Epichlorohydrin

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Report Abstract
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INTRODUCTION

Epichlorohydrin (chloromethyloxirane) is a clear liquid with a foul smell (resembling garlic/chloroform). It is slightly soluble in water and fully miscible in polar organic solvents such as alcohol and insoluble in non-polar organic solvents such as long-chain hydrocarbons. The chemical may be represented as shown below.

\[
\begin{align*}
\text{O} & \quad \text{Cl} \\
\end{align*}
\]

Epichlorohydrin

Commercial grade epichlorohydrin can be found listed as being of a minimum purity of 98.0 weight percent (with water content less than 0.1 weight percent), but more typically it is listed as having a minimum purity of 99.9 weight percent (with water content less than 0.05 weight percent).

Epichlorohydrin is an important commercial chemical, with a global annual demand of well over one million tons. Primary commercial applications are in the production of epoxy resins, elastomers, and synthetic glycerol. Glycerol production has been on the decline as byproduct glycerol from soap production and biodiesel have been able to meet most demand. Dow is the only remaining known producer of synthetic glycerol, with production in Stade Germany. Synthetic glycerol is only used when the highest purity is required, as in pharmaceuticals and some food grade products.

The availability of crude byproduct from biodiesel production has not only given rise to a reduced requirement of glycerol from epichlorohydrin but actually stimulated new world-scale epichlorohydrin plants based on crude glycerol feedstock. These world-scale plants currently under construction and scheduled to come on stream within the next three years will add to the existing smaller scale glycerol to epichlorohydrin plants which have recently come on stream.

This interesting situation has inspired Nexant to review this new technology and develop cost of production estimates for its commercial production at world-scale. Technology and cost of production estimates for the other current commercial technologies to epichlorohydrin via allyl chloride and via allyl alcohol, as well as speculative production costs for an acrolein based route are also reviewed. Key business developments and the technology licensing status with respect to all commercial processes is discussed. In addition, regional and global market supply, demand, and trade data are discussed.

CURRENT TECHNOLOGY

There are currently three process routes used to produce epichlorohydrin at an industrial commercial level. The chemistry and process technology of all of these routes are discussed in detail in the report.
1. Mature Allyl Chloride ("Conventional") Route

Epichlorohydrin was first introduced commercially in the mid-1930s by Shell using a process based on the high temperature chlorination of propylene to give allyl chloride and byproduct hydrogen chloride (HCl) as shown below. (At lower temperatures, the predominant reaction is the addition of chlorine to the double bond to give dichloropropane.)

\[
\text{CH}_2=\text{CHCH}_2\text{Cl} + \text{Cl}_2 \rightarrow \text{CH}_2=\text{CHCHCl}: \quad \text{HCl}
\]

Allyl chloride was then converted to glycerol chlorohydrin (dichloropropanol) by reaction with hypochlorous acid (HOCl was obtained by reaction of chlorine and water, with byproduct HCl also formed):

\[
2\text{CH}_2=\text{CHCH}_2\text{Cl} + 2\text{HOCl} \rightarrow \text{HOCH}_2\text{CHCH}_2\text{Cl} + \text{ClCH}_2\text{CHCH}_2\text{Cl}
\]

Dehydrohalogenation of the dichloropropanol with an alkali (base) such as calcium hydroxide gave epichlorohydrin and byproduct calcium chloride:

\[
\text{HOCH}_2\text{CHCH}_2\text{Cl} + \text{ClCH}_2\text{CHCH}_2\text{Cl} + \text{Ca(OH)}_2 \rightarrow 2\text{Cl}\text{Cl} + \text{CaCl}_2 + 2\text{H}_2\text{O}
\]

2. Mature Allyl Alcohol Route

In the mid-1980s, Showa Denko commercialized a process which reduces the chlorine consumption of the conventional allyl chloride process by using allyl alcohol as the key intermediate. Direct oxidation of propylene in the presence of acetic acid (catalyst) gives allyl acetate. Hydrolysis of the acetate results in allyl alcohol. Subsequent addition of chlorine in the presence of highly concentrated hydrochloric acid solution yields 2,3-dichloro-1-propanol (α-dichlorohydrin). The final step involves the treatment of the dichloropropanol with lime water (alkali) to obtain epichlorohydrin.
3. **New Glycerol Route**

The chemistry of producing epichlorohydrin from glycerol was patented in 1906 by German scientists. For a long time, nothing much happened. However, in the past 10 years, much research has been focused on the production of epichlorohydrin starting with glycerol, undoubtedly as a result of its relatively cheap availability as a byproduct of biodiesel production. Another advantage of this route is the glycerol feedstock is a renewable resource.

The glycerol to epichlorohydrin process is carried out without the use of solvents and is relatively simple. The process consumes hydrogen chloride as opposed to chlorine which is used in the conventional (allyl chloride based) processes, and will result in less chlorinated effluents being produced, making it more environmentally friendly.

**LITERATURE REVIEW**

Nexant has reviewed the literature and discusses its findings on alternative potential routes that have been researched (none of which have been commercialized). These include:

- Electrochemical Route
- Acetone Route
- Acrolein Route
- Ethane Conversion Route

**ECONOMICS**

Cost estimates for Epichlorohydrin production via the following processes have been evaluated:

- Allyl chloride route for plant capacities of 63.5 kta and 100 kta on a USGC basis.
- Allyl alcohol route for plant capacities of 63.5 kta and 100 kta on a USGC basis.
- Glycerol route for plant capacities of 100 kta on USGC basis.
- Speculative (non-commercial) acrolein route for plant capacities of 63.5 kta and 100 kta plant on a USGC basis.

The above cost estimates highlight the different process performances as they are all compared on a same capacity and location basis. However, the USGC location is not reflective of the developing industry as no new project is planned to be built in this region. Therefore, Nexant has also developed and compared the economics of production for the glycerol route to epichlorohydrin for the following regions as well:

- Glycerol route to epichlorohydrin for plant capacities of 100 kta in China
- Glycerol route to epichlorohydrin for plant capacities of 100 kta in Thailand
- Glycerol route to epichlorohydrin for plant capacities of 100 kta in Western Europe

All cost tables given in this report include a breakdown of the cost of production in terms of raw materials, utilities direct and allocated fixed costs, by unit consumption and per metric ton and
annually, as well as contribution of depreciation to arrive at a cost estimate (a simple nominal return on capital is also included)

COMMERCIAL APPLICATIONS & REGIONAL MARKET REVIEW

Epichlorohydrin is used in the manufacture of epoxy resins for surface coatings, castings, laminates and adhesives, as well as specialty resins for water treatment, paper treatment (particularly for tea bags) and ion exchange. Epichlorohydrin is also employed as a raw material for the manufacture of a multitude of glycerol (glycerin) and glycidol derivatives used as plasticizers, stabilizers, solvents, dyestuff intermediates, surface active agents and pharmaceuticals, and as intermediates for further synthesis.

The epichlorohydrin value chain is summarized in the figure below. The three commercial methods to produce dichlorohydrin (dichloropropanol) are shown.

- Global supply, demand and trade data are given and discussed.
- In addition, supply, demand and trade data is given and discussed according to region (North American, Western European, Asia Pacific and Rest of the World)
- A list of plants in each region above is given showing specific plant capacities, owning company, location and annual tonnage produced is given
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