15th PIN MEETING, CRANFIELD UNIVERSITY, 21 NOVEMBER 2007

MEETING MINUTES

Welcome/Introduction

Thirty five members attended the meeting, including a group of Cranfield postgraduate students. Colin Ramshaw welcomed us to Cranfield and then David Reay gave his talk on 'What's New Since the Last Meeting'. He outlined information on a new call on PI from the European Commission and also gave data on a new book on PI due out in 2008, written by David, Colin and Adam Harvey. The 'window' for the next meeting is May/June 2008, and offers to host it are invited.

This talk, together with several others given at the meeting will available on the PIN web site, www.pinetwork.org

Technical Presentations

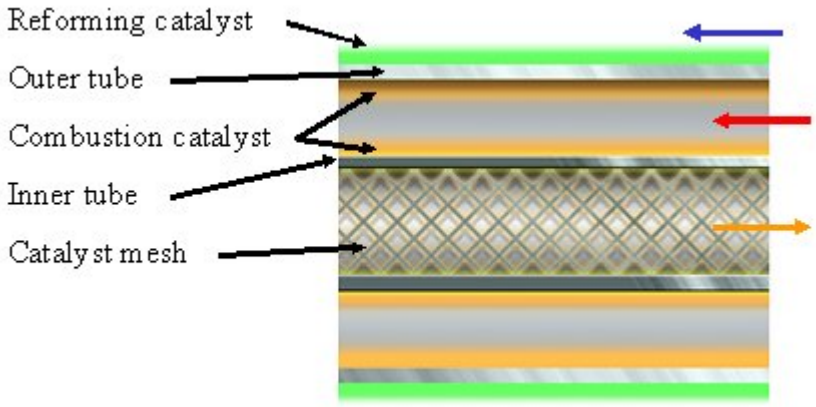
Cracking without steam: Arthur Gough, a consultant who also supervises research at Newcastle University, (Arthur.gough@waitrose.com) gave a comprehensive talk on 'cracking in the absence of steam'. This followed on from the talk on the subject at the 14th PIN meeting at Grangemouth earlier in 2007, where Mohamed Ellob introduced the concept of a much more compact cracker using ceramic tubes of 2-4 mm o.d., giving a reactor volume of 75 m^3, and a firebox volume of 300 m^3, much smaller than current fireboxes that are 8000 – 16,000 m^3. Arthur pointed out that cracking was the biggest petrochemicals process, and is used to make ethylene, propylene, butadiene and benzene, in particular. From the 1950s to today it has used copious quantities of steam, which has advantages but also several drawbacks.

Arthur pointed out that steamless cracking was probably limited to gaseous feedstocks such as ethylene, propylene, butane and light napthas. Steam is currently used because it enhances heat transfer, reduces coking (this aspect being part of the study that Mohamed had reported upon) and helps to remove coking that forms by reacting wit it to produce CO and CO_2. Steam also helps to improve the selectivity towards olefins. Steam has some disadvantages – it needs a lot of energy to generate the 100-150 tonnes/h for a typical plant, and it is not completely inert. As well as being involved in the coking reaction, it forms carboxylic acids, phenols etc., that are unwelcome, even if they are only created in the parts per million (ppm) range. If the steam is removed, there are benefits to capital investment, the environment and energy consumption. In the first case the firebox volume can be reduced fro 10,000 $m^3$to 300 m^3, and no dilutions steam system or caustic scrubber are needed. With regard to the environment, there are no problems relating to the disposal of spent caustic, such as Na_2CO_3 and NA_2S, and reduced disposal of contaminated process water (water containing phenols and organic acids). Currently waste heat recovery is practiced on crackers.

A conventional propane plant with an output of 269 t/h was described. This had a steam/propane ratio of 0.4, coil outlet temperature was 850^{o}C and the outlet gas was quenched to 340^{o}C, and the heat recovered as 80^{o}C water (100 MW) for a reboiler duty. Additionally h.p. steam is generated from the waste heat at a rate of 277 t/h, and this generates 68 MW of

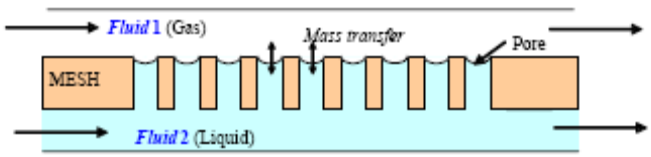
shaft power via a condensing turbine. Including the process heat recovery, the efficiency of the new conventional steam cracker would be 93-94%. Methane use was 31.4 t/h.

The new design without steam use was based upon the Protensive 'hot finger' reactor (see www.protensive.co.uk and the sketch below) in which the combustion mixture reacts with a surface catalyst to heat propane from 600 to 850^{o}C. In the reactor it is difficult to get combustion efficiency greater than 95% via the catalyst, but the 'hot finger' configuration can facilitate preheating of the incoming gas via an annular counter-current tubular recuperator. Upstream of this there would a gas turbine giving methane at 600^{o}C, and the reactor exhaust preheats the propane to 600C. However, there is in this new design no dilution steam for the quench tower, and only around 50 MW heat is available for the reboiler duty, about half that in the conventional scheme.



Summarising, Arthur said that the savings would be 2.6 t/h of methane and 1.4 t/h of methane credited as power generation, giving a total of 4-5.5 t/h of methane saved. Based upon a gas feedstock this would equate to 10% energy savings as GJ/t. If extrapolated worldwide, this would represent a saving of 9 million tonnes of CO_2 per annum. In discussions, Arthur was asked about coking. He sad that there was some on the surface but it took one hour to decoke the ceramic tube used. It was suggested that metal foam could be used to enhance heat transfer on the combustion side. However Arthur said that there could be a problem on the cracker side due to coking.

Mesh contactors as reactors: The second talk (*see the PIN web site for the overheads*) was by Asteros Gavriilidis of University College London (a.gavriilidis@ucl.ac.uk). Asterios described research on mesh contactors used as reactors for acetone stripping and hydrogenation. Particular applications would be in fine chemicals/pharmaceuticals where in the hydrogenation process for, as an example, phenyl ethanol production acetone is a byproduct and needs removing. As the acetone vapour pressure is higher it can be a little easier to remove, but one can also take out isopropanol at the same time.



Asterios showed the reactor concept, as in the figure above. A stainless steel mesh (76-100 microns pore size, 23% open area and 50 microns thickness) separates the liquid from the gas

flow and the liquid is introduced to the gas by capillary action through the mesh pores. Thereafter mass transfer talks place from the gas/liquid interface. The data presented included a comparison of modelled and measured nitrogen flow rate effects on acetone removal – showing good agreement – and a comparison between the performances of the mesh reactor and a batch reactor. The batch unit in this case was a flask with nitrogen bubbling through it at a high flow rate and the acetone removal rate was such that the concentration reduced from 0.1 mol/l to 0.075 mol/l in 30 minutes, while the mesh unit was able to strip off acetone so that 80% was removed (i.e. to less than 0.02 mol/l in only 5 minutes. It was also found that if the nitrogen was bubbled through isopropyl alcohol (IPA}the isopropanol was not stripped out, although it was pointed out that dry nitrogen was more effective at stripping acetone.

Asterios showed further data comparing batch and mesh reactors. The latter used less acetone, had a much lower residence time and a higher selectivity (by 5%). Good agreement between experiments and the reactor model, in terms of conversion prediction, was achieved. During discussion it was suggested that a polyelectrolyte membrane might be better in terms of giving positive separation between the liquid and the gas. Asterios said that this could be the case if the permeation rate could be sufficiently fast.

Asterios then highlighted an upcoming Conference, 31 August – 3 September 2008 in Belfast on Environmental Catalysis – see PIN web site (Asterios's talk) or www.centacat.qub.ac.uk/5icec

Precise processing in the food sector: Recent PIN meetings have reflected a growing interest in PI from the food sector, and Chris Wright (wright.cranfield@btinternet.com) used the phrase 'precise processing' to encompass the theme of PI as applied to his sector and described how the sector regards this concept. He said there were two areas – those involving large processes and basic foods, such as dairies, flour etc., and smaller operations where products such as sauces and purees were made. Now the centralised warehousing system impinges on distribution, and the biggest component transported is water (milk being 85% water, as an example). This offers an opportunity for smaller local units or a new concentration process.

Chris highlighted the spinning disc reactor (SDR) as being able to provide an acceptable concentrate without burning or other degradation of the product. The process could be extended to improve the taste of UHT products.

There are strong cost pressures in the sector, in/by the supermarkets and associated with energy costs and waste disposal. There is now pressure on local shops to supply local food, but this is not appropriate in all areas.-, BUT one can still have small-scale manufacture for local use.

The risks, as perceived by large processors, are quality, reliability, consistency and the employment of unproven technologies. The smaller specialists and batch producers, for example making fruit puree for yoghurts, (many purees being unique to each yoghurt) may consider precise processing. There would be benefits in fast turn-around and flexibility. For example large-scale spray drying may take 2-3 days, a small 200-300 kg unit would take hours and precise processing could be carried out in minutes. In terms of cost it might be difficult if one had to go from batch to continuous as batch production is regarded as being cheap and simple.

Chris pointed out that environmental issues were relevant to both groups (large scale and small producers). Specific factors include water use, waste raw materials and wasted chemicals. Precise processing could reduce volumes and help to recover contaminants downstream or reduce them in the first place. Chris saw significant opportunities in small batch processing, e.g. in freezing, and custard etc.

During discussion ideas floated included the merit of SDRs for custard, the increased use of microwaves. Richard Poynton saw precise processing being taken up by smaller specialist producers who are innovative.

Cracking in a gas turbine – the Turbo-cracker: Returning to the chemicals sector, Meihong Wang of Cranfield University (meihong.wang@cranfield.ac.uk) presented the concept of the Turbo-cracker for carrying out the process described earlier by Arthur Gough. Meihong started by reiterating the points made by Arthur about conventional crackers – the possibility of coke formation, the need for high heat fluxes through the tube walls and high surface temperatures, and the massive size. The idea put forward concerning the Turbo-cracker was to replace the conventional unit with a compressor and turbine. Heat is provided by compression in a gas turbine compressor, and the products of a tubular reactor outlet are expanded through the turbine section. *Meihong's overheads are on the PIN web site.*

Meihong said that the advantages of the Turbo-cracker would be higher selectivity (due to the higher temperatures achieved and the rapid expansion within the turbine) and the much reduced residence time (20-30 milliseconds). Coking should be less severe as there will be no heat transfer across a wall. A single gas turbine unit could replace several cracking furnaces.

Propane pyrolysis, based upon the Froment (1975) pilot plant data – see PIN web site for the full reference – was modelled using HYSYS and the agreement between the product composition of Froment's work and that predicted by HYSYS led to the conclusion that HYSYS could be used for the propane pyrolysis modelling.

Case studies were used to examine the criterion to achieve the same propane conversion in both systems, and to look at the effect of pressure. Cases examined included those where the conventional cracker was 95 m in length while the compressor component of the Turbo-cracker was only 2.5 m long. Other factors were scaled in proportion. Some were based upon Froment's kinetic data, but extended over a wider temperature and pressure range. For the Turbo-cracker simulation an industrial compressor of 23.3:1 pressure ratio was selected. Throughput was 84.5 kg/s air and it was 2.1 m in diameter and between 2.5 and 3 m long. The turbine part had eight stages, and was 1.5 m in diameter, 1 m long. Based upon the same feed as for Froment, it was calculated that one unit could reach 4.5 times the output of one furnace.

Challenges, according to Meihong, were uncertainties concerning the kinetics – in particular the behaviour of propane and naptha feed to the Turbo-cracker under high pressure conditions. There were also not enough data on conventional crackers, and the compressor in the Turbo-cracker unit might need more power than the turbine can deliver.

During discussion, concern was expressed about the potential for coking, as it was not only a function of the heat transfer across the wall (as in a tubular reactor). SAs the turbine exit temperature might be of the order of 350^{o}C, this would result in a lot of coke being laid down. A solution might be a 'steam only' decoke every 2-3 hours, but one would need to run with

multiple small turbines to avoid downstream disruption (as turbines were shut down for decoking).

Chemistry innovation: David Parker (david.g.parker@ntlworld.com) introduced the activities of the Chemistry Innovation Knowledge Transfer Network (CIKTN), in particular the area that he manages – manufacturing Design. The aim of the network is to induce interaction between industry and academia, and to deliver to the Technology Strategy Board the industrial needs with regard to Platform funding calls. *David's overheads are on the PIN web site.*

David said that priorities included catalysis and synthesis for fine chemicals and pharmaceuticals. There was an interest in the synthesis of tailored nano-particles and environmental catalysis. 'The Process is Key' is one theme, involving new process integration, reactions and separations using process intensification and reactive distillation and membrane separations. Target reactions for PI were amide formation avoiding poor reagents, and the reduction of amides, amongst others. More aspirational targets were the C-H activation of aromatics, 'green' fluorination methods.

Comparing interests in the sector in the USA with the UK, David included as a priority the activation of aromatics, followed by amide formation and further down the list, asymmetric hydrogenation. David looked in more detail at amide formation. He said conversion was currently 80% and this step was only one of perhaps eight to ten stages in the overall process – so selectivity is critical. There was a need for detailed mechanistic studies, and specific activities should focus on the critical aspect of water removal. Rapid heat transfer and short contact times could benefit - e.g. the spinning disc reactor. In the case of another important topic – asymmetric hydrogenation – David said that rapid reactions and rapid removal of product from the reaction zone were also needed.

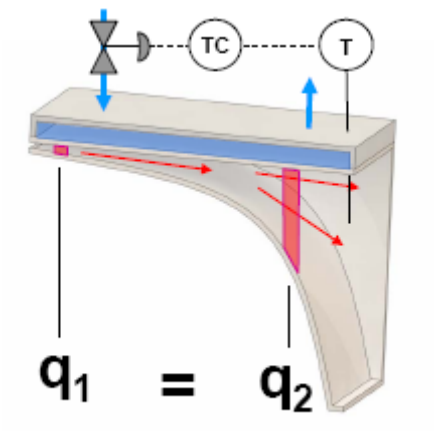
David invited comments on what would be sensible and realistic targets for the use of process intensification in fine chemical synthesis. Colin Ramshaw observed that in China Higee was already being used to manufacture nano-particles for pharmaceuticals. This involves high nucleation rates and one needs a high super-saturation, therefore rapid mixing.

Two new reactors: Robert Ashe of AsheMorris (Robert.ashe@ashemorris.com) introduced us to two new reactors – the first talk on these following the non-disclosure agreement. *(Robert's overheads are on the PIN web site).* With reaction times ranging from less than one second to more than 100 hours, one needed two solutions. The AsheMorris system allows one to run reactors of many types with a minimum number of components and simple configuration. Throughputs could be 100 g to more than 100 kg/h.

Robert outlined the criteria for reactors. They should be less than 5 m in length, have effective mixing, operate at any pressure but have a low pressure drop, and have good access for cleaning etc. For fast reaction times of 0-100 secs., one needs a fast reactor. A small channel solution is typical, but it has some disadvantages, such as pressure drop (high), potential for blockage and difficulty to access for cleaning. The solution is to give this performance but tackle the problems.

The Variable Channel Reactor: The variable channel reactor incorporates a profiled reactor channel which gets wider as the reaction progresses. The process heat load is thus constant

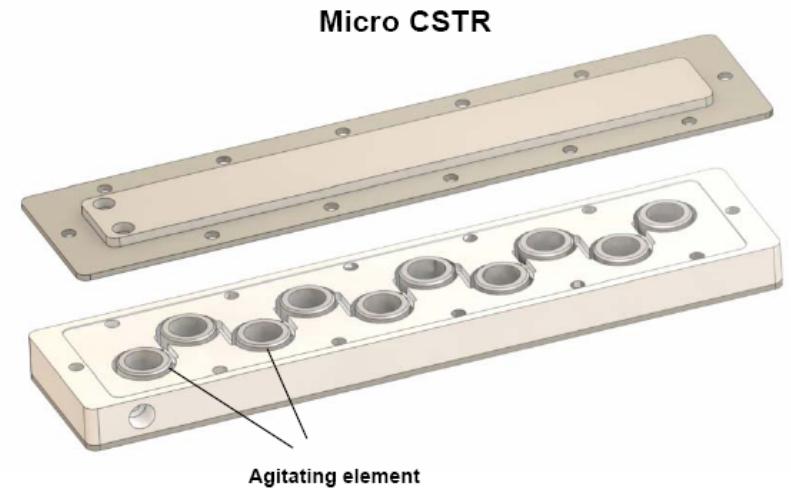
throughout the reactor, and this allows good temperature control of the whole reaction - see the figure below.



With other configurations, including the manufactured units, visible on the PIN web site, decisions needed were whether to adopt circular or rectangular channel cross-sections (the latter being chosen) and how to extend the channels while retaining a compact geometry. This was achieved by folding the flow paths like a concertina. The prototype had a channel size expanding from 0.2 mm to 2 mm.

Robert said that work was under way at Imperial College, London to compare the performance of conventional, compact and variable channel reactors – this may well be reported at the next PIN meeting. Data suggest that hot spots and cold zones have been eliminated and the pressure drop is much less. Cooling capacity was greater the 10^6 W/litre.

The Continuous Flow Stirred Tank Reactor or 'Agitated Cell Reactor' (ACR) : For slow reactions Robert said that the oscillatory baffle reactor (OBR) was one option, but he preferred the continuous flow stirred tank reactor ('batch in series'). However, the disadvantage of mounting conventions STRs in series was the high cost and complexity. So the breakthrough described here involves a block with a series of cells put into it, as shown below.



Each cell within the block has loose PTFE rings in it and a cooling plate covers all the cells. The whole assembly is mounted on an agitated platform – giving the ACR configuration. The

unit is cheap and the effect is to produce a continuous stirred tank reactor. The size of the agitation rings as one moves through the reactor can be changed to increase the cell size. Sampling and temperature measurements can be incorporated on each plate.

Robert concluded by describing the latest variants of his variable area concept, described at an earlier PIN meeting. Appropriate to controlling the throughput in large CSTRs and loop reactors, the use of multiple element jackets on STRs for example can allow one to vary the surface area for heat transfer, once the heat load is known. One can do very accurate heat balances on large reactors.

BioDiesel – Environmentally-friendly fuel: Richard Jackson of BHR Biofuels Ltd. (rjackson@bhrgroup.co.uk) introduced a relatively new activity within BHR Group, the development of bioDiesel manufacturing plant using PI technology. After giving the background on BHR and highlighting reasons for making bioDiesel (reduced viscosity, a tax rebate, the reduction of harmful acid species, better cold pour point and clouding issues), Richard said that the starting point is vegetable oil which is made of triglycerides. Continuing a brief description of the chemistry involved, Richard said that this was a natural product and was not clean in processing. The process is an ester – ester conversion and there is not a lot of heat involved in it. The target is 96.5% ester content, which is difficult to achieve because of some impurities in the feed, for example fish oils. The presence of water also causes soap formation and any free fatty acids increase the catalyst needs.

With regard to the physics, Richard said that a large scale adiabatic reactor was used with high mass transfer and near plug flow. Temperature is around 100^{o}C and the residence time can be seconds to a few minutes. The reactor pressure should be sufficient to suppress methanol boiling at the desired temperature. Challenges are associated with the mixing duty and the fact that operation is currently mainly batch mode.

The experimental work started with a small batch reactor and then moved to the BHR Flex-reactor, where temperatures were 70-150^{o}C and residence times 1-10 minutes. Trials were used to optimise operating characteristics with production of bioDiesel at 1 tonne/day. Scale up has now reached 75 tonnes/day and the target fuel specification was achieved first time. The plant can actually process 92 tonnes/day, 20% higher than the design value. BHR Biofuels is now working on a 150 tonne/day unit.

***Impromptu* Presentations**

There were 5 *impromptu* presentations.

Colin Ramshaw (colinramshaw@dsl.pipex.com) commenced the session with a description of his concept of rotating water electrolysis. Colin has just been awarded an EPSRC grant to look into this At Cranfield, and the concept is based upon the exploitation of the sensitivity of multi-phase systems to applied accelerations. Derived from work at ICI on rotating chlor-alk. cells operating at hundreds o ‘g’, the current work is directed at hydrogen production for fuel cells.

David Reay (DAReay@aol.com) discussed the different approaches to the impact of PI on energy efficiency and CO_2 reductions taken in the UK and on the Continent (in particular in The Netherlands). Arthur D Little has produced a major report highlighting opportunities for four key PI technologies in the chemicals and food sectors, in support of continental

organisations, but studies (also by ADL) for the UK Carbon Trust have led to the downgrading of PI as a potential carbon-reduction technology from one deserving high priority to a minimum position of warranting reviews 'to periodically reassess whether support is needed'. he concluded by saying that global warming will hopefully focus the minds of the funding bodies in the UK and open their pockets. *(See PIN web site for David's overheads).*

Richard Poynton (rp@richardpoynton.com) updated us on the work he reported upon at the Newcastle PIN meeting (13th) on progress in interesting the food sector in PI. Richard said that the sector was not used to analysing/optimising processes as in the past it had not been necessary. What is needed is a step change in design and processing, and this will need change at the business level. The CARBON agenda is a business problem, not a technical problem.

Richard said that he was trying to build a special interest group for like-minded people in the sector, and to bring in technical expertise from PIN members and others.

John Burns (john.burns@prosonix.co.uk) reported on attempts to use ultrasound in chemical processes. Areas of interest include pharmaceuticals where particle size control is important. Ultrasound is 'injected' into material via a probe, but one drawback of the process is that the probe is destroyed over time, and metal can be shed into the process. Probe overheating can also occur. However, the company has several successful ultrasound processes on the market – including Prosonitron reactors for carrying our duties such as sonocrystallisation, sonoprocessing and sonochemistry. The equipment at plant scale has been successfully used in alumina processing. One can achieve intense cavitation at the centre of the flow field with a low W/cm^2input without damaging the product. *(John's overheads are on the PIN web site, although we had problems showing them at the PIN meeting).*

Finally, **Matthew Tidmarsh** (Matthew.tidmarsh@ciktn.co.uk) introduced us to activities within the Manufacturing Design section of Chemistry Innovation. £42 million is the value of projects funded within the CIKTN of which £2 million is in Matthew's group. The target areas within manufacturing design are product efficacy and achieving the correct yield and maximising profits. The group studies new technologies that are available with a view to identifying where they can be used. Whole process design activities link with Britest, and facilities and infrastructure work is at CPI, Wilton. *(Matthew's overheads are on the PIN web site).*

Following thanks, many PIN members visited the bio-Diesel facility of BHR Biofuels.

Minutes prepared by David Reay from notes – 9 December 2007.