Isopropyl Alcohol by Direct Hydration of Propylene*

by Yasuharu Onoue**, Yukio Mizutani**, Sumio Akiyama**, Yusuke Izumi** and Hirofumi Ihara***

Summary: Tokuyama Soda has developed a new process for direct hydration of propylene to isopropanol in liquid phase. This process employs a highly active and selective catalyst system which essentially comprises an aqueous solution of polytungsten compounds within a selective pH range.

The first commercial plant, having a capacity of 30,000 metric tons of isopropanol per annum, has been successfully in operation since the beginning of June 1972 at Tokuyama Soda Co., Ltd.

The features of the process are simplicity, low value for propylene consumption and freedom from environmental pollution problems. These advantages make Tokuyama Process by far more economical than the conventional process for the manufacture of isopropanol.

1 Introduction

Isopropanol is an important derivative of propylene in petrochemical industry. It is used as solvent, dehydrating agent and disinfectant as well as a base for the manufacture of acetone and other compounds.

Since the first commercial production of isopropanol in 1920, most methods for hydrating propylene to isopropanol have been based on the use of concentrated sulfuric acid in a two-stage esterification-hydrolysis process. This process, although resulting in substantial conversion of propylene, has the problems of severe corrosion and disposal or reconcentration of dilute spent acid.

Many processes of direct hydration of propylene in one step in the presence of catalyst have been studied in order to avoid the disadvantages of the sulfuric acid process and to obtain the rapid conversion of propylene to isopropanol with the lowest possible amount of by-products.

It is quite lately, however, that some economical direct hydration processes for commercial isopropanol production have been developed. Now, with the rising market of isopropanol, the economic importance of isopropanol production by direct hydration has been well recognized.

Recently Tokuyama Soda has developed a new economical process for direct hydration of propylene to isopropanol in liquid phase. The first commercial plant of this process, having a capacity of 30,000 metric tons of isopropanol per annum, has been successfully in operation since the beginning of June 1972 at Tokuyama Soda Co., Ltd.

2 Hydration of Propylene

2.1 Reaction

Direct hydration of propylene is carried out in the presence of catalyst according to the following reversible equation:

\[ \text{C}_3\text{H}_6 + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{CH(OH)}\text{CH}_3 \]

The reaction is exothermic, and the heat of reaction calculated from available thermochemical data\(^1\) is about 12 kcal/mol over a range of 400 to 600°K in vapour phase.

The equilibrium constants by direct measurements\(^2\),\(^3\) for hydrating propylene are reported as follows:

\[ \log_{10}K_p = (1950/T) - 6.06 \quad \text{(vapour phase)} \]

\[ \log_{10}K_c = (2045/T) - 5.08 \quad \text{(liquid phase)} \]

For the hydration with liquid and vapour phases simultaneously present, the equilibrium compositions of both phases can be estimated\(^4\) by thermochemical data, together with vapour-liquid equilibrium data.

Although the formation of isopropanol is favored by low temperatures and high pressures, optimum combination of reaction conditions is selected in consideration of both rate limitation and equilibrium limitation.

The major by-products in the direct hydration of propylene are di-isopropyl ether, \( n\)-propanol

---

\* Received December 9, 1972.
** Research & Development, Tokuyama Soda Co., Ltd. (1-1, Mikage-cho, Tokuyama 745)
*** Development & Marketing, Tokuyama Soda Co., Ltd. (1-4-5, Nishi-Shinbashii, Minato-ku, Tokyo, Japan)
and propylene oligomers.

2.2 Catalyst and Process

In commercial realization of direct hydration, it is important to develop active catalysts and processes suitable for the effective application of the catalyst systems.

In recent years, various catalysts and processes for direct hydration of propylene have been proposed.

It seems necessary for a better understanding of Tokuyama Process to review some typical hydration processes briefly.

The catalysts most widely proposed for the vapour-phase direct hydration of propylene are mineral acids such as phosphoric acid and heteropoly acids on silica or diatomaceous earth, and solid acids of metal oxides.

The reaction is generally carried out by passing steam and propylene in a molar ratio of 0.5~2.0:1 through the catalyst bed at a temperature from 180 to 260°C and under a pressure from 10 to 65 atm to maintain the reactants in gaseous state. The VEBA process recently employed in commercial isopropanol production is based on the use of a supported phosphoric acid catalyst in vapour phase.

The vapour-phase direct hydration, however, has the substantial disadvantage of low conversion of propylene per pass, for example 5~6%, resulting in a high recycle rate. Consequently, the use of a propylene concentration of 99% or more is required for the feed. Moreover, the disadvantages inherent to supported mineral acid catalysts are decrease in hydration activity and the incidence of corrosion on the metal surfaces in contact with the product owing to migration and depletion of the acid. In order to avoid these difficulties, it is necessary to regenerate the catalyst and to neutralize the product.

The disadvantages of the low conversion and concomitant recycle problems in vapour-phase processes are overcome by the direct hydration in the presence of liquid water, since the propylene conversion to isopropanol is markedly raised by the increase in solubility of the product isopropanol in the excess liquid water.

The direct hydration with a solid catalyst under a high pressure at a high mole ratio of water to propylene can be preferably employed to obtain high per pass conversions of propylene. The reaction is generally carried out by passing propylene and liquid water at a mole ratio of water to propylene between 10 and 15 over the catalyst bed at a temperature from 230 to 270°C and a pressure from 200 to 300 atm. For the hydration in the presence of liquid water, tungsten oxide is widely used as an effective component of catalyst.

Tokuyama Soda has also proposed an active catalyst which comprises zirconium tungstate. This catalyst is suitable for both vapour-phase and liquid-phase processes. The examples...
of the results of propylene hydration with the zirconium tungstate catalyst in vapour phase and liquid phase are shown in Fig. 1 and Fig. 2, respectively, in comparison with the data of liquid-phase hydration over tungsten oxide catalyst by Zabor et al.\textsuperscript{18)}

The use of insoluble solid catalysts eliminates the difficulties of the remarkable migration and depletion of acid which take place in the hydration with supported acid catalysts. However, under the severe hydrothermal conditions in the liquid-phase hydration under high pressure, gradual depletion or crystallization of the effective components of catalyst is inevitable, and consequently both the decrease in hydration rate and some operating troubles will occur. Recently, Deutsche Texaco has developed a trickle process\textsuperscript{19)} in vapour and liquid phases applying cation exchange resins as catalysts under milder conditions of 130~150°C and 60~100 atm. One of the main problems in this process is probably the hydrolysis of sulfonic acid groups of the resin catalyst which causes the irreversible loss of catalytic activity.

In order to overcome the difficulties in the fixed bed processes with solid catalysts, the liquid phase hydration with the solid catalyst dispersed in water can be employed\textsuperscript{20)~22)}. In this process, propylene is treated with water at an elevated temperature and pressure in the presence of an aqueous suspension of fine particles of the catalyst. Although high space-time yields based on catalyst are obtainable by the suspension process, some operational difficulties of separation and circulation of the suspended particles can not be avoided.

Tokuyama Soda fully examined the disadvantages and difficulties in the typical processes described above through its own extensive experiments, and attained to a conclusion that the liquid-phase direct hydration with an aqueous solution of definite kinds of polytungsten compounds within a selective pH range. This system is also very stable because the catalyst components are strongly resistant to hydrolysis at high temperature and pressure in aqueous solution.

Tokuyama Soda studied systematically the catalytic activities and stabilities of aqueous solutions of various acid compounds in the direct hydration of olefins, and finally developed an excellent catalyst system of a stable aqueous solution under high temperature and pressure. It was found from the study that the rate of hydration was markedly increased by the presence of some kinds of polyatomic anions as shown in Table 1.

The activation energy of the propylene hydration with the catalyst solution of polyatomic anions is about 24 kcal/mol which is 6 kcal/mol higher than that in the case of the catalyst solution of sulfate anions.

According to the known mechanisms\textsuperscript{26)~29)} of olefin hydration in very dilute aqueous acid, the hydration rate is proportional to the acid concentration, and the counter anions have no effect on the rate. Since the medium effect on the activity coefficient of each component in very dilute acid solution is considerably small, the effect of the polyatomic anion on both the hydration rate and the activation energy is probably interpreted by assuming an intermediate of an activated complex containing the anion.

### 3 Tokuyama Direct Hydration Process

#### 3.1 Catalyst System

The catalyst system employed in Tokuyama Process\textsuperscript{30)~34)} essentially comprises a dilute aqueous solution of definite kinds of polytungsten compounds within a selective pH range. This catalyst system is highly active and remarkably selective for hydrating propylene to isopropanol. This system is also very stable because the catalyst components are strongly resistant to hy-

---

**Table 1** Effect of Anion on Rate of Propylene Hydration

<table>
<thead>
<tr>
<th>Anion</th>
<th>Concentration of Anion (mol/l) × 10(^\circ)</th>
<th>Relative Specific Rate of Propylene Hydration*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly-molybden Anion I</td>
<td>0.75</td>
<td>3.4</td>
</tr>
<tr>
<td>Poly-molybden Anion II</td>
<td>1.00</td>
<td>3.4</td>
</tr>
<tr>
<td>Poly-tungsten Anion I</td>
<td>0.75</td>
<td>2.8</td>
</tr>
<tr>
<td>Poly-tungsten Anion II</td>
<td>1.00</td>
<td>1.7</td>
</tr>
<tr>
<td>Sulfate</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Phosphate</td>
<td>1.5</td>
<td>1.0</td>
</tr>
<tr>
<td>Acetate</td>
<td>3.0</td>
<td>1.1</td>
</tr>
</tbody>
</table>

The kinetic experiments were carried out at 156°C and 14 kg/cm\(^2\)-G with the concentration of hydronium ion in the catalyst solution 3.0 × 10\(^{-4}\) mol/l.

* Relative values to the specific rate of hydration with sulfuric acid at unit pressure of propylene in vapour phase and at unit concentration of hydronium ion in solution.
hydrolysis. Such high stability of the catalyst system is well maintained at all times in operation by the careful control of poisons which cause the decomposition of the catalyst. The catalyst life is, therefore, very long in continuous operation. Tokuyama Process gives, moreover, higher per pass conversions of propylene owing to intimate contact between dissolved propylene and the catalyst solution in the liquid phase than in the case where solid catalyst systems are employed. Fig. 3 shows an example of the experimental results of propylene hydration with the Tokuyama catalyst system by a continuous flow reactor.

3.2 Kinetics of Hydration

In the hydration of propylene with the Tokuyama catalyst system, the reaction takes place between dissolved propylene and water in an aqueous solution. The hydration rate is controlled by the reaction step, provided equilibrium is at all times maintained in the distribution of propylene between vapour and liquid phases. Because of large excess of water, the rate is given by the following equation via a pseudo-first order kinetic treatment:

\[ r = k_i(C_p - C_i/K_i) = k_g(P_p - P_i/P_{w*}K_g) \]

where

- \( k_i, k_g \): rates of conversion of propylene to isopropanol in solution at unit concentration of propylene in solution, and at unit pressure of propylene in vapour phase, respectively.
- \( K_i, K_g \): equilibrium constants in liquid and vapour phases, respectively.
- \( C_p, C_i \): concentrations of propylene and isopropanol in solution, respectively.
- \( P_p, P_i \): partial pressures of propylene and isopropanol in vapour phase, respectively.
- \( P_{w*} \): equilibrium partial pressure of water in vapour phase.

This basic rate equation can be suitably applied to calculate conversion or space-time yield in process design and economic evaluation.

3.3 Process Description

The flow scheme of Tokuyama Process is shown in Fig. 4.

Liquid propylene is preheated and fed to a reactor under pressure. The catalyst solution recovered from the azeotrope column is preheated by heat exchange with the reactor effluent and fed to the reactor operating at 240~270°C and 150~250 atm. The reaction takes place in the liquid phase between dissolved propylene and water. The aqueous solution containing isopropanol and catalyst is withdrawn from the reactor and cooled by heat exchange and then flashed under reduced pressure in a gas separator where the unconverted propylene dissolved in the solution is separated and recycled. The

![Fig. 4 Flow Diagram of Tokuyama Process](image-url)
liquid is sent to the azeotropic column, from where azeotropic mixture of isopropanol and water is drawn off and sent to further distillation steps for purification and dehydration. The aqueous solution containing catalyst from the bottom of the azeotrope column joins with fresh water and is recycled to the reactor. The azeotrope alcohol is freed of the light impurities in the first rectifying column and then dehydrated in two further columns with benzene as the dehydrating agent. To obtain a high grade isopropanol (99.99% purity), another additional distillation step is necessary.

Under the optimum reaction conditions, the range of propylene conversion per pass is about 60~70% and selectivity to isopropanol based on the converted propylene is as much as 98~99%. The major by-product is di-isopropyl ether.

In Tokuyama Process, both the spent gas from the reactor and all the by-products drawn off at the purification section are completely utilized as fuel for heating in the system.

3.4 Features of Process

Tokuyama Process has a number of advantages based on its own catalyst system and process design. The features of the process confirmed in commercial operation are as follows:

1. The catalyst system comprises a homogeneous dilute aqueous solution which maintains high activity and excellent selectivity for hydrating propylene to isopropanol.
2. The catalyst solution is so highly stabilized that it is circulated repeatedly in the reaction system without any additional treatments. Catalyst life is, therefore, very long.
3. Since the reaction is carried out in aqueous solution under high pressure, the formation of isopropanol is markedly favoured by equilibrium effect.
4. The amount of unconverted propylene to be recycled is small owing to high conversion rate of propylene, and consequently this process does not require highly concentrated propylene feed. Commercial propylene of about 95% concentration is normally used.
5. The amount of by-products is remarkably small because the reaction takes place in an aqueous solution of highly selective catalyst. Organic acids and aldehydes are hardly detectable in the reaction product. A high grade isopropanol is easily obtained at the purification section.
6. Since the reaction is carried out in aqueous solution, the heat loss incidental to evaporation and condensation of water can be avoided.
7. Because of absence of corrosion in the system, easy operation and maintenance of equipments are possible.
8. The process is simple. It is also a completely closed system free from waste substances, and consequently the process can clear all the environmental protective regulations.

3.5 Quality of Product

Typical data of the product isopropanol obtained in Tokuyama Process are given in Table 2.

3.6 Economics

The economics of Tokuyama Process are shown in Table 3. They include the entire processing of propylene to 99.99% isopropanol.

3.7 Other Applications

Tokuyama Process is also applicable to the economical production of ethanol and butanols.

4 Conclusion

Besides the low value for propylene consumption, simpleness of process and freedom from environmental pollution problems by nature of the process itself make Tokuyama Process by far more economical than the conventional process for the manufacture of isopropanol.

Table 2 Typical Properties of Product

<table>
<thead>
<tr>
<th>Isopropyl Alcohol</th>
<th>99.99%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appearance</td>
<td>Colorless crystal</td>
</tr>
<tr>
<td>Color (Platinum-Coalt Method)</td>
<td>5</td>
</tr>
<tr>
<td>Specific Gravity (20°/20°C)</td>
<td>0.786</td>
</tr>
<tr>
<td>Distillation</td>
<td></td>
</tr>
<tr>
<td>Initial Boiling Point</td>
<td>82.4°C</td>
</tr>
<tr>
<td>Dry Point</td>
<td>82.6°C</td>
</tr>
<tr>
<td>Distillate</td>
<td>98%</td>
</tr>
<tr>
<td>Nonvolatiles</td>
<td>&lt;0.0002%</td>
</tr>
<tr>
<td>Water Content</td>
<td>&lt;0.001%</td>
</tr>
<tr>
<td>Free Acid (as Acetic Acid)</td>
<td>&lt;0.000%</td>
</tr>
</tbody>
</table>

Table 3 Economics of Tokuyama Soda

Direct Liquid-Phase Hydration Process

<table>
<thead>
<tr>
<th>Plant Capacity</th>
<th>30,000 metric tons of isopropanol per annum.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Investments, Battery Limits</td>
<td>2,000,000 U. S. dollars</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Consumption per metric ton of isopropanol</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Propylene</td>
<td>0.72 t</td>
</tr>
<tr>
<td>Catalyst &amp; Chemicals</td>
<td>50 cents</td>
</tr>
<tr>
<td>Steam (2.5 kg/cm²-G)</td>
<td>3.5 t</td>
</tr>
<tr>
<td>Electric power</td>
<td>200 kW-hr</td>
</tr>
<tr>
<td>Cooling water</td>
<td>15m³</td>
</tr>
</tbody>
</table>

Bulletin of The Japan Petroleum Institute
panol production toward direct hydration, Tokuyama Soda will greatly contribute to the proceeding of this trend through experience in its own commercial plant.

References

7) Hammer, W. F., ibid., 46, 1841 (1954); 48, 1621 (1956); 50, 1365 (1958); 52, 962 (1960).
15) Tokuyama Soda, Japan 43-6603 (1968).
24) Japan, Bureau of Industrial Technics, Japan 42-2411 (1967).
27) Taft, R. W., Jr. et al., ibid., 73, 3792 (1951).
28) Taft, R. W., Jr. et al., ibid., 74, 5372 (1952).
32) Tokuyama Soda, Japan Open, 47-31908 (1972).
33) Tokuyama Soda, Japan Open, 47-31909 (1972).
34) Tokuyama Soda, Japan Open, 47-31910 (1972).