CHEMSYSTEMS
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Methyl Methacrylate (MMA)

PERP 08/09-7

Report Abstract
March 2010

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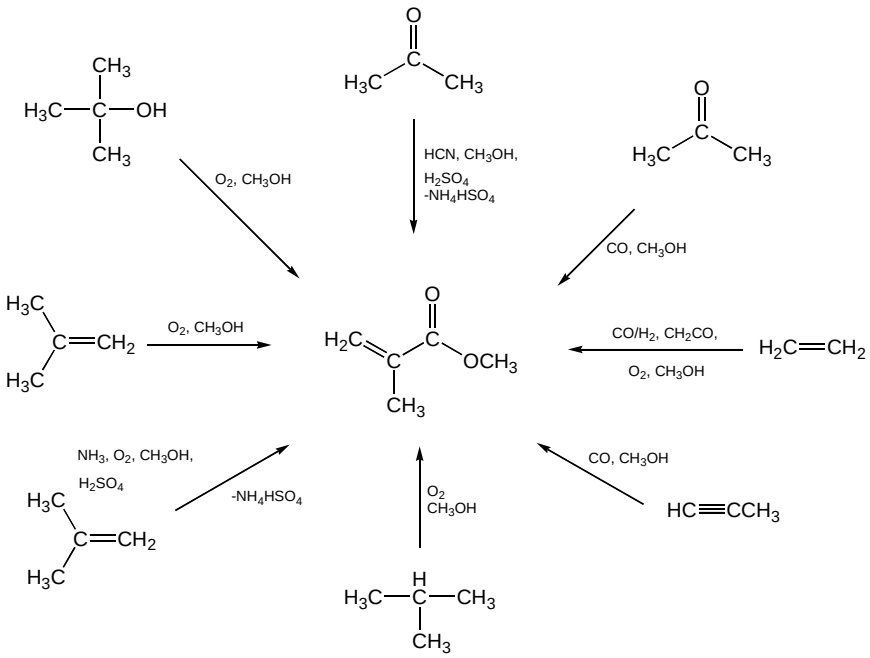
INTRODUCTION

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. At the end of 2008, there were almost 50 methyl methacrylate 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 1 500 to 360 000 metric tons per year (3.3 to 794 million pounds MMA per year). MMA can be commercially manufactured by a number of routes.

The conventional 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 byproduct. This byproduct 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. The Figure below summarizes the major chemistries and routes to MMA.

Routes to MMA



COMMERCIAL TECHNOLOGY

Six commercial process routes to MMA may be distinguished amongst current commercial operating plants and these are discussed in the report.

- **The ACH route:** The acetone cyanohydrin (ACH) route, starting from acetone and hydrogen cyanide (HCN) or from purchased acetone cyanohydrin and proceeding via dehydration, hydrolysis, and esterification to MMA.
- **The "i-C_4" route:** Two-stage gas-phase oxidation of isobutylene (or tertiary-butyl alcohol (TBA)) to methacrylic acid (MAA), followed by esterification. Such processes are operating commercially in the Far East.

  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 report, with a separate cost of production estimate to show when isobutylene and TBA are economically equivalent.
- **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 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 (MGC) developed this route. One commercial plant is operating in Japan.
- **The Lucite (formerly INEOS) "Alpha" Process:** 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 flow-sheet has been developed based on 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 byproduct propionic acid. One commercial plant is operating in Singapore and another is being planned.

DEVELOPING TECHNOLOGIES

The previous PERP report on MMA (04/05-2) covered some of the developing 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. The following are briefly discussed in the report:

- **Evonik's Aveneer® Process:** Evonik Industries AG has developed a route to MMA that avoids the use of sulfuric acid. Like the traditional ACH sulfur, the Aveneer® process is based on the starting materials ammonia, methane, acetone, and methanol, but without the additional use of sulfuric acid and without the necessity to recycle considerable amounts of spent acid. This not only eliminates the by volume largest feedstock (sulfuric acid), but also eliminates the sulfuric acid recovery section of the plant. Reprocessing is time-consuming and quite costly, and the elimination of the reprocessing of the spent sulfuric acid cuts both capital investment and energy use.

- **MGC New Process**

ECONOMICS

The following cost estimates have been developed and discussed in the report:

- Acetone cyanohydrin (ACH) route to produce MMA

  (including cost of production estimate for HCN from a using the Andrussow process)

- Isobutylene oxidation (" i-C_4") route to produce MMA

  (including cost of production estimate for isobutylene via MTBE cracking process)

- Tertiary butyl alcohol oxidation route to produce MMA
- BASF route to produce MMA

  (including cost of production estimate for syngas (H_2/CO=1/1) via methane steam reforming and cost of production estimate for formaldehyde (37 percent) via methanol oxidation using a silver catalyst)

- Asahi " direct metha" route to produce MMA
- MGC (including HCN recycle) route to produce MMA

  (including raw material consumption analysis for MGC process (HCN recycle) route versus MGC new process (NH_3 recycle) route to MMA)

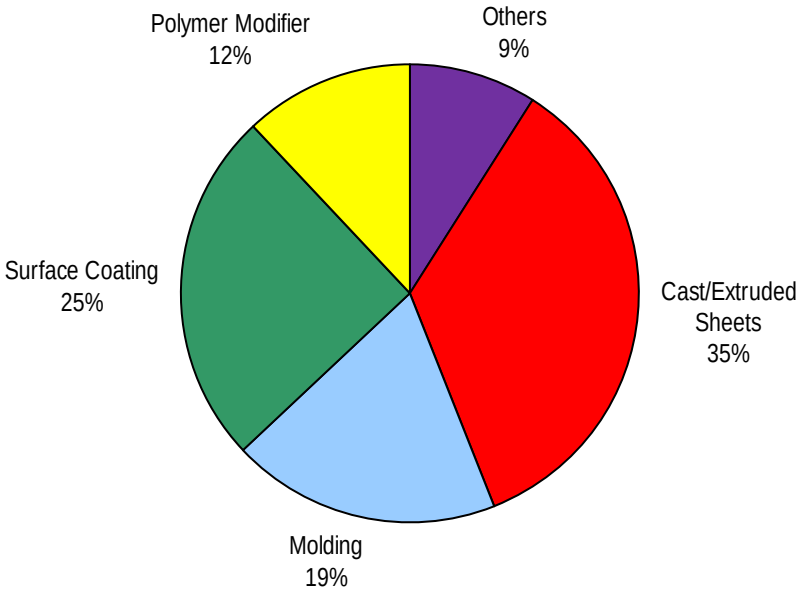
- Lucite-Alpha methyl propionate process to produce MMA
- Evonik's Aveneer® process to produce MMA

Also in this section, the sensitivity of the process economics as a function of feed price, utilities price, capital investment, and economy of scale are analyzed to illustrate the effects on the base case economics presented. These results can also be used to make approximate comparisons between cases for which detailed economics have not been provided by adjusting for capacity differences, alternative feedstock valuation, etc.

COMMERCIAL APPLICATIONS

Methyl methacrylate (MMA) is a mature product with well-established uses. MMA is used to make homopolymers (PMMA) and a wide variety of copolymers. PMMA has been widely used for many years as a substitute for glass due to its clarity, lightweight, and resistance to the effects of UV light and weathering. The end-uses for MMA are discussed further in the report.

Global MMA End-Uses



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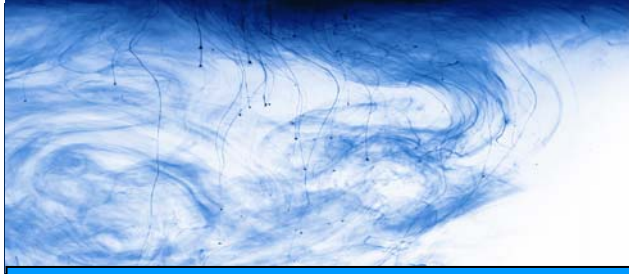
- Global demand is discussed
- Global supply is discussed including global capacity tables listing company, location specific plant capacity and production process utilized at site
- Global trade balance is discussed



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