Changes in the composition of wastewater as a result of dehydrochlorination of 1,3-dichloropropan-2-ol under different process conditions

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The results of dehydrochlorination of 1,3-dichloropropan-2-ol to epichlorohydrin are reported. The process ran in the reaction-stripping column system with a continuous removal of epichlorohydrin in a steam stream. The influence of 10 wt% alkali solution (NaOH, Ca(OH)$_2$) and the method of distillate collection on the 1,3-dichloropropan-2-ol conversion, selectivity of transformation to epichlorohydrin and by-products, and the composition of wastewater have been analysed.

Keywords: epichlorohydrin, dehydrochlorination, dichloropropanols, 1,3-dichloropropan-2-ol, wastewater.

INTRODUCTION

The process of dehydrochlorination of 1,3-dichloro-propan-2-ol (13DCP2OL) to epichlorohydrin (EPI) is currently an issue of interest at many scientific and research centres[1–5]. Epichlorohydrin is the epoxy compound that is used in the largest quantities in the reaction with bisphenol A in the production of epoxy resins[6]. It is also used in the production of elastomers[7], polyamide-epichlorohydrin resins[8–9], resins for water purification, glycidyl ethers, polyols, and many glycidyl derivatives.

World production of epichlorohydrin in 2010 was about 1.6 million Mg. The largest world producers of epichlo-rohydrin, according to generation capacity, include: Dow Chemical (31% of global capacity), Hexion Specialty Chemicals (12%), Solvay (6%) and Nan Ya (6%) (year 2010)[10]. The demand for epichlorohydrin in the world market is still increasing. Because of increasing restrictions aimed at the protection of natural environment, more economical and environment friendly methods have been introduced. The latest method, competitive to the traditional technology based on chlorine and propylene, is the one based on glycerol[1]. The process of dichlorohydrins dehydrochlorination in glycerol method is significantly different from the traditional chlorine process. In a new method a concentrated 1,3-dichloropropane-2-ol is subjected to the dehydrochlorination. Whereas in the chlorine method about 4 wt% aqueous solution of dichloropropanols with the prevailing contribution of 2,3-dichloropropan-1-ol is used.

A leading company in the production of epichlorohy-drin based on glycerol (which is waste from the production of biodiesel) is the Solvay International Chemical Group[11]. This process is being developed under the name of Epicerol®[12]. The Solvay company developed a new class of catalysts of hydrochlorination of glycerol, whose compositions and structures are confidential, and the process is the basis for 38 patent applications. Some applications were patented in various countries of the world. The innovative process based on glycerol used for the production of epichlorohydrin was initiated in the mid-2003. The installation was built in the laboratory Neder-Over-Heembeek Research & Technologies and in April 2007 the syntheses were conducted on a pilot plant in Tavaux in France. Because of much increased environmental requirements, this process has been fully optimized. The installation is supplied with glycerol from the transesterification of rapeseed oil and has been working continuously since 2007 with epichlorohydrin production capacity of 10 000 Mg/y. Recently the Solvay company launched another plant of epichlorohydrin in Map Ta Phut in Thailand with a production capacity of 100 000 Mg/y. Another installation (in 2014) based on the Epicerol® process is to be opened in 2014 in Jiangsu Taixing in China[13].

The main advantages of the Epicerol® process over the traditional chlorine method are as follows.
– Significant reduction in the consumption of chlorine, and consequently formation of much smaller amounts of chlorinated organic compounds as by-products:
   – Lower amounts of post-production wastewater;
   – The use of non-toxic and flame retardant materials;
   – The use of renewable raw materials, the process consumes 50% less of non-renewable materials in comparison with the standard process.

Asia's share in world production of epichlorohydrin currently exceeds 50%. In Europe 350 000 Mg/y resins with epichlorohydrin are produced. In Poland, the only manufacturer of epichlorohydrin is Zachem-Ciech which has been working since 1976 and has employed the chlorine method. The production capacity of the installation is 30 000 Mg/y. In Central Europe epichlorohydrin is produced also in the Czech Republic (Spolchemie). Despite the fact that there are plants, which produce epichlorohydrin from glycerol, and new such plants are being actively built, the process of dehydrochlorination of the concentrated dichlorohydrins obtained from the glycerol is still poorly understood. In particular, as far as we know, there are no optimal process conditions reported in the literature for the combined reactive-distillation reactor.

In this study the changes in composition of the waste-water obtained after the process of dehydrochlorination of 1,3-dichloropropan-2-ol (prepared by the glycerol method) are analyzed versus the technological parameters used. The results indicate that the course of dehydro-chlorination in the reaction-stripping column by means

of 10 wt% Ca(OH)$_2$ is more preferable than that with a NaOH solution.

EXPERIMENTAL

Materials

The following raw materials were used in the studies: 1,3-dichloropropan-2-ol of 98 wt% purity containing 2% 2,3-dichloropropan-1-ol (Merck, Warsaw). Dehydrochlorination was carried out with calcium hydroxide (96 wt% Ca(OH)$_2$ and 3 wt% CaCO$_3$) and sodium hydroxide (98.8 wt% NaOH and 0.7 wt% Na$_2$CO$_3$) both produced by Chempur, Poland.

Analytical methods

The organic and water layer of distillate and wastewater were analyzed by the Trace GC 2000 Thermo apparatus, equipped with a flame ionization detector (FID) and a capillary column TR-WAX (30 m x 0.25 mm x 0.5 μm). The analytical conditions were the following: detector temperature: 250°C, carrier gas: He, flow rate 1.8 cm$^3 \cdot$ min^{-1}, air flow 350 cm$^3 \cdot$ min^{-1}, hydrogen-flow 35 cm$^3 \cdot$ min^{-1}. The oven temperature was maintained at 55°C for 2 min, then it was increased to 160°C at a rate of 15°C $\cdot$ min^{-1}, held for 3 min, then increased by 25°C $\cdot$ min^{-1} to 240°C and maintained at 240°C for 4 min. A sample was introduced to a feeder with a partition (split 10:1) at 200°C.

The identification of the peak on the chromatograms was performed on the bases of retention times of the standards. The quantitative determinations of the composition of the distillate and wastewater were made with the help of the internal standard method, with octane.

The concentration of chlorine in inorganic compounds or complexes was determined by the argentometric method. Titrator TitroLine Easy module 3 produced by Schott was used for the determination. The amount of water in the organic layer of the distillate was determined by modified coulometric method on KF831 apparatus produced by Metrohm. Glycerol concentration in the wastewater from the reboiler was determined by the periodate method.

Experimental procedure

The solutions used in the process were 88 wt% aqueous solution of 13DCP2OL and 10 wt% aqueous solutions of calcium and sodium hydroxide. Dehydrochlorination was carried out in the apparatus described in literature[14]. The syntheses were performed using two types of dehydrochlorinating agents and the epichlorohydrin distillate was collected from the top of the reaction-stripping column or from the reboiler. After condensation, the distillate was separated into an organic layer and a water layer. Both the layers and the wastewater were analyzed quantitatively by gas chromatography and on the basis of this analysis the mass balances of each synthesis were performed. Concentrations of the following compounds were determined: 13DCP2OL, 2,3-dichloropropan-1-ol, 3-chloropropane-1,2-diol, glycerol, glycidol and diglycidyl ether.

RESULTS

Dehydrochlorination with a 10 wt% solution of calcium and sodium hydroxide using two methods of epichlorohydrin distillate collection

If the product is collected in the form of a distillate from a reaction-stripping column regardless of the type of alkali, a high selectivity of transformation to epichlorohydrin is obtained (98–99%). If the distillate is collected from the reboiler, a decrease in selectivity to 85–87% is observed (Table 1), however then the 13DCP2OL conversion is almost complete (99.1 and 99.7%). A much lower conversion of 90% is obtained when the distillate is collected from the column, which is a result of the method of operation of the reaction-stripping system. When epichlorohydrin is collected from the column, it spends less time in the alkaline reaction medium, which limits the possibility of its subsequent conversion into such products as: 3-chloropropane-1,2-diol, glycidol, glycerol, diglycidyl ether and polyglycerols. As a result of epichlorohydrin hydration, 3-chloropropane-1,2-diol is obtained and its dehydrochlorination leads to glycidol. Glycidol in an alkaline medium and at elevated temperatures hydrates to glycerol. As a consequence of the reaction of glycerol with glycidol or condensation of glycerol molecules, di–, polyglycerols and cyclic digly-

epichlorohydrin   3-chloropropane-1,2-diol   glycidol   glycerol   diglycerol   polyglycerols
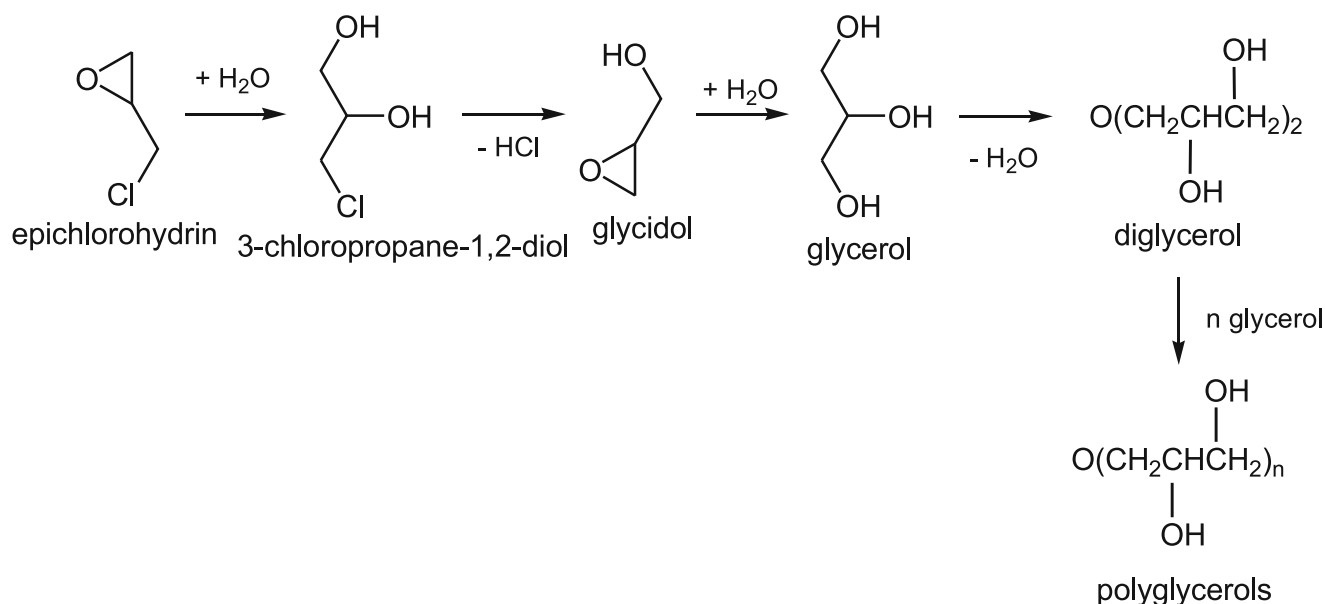
cerol are formed. The course of these reactions can be summarized as follows:
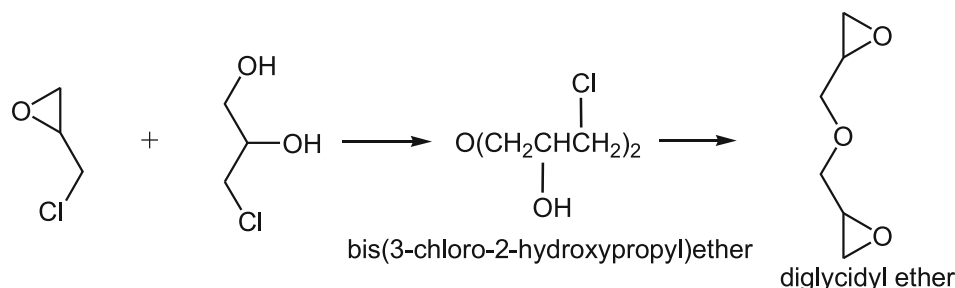
In the independently performed experiments, the formation of diglycidyl ether in the reaction of epichlo-

bis(3-chloro-2-hydroxypropyl)ether

diglycidyl ether

rohydrin with 3-chloropropane-1,2-diol in an alkaline medium was confirmed.

Glycerol and polyglycerols occur only in wastewater, the other products can be present in the distillate. Greater amounts of by-products are obtained when the distillate of epichlorohydrin is collected from the reboiler than from the column (Table 1). Wastewater from the reboiler can contain unreacted 13DCP2OL, 2,3-dichloropropan-1-ol, 3-chloropropane-1,2-diol, glycerol, glycidol, diglycidyl ether and polyglycerols, regardless of the type of dehydrochlorinating agent. When the distillate was collected from the column, the wastewater did not contain 3-chloropropane-1,2-diol and diglycidyl ether, the concentration of epichlorohydrin decreased from 0.306–0.503 wt% to 0.000 wt% and the content of glycidol was lowered.

The dehydrochlorination of 13DCP2OL with the use of a 10 wt% aqueous solution of lime milk and collection of epichlorohydrin in the form of the distillate from the column is more beneficial. Although the 13DCP2OL conversion in these conditions is not complete (90%),

but the selectivity of transformation to epichlorohydrin is the highest possible, of 99%.

In the working system of the reaction stripping-column applied it is preferable to run the process at the highest selectivity of epichlorohydrin and at a slightly lower conversion of 13DCP2OL than in the opposite way of working. A distillate from the reaction-stripping column undergoes liquid-liquid phase separation into the aqueous and organic layers. 13DCP2OL dissolved in the aqueous layer of the distillate (0.5–2.0 wt%) can be recycled with all the aqueous layer onto the column. The organic layer containing 1–5 wt% 13DCP2OL must then be rectified on a typical distillation column for the separation of pure epichlorohydrin and 13DCP2OL. Owing to this, 13DCP2OL recovered can be recycled to the reaction-stripping column. A smaller amount of 13DCP2OL is lost in the form of by-products. The conversion of the raw organic material to by-products would then be smaller than in the process without recirculation. A better utilization of 13DCP2OL is achieved owing to the recirculation.

Besides the unreacted calcium hydroxide, calcium carbonate and calcium chloride, some small amounts of unreacted 1,3-dichloropropan-2-ol, glycerol and polyglycerols are present in the wastewater.

Table 1. 1,3-dichloropropan-2-ol conversion, selectivity of transformation to epichlorohydrin and wastewater composition, in the processes when the distillate was collected from the reaction-stripping column and from the reboiler

Site of distillate collection		Column		Reboiler	
Type of alkali solution		10 wt% Ca(OH)$_2$	10 wt% NaOH	10 wt% Ca(OH)$_2$	10 wt% NaOH
Molar ratio of alkali to 13DCP2OL	[mol · mol^{-1}]	0.45:1	0.91:1	0.48:1	0.98:1
Temperature	[°C]				
– pre-reactor		80.3	39.7	69.5	37.8
– reactor		76.1	68.0	72.5	68.3
– reboiler		82.1	67.7	79.6	68.1
pH in distillation reboiler		9.4	8.2	9.5	8.8
Pressure	[kPa]	52.7	53.2	53.1	52.2
Flow rate of 88 wt% 13DCP2OL solution	[cm^3 · min^{-1}]	3.0	14.0	3.0	14.0
Flow rate of alkali solution	[cm^3 · min^{-1}]	9.1	40.0	10.1	42.0
Flow rate of steam	[dm^3 · min^{-1}]	4.3	6.2	2.5	6.2
Reaction time	[min]	120	50	120	50
		WASTEWATER COMPOSITION			
weight	[g]	1044.1	2508.0	1790.6	2590.9
Concentrations:	[wt%]				
– epichlorohydrin		0.000	0.111	0.286	0.503
– 1,3-dichloropropan-2-ol		0.020	0.072	0.020	0.011
– 2,3-dichloropropan-1-ol		0.000	0.018	0.009	0.017
– 3-chloropropane-1,2-diol		0.000	0.000	0.210	0.191
– glycidol		0.000	0.133	0.176	0.161
– glycerol		0.147	0.153	0.365	0.881
– diglycidyl ether		0.000	0.000	0.007	0.012
		TECHNOLOGICAL INDICATORS			
13DCP2OL conversion	[%]	89.5	83.5	99.6	99.1
Selectivity of EPI	[%]	98.3	98.7	86.5	85.2

The composition of wastewater left after dehydrochlorination of 1,3-dichloropropan-2-ol with a 10 wt% solution of calcium hydroxide under variable flow rate of reactant streams

Having established that the dehydrochlorination of aqueous solution of 13DCP2OL of a concentration of 88 wt% with the use of a 10 wt% calcium hydroxide solution and with collecting of epichlorohydrin in the form of distillate from the column leads to the highest selectivity of transformation to EPI, a series of tests was carried out for a varied flow rate of raw materials.

The concentration of the substrates and other technological parameters were kept constant. Table 2 presents the data illustrating the effect of changes in the reactant streams flow rates on the composition of wastewater. The increase in the flow rate of reactants reduces the temperature of the pre-reactor. With increasing the total flow rate of the substrates from 12.1 $cm^3 \cdot min^{-1}$ to 70 $cm^3 \cdot min^{-1}$ the pre-reactor temperature is reduced from 80.3°C in the synthesis of 1 to 38.1°C in the synthesis of 6. The increasing flow rate of reactants reduces the temperature in the pre-reactor, because at the time the reactants were mixed they had the ambient temperature. This does not affect the operating temperature of the reactor, because of additional heating of its much larger area. However, the increasing flow rate of the reactants has impact the content of organic compounds in wastewater, conversion of 13DCP2OL and selectivity of transformation to epichlorohydrin and by-products. The most appropriate temperature of the pre-reactor is 70–80°C and it occurs at the total flow rate stream reactants in the range of 12.1–36.0 $cm^3 \cdot min^{-1}$. A good mixing of 13DCP2OL and calcium hydroxide solution is also important. Comparable results of 13DCP2OL conversion and selectivity of transformation to epichlorohydrin indicate that this occurs at the above indicated flow rate of the reactants. The pre-reactor temperature is therefore important to obtain the maximum of 13DCP2OL conversion and selectivity of transformation to epichlorohydrin. It is the place in which the majority of 13DCP2OL introduced is dehydrochlorinated. The flow rate of the reactants close to 70.0 $cm^3 \cdot min^{-1}$ is too much column burden, which results in an irregular flow of streams and a periodic shift of part of the reactants from the column into the receiver. Consequently, the 13DCP2OL conversion and selectivity of transformation to epichlorohydrin decreases. Although the exchange of mass (intense mixing) is good, the share of unreacted 13DCP2OL in the wastewater increases. In relation to the amount of reactants, the steam stream flow is too weak for a complete removal of epichlorohydrin from wastewater. In all the experiments in this series, epichlorohydrin was present in the wastewater. However, at low flow rates of reactants of 12.1–36.0 $cm^3 \cdot min^{-1}$, its share in the wastewater is small (0.001–0.024 wt%) and increases to 1.53 wt% when raising the flow rate to about 70.0 $cm^3 \cdot min^{-1}$. More pronounced is the effect of the flow rate of reactants on the contents of unreacted 13DCP2OL and glycerol. With increasing flow rate of reactants the concentration of 13DCP2OL in the wastewater increases. The concentration of glycerol in the wastewater is at a similar level (0.09–0.15 wt%) in all experiments, which means a loss of unreacted 13DCP2OL. Moreover 2,3-dichloropropan-1-ol is present in the wastewater at a constant level of about 0.05 wt%. Most of it was introduced with 13DCP2OL. The presence of glycidol and 3-chloropropano-1,2-diol in the wastewater is not related to the flow rate of the reactants. The highest concentration of 3-chloropropane-1,2-diol in one of the samples reached the value of 0.12 wt%. However, in most experiments its content was lower. Glycidol occasionally occurs in the wastewater as a result of dehydrochlorination of 3-chloropropane-1,2-diol but it immediately reacts to glycerol. The selectivity of transformation to epichlorohydrin and the compositions of wastewater in experiments 1–6 are shown in Table 2.

Table 2. Changes in the technological indicators (conversion and selectivity) and in wastewater composition in response to an increased flow rate of the reactants

Number of experiments		1	2	3	4	5	6
Molar ratio of Ca(OH)$_2$/13DCP2OL	[mol · mol^{-1}]	0.44:1	0.44:1	0.44:1	0.43:1	0.58:1	0.48:1
Temperature	[°C]						
– pre-reactor		80.3	72.2	70.2	67.1	65.1	38.1
– reactor		77.1	76.4	73.0	72.5	69.3	71.7
– reboiler		82.1	81.0	76.2	80.8	77.0	76.7
pH in distillation reboiler		8.4	8.3	8.4	8.2	8.6	8.4
Pressure	[kPa]	52.7	54.4	51.1	53.0	53.7	53.2
Flow rate of 88 wt% 13DCP2OL solution	[cm^3 · min^{-1}]	3.0	6.0	8.0	14.0	13.0	20.0
Flow rate of calcium hydroxide solution	[cm^3 · min^{-1}]	9.1	19.0	28.0	35.0	41.3	50.0
The total flow of reactants	[cm^3 · min^{-1}]	12.1	25.0	36.0	49.0	54.3	70.0
Flow rate of steam	[dm^3 · min^{-1}]	4.3	4.1	4.3	4.3	4.3	5.2
Reaction time	[min]	120	60	60	60	50	40
WASTEWATER COMPOSITION COMPOSITION							
weight	[g]	1044.1	1075.7	1532.2	2589.6	2313.3	2001.6
Composition:	[wt%]						
– epichlorohydrin		0.001	0.040	0.024	0.562	1.163	1.531
– 1,3-dichloropropan-2-ol		1.225	1.515	1.535	1.808	2.642	3.866
– 2,3-dichloropropan-1-ol		0.050	0.055	0.051	0.060	0.052	0.056
– 3-chloropropane-1,2-diol		0.000	0.076	0.000	0.114	0.092	0.125
– glycidol		0.000	0.000	0.002	0.112	0.003	0.000
– glycerol		0.086	0.099	0.126	0.098	0.134	0.148
– diglycidyl ether		0.000	0.000	0.000	0.000	0.002	0.012
TECHNOLOGICAL INDICATORS							
13DCP2OL conversion	[%]	89.5	83.6	89.4	80.5	80.6	78.4
Selectivity of EPI	[%]	98.3	98.9	99.6	98.3	96.2	96.1

CONCLUSIONS

As follows from the above described results, a higher conversion (89.5%) at a comparable selectivity of transformation to epichlorohydrin (98.3% and 98.7%) is obtained in dehydrochlorination with a 10 wt% solution of calcium hydroxide than with a 10 wt% solution of sodium hydroxide. A better effect of the reaction is obtained when the distillate is collected from the column rather than when it is collected from the reboiler. The technological parameters of the process are as follows: pre-reactor temperature 70°C, reactor 73°C, reboiler 76°C, pressure 51.1 kPa, the molar ratio of $Ca(OH)_2$/13DCP2OL = 0.44:1, flow rate of 88 wt% 1,3-dichloropropan-2-ol solution 8.0 $cm^3 \cdot min^{-1}$, flow rate of 10 wt% $Ca(OH)_2$ solution 28.0 $cm^3 \cdot min^{-1}$. In these conditions a smaller amount of by-products is formed and the wastewater contains a small amount of unreacted 13DCP2OL with contaminating 2.3-dichloropropan-1-ol and glycerol. To achieve high selectivity of transformation to epichlorohydrin and high 13DCP2OL conversion is very important to maintain a temperature of about 70–80°C in the pre-reactor, at the time of mixing the reactants and ensure good mixing. In this element of the apparatus the most intensive dehydrochlorination takes place immediately followed by distillation of forming epichlorohydrin. An increase in the flow rate of reactants in the range from 12.1 to 49.0 $cm^3 \cdot min^{-1}$ results in the increased content of epichlorohydrin and unreacted 13DCP2OL with 2,3-dichloropropan-2-ol in wastewater. Glycerol occurs at an almost constant level of concentration in the wastewater. Increasing the flow rate of reagents decreases the process indicators and increases the total content of organic compounds in the wastewater.

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