Microwave chemistry heats up

Australia is a world leader in microwave heating technology, a clean, efficient and flexible alternative to the glassware traditionally used in practical chemistry.

Bryony Bennett

Wendy Eason

Chemical reactions are faster in the microwave reactor, saving time and energy.

Microwave energy, despite its widespread use in modern kitchens, has never replaced conventional heating methods in chemical laboratories.

Advances in the technology, however, have improved the performance of microwave equipment in chemical processing. For manufacturers facing tight restrictions on solvent use and waste output, microwave heating now offers a competitive advantage in the lucrative market for high-value chemicals.

The use of microwave heating in chemical manufacture is one of a number of areas of research in chemistry at CSIRO's Division of Chemicals and Polymers in Melbourne. The work of the group is at the forefront of international efforts in this new area. A team led by Dr Christopher Strauss developed the division's first prototype microwave reactor four years ago. An industry-scale model, manufactured by a commercial partner, is due to be available by 1995.

Strauss says many opportunities for innovation in manufacturing technology have flowed from the worldwide focus on ecologically sustainable development. In some cases established manufacturing processes are unacceptable on environmental grounds, yet there is demand for a higher level of production of these chemicals.

Australia, which imports $4 billion worth of chemicals a year, has the skill and raw materials to compete in this market, but only if the nation quickly adopts 'clean', efficient manufacturing technology. Either new materials (new chemical entities) or new processes must be invented. CSIRO's leading position in the field of microwave heating provides a valuable head start.

Ceramic membranes enhance urea reaction

The drive toward more efficient production in the chemical industry is fuelled by concerns about both costs and the environment. One of the diverse strategies being explored involves membrane technology, developed at CSIRO's Division of Chemicals and Polymers.

Scientists from the division, working with Brisbane company Incitec, have been studying the use of membranes to achieve higher yields in the production of urea.

The impact of more efficient urea production would be significant because it is the world's fourth most traded commodity after oil, coal and iron ore. It is made at 400 production plants worldwide and is commonly used as fertiliser and stockfeed.

Senior development officer at Incitec's Gibson Island Works, Tony Brown, says the company's existing reactor converts up to 80% of raw materials (liquid carbon dioxide and liquid ammonia) to urea. The by-products of this process (ammonium carbamate and water) then need to be converted back to their original form for recycling in the reactor.

Membrane processing technology has proven capable of enhancing the urea reaction, Brown says. A small-scale reactor built to test the process improved the 'first pass' yield to more than 90%. This suggests that significant savings in energy consumption and capital input could be made if the process can be perfected at a commercial scale.

Dr Alastair Hodges, a CSIRO scientist working in the membrane area, says the membrane improves the efficiency of the reaction by helping to separate the by-products (in this case water) from the desirable product (urea). By removing water from the reactor, a backward or 'competing' reaction (in which ammonium carbamate is formed from water and urea) is prevented. It is this backward reaction which normally prevents full conversion of the raw materials.

The technology has the potential to attract worldwide interest (particularly as the membranes can be fitted to existing reactors) when proven on a commercial scale. To achieve this, there is a need for membranes that withstand for longer periods the harsh conditions experienced during urea production. Hodges says researchers in the United States are developing ceramic membranes with the required properties. Australia has worldwide intellectual property rights on the use of membranes to enhance urea production.

Incitec, Australia's only urea manufacturer, has invested significant funds in the membrane process, for which it has secured an international patent. Membrane technology has the potential to be applied to a range of other chemical processes.

Chemical solutions

The value of the microwave reactor lies in its energy efficiency and its ability to reduce the impact of chemical processing on the environment.

In conventional heating methods, the vessel is heated, transferring energy to its contents. This process is slow and can result in severe temperature gradients within a reaction mixture, sometimes yielding variable chemical results.

Microwave heating, on the other hand, is rapid, because energy is absorbed directly by the material being heated. The temperature of the reaction mixture is more uniform. Also, the temperatures reached can be much higher than under normal conditions. A further saving of energy is achieved because the higher temperatures allow faster reactions.

To facilitate high-temperature reactions, the chemicals inside the reactor are held in a pressurised environment. The small (100 millilitre) vessel that houses the reactions is made from an inert polymer. A ceramic chamber lined with polymeric material has been developed to contain the vessel under pressure, yet remain transparent to the microwaves.

Under these conditions of high pressure and temperature, water, long assumed unsuitable as a solvent in organic reactions, takes on the properties of an 'organic solvent'. Many organic compounds which did not normally react in water do under these conditions.

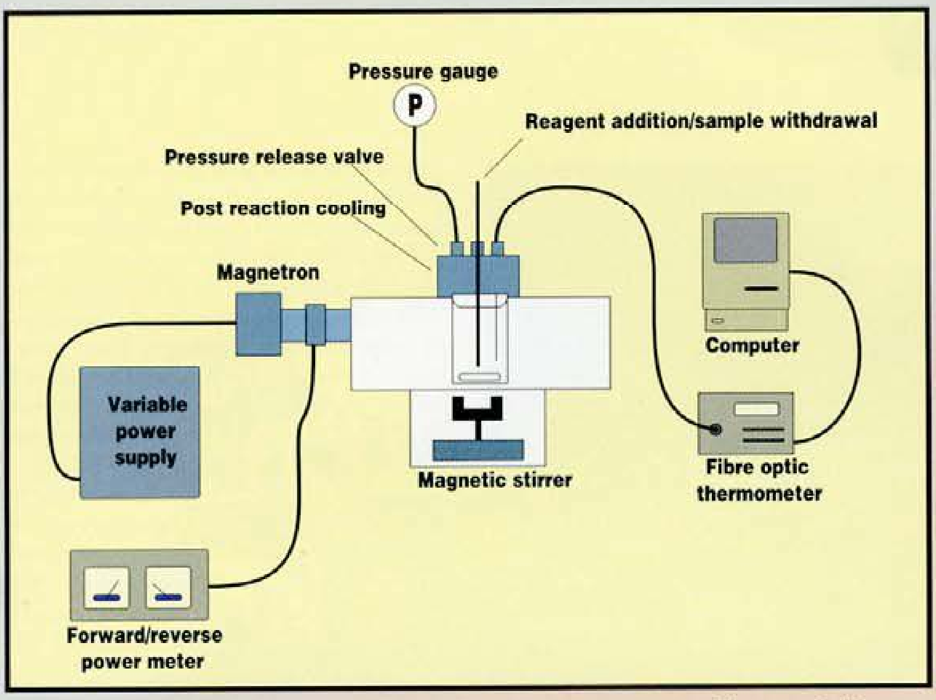
Dramatic changes in physical and chemical properties at elevated temperatures combine to make the solvent properties of water at 300°C roughly equivalent to those of the organic solvents such as acetone, at 25°C.

That water can replace solvents in many chemical reactions is most important. The key to cleaner chemical production lies in developing efficient processes that minimise the use of organic solvents. This has encouraged the CSIRO researchers to continue their exploratory work.

Organic solvents are used in conventional synthesis of chemical products such as paints, industrial cleaners, printing inks and pharmaceuticals. But many of these solvents are toxic to varying degrees and are being phased out by governments keen to embrace the principles of ecologically sustainable development.

A consequence of solvent use is the production of effluent requiring detoxification and disposal. In chemical processing, this can account for up to 80% of production costs. Strauss says a more efficient approach is to produce less waste in the first place, either by reducing the quantity of solvent used, or by replacing organic solvents with water. He says that in many cases this can be achieved through the use of microwave heating.

Investigation of particular reactions

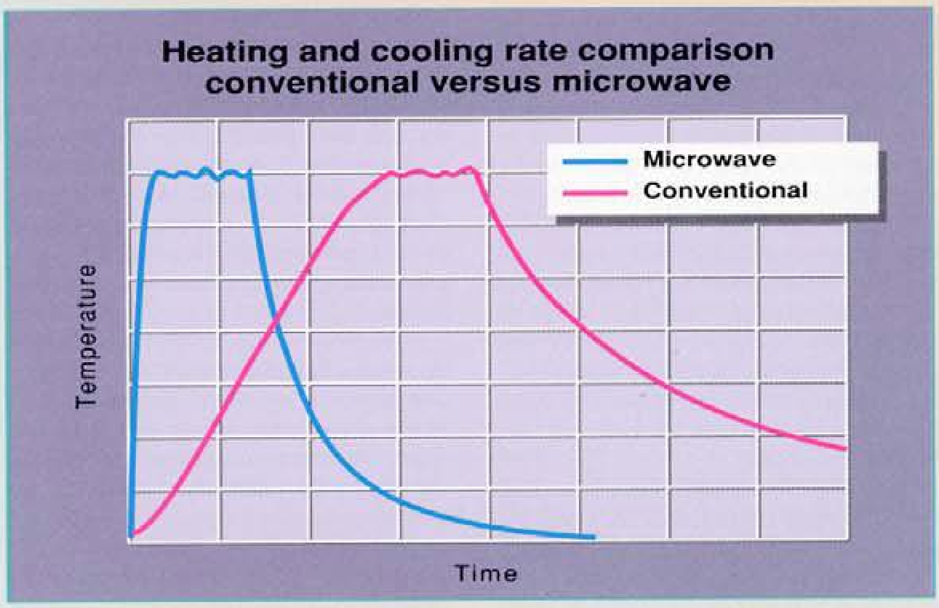


The microwave reactor: controlling the flow of microwave energy was one of the many challenges to be met before the equipment could be ready for commercial application.

in the microwave reactor has shown the capability of the technology. The scientists have found that several reactions, difficult to achieve by conventional heating at atmospheric pressure, proceed easily and with high selectivity in a microwave environment.

In one example, they were able to hydrolyse a tertiary amide with dilute hydrochloric acid within a few minutes at 200°C, after the conventional method had failed to produce the desired outcome, even after hours of heating. They have also produced in significant quantity, highly reactive substances such as phenyl vinyl ketone, by a microwave process requiring rapid heating to afford the product, but where excessive heating could subsequently destroy it.

The research team has also successfully produced chemicals under solvent-free conditions, when it had been thought previously that these reactions needed to be conducted under high dilution in the presence of high-boiling organic solvents.



Microwave heating is more rapid than conventional techniques because energy is absorbed directly by the material being heated.

Chemistry and beyond

Developing a microwave reactor requires a range of expertise extending beyond the field of chemistry. Although some of the early prototypes might have looked suspiciously domestic, the model now used in the laboratory bears little resemblance to its culinary counterpart.

Controlling the flow of microwave energy was just one of many challenges to be met before the equipment could be ready for commercial application. Colleagues from the Division of Applied Physics provided much help in meeting these challenges.

One of the most costly parts of the microwave reactor is a fibre-optic thermometer. Linked to a computer, this gives the required accuracy to control the temperature and pressure, and thus the chemical reactions occurring inside the reactor. A magnetic stirrer incorporated within the reactor ensures uniform temperatures.

Years of development have culminated in the integration of these and other components into a chemical processing system that is now being patented. According to Strauss, however, the real know-how that gives his team the edge in the development of microwave technology lies not in heating the reaction mixture, but in cooling it. The requirement for controlled cooling of the reaction mixture is vital to the viability of the technology.

Understandably, the knowledge behind the cooling process is something Strauss won't be parting with until after the process has been protected by law.

Strauss is confident that microwave heating will become commonplace in chemical laboratories within the next two decades. He says because of its speed and convenience, the method will be adopted as a valuable alternative to the glassware traditionally used in practical chemistry.

New and better chemical processes requiring microwave technology will be developed, Strauss says. These should be more energy-efficient and clean, and will be particularly useful for the manufacture of low volume, high value chemicals such as pharmaceuticals or synthetic building blocks such as those used in the manufacture of plastics.

In the meantime, the CSIRO team is concentrating on developing techniques for manufacturing new chemicals for which no commercial techniques or equipment are yet available.