PERP Program – Methyl Methacrylate
New Report Alert
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Nexant’s ChemSystems Process Evaluation/Research Planning program has published a new report, *Methyl Methacrylate (04/05-2)*. To view the table of contents or order this report, please click on the link below:

Introduction

Methyl Methacrylate (MMA) is a key intermediate chemical, due to its ability to undergo polymerization and copolymerization. Polyacrylates, a family of clear and relatively durable thermoplastics, are the major source for the consumption of MMA. MMA can be commercially manufactured by a number of routes. Global demand for MMA is in excess of 2.4 million tonnes (about 4.5 billion pounds) and newer applications such as flat panel displays for polyacrylates and the Asian region growth are fueling MMA demand. This PERP examines some newer technological developments and in particular the new so-called Alpha process developed by Lucite, and also looks at the continuously evolving commercial outlook, especially the Asian scene.

The conventional methyl methacrylate (MMA) process centers on the reaction of hydrogen cyanide (HCN) and acetone to give acetone cyanohydrin. The cyanohydrin then undergoes acid assisted hydrolysis and esterification with methanol to give methyl methacrylate. This process (known as the ACH route) whilst quite economical if a producer has access to a low cost source of HCN, creates large amounts of ammonium bisulfate by-product. About 1.2 tons of ammonium bisulfate is formed from every ton of MMA produced. This by-product disposal issue and the handling of the highly toxic HCN, has prompted a great deal of research over the years aimed at developing newer cleaner and more cost effective process technologies for making MMA.

A number of alternative routes have been commercialized over the last two decades and more are claimed to be close to commercialization. These new routes range from using new feedstocks, such as isobutylene, ethylene, or even methylacetylene to developing techniques for recycling the HCN and/or the ammonium bisulfate. Figure 1 summarizes the major chemistries and routes to MMA. Table 1 outlines the key currently commercial and also the speculative MMA routes that this PERP examines in detail.

Current Commercial Technology

At the end of 2004, there were at least 30 MMA Manufacturing plants globally (some uncertainty exists over the precise number of plants in China where the very small localized plants are scattered over a wide geography) with plant sizes ranging from 10,000 to 360,000 metric tons per year (66 to
794 million pounds MMA per year), and with a total capacity of around 2.5 million metric tons MMA per year.

**Figure 1** Routes to MMA

![Figure 1: Routes to MMA](image)

**Table 1** MMA Process Technologies Assessed in This Report

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Five process routes to MMA may be distinguished amongst current commercial operating plants:

- **The ACH Route**: The acetone cyanohydrin route, starting from acetone and hydrogen cyanide (or from purchased acetone cyanohydrin) and proceeding via dehydration, hydrolysis and esterification to MMA.

- **The "i-C4" Route**: Two-stage gas-phase oxidation of isobutylene (or TBA) to methacrylic acid, followed by esterification. Such processes are operating commercially in the Far East.

- **The BASF Route**: Hydroformylation of ethylene to propionaldehyde, condensation with formaldehyde to methacrolein, followed by oxidation and esterification. The first and only company to commercialize this route is BASF.

- **The Asahi Chemical "Direct Metha" route**: A new process in which isobutylene (or TBA) is first oxidized in the gas phase to methacrolein. The methacrolein is recovered as liquid, mixed with methanol and then oxidized with air in the liquid phase over a Pd/Pb catalyst with simultaneous esterification to MMA.

- **The "MGC" or Mitsubishi route**: A recycle version of the ACH route in which ACH is made as usual from acetone and HCN and is then hydrolyzed to alpha-hydroxyisobutyramide, which is reacted with carbon monoxide and methanol under pressure to yield formamide and methyl-alpha-hydroxyisobutyrate. The latter compound is dehydrated to MMA, while the co-product formamide is dehydrated to HCN for recycle. Mitsubishi Gas Chemicals developed this route. One commercial plant is operating in Japan.

The conventional two-stage gas-phase oxidation of isobutylene is very similar technically to the gas-phase oxidation of TBA and these processes are therefore considered together in this study, with a separate cost of production estimate to show when isobutylene and TBA are economically equivalent. The Asahi Chemicals’ Direct Metha route has replaced another unique process formerly operated by Asahi Chemical based on methacrylonitrile.

The above five process routes to MMA, selected to represent current commercial practice, are designated as ACH, i-C4 (and TBA), BASF, ASAHI, and MGC, respectively, in this report.

Detailed process flow diagrams and descriptions are provided for each of these processes.

Many of the newer capacity announcements and plants under development are in the 90 Kt 140 kT/year range. We have therefore selected a nameplate capacity of 300 million pounds per year (136,000 metric tons per year), in the middle range for the ACH route, for typical "base case" economics.
A comparison of the estimated economics of currently commercial MMA processes is presented, using the US Gulf Coast as reference location:

- **ACH-L**: Conventional MMA production route from acetone and HCN via acetone cyanohydrin, on a scale of 300 MM lbs/year (136,080 metric tons/year) that is approximately the size of some of the larger existing installations. Assumed integrated with sulfuric acid recovery to meet effluent regulations and using transferred HCN costing.

- **i-C4**: Plant based on isobutylene notionally produced by cracking purchased MTBE. The plant scale is for producing 198 MM lbs/year (90,000 metric tons/year) of MMA by two-stage gas-phase oxidation of isobutylene (or TBA) followed by liquid-phase esterification.

- **BASF**: Plant based on high-pressure ethylene hydrocarbonylation to propionaldehyde, condensation with formaldehyde, oxidation and esterification as practiced by BASF. Assumed plant scale is 198 MM lbs/year (90,000 metric tons/year) with ethylene priced at market.

- **ASAHI**: The new Asahi Chemical "Direct Metha" route in which isobutylene (or TBA) is first oxidized in the gas phase to methacrolein. The methacrolein is recovered as liquid, mixed with methanol and then oxidized with air in the liquid phase over a Pd/Pb catalyst with simultaneous esterification to MMA. Assumed plant scale is 198 million lbs/year (90,000 metric tons/year) that is larger than the existing plant.

- **MGC**: Mitsubishi Gas Chemicals modified ACH process, in which HCN is recovered and recycled, leaving only a small make-up requirement to compensate for losses. This also eliminates the effluent problem and therefore the requirement for the expensive sulfuric acid recovery plant. However, the process route and equipment is complicated for the MGC process. The same scale is considered, i.e., 198 million lbs/year (90,000 tons/year).

- **ACH-S**: As for ACH-L at the beginning of this list, except smaller (198 MM lbs/year, 90,000 metric tons/year).

The production costs of the five processes are assessed in the report. The Asahi "Direct Metha" route emerges as the most economical for a completely new MMA plant on the USGC. The current high HCN and acetone transfer price and market price situation, coupled with very good by product pricing for the rival plants’ acetic and acrylic acids, makes the ACH routes less competitive today than they were when previously analyzed in the 1996 and 2000 PERP reports. Additionally, the rival plants to the ACH process have this time been analyzed at a capacity of 90,000 tons per year and not 45,000 tons per year as in the previous cases. This makes the non-ACH routes more competitive at the larger scale.
New Developments

This section of the report covers some of the newer process routes to MMA, most of which have been or are being developed through the pilot plant stage and some of which have the potential eventually to evolve to full scale plant designs. In fact one of them has recently been announced for commercial implementation (The Lucite-Alpha ethylene based process). Three of the processes are improved ethylene-based routes that could be compared to the existing BASF ethylene-based operating plant. These three processes are:

- **The Lucite (Formerly INEOS) “Alpha” Process** that relies on combined carbonylation and esterification of ethylene to methyl propionate. The methyl propionate is reacted with formaldehyde under almost anhydrous conditions to form methyl methacrylate. A tentative flow sheet has been developed based on Shell/ICI/Ineos/Lucite patents to allow for removal of water from feed formalin, recovery of unreacted formaldehyde, separation, the recycle of a large stream of methyl propionate plus methanol and the purification of MMA product and of by product propionic acid. This process is a major focus of this PERP as Lucite have recently announced that it would use this technology for their new 120,000 tons per year plant to be built in Singapore (2008 start up), and also that the same technology will be used for a subsequent even bigger plant (250,000 tons) plant 2010–2011 period.

- **The RTI-Eastman-Bechtel Three-Step Process** based on hydro-carbonylation of ethylene to propionic acid followed by condensation with formaldehyde to methacrylic acid and esterification to produce MMA. This route is primarily syngas based. Eastman is a commercial producer of propionic acid and hence its focus. A fundamental challenge with this route has been the relatively shorter lifetime of the condensation catalysts. The published information indicates selectivity to MAA in the condensation reaction to be somewhat lower than in the Lucite-Alpha process. Without key patent based guidance on the other products made, it has not been possible to estimate overall process flows or net raw materials costs after allowing for by-products credits.

- **BASF Route Involving Carbonylation/Esterification of Ethylene** to methyl propionate, followed by condensation with methylal to MMA, in a simplification of the industrial BASF route. Condensation catalyst life is unknown but in laboratory tests fresh catalyst displayed almost quantitative selectivity combined with high conversion, albeit with rather low turnover. An idealized version of this process, assuming a long-lasting condensation catalyst could be found, results in favorable economics for the obvious reasons of process simplicity, high conversions per pass and very high selectivity. This process has never been commercialized probably because of inability to achieve a satisfactory life for the condensation catalyst.

The other four potential MMA processes are:
• **Isobutane Oxydehydration to Methacrolein/Methacrylic Acid**: An analogous process to the established isobutylene (isobutene) selective oxidation. Various process developers have worked on this route, the most advanced being Arkema and Sumitomo. The process has the attraction of lower cost raw materials.

• **Carbonylation/Esterification of Methyl Acetylene (Propyne) Directly to MMA**: This process was developed in detail by Shell and the technology now belongs to INEOS. This process is very simple in concept. The main limitation is the restricted availability of the raw material.

• **The HCN recycle route** was developed by Mitsubishi Gas Chemical (MGC) to meet their own circumstances of restricted HCN supply and effluent restrictions. They have now developed an improved process, the MGC New Process, which recycles ammonia rather than HCN. The raw materials net costs are not much improved but there are advantages apparent in capital equipment costs and ready availability of the raw materials required.

• **Carbonylation of propylene to isobutyric acid**, followed by dehydrogenation to methacrylic acid and esterification to MMA. This technology has been neglected in recent years despite competitive basic economics, possibly because of equipment design difficulties and capital costs issues.

The Lucite Alpha route, based on carbonylation and esterification of ethylene to methyl propionate followed by condensation with formaldehyde, does not appear to offer any significant saving in net raw materials costs over the established BASF ethylene-based process. However, the Lucite Alpha route should enjoy significant savings in capital and related charges such as fixed costs and finance costs. Detailed speculative capital and production cost estimates are provided for the Lucite Alpha process.

**Commercial Status**

Global consumption of MMA today exceeds 2.5 million metric tons per year, of which more than two million tons is for MMA polymers. The other primary product of this industry is crude methacrylic acid (crude MAA), which is produced by similar technology but often in separate plant units. MAA capacity and production are not generally published. Production of crude MAA (for uses other than MMA) is about 20 percent of the total production of MMA.

The crude MAA produced for purposes other than MMA production is not used directly. It is first processed into either or both of two other products: butyl methacrylates and "glacial" MAA. Butyl methacrylates (i.e., normal- and isobutyl methacrylate) are made by esterification with n-butanol or with isobutanol, respectively. Glacial MAA is highly purified crude MAA. These two products are marketed as such, and are also used as intermediates for downstream products.
Glacial MAA is used directly as a comonomer in various polymers. Glacial MAA is also used to make a variety of small volume specialty methacrylates. Some of the higher methacrylate esters are also made by transesterification of MMA, more particularly in Western Europe and Japan.

The largest volume uses of MMA are for pure or almost pure homopolymers (PMMA), but there is also a wide variety of copolymer uses. Within the PMMA consumption categories, the largest is for cast and extruded transparent acrylic sheet (PMMA sheet). Acrylic sheet is used for glazing, lighting, signage, displays, sanitary ware, and miscellaneous other applications. Its largest markets are in skylights, architectural applications, security glazing, and displays.

Molding resins (excluding the resin beads prepared for extruded acrylic sheet production) are the next largest consumer of MMA. Most of the final products are destined for automotive parts and electrical appliances. In transportation the typical uses are taillight lenses, instrument panel covers, control dials and knobs, and assorted other uses and decorations. The appliance market uses molded acrylics for knobs, housings, nameplates, dials, control panels, hair dryer hoods, and vending machine housings. Acrylic moldings also have miscellaneous minor uses in houses, offices and institutions, including lighting fixtures, accessories, and furniture parts.

Surface coatings are the next largest consumer of MMA, both for industrial solvent-based systems and, increasingly, for water-based acrylic dispersions for domestic and industrial use.

MMA provides a hard, glossy component in paint resins, where it is often combined with other acrylate and methacrylate monomers to form copolymers with appropriate properties both for aqueous dispersion (latex) and solvent-based (acrylic lacquers and enamels) surface coatings. Nonacrylic comonomers with MMA are also important in surface coatings, like the acrylic urethanes. Solvent-based systems were developed first, but the aqueous dispersions are now much more important, accounting for 75-80 percent of MMA used in surface coatings.

MMA is used in water-based acrylic dispersions for exterior masonry and wood coatings and semigloss emulsions for interior decorative coatings. These resins are essentially copolymers of MMA, other methacrylates and acrylates, and comparatively low levels of acrylic acid and/or MAA to provide some hydrophilic components. Vinyl resins compete in these areas but do not match acrylics for gloss and weatherability. Demand growth for water-based acrylic paints depends to some extent on new building activity, but it is also sustained by maintenance use and by increasing reluctance to use solvent-based surface coatings on environmental grounds.

The use of MMA in industrial coatings (trade paint) is primarily in the form of solvent-based acrylic resins. There is a growing use of acrylic water-based industrial coatings that are seen as a future growth area. The total consumption of MMA for industrial surface coatings has been falling with moves toward high-solids and powder coatings, where polyesters are the preferred resin type. Original and refinishing acrylic topcoats for automobiles are still slowly growing markets for MMA.
By far the biggest emerging application of acrylics has been in Liquid Crystal Displays (LCD), and the enormous current and projected growth for large LCD screens for home theatre etc has been a major driver for MMA expansions, especially in Asia where virtually all the LCD manufacturing market now concentrates. The anticipated demand has been responsible for a spate of recent announcements for planned capacity addition by Lucite-MRC, Sumitomo, Degussa, etc. If demand is not realized there could be a risk of an MMA over-supply for years to come. The current trend, however, shows that LCD home theatre is replacing conventional CRT TVs at a much faster rate than anticipated.

Demand growth in Asia as a whole is projected to be around seven to eight percent per year for the period 2005–2008. LCD demand in Japan, South Korea and Taiwan, the hub of the home theatre manufacturing industry expanded 40 percent in the period 2001–2004, and is expected to increase by about half as much again over the period 2005–2008.

Figure 2 shows the breakdown of MMA consumption by end use and the dominance of PMMA in industrial coatings, extruded sheet, and injection molded articles.

![MMA End-Use Breakdown, 2005](image)

The report also covers the global and regional supply and demand for MMA and global trade in MMA. Nexant’s projections take into account geographical population and economic growth dynamics, as well as current, planned and announced, and speculative MMA capacities. Speculative capacities consist of two elements – speculative debottlenecks in existing capacity and speculative additions of new capacity (both new grassroots plants, as well as additional production trains
supplementing existing ones) based on dynamics of trade, operating rates, anticipated tightening of supply and investment history.

Global MMA consumption by region is shown in Figure 3.

**Figure 3**  Global MMA Consumption by Region, 2005

Detailed supply, demand, and trade data are provided for the United States, Europe, and Asia-Pacific, covering the period 2004 to 2015.