Use of Ultrasound for Monitoring Reaction Kinetics of Biodiesel Synthesis: Experimental and Theoretical Studies.

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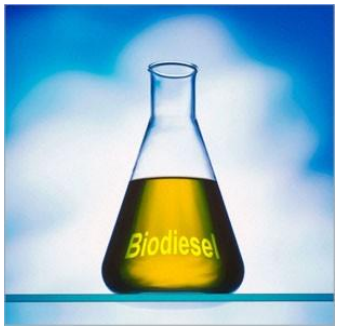

Water and Energy Workshop
15 – 17 February 2015
Doha, Qatar

Content

- Introduction
- Various Issues with Biodiesel
- Biodiesel Production (Experimental Procedure)
- Modelling using gPROMS
- Use of Ultrasound (Novel Technique for Monitoring Reaction Rates)
- Further Work
- Other Aspects of Biodiesel at UoB


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SCOTLAND
WALES
Population
Less than 10000
10000 - 50000
50001 - 100000
100001 - 300000
300001 - 1000000
Over 1 Million People
Motorway
Dual Carriageway
0 30 60 miles
0 50 100 kilometres
Berwick
Embleton
Alnwick
Amble
Rothbury
Morpeth
Blyth
Haltwhistle
Hexham
Newcastle
Sunderland
Carlisle
Wigton
Durham
Maryport
Workington
Whitehaven
Penrith
Keswick
Appleby
Shap
Darlington
Stockton
Hartlepool
Middlesbrough
Whitby
Seascale
Ambleside
Kendall
Richmond
Leyburn
Pickering
Scarborough
Thirsk
Barrow In Furness
Morecambe
Lancaster
Settle
Skipton
Harrogate
Ripon
Knaresborough
York
Bridlington
Hornsea
Beverley
Blackpool
Preston
Bradford
Leeds
Selby
Hull
Goole
Withernsea
Penrith
Bolton
Wigan
Manchester
Doncaster
Scunthorpe
Grimsby
Liverpool
Warrington
Rotherham
Saltfleet
Mablethorpe
Sheffield
Worksop
Macclesfield
Buxton
Bolsover
Lincoln
Spilsby
Chester
Congleton
Matlock
Coningsby
Crewe
Kidsgrove
Wrangle
Whitchurch
Stoke
Derby
Nottingham
Sleaford
Boston
Wells next the Sea
Market Drayton
Grantham
West Felton
Stafford
Spalding
Kings Lynn
Shrewsbury
Coalville
Great Yarmouth
Leicester
Stamford
Wisbech
Norwich
Wolverhampton
Peterborough
Birmingham
Corby
Lowestoft
Coventry
Kettering
Thetford
Ludlow
Rugby
Leominster
Northampton
St Ives
Bury St. Edmunds
Cambridge
Worcester
Stratford upon Avon
Stowmarket
Bedford
Ipswich
Hereford
Banbury
Buckingham
Sudbury
Letchworth
Cheltenham
Luton
Colchester
Gloucester
Harlow
Cirencester
Oxford
Chelmsford
Hemel Hempstead
Didcot
Basildon
Cardiff
Swindon
London
Clevedon
Bristol
Newbury
Rochester
Margate
Bath
Devizes
Weston-Super-Mare
Trowbridge
Basingstoke
Farnborough
Maidstone
Canterbury
Burnham on Sea
Frome
Warminster
Farnham
Guildford
Deal
Lynton
Minehead
Glastonbury
Tonbridge
Crawley
Tunbridge Wells
Dover
Bridgewater
Taunton
Salisbury
Winchester
Hythe
Folkestone
Bideford
Petersfield
Yeovil
Tiverton
Southampton
Lewes
Hailsham
Bude
Okehampton
Hythe
Worthing
Hastings
Lyme Regis
Dorchester
Portsmouth
Brighton
Eastbourne
Exeter
Poole
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Exmouth
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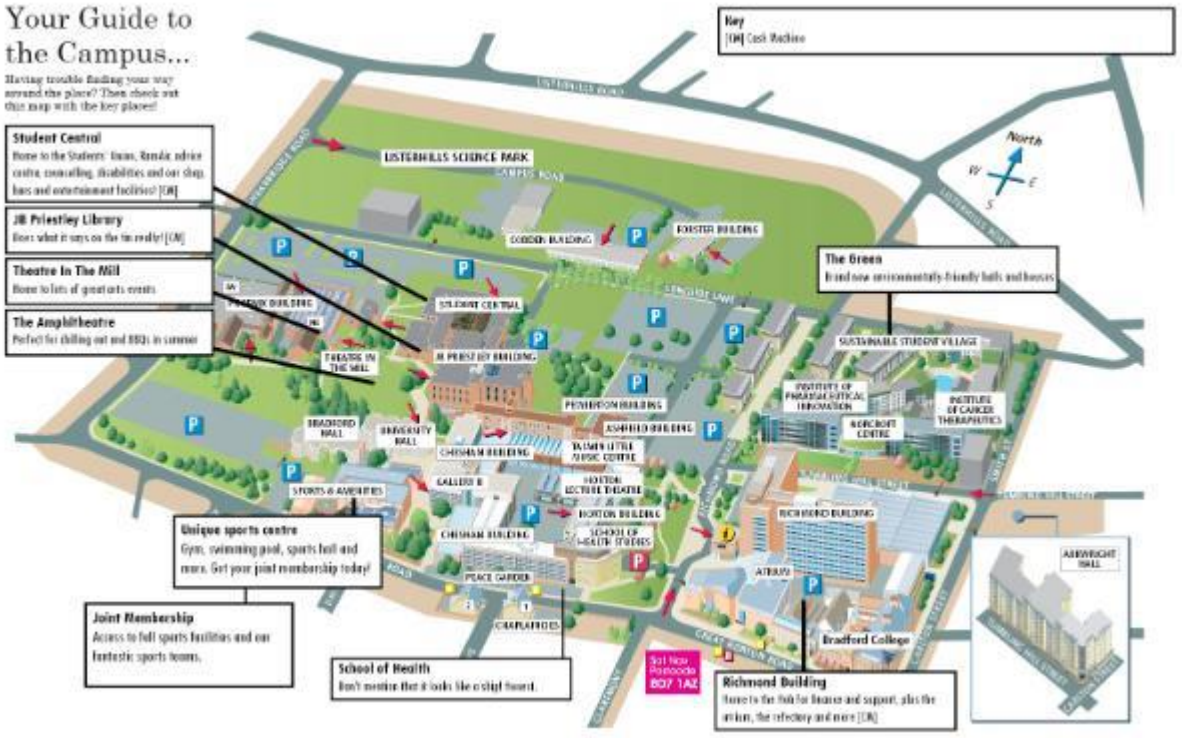
Campus



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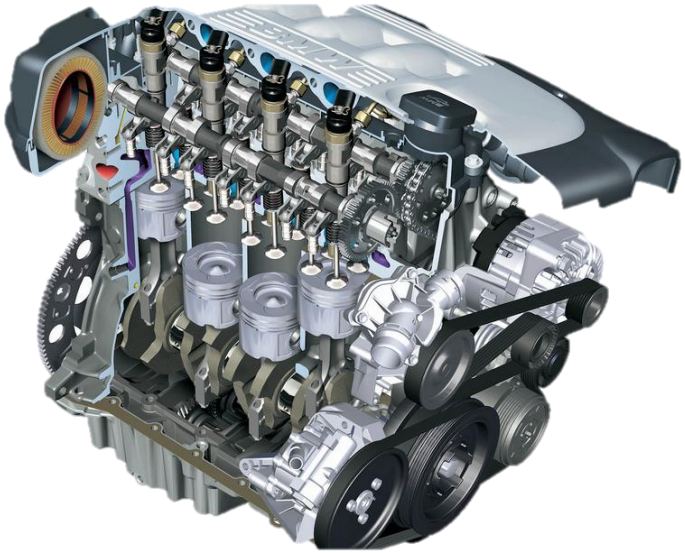
- Faculty of Social & International Studies

Introduction

- Biodiesel is an upcoming fuel intended to be a substitute for conventional diesel.
- Has no sulphur and lower aromatic content compared to diesel.
- Biodiesel can be used in most diesel engine vehicles.
- Renewable



Facts and Figures

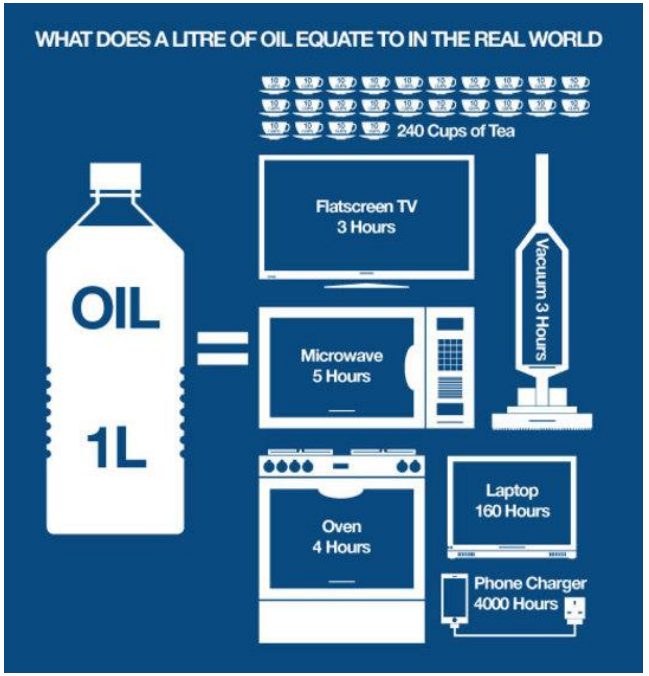
- To help combat climate change the UK has a target to reduce carbon emissions by 80% by 2050.

- 30% of the UK renewable energy could come from biomass heat and electricity by 2020.

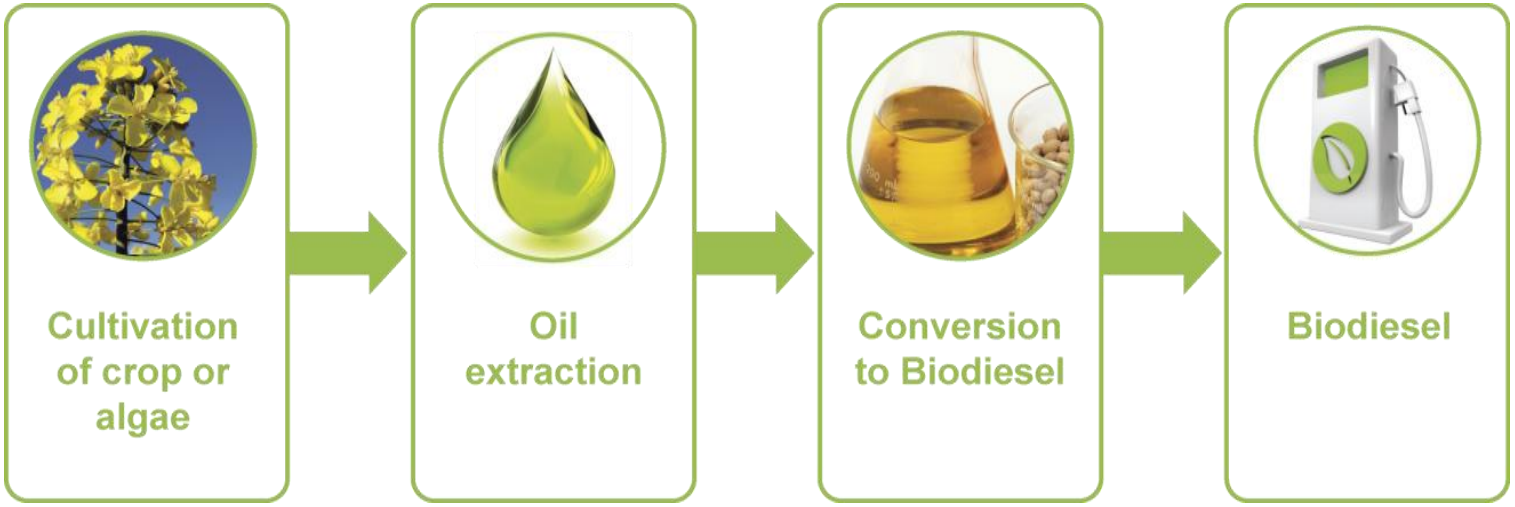
- To meet the European Renewable Energy Directive, the UK is aiming for 10% of transport energy to be from renewable sources by 2020.

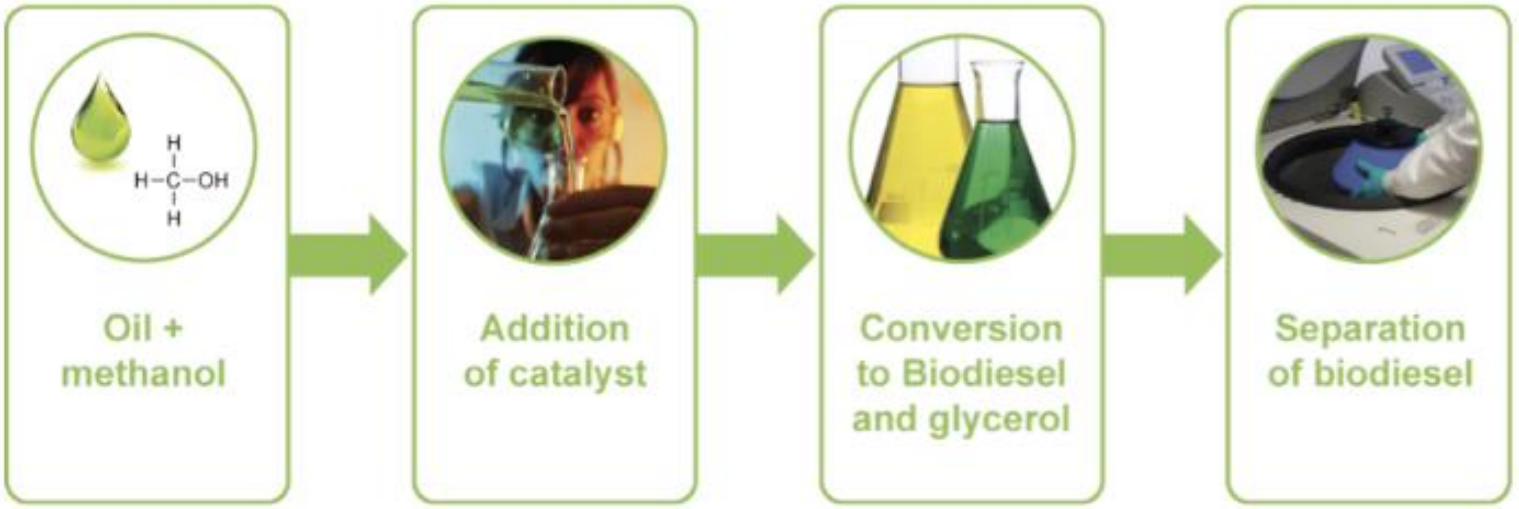
- By 2020, 8% of our petrol and 5% of our diesel could come from crops grown in the UK.

- 129,000 tonnes of used cooking oil is disposed by households each year in the UK (140,000,000 Litres)



http://www.livingfuels.co.uk/did_you_know


Cultivation of crop or algae
Oil extraction
Conversion to Biodiesel
Biodiesel


H
H–C–OH
H
Oil + methanol
Addition of catalyst
Conversion to Biodiesel and glycerol
Separation of biodiesel

Types of Renewable Feedstock

Coconut
Corn
Cottonseed
Crambe
Lard
Palm
Waste Vegetable Oil
Peanut
Rapeseed
Soybean
Sunflower
Tallow
Canola

Homogeneous

Sodium Hydroxide

Sodium Methoxide

Potassium Hydroxide

Potassium Methoxide

Heterogeneous

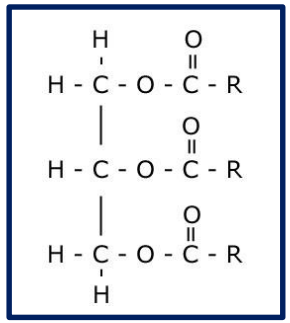
Heterogeneous acid catalyst:

- Ruthenium catalyst
- Zinc stearate immobilized on silica gel
- Sulphate tin oxide
- Hetropoly acid
- Silica functionalised with 4-ethyl-benzene sulfonic acid group.

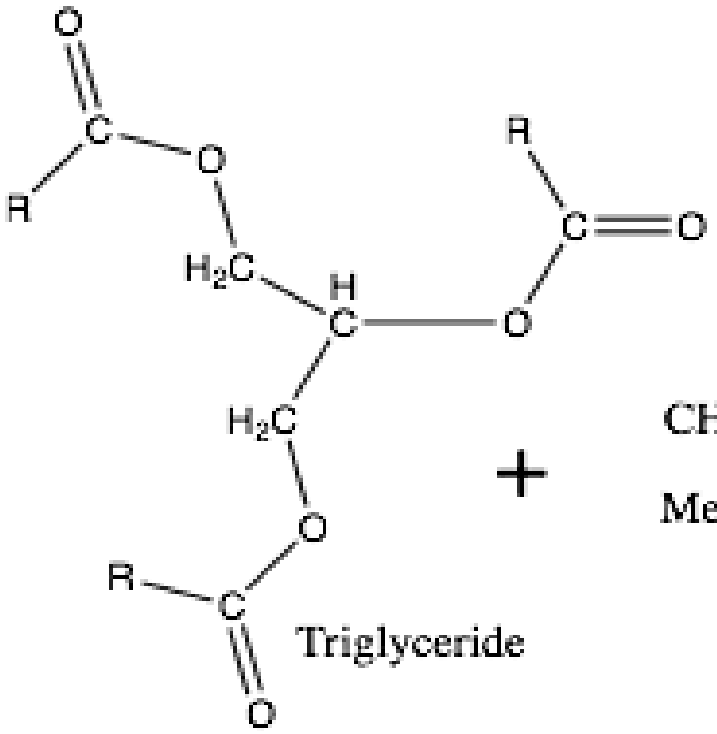
Heterogeneous solid base catalyst:

- MgO
- CaO
- SnO
- Waste eggshell
- Golden apple
- Meretin venus
- A/Mg Hydrotalcite
- KNO_3/Al_2O_3
- Montmorillonite KSF

Biodiesel Production (Homogeneous)



- Biodiesel can be produced from vegetable oil by transesterification (basically means reducing the viscosity)
- Methanol + Vegetable Oil $\xrightarrow{\text{Catalyst}}$ Glycerol + Biodiesel
- Typical vegetable oils: Palm, Rapeseed, Canola, Sunflower Oil, Waste Vegetable Oil (WVO) All are Triglycerides
- Typical Catalysts: Sodium Hydroxide, Potassium Hydroxide.



Triglyceride

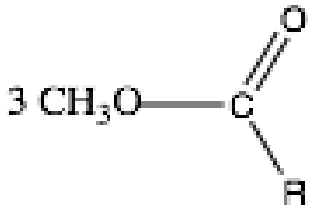
+

CH_3OH

Methanol

NaOH

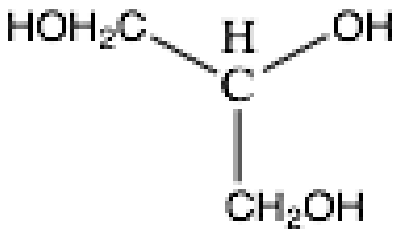
Catalyst



Fatty Acid Methy Ester

(FAME)

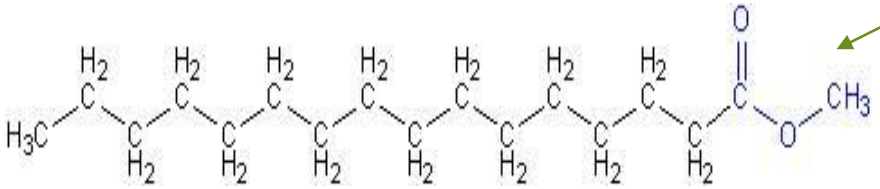
+



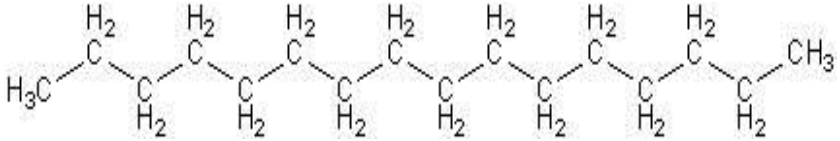
Glycerol

Biodiesel : Diesel Comparison

Ester



Typical Biodiesel Molecule



Typical Diesel Molecule

Reaction Mechanism (1)

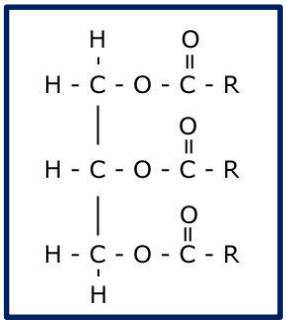
The process involves reacting triglyceride with methanol to produce methyl ester (Biodiesel) and a by-product, glycerol

$$TG + CH_3OH \overset{k1,k2}{\Longleftrightarrow} DG + R_1COOCH_3$$

$$DG + CH_3OH \overset{k3,k4}{\Longleftrightarrow} MG + R_2COOCH_3$$

$$MG + CH_3OH \overset{k5,k6}{\Longleftrightarrow} GL + R_3COOCH_3$$

$$TG + 3CH_3OH \leftrightarrow GL + 3RCOOCH_3$$ Overall Reaction



Three Fatty Acids (Triglyceride)

Reaction Mechanism (2)

ODEs

$$\frac{dC_{TG}}{dt} = -k_1 C_{TG} C_A + k_2 C_{DG} C_E$$

$$\frac{dC_{DG}}{dt} = -k_1 C_{TG} C_A + k_2 C_{DG} C_E - k_3 C_{DG} C_A + k_4 C_{MG} C_E$$

$$\frac{dC_{MG}}{dt} = k_3 C_{DG} C_A + k_4 C_{MG} C_E - k_5 C_{MG} C_A + k_6 C_{GE} C_E$$

$$\frac{dC_E}{dt} = k_1 C_{TG} C_A - k_2 C_{DG} C_E + k_3 C_{DG} C_A - k_4 C_{MG} C_E + k_5 C_{MG} C_A - k_6 C_{GL} C_E$$

$$\frac{dC_A}{dt} = -\frac{dC_E}{dt}$$

$$\frac{dC_{GL}}{dt} = k_5 C_{MG} C_A - k_6 C_{GL} C_E$$

$$k_i = a_i e^{-\frac{b_i}{T}}$$

Where C_{TG}, C_{DG}, C_{MG}, C_E, C_A, C_{GL}, are concentrations of triglycerides, diglycerides, mono glycerides, methyl ester, methanol and glycerol –

Model Simulations Carried Out Using gPROMS

Reaction Mechanism (3)

Many researchers have calculated rate constants…….

Rate Constants Used in this Study

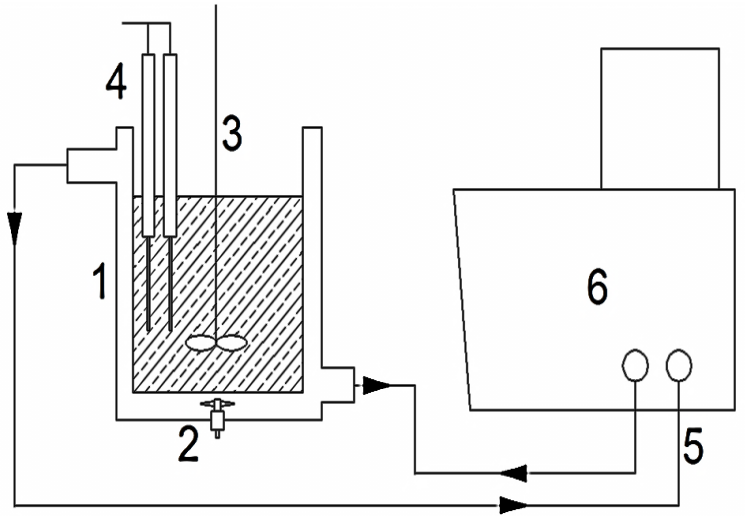
Table 2. Apparent Rate Constants

temp (°C)	catalyst concn (%)	k_1' ($L \cdot mol^{-1} \cdot min^{-1}$)	k_2' ($L \cdot mol^{-1} \cdot min^{-1}$)	k_3' ($L \cdot mol^{-1} \cdot min^{-1}$)	k_4' ($L \cdot mol^{-1} \cdot min^{-1}$)	k_5' ($L \cdot mol^{-1} \cdot min^{-1}$)	k_6' ($L \cdot mol^{-1} \cdot min^{-1}$)	sum of absolute errors
25	0.5	0.07	0.25	0.15	0.14	0.22	0.0160	0.1034
35	0.5	0.20	0.98	1.67	2.18	0.27	0.0110	0.2618

Vicente, G., Martinez, M., Aracil, J., Esteban, A., 2005. Kinetics of sunflower oil methanolysis. Ind. Eng. Chem. Res. 44, 5447-5454

Experimental Procedure

- Alcohol/oil mixture added to reactor
- Water bath set to desired temperature
- Mixture stirred for 40 minutes (typical reaction time)
- pH & temperature monitored



1. Jacket Tank Reactor
2. Reactor Tap
3. Agitator
4. pH electrode & Temperature Sensor
5. Water Pipes
6. Water Bath

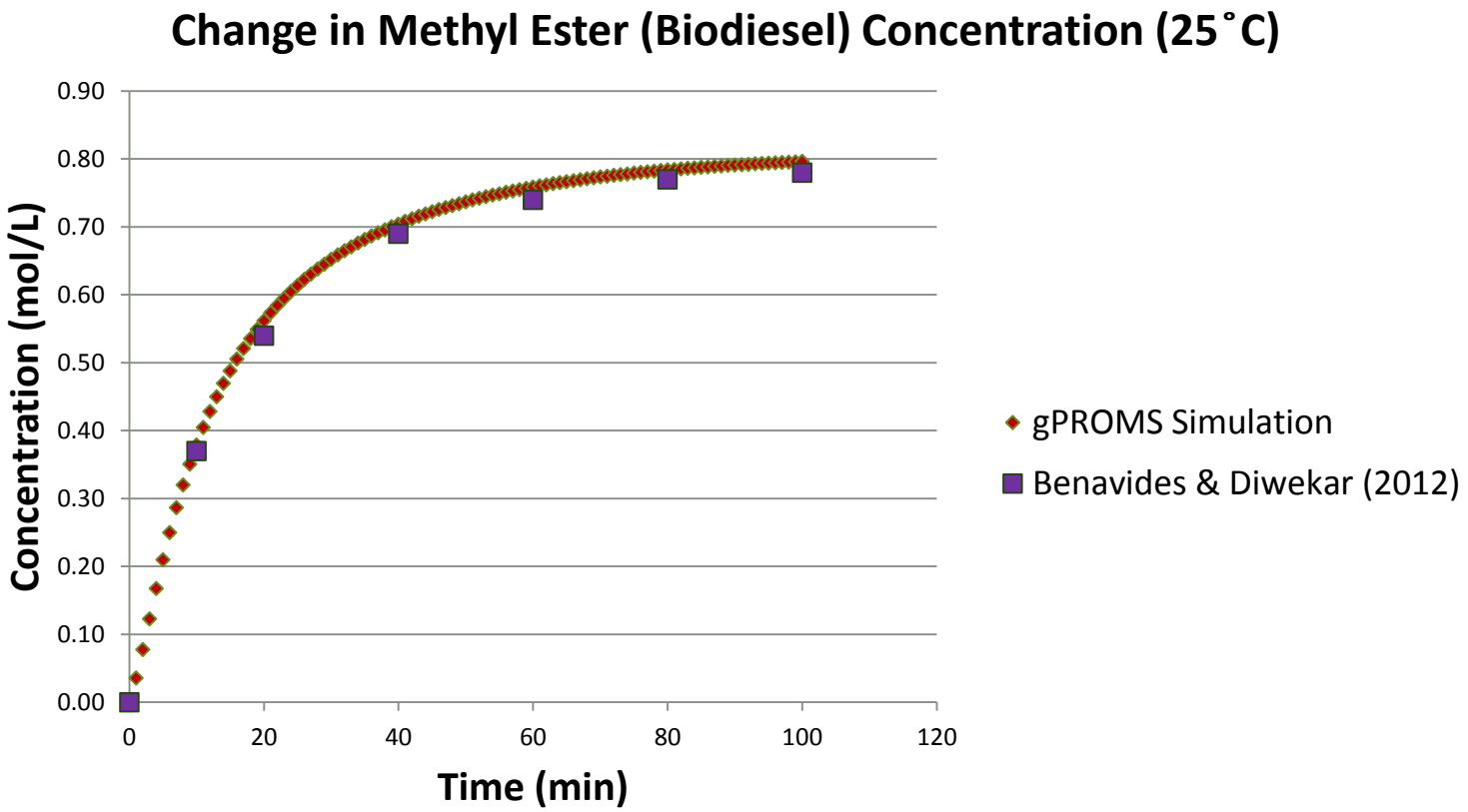
Experimental Procedure (2)

- **Ratio of Methanol to Sunflower Oil** **6:1 (molar basis)**
- **Temperature:** **25 °C and 35 °C**
- **Total Reactor Volume:** **375 mL**
- **Catalyst:** **1.35g KOH dissolved in methanol**

$$C_3H_5(RCOOH)_3 + 3CH_3OH \leftrightarrow 3RCOCH_3O + C_3H_5(OH)_3$$

Sunflower Oil Methanol Biodiesel Glycerine

Comparison of gPROMS Model Prediction

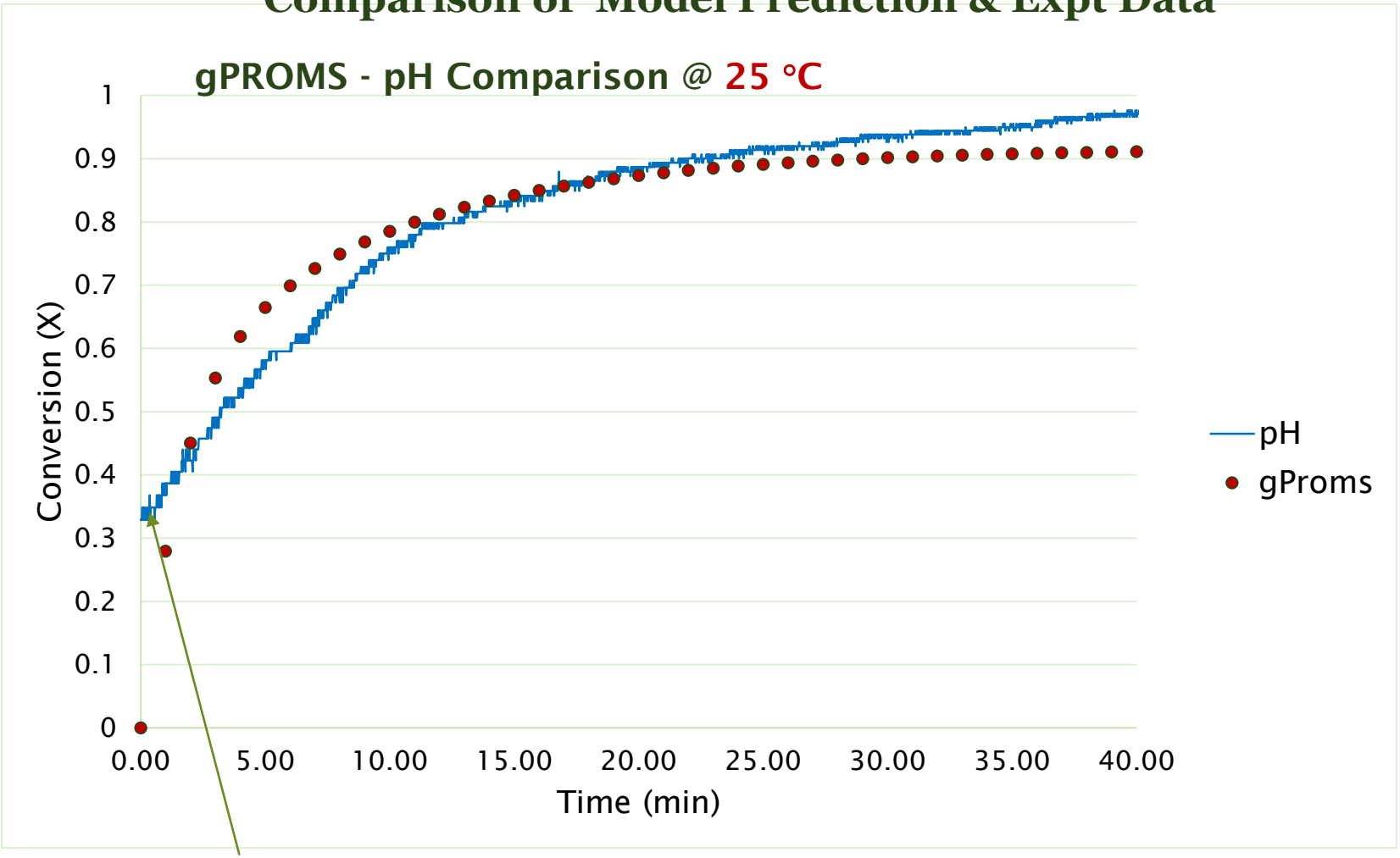


Benavides & Diwekar (2012); ODEs integrated using explicit Runge-Kutta Fehlberg (RKF) method.

Experimental Measurements
Conversion of Biodiesel From pH measurements

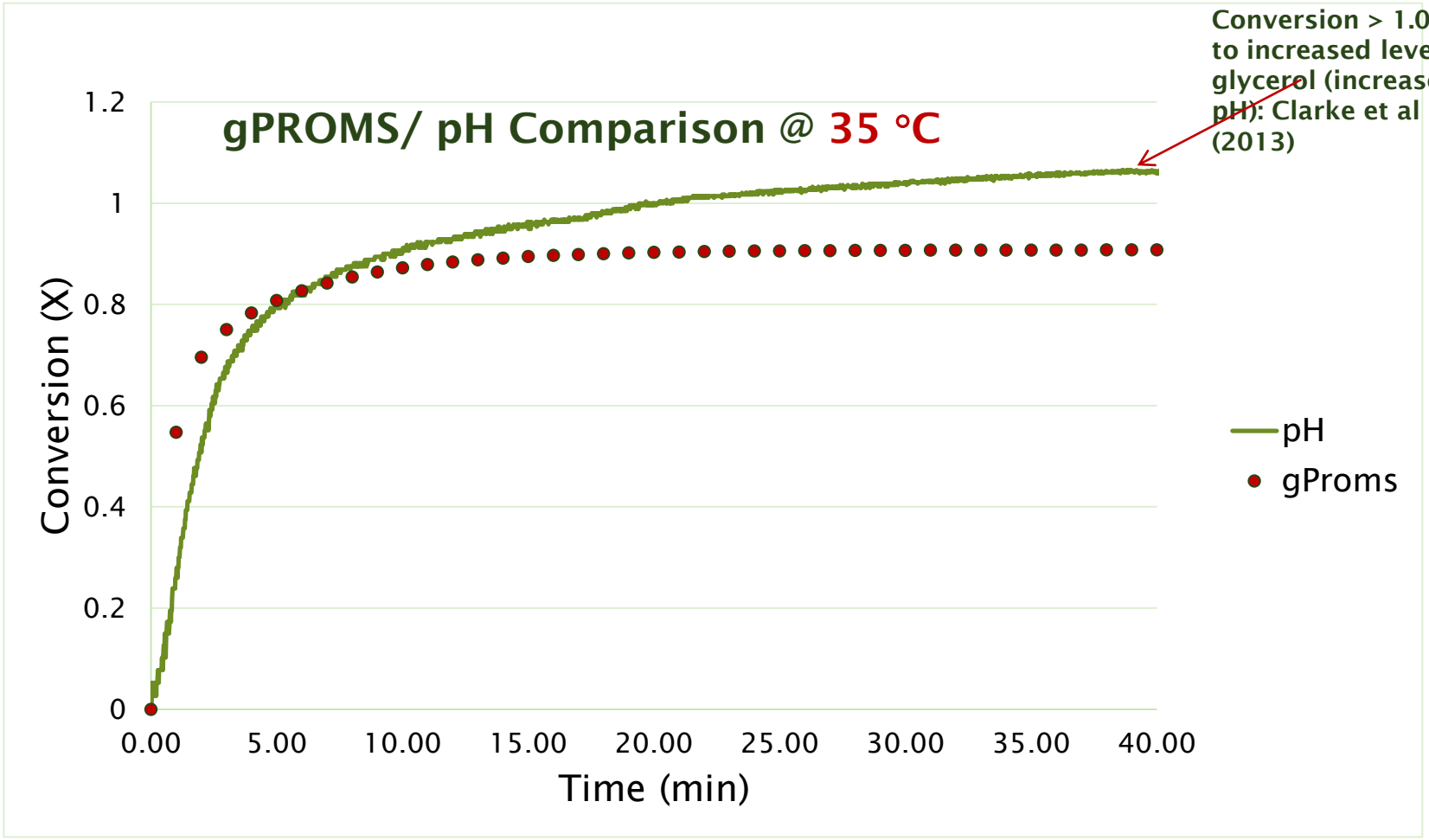
$$X_{(t)} = \frac{10^{-(14-peak\ pH)} - 10^{-(14-pH\ at\ t)}}{10^{-(14-peak\ pH)} - 10^{-(14-final\ expected\ pH)}}$$

Comparison of Model Prediction & Expt Data



Tend to get discrepancy when alcohol first added

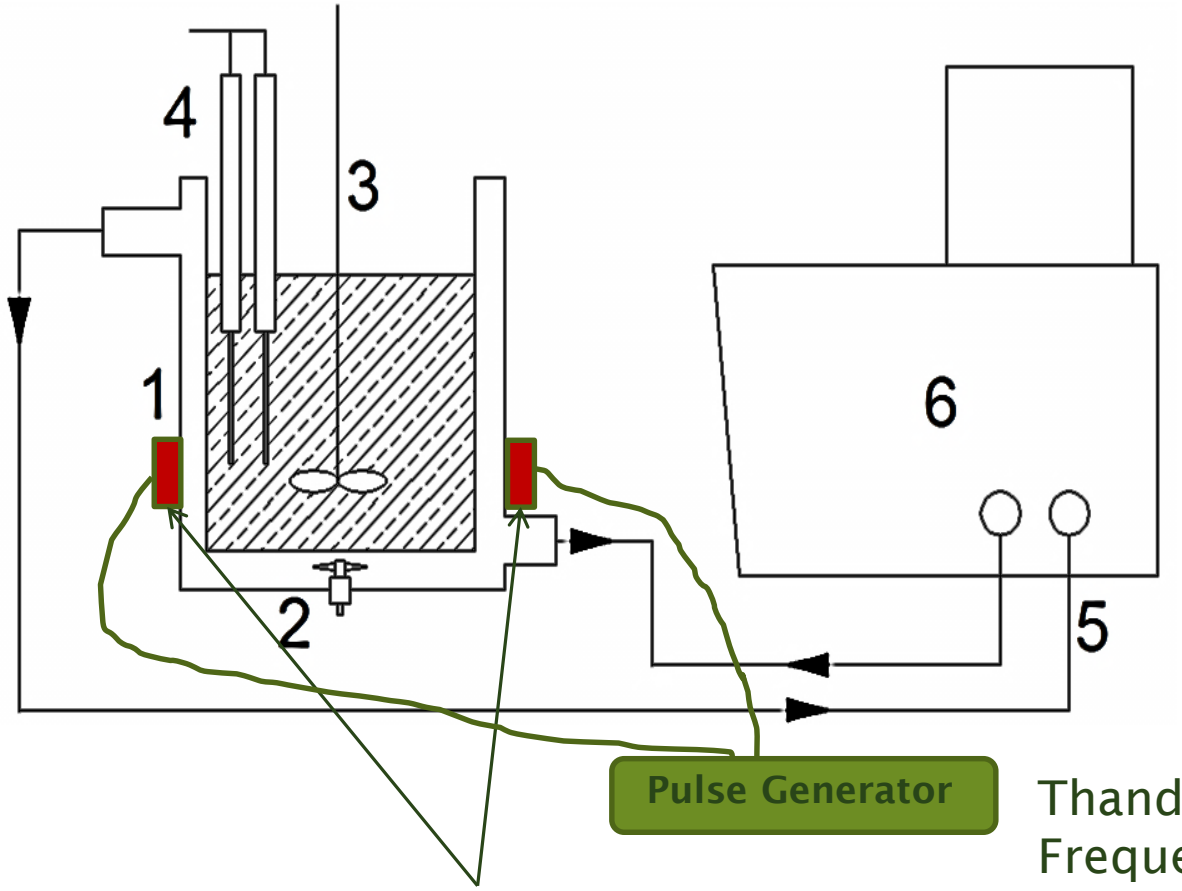
Comparison of Model Prediction & Expt Data



Using Ultrasound to Monitor Conversion

- Ultrasound can be used to monitor in-process conversion (It is a bulk measurement and therefore more representative rather than spot measurements e.g pH)
- Biodiesel has a lower viscosity than vegetable oil & WVO
- Change in velocity would indicate progress in the reaction
- Need to use appropriate frequency & pulse width

Ultrasound Set-up



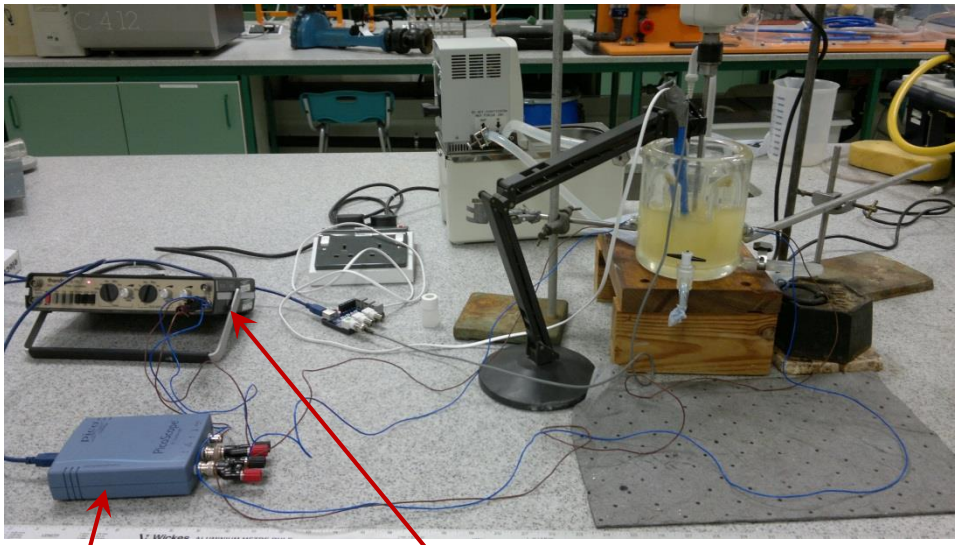
Ultrasound Probes

Type: Cylindrical
Diameter: 13mm

Data Capture: Picoscope Oscilloscope

Thandar – TG 105
Frequency : 200μs
Pulse Width: 1000 μs

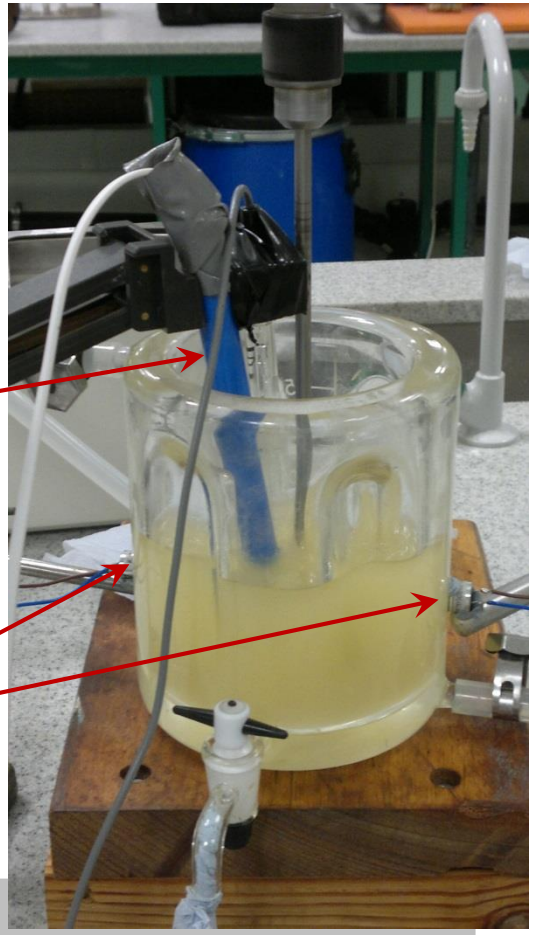
Ultrasound Set-up



Pico - Oscilloscope

Pulse Generator (Analogue)

pH Probe

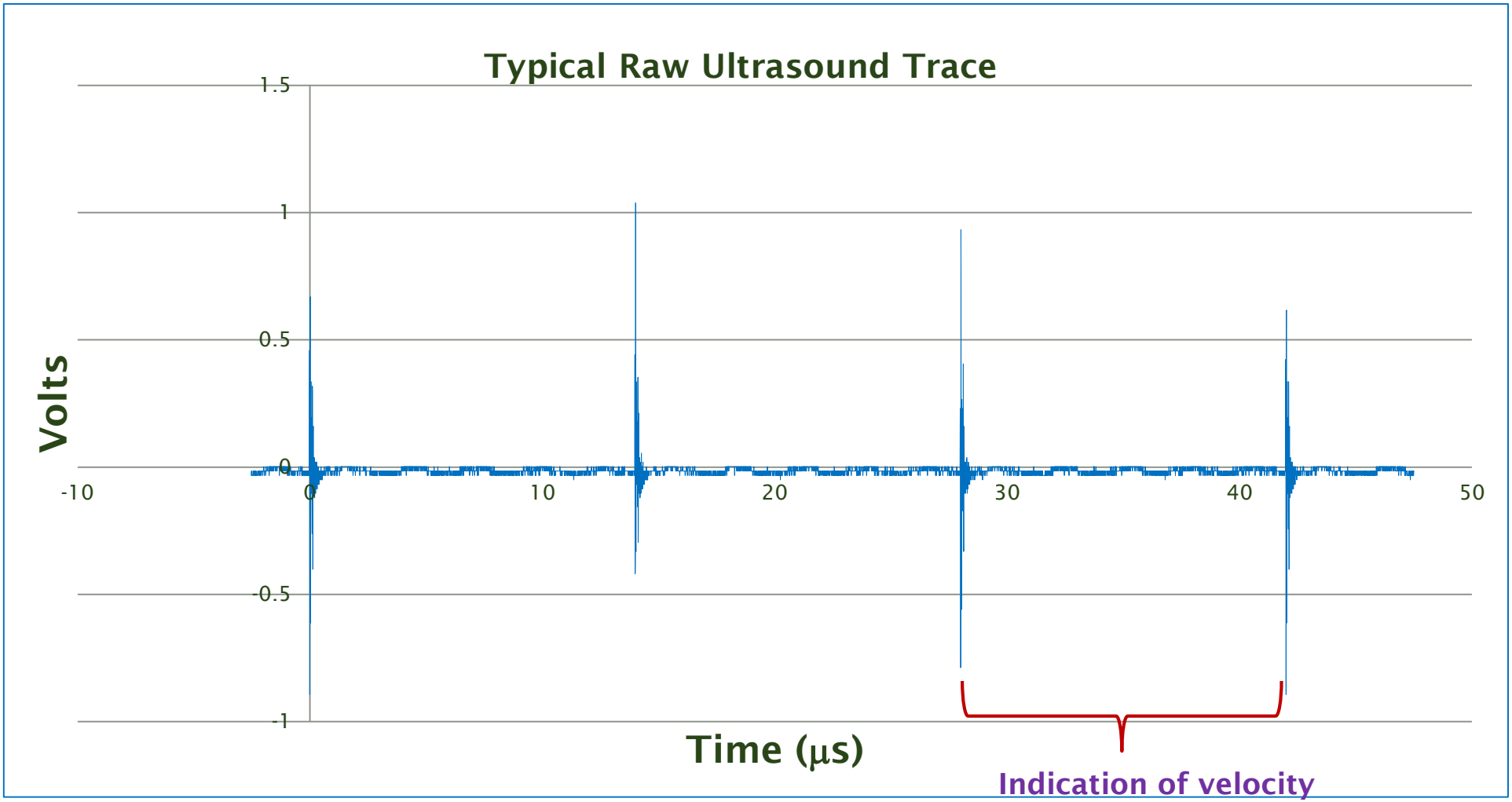


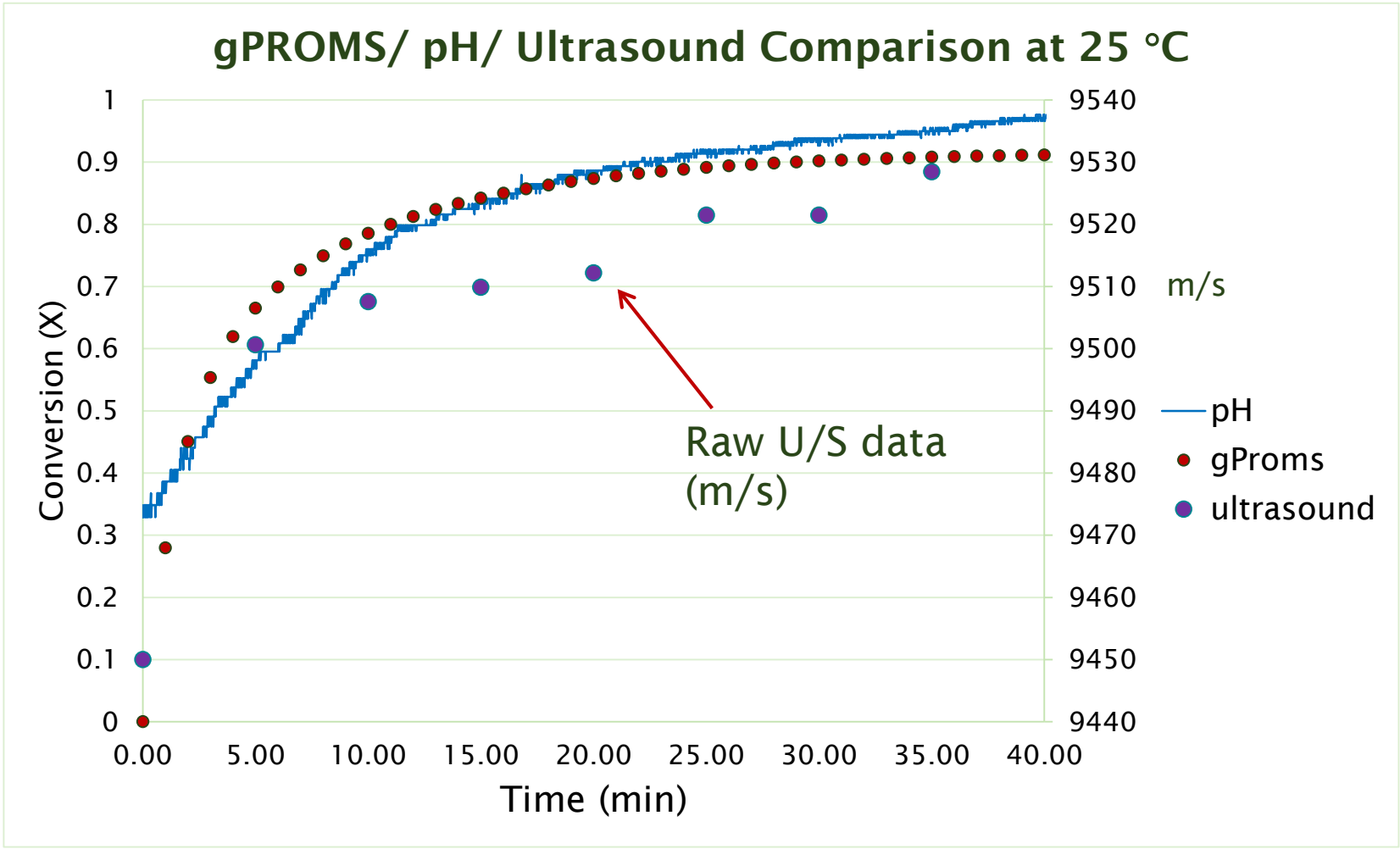
Ultrasound Probes

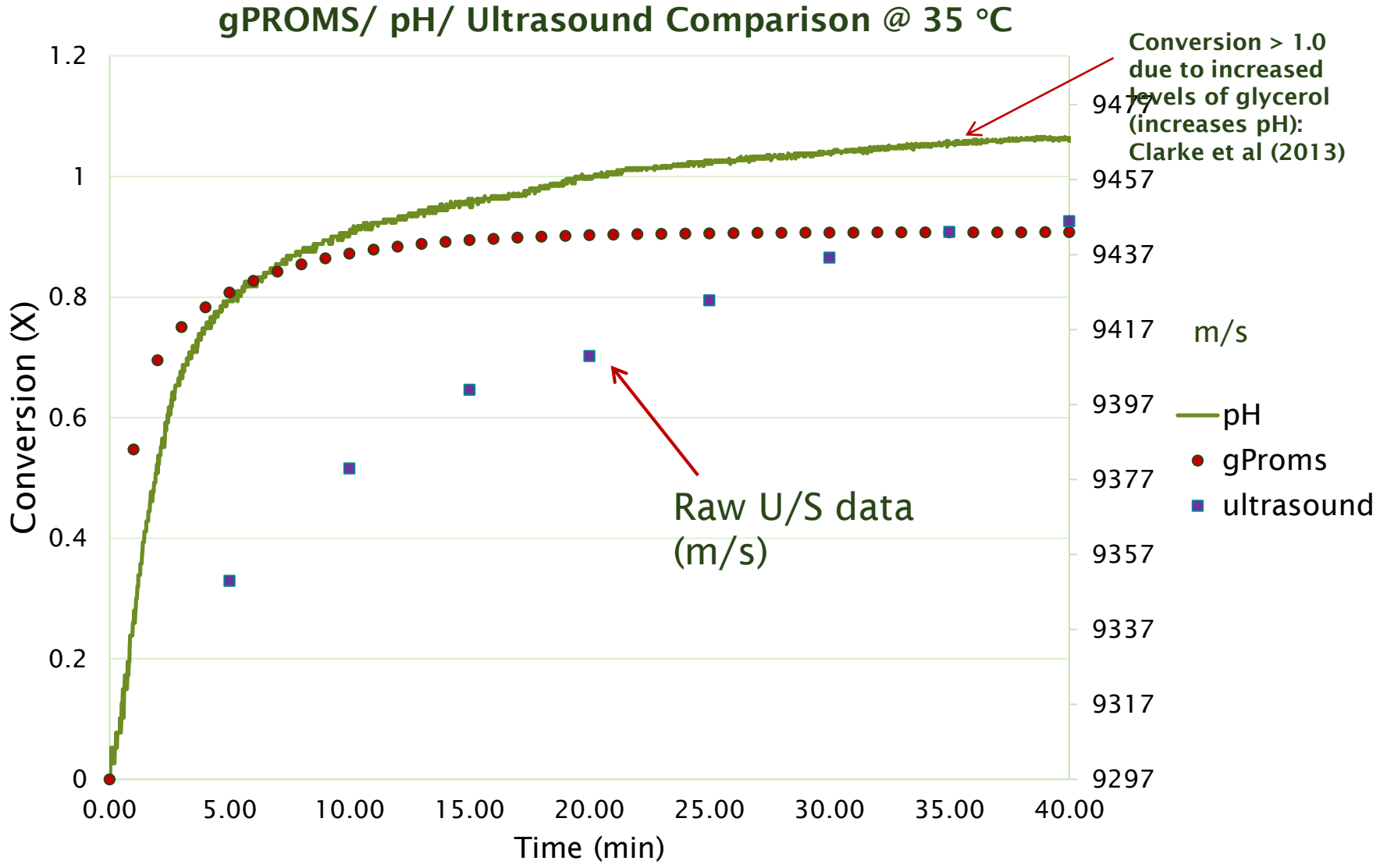
Ultrasound Issues

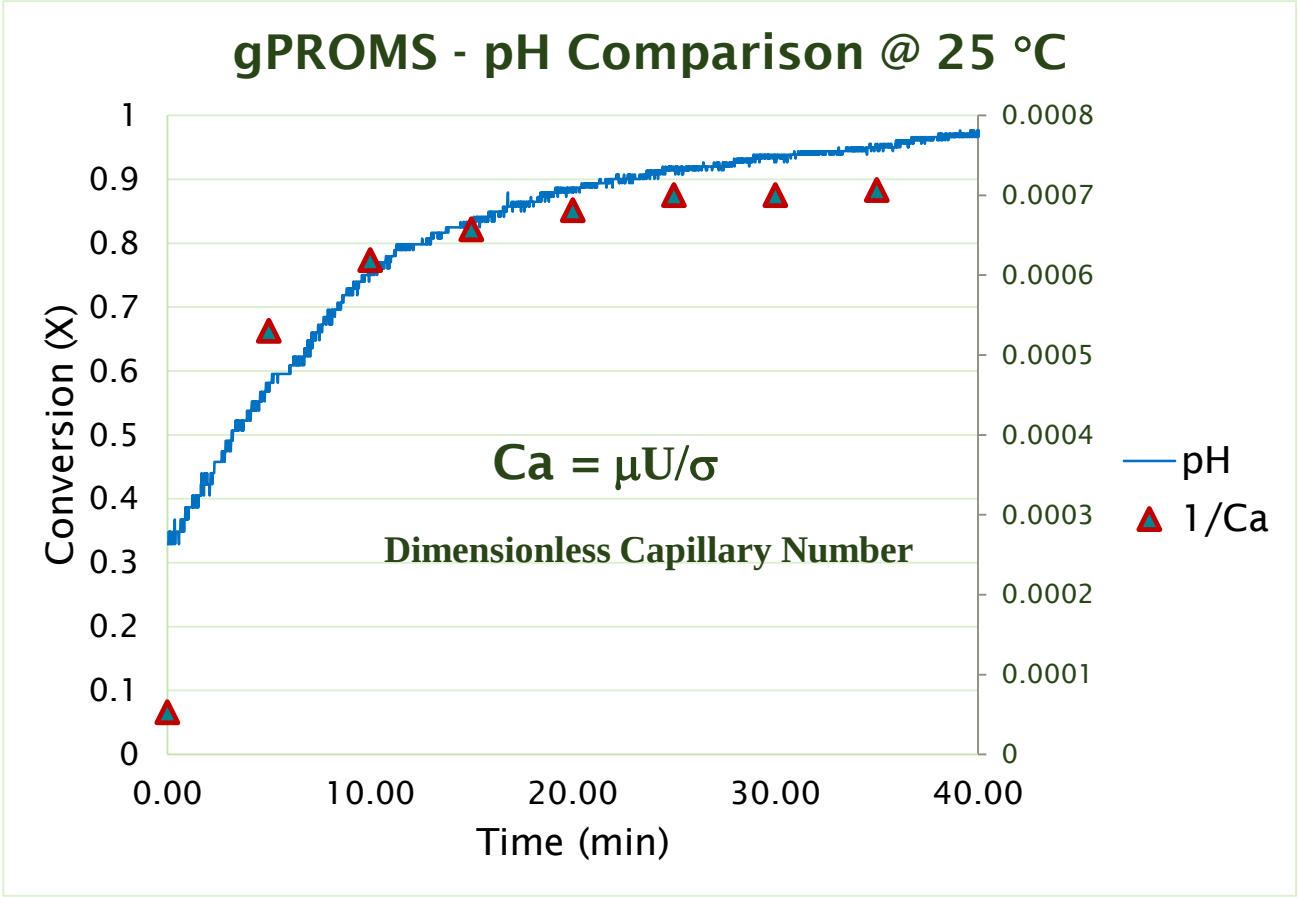
- Initially had difficulties – Ultrasound waves travelling through the base/bench giving spurious data.
- Therefore good insulation is essential
- Homing in on the frequency and pulse width – time consuming

Ultrasound Data



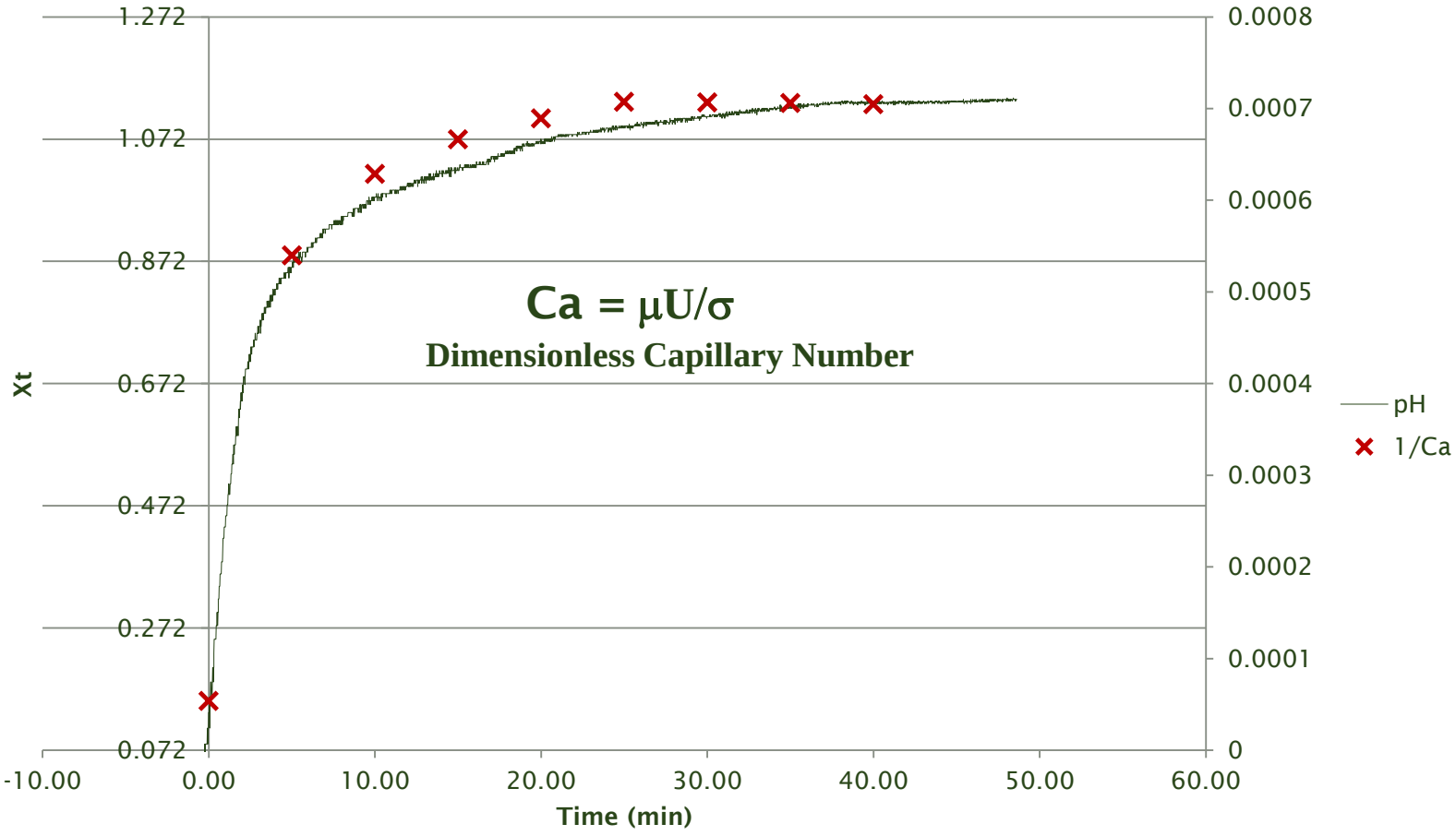

gPROMS/ pH/ Ultrasound Comparison at 25 °C
Conversion (X)
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
9540
9530
9520
9510
9500
9490
9480
9470
9460
9450
9440
m/s
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
Time (min)
Raw U/S data (m/s)
pH
gProms
ultrasound


gPROMS/ pH/ Ultrasound Comparison @ 35 °C
Conversion > 1.0 due to increased levels of glycerol (increases pH): Clarke et al (2013)
Raw U/S data (m/s)
Conversion (X)
Time (min)
m/s
pH
gProms
ultrasound
0
0.2
0.4
0.6
0.8
1
1.2
0.00
5.00
10.00
15.00
20.00
25.00
30.00
35.00
40.00
9297
9317
9337
9357
9377
9397
9417
9437
9457
9477



Naoko Ellis et al, Chemical Engineering Journal 138 (2008) 200–206

Conversion sunflower oil to biodiesel at 35 Deg C based on pH



Conclusions – Further Work

- Need to repeat trials - reproducibility
- Need to re-evaluate the rate constants for the sunflower oil
- Different ultrasound probes (larger ones – better signals)
- Digital Pulse Generator
- All factors need to be investigated (Temperature, Mole Ratios, Raw Materials)
- Scale-up with Ultrasound Measurement
- Characterisation of product (Calorific Value, Rheology etc)
- Correlation of Ultrasound data with conversion obtained from pH measurements

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- Separation of Waste at Source

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Biodiesel Production: Engineering a Greener Future

Oil to be collected from Food-on-Campus outlets, Restaurants & Take-aways, converted and returned to provide fuel for UoB vehicles and facilities. The central component of this process is the FuelPod™, an easy to use reactor.

It is important to ensure the quality of the fuel produced, with analysis performed in the UG teaching labs, where small scale production experiments are also conducted.

Thank You
&
Any Questions