9^{TH} PIN MEETING

UNIVERSITY COLLEGE LONDON, 14 MAY 2003.

MEETING MINUTES

The 9th PIN meeting was hosted by the Chemical Engineering Department of UCL on 14 May 2003. The attendance was 40.

Introductory Talks

Colin Ramshaw welcome members to the meeting and then introduced Prof. Alan Jones, Head of Chemical Engineering at UCL, who was a colleague of Colin's at ICI 'some years ago'. Alan pointed out that Engineering Sciences would be housed in a new building, currently being constructed with the help of an infrastructure grant.

David Reay (DAReay@aol.com) then updated members on PIN activities since the last meeting. His presentation is available on the PIN web site, he pointed out that some sponsorship had been received for the current financial year, and the increase in meeting fees, it was hoped, would make up some of the reduction in sponsorship. (New sponsors are invited, contact David). PIN membership has expanded to 350, of which more than 50% are from industry and over 25% outside the UK.

Colin Ramshaw (Colin.Ramshaw@bun.com) briefly reported on the AIChE Spring meeting which he attended in New Orleans. There was a session on PI and keynotes on spinning disc reactors (SDRs) and catalytic plate reactors. US funding agencies would support 'step out' technologies, including PI. The AIChE is looking at a US version of PIN, and Colin said that they might end up doing their own thing, while maintaining some collaboration with us.

At the last PIN Committee meeting, Colin said that ways for influencing undergraduate (UG) courses was discussed. One idea was to identify UG experiments with an emphasis on PI. Equipment could be supplied to appropriate Departments. Industrial sponsorship would be needed, and Colin invited ideas/feedback.

Technical Presentations

Lab on a Chip and Micro-reactors: Tim Ryan of Epigem, (www.epigem.co.uk) which Tim described as a 'polymer foundry', introduced us to the lab on a chip project and the opportunities for fabricating micro-reactors. He gave us background on the LINK Foresight project which led to lab on a chip toolkits for product and process development, and described the launch of 'Fluence' micro-fluidic process systems, within a consortium involving GSK, Kodak, Newcastle University, Imperial College etc., directed at a 'synthesis demonstrator'.

This is associated with high throughput synthesis and screening, (nanolitres to millilitre fluid volumes), in a 'plug and play' system. This is based upon using a baseboard which allows interconnection of any functions one is interested in. Polymer chips (as in electronic chips) are used as system building blocks, and these have roles such as flow/pumping, reaction, analysis, separation processes etc. 'Scale out' is achieved by putting lots of reactors together – up to 1 million for large scale production. The motivation for this includes high sample throughput, parallel processing and the achievement of high yields with faster analysis. Cost reduction is also a driver – energy and reagent use is minimised, and the systems can be 'disposable', for home healthcare. Tim said that the processes could be put on something like a credit card!

Environment and health uses include portable on-site or remote sensors, safer hazardous reaction synthesis, and the opportunity to do some reactions beyond the explosion limit (because they are done at a small scale). Tim compared diffusion times against characteristic lengths, emphasising the very short times for micrometer lengths compared to those at the 'large' scale. Statistics on reactions at the micro-scale indicated that, for an alkylation, in a flask it took 6 hours and gave 28% yield, while in micro-channels it took 3 seconds and the yield was 85%.

Operational advantages of micro-reactors include the ability to carry out diffusion-limited reactions in a laminar flow regime. One can use electro-kinetic (e.g. electro-osmotic flow) and hydrodynamic pumping. Computer control and monitoring is feasible, also. The chemical advantages of the units include rapid optimisation; the ability to generate 'in situ' reagents[1], the achievement of unique thermal and concentration gradients, and the output of higher purity products.

Tim described the 'Fluence' toolkit, which has two baseboards and 50 chips, (or it can be customised). The cost is about £5k. It can accommodate 100 input/output points, and can feature tiling, stacking or racking of the chips. A range of polymers can be used for its fabrication, and heating or cooling can be included on baseboard substrates. The uses include micro-biology and micro-chemistry (liquid-liquid reactions, extractions, for example). Chip design was done at Imperial College.

The polymers used can tolerate up to 100 bar and 100^{o}C, and PEEK can be used for higher temperatures. The system can be integrated with printed circuit boards, micro-optics etc., and with surfaces having customised surface chemistry characteristics.

During discussion, questions centred on safety, manifolding, 'scale out' and in-line analyses.

Towards a Sustainable European Chemical Industry: Frank Agterberg of CEFIC Research & Science, (AGT@cefic.be) has been seconded to CEFIC for 3 years from DSM to help develop CEFIC's programmes. He started his talk by highlighting a number of factors relating to the chemicals sector in Europe, such as societal acceptance (innovative chemistry is OK, production technology raises fears and concerns). The size of the European sector is large – a good reason for keeping it here. It has two million employees and in 2001 had a sales value of Euro 519 billion, with a positive trade balance. A major question to be answered is 'how can we keep production technology here?' CEFIC has a vision and mission to assist this, and the research and science department where Frank works looks at EU policy on chemicals, climate change and energy use, and the safe distribution/transport of chemicals. The objective is to integrate research and science.

Sustainable development is the key phrase Frank used, and a paper on this can be found on www.icca-chem.org A key factor analysis is looking at drivers of importance, such as innovation and sustainable development, these being highlighted out of 38 key factors. The key aim is 'eco-efficiency'. As an example, Frank cited the 'rent a solvent' concept whereby used solvent is shipped back to the supplier – one is buying 'solvent power', not a solvent. Another example was the Mercedes A class car, which is painted 'on spec' rather than the manufacturer buying paint in bulk.

SUSTECH aims include the prioritisation of R&D programmes, and to position SUSTECH as a partner of choice for the European Commission. Within SUSTECH are cluster networks such as HyNet, which deals with hydrogen, and IMPULSE, which proposed to investigate multiscale

[1] One can overcome problems associated with unstable intermediates, e.g. for cleaning fluids. The reagents can be generated at the point of use.

process units and locally structured elements, (it was not approved as it was too vague). There is, said Frank, room for PI within this, in the physico-chemical transformations area.

Looking ahead, the EC is proposing a 'technology platform' for a for multi-stakeholder groups, in areas such as water and 'white biotechnology'. (*Frank's overheads will be available shortly on the PIN web site).*

Micro-engineered Reactors: Asterios Gavriilidis (A.Gavriilidis@ucl.ac.uk), our host, told us about his research on micro-reactors. These have features in the range of a few microns to 100's of microns. They are constructed in part using microtechnology, and micro- and precision engineering. The advantages are efficient mass transfer, good heat transfer coefficients (better than conventional vessels) and better control of the processing environment.

The UCL activities centre on design, fabrication, modelling and evaluation of the systems. The design includes consideration of the geometry and catalyst incorporation. Materials for construction are silica/glass and metals. The evaluation covers oxygen dehydrogenation reactions, epoxidation and hydrogenation, dealing respectively with gases, liquids and two-phase reactions. Some are highly exothermic, with contact times of less than 0.01 seconds. Asterios showed us the fabrication methods, and gave data on the impact of variables, such as oxygen concentration, on performance. Channel depth was interesting – smaller channel depths gave better conversion but lower selectivity.

Asterios showed work on a zeolite reactor (in conjunction with Hong Kong University), with 'T' or serpentine passage designs. The trapezoidalcross-section was achieved by KOH etching, and there were methods for growing zeolite on the surfaces of the reactor. It was used for the epoxidation of 1-pentene with 1 mm channels giving the best yield (at 28%). In order to counter catalyst deactivation, calcination was used to get rid of deposits. Stable operation was achieved for a period of a few hours. With IMM in Germany, UCL was also working on a falling film reactor. This comprised a plate with 64 channels, each 300 microns wide by 100 microns deep. The gaseous phase diffuses rapidly through the liquid falling film onto the catalyst underneath. A reaction here would be hydrogenation of nitrobenzene in ethanol over Palladium. Flow is 0.35 ml/min, 10 seconds residence time and 50 micron liquid film thickness. Asterios showed us the catalyst stability data, and ways of reactivating the catalyst.

A Taylor flow reactor was the next example shown. This comprises bubbles of gas in a liquid in a tube, and the hydrodynamics at tube entry are being examined, together with heat and mass transfer. Mechanisms controlling axial dispersion were being sought. Scale out of micro-reactors was another subject of interest. Asterios showed bifurcated and 'consecutive' structures as two options. The former gave equi-partitioning of the flows, regardless of the flow rate.

In conclusion, Asterios said that isothermal operation and efficient mass transfer were achieved, the hydrogenation environment can be precisely controlled, and catalysts of controlled thicknesses can be precisely engineered.

Micromesh Contactors for Reactions: John Shaw of CRL (jshaw@crl.co.uk and www.crl.co.uk) said that he worked mainly in the bio- side but also in two-phase reactions. CRL is part of Scipher Ltd., and John is in the area of micro-fluidics and high throughput screening. The collaborations involve CRL and IMM on device fabrication, Rhodia and Limerick University on catalyst preparation, CNRS Lyon on device operation and UCL on modelling. Also involved were BP and Strathclyde University. Systems being examined are gas-solid (not CRL), liquid-liquid (isomerisation of alcohols), gas-liquid-solid and liquid-liquid-solid. Materials used include glass/silicon for corrosion resistance (in particular in 2-phase reactions), and John said that polymers were not so good with organic solvents).

John then described the system set-up, including the range of micro-devices, which covered emulsion, slug and falling film reactors (all IMM) and mesh contactors for reactions (CRL). These are liquid-liquid and gas-liquid (g-l) devices, with solid catalysts on the wall or on the mesh. (By looking at air and ammonia with fluorescence, one could visualise what would happen in a g-l reactor). He pointed out the advantages of microchemistry at such small dimensions, where flow is laminar and transport is by migration. A critical parameter is the diffusive mixing, related to Dt/l^2 where D is diffusion coefficient, t time and l length. If this is unity, one achieved good mixing, and this determines the characteristic length l of 50-100 microns – hence the size of micro-devices! Contact times between components are relatively well defined and in micro-contactors two immiscible fluids are brought together and then separated without mixing – this is the PI part, said John. (The explanation for the ability to keep the fluids apart is based upon surface tension effects). For micro-reactors the advantage lies in high speed where diffusion would be limited in macro-systems – e.g. in a 1 mm channel diffusion takes 100 secs. (in liquid systems), while in a 50 micron channel it takes just 2 secs. A 50-100 micron channel could have a throughput of typically 1 ml/day.

John showed us a multiple assembly of micro-channel systems which could process 0.5 l/h, but said it was not cheap!

With regard to mesh devices, mesh pore size was 5-10 microns, pore length 5 microns and open area 30%. Contact times in continuous flows were a few seconds, or it could reach hours in 'stopped' flow. Nickel meshes were used a lot, and the mesh was arranged like a segment of a circle. Liquid-liquid systems were shown by CRL to work, and thus hydrolysis of esters was carried out. In g-l systems, UCL was modelling a pyrogallol reaction. *(John's talk will be on the PIN web site soon).*

Links between PI and Nanotechnology: Jeff Howarth (currently Jhowarth@NEL.uk but moving end of June to Highland & Island Enterprises) reported upon the study he is carrying out for the DTI on nanotechnology and PI. He said that this was a real prospect for funding, and for bringing the PI and 'nano' communities together. Germany has linked micro-technology and 'nano' very well, but Jeff said that the UK has not yet got the microsystems infrastructure. One of Jeff's questions was: 'Can nano technology help PI deliver what is promised?'

Jeff said that the nanotechnology programme might have £600 million over 10 years, with £80 million in the first year. Areas to be covered could include photonics, electronics, materials, genetics and micro-systems. Jeff, as part of his study, is talking to a number of PIN members and is contacting 15-20 organisations. At this PIN meeting, Jeff was looking for feedback (see WORKSHOP report below). After giving an outline of nanotechnology, Jeff illustrated its importance by stating that BASF estimated that in 2002 the world-wide nano-particle market was worth 40,000 million Euros. *(See PIN web site for Jeff's overheads, available soon)*

WORKSHOP

Jeff (JH) invited initial reactions to his talk.

Andrew Green (BHRG) kicked off by saying that the links to nanotechnology were fine, but how do we get beyond this point? It seems that the UK is not so good as Germany at microsystems, and does this imply that the micro-reactor community in the UK is not so strong either.

Nanotechnology may be a way of strengthening this. JH said that PI can be used to make nano particles, and adds a unique dimension to PI. One could include polymers. David Reay felt that micro-technology was not so weak in the UK, (e.g. RHL, and University specialised centres). Paul Langston of Heatric said that there was point of use manufacturing capability here for microreactors, but an application had not been found.

Tim Ryan said that the EC 6th Framework Programme ‘hit rate’ on nanotechnology proposals was 1 in 10, therefore lots of UK organisations were likely to be resubmitting to the DTI. Curt Koenders (Kingston Univ.) said that he had to process nano-particles. He was working with RAL, Harwell on a project involving 100 nanometre particles in fluidic devices. John Shaw said that there was still a lack of understanding on what one could do with nano-particles. He suggests talking to academics about this and this would help companies such as CRL direct what to do with the fluidics etc. around them. Therefore an awareness of the point of nano-particles is necessary. Janet Etchells (HSE) said we should think of the environmental and safety aspects, e.g. the toxicity of small particles. This should be thought through right from the start. JH pointed out that one could target reactions with complete specificity, therefore there were no by-products.

Frank Agterberg agreed with the safety side. A new SUSTECH activity in this area was possible, and there are ‘roadmaps’ in FP6. Mike Jones of Protensive said that we did not need other studies, as all the data were out there. PI has concentrated too much on processing without knowing what one is doing. Colin Ramshaw said that you did not need a nano reactor to make nano particles (e.g. polymers).

In other areas, Andrew Green said that PI has given us a better knowledge of fluid dynamic conditions at the small scale, (crystallisation, mixing, heat transfer). Other issues were the supply chain and intellectual property. He suggested selling ‘kit and chemicals’. Tim Ryan said that a continuity of calls was needed from the DTI.

Other points discussed included the role of PIN in this, and the possible formation of consortia interested in working in nanotechnology.

Impromptu Presentations

Four impromptu presentations were given in the afternoon session.

PI and Fouling Minimisation in Boilers: Stavroula Balabani of King’s College London (Stavroula.Balabani@kcl.ac.uk) discussed how active (flow oscillations) and passive (tube layout changes) measures could be used to minimise fouling deposition in lignite boilers. This project had been carried out with National Technical University, Athens and GRETh in France. Particle deposition was examined experimentally, and Stavroula showed the vortex shedding behind tubes, and measurement of the particle deposition patterns. The work led to the design of a new heat exchanger with oval tubes.

DTI PI Workshop Project: Andrew Green of BHRG (Agreen@bhrgroup.co.uk) announced DTI funding for a new project to run two workshops to raise the awareness of PI plant and to help make a ‘technology road map’. The first workshop will be a small working group to identify technical issues for PI plant, and key themes to aid business uptake. This will lead to focussed presentation for the second workshop, which will be ‘open’. The second one may be associated with a PIN meeting, and the outcome will be an agreed action plan for resolving main barriers to business uptake. *(Data from Andrew are on the PIN web site).*

Microwave Heating of Tubular Reactor: Lionel Estel of the Laboratory of Process & Chemical Risk, INSA, (Lionel.estel@insa-rouen.fr) is studying chemical process intensification, using microwaves and plasmas to enhance reactions. Showing examples where reaction temperature is controlled by surface exchange, influenced by high gradients in the boundary layer between the reactor wall and the reactants, Lionel went on to describe a continuous flow tubular microwave reactor. This could control heating of the catalyst bed, and the theoretical analysis is based on solving Maxwell's equation coupled with the heat diffusion equation. The results have been validated using i.r. thermography.

PI Issues in Thermal Metrology: Thermal metrology deals with temperature, humidity, thermophysical properties of fluids, etc., and much research in the UK is centred on NPL and NEL. As characteristic dimensions decrease and time-scales decrease, (to nano-scale and micro-seconds), such properties become increasingly important, and some of the heat/mass transfer corrrelations used at the macro-scale become inaccurate and some thermophysical properties become critical (e.g. viscosity). The needs of the PI sector can be addressed by the new Thermal Metrology programme funded by the DTI. Guidance from the PI community is needed. Contact DAReay@aol.com

Laboratory Visit

We were then shown round the micro-reactor laboratories, with several experiments being introduced to groups of PIN members by researchers at UCL.

Thanks are due to Asterios Gavriilidis and his colleagues for the organisation and hospitality.

These minutes were written by David Reay on the basis of notes prepared by him.
6 June 2003.