news letter
GREEN CHEMISTRY DOWNUNDER

Centre for Green Chemistry *Issue 3 - April, 2001*

From the Director

Professor W. Roy Jackson, Director
Centre for Green Chemistry, Monash University

The great news from the Centre is that our builders did a fantastic job and completed their work on time. We took possession of the new facility on 2nd April and are delighted with the quality of the workmanship. It appears that our planning sessions and Elizabeth Jeffreys' good liaison with the university building officers, Bruce Dunlevie and Jack Izowski made sure that all major and most minor problems were dealt with as building progressed with a minimum of fuss. All of us in the Centre thank the Monash Building Staff and the builders for doing such a good job.

The changes in the Centre's administration forced on us by Colin Raston's departure have taken place and Chris Strauss and Janet Scott have become co deputy directors. Chris has moved across from CSIRO and can now be found in my old office (Room 163, Building 23, telephone number +61 3 9905 9630). He is taking a special interest in extending our interactions with industry and together with Jens Mohr, a member of our Advisory Committee and a former head of Hoechst Australia, is arranging a series of visits to targeted companies in the Melbourne area. Janet is taking a special interest in educational matters as well as coping with an expanding research group, together with teaching and administrative duties. She has obtained a large grant from Monash University's Strategic Innovations Fund to facilitate the preparation of modules, which will be used as part of a postgraduate diploma.

The year 2001 has seen the commencement of 15 new projects boosted by the use of unspent funds from the Centre's initial year and the termination of two projects. A project review committee consisting of Dr Geoff Knights, Dr Mark Schapper and the Director is critically examining the extent of progress in each project. Additional input to this committee comes from our two academic members of the advisory committee, Professors Martin Banwell (ANU) and John Warner (University of Massachusetts) who evaluated all of the proposals.

The list of new projects contains three that involve cooperation with Professor Milton Hearn, Dr Steve Bottomley and Dr Robert Pike, members of the Department Biochemistry and Molecular Biology. These projects represent our initial attempts to introduce a strong biotechnological element into the research profile of the Centre. Most of these new projects have already commenced and the Centre now has twenty two postgraduate students and seven postdoctoral research fellows. Eighteen members of Monash academic staff in Science, two in Medicine and one in Engineering together with four CSIRO personnel and staff in the Universities of Newcastle, NSW; Leeds, U.K. and Ruhr, Germany are involved. Not surprisingly the new laboratory will be completely full in a couple of month's time and already twelve of the thirteen benches are occupied.

Projects involving collaboration with industry are slowly increasing. Patrick Perlmutter and myself, together with Chris Such and Algi Seralis have been successful in obtaining support from the Orica Strategic Research Fund. Orica has committed $240K over three years to support research on *"New organometallic catalysts for environmentally benign polymerisation processes"*. Chris Strauss is optimistic, after discussions with an overseas company, that significant support for a microwave based project will eventuate. The benefits of talking to industry and community groups are exemplified by Janet Scott's presentation to PACIA and the SET Futures workshop. This resulted in a representative of a large company asking us to submit proposals based on our expertise in two areas. This is about to occur.

Our educational outreach program has been a little delayed by the late withdrawal of an exceptionally qualified candidate. We continue to search for a suitable person to fill this role. As stated above, Janet Scott is busy writing modules for postgraduate diploma courses and together with Leone Spiccia and Tony Patti is collaborating with members of the Chemical Teachers Association in producing a manual of Green Chemistry experiments for schools.

Finally, the Grand Official Opening. This will take place on Monday 9th July. The Hon. Kay Patterson, Senator for Victoria, will carry out the official opening. There will be a Seminar from 2.30 to 4.30 in the afternoon in which highlights of some of our projects will be described.

2001 New Projects:

- Humic Substances, Al & Fe: Effects on "Plant Available" P & Fertiliser Formulation Implications [A. Patti & W.R. Jackson]
- Medicinal Chemistry in Green Reaction Media [A. McCluskey & J.L. Scott]
- Chemical Reactions in Salt Water Containing Clathrated CO_2 and/or CH_4 [C.R. Strauss & J.L. Scott]
- Thermolysis and Aquathermolysis of Carbohydrates under Microwave Heating [C.R. Strauss]
- Bioconversion of Coal/Biomass to Humic Material, Clean Fuel & Other Chemical Products [A. Chaffee & A. Patti]
- Non-Addictive Opiod Analgesics [W.R. Jackson]
- Greening Bismuth Chemistry and Compounds [P. Andrews, G.B. Deacon, W.R. Jackson]
- Biotechnology in Green Chemistry [M. Hearn]
- Novel Supported Catalyst Systems [C.R. Strauss & J.L. Scott]
- A Benign Approach to New Schiff Base Ligands: Synthesis, Structure, Applications [J.L. Scott & B.A. Roberts]
- Green Corrosion Inhibitors for Coating Applications [G.B. Deacon & M. Forsyth]
- Engineering Biological Catalysts [V.McCarl, P.Duggan, S.Bottomley]
- Tailored Carbons for Hydrogen Storage [A. Chaffee]
- Synthesis of Cyclic-α and β-Amino acids Involving Enantioselective Hydrogenations in s.c. CO_2 [A. Robinson, W.R. Jackson]
- Green Approaches to Anticoagulants [P. Duggan, S. Bottomley, R. Pike]

RESEARCH ACTIVITIES

"Green" Chemistry with Microwaves

An increase of 10°C in reaction temperature can lead to a halving of the requisite reaction time. If a reaction taking 16 hours at 100°C could be performed at 200°C, the time expected would be about 1 minute *i.e.* in the order of 2^{10} faster! Thus, higher temperatures than normal offer opportunities for efficiencies in time and energy. If reaction mixtures are sufficiently mobile, it should be possible to transform lengthy batch processes into continuous operations merely by changing the reaction temperature.

For reaction temperatures of 200°C or above at atmospheric pressure, the choice of solvents is limited and high-boiling solvents are inconvenient to remove and to repurify. These disadvantages can be avoided by heating low-boiling solvents (including water) in closed systems. Increases in boiling points of many commonly used solvents are significant with modest rises in pressure and at 2-3 MPa, relatively high temperatures can be attained safely for a variety of solvents. Such conditions cannot be obtained readily with typical glassware. The continuous microwave reactor (CMR) was the first microwave system designed for reactions in organic solvents at high temperature and under pressure. A commercially available embodiment that can operate at 220°C and 3 MPa, has a volume of 120 ml within the microwave zone, 80 ml within the cooling zone and a pump that can produce flow rates up to 100 ml/min. Residence times in the microwave zone (which for convenience, are also defined as reaction times) are typically 2-10 min.

A complementary laboratory-scale microwave batch reactor (MBR) is available within The Centre. With a capacity of 25-200 ml, it is capable of operation at up to 260°C and 10 MPa.

Priorities for safety and the environment, as well as economy of operation, emphasize needs for decreased usage of many organic solvents in laboratories and in industrial processes. Accordingly, water has been intensively investigated as a medium for organic reactions. At ambient T & P, water is a poor solvent for most organic compounds, but its ionic product increases one thousand-fold between 25°C and 240°C, so it becomes a stronger acid and base. The dielectric constant decreases from 78 at 25°C to 20 at 300°C, indicating that the polarity is lowered with temperature increase. If this apparently anomalous behaviour were better understood it would be more predictable and new clean methods could result.

Investigations into organic synthesis in high-temperature water have been carried out with the MBR and CMR. Biomimeticreactions that normally would be acid-catalysed, can proceed on underivatised compounds in the absence of added acidulant. Cooling of such mixtures renders the products insoluble, readily isolable and the aqueous phase does not require neutralisation before work-up. This approach is attractive to the flavour and fragrance industry, where biomimetic products derived by clean processing can command a premium.

The Centre's Dr Ulf Kreher carrying out experimental work on the Microwave Batch Reactor.

Customarily organic products are recovered from water by extraction with organic solvent. The aqueous phase becomes saturated with the solvent, thereby complicating disposal and offsetting environmental benefits gained through using water as the reaction medium in the first place. Alternatively, hydrophobic resins can be employed for concentration and isolation of the products from aqueous media. Organics are retained on the resin and later desorbed with a solvent such as ethanol which is a useful solvent for "green" chemistry as it is readily recyclable and is both renewable and biodegradable. Advantages of non-extractive processes include convenience, high throughput and low waste owing to ready disposal of the spent water, recyclability of the resin and the solvent used for desorption.

Solvent-free conditions employing elevated temperatures with less catalyst, a milder catalyst or without addition of catalyst, also represent an attractive alternative to those utilising aggressive reagents at lower temperatures. For example, a new catalytic, thermal etherification that can be performed conveniently in the MBR or CMR, produces minimal waste and is carried out near neutrality. Advantages are high atom economy, no salt formation, no addition of strong acids is required and water is the major by-product.

The MBR and CMR are portable, multi-purpose and self-contained, advantages that could become increasingly important for industrial chemical reactors. Their capabilities for rapid throughput and the materials of construction enable easy cleaning for reuse and promote short turnaround times. Safety advantages include control and method of energy input, low volumes undergoing reaction at one time and opportunities for remote, programmable operation.

Community Outreach Officer

A part-time community outreach officer is required to develop and deliver presentation and demonstration material promoting the principles of Green Chemistry to schools, community organisations and undergraduate students, under the direction of Dr Janet Scott, Deputy Director.

Skills Required: A background in chemistry is essential. Experience in the use of presentation software (e.g. Power Point). Lecture presentation skills and the ability to interact with a wide range of audiences.

Benefits: $35,594-$48,304 pa (pro rata) - Level A.

Duration: One-year appointment (part-time – hours negotiable).

Applications, by 1st June, to the address below. Include C.V. and the names, with phone, fax and email (where possible) contacts of three referees in your application.

Scholarships

The Centre for Green Chemistry has postgraduate scholarships available for study towards a PhD degree. Benefits and conditions will be as offered under the APA(I) Scholarships programs. The scholarships will be for a period of three years. Applicants should have good, recent Honours degree in Chemistry and are required to be Australian citizens or have permanent residence status in Australia. For an indication of types of projects available visit http://web.chem.monash.edu.au/greenchem ('Current Projects'). Submit letter of application, indicating areas of interest and including academic record and two referees, to: Director, **Centre for Green Chemistry, PO Box 23, Monash University, Clayton Vic. 3800.**

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