ACRYLICS FOR THE FUTURE

One of the four finalists in this year's MacRobert Award was Lucite International with its Alpha process. Alpha is a cheaper, greener way of making methyl methacrylate, the key ingredient in acrylic plastics. Dr Ben Harris, the R&D Manager at Lucite, explains how the company developed and commercialised a process plant capable of producing 120,000 tonnes of methyl methacrylate a year.

Many of the things we use each day, whether they are motorcycle helmets, the casings of car headlights, artificial nails, kitchen surfaces or lightweight and scratch-resistant laptop screens and back lighting panels, rely on an often unrecognised material, a colourless liquid known as methyl methacrylate (MMA).

MMA is the monomer (or building block) for the polymer poly-methyl methacrylate (pMMA), which is commonly called by brand names such as Perspex and Lucite, or simply known as acrylic. The properties of pMMA include high visible light transmittance and very low UV absorbance resulting in a stable, weather-resistant polymer. It can be easily coloured, moulded and recycled.

These properties make pMMA ideal as a lightweight, shatterproof substitute for glass in applications including mobile phone screens, giant aquaria and viewing ports of submarines; as well as numerous applications in the photonics and semiconductor industries. MMA and pMMA work well with the human body too, making them ideal for applications such as artificial lenses, bone cement and dentures. MMA is also used in combination with other monomers in the creation of many other polymers and resins (see *Speciality Monomers*).

This wide range of applications has fuelled a 4% year-on-year demand growth for MMA. However, challenges in the manufacture of MMA have traditionally limited the availability of this monomer.

TRADITIONAL MMA MANUFACTURE

MMA was first made by ICI and DuPont in the 1930s using a technique known as the ACH process and this is still the most widely-used method of making MMA today. However, the ACH process starts with extremely toxic and corrosive chemicals such as hydrogen cyanide and sulphuric acid. Using such chemicals means that strict safety measures have to be considered when planning a plant's construction and operation. These requirements bring significant additional costs to the plant and also limit its scale. Another factor that raises the costs of operation is that the feedstock itself, especially acetone, is expensive. An alternative, the C4 process, was developed in Japan in the 1970s but it has similar constraints and the process is only used in the Far East.

Now there is another option for making MMA. The Alpha process, developed by Lucite International, is a two-stage, high-yield route to MMA that starts from simple, widely-available chemicals: ethylene, methanol and carbon monoxide. In the fourth quarter of 2008, the company commissioned its 'first in class' Alpha MMA plant based on Jurong Island in Singapore. This process plant is 30-40% cheaper to build and run than conventional systems, produces virtually no waste and the feedstocks can even be made from biomass.

DEVELOPING THE ALPHA PROCESS

The new Alpha plant is the result of nearly two decades of research and development work carried out by scientists and engineers at Lucite International's R&D centre at Wilton,

An engineer programming external LED signage for Fort Dunlop. This sign was awarded Best UK Sign of the Year and Best Illuminated Sign by the Sign Industry Awards when it was created a new shopping centre in Birmingham. It is made from Perspex (based on methyl methacrylate) from Lucite International © Lucite International

Alpha 1 plant, Jurong Island Singapore. This is the first-in-class plant using Lucite's Alpha technology. It was commissioned in the latter part of 2008 and cost $230 million to engineer and construct © Lucite International

UK, starting with preliminary catalyst trials and conceptual process design studies that began in 1990.

This research revealed the potential of a new two-step process using commodity starting materials and novel catalysts. The first stage involves reacting carbon monoxide, ethylene and methanol together in a single homogeneous catalysed reaction step to produce methylpropionate (MeP). In the second reaction step, MeP is reacted with formaldehyde in a single heterogeneous reaction step to form MMA (see: *The Alpha MMA process*).

Once the initial screening and concept development had been carried out, it was clear that the proposed process was radically different from existing MMA processes. New chemistry, novel reactive distillations and a dearth of process design information presented significant challenges. The development team needed to determine and develop reaction mechanisms, kinetics, physical property models and data for the principal components and minor impurities. These challenges were compounded by the requirements for very high purity that many applications place on the MMA. The team needed to ensure that the chemistry of all the intermediates and potential by-products – some of which had never been characterised before – was fully understood. Furthermore, given the exacting specifications for MMA, it was concluded that it was necessary to pilot the new process to replicate all reaction steps, separation operations and impurity recycle streams. The scale selected for the MMA pilot was 0.5kg/hr and Lucite worked with Davy Process Technology (now part of Johnson Matthey) to design this micro-scale plant so that it would faithfully reproduced the behaviour of the full-scale plant (see: *Micro-Scale plant concept*).

PROCESS SCALE-UP

Once the process had been studied and understood, Lucite took the bold move of scaling up from pilot to production scale without further intermediate, non-commercial, steps. The anticipated scale of the first production unit was 120,000 tonnes per annum so that required a scale-up by a factor of more than 25,000:1. Although this was not outside the range of scale-up that had been achieved by Davy Process Technology in the past, the MMA flow-sheet was significantly more complicated than the processes previously developed in this manner. In particular, the reactive nature of the product MMA (its propensity to polymerise), reactive reaction intermediates (formaldehyde adducts and by-products) and the associated impurities made the proposed design and scale-up exercise unique.

A strategy was adopted to minimise the risk of the technology not performing as expected. Firstly, it was decided that the process should not try to operate outside the bounds of established unit operations in terms of hardware and processing technology. Secondly, the Alpha pilot plants should be used to confirm fundamental process technology data to allow process design. The third element of the strategy was that the pilot plant should reflect the final plant configuration: all principal separations should be included, all recycle streams should be closed and the construction materials should be the same as for the full-scale plant. Finally, as product quality was critical, the pilot-plant product had to be qualified in end-use applications.

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FULL-SCALE PROCESS

The first step in the process, the MeP synthesis reaction, is done in a continuous-stirred tank reactor under moderate conditions of temperature and pressure. A proprietary agitation and gas-liquid mixing arrangement is used to ensure that the reaction conditions, in terms of reactant concentration and mass transfer rates, are optimal.

The subsequent MMA synthesis from MeP and formaldehyde takes place over a fixed bed of catalyst. This catalyst has caesium oxide on silica as its active component and it achieves a selectivity to MMA from MeP of approximately 93% and 85% on formaldehyde to MMA. Two parallel MMA reactors are needed because of the formation of a small amount of heavy, relatively-involatile compounds. These form coke (solid carbonaceous material) on the catalyst that causes some loss of activity and selectivity. The coke is easily removed and catalyst activity and selectivity restored by controlled, in-situ regeneration whilst maintaining production through the other reactor.

The reactor product stream is separated in a primary distillation so that a crude MMA product stream, free from water, MeP and formaldehyde, is produced. Unreacted MeP and water are recycled via the formaldehyde dehydration process.

Pure MMA (>99.9%) is produced from the crude MMA in a series of vacuum distillations and one proprietary reactive

THE ALPHA MMA PROCESS

Stage 1 reaction:

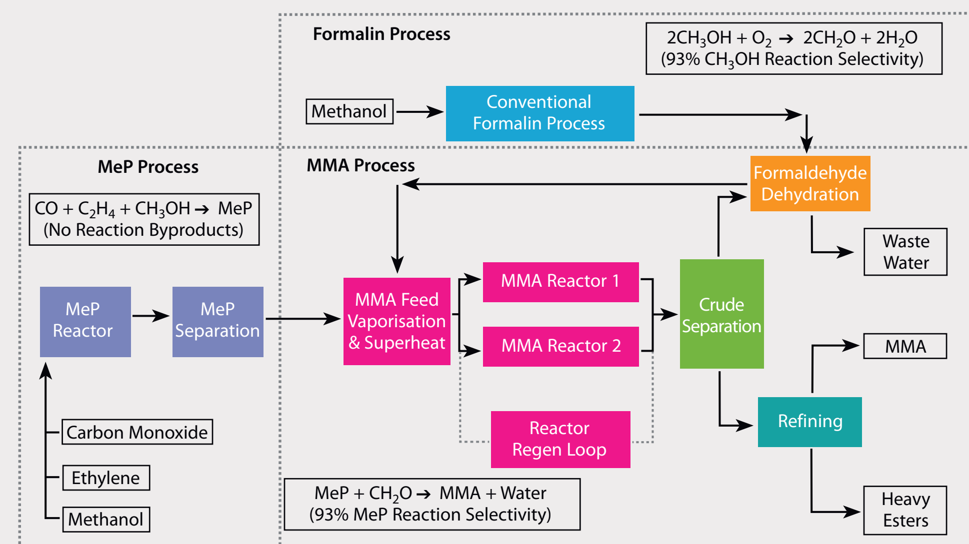
$CH_2 = CH_2 + CO + CH_3OH \longrightarrow CH_3CH_2CO_2CH_3$

Ethylene + Carbon Monoxide + Methanol ⟶ Methyl Propionate

Stage 2 reaction:

$CH_3CH_2CO_2CH_3 + CH_2O \longrightarrow CH_3(CH_2)CCO_2CH_3 + H_2O$

Mep + Formaldehyde ⟶ MMA + Water



SPECIALTY MONOMERS

Specialty Monomers (SpMAs) form a separate category of related monomer-based products – these can be readily produced from MMA. Chemical modification enhances the properties of the monomers, which are then used in more specialised end-applications where one or more particular performance characteristics are required.

Methacrylic Acid – properties such as adhesion, improved pigment wetting and cross linking ability make it ideal for use in flexible and semi-rigid packaging for the food industry, automotive, architectural and industrial coatings, floor polishes and textile finishes as well as coatings for golf balls.

Specialty Methacrylates – where properties such as weatherability, film forming, gloss finish, solubility, toughness and fast curing properties are used to beneficial effect in electronics, toys, adhesives, inks and high performance coatings.

One of the biggest growth sectors for Lucite's SpMAs is in surface coatings, which include automotive finishes, lubricants, inks and adhesives. Its durability has made it attractive to the surface coatings industry, as has worldwide environmental legislation which is driving the increased use of waterborne coatings with low solvency ratings.

MMA was the raw material for this ground-breaking aquarium, which forms the centrepiece of Berlin's DomAquaree hotel and leisure complex. Suspended 8 m off the ground, the cylindrical aquarium is made from 150 tonnes of high-optical clarity acrylic. A seven-minute narrated elevator ride through the structure allows a good view of more than 2,500 fish swimming in the one million litre artificial seascape © Christian Gahl

separation. In all cases, the separated streams are returned to the process; there is only one (small) heavy ester purge stream. This is readily disposed of in a thermal oxidizer with heat recovered for use in the process.

The catalyst for the first step is a palladium bisphosphine, developed in collaboration with Professor Peter Edwards at Cardiff University, Wales. This catalyst displays enzyme-like selectivity (>99.9% to methyl propionate from its raw materials) with excellent activity. Because the reaction is highly selective, no by-products are formed. This makes the separation and purification of methyl propionate straightforward. The catalyst is fully soluble in the reaction mix so it can be continuously recycled to the reaction stage, while pure MeP (>99.9% purity) can be produced.

To ensure high selectivity to MMA and to avoid excessive ageing of the catalyst, the formalin used in the process must be dehydrated to give an anhydrous feed. Commercially-available formalin processes typically produce a formalin product with a maximum concentration of 55%wt formaldehyde, 1% methanol, and the balance water. To resolve this issue, the Alpha process includes a patented separation process that was developed in-house to dehydrate formalin.

ADVANTAGES OF THE PROCESS

The Alpha process offers many benefits over the other technologies. Firstly, there is the minimization of societal and environmental risks. The new process has no significant inventories of hazardous chemicals and the principal hazards are only those associated with flammability of inventories. In addition, by-product formation is low so the waste treatment requirements are minimal.

The process also benefits from efficient resource utilisation. The raw material efficiency is better than the other demonstrated technologies and the feed-stocks can all be (syn) gas-based. There is also excellent co-gen fit: the reactions are mildly exothermic and the chosen separation and refining scheme use low-grade heat.

Operating and capital costs are also lower for Alpha than for the other MMA processes. This is because the process uses more readily available feedstocks (carbon monoxide, methanol and ethylene). A significant advantage is that capital cost is approximately 30-40% lower than equivalent-scale ACH or C4 plants.

Location and scale flexibility benefits have also been linked to the feedstocks. Because feedstock availability is not a constraint, there are many potential Alpha plant locations. In addition, no engineering scale limitations have been found for plants to produce at least 250,000 tonnes per annum.

These benefits have been reflected in Lucite's experience with the plant since it opened. The MeP plant met its 100% flow-sheet rate acceptance test within three days of starting production and the MMA plant met its 100% acceptance test within three weeks. Since then, the company has run the plant at >100% rate and sold everything that has been made. Plant production performance has exceeded year one budget expectations and production to date in 2010 is in excess of 10,000 tonnes per month.

Lucite International now has well-advanced plans for an Alpha 2 plant – the location is yet to be decided but options include China, the Far and Middle East. The new plant will take advantage of Alpha technology's innate scalability – options for designs in the range of 200,000-250,000 tonnes per annum are being examined and optimized, and the design is likely to incorporate advanced heat-integration steps to further improve the process economics.

For further information visit www.luciteinternational.com

MICRO-SCALE PLANT CONCEPT

Usually new processes are tested in a pilot plant of substantial capacity that requires a clear understanding of the process design parameters before it is built. However, the concept of the micro-scale plant is based on the use of laboratory-scale set-ups that include all the design elements of a commercial plant and are made of the same materials and subject to the same chemical and physical reaction conditions. The Alpha pilot plant is operated on a scale that is 1/25,000th of the final size. Key process steps are fully integrated to allow the entire operation to be evaluated and then optimised.

A micro-scale plant generates comprehensive design information for each element of the plant before all the systems are inter-connected. The result is a wealth of data that allows the entire plant performance to be determined accurately. A key aspect is the evaluation of scaling-up effects; each piece of equipment is tested to its boundary conditions and an accurate computer simulation of the entire process is then prepared.

This enables a strategy for process operation to be developed that takes into account how changing conditions in one part of the plant affect operations elsewhere. Such a strategy is critical to the building of a comprehensive process model that provides the basis for the successful scale-up to commercial plant size.

Lucite International's Alpha pilot plant is located at Wilton, UK. It fully reproduces the plant that was commercialised in Singapore in 2008 but at 1/25,000th of that scale. It is manned by two operators and one analyst 24 hours a day, 330 days a year. Lucite continue to run the pilot plant to test improved catalysts and process enhancements and to develop the next generation of MMA technology based on the Alpha chemistry © Lucite International

BIOGRAPHY

Dr Ben Harris is the R&D Manager at Lucite International, now part of Mitsubishi Rayon Co. He studied chemical engineering at the University of Canterbury, New Zealand followed by PhD Studies at Cambridge University. He joined ICI in 1992 and ICI Acrylics (now Lucite International) in 1995. He has experience in technical, operations and manufacturing management on high hazard ACH processes at Billingham. Ben Harris joined the Alpha RT&E team in 2006.

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