Clean technology in the production of epichlorohydrin

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The conventional production of epichlorohydrin takes place via allyl chloride and dichlorohydrin. A major disadvantage of this chemical process is the formation of a large amount of chlorinated organic by-products, which are found partially in the voluminous effluent. In order to reduce this emission to surface water, measures have to be taken. Technical measures varying from end-of-pipe techniques to alternative processes have been evaluated. Application of end-of-pipe techniques is not the optimal solution for emission reduction, either technically or economically. Results from in-process measures focused on reduction of the amount of waste water and contaminants are more promising. However, the development of an alternative route is necessary in order to obtain a process with minimal emissions and minimal costs.

Keywords: clean technology; epichlorohydrin; chemical industry

Introduction

In the early 1950s, the first industrial production of epichlorohydrin (ECH) took place. Nowadays, there are about 20 production locations worldwide at which ECH is produced by the conventional route starting with propene and chlorine via allyl chloride (AC) and dichlorohydrin (DCH) to ECH. The world production capacity of ECH amounts to about 800 kton per year. ECH is mainly used for the production of epoxy resins (about 50% of the ECH produced) and glycerin (about 20%). The primarily chlorine-free epoxy resins are applied in paints, electric circuits, construction, gum, and so on. Important properties of epoxy resins are chemical inertness, insensitivity to corrosion and aggressive chemicals, and good electrical isolation and adhesion properties. ECH is considered as an irreplaceable chemical compound for the production of epoxy resins at the moment.

A major problem with the conventional production process for ECH is the formation of a large amount of chlorinated by-products, which are found partially in the voluminous effluent. The amount of by-products is about 0.3 kg per kg ECH produced. The by-products are generally considered as waste and incinerated. Without waste water treatment facilities, about 1 to 3 g EOCI (extractable organochlorine compounds) per kg ECH produced is present in the effluent. In western countries, ECH production plants usually have waste water treatment facilities. However, the EOCI reduction obtained is considered to be insufficient from an environmental point of view.

Within the framework of the Dutch government programme SPA (focused on pollution prevention, clean technology and advanced waste water treatment), a project has been set up by RIZA (Institute for Inland Water Management and Waste Water Treatment) and Comprimo Consulting Services (engineering and consulting company), in which the possibilities of end-of-pipe techniques, in-process measures and clean production processes for reduction of the EOCI emission to surface water are compared.

Conventional production of ECH

The chemistry of ECH production is briefly discussed. Details about technical aspects of this production process can be found elsewhere. The synthesis of ECH can be divided into four steps:

- synthesis of allyl chloride (AC)
- synthesis of dichlorohydrin (DCH)
- synthesis of epichlorohydrin (ECH)
- synthesis of hypochlorite (HOCl)

The main reaction equations are given in Scheme 1.
\[
\begin{align*}
\text{H}_2\text{C} &= \text{CH-CH}_3 + \text{Cl}_2 \rightarrow \text{H}_2\text{C} = \text{CH-CH}_2\text{Cl} + \text{HCl} \\
\text{propene} &\quad \text{allyl chloride} \quad \text{hydrochloric acid} \\
\text{H}_2\text{C} &= \text{CH-CH}_2\text{Cl} + \text{HOCl} \rightarrow \text{CH}_2\text{Cl-CHOH-CH}_2\text{Cl} + \text{CH}_2\text{OH-CHCl-CH}_2\text{Cl} \\
\text{allyl chloride} &\quad \text{hypochlorite} \quad \text{1,3-dichlorohydrin} \quad \text{1,2-dichlorohydrin}
\end{align*}
\]

Scheme 1 Reaction equations for the synthesis of (1) allyl chloride, (2) dichlorohydrin, and (3) epichlorohydrin

**Synthesis of AC**

The synthesis of AC takes place by reaction of propene with chlorine at a temperature of 500–520°C (equation (1) in Scheme 1). The selectivity of this reaction is rather low; by-products such as mono- and dichloropropene and mono- and dichloropropane are formed.

**Synthesis of DCH**

The reaction of AC and HOCl to form DCH is performed in water at a temperature of 30°C (equation (2) in Scheme 1). Excess water has to be used in order to prevent formation of an organic phase, as the undesirable side-reaction of AC to form 1,2,3-trichloropropane (TCP) takes place in the organic phase. The low solubility of AC in water makes the large amount of water necessary\(^2\). Besides TCP, chlorinated ethers are formed as by-products. They originate from the reaction of the reactive intermediate species (chloronium ions) with DCH. Their formation is suppressed by the large amount of water.

**Synthesis of ECH**

ECH is formed by dehydrochlorination of DCH with \(\text{Ca(OH)}_2\) in water at a temperature of 90°C (equation (3) in Scheme 1). ECH is immediately removed from the solution in order to prevent formation of monochlorohydrin (MCH) and consequently glycerol\(^3\).

**Synthesis of HOCl**

The HOCl solution is used in the DCH synthesis is prepared by the reaction of chlorine and calcium hydroxide (Ca(OH)_2). HOCl is partially converted into other chlorine-containing inorganic compounds, which play a role in the formation of chlorinated organic by-products.

**Environmental aspects of the conventional process**

As mentioned earlier, the conventional production process for ECH is characterized by a large amount of by-products and a voluminous waste water flow. In nearly all processes, the by-products (~0.3 kg per kg ECH produced) have to be considered as waste and are incinerated. About 80% of the effluent (about 40 m\(^3\) per ton ECH) originates from the DCH synthesis. The effluent contains not only CaCl\(_2\) in high concentration, but also EOCl compounds. Typical concentrations are 25–75 mg l\(^{-1}\), which corresponds to an EOCl emission of 1–3 kg per ton ECH produced. In some cases, the effluent of the ECH plant is biologically treated before it is emitted to surface water. Generally the EOCl compounds are only partially removed by biological treatment. Therefore, additional measures are necessary.

In this paper, three points of view for emission reduction are considered: (i) end-of-pipe techniques and combinations of end-of-pipe techniques; (ii) in-process measures; and (iii) alternative, cleaner processes. It will be shown that for the production of ECH, application of most end-of-pipe techniques is insufficient for reaching an EOCl level of 0.1 mg l\(^{-1}\). From both an environmental and an economic point of view, in-process measures and especially alternative process routes are much more promising.

**Application of end-of-pipe techniques**

Several end-of-pipe techniques and combinations of these techniques are theoretically considered for treatment of the ECH effluent. These include (i) biological treatment, (ii) biological treatment, reverse osmosis and evaporation of the concentrate flow, (iii) biological treatment and active-carbon adsorption, (iv) biological treatment, active-carbon adsorption and wet-air oxidation for regeneration of the carbon, and (v) evaporation.

Table 1 shows the assumed removal levels and a rough estimate of the costs of the techniques for a typical production plant with a capacity of 24 kton per year. By biological treatment, about 50% of the EOCl is removed. Additional application of reverse osmosis or active-carbon adsorption results in EOCl removal of 90%. Evaporation yields 100% EOCl removal. Only by application of evaporation can the desired EOCl level of 0.1 mg l\(^{-1}\) be reached. The costs of this technique are estimated to be about 800 guilders (fl) per ton ECH produced, which is high compared to the cost price of ECH (about 3000 guilders per ton). Application of the other techniques is cheaper, but their performance is insufficient.

It is concluded that application of end-of-pipe...
techniques is not the optimal solution for EOCI emission reduction. This is caused by the large amount of waste water which has to be treated (~40 m³ per ton ECH produced). It is advisable to reduce the amount of waste water first by in-process measures and subsequently treat the smaller waste water flow.

In-process measures

In-process measures are aimed at reducing the amount of waste water and the amount of EOCI in the effluent. As the largest amount of waste water and contaminants is formed during the DCH synthesis, in-process measures are focused on this reaction step. The DCH synthesis will be discussed in more detail in order to understand the possible measures.

The mechanisms for the formation of chlorinated compounds during DCH synthesis are given in Scheme 2.5. 2. The chloronium ion is the reactive intermediate species in DCH synthesis. During this reaction step, this ion reacts with water to form 1,3- and 1,2-DCH. However, the chloronium ion also reacts with other nucleophilic species in the aqueous phase, like chloride ions, to form TCP (equation (4) in Scheme 2). TCP can also be formed in an organic phase by reaction of Cl₂ and AC, which is shown in equation (5) of Scheme 2. Tetrachloropropylether is formed by reaction of the chloronium ion with DCH (equation (6) in Scheme 2).

It is shown that EOCI compounds are formed via several mechanisms. This makes it difficult to predict the effect of a measure on the final EOCI emission, as a measure can result in different effects. The effect of the desired minimization of the amount of water is discussed as an example.

Excess water is primarily applied for preventing the formation of by-products. With excess water, formation of the organic phase is prevented. So, TCP formation originating from AC in the organic phase does not occur. Excess water also limits the formation of ether and TCP. Minimizing the amount of water will result in an organic phase and in higher DCH and chloronium ion concentration. These effects result in higher EOCI concentration, as explained earlier. Therefore, reduction of the amount of water used is not that easy.

In-process measures for EOCI reduction are focused on minimizing the Cl₂ and Cl⁻ concentration, since these species are also responsible for the formation of EOCI compounds. As Cl₂ and Cl⁻ ions originate from the HOCI solution, it is advisable to decrease their concentration in that solution. This is difficult, since the HOCI synthesis is an equilibrium reaction. Recently, an alternative pathway for the production of HOCI has been commercialized, in which a more concentrated HOCI solution is prepared. It is interesting to study whether this Olin process can be integrated in the ECH production process. The expected reduction in waste water is about 30 m³ per ton ECH. The effect on the EOCI level is not known and is difficult to predict. TCP formation will probably not occur, but the formation of chlorinated ethers can increase. This must be studied in practice.

\[
\text{CH}_2\text{C} = \text{CH} - \text{CH}_2\text{Cl} + \text{Cl}^- \rightarrow \text{CH}_3\text{Cl} - \text{CHCl} - \text{CH}_2\text{Cl} \\
\text{Cl}\quad \text{chloronium ion} \quad \text{trichloropropane}
\]

\[
\text{H}_2\text{C} = \text{CH} - \text{CH}_2\text{Cl} + \text{Cl}_2 \rightarrow \text{CH}_3\text{Cl} - \text{CHCl} - \text{CH}_2\text{Cl} \\
\text{allyl chloride} \quad \text{chlorine} \quad \text{trichloropropane}
\]

\[
\text{CH}_2\text{Cl} - \text{CHCl} - \text{CH}_2\text{OH} + \text{CH}_2\text{C} = \text{CH} - \text{CH}_2\text{Cl} \rightarrow \text{CH}_3\text{Cl} - \text{CHCl} - \text{CH}_2\text{O} - \text{CH}_2 - \text{CHCl} - \text{CH}_2\text{Cl} + \text{H}^+ \\
\text{dichlorohydrin} \quad \text{chloronium ion} \quad \text{tetrachloropropylether}
\]

Scheme 2 Three mechanistic pathways for the formation of chlorinated organic by-products: (4) trichloropropane in the aqueous phase, (5) trichloropropane in the organic phase, and (6) tetrachloropropylether
As the effects of in-process measures are not completely clear, it is interesting to study the possibilities of alternative, cleaner process routes.

Alternative process routes

Patent literature shows that research on several alternative routes for ECH has been performed. In most cases, propene is used as a feedstock. Propene is converted into allyl chloride, allyl alcohol, or dichloropropylacetate. Almost all routes include the conversion of DCH to ECH as a final step. A survey of these routes can be found elsewhere. A selection of these routes is made, based on selectivity and waste water production. This has resulted in three promising routes.

One of these promising routes is commercialized – the Showa-Denko process. It is developed due to a lack of Cl₂. The chemistry will be discussed briefly; technical details can be found elsewhere. Four reactions play a role, which are shown in Scheme 3:

- synthesis of allyl acetate
- synthesis of allyl alcohol
- synthesis of 1,2-dichlorohydrin
- synthesis of epichlorohydrin

In the Showa-Denko process, only 0.035 kg organic by-products per kg ECH produced is reported to be separated and incinerated. This is ten times lower than in the conventional production process. The amount of waste water is 8 m³ per ton ECH, which is a decrease of about 80% compared to the conventional process. Details about the EOCI level in the effluent are not known.

It is estimated that the total amount of organic material in the effluent is about 60 kg per ton ECH, which is 50% lower than in the conventional process. Although the selectivity of the reactions in this process is higher than in the conventional process, TCP formation still occurs. If the mechanism is comparable to that of the conventional route (via the chloronium ion), the formation of chlorinated ethers can also be expected. Unfortunately, no information about the emission of these compounds is known at the moment. This is an important topic for further research.

Mainly as a result of the lower production of by-products and waste water and the lower costs for feedstock, the estimated cost price for ECH is about 20% lower than that of conventionally produced ECH.

Concluding remarks

This study has shown that application of end-of-pipe techniques is not the optimal solution for EOCI emission reduction. Due to the large amount of waste water that has to be treated, these techniques become very expensive. It is advisable to minimize the amount of waste water first, before these techniques are installed. Therefore, in-process measures have to be taken. A problem with in-process measures is that by minimizing the amount of water, the EOCI load can increase.

The most elegant solution is to develop a new process in which environmental aspects are also taken into account. One alternative process has been commercialized in Japan – the Showa-Denko process. This process is worth studying in more detail, especially the environmental aspects. The non-commercialized routes are also interesting to study in more detail as, compared to the conventional process, their selectivity is higher and waste water formation is less. This study has shown that research must not be focused on end-of-pipe techniques, but that the total industrial process must be involved.

References

4. de la Mare, P.B.D. and Galanadour, S. J. Chem. Soc. 1958, 36