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A new route for the synthesis of methacrylic acid from 2-methyl-1,3-propanediol by integrating biotransformation and catalytic dehydration

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Graphical abstract

2-Methyl-1,3-Propanediol $\xrightarrow{G.\text{oxydans}}$ 3-Hydroxy-2-methylpropanal $\xrightarrow{\text{TiO}_2} 195-210^\circ\text{C}$ 3-Hydroxy-2-methylpropionic acid $\xrightarrow{\text{TiO}_2}$ Methacrylic acid

1 2 3 4
A new route for the synthesis of methacrylic acid from 2-methyl-1,3-propanediol by integrating biotransformation and catalytic dehydration†

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Methacrylic acid was produced at high yield by an integrated process involving bioconversion of 2-methyl-1,3-propanediol (2M1,3PD) to 3-hydroxy-2-methylpropionic acid (3H2MPA) via 3-hydroxy-2-methylpropanal (3H2MPAL), and catalytic dehydration of the resulting acid. Whole cells of *Glucobacter oxydans* grown on glycerol-based culture medium were used as catalyst for oxidative biotransformation that involved alcohol dehydrogenase (ADH) and aldehyde dehydrogenase (ALDH) enzymes in the organism. The effect of several reaction parameters on bioconversion in a batch system was investigated to obtain 95-100% conversion of 2M1,3PD with over 95% selectivity to 3H2MPA. The optimum conditions for bioconversion were pH 6.7-7.5, 25-30 °C, 5-10 g substrate and 2.6 g cell (dry weight) per liter. Higher substrate concentrations led to enzyme inhibition and incomplete conversion. Loss of catalytic activity was noted during recycling of the cells. The cells were active for a longer period when used for biotransformation of 20 g/L substrate in a continuous reactor with cell retention. The product of the bio-oxidation, 3H2MPA was converted using titanium dioxide at 210 °C to give methacrylic acid (MA) with a yield of over 85%. The integrated process provides a new environmentally benign route for production of methacrylic acid from 2-methyl-1,3-propanediol, an industrial by-product, compared with the conventional acetone-cyanohydrin (ACH) process.

**Introduction**

Methacrylic acid (MA) and methyl methacrylate (MMA) are important monomers for a range of polymer products; the major product is poly(methyl methacrylate) (PMMA), with an annual global consumption of 2.1 million tonnes.1 Approximately 80% of the global production of MMA is achieved using the well known acetone-cyanohydrin (ACH) process, in which acetone and hydrogen cyanide are reacted with excess concentrated sulphuric acid to produce the methacrylamide acid sulphate 2, followed by treating with excess aqueous methanol, and hydrolysis and esterification of the amide to yield a mixture of MMA and MA. However, there are serious problems with this route due to the use of highly toxic raw materials, high process cost, and formation of significant amounts of by-products, which have to be disposed.3-5 The ACH process is estimated to result in emission of 5.5 kg CO₂/kg MMA, which is much higher than that from other platform chemicals such as propylene (1.1 kg CO₂/kg), ethylene (1.1 kg CO₂/kg), and vinyl chloride monomer (1.5 kg CO₂/kg).3 Therefore, among several platform chemicals, a greener production route of MMA can be expected to be highly beneficial for the environment. Different alternative processes have been proposed since the 1980s to replace the ACH technology. Some of them are close to commercialization, while others, although attractive from environmental and economic points of view, are still in the research stage.6

An earlier study has reported the production of an analogous compound, acrylic acid from 3-hydroxypropionic acid in a continuous process with >98% conversion and >99% selectivity using titanium oxide as the catalyst at 180 °C.4 Also, dehydration of lactic acid to obtain acrylic acid has been studied,5-6 but the product yield was too low for commercial application. A similar process for the production of methacrylic acid would require 3-hydroxy-2-methyl propionic acid (3H2MPA, isohydroxybutyric acid) as the substrate. Synthesis of this chemical has been achieved by enantioselective oxidation of 2-methyl-1,3-propanediol (2M1,3PD) using an acetic acid bacterium, *Acetobacter pasteurianus*.7 2M1,3PD is a by-product of the butanediol production process involving hydroformylation reaction of allyl alcohol and CO/H₂ gas mixture in the presence of a catalyst, and hence is a cheap and commercially available substrate.7-8 Recently, the possibility of 2M1,3PD production

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† Electronic Supplementary Information (ESI) available: [S1. Gas chromatograms. S2. GC-MS and NMR data]. See DOI: 10.1039/b000000x/
from renewable resources has been suggested by fermentation of
glycerol and thin stillage obtained from biofuel production
process, by *Citrobacter freundii*.10

In the present report, a process comprising oxidation of
2M1,3PD to 3H2MPA via 3-hydroxy-2-methylpropionaldehyde
(3H2MPAL), followed by catalytic dehydration is proposed as a
new synthetic route to produce methacrylic acid. *Gluconobacter oxydans* was selected as the microorganism for oxidation of
2M1,3PD to 3H2MPA, which was subsequently dehydrated to
methacrylic acid using TiO2 (Scheme 1). The latter has been used
as an environmentally friendly photocatalyst in water treatment
and organic synthesis, and is known to be a non-toxic and biocompatible material.11,12

![Scheme 1. Conversion of 2-methyl-1,3-propanediol to methacrylic acid via 3-hydroxy-2-methylpropionic acid by microbial conversion and catalytic dehydration.](image)

**Materials and Methods**

**2.1. Materials**

2-Methyl-1,3-propanediol was a product of Perstorp AB (Sweden). Methacrylic acid, 2,4-dinitrophenylhydrazine (99%,
DNPH), CDCl3, DMSO-d6, CaCO3, and glycerol were purchased from Sigma-Aldrich (St. Louis, MO, USA). Potassium phosphate
salts, acetonitrile, ethyl acetate and dichloromethane were
purchased from MERCK (Germany), while Trizma™ was from VWR international, and yeast extract (Bacto™) was obtained
from BDH (NJ, USA). *G. oxydans* (DSM 50049) was purchased from DSMZ (Deutsche Sammlung von Mikroorganismen,
Germany).

2.2. Maintenance and cultivation of *G. oxydans*

*G. oxydans* was maintained on solid medium containing per liter: 50 g glucose, 10 g yeast extract, 20 g CaCO3, and 15 g agar-agar
at pH 6.8. The agar slants were inoculated with the stock culture of
the microorganism in 20 % (v/v) glycerol, and incubated at 28
°C for 2 days, and then stored at 4 °C. To prepare the preculture,
cells from the surface of the slants were transferred to 100 mL
fermentation medium in 1 L baffled Erlenmeyer flask, containing
(per liter): 10 g glycerol, 10 g yeast extract, 5 g KH2PO4 at pH
5.5. The flasks were incubated in an orbital shaker incubator
(New Brunswick, Innova 4430, Edison, USA) at 28 °C and 200
rpm for 4 days. The pre-culture (75 mL, OD600 = 2.8) was used to
inoculate 1.5 L fermentation medium in a 3 L bioreactor
(Applikon, Microbial Biobundle, The Netherlands). The fermentation was monitored and controlled through ez-control
unit. The temperature was controlled at 28 °C and pH at 5.5
through addition of 5 N NH4OH and 5 N HCl. Stirrer speed was
500 rpm and a constant airflow at 1vvm was maintained during
the whole fermentation. Sterile polypropylene glycol in water
(1:1) was used as antifoam and was added when required. The fermentation lasted for 2 days and samples were collected and
analysed for optical density (OD), cell dry weight (CDW) and
concentration of glycerol, acetic acid, succinic acid, and dihydroxyacetone (DHA) using HPLC. After 48 hours, the
fermentation was terminated and the cell broth was harvested and
stored at 4 °C until use.

2.3. Biotransformation of 2-methyl-1,3-propanediol to 2-methyl-3-hydroxypropionic acid

*G. oxydans* cells were obtained by centrifugation of the culture broth at 10 000 × g for 2 min and followed by washing with 0.1
M Tris-HCl buffer (pH 7.2) to remove the residual culture media.
Oxidation of 2M1,3PD (2.5-30 g/L) using *G. oxydans* cells was studied in 1 mL reaction volume in 5 mL vials placed in a thermomixer (MKR 13, HLC Biotech, Germany) at 500 rpm. The reaction conditions were optimized with respect to reaction time,
substrate- and cell concentration at 28 °C and pH 7.2.

![Fig. 1. Bioreactor system used for continuous biotransformation of 2-methyl-1,3-propanediol to 3-hydroxy-2-methylpropionic acid using resting cells of *G. oxydans*. The cells were retained by a tangential flow microfiltration module (3) integrated with the bioreactor (1). Pump (2) was used to feed the substrate 2M1,3PD to (1) and remove the cell-free product from the membrane filter at a rate of 0.5 mL/min, while pump (4) was used to recirculate the reaction suspension with the cells between the reactor and the microfiltration unit at a rate of 30 mL/min.](image)

Continuous biotransformation of 2M1,3PD was performed using the system illustrated in Fig. 1, composed of a 3 L
bioreactor connected to a tangential flow microfilter, (Pellicon
XL, 0.45 µm, 50 cm² filtration area, Millipore, Bedford, MA).
Two pumps were used – one for re-circulating the reaction suspension between the bioreactor and the filtration system at a rate of 30 mL/min, and the other for feeding the fresh substrate solution and removing the cell-free product stream at a constant
rate. During the whole run, the stirrer speed was kept constant at
1000 rpm, air flow at 1 vvm, pH at 7.2 though addition of 5 N
NH4OH, and temperature at 28 °C. The cells used for the biotransformation were previously grown as described above,
recovered from the fermentation broth by centrifugation at 15 000
× g for 10 min. The reaction was performed in 1 L working volume containing 5 g 2M1,3PD and 5.85 g cells (dry weight) in
0.05 M Tris-HCl (pH 7.2), initially in a batch mode for 7.2 h
followed by a continuous mode by feeding 20 g/L 2M1,3PD in
the same buffer at a dilution rate of 0.03 h⁻¹, removing the cell-
free product as a permeate from the microfiltration unit while
recycling the retained cells, for a period of 107 hours.

The biotransformation experiments were performed in two independent runs and analyses of the reaction components was performed in duplicates.

2.4. Catalytic dehydration of 3-hydroxy-2-methylpropionic acid to methacrylic acid
3H2MPA, obtained as a product of batch biotransformation using *G. oxydans* cells, was used without further treatment for catalytic dehydration. A simple flow reaction cell was designed using a stainless steel (4.5 x 200 mm) packed with 3 g TiO$_2$ and placed in an oven. Twenty five millilitres of a pre-heated 3H2MPA solution (5 g/L) was fed to the pre-heated reaction tube using a quantitative pump (Pump 2248, Pharmacia LKB, Sweden) at different flow rates for providing different residence times. The reaction temperature was varied in the range of 175-210 °C. The eluate containing MA was condensed in a cold water bath and collected.

### 2.5. Analyses and structure elucidation

Growth of *G. oxydans* cells was monitored by measuring optical density (OD) at 620 nm (UV-Vis Spectrophotometer, Utruospec 1000, Pharmacia Biotech, Sweden). For determination of cell dry weight, cells were recovered from 10 mL broth by centrifugation (10 000 × g for 2 min), and washed using distilled water and dried overnight in an oven at 110 °C.

The concentrations of glycerol and dihydroxyacetone (DHA) were determined by HPLC (Dionex, Ultimate RS 3000 system, USA) equipped with UV/VIS (RS-3000 RI-101 Shodex), and an oven (RS 3000). Separation of the compounds was done on an Aminex HPX 87-H ion exclusion chromatographic column (300 mm long, ID 7.8 mm, particle diameter 9 μm, Bio-Rad Laboratories, CA, USA). The column temperature was maintained at 40 °C. Samples from the bioreactor were diluted with MilliQ quality water. Thirty microliter sample was injected into the column and eluted using water/acetonitrile (65:35) containing 0.5 mM sulfuric acid as the mobile phase at a flow rate of 0.5 mL/min, and the eluted products were detected at 270 nm. For determination of acetic acid and succinic acid, the same chromatographic column was used, and peak separation was done using 5 mM sulphuric acid at a flow rate of 0.6 mL/min. Oven temperature was kept at 55 °C and detection was done using RI detector (ERC-inc, Kawaguchi, Japan).

Quantitative analyses of reaction components were performed using gas chromatography (GC, Varian 430-GC, Varian, USA) equipped with FactorFour Capillary column, VF-1ms (Varian, 15M × 0.25mm) and a flame ionization detector. The initial column oven temperature was increased from 50 to 250 °C at a rate of 20 °C/min. The samples, diluted with acetoniitrite to a concentration of 0.1-1 g/L, were injected in split injection mode of 10 % at 275 °C. The percent conversion of 2M1,3PD and formation of the products were calculated from the peak areas on the gas chromatograms (Supplementary data). Commercially available 2M1,3PD and MA were used as standards, while 3H2MPA was prepared from reaction of 2M1,3PD using sufficient amount of cells to reach 100 % conversion. All samples were analysed in duplicates and data provided is an average of the replicates. The molecular masses of all substances were measured by GC-MS (Varian 431-GC, Varian 210-MS) equipped with FactorFour Capillary column, VF-5ms (Varian, 30M × 0.25 mm). The initial column oven temperature was increased from 50 °C to 275 °C at a rate of 15 °C/min. The diluted samples were injected at 275 °C.

The kinetic parameters for the oxidation of 2M1,3PD and 3H2MPAL by ADH and ALDH, respectively, were determined from the Lineweaver–Burk plot of the initial reaction velocity vs. the substrate concentration:

\[
\frac{1}{v} = \frac{(K_m/V_{max})/\left[S\right]}{1/V_{max}} + \frac{1}{V_{max}} \quad (\text{Eq. 1})
\]

where [S], $V_{max}$, and $K_m$ are substrate concentration, maximum reaction rate and Michaelis constant, respectively.

The identity of 3H2MPAL was confirmed by reactive extraction with DNPH, which is a general method for confirming aldehydes. To the reaction solution recovered after centrifugation, was added 0.1 M DNPH solution followed by extraction with ethyl acetate. The organic phase was dried and subjected to $^{13}$C-NMR analysis (Supplementary data).

3H2MPA was isolated from the reaction mixture by simple filtration followed by water evaporation under reduced pressure. The structure of 3H2MPA was elucidated by $^1$H and $^{13}$C-NMR using 400 MHz NMR (Bruker, UltraShield Plus 400, Germany), (Supplementary data).

### 3. Results and discussion

#### 3.1. Cultivation of *G. oxydans* cells

Acetic acid bacteria are characterised by their ability to catalyse incomplete oxidation of alcohols and sugars to the corresponding aldehydes, ketones and organic acids. This was translated into several industrial processes for production of valuable chemicals such as dihydroxyacetone (DHA) from glycerol, L-sorbose and L-sorbosone from D-sorbitol, and D-gluconic acid, 2-keto- and 2,5-diketo-gluconic acid (precursor of vitamin C) from glucose using *Gluconobacter oxydans* and acetic acid from ethanol using *Acetobacter* spp.

In this study, *G. oxydans* DSM 50049 cells obtained by cultivation in a glycerol-based culture medium were used to catalyse the conversion of 2M1,3PD to 3H2MPA. The growth curve of *G. oxydans* showed no lag phase and the microorganism grew logarithmically at maximum specific growth rate ($\mu_{max}$ of 0.213 h$^{-1}$) and doubling time ($t = 3.25$ h) during the first 12 hours of cultivation (Fig. 2).

![Fig. 2. Growth curve of *G. oxydans* showing Ln OD$_{620}$ nm for calculation of growth rate (x), % dissolved oxygen / 10 (●), and concentrations of glycerol (▲), DHA (■), acetic acid (*), and succinic acid (○). The values are the mean of two independent runs, and measurements performed in duplicates.](image-url)

This was accompanied by increase in oxygen uptake rate as shown by the decrease in the dissolved oxygen (%DO) from 90 to 5% of saturation. Complete consumption of glycerol and production of 9.3 g/L DHA was observed after 18 hours of cultivation. Subsequently, the microorganism assimilated the produced DHA via the pentose phosphate pathway and the growth rate was decreased to 0.04 h$^{-1}$ ($t = 17.3$ h). During this period the %DO was stabilized around 20% and then increased...
gradually to 100% at the end of day 2. The final cell density reached was 1.3 g cell dry weight per liter. These cells were collected for use in the biotransformation of 2M1,3PD.

3.2. Bioconversion of 2-methyl-1,3-propanediol by G. oxydans

3.2.1. Characterization of bioconversion and reusability of cells

Oxidative biotransformation of 2M1,3PD using resting cells of G. oxydans was investigated under conditions considered optimal (25-30 °C and pH 6-8) for the organism. The reaction was studied in 1 mL volume at varying substrate concentration (5, 7.5, 10, 12.5, 15, 20 and 30 g/L), pH 7.2 (0.1 M Tris-HCl), 29 °C using 2.6 mg of cell dry weight/mL. Substrate conversion, reaction rate and product formation were followed and are summarised in Table 1. Complete conversion of 5 g/L 2M1,3PD was achieved in 9-12 h (not shown), while 98% of 7.5 g/L was converted to 3H2MPA in 24 hours (Fig. 3).

Higher substrate concentrations, 10-12.5 and 15 g/L resulted in 89% and 80.5% conversion, respectively, in 24 h. 3H2MPA and its methyl ester, known as Roche ester, can be used as major building blocks in organic synthesis. Molinari et al. have earlier reported the oxidative conversion of several aliphatic alcohols such as 1-propanol, 1-butanol, 2-methyl-1-butanol, and 2M1,3PD to the corresponding carboxylic acid mainly by Acetobacter spp. Also enantioselective oxidation of (R,S)-2-phenyl-1-propanol to (S)-2-phenylpropanoic acid was achieved at 45-50% molar conversion in 24 h by G. oxydans. Two membrane-bound enzymes in G. oxydans, ADH and ALDH are suggested to be involved in the conversion of the diols to the hydroxyacid. The evidence for the involvement of the membrane-bound quinohemoprotein ADH in G. oxydans DSM 2003 for biooxidation of 1,2-propanediol to lactaldehyde, was recently obtained in a study using ADH deficient mutant. This study also proved the contribution of several ALDHs towards the subsequent oxidation of lactaldehyde to D-(-)-lactic acid.

Table 1. Results of biotransformation of varying concentrations of 2-methyl-1,3-propanediol by 2.5 mg dry weight/mL G. oxydans cells at 29 °C and pH 7.2 during initial 3 h

<table>
<thead>
<tr>
<th>Run</th>
<th>Substrate (2M1,3PD) Initial</th>
<th>Product</th>
<th>ADH reaction</th>
<th>ALDH reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>g/L M</td>
<td>2M1,3PD (M)</td>
<td>3H2MPAL (M)</td>
<td>3H2MPA (M)</td>
</tr>
<tr>
<td>1</td>
<td>5 0.055</td>
<td>0.017</td>
<td>0.000</td>
<td>0.038</td>
</tr>
<tr>
<td>2</td>
<td>7.5 0.083</td>
<td>0.031</td>
<td>0.005</td>
<td>0.046</td>
</tr>
<tr>
<td>3</td>
<td>10 0.111</td>
<td>0.053</td>
<td>0.009</td>
<td>0.049</td>
</tr>
<tr>
<td>4</td>
<td>12.5 0.139</td>
<td>0.071</td>
<td>0.014</td>
<td>0.054</td>
</tr>
<tr>
<td>5</td>
<td>15 0.166</td>
<td>0.098</td>
<td>0.019</td>
<td>0.050</td>
</tr>
<tr>
<td>6</td>
<td>20 0.222</td>
<td>0.163</td>
<td>0.027</td>
<td>0.032</td>
</tr>
<tr>
<td>7</td>
<td>30 0.333</td>
<td>0.278</td>
<td>0.045</td>
<td>0.010</td>
</tr>
</tbody>
</table>

Abbreviations: 2M1,3PD: 2-methyl-1,3-propanediol, 3H2MPAL: 3-hydroxy-2-methylpropanal, 3H2MPA: 3-hydroxy-2-methylpropionic acid. aConversion of 2M1,3PD. bSubstrate calculated as sum of 3H2MPAL and 3H2MPA used in ALDH reaction. cConversion to 3H2MPA

Fig. 3. Profiles of reaction substrate (●, 2-methyl-1,3-propanediol), intermediate (■, 3-hydroxy-2-methylpropanal), and product (▲, 3-hydroxy-2-methylpropionic acid) with time during biotransformation using 2.6 mg cells (dry weight) G. oxydans at pH 7.2 (0.1M Tris-HCl), in 1 mL reaction volume in 5 mL vial at 29 °C. The reaction was carried out using 7.5 g/L substrate. The values are the mean of two independent runs, and measurements performed in duplicates.

As seen in Fig. 4A, the rate for ADH catalysed reaction increased with increase in 2M1,3PD concentration up to 0.2 M and then decreased suggesting substrate inhibition. Product inhibition by the aldehyde intermediate 3H2MPAL could be ignored since it was continuously converted to 3H2MPA by ALDH reaction, and hence its concentration was kept sufficiently low (below 0.05 M). The amount of substrate for ALDH catalysed reaction was calculated as sum of residual 3H2MPAL and the product 3H2MPA (Table 1), which showed that the reaction rate was faster than that of ADH reaction at the prevailing substrate concentrations (Fig. 4A).
Kinetic parameters were determined from the Lineweaver–Burk plot (Fig. 4B); $K_m$ (M) and $V_{max}$ ($\mu$mol/min/mg) values for ADH were 0.122 and 0.265, and for ALDH were 0.059 and 0.213, respectively (Table 1). It seems that the inhibition for the ALDH reaction occurs at lower substrate concentration than that for the ADH reaction. On the other hand, product inhibition was not apparent since 3H2MPA could not be produced at sufficiently high concentration due to the inhibitory effect of the substrate.

Recycling of the cells for the biotransformation of 2M1,3PD was investigated. As seen in Fig. 6, while the substrate conversion was efficient during the first run, the activity of the cells during the second run was decreased resulting in a mixture of 28% unconsumed substrate, 33% aldehyde intermediate and 39% acid product. In the subsequent run, only 30% conversion of substrate took place to give 4% acid and 26% aldehyde, suggesting faster inactivation of ALDH.

Different concentrations of 2M1,3PD were treated with varying cell concentrations (2.5-10 mg/mL). The plot of reaction rate versus substrate concentration indicates decrease in specific reaction rate with increase in cell concentration, although showing similar trend of substrate inhibition above 0.2 mM 2M1,3PD at each cell concentration used (Fig. 5).

The loss of activity of the cells is most likely partly due to the limitation of dissolved oxygen during transfer from one batch to the other; acetic acid bacteria are known to be highly sensitive to oxygen limitation. Moreover, the accumulation of the aldehyde intermediate as seen in Fig. 6 would also lead to enzyme inhibition.

### 3.2.2. Biotransformation in continuous cultivation with cell retention

The oxidative biotransformation of 2M1,3PD was then studied using the *G. oxydans* cells in a bioreactor integrated with membrane filtration to enable cell retention and recycle (Fig. 7). Initially the reaction was started in a batch mode using 5 g/L 2M1,3PD, which gave 90% conversion in 7.2 h. The reaction was then shifted to a continuous mode at residence time of 33.3 h using a feed of 20 g/L substrate. The concentrations of both substrate and product increased gradually in the outlet stream.

The 3H2MPA concentration in the outlet reached a maximum of 8.5 g/L after 66.8 hours from the start of the feeding and subsequently the concentration was decreased down to 5.4 g/L when the reaction was terminated. The substrate concentration continued increasing gradually and reached 13.7 g/L at the end of the experiment. The dissolved oxygen was constant during the entire process. Compared to results obtained above with the recycled cells (25 h), the cells in the continuous mode were maintained with higher catalytic activity for a longer period of time (~120 h) and left no residual aldehyde intermediate during the entire reaction time, even though the substrate concentration used was at an inhibitory level for the activity of the cells.
could be due to more favorable conditions such as oxygen supply and pH control maintained by feeding NH₄OH. Comparison between different processes used industrially or experimentally for acetic acid production from ethanol by Acetobacter spp. showed that industrial bioreactors such as Frings acetator, submerged and semi-continuous are characterized by higher final acid concentration but limited volumetric productivity, while in the high-cell-density bioreactors with cell-recycle, the volumetric productivity was almost 10 times higher despite the 2-3 times lower final acid concentration obtained.

3.3. Production of methacrylic acid by dehydration of 3-hydroxy-2-methylpropionic acid

3H2MPA was subjected to dehydration by passing through a bed of TiO₂. Ti is the ninth most abundant element on Earth; more than 5.28 millions tons being produced in 2008, which has been investigated with increasing interest, during past couple of decades, as one possible route for inexpensive industrial by-product. All reactions were performed in aqueous media without using organic solvents, and separation and/or pre-treatment were not required due to high purity yield in each step. The process provides significant environmental advantages over the acetone-cyanohydrin process used for methacrylic production, which is based on fossil gas or oil as raw material, uses corrosive sulfuric acid and toxic HCN, and produces 1.5 tons of ammonium bisulfate as waste per ton of MMA. Hence, it provides a good model for comparing life cycle assessment of the new and the traditional routes. The approach is applicable for the selective oxidation of other polyols. Further investigations are however required to develop the system to allow effective conversion of higher concentrations of substrate such as in the process for the production of acetic acid from ethanol using Acetobacter sp.

Fig. 8. Effects of reaction temperature and feeding rate on dehydration of 3-hydroxy-2-methylpropionic acid. The reactions were carried out using 25 mL of 5 g/L substrate. The symbols represent feeding rate at 0.025 mL/min (○) and 0.1 mL/min (■). Insert shows the effect of feeding rate at 210 °C.

Fig. 7. Time course of the biotransformation of 2-methyl-1,3-propanediol (●) to 3-hydroxy-2-methylpropionic acid (▲) via 3-hydroxyl-2-methylpropanal (■) using 5.85 g cell dry weight/L in batch and continuous modes. Initial batch mode reaction using 5 g/L substrate for 7.2 h was followed by the reaction in continuous mode using feeding solution of 20 g/L substrate at a dilution rate of 0.03 h⁻¹, 28 °C, 1000 rpm, and 1 vvm.

Conclusions
This study provides an alternative greener route for the synthesis of methacrylic acid from 2-methyl-1,3-propanediol, an inexpensive industrial by-product. All reactions were performed in aqueous media without using organic solvents, and separation and/or pre-treatment were not required due to high product yield in each step. The process provides significant environmental advantages over the acetone-cyanohydrin process used for methacrylic production, which is based on fossil gas or oil as raw material, uses corrosive sulfuric acid and toxic HCN, and produces 1.5 tons of ammonium bisulfate as waste per ton of MMA. Hence, it provides a good model for comparing life cycle assessment of the new and the traditional routes. The approach is applicable for the selective oxidation of other polyols. Further investigations are however required to develop the system to allow effective conversion of higher concentrations of substrate such as in the process for the production of acetic acid from ethanol using Acetobacter sp.

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Notes and references

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