Process Intensification Network

14TH PIN Meeting, INEOS Exhibition Centre, Grangemouth, Scotland,

26 April 2007.

MEETING MINUTES

The 14th meeting of PIN was hosted by INEOS Manufacturing Scotland Ltd. at Grangemouth. Approximately 35 members attended, with a high proportion from industry.

Following the welcome by Gay Newman, INEOS Engineering Standards Manager, Colin Ramshaw, Chairman for the morning session, invited David Reay to updated members on the PIN activities, including recent calls for proposals that might be relevant. He also invited case studies for a book planned on PI. David's overheads are on the PIN web site.

Technical Presentations

(Note that most of the overheads from talks will be available on the PIN web site – www.pinetwork.org)

Ian Laird of NiTech Ltd. (Contact X.Ni@hw.ac.uk) started by showing a movie of the flow patterns that occur on an oscillatory baffle reactor (OBR). He than cited the installation at James Robinson as an example, where a reactor of 27m in height was reduced to 2.5m, moving from a stirred batch to an OBR. The features of an OBR, Ian said, were good mixing, dispersion and solids control. The systems can be made continuous – the COBR.

The start of the OBR story was expertise in baffled mixing, which led to PI and allowed the demonstration of business advantages, such as innovative supply chains. In the words of Ian: 'good technology is not enough, one wants….value creation'. Radial mixing with good dispersion was demonstrated.

Ian described several basic reactor types. For liquid-gas reactions, such as biopolymer fermentation, the benefits include reduced reaction time, and good gas dispersion (eg in hydrogenation processes). Liquid-liquid reactions can be aided by good mixing, eg C8 mixing in water. A key characteristic of the OBR is that it can deal effectively with solids. A range of particle sizes can also be controlled.

In terms of OBR control, continuous temperature and pH control is possible. There are challenges in crystallisation, and the COBR gives greater process condition control, leading to greater product consistency. The cooling rate can also be controlled.

Other examples of the COBR use met various process needs. In one, where improved yield was the driver, 150m^3 of a product was produced in 12 min., not 90 min. Waste reduction was another need, and in the case of energy savings a reduction in process temperature from 140^{o}C to 70^{o}C of a 100m^3 batch coincided with a process time reduction from 120 to 30 minutes.

During discussion, points were raised on the adaptability of the OBR, heat exchanger anti-fouling, and blood oxygenation (an early OBR).

Mohammed Ellob of Newcastle University PI Centre (Contact Jon Lee on j.g.m.lee@newcastle.ac.uk) introduced us to the research he is doing on steamless cracking. Mohammed started with the question: 'Does steam cracking need steam?' He then highlighted the predicted trends in the demand for olefins up to 2010. These comprise a 405% pa increase in ethylene/propylene with a production capacity growth of 5% pa for each product. The conventional cracking process has an overall furnace efficiency of 95-97%, but the firebox efficiency is around 65%. The use of steam covers three areas: the enhancement of heat transfer, the reduction in coke formation and the improvement of ethylene selectivity. The main process limitation is coke formation.

Mohammed then moved on to describe the PI aspects of his research, in particular the use of a catalytic plate reactor. As an example he showed the Velocys olefins unit (*see John Brophy papers at two previous PIN meetings*) and described the advantages of their concept. The question remains, however: 'Can it be used for cracking if coke formation occurs?'

After describing the three types of reaction that can lead to coke formation and how these might be avoided. The heterogeneous catalysis reaction was a possibility as was this type of reaction without a catalyst. Homogeneous non-catalytic reactions could have coking minimised by trying to adjust the operating condition and condensing outside the reactor. Mohammed went on to describe the objectives of his research and the benefits of the process, such as reduced amounts of contaminated water (due to lower steam needs).

The experimental set-up at Newcastle can adapt to accommodate several variables, including reactor material/coatings, the size and channel dimensions, temperatures, pressures and flows, and the run time of the reaction. With regards to results, Mohammed showed the conversions achieved at various flow rates, and the coke yield vs. flow – indicating a decease in coke rate as flow increases. Coke rate also was shown to increase with pressure. On the basis of these data he was able to determine the optimum conditions for an acceptable coking rate.

Mohammed concluded by stating that 90% conversion could be achieved in 2mm i.d. fused silica reactor channels. This is associated with reduced steam use, high olefin yield and low acetylene and C_4^+ yield. It was estimated that a run time of 2-3 weeks was possible before decoking was needed.

Questions covered the effect of pressure on ethylene yield (Ans. A pressure of 1.35 bar downstream was adequate); how the reactor is cooled; the application of catalytic combustion on the other side of the reactor, and heat fluxes. Colin Ramshaw gave data in this context on Palladium on alumina, where at 1 bar 10 kW/m^2 could be achieved, while at 10 bar a heat flux of 100 kW/m^2 was possible. He also said that as temperatures were around 800^oC, one would be operating below a significant NOx threshold.

We returned to OBRs (and other reactors) when **Denis Wray, Centre for Process Innovation, Wilton** (denis.wray@uk-cpi.com) described work in the Advanced Processing Section on comparing OBRs and stirred tank reactors (STRs). The CPI was set up in April 2004 and attempts to give the chemicals/related sectors an edge using new technology. It operates by collaborating with users etc. and makes plant available for companies to run ‘proof of concept’ experiments. Denis pointed out that it was…”easy to turn money into science, but more difficult to turn science into money!’

The COBR project was then described. Denis firstly described the key features that allowed one to go from batch to continuous operation. He then described what it is like to work with a COBR. Regarding consistency and reproducibility, he showed they were analogous to photocopiers. The STR on the other hand had no consistency of performance and if there was a hiccup it could be difficult to find where it came from. A COBR gave, for a batch hydrogenation, product purity of 99% plus over a period of 20 hours consistent output, (equivalent to 300 kg/week of product).

Cleaning of he COBR was quicker, easier and cheaper than cleaning of the equivalent STR. There are reduced problems in solvent disposal as much less is needed in the former case. Safety is superior and the control of, for example, crystallisation is better – in an STR one gets a mixture of crystal sizes, while in an OBR one can control temperature, pH etc. to get a small bandwidth of crystal sizes.

Denis said that CPI had now purchased a Spinning Disc Reactor (SDR) which was being commission at the end of April. He invited interested parties to ‘come and try it’. Also planned is a structured reactor.

During discussions, it was suggested that 5000 cP was around the current upper limit for fluid viscosities in OBRs, and the reactions were mainly exothermic. A typical COBR residence time might be8 to 12 minutes, but the batch size in this example was not known.

Zac Meadows of FujiFilm Imaging Colorants (zac.meadows@fujifilmic.com) then took us through the exercise resulting in a PI process at the local Grangemouth plant (which we were to see later in the day). The challenge was to make economically an inkjet colorant for a major customer. Production is required to be 2 tonne/a. A high cost intermediate is needed and there was no capability to make more than 100 kg. The current batch size was 5 kg, from a 200 litre vessel, while for 1 tonne a $60m^3$ vessel would be needed. This would involve high working capital, long lead time and high risk. The construction of a new batch asset would cost £millions and have a long payback period.

Thus the Company decided that it needed an alternative route.

Zac described the start of the exercise, where qualitative studies of the synthesis process were performed. This allowed the identification of PI opportunities, where one could negate side reactions, produce a better quality product and utilise a smaller plant. Then quantitative studies were needed, followed by data acquisition, including experiments. Data processing included reaction kinetics, where residence time was a key piece of information.

The design challenge in part arose because the process comprises three consecutive reactions. Intensified isolations are difficult, but post-purification is possible using nano-filtration. In order to do this one had to minimise side reactions.

The three reactors in the PI plant are: firstly a continuous stirred tank reactor (CSTR), secondly a pH-controlled tubular reactor involving static and jet mixers with a less than 10 sec. residence time and finally a CSTR with pH control. Cost-wise the PI lab scale unit cost £15,000 and can produce 2 kg/h, while the old pilot plant produced 5 kg in 2 days. Benefits of the new solution are low capital cost, reduced working capital, reduced hazardous inventory, reduced effluent and minimum scale-up risks – in fact no scale-up is needed!

Wouter Siemers of SenterNovem in The Netherlands (W.Siemers@senternovem.nl) introduced us to the Dutch PI activities, which have been stimulated by the major programme 'Energy Transition' which envisages major changes in energy supply in The Netherlands over the coming years to reduce reliance on imported energy.

Before detailing the implications of this, Wouter gave an overview of SenterNovem and the Dutch PI Network – PIN-NL. This was started in 1997 and since 2006 the funding position has been strengthened by a membership fee of 1000 Euros/a paid by large companies. There are currently 20 paying members.

With regard to the transition policy, the drivers centre around the Dutch dependence on oil imports and the need to achieve sustainable energy supplies by 2050 – e.g. via bio-based supplies. There are several 'platforms', and chain efficiency is one of these, the one in which PI is regarded as important, via reduced energy use. Arthur D Little (ADL) carried out a major study to see what impact PI could have on energy use/emissions by 2015 and 2030 and specified a number of 'enabling applications'. However, Wouter said they were still some distance from finding good PI implementation in industry.

The ADL study concentrated on four PI technologies – microreactors, HiGee types of plant, microwaves and multifunctional units. The sectors addressed included food as well as chemicals. The CO_2 savings potential was found to be very good.

The Dutch group has strong links with European activities, including the EFCI PI Working Party and EU projects. Wouter said that interactions with stakeholders were very important to make progress. The offering of a PI Quick Scan activity, whereby for 1-2 man-days of effort at a company the possibilities of PI there and the research and technology needs could be summarised, was seen as a useful way in to organisations.

Following lunch, **Philippe Caze of Corning SAS in France** (cazep@corning.com) introduced the Company's micro-reactor technology. Corning produce optical fibres, LCD screen and catalytic exhaust systems for vehicles. The latter involve a monolith with 1000 channels in which a gas-solid chemical reaction takes place. This gives the Company a deep understanding of heat and mass transfer in micro-channels. Secondly, Philippe said that Corning was a glass company – making anything involving an oxide (e.g. Zircon). The Company developed micro-structure technologies 10-15 years ago and is able to generate features in materials with mm to micrometer aspect ratios. Combining these two areas leads to the micro-reactor activity that Philippe reported upon.

The target of the development is to replace batch pharma plant with throughputs to 10 kt/a upwards with the micro-reactor technology. As well as pharma, speciality and fine chemicals are seen as markets. Corning has worked with seven companies who have provided challenging applications for their reactor. The system was launched at AChEMA in 2006.

Philippe showed the micro-structure layers, with a mass transfer layer where the reaction takes place and a heat transfer layer for heating/cooling. Sheet size is 10 x 15 cm, thickness 1-1.32 mm. Validation pressure is 20 bar and the temperature range -80 – 250^{o}C (a function of the polymeric connecting material). Shock resistance is similar to Pyrex – i.e. it can withstand an excursion from -200 to +200°C. Throughputs are typically 0.5 – 20 l/h, with a mean of 40 tonne output/a

Configurations include single and multiple injection reactors. In the latter case this can include a preheat section, followed by splitting of streams. This allows better temperature management along the flow path and decreases the potential for hot spots. Also it avoids local over-concentration of active species. Examples of uses include liquid/liquid polystyrene precipitation and liquid/gas reactions.

Describing an end-user application, Philippe was able to outline the methodology. This firstly involved getting the chemical know-how and examining rector fundamentals. This was followed by a basic engineering exercise to chemistry to heat and mass transfer needs, concluded by detailed reactor engineering. The application, in a pharma plant, involved a process dealing with 40 kg/week/reactor with raw materials costs greater than 500 Euros/kg and 99% conversion with impurities of less than 1%. The total internal volume of the reactor to carry out this duty was 70 ml.

Other uses include nitration. A modular concept is emerging, and Corning is working with Zeton in the Netherlands to bring an integrated approach to commercial production. One aspect of this is an industrial mobile multi-purpose microreactor unit that can be taken into companies.

***Impromptu* Presentations.**

There were three 'impromptus' at the meeting, covering support, space Shuttle materials and a polymer microreactor.

Bob Tucker of Zerontec (robertjtucker@zerontec.com) described a high emissivity coating that could be applied to walls (e.g. in furnaces). 'Emisshield' is obtained from Wessex Inc., a US company that has a licence from NASA, which uses the material to protect the Space Shuttle during re-entry. The emissivity is 0.93.

Bob suggested that the coating could be applied in the radiant sections of reformer furnaces, and pit onto the tube surfaces. With a high emissivity across the whole of the wavelength spectrum, it was calculated that the application would result in a 12% improvement in furnace output. The coating can be sprayed on.

Kimm Sutter of RADIKAL at Heriot-Watt University (k.sutter@hw.ac.uk) described some of the funding and collaboration opportunities that existed for SMEs in collaboration with Universities. While largely of a Scottish flavour, Kimm said that schemes within RADIKAL (the Research And Development, Innovation, Knowledge Adoption and Liaison project) could extend south. Support options included access to MSc students to carry out projects on behalf of companies, industrially-focussed PhD studies which could involve substantial industrial secondments, and support for feasibility studies. Currently RADIKAL is involved in transferring advanced engineering and innovative manufacturing expertise in three technical areas: Photonics, Digital Tools and Microsystems.

Christian Hornung of the University of Cambridge (ch376@cam.ac.uk) brought us up to date on the micro-capillary flow reactors that were described by Bart Hallmark at the last PIN meeting in Newcastle. The new variant is a micro-capillary flow disc reactor, with polymer micro-capillaries in an extrusion, having holes of 30-500 microns wrapped in a spiral format. The device will be used for flow chemistry, each disc having capillaries of 5-40 m in length, giving a hold-up of to 25 ml. Typical residence time is 250 minutes and organic liquid phase reactions are being studied.

For a kg scale reactor, Christian said that 8 discs would be used in parallel, giving 6 km of micro-channel. As an example he cited the Diels-Alder reaction, where the unit could process 4 kg/day with a 93% conversion.

Conclusions & Site Visit

At the close, thanks were expressed to INEOS for their hospitality, FujiFilm for organising the site visit, and all speakers.

The site visit to FujiFilm allowed us to compare the massive STRs with the ‘pilot’ plant using PI technology, and was an eye-opener as far as what ‘real’ PI can do.

Minutes prepared by David Reay, 2 May 2007.