# A Green & Clean Process for the Production of Methacrylic Acid and Methacrolein from Biofuel

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## ABSTRACT

Excessive consumption of fossil fuels for energy and chemical production has led to global warming and other negative impacts worldwide in recent years. About 10% of U.S. crude oil imports are used to feed its chemical industry, while only about 4% of chemical sales are attributable to renewable origin. Shifting from fossil fuels based to biomass based chemical productions requires enabling technologies. Methacrylic acid and methyl methacrylate are important monomers for the productions of many valuable methacrylate polymers. The annual methacrylate market is about $2.1 and $8.1 billion in the US and worldwide, respectively. Methacrylate is produced mainly from acetone and HCN via the so-called ACH process, which also uses large sums of $H_2SO_4$ and has serious environmental, health and safety issues. A green and clean catalytic process is being investigated, aiming at achieving a sustainable methacrylate production from bioisobutanol, a $2^{nd}$ generation biofuel, as well as to avoid all of the negative issues associated with the ACH process.

*Keywords*: biofuel, bioisobutanol, methacrylic acid, methacrolein, methacrylate.

## 1 INTRODUCTION

Fossil fuels, including coal, petroleum and natural gas, are the primary resources for energy generation and for producing many chemicals in the modern world. The rapid and excessive consumption of non-renewable fossil fuels in recent decades has unfortunately led to not only a substantial depletion of the fossil fuel resources, but also an alarming accumulation of greenhouse gases, which, in turn, has led to global warming and induced ecological imbalance and disastrous climate changes. The dependence on fossil fuels has further caused disputes among nations and exposes countries and businesses alike to economic and social uncertainties. There is urgency for the US and the rest of the world to explore renewable resources for energy and chemical production to sustain the ever expanding human activities while protecting the earth environment and reducing the resources related disputes among nations.

While the need for sustainable energy generation can be met by utilizing various types of renewable resources, such as solar, wind and geothermal, biomass is the only renewable resource that can be used to produce carbon-based fuels and chemicals. The US chemical industry is a $460+ billion enterprise[1]. It is a key element of the US economy and constitutes about 26% of the global chemical production. Approximately 10% of the U.S. crude oil imports are used to feed the chemical industry[2]. The United States has over a billion tons of sustainable biomass resources that can be turned into biofuels for power generation and chemical production. However, recent data indicate that only about 4% of the US chemical sales are attributable to renewable resources[2].

As part of the efforts to gain energy independence, the US Department of Energy has been leading the innovation for the production of bioenergy and bio-based products in the United States[3]. Consistent with its mission, the DOE recently also sponsored our exploratory effort to demonstrate the feasibility of a green and clean technology for the production of methacrylate from bioisobutanol[4].

## 2 METHACRYLATE AND THE FOSSIL FUEL BASED PRODUCTION ROUTES

Methacrylic acid (MAA) and its ester derivatives are common monomers for the production of many polymers. Among all the esters, methyl methacrylate (MMA) is the most useful one and a majority of crude MAA is used for MMA production. MMA is the building block for the production of P-MMA and a variety of co-polymers, which are widely used in construction, transportation, automobile, lighting, electronic and many other businesses. As shown in Fig. 1, the annual MMA market is about $2.1 and $8.1 billion in the US and worldwide, respectively.
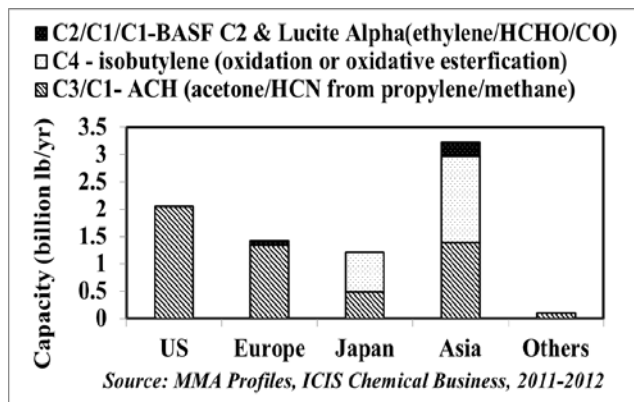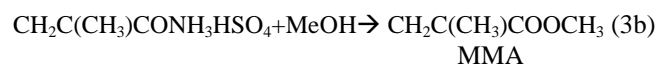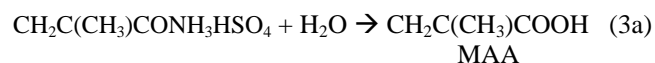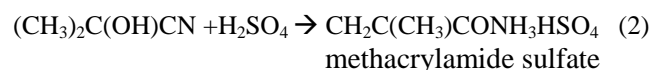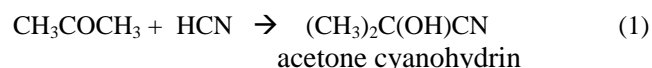


**Fig. 1  MMA Production by Region and Technology**

Also as shown in Fig. 1 and will be discussed in more details below, the ACH process is the predominate technology for MAA and MMA production in the United States and further accounts for about 65% of the methacrylate production worldwide. The second most used production method is the isobutylene process commercialized in Japan and Asia. Together, the ACH and isobutylene processes are the two existing processes accounting for about 95% of MMA produced worldwide.

## 2.1 ACH Process

The commercial production of MMA began in around the 1930s, using a process widely known as the acetone cyanohydrin (thus, the ACH) process. The ACH process starts with expensive feedstocks, acetone and hydrogen cyanide (HCN), which is also highly toxic (eq. 1). The resulting intermediate, acetone cyanohydrin, is subsequently converted to a sulfate ester in the second step with an excessive amount of concentrated sulfuric acid as the catalyst and solvent (eq. 2). The third step is a hydrolysis step leading to MAA (eq. 3a), or an esterification step with methanol leading to MMA (eq. 3b).

$$CH_3COCH_3 + HCN \rightarrow (CH_3)_2C(OH)CN \qquad (1)$$
$$\text{acetone cyanohydrin}$$

$$(CH_3)_2C(OH)CN + H_2SO_4 \rightarrow CH_2C(CH_3)CONH_3HSO_4 \quad (2)$$
$$\text{methacrylamide sulfate}$$

$$CH_2C(CH_3)CONH_3HSO_4 + H_2O \rightarrow CH_2C(CH_3)COOH \quad (3a)$$
$$\text{MAA}$$

$$CH_2C(CH_3)CONH_3HSO_4 + MeOH \rightarrow CH_2C(CH_3)COOCH_3 \quad (3b)$$
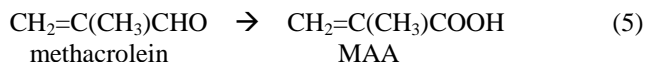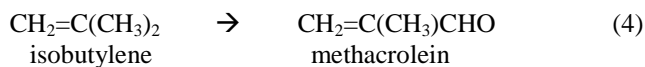$$\text{MMA}$$

For each pound of MAA produced, 0.31 pound of hydrogen cyanide is required as the feedstock, even if the reaction and operation can run at the theoretical efficiency of 100% in each step. For each pound of MAA or MMA produced, the conventional ACH process also requires the use of 1.6 pound of concentrated sulfuric acid as the solvent and the catalyst[5]. Thus, for the annual production of 2 billion pounds of MAA/MMA in the US, in excess of 0.62 billion pounds of HCN must be used, of which the excess amount goes to the toxic streams. Furthermore, about 3.2 billion pounds or more of concentrated sulfuric acid must be used and subsequently regenerated from the diluted discharge, and up to 5 billion pounds of corrosive by-product, ammonium bisulfate, is generated for disposal[6].

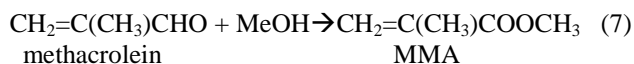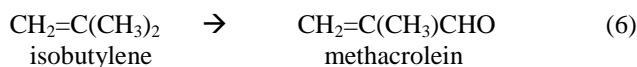## 2.2 Isobutene Routes for MAA and MMA Production

To overcome the drawbacks of the ACH process, various alternative processes for the production of MAA or MMA have been explored over the years. The first alternative process is the two-step direct oxidation process for MAA production from isobutylene (eq. 4-5). This direct oxidation process was developed and commercialized by Mitsubishi Rayon, Sumitomo and Kyodo Monomer, respectively, in 1982 in Japan[7].

$$CH_2=C(CH_3)_2 \rightarrow CH_2=C(CH_3)CHO \qquad (4)$$
$$\text{isobutylene} \qquad \text{methacrolein}$$

$$CH_2=C(CH_3)CHO \rightarrow CH_2=C(CH_3)COOH \qquad (5)$$
$$\text{methacrolein} \qquad \text{MAA}$$

In this process, isobutylene is converted to methacrolein in the first reactor using a MoBiFeCo- containing catalyst, which was derived from the well-known SOHIO Mo-Bi oxides. The resulting methacrolein is subsequently oxidized in a second reactor over heteropoly compounds which contain MoP as the key elements and exhibit Keggin-type structures. An overall MAA yield up to 69% was reported[8].

Another alternative process was developed and commercialized by Asahi in 1998, which produces MMA from isobutylene in two steps.

$$CH_2=C(CH_3)_2 \rightarrow CH_2=C(CH_3)CHO \qquad (6)$$
$$\text{isobutylene} \qquad \text{methacrolein}$$

$$CH_2=C(CH_3)CHO + MeOH \rightarrow CH_2=C(CH_3)COOCH_3 \quad (7)$$
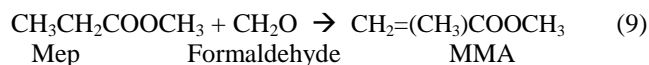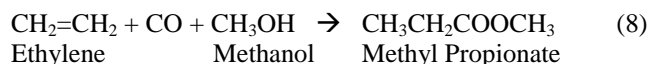$$\text{methacrolein} \qquad \text{MMA}$$

In the first step (eq. 6), isobutylene is converted to methacrolein using the same MoBiFeCo oxide catalyst used in the direct oxidation process. In the second step(eq. 7), methacrolein is directly converted to MMA in the liquid phase using a Pd-Pb- containing catalyst, which achieves up to 93% yield of MMA from methacrolein[9].

Although isobutylene is contained in the C4 stream of gasoline cracking, its separation is not an easy task, as the boiling points of isobutylene and other C4 streams are similar and difficult to separate by distillation. The isobutylene feedstock used for the above processes is obtained from the dehydration of t-butanol, or the cracking of methyl t-butyl ether (MTBE). The above mentioned isobutylene processes are not deployed in the US or Europe some 30 years after its commercialization in Japan, likely due to the limited availability of pure isobutylene and its high and fluctuating cost.

## 2.3 Other Routes for MAA and MMA Production

The newest technology commercialized for MMA production is the 2-step Alpha process. Its development started at ICI in the early 1990s, and the commercialization took place in 2008 in Singapore by Lucite International, which was subsequently acquired by Mitsubishi Rayon in 2009. Methyl propionate is produced in the 1st step from ethylene, carbon monoxide and methanol (eq. 8). The gas

phase condensation of methyl propionate and formaldehyde takes place in the 2$^{nd}$ step to produce MMA (eq. 9).

$$CH_2=CH_2 + CO + CH_3OH \rightarrow CH_3CH_2COOCH_3 \qquad (8)$$
Ethylene       Methanol     Methyl Propionate

$$CH_3CH_2COOCH_3 + CH_2O \rightarrow CH_2=(CH_3)COOCH_3 \qquad (9)$$
Mep      Formaldehyde      MMA

The Alpha process uses less hazardous starting material and generates less toxic wastes, as compared to the ACH process. While the reaction parameters in the first stage are satisfactory, further improvements in stability and reactivity for the second stage catalyst would be beneficial[10]. Mitsubishi Rayon is the owner of newly developed Alpha process, and is the only manufacturer concurrently utilizing all three technologies for MAA and MMA productions.

Besides the above 3 technologies "in-use" for MAA or MMA productions, there are a number of other technologies that are still under development, not yet-utilized, or abandoned[10]. Among these, the isobutane process is unique in that the feedstock, isobutane, is an underutilized hydrocarbon and the cheapest feedstock than all of the other feedstocks. The early investigation through the 1990s focused mainly on Keggin-type heteropoly compound $H_3PMo_{12}O_{40}$ or its derivatives[11], which exhibit modest activities in converting isobutane to MAA in gas phase oxidation, but tend to suffer from short catalytic lifetime at the high temperatures and other conditions required for isobutane oxidation[12]. Recently, we reported a class of novel metal oxide catalysts achieving a modest isobutane conversion and up to 70% oxygenates selectivity[13]. Further improvement upon this patented process and the catalytic system will enhance its attractiveness for commercial implementation.

## 2.4 Technologies Tied to Fossil Fuels Derived Feedstocks

Whether via the above-mentioned aged ACH process, the isobutylene process, the most recently commercialized Alpha process or the isobutane process under development, all of the feedstocks are fossil fuels based. Acetone is a downstream product from propylene; isobutane is a naturel gas component; while ethylene, propyne, isobutene, t-butanol, MTBE, formaldehyde and carbon monoxide are from C2, C3 and C4 streams or other derivatives of petroleum cracking. The consumption of fossil-fuel derived feedstock speeds up the depletion of fossil resources, thus leading to rapidly increasing production costs, as reflected by the tripling of the petrochemical pricing index in the last two decades from 1993 to 2012[14]. The consumption of fossil fuel based feedstock further contributes to the substantial net $CO_2$ emission, which is likely to speed up the global warming and other disastrous climate changes as observed in the recent years.

## 3 BIOISOBUTANOL AND THE CLEAN AND SUSTAINABLE ROUTE

The concerns over the dependence on fossil resources and climate change can only be addressed by developing sustainable productions of energy and chemicals. Since biomass is the only renewable resource for the sustainable production of carbon based chemicals, there is an urgent need to develop the corresponding technologies using biomass derived feedstocks for the production of chemicals, especially those large volume commodity chemicals, such as MAA/ MMA

## 3.1 Biobutanol - a 2$^{nd}$ Generation Biofuel

Bioethanol is the first generation and most common biofuel produced worldwide and used in petro engines as a direct replacement for gasoline. Biobutanols, mainly n-butanol and isobutanol, are so-called 2$^{nd}$ generation biofuels that are more desirable as gasoline replacements than bioethanol. Biobutanols have superior physical properties, such as higher energy density (29.2 MJ/l) than that of bioethanol (19.6 MJ/l), lower Reid Vapor Pressure, and full compatibility for blending with gasoline. These superior properties can translate into substantial economic and social benefits. Biobutanol can be blended to 16-20 % by volume without compromising the gasoline performance, vs. 10% with bioethanol. Furthermore, the resulting biobutanol/ gasoline blends require no modification on the existing infrastructure of the blending facilities, storage tanks or retail station pumps. As the fuel market is about $700 billion[15] in the United States alone, the incentives are huge in driving the technology development and production of biobutanols to fill the biofuel market. The world's first commercial production of bioisobutanol was successfully commenced in the US by Gevo in May 2012[16].

## 3.2 Sustainable Production of Methacrylate

Besides the intended use as a biofuel, bioisobutanol, with the branched C4 carbon structure, can be a superior feedstock for methacrylate production. The production routes from bioisobutanol to MMA are illustrated in Fig. 2.
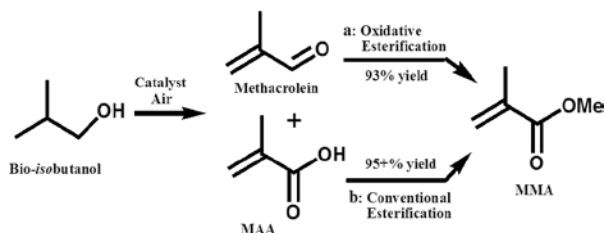


**Fig. 2 Production Routes from bioisobutanol to MMA**

In principle, methacrolein and / or MMA can be produced from bioisobutanol through the combination of dehydration and oxidation reactions in the presence of air and suitable catalyst(s). MMA can be produced in high yield via the esterification of MAA through the well-known conventional processes. MMA can also be produced in

high yield from methacrolein through the oxidative esterification process[9] established in the 1980s and commercialized in the 1990s.

The feasibility of the bioisobutanol route for methacrylate production depends on the successful development of an effective catalytic system. The technical feasibility of this process can be established when methacrolein and / or MAA can be produced in reasonable yields. However, higher methacrolein and/or MAA yields and a stable catalytic system are required for the technology to be commercially feasible and economically viable.

## 3.3 Petro-based Isobutanol and Attempted Usage for Methacrolein/MAA Production

Before the biofuel age, isobutanol could only be produced using petro-based feedstock. The most common industrial process for the petro-based isobutanol production is a two-step process (shown in Fig. 3) through propylene carbonation followed by hydrogenation of the two butyraldehydes and the subsequent separation of isobutanol from n-butanol[17].
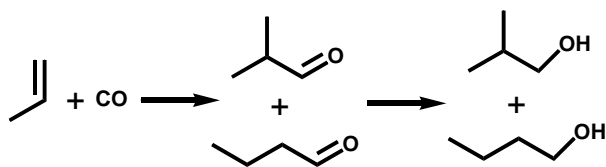


**Fig. 3    Production of Petro-based Isobutanol**

Compared with other petro-based feedstocks such as acetone or isobutylene, petro-based isobutanol thus produced cannot be an economically viable feedstock for methacrylate production. However, in the 1980s as an offshoot when isobutylene processes were developed, a Keggin-type $P_aMo_bX_cY_dO_n$ heteropoly compound (HPC) was reported to achieve a 38 – 45% combined yield of methacrolein and MAA[18]. In addition to the inadequate yields, Keggin-type HPCs are known to decay in short time under the required reaction conditions. No follow-up research has been published with respect to this $P_aMo_bX_cY_dO_n$ catalyst.

## 3.4 Status and Technical Challenges in Developing the Bioisobutanol Process

Our investigation to explore the feasibility of the bioisobutanol process started with the validation of the $P_aMo_bX_cY_dO_n$ Keggin-type catalytic system. The reported methacrolein and MAA yields were confirmed in our laboratory. As expected, however, noticeable degradation of the catalyst activity and selectivity were also observed in very short periods of time under the required reaction conditions. Because of such fatal defects in the catalyst stability, Keggin-type HPCs are not good candidates for the bioisobutanol process.

Our subsequent exploration concentrated on metal oxide-based catalytic systems. Several promising leads exhibiting reasonable stability and productivity have been identified. To advance the productivity to a commercially viable level, we still need to overcome various technical challenges, such as promoting the selective pathway to the desired products, minimizing destructive side reactions, and / or slowing down the further oxidation of the desirable products.

## 3.5 Benefits of the Sustainable Process

The benefits for this green and clean technology are obvious, once it advances to a commercially viable stage and deployed. As a clean process involving no toxic substances, it will eliminate all of the undesirable issues inherent in the existing ACH process. As a green process with a biofuel as the feedstock, it further avoids the consumption of fossil-fuel based feedstock and produces no net $CO_2$ emission. It helps transforming the current petro-based chemical production towards a sustainable direction, while reducing the consumption of fossil fuels. It further offers the emerging biofuel industry with a high value application for bioisobutanol.

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