Environmentally benign biodiesel production from renewable sources

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Outline

- Professional background and responsibilities
- Research highlights
- Current research activities
- Conclusions

Professional Background

- Founding Director (2012 - present), Centre for Green Process Engineering (CGPE) – London South Bank University (LSBU)
- Research Lead (2014 - present) – School of Engineering, LSBU
- Research Lead (2011 - 2014) – Department of Applied Sciences, LSBU
- Graduate Advisor (2011 – 2014) - Department of Applied Sciences, LSBU
- Professor of Chemical and Process Engineering (2010 – present) – LSBU
- Visiting Professor (2011) – University of Barcelona, Spain
- Reader in Chemical Engineering (2008 - 2010) & Director of Postgraduate Studies (2005 – 2010) – Loughborough University, UK

Professional Background

- Visiting Professor (2007) – Saga University, Japan
- Visiting Professor (2006) – University of Burgos, Spain
- Senior Lecturer (2004 - 2007) & Director of Postgraduate Studies – Chemical Engineering Department, Loughborough University, UK
- Royal Academy of Engineering Industrial Secondee (2002) - Syngenta Ltd., Process Technology Group (PSG), Huddersfield, UK
- Lecturer (1999 - 2003) – Chemical Engineering Department, Loughborough University, UK
- Post-doctoral Research Associate (1997 - 1999) – Chemical Engineering Department, Loughborough University, UK

My Research Interests & Activities

- Advanced Separation Processes - development of novel adsorbents for environmental remediation
- Greener and sustainable chemical technologies (includes process intensification - e.g. reactive distillation, reactive chromatography etc.)
- Conversion of CO_2 to valuable chemicals/fuels
- Renewable and sustainable energy solutions

Development of Novel Adsorbents

- Ion exchange resins (granular and fibrous)
- Hyper-cross linked (Macronet) polymers
- Solvent impregnated resins (SIR)
- Engineered activated carbons (granular and fibrous)
- Functional and carbonised polymers
- Granular ferric hydroxide (GFH)

Saha et al., In "Ion Exchange and Solvent Extraction", SenGupta, A. K. and Marcus, Y. (Eds.), Marcel Dekker, Inc., New York, USA, 2004, Volume 16, Chapter 1, pp 1-84.

Saha, B., In "Water Encyclopedia: Water Quality and Resource Development", Lehr, J.H. and Keeley, J. (Eds.), John Wiley & Sons, Inc., New Jersey, USA, 2005, pp 79-86.

Saha et al., *Reactive and Functional Polymers*, 2010, 70, 531–544.

Target Pollutants

- **Trace toxic heavy metals**
- **Herbicides, pesticides and fungicides**
- **Chlorinated hydrocarbons**
- **Endocrine disrupting compounds (EDC)**
- **Aviation hydraulic fluid**

Saha et al., *J. Colloid and Interface Science*, 302 (2), 2006, 408-416.
Saha et al., *Industrial and Engineering Chemistry Research,* 2008, 47, 6734-6741.
Saha et al., *Separation Science and Technology,* 2009, 44 (16), 3950 - 3972.
Saha et al., *Environmental Geochemistry and Health Journal*, 2010, 32, 341–347.
Saha et al., *Reactive and Functional Polymers*, 2010, 70, 531–544.

Environmentally Benign Biodiesel Production

- A majority of the world’s energy is supplied through petrochemical sources, coal and natural gases
- It has been predicted that by 2035, global energy consumption will increase by 49%, with an increase of 1.4% every year
- Within the EU, the demand for diesel fuel was forecasted to grow by 51% from 2000 to 2030
- EU Directive requires that 10% of the energy used for transport to come from renewable sources by 2020
- It is increasingly necessary to develop renewable energy resources to replace the traditional sources

Environmentally Benign Biodiesel Production

Environmentally Benign Biodiesel Production by Heterogeneous Catalysis

Collaborators: Greenfuel Oil Co. Ltd., Purolite International Ltd., Novozymes Ltd.

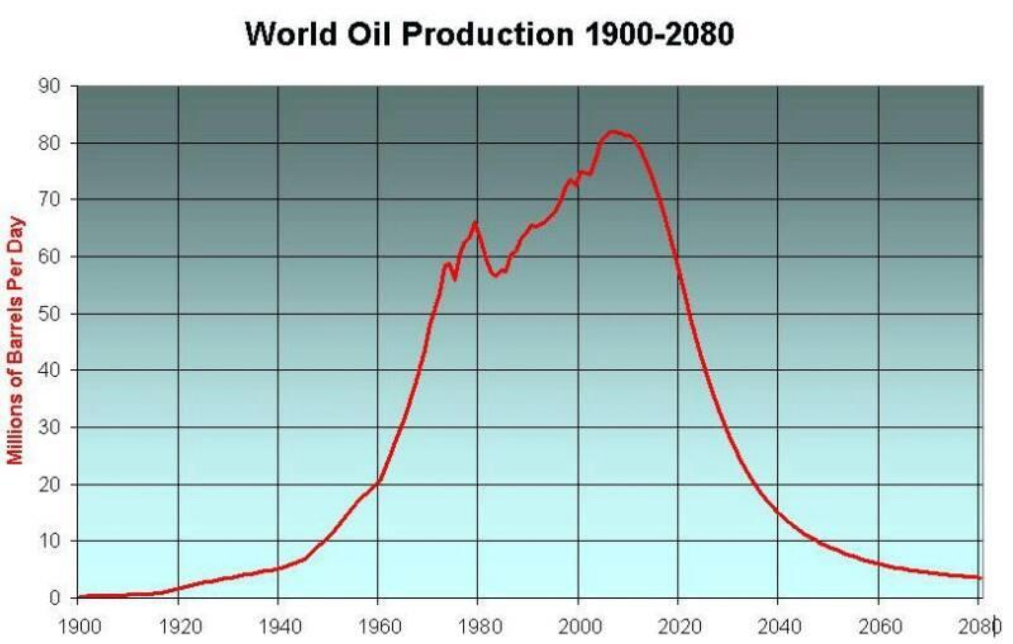
Starting material – Used Cooking Oil (UCO)

The main reactions investigated:

- Esterfication (Pre-treatment)
- Transesterfication (Biodiesel Production)

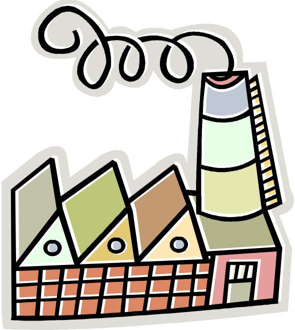
Saha *et al., Progress in Colloid and Polymer Science, 2012*, 139, 19-23
Saha *et al., Ind. Eng. Chem. Res., 2012*, 51, 14653−14664
Saha *et al., Canadian Journal of Chem. Engineering,* 2013, 9999, 1-8.
Saha *et al., Fuel,* 2013, 111, 186–193.
Saha *et al., Chemical Engineering Research and Design,* 2014, 92, 713-719.
Saha *et al., Processes,* 2014, 2, 311-332.

Why Investigate Alternative Fuels?

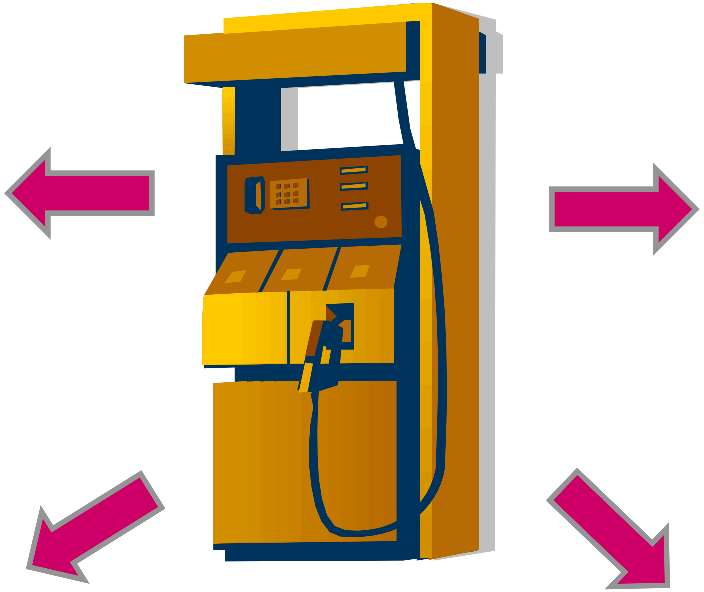


Biodiesel Production

Why Biodiesel?



Work in existing infrastructure



Green fuel

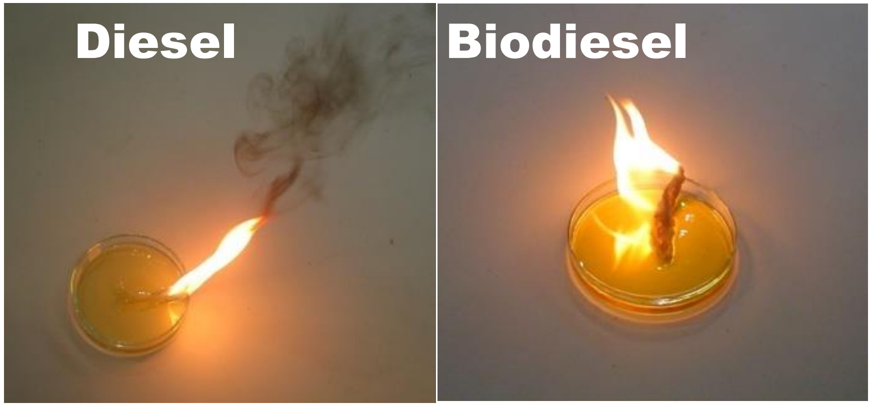
Stimulates agriculture

Reduce reliance on fossil fuel

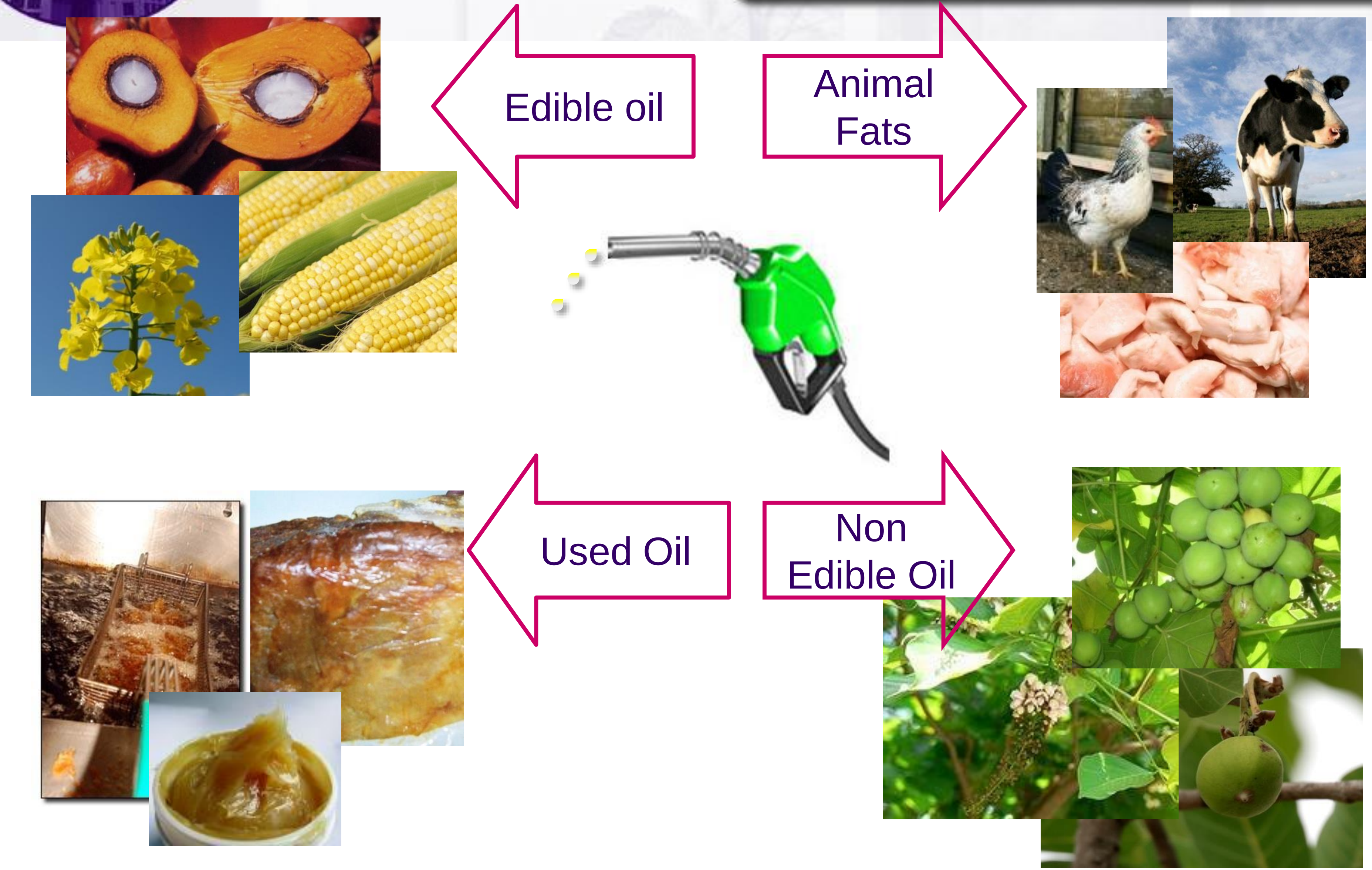
Biodiesel Production

Advantages of Biodiesel

- ‘Green’ emission - less CO_2 and free of sulphur
- Less smoke and particulates
- Lower carbon monoxide and hydrocarbon emission
- Higher cetane numbers
- Renewable energy
- Biodegradable and non-toxic
- Pleasant exhaust fume



Feedstock Choices for Biodiesel Production



Edible oil

Animal Fats

Used Oil

Non Edible Oil

Feedstock Choices

Feedstock for This Study

- Feedstock – Used Cooking Oil (UCO)
- Supplier – Greenfuel Oil Co. Ltd.
- Why Used Cooking Oil?
  - ✓ Cheap and renewable sources
  - ✓ Non-food competing feedstocks
  - ✓ Improve environmental awareness
    - reduce environmental pollution and groundwater contamination

Free Fatty Acids

- **What is free fatty acids?**
  - Fatty acids that are not bound or attached to other molecules (e.g. triglycerides)
  - Degradation products of the vegetable oil
- **Oil feedstocks with a high FFA content**
  - Non-edible oil, animal fats, used oil
  - Mahua: 20%, Jatropha:14%, Waste oil: 6-30%
- **Why do we need to remove free fatty acids?**
  - Difficulties with biodiesel production & separation – saponification
  - Level of FFA - below 1% - to avoid saponification
  - Biodiesel specifications

Composition of Fatty Acid in UCO

Component	% Composition
Palmitic acid (C16:0)	11.34
Stearic acid (C18:0)	3.18
Oleic acid (C18:1)	43.95
Linoleic acid (C18:2)	36.44
Linolenic acid (C18:3)	5.09

Biodiesel Production

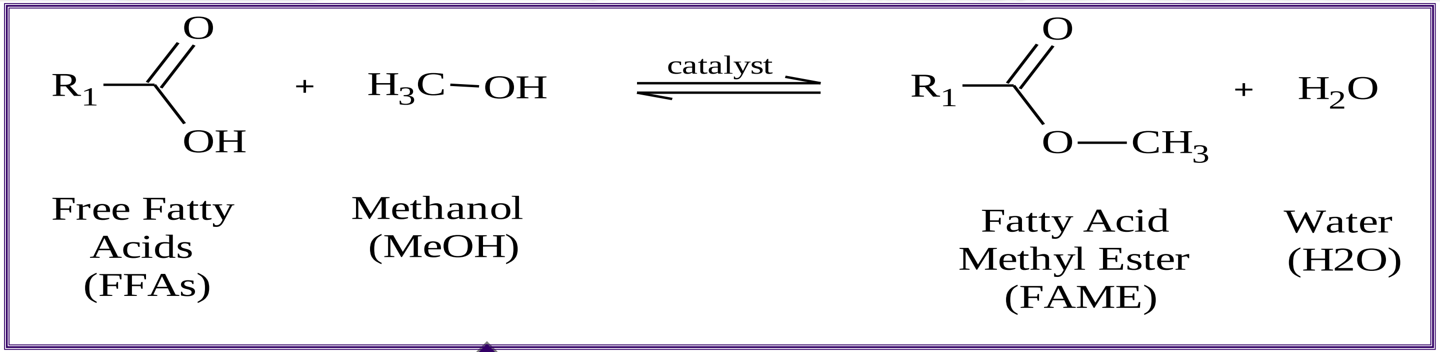
Esterification

- Also known as the **acid catalysed process**
- Used as a **pre-treatment** step to reduce the large amount of FFA in feedstocks
- **Converts free fatty acids (FFAs)** to methyl ester before goes to transesterification reaction

Transesterification

- Also known as **alkali catalysed process**
- **Faster, higher yield and purity** compared to acid catalysed process
- **Converts triglycerides** to methyl ester (biodiesel)
- **Sensitive to the quality of feedstock** – feedstock with high FFA will lead to saponification reaction

Proposed Reaction Scheme



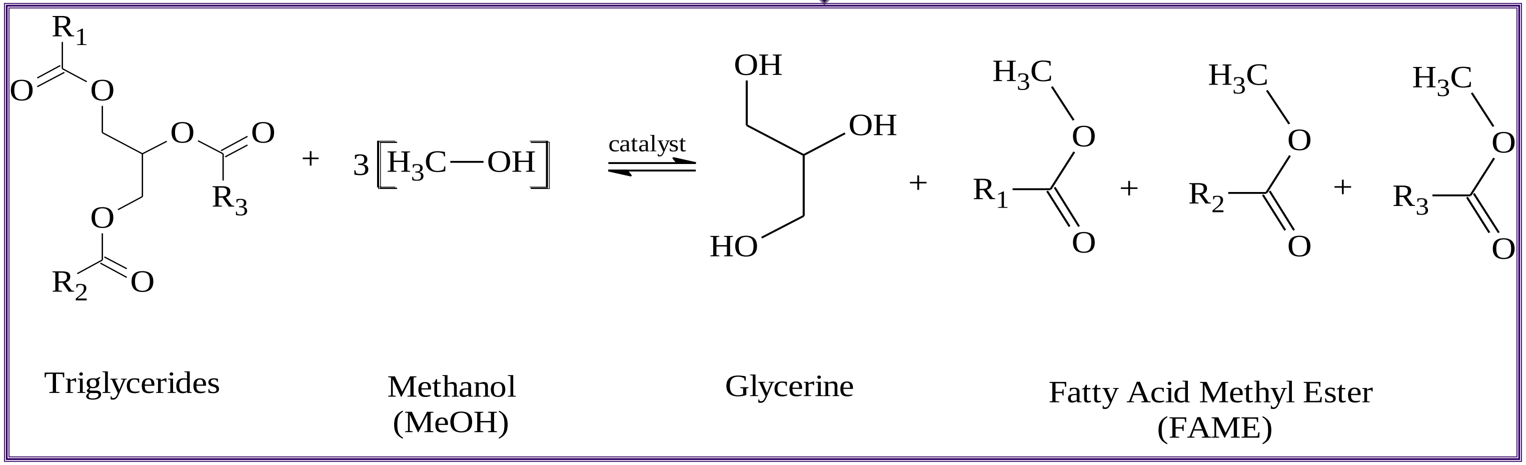
Free Fatty Acids (FFAs)

Methanol (MeOH)

Fatty Acid Methyl Ester (FAME)

Water (H2O)

UCO → **Esterification** → **Transesterification** → **Biodiesel**



Triglycerides

Methanol (MeOH)

Glycerine

Fatty Acid Methyl Ester (FAME)

Biodiesel Production

Catalysts investigated

	Purolite D5081 & D5082 Amberlyst 36	Novozyme 435
Type	Cation-exchange resin	Immobilised Enzyme
Description	Sulphonated polystyrene cross-linked with divynlbenzene	Candida Antarctica lipase B (CALB) immobilised on acrylic resin
Particle Size (μm)	~482	450
Image		

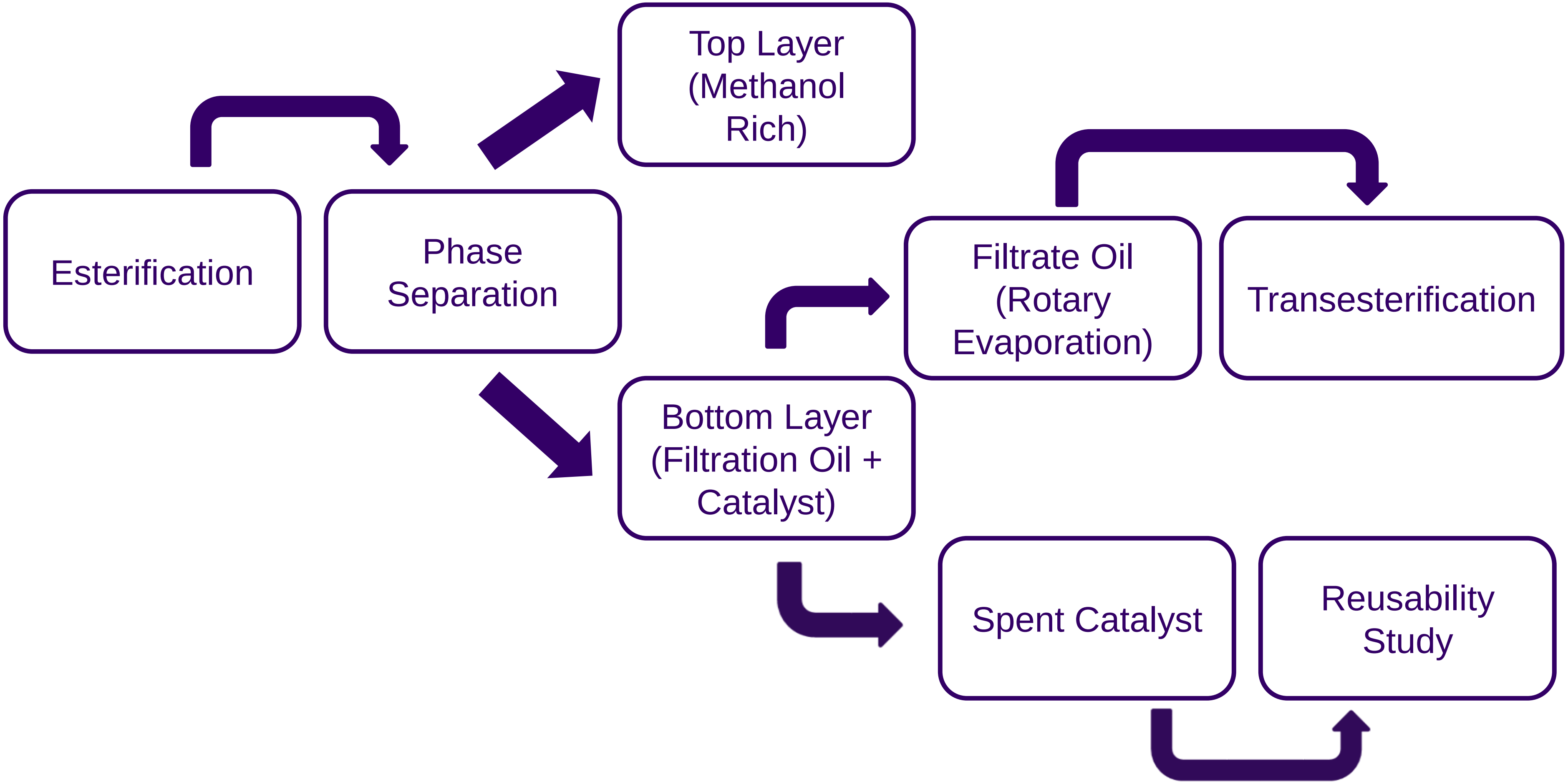
Catalysts Properties

Catalyst Properties	Purolite D5081	Purolite D5082	Amberlyst 36
Physical Appearance	Black spherical beads	Black spherical beads	Black spherical beads
Cross-linking level	High	High	Low
Matrix	Hypercrosslinked	Hypercrosslinked	Macroporous
Particle Size, (µm)	396	482	341
BET Surface Area(m^2/g)	514.18	459.62	30.0
Total Pore Volume (cm^3/g)	0.47	0.36	0.19
Average pore diameter (Å)	36.9	31.4	254.2
True Density (g/cm^3)	1.311	1.375	1.568

Elemental Analysis

Catalyst	% C	% H	% N	% S	% O*
Fresh D5081	77.04	5.32	0.95	4.09	12.61
Fresh D5082	68.87	4.44	0.13	5.92	20.65
Fresh Amberlyst 36	42.18	4.10	0.10	18.27	35.35

Proposed Process Scheme



Esterification

Phase Separation

Top Layer (Methanol Rich)

Bottom Layer (Filtration Oil + Catalyst)

Filtrate Oil (Rotary Evaporation)

Transesterification

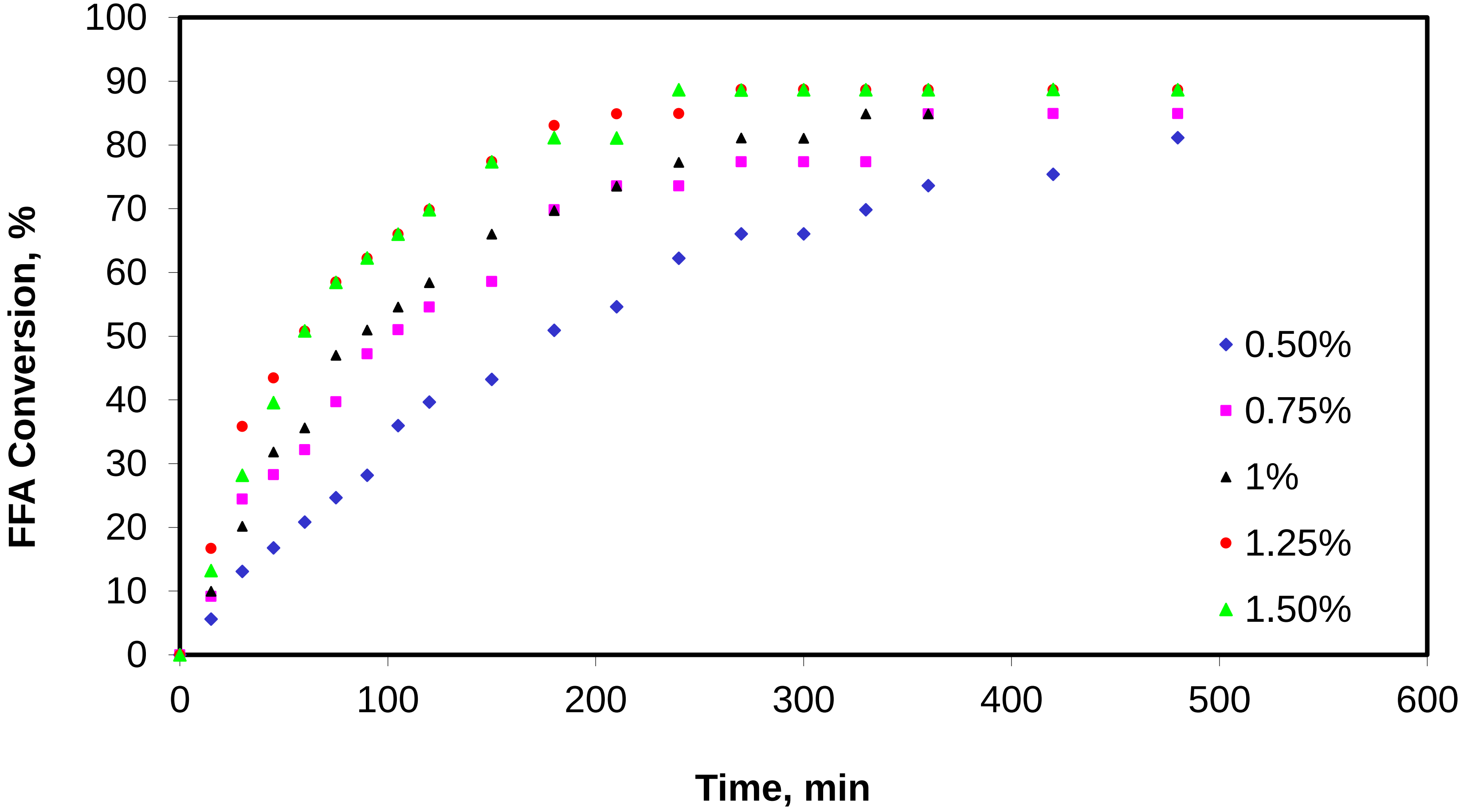
Spent Catalyst

Reusability Study

Comparison of Catalysts

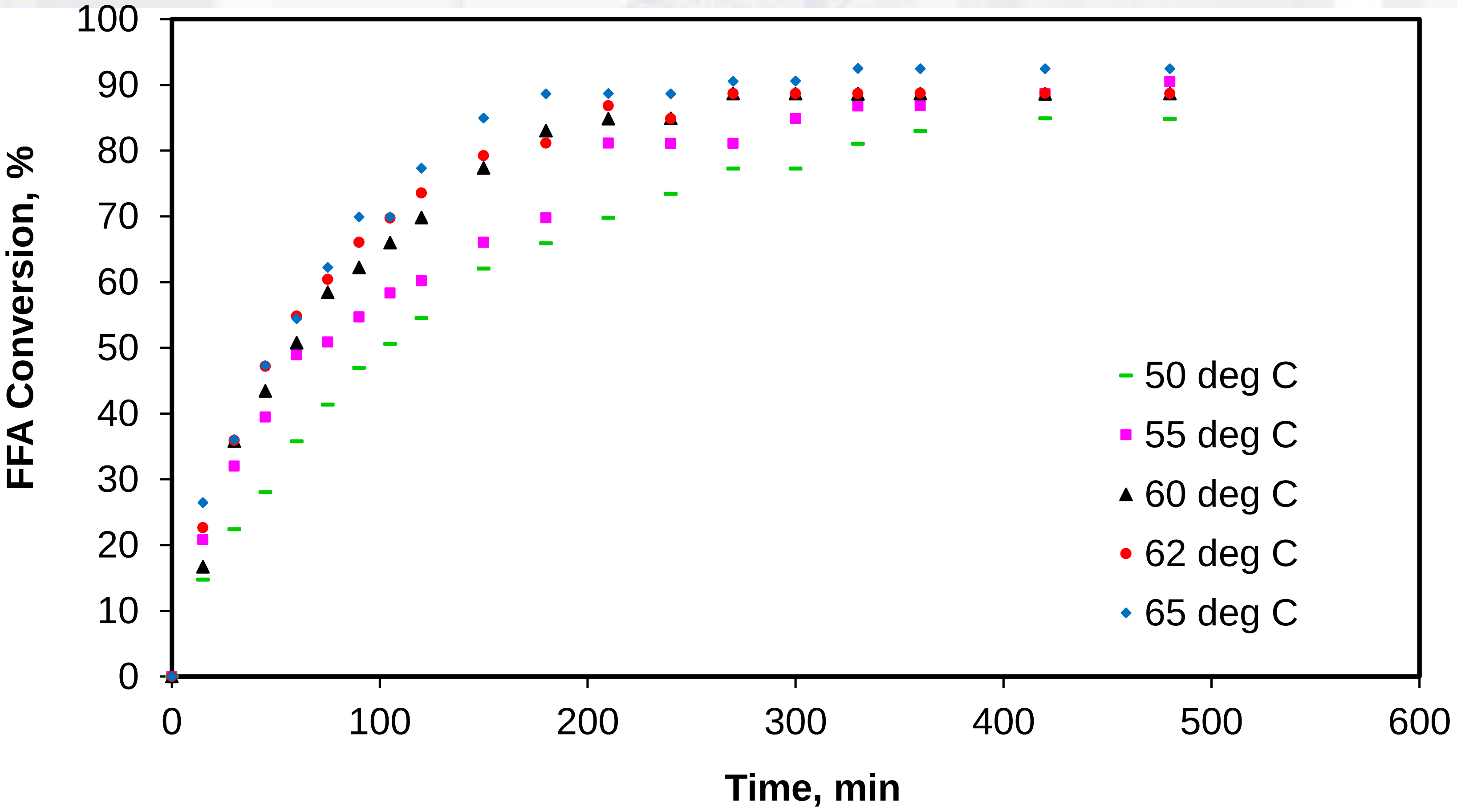
FFAs Conversion	Purolite D5081	92%
	Purolite D5082	82%
	Amberlyst 36	38%
Largest specific surface area and pore volume (BET analysis):	D5081	
High DVB cross-linking:	D5081 then D5082	
Smallest average particle size:	D5081	
Best catalytic performance:	D5081	

Catalyst (D 5081) Loading



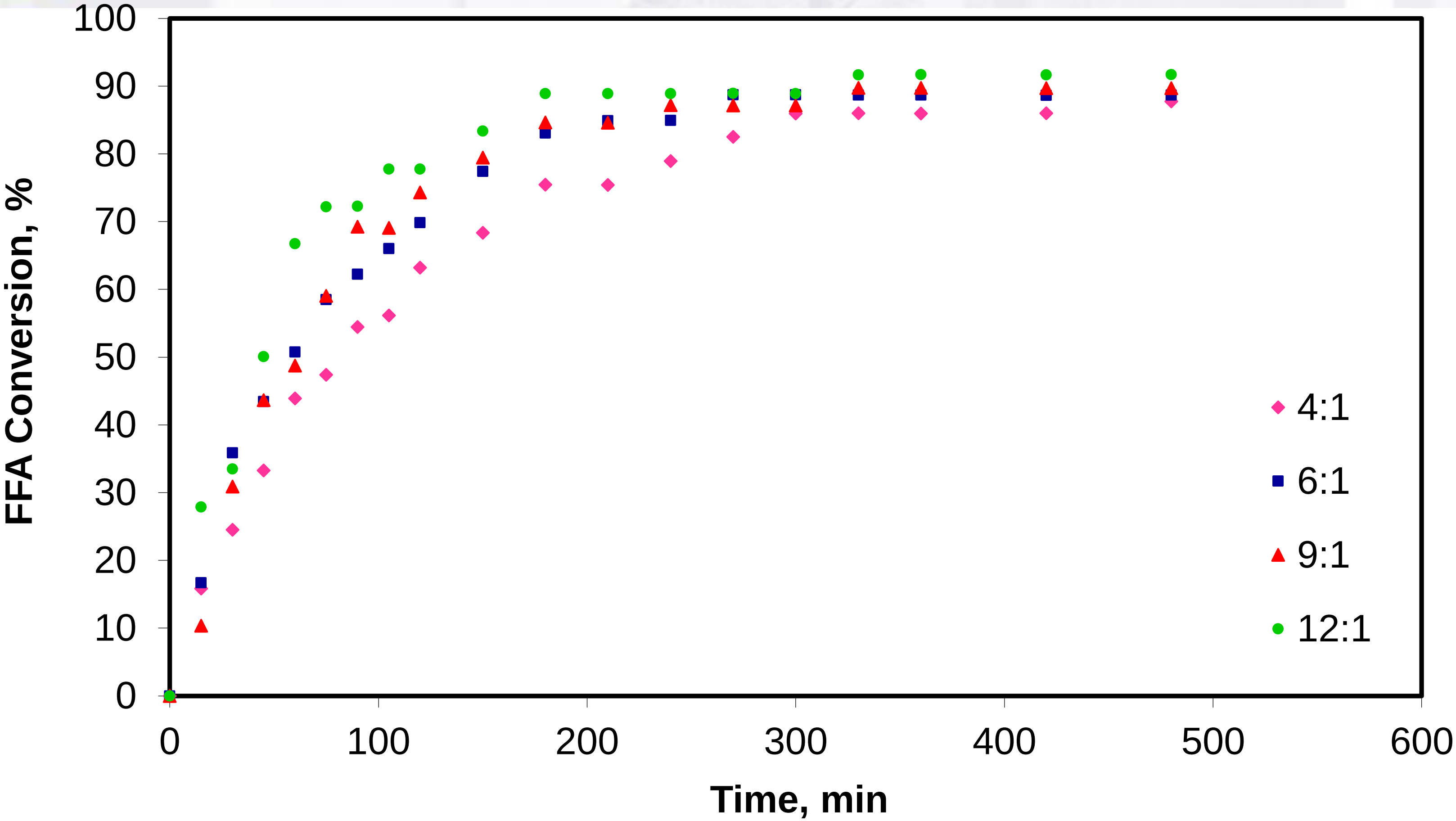
- 1.25 wt% selected as optimum catalyst loading

Reaction Temperature



- High temperature decrease viscosity, improving contact (catalyst: D 5081)
- The boiling point of methanol is 64.7 °C

Methanol to Oil Molar Ratio



- Optimum mole ratio 6:1 (catalyst: D 5081)

Results Summary

- Very high conversion of FFAs is possible with ion-exchange resin catalysts
- Purolite D5081 gave the largest reduction of FFAs, with a catalyst loading of 1.25 wt%, at 60 °C and a mole ratio of 6:1 giving FFAs conversion of 92%
- Purolite D5081 has the largest surface area, largest pore volume and smallest average particle size
- Triglycerides, proteins, phospholipids or other impurities present in the UCO could potentially foul Purolite D5081 catalyst
- Good separation prior to transesterification is possible

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Saha *et al., Ind. Eng. Chem. Res., 2012*, 51, 14653−14664
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Biodiesel Production

- Current Work
  - to study the feasibility of continuous flow reactor for the production of biodiesel
- FlowSyn Continuous Flow Reactor
  - Developed by Uniqsis Ltd
  - A fully integrated continuous flow reactor for reaction optimisation
- Advantages
  - Accessible, flexible, reproducible scalability

FlowSyn Continuous Flow Reactor

Methanol

Flow Reactor

Product Bottle

User Interface

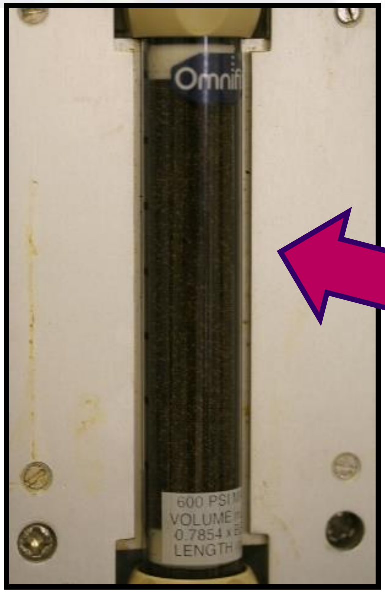
Solvent

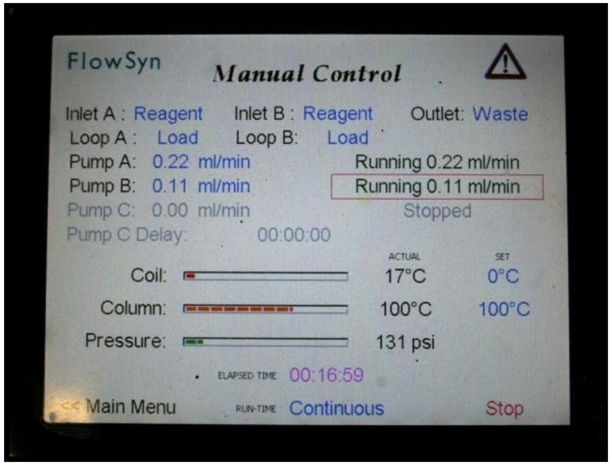
Used Oil

Pump

Coil Reactor

FlowSyn Continuous Flow Reactor





FlowSyn
Manual Control

Inlet A : Reagent Inlet B : Reagent Outlet: Waste
Loop A : Load Loop B: Load
Pump A: 0.22 ml/min Running 0.22 ml/min
Pump B: 0.11 ml/min Running 0.11 ml/min
Pump C: 0.00 ml/min Stopped
Pump C Delay: 00:00:00

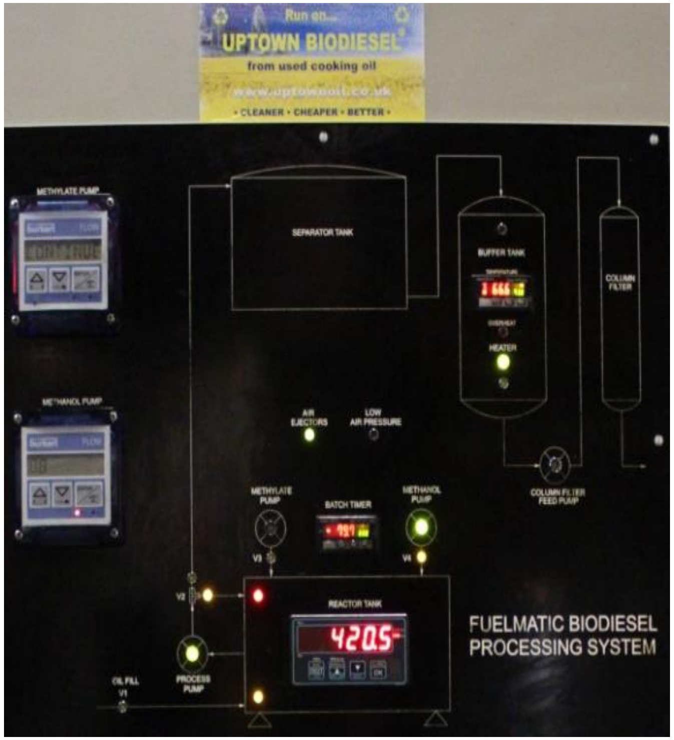
	ACTUAL	SET
Coil:	17°C	0°C
Column:	100°C	100°C
Pressure:	131 psi	

ELAPSED TIME 00:16:59
<< Main Menu RUN-TIME Continuous Stop

Collaboration with Uptown Oil Ltd and PwC: Specific areas of focus

- Optimised the conversion process at Uptown Oil Ltd and produced biodiesel meeting EN14214 standards
- Scaled up production from ~40 tonnes/week to ~70-80 tonnes/week at Uptown Oil Ltd
- Embedded both technological developments and scale-up into standard operating procedures at Uptown Oil Ltd ensuring ongoing consistency of output
- Recently worked with PricewaterhouseCoopers (PwC) to monitor the quality of the biodiesel samples

Production at Uptown Biodiesel Ltd



We have optimised the process to scale up biodiesel production from ~40 tonnes/week to ~70-80 tonnes/week at Uptown Oil Ltd, London

Highlights – biodiesel production process

- Successfully investigated catalytic properties of newly developed catalysts in collaboration with Purolite International Ltd
- Successfully developed an innovative two stage catalysed biodiesel production process
- Optimised reaction parameters to produce a greener process methodology and provide support to Uptown Oil to implement the process technology for supplying EN14214 standard biodiesel to PwC for commissioning the trigenerators at their site
- The collaboration has allowed PwC to run its CHP engine with clean carbon neutral fuel, thus reducing the buildings EPC to 11 representing an A rating
- PwC (Embankment Place, London) has created the most sustainable building in the world and achieved the highest BREEM rating record worldwide

Highlights – biodiesel production process

PwC (1 Embankment Place, London) has created the most sustainable building in the world and achieved the highest BREEM rating record worldwide (include a heat and power system run on recycled waste vegetable oil)

Highlights – biodiesel production process

- PwC building achieved Environmental Performance Certificate A and a BREEAM score of 96.31% – surpassing all others internationally
- Today the building emits 40% less carbon than one typical of its size and 20% of heat and 60% of its energy needs are produced on-site
- Estimates suggest a utility bill saving of £250,000 a year, but PwC forecasts more: electricity (-221%); gas (-11%); and water (-33%)
- The transformation will help it achieve PwC's 2017 targets to reduce carbon emissions by 50% and energy use by 25%

http://www.theguardian.com/sustainable-business/sustainability-case-studies-pwc-one-embankment-place?CMP=twt_gu

http://www.breeam.org/podpage.jsp?id=666

Conversion of CO_2 to Value Added Chemicals

- CO_2 is the focus of global attention because of its position as the primary greenhouse gas
- In 2012 global CO_2 emission from fossil fuels was ~ 7000 million metric tons carbon
- Atmospheric CO_2 concentration changed from 280 ppmv in 1000 to 295 ppmv in 1900, but increased to 315 ppmv in 1958 and further to 377 ppmv in 2004, and 400 ppmv in 2014
- The need to reduce CO_2 emissions is now firmly in the public focus
- Something needs to be done now to be able to play a leading role in future commercial landscape

Adeleye, A. I., Patel, D., Niyogi, D., Saha, B., *Ind. Eng. Chem. Res.,* 2014, 2014, 53, 18647-18657.

Saada, R., Kellici, S., Heil, T., Morgan, D., Saha, B., *Applied Catalysis B: Environmental*, 2015, 168 , 353–362.

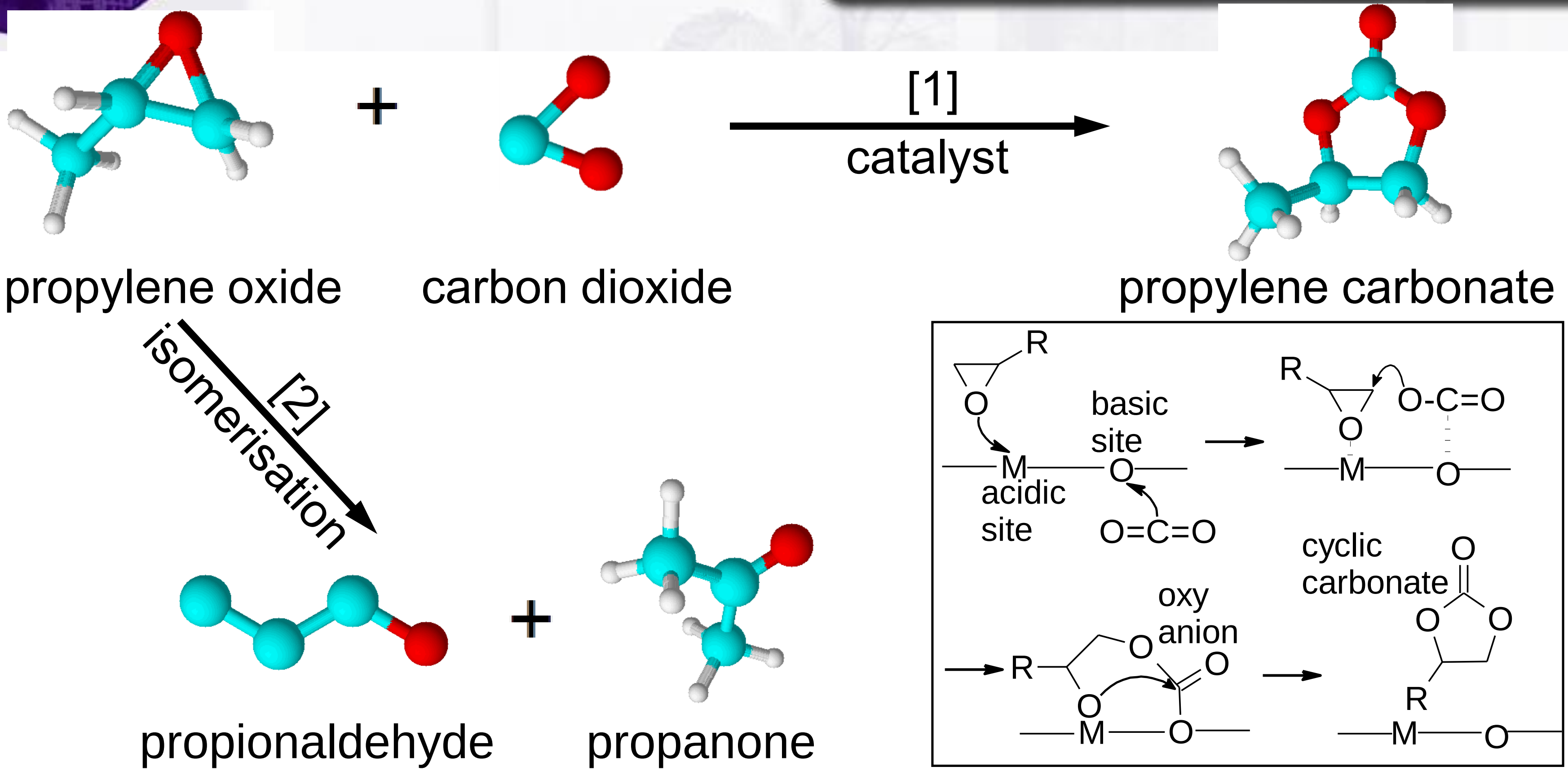
Adeleye, A. I., Kellici, S. Saha, B., *Catalysis Today*, 2015, in press, doi http://dx.doi.org/10.1016/j.cattod.2014.12.032.

Conversion of CO_2 to Value Added Chemicals

- We are currently investigating a detailed study for the conversion of CO_2 to value added chemicals in collaboration with MEL Chemicals
- MEL Chemicals - one of the world’s leading producers of inorganic chemicals specialising in zirconium based catalysts and hydrotalcites
- In our work, CO_2 is reacted with epoxides to produce carbonate(s) and poly(carbonate)s using heterogeneous catalysts in collaboration with MEL Chemicals
- Continuous hydrothermal flow synthesis reactor is used for the synthesis of advanced graphene inorganic nanocomposite functional materials for converting CO_2 into propylene carbonate
- We are also investigating cyclic carbonate synthesis from supercritical CO_2 and epoxide using heterogeneous catalysts

Adeleye, A. I., Patel, D., Niyogi, D., Saha, B., *Ind. Eng. Chem. Res.,* 2014, 2014, 53, 18647-18657.

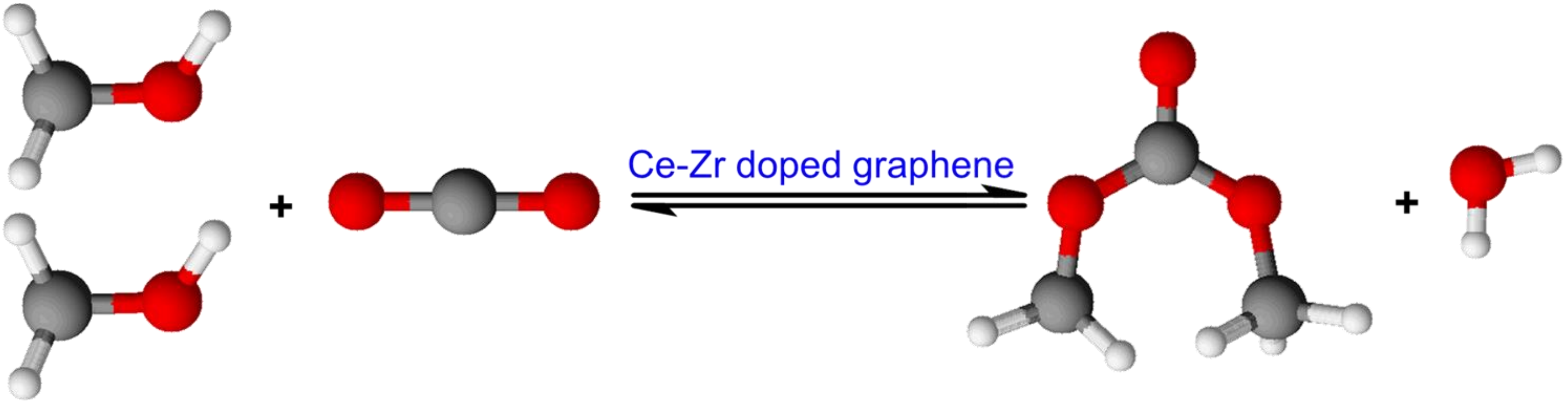
Reaction Scheme



Catalysts: Ceria and lanthana doped zirconia (Ce-La-Zr-O), ceria doped zirconia (Ce-Zr-O), lanthana doped zirconia (La-Zr-O), lanthanum oxide (La-O) and zirconium oxide (Zr-O)

Saha, B. et al., *Ind. Eng. Chem. Res.,* 2014, 2014, 53, 18647-18657.

Reaction Scheme



Methanol
(MeOH)

Carbon dioxide
(CO_2)

Dimethyl carbonate
(DMC)

Water
(H_2O)

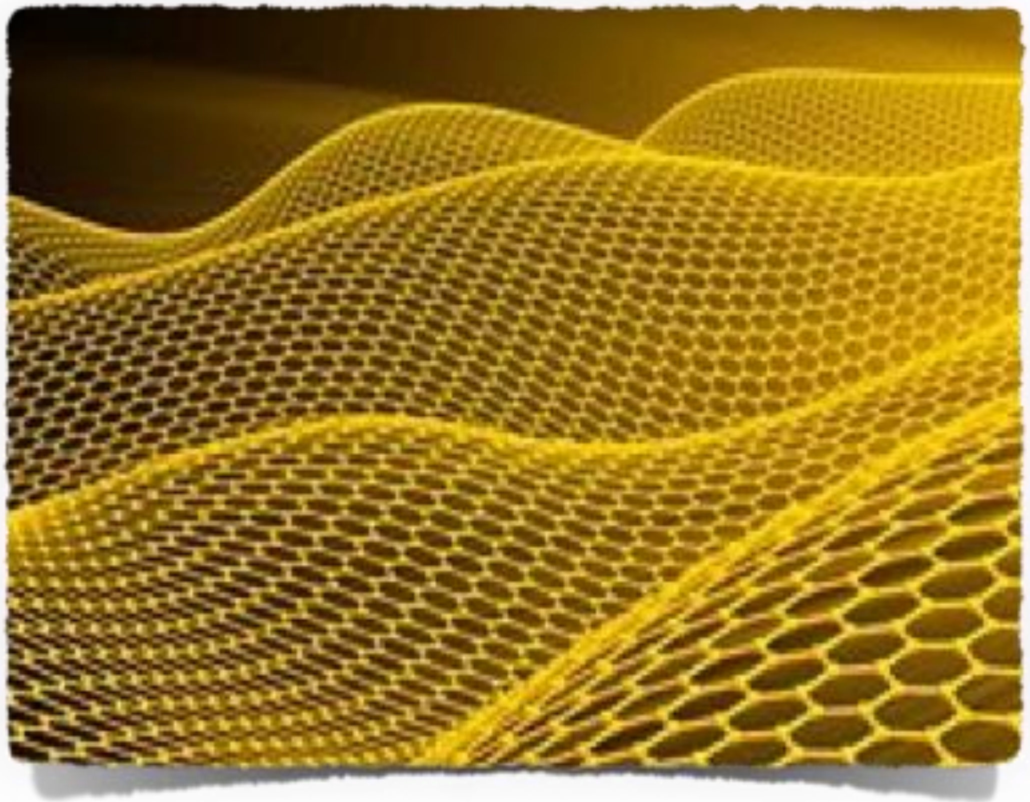
Saada, R., Kellici, S., Heil, T., Morgan, D., Saha, B., *Applied Catalysis B: Environmental*, 2015, 168 , 353–362.

Graphene Inorganic Nanocomposite (GIN) from SCF

- Graphene 2D, plate like structure - it offers an attractive substrate for deposition of inorganic nanoparticles (NP) to give functional materials with enhanced properties
- Advanced functional materials *via* Continuous Hydrothermal Flow Synthesis (CHFS)
- An innovative approach is utilised for synthesising graphene-inorganic nanoparticles (GIN) *via* utilisation of sc-CO_2
- sc-CO_2 allows homogeneously disperse various metal nanoparticles onto graphene in a single step
- The density of NPs on graphene is modulated by modifying NP precursor to graphene ratio
- These materials are currently being tested for gas–sensing properties

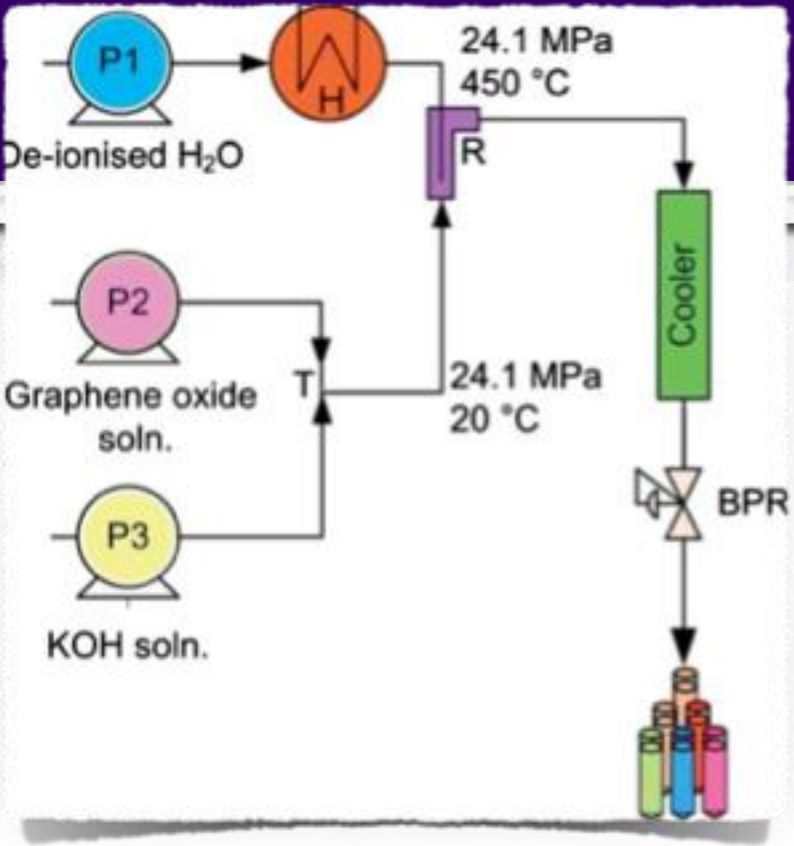
Making Reduced Graphene Oxide (rGO)

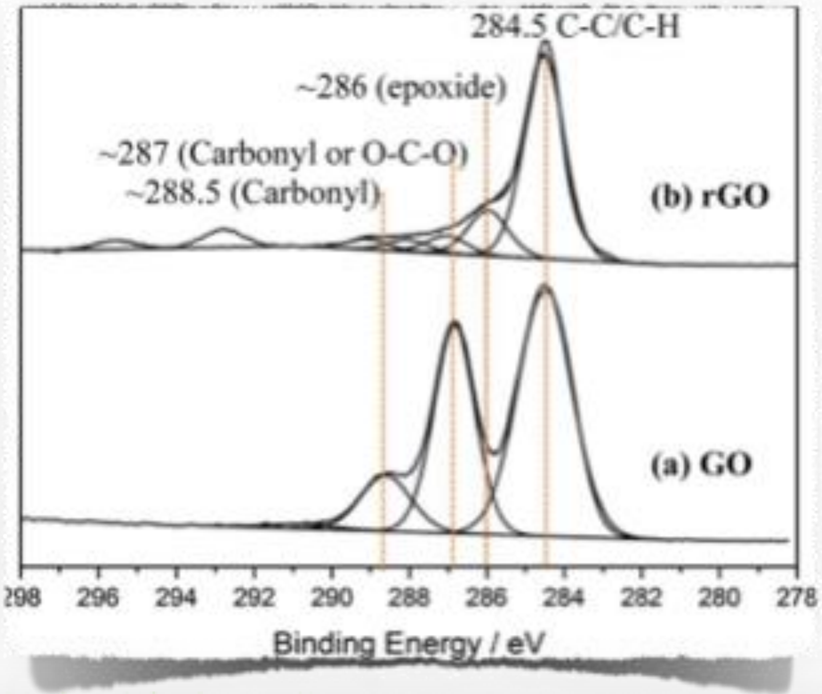
We are developing a novel and rapid approach using the exotic environment of supercritical water to make advanced graphene based functional materials with antibacterial properties



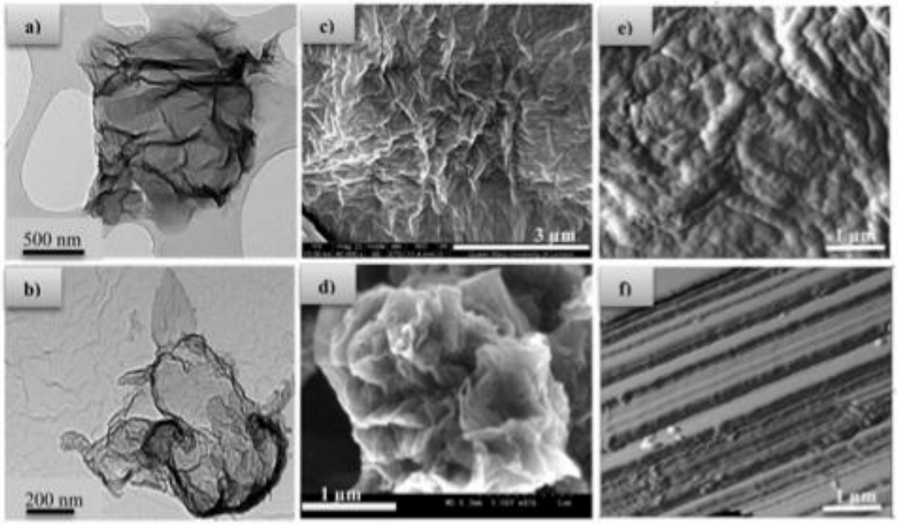
Making rGO

S. Kellici, J. Acord, J. Ball, H. Reehal, D. Morgan and B. Saha, *RSC Adv.*, 2014, 4, 14858-14861



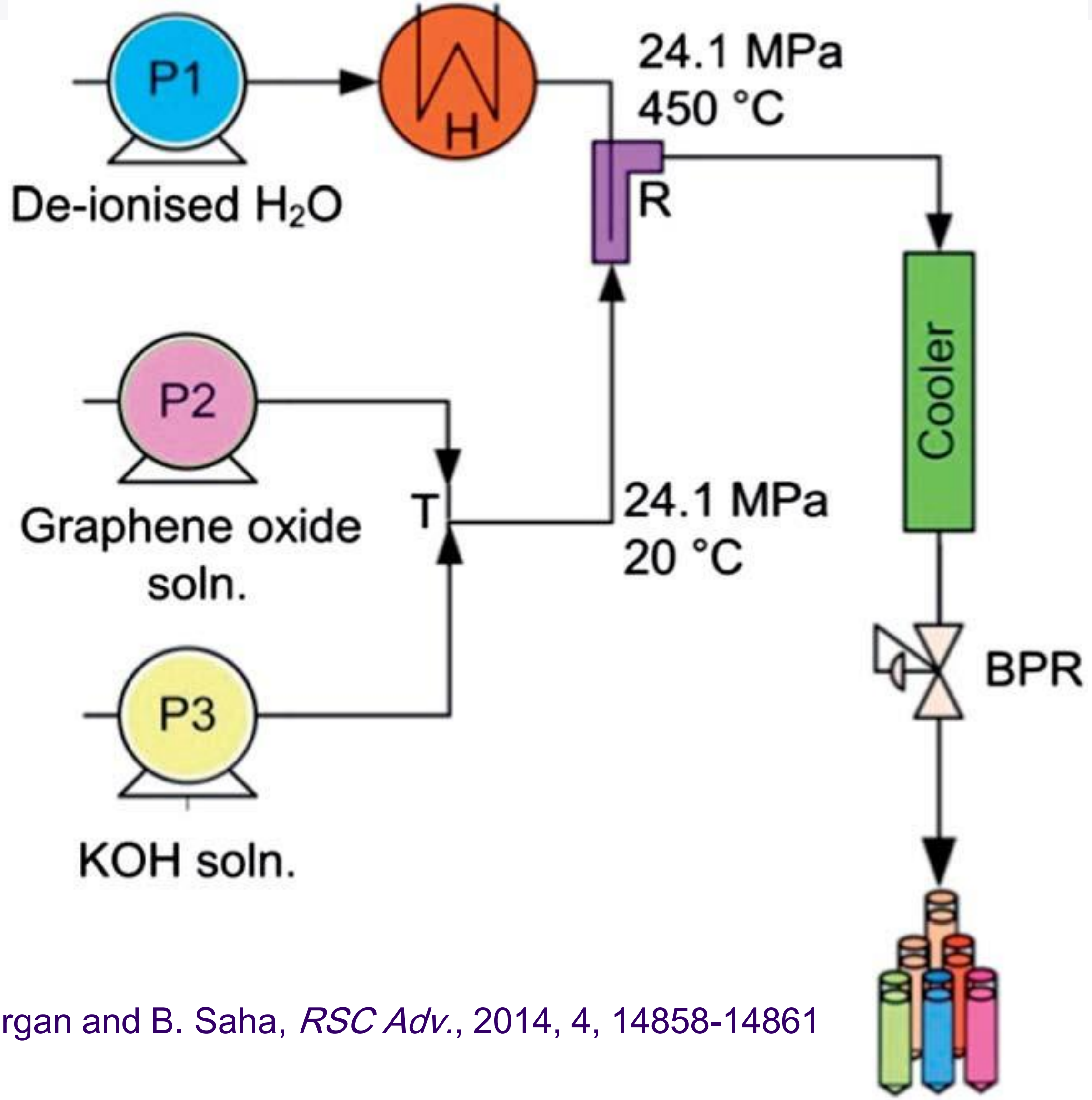


XPS spectra of (a) GO and (b) rGO which revealed a significant reduction in peak intensities of the oxygen containing functional groups for rGO sample. This confirms that CHFS is very effective in dehydrating/reducing GO.



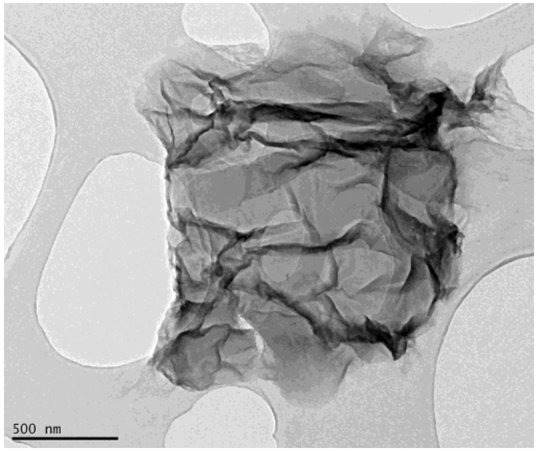
GIN Synthesis from SCF

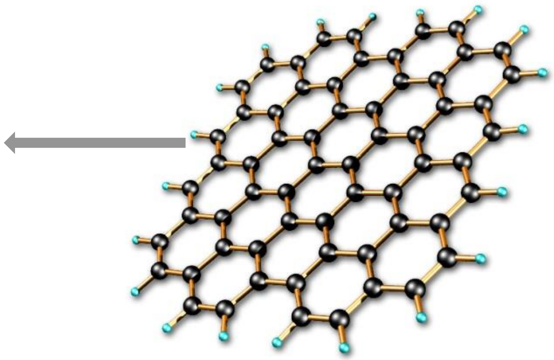
- Mix aqueous salt with scH_2O
- Rapid precipitation and crystallisation
- Single step, rapid synthesis
- Efficient synthesis of various functional materials
- Novel materials with improved properties

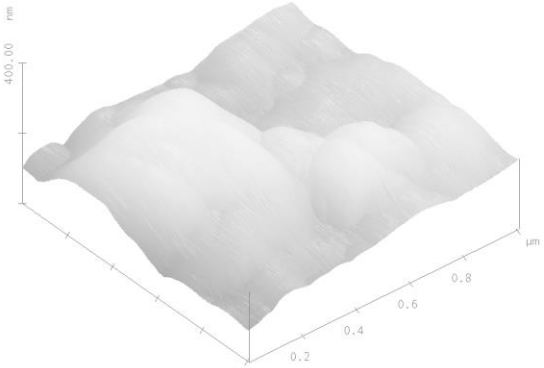


S. Kellici, J. Acord, J. Ball, H. Reehal, D. Morgan and B. Saha, *RSC Adv.*, 2014, 4, 14858-14861

GIN from SCF



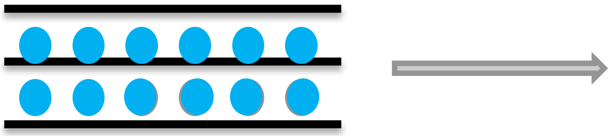




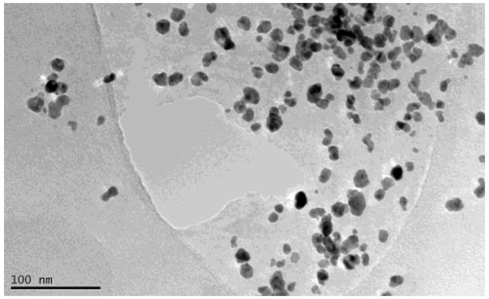
Pd

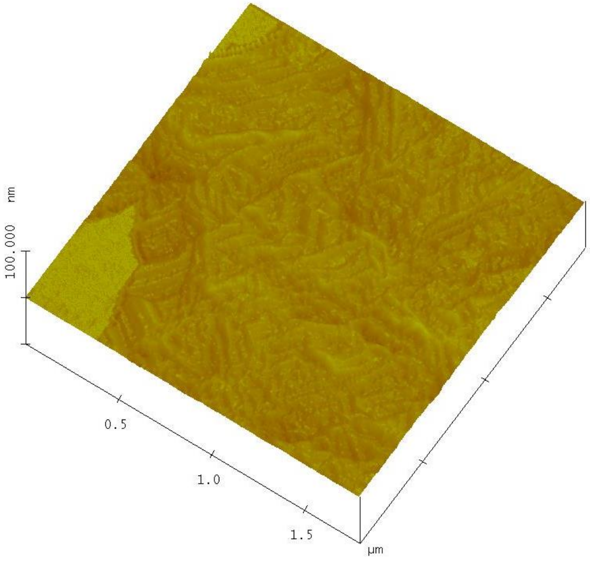
precursor

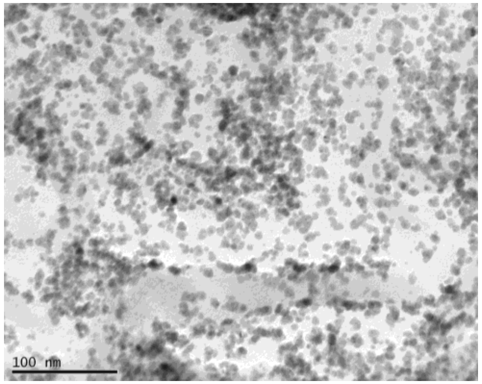
sc-CO_2



Pd-decorated graphene

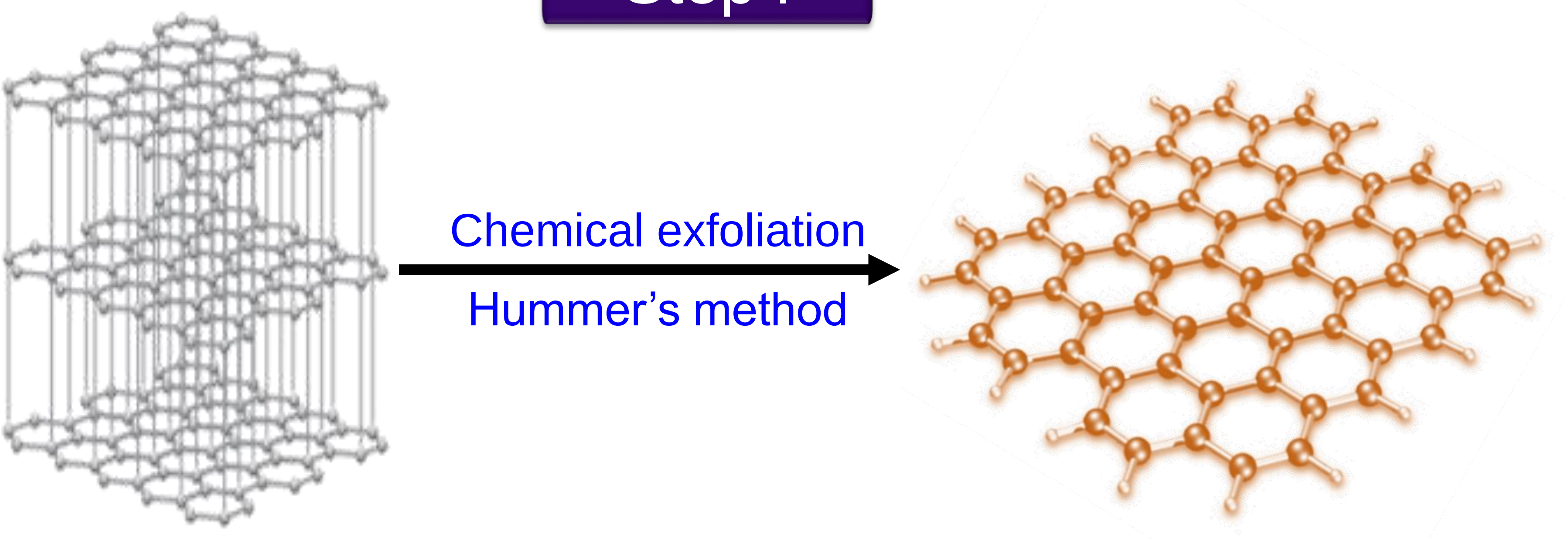






Schematic of Catalyst Preparation

Step I



Chemical exfoliation

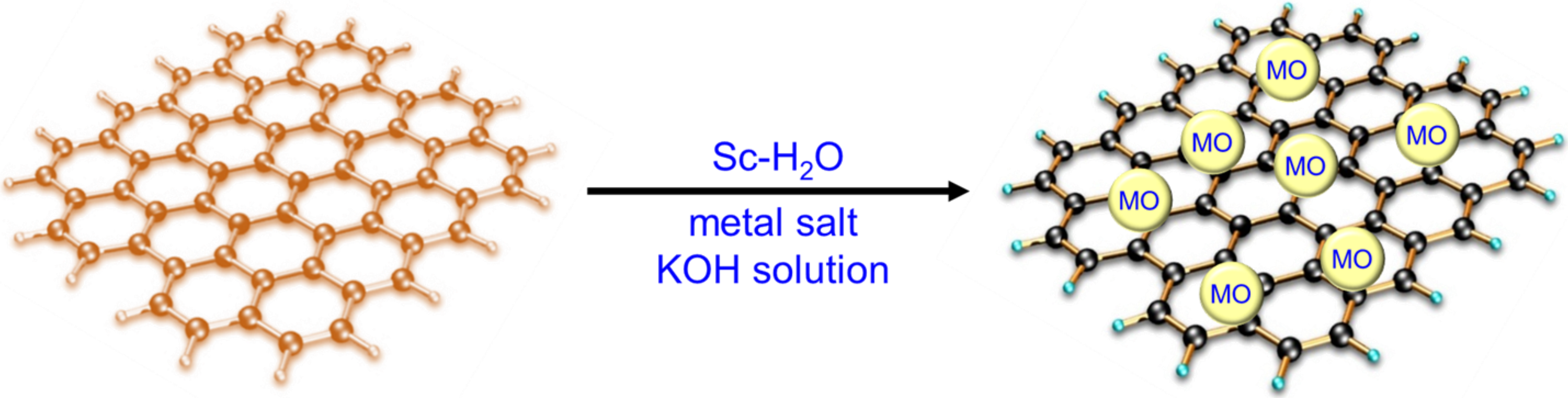
Hummer’s method

Graphite

Graphene oxide

Schematic of Catalyst Preparation

Step II



Sc-H_2O

metal salt
KOH solution

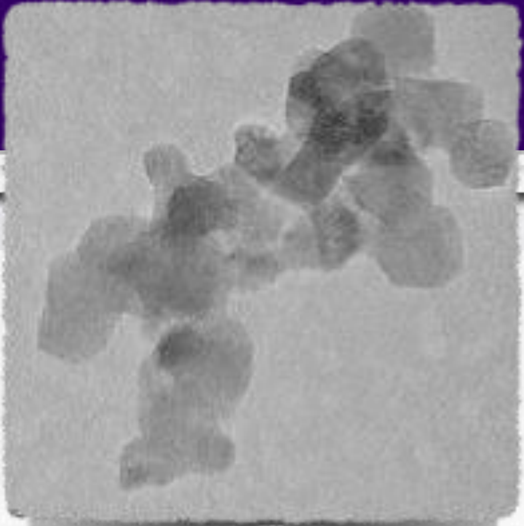
Graphene oxide
(GO)

Ce-Zr decorated graphene
(Ce-Zr-GO)

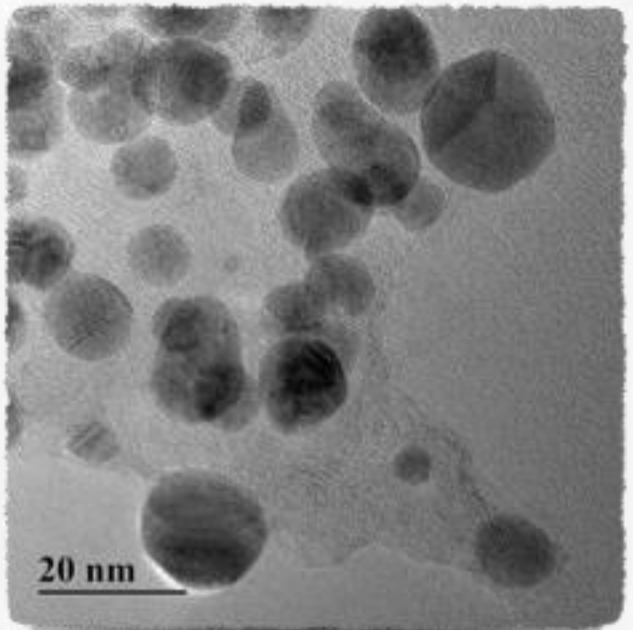
MO: metal oxide CeO_2-ZrO_2

Other Materials

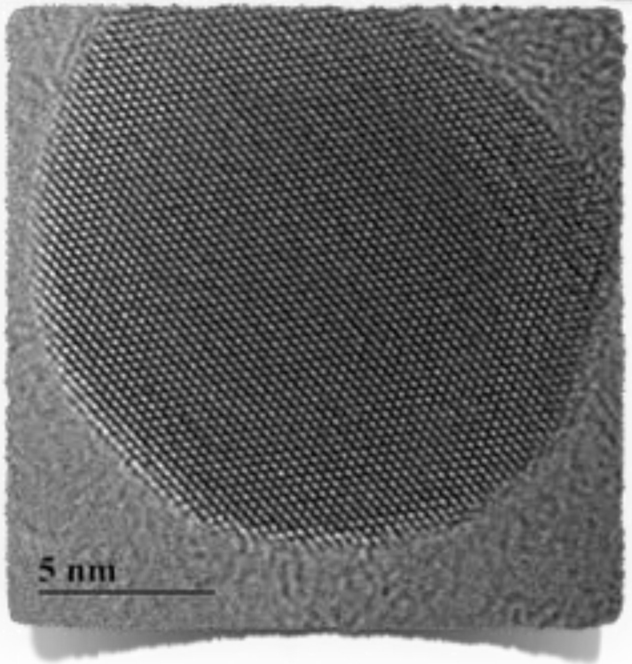
Broad range of applications such as catalysts, biological imaging to solar cells.



Various heterogenous metal oxides - GO for greener synthesis of PC and DMC



Ag-GO



Delivering Low Carbon Energy from Biomass Resources

- With a growing global population and developing economies there is an ever increasing demand for energy
- With finite fossil fuel resources, one of the contributors to the energy balance is the use of biomass
- Biomass does not automatically mean renewable, sustainable or low carbon
- To achieve this requires careful resource selection and management
- My current research focuses on delivering low carbon energy from waste and biomass

Delivering Low Carbon Energy from Biomass Resources

- In 2012, the UK government published a bioenergy strategy linked to three main energy sectors: transport, heat and electricity generation
- It emphasized that biomass energy can be applied more flexibly than other renewable energies
- It can play an important role in meeting the 2020 renewables targets (15% of total energy consumption) and the 2050 carbon reduction targets (80% reduction of greenhouse gas emissions by 2050)
- The latest estimates show that over 20% of the renewable energy targets in the UK can be met using biomass alone
- I would like to explore this area which could drive the implementation of biomass technologies towards 2020 and beyond

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THE ROYAL SOCIETY

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The Royal Academy of Engineering

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Research continues…

Questions?

Thank you for listening!

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