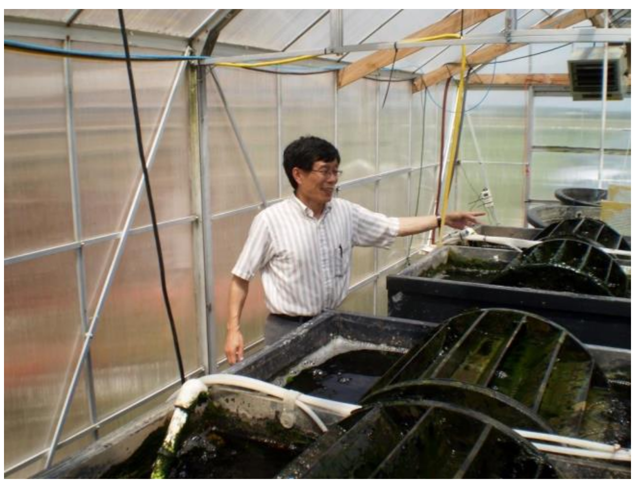


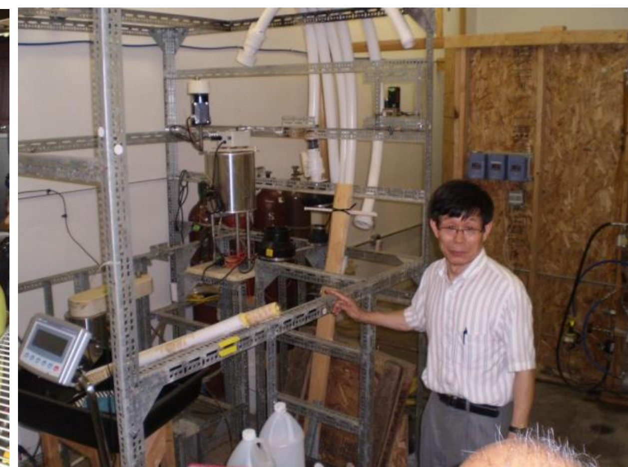
UNIVERSITY OF BIRMINGHAM
COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

BRIDGE

Collaborator Dr B.K. Sharma





UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

UIUC University of Illinois Urbana Champaign, Illinois Centre for Sustainable Technology
BRIDGE (BiRmingham-Illinois Partnership for Discovery EnGagement and Education)

Prof. Joe Wood BRIDGE feasibility project on bio-oil hydrodeoxygenation using bio-Pd catalysts

(developed by Prof. Lynne Macaskie)

BioPd: Average metal particle size
3.34 ± 0.09 nm
Bacterial cells 2.8 μm

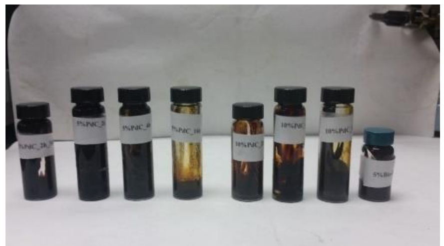
Feed: 15 g *Chlorella* derived HTL bio-oil

↓

5-10 wt % Catalyst (Pd/C, Pd/bio-C)

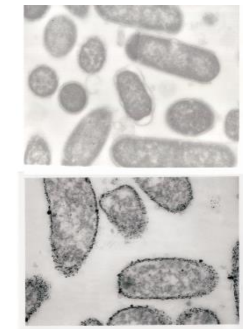
↓

Temperature (300, 325 °C), Pressure (2000 Psi at final Temperature), Reaction time 2, 4 or 16 hours



Characterization

- **Oil** → Simdist, Elemental, HHV, GC-MS, NMR and FTIR
- **Coke** → TGA
- **Catalyst** before and after reaction → XRD, SEM

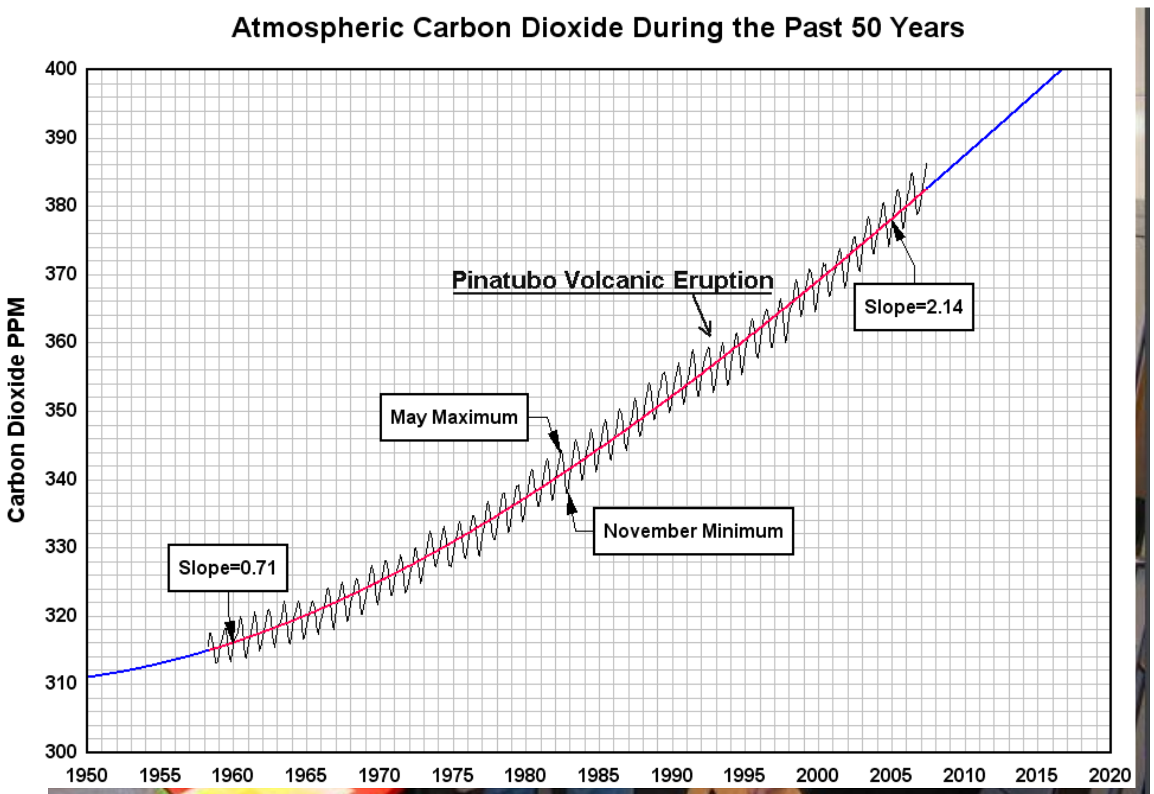


Catalyst	Temp (°C)	Time (h)	Catalyst wt%	Liquid Yield wt%	%C	%H	%N	%O	%S	HHV (MJ/kg)
Bio-crude oil					73.5	8.9	6.6	10.8	0.72	35.7
Pd/C	300	2	5	87	74.6	10.2	4.6	10.4	0.11	38.0
Bio-Pd/C	325	4	5	77	80.7	10.1	4.9	3.9	0.3	41.0

UNIVERSITY OF BIRMINGHAM | ILLINOIS

J. Wood, S. Deilami, B. Kunwar, L.E. Macaskie, B.K. Sharma, Catalytic Upgrading of HTL Bio-Oil Using Bio-Pd/C Catalyst. Oral presentation at the Euro Biomass International Conference Birmingham UK, August 8-9th 2016.

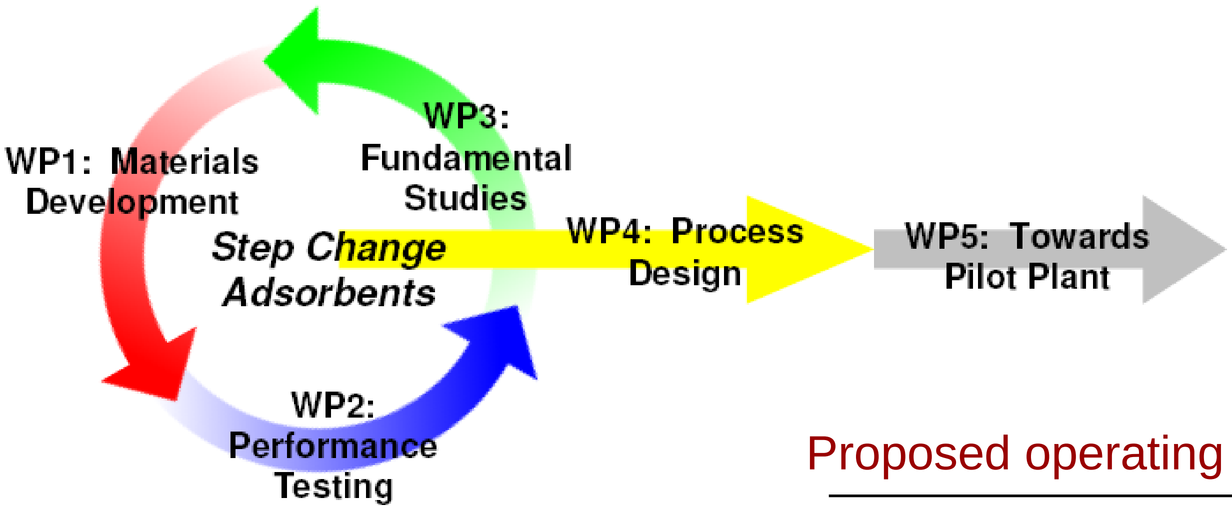
Post Combustion CO2 Capture



Mauna Loa Observatory, Hawaii, Monthly Average CO2 Concentration
Data from Scripps CO_2 Program

UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

Step Change Adsorbents



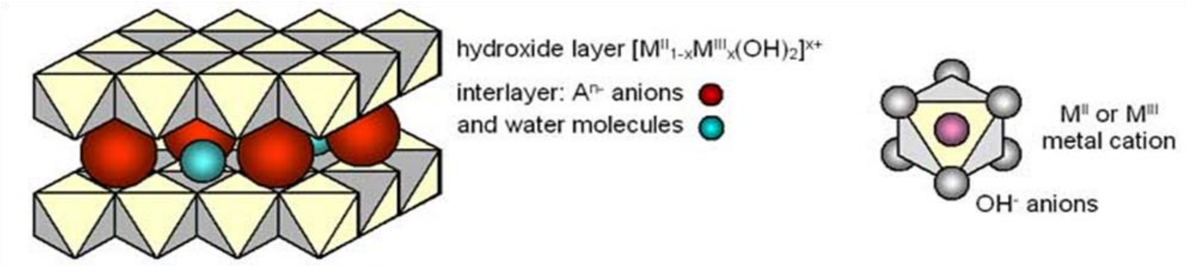
Proposed operating conditions for capture plant

Performance Parameter	Target
Operating : adsorption	40 – 80 °C
Temperature : desorption	85 – 160 °C
Cyclic capacity	> 3 mmol g^{-1}
Operating pressure	~1015 mbar
CO_2 product purity	> 95 %
CO_2 capture	> 80 %

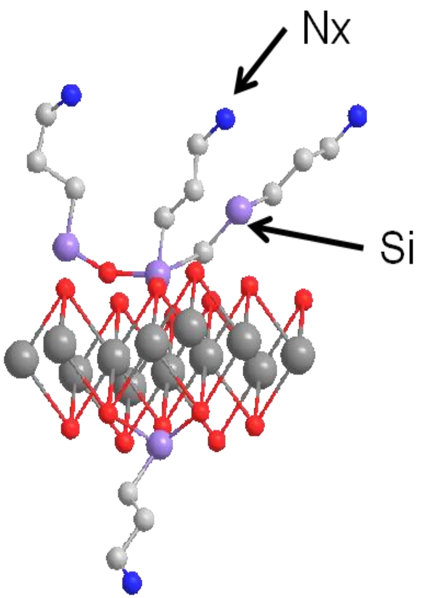
UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

T. C. Drage et al., 2012, *J. Materials Chem.* 22, 2815.

Amine Modified Hydrotalcites



Layered crystal structure of hydrotalcite-like compounds

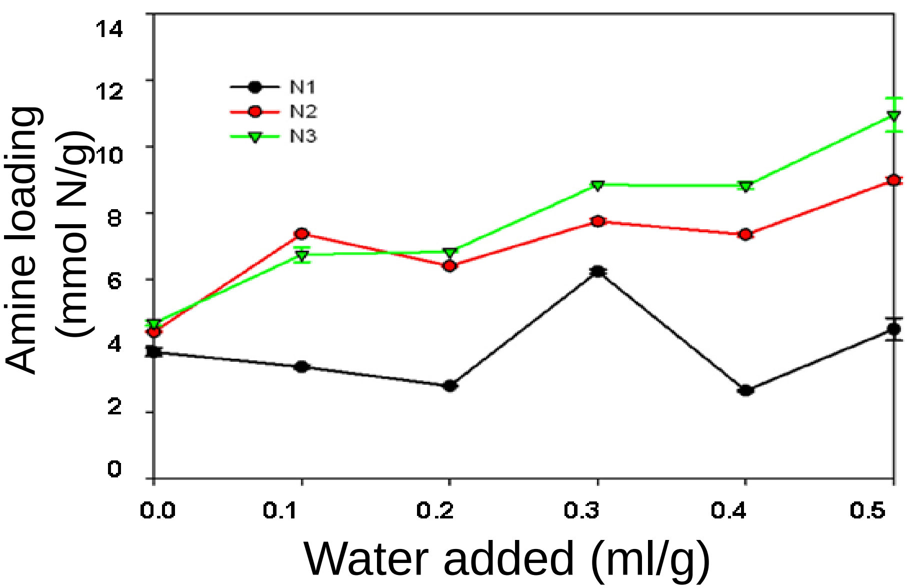


UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

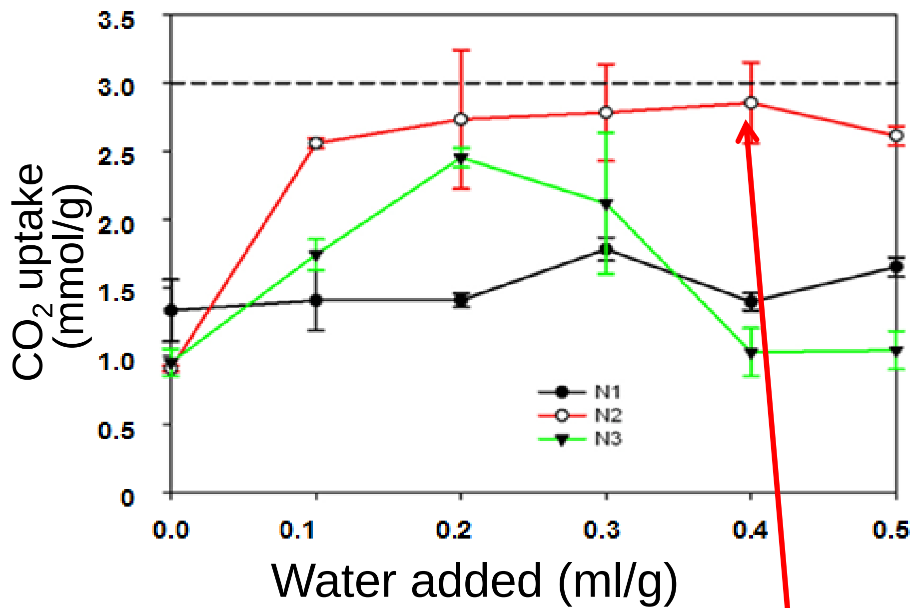
J. Wang, L. Stevens; T.C. Drage; J. Wood., 2012, *Chem. Eng. Sci.* 68, 424 – 431.

Adsorbent Performance

Flash EA 1112 elemental analyzer (Amine loading)



Netzsch TG 209 F1 thermogravimetric analyzer (CO_2 uptake)



Optimal formulation

UNIVERSITY OF BIRMINGHAM
COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES

Acknowledgements

EPSRC
Petrobank
Touchstone Exploration
Petrochina
The Steam Oil Company
E.ON
ETI
Johnson Matthey
Shell
Natureworks

Prof Mike Winterbottom
Prof Mark Simmons
Dr Andreas Tsolikgas
Prof Sean Rigby
Dr Bushra Al-Duri
Dr Jiawei Wang
Dr Faiza Hassan
Prof Lynne Macaskie
Dr James Bennett
Prof Gary Attard
Dr Angela Murray
Dr Iryna Mikheenko

Prof Colin Snape
Dr Simon Caldwell
Bilaal Hussain
Prof Michele Clarke
Dr Artur Majewski
Prof Malcolm Greaves
Dr Rob Fishwick
Dr Amjad Shah
Dr Abarasi Hart
Dr John Robinson
Dr BK Sharma
Prof Karen Wilson

PACT Facilities Sheffield
Lu’an Corporation

My past and current research students, colleagues and collaborators
Support staff, Dave Boylin

UNIVERSITY OF BIRMINGHAM | COLLEGE OF ENGINEERING AND PHYSICAL SCIENCES