Trends and Future of Monomer - MMA Technologies

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MMA production is one of the core businesses of the Basic Chemicals Sector of Sumitomo Chemical, and its demand and capacity is continuously going to be expanded, mainly in Asia. Now five technologies for monomer-MMA production coexist in the world, and none of them is the predominant process. Among those technologies, the C_4 methods are going to be adopted in many production plants. Sumitomo Chemical also selected this technology for its MMA production. In this paper, the current processes, mainly for C_4 methods, and the next generation of potential technologies will be reviewed.

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Introduction

Polymethyl methacrylate (PMMA) can be considered the queen of resins, because it is the most beautiful of synthetic resins. Making use of its superior transparency, weather resistance and other characteristics, the demand for its use in signboards and displays, lighting equipments, automotive parts, construction related materials and the like has increased. Recently, we have seen a rapid expansion in new fields related to IT, making even greater use of its optical characteristics, for example in light-guiding plates and light diffusion plates for flat panel displays. Not only are there uses for methyl methacrylate (MMA), in the form of monomers of these resins, but also there is a demand for comonomers in fields such as coatings, adhesives and plastic modifiers. In addition, higher esters like butyl-ester produced by esterification of methacrylic acid (MAA), which is an intermediate in MMA synthesis, or by transesterification of MMA, are used in a variety of applications.

MMA production is one of the core businesses of the Basic Chemicals Sector of Sumitomo Chemical Co., Ltd., and we are actively expanding these operations in Asia, where the demand for monomers and polymers is increasing rapidly. The world demand for MMA is growing steadily, and it exceeded 2.3 million tons in 2003. **Fig. 1** shows the demand and supply predictions estimated by the Sumitomo Chemical Methacrylates Division. A great amount of growth will be expected in Asia, especially in China.

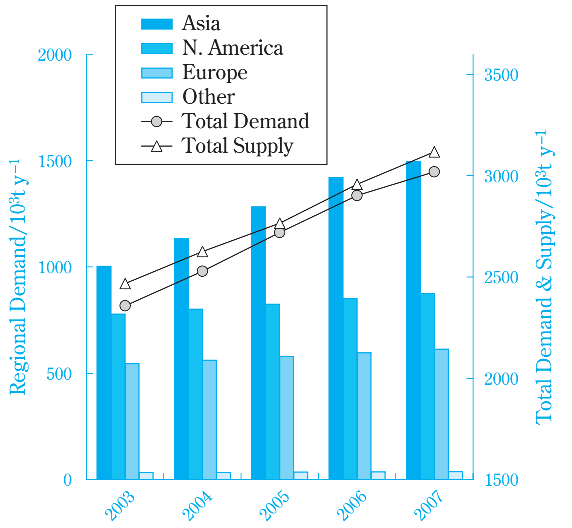


Fig. 1 Forecast world MMA demand and supply (estimated by Sumitomo Chemical Methacrylates Division).

In this article, we will comment on the trends in MMA production technologies. It is usual in bulk chemicals production that the one or two most competitive methods will survive, but there is a special situation in MMA production, where five methods currently coexist. Furthermore, in contrast to the fact that in Europe and the U.S. the most extended method is the traditional acetone cyanohydrin (ACH) process as shown in **Fig. 2**, other methods are already dominant in Japan and Asia. Most of these new methods have been developed in Japan.

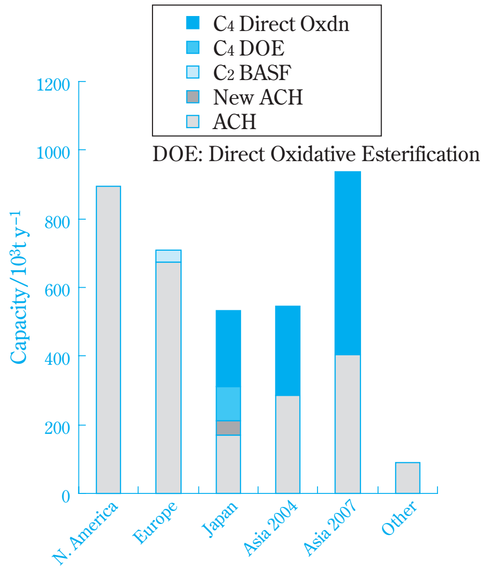


Fig. 2 World MMA capacity and technologies (2004).

Sumitomo Chemical has commercialized a direct isobutylene oxidation method in cooperation with Nippon Shokubai Co., Ltd. This was introduced in the journal SUMITOMO KAGAKU in 1992,$^{1)}$ and this article is a continuation of that one. The Sumitomo Chemical / Nippon Shokubai technology has expanded to five plants, including plants in Korea and Singapore, and another plant is being constructed. Moreover, plans for further expansion are also progressing. **Table 1** shows the history of Sumitomo Chemical's MMA operations.

Table 1 History of MMA in Sumitomo Chemical.

1962	Start to research on C_4 direct oxidation
1964	Introduction of SOHIO acrylonitrile (Niihama)
1967	Introduction of MMA polymer (Sumipex) from ICI
1967	Start production of monomer-MMA (ACH process)
1982	Semicommercial C_4 Direct Oxidation by Nippon Shokubai (Himeji)
1982	Foundation of Japan Methacryl Monomer (J/V with Nippon Shokubai)
1984	Start JMM Niihama plant
1889	Start JMM Himeji plant
1993	Start LGMMA plant (Korea)
1998	Start SMM plant (Singapore)
2002	Business exchange Acrylic acid and MMA with Nippon Shokubai
2003	Start LGMMA 2nd plant
2005	Scheduled start SMM 2nd plant

History of MMA Production

Methacrylic resin is old, having been introduced to the world by Rohm & Haas in the 1930's. Then, ICI developed and commercialized the ACH process in 1937. In Japan, Asahi Glass Co., Ltd. and Fujikura Kasei Co., Ltd. started production in 1938. After that, the ACH method was actually the only industrial production method for MMA for 45 years until Mitsubishi Rayon Co., Ltd. and Nippon Shokubai independently commercialized the direct oxidation method in 1982. The raw materials for the ACH process are acetone and hydrogen cyanide. With the sudden rise and development of petrochemistry following World War II, it was possible to obtain acetone as a byproduct of phenol and hydrogen cyanide as well as from acrylonitrile production. In this way, there is an aspect of concerted development along with these products. Sumitomo Chemical also entered the MMA business after introduction of the Sohio acrylonitrile process.

However, with the increase in demand for MMA and with the changes in the world's way of looking at industrial activity in terms of pollution problems and the like, important weaknesses in the conventional ACH method were revealed, and there was a strong demand for changing the production method. The first weakness of the ACH method is the difficulty of acquiring the cyanide. In Japan in particular, almost all of the cyanide raw material for ACH is the byproduct of the Sohio acrylonitrile process, and for conventional Japanese makers who produced only several ten thousands of tons MMA per year, cyanide synthesis on purpose could not be feasible. The second weakness of the ACH method is processing the waste acid originated from the use of sulfuric acid. The ACH process produces a large volume of ammonium bisulfate contaminated with organic materials as a byproduct. At one time, there were cases of this waste acid being disposed of in the ocean. In addition, it is said that deep well processing, the name for disposing of something deep in the earth without processing it, has been adopted in the U.S. and other places. Since these methods are no longer permissible, recovery as ammonium sulfate with addition of ammonia, or recovery as sulfuric acid by investing in facilities for super corrosion resistant materials, as well as a need for large amounts of energy, is becoming a large financial burden.

In Europe and the U.S., it can be assumed that there has been little progress in changing the production method because there are large plants for which the costs are feasible even if hydrogen cyanide is produced by synthesis, and since the pressure on waste acid treatment has not been intense. However, the situation in Japan is as described above, thus all MMA makers have converted to their own new methods, even though there are some companies retaining some ACH processing.

Table 2 lists the capacities and production methods for six Japanese MMA producers. In addition, there have been repeated alliances and ruptures among Western MMA makers, and now there are four groups. The history of their rearrangements and capacities is shown in **Fig. 3**.[2)]

Table 2 Japanese MMA makers.

Company, Group	Technology	Capacity 10^3 t/y	Remarks
Mitsubishi Rayon	ACH	107	
	C_4 DO*	110	
Thai MMA (MRC45%)	C_4 DO	70	2004 +15 debottleneck
China	C_4 DO	(90)	2006 start
Sumitomo Chemical (Nippon Shokubai)	C_4 DO	90	(NS 18)
Korea, LGMMA (SC25%, NS25%)	C_4 DO	100	
Singapore, SMM (SC100%)	C_4 DO	53	2005 +80 increase
Asahi Kasei	C_4 DOE**	100	
Kuraray	ACH	65	
	C_4 DO	20	Kyodo Momomer
Mitsui Chemical		20	
Korea, Honam Petrochemical (licence)	C_4 DO	40	
Mitsubishi Gas Chemical	New ACH	51	

*C_4DO: Isobutylene Direct Oxidation

**C_4DOE: Isobutylene Direct Oxidative Esterification

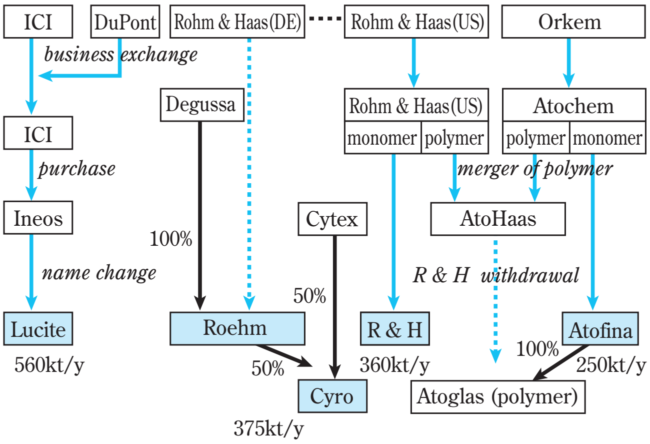


Fig. 3 Relations between Western MMA makers.

MMA Synthesis Routes

Methyl methacrylate or methacrylic acid are simple molecules, but many routes have actually been thought up for making them from even simpler molecules, and a variety of raw materials, C_1 through C_4, are used. Besides the routes described below, there are many for which patent applications have been made as variations and possible routes. We will describe the routes that are already commercialized and those that were once commercialized. We will also discuss processes for which there have been announcements of future commercialization and the isobutane process, which has

Table 3 MMA production technologies.

Process	Raw materials (without methanol)	Feature, Issue	Important catalytic reaction	Maker	Industrialized
ACH	Acetone HCN, H_2SO_4	Supply of HCN Waste treatment			1937–
C_4 Direct Oxidation	Isobutylene (TBA)	2 step oxidation and esterification	1st oxidation; Mo-Bi 2nd oxidation; Mo-P	Mitsubishi Rayon Sumitomo/Nippon Mitsui/Kuraray	1982–
MAN	Isobutylene NH_3, H_2SO_4	Via methacrylonitrile Waste treatment	Ammoxidation; Mo-Bi	Asahi Kasei	1984–1999
C_4 DOE*	Isobutylene (TBA)	Oxidative esterification of methacrolein	1st oxidation; Mo-Bi Oxidative esterification; Pd-Pb	Asahi Kasei	1999–
New ACH	Acetone (HCN) $HCOOCH_3$	HCN recycle Not use H_2SO_4 Too many steps	Amidation; MnO_2 Esterification; NaOMe Dehydration; Zeolite	Mitsubishi Gas Chemical	1997–
C_2 BASF	Ethylene CO, H_2, HCHO	Use two C_1 compounds Via propionaldehide	Condensation; Amine Oxidation; Mo-P	BASF	1989–
Alpha Process	Ethylene CO, HCHO	Use two C_1 compounds Via methylpropionate	Carbonylation; Pd complex Condensation; Cs/SiO_2	Lucite	Plan (2008)
Propyne	Propyne, CO	Yield 99% Lack of resource	Carbonylation; Pd complex	Shell (Lucite)	Not yet
Isobutane	Isobutane	1 step oxidation	Oxidation; Mo-P		Not yet

*DOE: Direct Oxidative Esterification

the greatest expectations for the future.

Naturally, there are strict quality requirements for MMA, but it is a bulk chemical that is popular for swapping. Since it is not a product that gets added value from product function or quality, the only point motivating the comparison and investigation of various processes is the production at the lowest cost. The cost can be calculated from variable costs for the main raw materials (price and amount), steam, electric energy and the like, and fixed costs focusing on the cost of facilities. However, the price of the raw materials normally varies by location, and it varies greatly according to whether the company has to purchase the raw materials or produces them itself. It is difficult to accurately estimate facilities costs and the amount of steam, secondary raw materials, catalysts and the like unless one is involved in the process development. For example, there are frequently minute amounts of byproducts that must not be in the product, and a large amount of energy being required to separate them out. Each company has its own situation concerning this point, and it is difficult to accurately compare and evaluate the processes without knowing the prerequisite conditions. Therefore, this article will only cover the general characteristics of each production method and a qualitative evaluation.

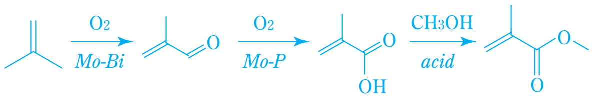
Simple profiles of the various production technologies are brought together in **Table 3**. Most of the development effort for all of the technologies is spent in catalyst development, but reviews focusing on catalyst techynology 3) – 6) and descriptions focusing on processes 7), 8) have already appeared.

Industrialized processes

1. ACH Process

The ACH process is the predominant method in Europe and the U.S., but as it is a technology from the past, we will not discuss it in this article.7) – 9)

2. Direct Oxidation Process



Direct oxidation processes have as their raw materials isobutylene or tert-butyl alcohol (TBA), and MMA is produced by esterification of methacrylic acid (MAA), which is obtained by a two-step oxidation reaction.

It has already been 20 years since the isobutylene direct oxidation process was commercialized. It was independently developed by three groups in Japan; Mitsubishi Rayon, Japan Methacryl Monomer (Sumitomo Chemical and Nippon Shokubai) and Kyodo Monomer (Kuraray and Mitsui Chemicals), and all three groups not only have domestic plants, but also have progressed overseas with plants in South Korea (Sumitomo Chemical / Nippon Shokubai, Kuraray / Mitsui), Singapore (Sumitomo Chemical / Nippon Shokubai) and Thailand (Mitsubishi Rayon). Mitsubishi Rayon is constructing a plant in China. It can be assumed that this proves that, at least based on new construction in Asia, this method is clearly superior to the ACH process economically. The reaction routes for the three processes are basically the same, but while the Sumitomo Chemical / Nippon Shokubai method has isobutylene as raw material, the Mitsubishi Rayon and Kuraray / Mitsui Chemicals have TBA. Furthermore, while the Sumitomo Chemical / Nippon Shokubai method is a two-step direct combination, the Mitsubishi Rayon method differs in separating methacrolein from a gas produced in the first step and afterwards carrying out the second oxidation reaction. Comparatively detailed reports have been published on Japan Methacrylic Monomer and Mitsubishi Rayon.10) – 12)

As will be discussed later, the Asahi Kasei Corp. methacrylonitrile (MAN) method and the direct oxidative esterification process have TBA as the raw material. However, isobutylene is contained in the C_4 stream at ethylene plants or cracked gasoline plants (FCC), leading to a situation where the technology for separating it had to be developed at the same time as the MMA process. Since the boiling points of isobutylene and 1-butene in the C_4 stream are similar, it is difficult to separate them by distillation. All the companies developed processes for reaction and separation that used catalyst technology. Sumitomo Chemical obtains high purity isobutylene using a method that works via methyl tert-butyl ether (MTBE). This method is also effective when one wants to obtain the high purity 1-butene used in LLDPE comonomers. This was made practical through the development of a highly selective, long-life, unique solid catalyst as the decomposition catalyst for MTBE, in which silica was impregnated with a metal sulfate and heat-treated. The Mitsubishi Rayon and Asahi Kasei processes are methods that have a strong acidic ion exchange resin and a heteropolyacid aqueous solution, respectively, as the catalyst, and selectively hydrate the isobutylene in the C_4 stream for synthesis and separation as TBA. The Asahi Kasei method of using a concentrated aqueous heteropolyacid solution is unique from the standpoint of catalyst technology.14)

After the commercialization of direct oxidation methods, there was a sudden expansion in the demand for MTBE as a gasoline additive, so that the byproducts of naphtha cracker, FCC and the Oxirane process (propylene oxide) were insufficient. Therefore, dehydrogenation of isobutane in C_4LPG has come to be carried out on a large scale. The fact that MTBE exists in large quantities as a product means that there is a possibility for acquiring the raw material for the direct oxidation process anywhere in the world, but in turn, since its cost moves with the price of expensive gasoline, it is hard to purchase as a MMA raw material, and this can be thought of as one reason that the C_4 direct oxidation process has not disseminated to Europe and the U.S. MTBE has been related to well water contamination due to leakage from underground gasoline tanks in the U.S., and starting with California, various states prohibited it, with the U.S. prohibiting it several years later. This should not immediately spread to Europe, but (Japanese oil companies abolished it voluntarily) the U.S. was the largest consumer of MTBE, so its influence will be great. Since there is a worldwide excess in facilities for MTBE, we can think that there will be a trend toward easily acquiring raw materials for Sumitomo Chemical / Nippon Shokubai with their process that uses decomposition of MTBE.

When Sumitomo Chemical / Nippon Shokubai uses isobutylene as the raw material, the first step reaction is somewhat different from the methods of Mitsubishi Rayon and Kuraray / Mitsui Chemicals that use TBA. Being able to use TBA in the same manner as isobutylene is due to the fact that it easily breaks down into isobutylene and water at high temperatures on the first step catalyst. This reaction is endothermic, and since the inlet catalyst does not work effectively as a methacrolein synthesis catalyst, an inexpensive decomposition catalyst such as alumina can be used. In addition, since the first step reaction is possible under anhydrous conditions, not only is a number of moles of water equal to that of isobutylene always generated with TBA, but also a small amount of water is normally included in the TBA raw material in connection with purification. Thus, there are differences with the isobutylene process in terms of the nature of the first step reaction and the input and release of energy. However, since it can be assumed that the energy for producing TBA is less than the energy for producing isobutylene, this difference may compensate the additional energy required for the TBA dehydrogenation to isobutylene.

In addition, there is a large difference in the process makeup between the Sumitomo Chemical / Nippon Shokubai first and second step direct combination (tandem method), and the Mitsubishi Rayon methacrolein separation method (separation method). **Fig. 4**15) and **Fig. 5**16) show the oxidation processes for both. From the standpoints of facilities and energy, the tandem

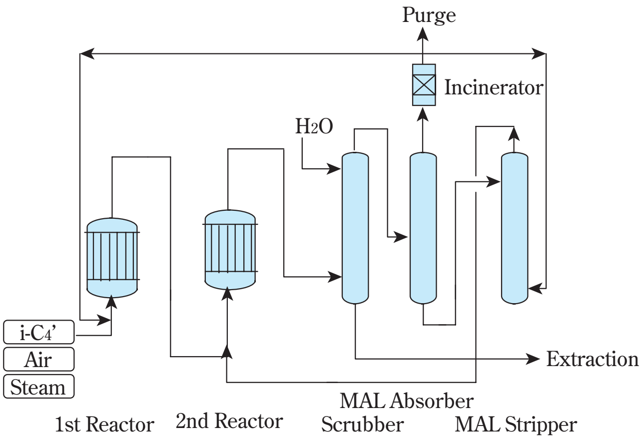


Fig. 4 Tandem C_4 direct oxidation process15).

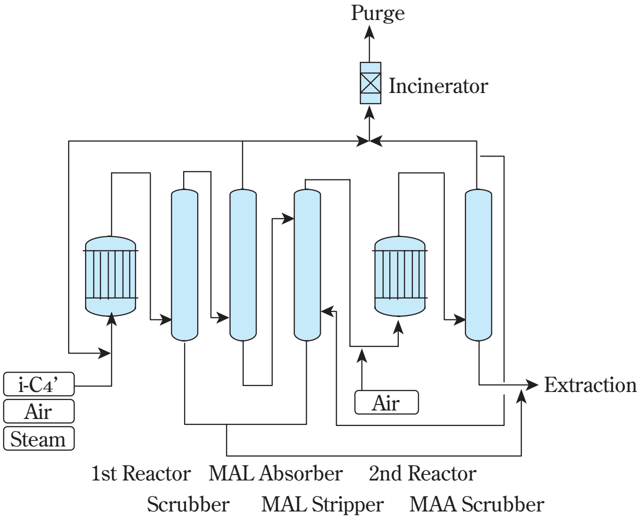


Fig. 5 Separate C_4 direct oxidation process 16).

method is advantageous. With the separation method, the equipment for methacrolein recovery is not only large and complicated, but also needs the energy for it. In addition, the air required must be separated for the first and second steps, and excess power and preheating are applied. On the other hand, the separation method is advantageous in terms of reaction. The gas generated in the first stage is supplied directly to the second step in the tandem method, so the unreacted isobutylene and high boiling point byproducts are brought to the second step without alteration. Since isobutylene, in particular, inhibits the second step reaction, the first step conversion must be as high as possible. Since the reaction in the second step is inhibited by isobutylene and the byproducts, and there is a limit to the methacrolein concentration, a large reaction vessel is necessary for the tandem method, and there are many restrictions compared with the separation method. With the tandem method, the requirements for catalyst performance can be said to be strict, but the problem has been solved by Sumitomo Chemical / Nippon Shokubai using a first step catalyst that has an extremely high conversion rate without lowering the yield, and a tough, long-life second step catalyst that exhibits sufficient capacity even in the presence of poisonous materials.

The heart of the direct oxidation process is the catalytic two-step oxidation reaction. This reaction is similar to the synthesis of acrylic acid by direct oxidation of propylene. Our research into direct oxidation of isobutylene started at about the same time as that for propylene oxidation, but commercialization was ten years later than acrylic acid. The fact is that it was that difficult to develop the catalysts. The first step catalyst is a Mo-Bi multi component composite oxide catalyst similar to that for propylene oxidation. In contrast, the catalyst developed for the second step is a PMo heteropolyacid catalyst with a structure that differs from the Mo-V catalyst for acrolein oxidation.

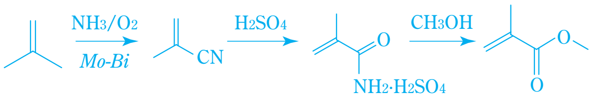
The first step catalyst is a Mo-Bi-Fe-Co/Ni-A (A: alkali metal, alkaline earth, Tl) composite oxide, and is similar to that for propylene oxidation. However, as the reactivity of isobutylene is different from that of propylene, if a propylene oxidation catalyst is used as is, the activity would be too high, with progression to complete oxidation and low yield. This was optimized for isobutylene by increasing the amount of alkali metal additive.

The second step catalyst is based on a heteropolyacid with an anion structure known as the Keggin structure of $[PMo_{12}O_{40}]^{3-}$. It has uniformly strong Broensted acidity because of the presence of protons as paired cations and suitable oxidation strength originating in Mo. Free 12-molybdophosphoric acid ($H_3PMo_{12}O_{40} \cdot nH_2O$) itself does not exhibit such a good yield, and as a fatal defect, its thermal stability is poor and the structure breaks down, so the catalyst life is short. It was found early on that forming a heteropolyacid with a configuration where some Mo atoms are replaced with V, and a crystal structure with a salt structure where some protons are replaced with alkali metals was effective for the yield and life. It was brought to the level of a practical catalyst by controlling the addition of other minute components, surface area and the volume of micropores.

However, the level of the second step catalyst performance is not at all satisfactory yet. Compared with acrylic acid, the selectivity is insufficient, and if the conversion is raised it gets worse. Since the activity is insufficient and there is a problem with the life, the productivity per unit catalyst is low. This is one major reason for the isobutylene direct oxidation process not having established a firm position as that of the direct propylene oxidation process for acrylic acid. Therefore, a great effort, including that by Sumitomo Chemical, is continuing to be put into improving the performance. Many patents have been issued regarding catalyst composition, and P and Mo are necessary, but almost every element in the periodic table has been claimed as an additive. However, there have been investigations recently into catalyst preparation methods such as additives, molding methods, forming and calcination. Sumitomo Chemical has developed good catalysts with superior durability using its own catalyst preparation methods, and it has been possible to achieve good productivity. Catalysts that not only increase yields but also improve the work rate through increased life and can handle increased production due to increasing loads have great merits recently with the strong demand for MMA.

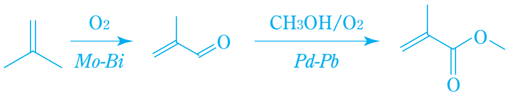
Efforts toward further improvements are also continuing at present for processes such as for example acrylonitrile and ethylene oxide, which have been already completed, and if we consider the fact that compared with the first commercialization time, the performance has assuredly improved, we can assume that efforts toward steady improvements in performance in the future will be indispensable for the relatively new process of direct oxidation to survive as a competitive MMA production method.

3. MAN Process



Asahi Kasei developed a route through methacrylonitrile, using isobutylene (TBA in fact) as raw material and commercialized it in 1984.[19] Acrylonitrile is produced in large quantities by the ammoxidation of propylene known as the Sohio process, but it is also possible to convert isobutylene to methacrylonitrile through a similar catalytic reaction. Asahi Kasei developed a catalyst for this reaction by modifying an acrylonitrile catalyst, based on existing patents, with a similar yield to that of acrolonitrile. In addition, the hydration and esterification processes that follow are similar to the ACH method, and since the yield is high, it can be assumed that the yield from isobutylene is superior to that of direct oxidation. However, the disadvantage of using ammonia as a secondary raw material is a large waste, and as with the ACH process, the production of ammonium bisulfate cannot be avoided. Because of these problems, Asahi Kasei developed the direct oxidative esterification process that will be discussed next and changed the production to the new method in 1999.

4. Direct Oxidative Esterification Process

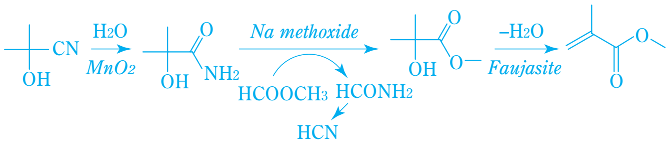


Asahi Kasei developed and commercialized the method known as the direct oxidative esterification process as one that uses TBA as the raw material but does not produce ammonium bisulfate as a byproduct. The first step reaction is the same as direct oxidation, and methacrolein is obtained from gas phase oxidation of TBA. In the later step, oxidative esterification of the methacrolein is carried out in a liquid catalytic reaction in methanol to obtain MMA directly.[20), 21)] Not only are ammonia and sulfuric acid unnecessary, but there is a reduction of processes compared with direct oxidation. Since the yield is higher than that of direct oxidation, this can be basically assumed to be a competitive method. There are many inquiries from overseas, and there has been a joint F/S announcement with a company in Taiwan, but no specific plan has been announced yet.

Asahi Kasei discovered that this reaction progresses selectively and well with a Pd-Pb catalyst, but investigations into this method were frozen temporarily with the commercialization of the MAN method. It was necessary to overcome the problems of productivity, byproducts and catalyst life for commercialization, but with ingenuity in precision synthesis of intermetallic compound catalysts, carriers and catalyst supporting methods, and breakthroughs such as the use of a “reductive oxidation reaction environment” with a lower partial pressure for oxygen, it could be built up commercially with success.

The merits of this method compared with the direct oxidation method allow lower facilities costs, because the second stage gas phase oxidation can be eliminated and the total yield is high. On the other hand, the collection of methacrolein, recycling of excess methanol, separation of byproducts and the like can be assumed to require a large amount of energy. It appears that there is a problem of the yield dropping when trying to raise productivity and reducing the excess methanol to reduce recycling. We can assume that selectivity does not exceed the 95% stated in the patents. In addition, since the direct oxidation process is carried out at high-temperature in gas phase, the reaction heat is recovered almost completely. It is highly possible that most of the reaction heat in the liquid phase reaction at 100°C or less is wasted. It is said that the life of the catalyst for the later step oxidative esterification reaction is sufficiently long, but the initial investment is very large, and the trends in the price of Pd may affect the adoption of this method. Even with these problems, among the methods being used, the direct oxidative esterification process is the greatest rival technology for the direct oxidation, and we can assume that it will be necessary to follow the trends in the future.

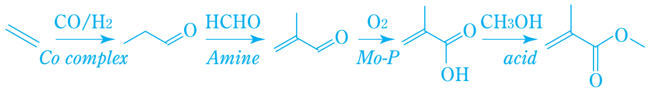
5. New ACH Process



The problems for the conventional ACH process were the problems in the cyanide supply and with large quantities of ammonium bisulfate byproducts. However, Mitsubishi Gas Chemical Co., Inc. developed a new ACH process that solves these two problems and commercialized it in 1997.[22] First of all, the reaction hydrates ACH using a catalyst based on manganese oxide that does not use sulfuric acid, making α-hydroxyisobutyramide, and next forming methyl α-hydroxyisobutyrate by means of an amide ester substitution reaction using methyl formate. Sodium methoxide is used in this catalyst. This methyl formate becomes formamide, generating hydrogen cyanide in the formate dehydration, which is recycled and used in the ACH synthesis process. MMA is made through a dehydration reaction with methyl α-hydroxyisobutyrate. The two dehydration reactions are carried out in the gas phase using solid catalysts.

This process solves the cyanide problem and waste problem of the ACH process with an admirable course of action, but there are a large number of reaction steps, and since each step requires separation and purification, increased consumption of energy cannot be avoided. In addition, the comparatively specialized intermediate methyl formate is required, which is produced at a special site of Mitsubishi Gas Chemical, so a business in this process could be started.

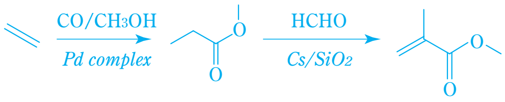
6. BASF Process



One of the MMA production methods that uses ethylene as a raw material was developed by BASF, and a plant that produces 40,000 t/y of MMA along with 5,000 t/y of methacrylic acid was built in 1989.[23] The reaction of propionaldehyde and formaldehyde is an almost completely quantitative reaction carried out in a tubular reactor in the presence of a secondary amine and acid. The processes after methacrylic acid synthesis are the same as for the isobutylene direct oxidation process, and the BASF oxidation catalyst is a heteropolyacid similar to those developed by various Japanese companies. BASF already had propionaldehyde and formaldehyde, and the new construction was for the methacrolein synthesis process onward. This is a production method suited to the conditions of the BASF location, and in terms of the BASF circumstances, it can be assumed that they wanted not only MMA but also higher esters, so the method of taking this out as methacrylic acid was used. Therefore, it is difficult for this to become a general MMA production method, and subsequently there has been no announcement of more new facilities.

Other processes in development

1. Alpha Process

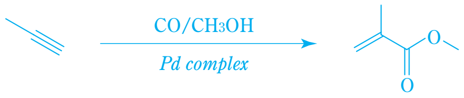


For a long time, many companies have investigated the route through propionic acid or methyl propionate with ethylene as raw material, but recently Lucite established this method as the alpha process and is currently carrying out pilot tests. It has been announced that it will be commercialized by around 2008.[24]

Propionic acid has already been commercialized, but the alpha process newly employs a process for directly synthesizing methyl propionate from ethylene, methanol and CO. MMA is obtained through gas phase condensation of methyl propionate and formaldehyde. It is a simple process for deriving MMA in a two-step reaction from C_2 ethylene. Because of the development of a Pd complex catalyst, the methyl propionate synthesis progresses substantially quantitatively. The condensation process that follows is the key to its practical application. The reaction occurs in the gas phase, and a Cs/SiO_2 solid base catalyst is used for the catalyst. These catalysts have been studied for a long time by Amoco and Mitsubishi Rayon, but while both have a high selectivity of 80 – 90%, the reactivity is not greater than 20 – 30% in a single pass. In addition, it is said that there is a problem with catalyst life, and just how far the catalyst performance can be improved is extremely interesting.

The economics of the process are largely controlled by the raw material situation, but the raw materials necessary for this process are ethylene, CO, methanol and formaldehyde. All of them are general-purpose raw materials that are produced in large quantities, but it is difficult to say if the alpha process, which must purchase all of them on a market price basis, is better than the direct oxidation process or the ACH process. If there is a location that has inexpensive ethylene and large methanol and formaldehyde plants, the circumstances probably change greatly.

2. Propyne Process

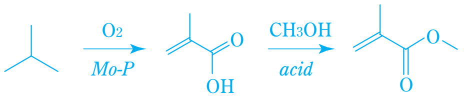


The propyne process developed by Shell is an extremely fascinating process that produces MMA with a yield of 99% in a one step reaction. The production of acrylic acid by carbonylation of acetylene (Reppe process) has been replaced with direct oxidation of propylene, and BASF has already shut down its last plant. However, for propyne the yield was insufficient with a reaction system similar to that for acrylic acid synthesis. Shell found that this reaction progressed with a good yield with a system made up of palladium acetate, organic phosphine and a protonic acid. For example, a system using 2,6-bis (diphenylphosphine) pyridine achieved a very good reaction record with a yield of 99%, 100,000 mol MMA/mol Pd.[27]

A separation process combined with distillation that includes an amount of ethylene of several percent in a naphtha cracker C_3 stream for the raw material propyne (and propadiene), extraction and isomerization of propadiene, was developed, but even at a 1,000,000 t/year ethylene center, there will only be 40,000 – 50,000 t/y of MMA, and the major limiting condition is the problem of raw materials. At present, this process technology has been assigned to ICI by Shell and can be thought of as belonging to Lucite, but it seems that they have no will to commercialize it now.

Moreover, there is also the isobutyric acid process among the methods that were actively researched in the past for processes using C_3 as a raw material. Isobutyric acid is synthesized by means of an HF catalyst from propylene and CO, and methacrylic acid is derived by oxidative dehydrogenation. The performance of the later step catalyst is insufficient, and it has been abandoned.

3. Isobutane Process



All of the methods discussed up to the present have unsaturated hydrocarbons as the raw material, but we will focus on a method that uses isobutane as the raw material and obtains methacrylic acid in a single step. Unsaturated hydrocarbons, which are the raw materials for petrochemistry, are made by investing a large amount of energy in saturated hydrocarbons, natural raw materials. For example, to produce 1 kg of ethylene from naphtha, approximately 20 MJ of energy are required, and approximately 0.4 kg are necessary per hydrocarbon fuel calculations. The basic situation for isobutylene is the same. If direct synthesis of MAA from isobutane (separated from C_4LPG), which is an upstream resource, was possible, it can be assumed that a process that is advantageous in terms of energy and economics could be obtained, and effort is being put into its development.

Rohm & Haas discovered that this reaction progresses with a heteropolyacid catalyst composed of Mo-P-Sb-O,[28] and after that Asahi Kasei, Sumitomo Chemical and Mitsubishi Rayon and others discovered that with a heteropolyacid catalyst similar to the current methacrolein oxidation catalyst approximately 70% selectivity for methacrylic acid and methacrolein could be achieved. One of the three equivalent methyl groups on isobutane is kept, another methyl group is dehydrogenated, while the third is carboxylated. It can occur on the same catalyst, even though it is surprising for a high level chemical reaction. At present this has not reached a catalytic performance level that makes commercialization possible, and it is thought that a practical application will take just a little more time.

As a part of the NEDO Simple Chemistry Project, we are participating in the development of saturated hydrocarbon selective oxidation reaction technology, and since reaction mechanisms have been examined and processes evaluated, an outline is given below.[32)–35)]

The catalyst used is a heteropolyacid catalyst formed from Mo-P-V-As-Cu, which has exhibited a good record in current methacrolein oxidation. **Fig. 6** shows a typical reaction performance. If the conversion rate is high, the selectivity suddenly falls, and a yield of only about 10% is obtained.[35]

Fig. 7 shows the reaction paths that can be considered. Isobutylene is the first intermediate, and it has been confirmed that this is the rate-limiting step. **Table 4** shows the rate constants for each step.[34] It is known that the isobutylene formed by dehydrogenation pro-

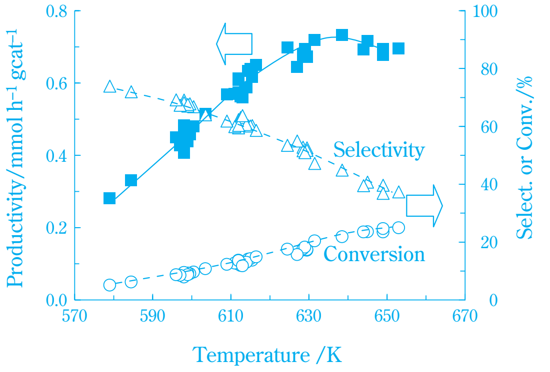


Fig. 6 Typical reaction performance. (■) productivity of MAL+MAA, (○) conversion of isobutane, and (△) selectivity to MAL+MAA. Feed composition: [isobutane]=25 vol.%, [O_2]=25 vol.%, [H_2O]=15 vol.%, [N_2]=balance. Operating conditions: SV=1000 ml$g^{-1}h^{-1}$, P=150 kPa, Contact time=5.4 s.

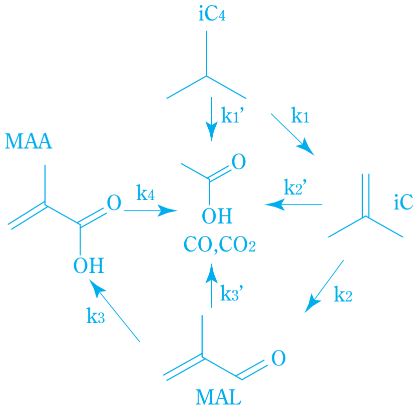


Fig. 7 Scheme of isobutane selective oxidation reaction.

Table 4 Kinetic parameters of isobutane oxidation reaction on Mo-P-V-As-Cu-Cs heteropolyacid catalyst.

	Ea_x/kJ mol^{-1}	k_x/s^{-1} (at 573K)	k_x'/s^{-1} (at 573K)	$k_x/(k_x + k_x')$
iC_4 (x=1)	84.3	0.0084	0.0015	0.85
iC_4' (x=2)	57.0	4.10	1.03	0.8
MAL (x=3)	60.5	1.16	0.06	0.95
MAA (x=4)	135	0.0185		

$$d[iC_4]/dt = -(k_1+k_1')[iC_4]$$
$$d[iC_4']/dt = k_1[iC_4] - (k_2 + k_2')[iC_4']$$
$$d[MAL]/dt = k_2[iC_4'] - (k_3 + k_3')[MAL]$$
$$d[MAA]/dt = k_3[MAL] - k_4[MAA]$$

gresses to methacrylic acid comparatively rapidly and with high selectivity, but the target MAA is oxidized at a rate twice that of the isobutane reaction, causing the selectivity to drop. However, it is known that the MAA combustion is inhibited by the coexistence of isobutane, thus even if the conversion is low, if the isobutane concentration and the pressure are increased, this process can be taken to a level that is not inferior to the isobutylene direct oxidation method, in terms of MAA productivity. **Fig. 8** shows data on the pressure dependency of productivity.[35]

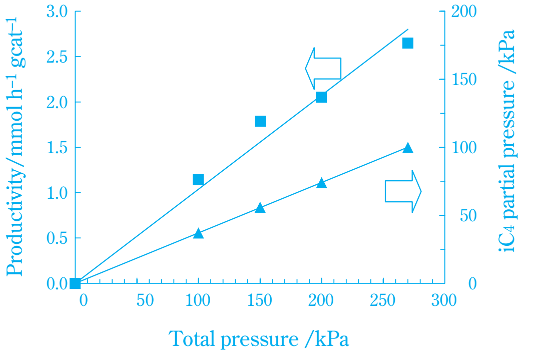


Fig. 8 Influence of the total pressure, at constant P/SV ratio=0.1, on (■) productivity of MAL+MAA, and (▲) isobutane partial pressure. Feed composition: [isobutane]=37 vol.%, [O_2]=37 vol.%, [H_2O]=15 vol.%, [N_2]=balance. Operating conditions: SV=1000–2700 ml$g^{-1}h^{-1}$, P=100–270 kPa, T=623 K, Contact time=3.5 s.

Based on this reactivity, we have proposed a recycling process as shown in **Fig. 9**, and estimated the material balance, energy budget and the like. **Table 5** gives the results of a comparison with the direct oxidation process.[32] The recycling yield is approximately 52%, but the part going to the combustion reaction can be recovered as energy (steam). Assuming that isobutylene is synthesized by the isobutane dehydrogenation process (the UOP Oleflex process,[36] for example), calculating only the energy invested, we get

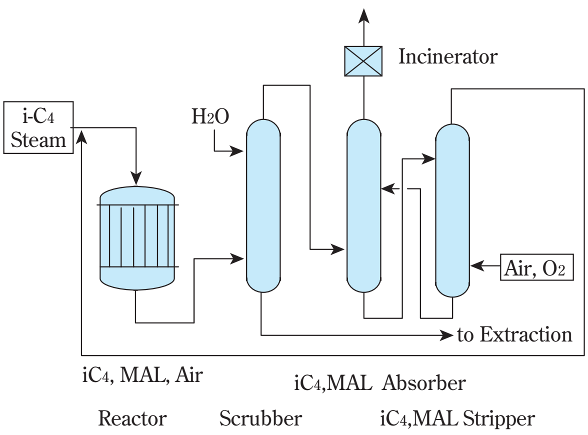


Fig. 9 Supposed isobutane direct oxidation process.

Table 5 Comparison of isobutane process with isobutylene direct oxidation process.

Isobutylene direct oxidation process

Reaction performance			
iC_4’ conv.	100%		
MAA yield	65%		
	Unit consumption /tMMA	**as Fuel/t**	**$/t**
iC_4’	0.86 t	0.991	310
Power	500 kWh	0.10	40
Steam	–1 t	–0.06	–12
Sum		**1.03**	**338**

Supposed unit price

C_4LPG	200 $/t	Power	0.08 $/kWh
Isobutylene	360 $/t	Steam	12 $/t
Isobutane	240 $/t	93%O_2	0.37 kWh/Nm^3

Isobutane direct oxidation process

Reaction performance			
iC_4 conv.	10%		
(Recycle conv.)	96%		
MAA select.	50%		
MAL select.	5%		
(Recycle MAA yield)	52%		
	Unit consumption /tMMA	**as Fuel/t**	**$/t**
iC_4	1.124 t	1.12	270
Power	650 kWh	0.13	52
Steam	–4.5 t	–0.28	–54
93%O_2	1160 Nm^3	0.09	34
Sum		**1.06**	**302**

per 1ton fuel

Power	5000 kWh
Steam	16 t
(Heat	46 GJ)

a value equivalent to 1.15 times the isobutane. This isobutane method requires oxygen enriched air, and energy is necessary for applying pressure and recycling, so with the current catalyst performance it does not reach the isobutylene process in terms of energy by a small margin. If isobutylene is produced from isobutane, the price cannot be 1.15 times, and if the price of isobutylene is as shown in Table 5, calculations of the variable cost advantage of the isobutane process can be established with these figures. However, isobutylene is currently valued as a byproduct of ethylene, cracked gasoline and the like. On the other hand, C_4LPG, which is the raw material for isobutane, is valued independently from naphtha for trading, so the situation is such that isobutane cannot always be called advantageous. It is also necessary to surpass the present methods in terms of energy consumption, and the development of a higher performance catalyst is the key to the realization of this process. The direction of the future improvement of the catalyst that came to the surface from the investigation of the reaction mechanism is moving to a catalyst that has strong durability for the absorption poisoning of isobutylene present as an intermediate, controls the consecutive oxidation of the methacrylic acid produced, and improves selectivity.

Conclusion

A large number of production technologies for MMA monomers have been established in parallel at present, and it seems that the C_4 processes will play a leading role in the near future. The process for obtaining MAA in air oxidation using an unmodified branched C_4 structure should be reasonable. There is a need to follow the future trends in the direct oxidative esterification process and alpha process. However, in order to nurture the direct oxidation process, Sumitomo Chemical / Nippon Shokubai method, as the most competitive MMA technology, we should continue improving the catalytic performance. In particular, concerning the second step heteropolyacid catalyst in the tandem process, a catalyst resistant to isobutylene poisoning is required. In addition, the development of a catalyst with high selectivity that controls the overoxidation of methacrylic acid is desired. This is the direction of the development of isobutane process catalysts. Increasing the performance of current catalysts can be thought of as being directly connected to the development of catalysts for the isobutane process, which is the technology for the future.

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