Newcastle University
School of Chemical Engineering &Advanced Materials

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pig MONTHLY

process intensification group | www.pig.ncl.ac.uk | www.pinetwork.org

Introduction

Welcome to Issue #4 of the process intensification group newsletter, covering activity from April and May 2017. In addition to an update on research activity, this issue contains the second research spotlight article, covering the *Sustainable Polymers* project, and an article explaining the PIG's involvement in the *IbD (Intensified by Design)* project. As with previous issues, upcoming events are also advertised.

ISGC2017

The 4th International Symposium on Green Chemistry (ISGC) was held in La Rochelle, France, from 15-19 May. Over 700 researchers from approximately 50 countries were in attendance. A full programme consisting of 8 plenary lectures (1 hour), 17 keynote presentations (30 min), 126 oral communications (20 min), 180 flash communications (10 min) and 224 posters was presented. The main topics of the symposium were: (1) renewable carbon/valorization of waste, (2) smart use of fossil fuels, (3) polymers, (4) environmental impact and LCA, (5) mechanism study, (6) catalysis, (7) alternative solvents, (8) biotechnologies, (9) non-thermal activation methods, and (10) networking and education. The PI group was represented by five researchers: Dr Anh Phan, Dr Ana Lopez, Abdul Rehman, Mohamad Faiz Gunam Resul and Jonathan McDonough who each presented either oral or flash communications. Details of these can be found on the next page. Abstracts can also be found on the scientific programme available **here**.

In This Issue

Left to right: Abdul Rehman, Dr Anh Phan, Dr Ana Lopez, Jonathan McDonough, Mohamad Faiz Gunam Resul

Mohamad Faiz Mukhtar Gunam Resul

Green Sustainable Epoxidation of Terpenes using Continuous meso-scale Oscillatory Baffled Reactors

Part of the *Sustainable Polymers* project

Oral Communication, Wed 17th May, 09:30-09:50

Jonathan McDonough

Solvent-free synthesis of an exothermic imination reaction passively cooled in flow using a Heat Pipe Oscillatory Baffled Reactor (HPOBR)

Oral Communication, Wed 17th May, 09:30-09:50

Dr Anh Phan

Direct conversion of waste glycerol from biodiesel production into value-added products

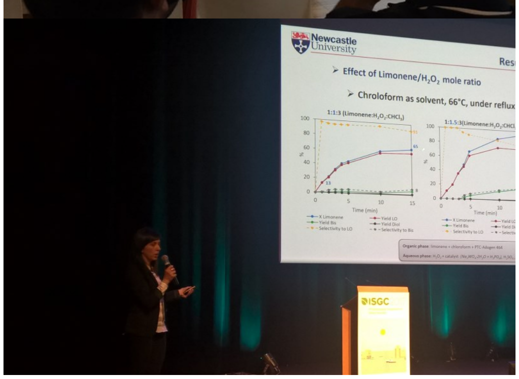
Oral Communication, Wed 17th May, 09:50-10:10

Abdul Rehman

Catalytic synthesis of cyclic carbonates from CO_2 and renewable terpene-based epoxides: Batch to Continuous

Part of the *Sustainable Polymers* project

Flash Communication, Wed 17th May, 17:10-17:20



Dr Ana Lopez

Sustainable method for terpenes epoxidation with hydrogen peroxide under conventional heating and microwave irradiation

Part of the *Sustainable Polymers* project

Flash Communication, Wed 17th May, 17:30-17:40

Upcoming Conferences

- **5th International Conference on Green Chemistry and Technology** (24-26 July 2017, Rome, Italy).
- **16th International Conference on Sustainable Energy Technologies** (17-20 July 2017, Bologna, Italy). Early Bird Registration Deadline: 9th June
- ***WCCE10+ECCE11+ECAB4+IPIC*** (1-5 Oct 2017, Barcelona, Spain). Early-Bird Registration Deadline: 30th June
- **2017 *AIChE* Annual Meeting** (Oct 29-Nov 3 2017, Minneapolis, US). Early Registration Deadline: 18th Sep
- **Global Biotechnology Congress** (10-13 July 2017, Boston, US). Abstract Submission Deadline: 10th June
- **15th UK Heat Transfer Conference** (4-5 Sep 2017, Brunel University, London). Extended Abstract Submission Deadline (2 Pages): 16 June
- **Green Materials & Technology Conference** (4-8 Feb 2017, Singapore). Abstract Submission Currently Open
- **25th International Symposium on Chemical Reaction Engineering, ISCRE25** (20-23 May 2018, Florence, Italy). Abstract Submission Deadline: October 2017
- **ChemEngDayUK2018** (27-28 March 2018, Leeds, UK). Abstract Submission Opening: September 2017

PIG News

- Marko Paavola, from the University of Oulu (Finland), will be visiting the group for the next 10 weeks working on the HORIZON 2020 IbD (Intensified by Design) project and other areas where his control and modelling expertise will be valuable. You will be able to meet Marko at the next PIG seminar or PIN meeting.
- Dr Marija Vicevic has rejoined the group working as a Teaching Fellow. This is Marija's second time working with the group, having previously worked with Kamelia on spinning disc reactors.
- The PIG would like to welcome the following new postgraduate students:
  - Akmal Bin Abdul Rahim. *Intensification of epoxidation of vegetable oil*. Supervised by Prof Harvey and Dr Phan
  - Eka Utuk. *Real time monitoring of water pollution using microbial fuel cells*. Supervised by Dr Velasquez-Orta

New Publications

- Eze, V.C., Fisher, J.C.; Phan, A.N., Harvey, A.P. Intensification of carboxylic acid esterification using a solid catalyst in a mesoscale oscillatory baffled reactor platform. Chemical Engineering Journal 322 (2017) 78-107
- McDonough, J.R., Ahmed, S.M.R., Phan, A.N., Harvey, A.P. A study of the flow structures generated by oscillating flows in a helical baffled tube. Chemical Engineering Science 171 (2017) 160-178
- Outram, V., Lalander C-A, Lee J.G.M., Davies, E.T., Harvey, A.P. Applied *in situ* product recovery in ABE fermentation. Biotechnology Progress (2017). 10.1002/btpr.2446
- Velasuez-Orta, S.B., Werner, D., Varia, J.C., Mgana, S. Microbial fuel cells for inexpensive continuous *in-situ* monitoring of groundwater quality. Water Research 117 (2017) 9-17
- Wang H., Mustaffar A., Phan A., Zivkovic V., Reay D., Law R., Boodhoo K. A review of process intensification applied to solids handling. Chemical Engineering and Processing: Process Intensification 118 (2017) 78-107 http://www.sciencedirect.com/science/article/pii/S0255270116306742
- Yang, H., Zhang, B.F., Li, R., Zheng, G., Zivkovic, V. Particle dynamics in avalanche flow of irregular sand particles in the slumping regime of a rotating drum. Powder Technology 311 (2017) 439-448
- Zhang, K., Zhang, G., Liu, X., Phan, A.N., Luo, K. A study of CO_2 decomposition to CO and O_2 by the combination of catalysis and dielectric-barrier discharges at low temperatures and ambient pressure. Ind. Eng. Chem. Res. 56(12) (2017) 3204-3216
- Zheng, Q., Russo-Abegao, F.J., Sederman, A.J., Gladden, L.F. *Operando* determination of the liquid-solid mass transfer coefficient during 1-octene hydrogenation. Chemical Engineering Science (2017). doi.org/10.1016/j.ces.2017.04.051

Upcoming PIG Seminars

- Fri 2nd June, 12:00-13:00. Ahmed Al-Hatrooshi: Marine Waste Biorefinery
- Fri 9th June, 12:00-13:00 Dr Ahmad Mustaffar
- Fri 16th June, 12:00-13:00 Faisal Saleem
- Fri 30th June, 12:00-13:00 Salihu Musa
- Fri 7h July, 12:00-13:00 Tobechi Okoroafor
- Fri 14th July, 12:00-13:00 Muayad Al-Karawi

Other Information

- Full contact details and research profiles for the PI group members can be found at the website: www.pig.ncl.ac.uk
- For enquires about collaborations or PhD study, see the website: www.pig.ncl.ac.uk
- If anyone would like to contribute any articles, or if anyone has any ideas regarding the newsletter please contact Jonathan McDonough: jonathan.mcdonough@ncl.ac.uk

CEAM PGR Conference Success

The annual CEAM postgraduate research conference took place on Friday 26th May. The conference offers the chance for students to demonstrate their research to the entire school via poster (1st year) or oral presentation (2nd and 3rd years), and prizes are awarded to the top three students in each cohort. This year, six of the prizes were awarded to students from the PI group:

- 1st Year | *Poster* | Pichaya In-Na (1st), Ibrahim Mohammed (2nd), Aumber Abbas (3rd)
- 2nd Year | *Presentation* | Luma Al-Saadi (1st) and Faisal Saleem (3rd)
- 3rd Year | *Presentation* | Abdul Rehman (3rd)

A list of all talks given by PIG members can be found on the group's website on the "**seminars and events**" page.

Recent PIG Seminars

- Dr Greg Mutch. Carbon Capture and Storage: Investigating Surface Chemistry by *in-situ* Vibrational Spectroscopy. 7th April
- Safaa Ahmed. Mass Transfer Enhancement as a Function of the OBR's Design. 21st April
- Phuet Prasertcharoensuk. Gasification of waste wood for hydrogen production. 28th April
- Luma Al-Saadi. Use of 4-Dodecylbenzenesulfonic Acid (DBSA) Catalyst on the Methanolysis of the Rapeseed oil in Meso– Integral Baffled Reactor. 5th May
- David Okot. Briquetting of waste biomass for pyrolysis. 12th May
- Abbas Umar. CO_2 mitigation using algae bio-composite. 19th May

PIN & HEXAG Annual Meetings

- The Heat EXchanger Action Group (HEXAG) meeting will be held in CEAM on Tuesday 20 June 2017
- The Process Intensification Network (PIN) meeting will be held in CEAM on the following day, Wednesday 21 June 2017
- Offers of short 'impromptu's' are still welcome. Please contact either David Reay (HEXAG) or Adam Harvey (PIN)

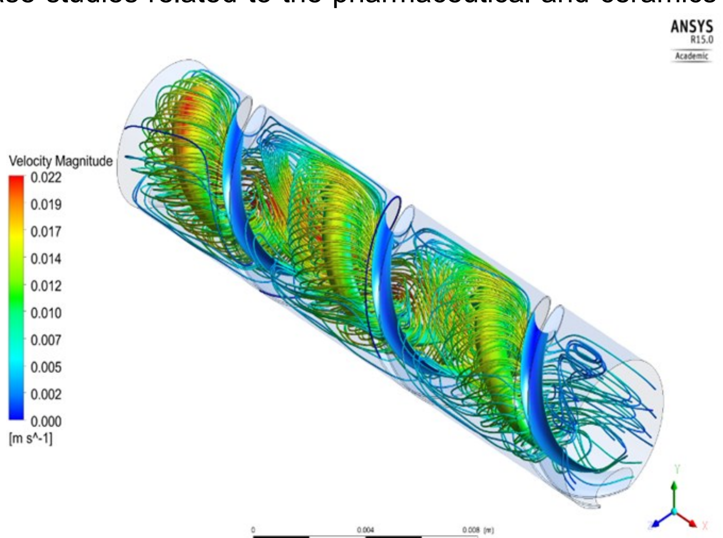
The IbD® project, awarded as part of Horizon2020 SPIRE-08-2015 call on “Solids handling for intensified process technology” (funding value €8.5M), brings together a consortium of 22 academic and industrial partners across Europe.

IbD® will create a holistic platform for facilitating process intensification in processes in which solids are an intrinsic part, the cornerstone of which will be an intensified-by-design® (IbD). The IbD approach involves the use of robust data about a process to ‘redesign’, modify, adapt and alter that process in a continuous, intensified system, and will be the new paradigm in the intensification of processes based on statistical, analytical and risk management methodologies.

The IbD Project will deliver the EU process industry with an affordable and comprehensive devices-and-processes design-platform endeavoured to facilitate process intensification (PI), which specially targets - but is not limited to - solid materials processing. Five industry case studies will be implemented in mining, ceramics, pharmaceutical, non-ferrous metals and chemicals industries to validate the IbD methodologies, tools, PI modules, control and fouling remediation strategies and the ICT Platform itself for the industrial implementation of PI in processes involving solids.

The School of Chemical Engineering and Advanced Materials, Newcastle University, is represented in this project by Dr Kamelia Boodhoo, Dr Anh Phan and Dr Vladimir Zivkovic, with a share of the total funding awarded of €638,913. The contribution of the research team at Newcastle University involves characterisation of the capabilities of existing PI modules such as spinning disc reactors and oscillatory flow reactors as well as more novel PI concepts such as the Heat Pipe Screw Dryer (HPSD), the Twin Screw Granulator (TSG), Taylor-Couette and micro-fluidic technologies for solids processing applications. These data will be combined with control and fouling remediation strategies for incorporation into the IbD Platform in order to enable a design envelop to be formulated for each technology. Collaboration with industrial partners on specific case studies related to the pharmaceutical and ceramics industries are currently underway.

Programme: Industrial Leadership: Leadership in enabling and industrial technologies - Advanced manufacturing and processing
Innovation Action – Consortium of 22 partners
Project Coordinator: Innovacio i Recerca Industrial i Sostenible SL (IRIS), Spain
Principal Investigator at Newcastle: Dr Kamelia Boodhoo, School of Chemical Engineering & Advanced Materials
Website: www.ibd-project.eu



CFD profile of flow in screw dryer (courtesy DSC-Analisis)

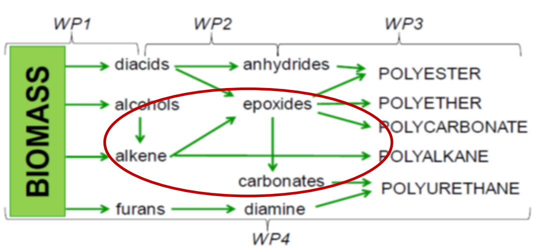
Sustainable Polymers

Dr Ana Lopez, M.F.M. Gunam Resul, Abdul Rehman, Prof Adam Harvey

Due to global concerns regarding CO_2 emissions and the depletion of petroleum based oil, it is necessary to develop environmental friendly sustainable polymers or “green materials”. Sequestering CO_2 incurs significant capital and running costs. Instead, CO_2 should be used as a chemical feedstock. Reaction of CO_2 with intermediates from terpene-derived biomass has been identified as a pathway for the production of monomers and sustainable polymers. One route for the production of these polymers is by reacting bio-based epoxides with CO_2 for the synthesis of cyclic carbonates, which can be used as intermediates in the green polymer industry. Terpenes epoxides are also useful chemical intermediates in the synthesis of fragrances and flavours. Therefore the overall aim of this project is to produce monomers and polymers from CO_2 and sustainable waste materials.

The aim of the PI group in this project is to explore novel technologies for green polymers synthesis. The main areas of investigation are flow chemistry, in mesoscale oscillatory baffled reactor (OBRs), and the application of microwaves. Microwaves are specifically being tested in two process steps: the synthesis of terpene epoxides, and the synthesis of cycles carbonates from CO_2 and terpenes-based epoxides.

The project is composed of four interconnected work packages (WP) as shown in figure 1, involving collaboration between four different research groups. Prof North’s group from the Green Chemistry department at York University and Prof Williams’ group from Oxford University are concerned with the synthesis and characterization of new monomers and polymers from waste biomass. Prof Shah´s group from Imperial College London is responsible for a life cycle assessment (LCA) of the process and Prof Harvey’s group from Newcastle University is responsible for applying process intensification to the whole system. WP4 is focused on optimizing process synthesis though the network shown in figure 1, which involves intensification and optimization of the process steps associated with the production of the intermediates. It is here where our research group play a crucial role.



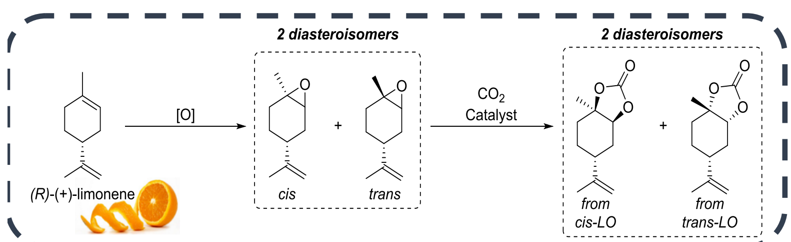


Figure 1. Work Packages

Figure 2. Limonene epoxidation and cycloaddition of CO_2

Process intensification of terpenes epoxidation

Conventional industrial epoxidation processes rely heavily on batch reactors that also use toxic oxidants. A continuous process offers advantages including better control of operating conditions, decreased reactor volume and reduced operating/capital costs. Also, microwave irradiation in chemistry is considered one of the best process intensification strategies because it enables faster reaction rates, better yield and purity, selective heating, and very rapid heat transfer rates. In the course of our research, the epoxidation of terpenes (limonene and pinene) was investigated in a laboratory scale batch reactor and continuous mesoscale-OBR (figure 3). Studies were also performed using a batch reactor under microwave irradiation, in order to compare the effect of source heating.

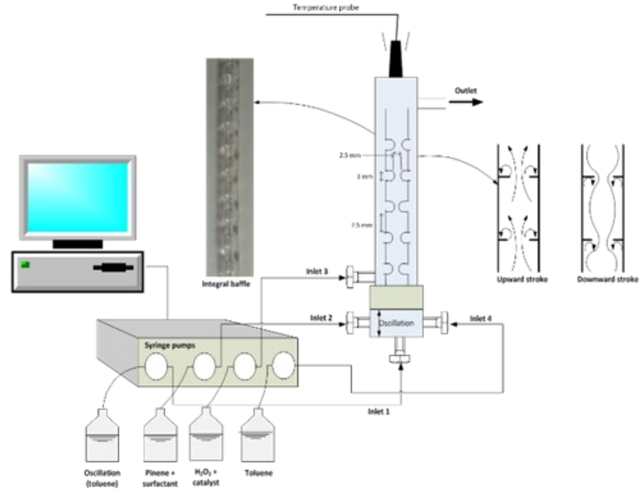


Figure 3. Mesoscale oscillatory baffled reactor platform

From batch to continuous using mesoscale-OBRs

Terpene epoxidation is conducted in an organic-aqueous biphasic system, consisting of a tungsten-based polyoxometalate catalyst, a phase transfer catalyst, an organic solvent, the inorganic salt Na_2SO_4, and H_2O_2 30% as oxidant. The main products for pinene and limonene substrates are pinene *1,2* oxide, and limonene *1,2* oxide/bis-epoxide respectively. However, terpene epoxidation is a very complex process because secondary reactions (under acid aqueous phase conditions) and the formation of by-products (such as diol) occur. The reaction pathways for the limonene epoxidation are shown in figure 4. The effect of various process parameters such as terpene/oxidant molar ratio, reaction time, temperature, type of solvent were evaluated. Experiments were first performed in batch followed by a continuous mesoscale-OBR (5 mm diameter, 30 mL volume) fitted with an integral baffled where the effect of mixing intensity and net flow rates were also investigated. Results showed that the reaction was strongly affected by the pH of the reaction and the type of solvent, with limonene in excess giving a higher yield (figure 5). Although increasing the temperature from 30 to 60 °C significantly increased the reaction rate, these higher temperatures also favoured the hydrolysis of the epoxides leading to diol formation.

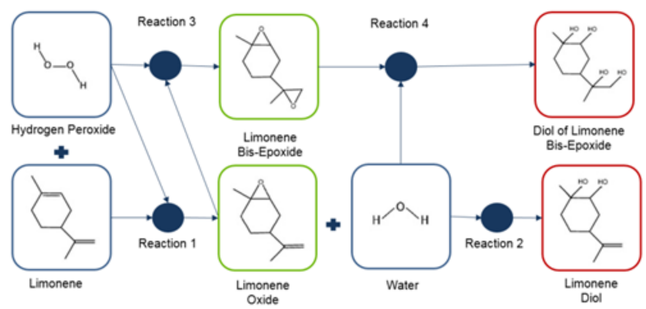


Figure 4. Reactions in the limonene epoxidation pathway

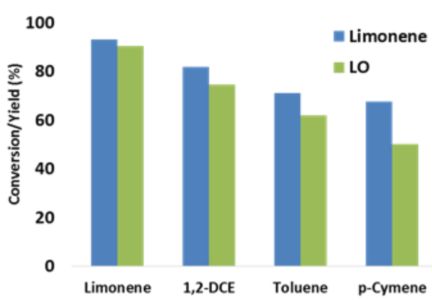


Figure 5. Effect of solvent type on limonene epoxidation in a batch reactor. 1:1:3 (limonene:H_2O_2:solvent) molar ratio, 50°C, 30 min reaction time

The continuous process showed comparable reaction conversion with the batch reactor, whilst decreasing the amount of solvent required, enhancing temperature control, reducing the exothermicity because of the higher surface-to-volume ratio, and reducing the amount of waste and energy associated with the process.

Terpenes epoxidation under microwave irradiation

Limonene epoxidation was also studied using the Sairem MiniFlow 200SS (figure 6) from York's partners. Experiments were performed in batch reactor under reflux conditions, in order to work under isothermal conditions under conventional heating (CH) and microwave (MW) irradiation. Results showed high limonene conversion, 100% selectivity to epoxides in really short reaction times, 15 minutes. A slightly increase of the oxidant amount improved the selectivity to limonene

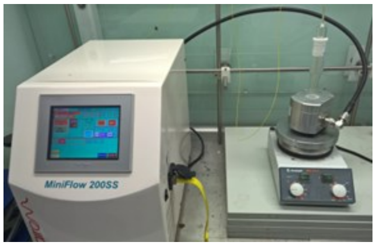


Figure 6. Sairem MiniFlow 200SS Microwave

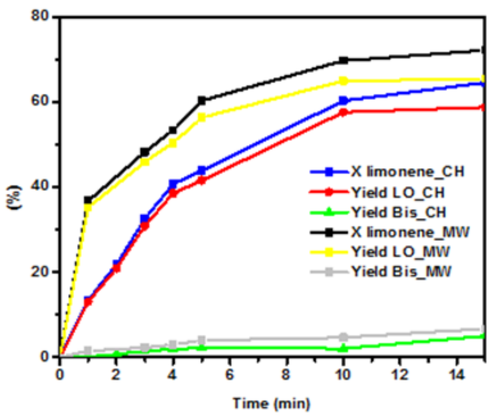


Figure 7. Experimental results for limonene epoxidation under CH and MW heating. Conditions: 1:1:3 (limonene:H_2O_2:$CHCl_3$) molar ration, 66°C, 10W,

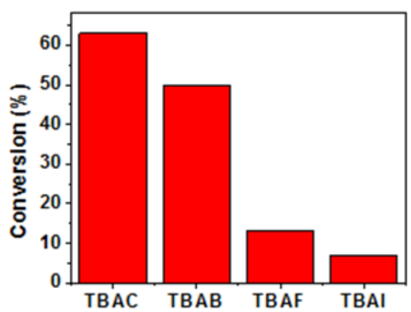


Figure 8. Limonene oxide conversion to limonene carbonate with different catalyst. Conditions: 6 mol% TBAX, 120°C, 40 bar CO_2, 7h

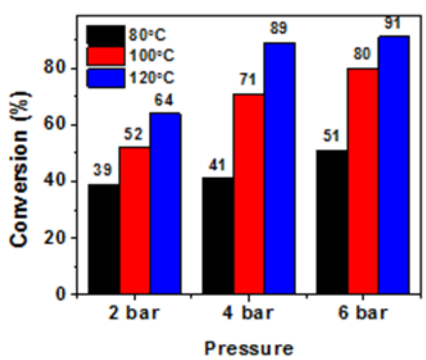


Figure 10. Effect of pressure and temperature in the synthesis of cyclic carbonates from styrene oxide in a flow reactor. Conditions: 4.5M SO, TBAB/$ZnBr_2$ 0.4/0.1, 30 min (0.075 mL/min)

bis-epoxide. The heating method did not affect the selectivity of the products. However, the initial reaction rates strongly depend on the applied heating method. 40% limonene conversion was achieved in 1 min under MW, while 13% was achieved under conventional heating.

Synthesis of cyclic carbonates from CO_2 and epoxides: batch to continuous

The synthesis of cyclic carbonates from epoxides and CO_2 is a typical gas-liquid multiphase catalytic process, involving gas-liquid mixing/mass transfer. Therefore, a highly efficient reactor in terms of good mass transfer is required. In this work, a continuous method for synthesis of cyclic carbonates by chemical fixation of CO_2 with epoxides in the presence of homogeneous catalyst is described. The initial research was performed in a batch reactor, using limonene *1,2 o*xide (LO) as the substrate. TBAC was found to be the optimal catalyst, producing >60% LO conversion (figure 8). Then cycloaddition of CO_2 using styrene oxide as a model compound was performed in a tube-in-tube gas liquid micro-reactor (figure 9). The effect of different parameters in the synthesis of carbonates were investigated: temperature, pressure, reaction time and catalyst amount. Exceptionally high CO_2 gas permeation though the membrane tubing resulted in high conversion of epoxides to cyclic carbonates. Furthermore, the high surface area to volume ratio of the micro-reactor resulted in an enhanced rate of heat and mass transfer, which significantly reduced the reaction time compared to batch reactor. An increase in temperature and pressure involved considerable enhancement of epoxide conversion, with ~90% obtained in just 30 min at 120 °C, 6 bar using TBAB/$ZnBr_2$ catalyst (figure 10).

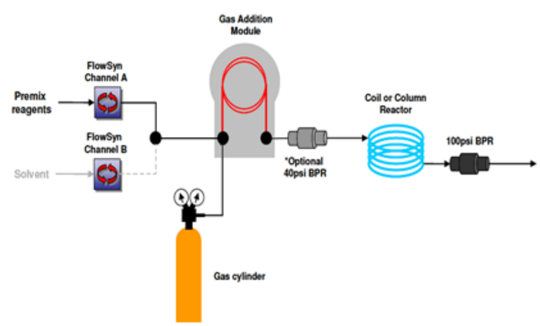


Figure 9. Flow reactor system

These results have been presented at the 5th Conference on Carbon Dioxide as Feedstock for Fuels, Chemistry and Polymers (December 2016) in Cologne, Germany by Abdul Rehman. Additionally, recent results from the project were disseminated by Dr Ana Lopez, Faiz Gunam and Abdul Rehman at ISGC2017, La Rochelle, France (May). Future results will be outlined at the forthcoming 10th WCCE.

Summary

- Limonene epoxidation performed in a continuous mesoscale-oscillatory baffled reactor produced similar conversion to an equivalent batch reactor, without by-products formation, with better control of temperature and with a reduction in solvent use.

- Limonene epoxidation was performed in a batch reactor under conventional heating and microwave irradiation. The same conversion was achieved in both systems, but the initial reaction rate was clearly enhanced by the use of microwave irradiation.

- High conversions of epoxides to cyclic carbonates by the cycloaddition of CO_2 were achieved in batch and flow reactors. However, flow reactor showed clearly enhanced rates of heat and mass transfer, which significantly reduced the reaction time compared to batch.