

Dehydrochlorination of 1,3-dichloropropan-2-ol by calcium and sodium hydroxide solutions

Anna Krzyzanowska*, Eugeniusz Milchert, Marcin Bartkowiak

West Pomeranian University of Technology, Szczecin, Institute of Organic Chemical Technology, Pułaski 10 Street, 70-322 Szczecin, Poland

*Corresponding author: e-mail: akrzyzanowska@zut.edu.pl

The results of dehydrochlorination of 88 wt% aqueous solution of 1,3-dichloropropan-2-ol to epichlorohydrin are reported. The process was carried out in the reaction-stripping column system with a continuous removal of epichlorohydrin in the steam stream. Aqueous solutions of sodium and calcium hydroxides at concentrations in the range of 3–14 wt% were used for the dehydrochlorination. The influence of the type and concentration of dehydrochlorination agent on 1,3-dichloropropan-2-ol conversion, the selectivity of transformation to epichlorohydrin and by-products, and the composition of distillate and wastewater were studied.

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

INTRODUCTION

Epichlorohydrin is a compound used primarily in the production of epoxy resins¹. Currently, the epichlorohydrin is produced on an industrial scale mainly by the chlorine method². This technology uses large amounts of chlorine and propylene, obtained by pyrolysis of hydrocarbons. Epichlorohydrin produced by this method is 99.9% pure, which is the undoubted advantage, however, the multi-step process involves the formation of considerable amounts of organic and inorganic products. The inorganic by-products comprise calcium or sodium chloride (depending on the type of hydroxide used in the process) and hydrogen chloride. The organic by-products include: unreacted allyl chloride, 2-chloroprop-1-ene, 1-chloroprop-1-ene, 2-chloropropane, 1-chloropropane, 1,3-dichloroprop-1-ene, 2,3-dichloroprop-1-ene, 1,2-dichloropropane, 1,2,3-trichloropropane, glycerol and polyglycerols.

In the conventional technology allyl chloride is obtained in the reaction of propylene with chlorine. After chlorohydroxylation of allyl chloride is formed an aqueous solution of dichloropropanols at a concentration of 2–5 wt%, with prevailing fraction of 2,3-dichloropropan-1-ol isomer. A low solubility of allyl chloride in the water precludes the preparation of more concentrated solutions. The selectivity of transformation to dichloropropanols decreases rapidly at higher concentrations of these solutions. Allyl chloride and by-products: 1,2,3-trichloropropane and chloroethers form a separate organic layer, what considerably intensifies the formation of additional amounts of these compounds. With regard to the significant consumption of steam for distillation of the epichlorohydrin in the dehydrochlorination stage (more than 57 Mg/Mg epichlorohydrin) as well as water in the stage of chlorohydroxylation, a substantial amount of wastewater is generated in this process.

In a newly proposed method for the production of epichlorohydrin³ the first stage (hydrochlorination of glycerol) yields dichloropropanols as the main products at the concentration range 40–61 wt% with prevailing fraction of more active 1,3-dichloropropan-2-ol (13DCP2OL). Additionally 3-chloropropane-1,2-diol and 2-chloropropane-1,3-diol were formed as the by-products. The post-reaction solution also contains unreacted glycerol and

the catalyst that can be recycled into the process. The second stage is the dehydrochlorination of dichloropropanols, which gives epichlorohydrin and the following by-products: glycidol, 3-chloropropane-1,2-diol, diglycidyl ether, glycerol and polyglycerols. The latest method for the production of epichlorohydrin allows management of glycerol which is a by-product of the synthesis of fatty acid methyl esters (FAME). These esters are the basic biocomponents used for production of diesel fuel or they are used as a stand-alone fuel. Sure advantages of the new technology are generation of a much smaller amounts of by-products and wastewater and lower energy consumption than in the conventional chlorine method. The glycerol technology of epichlorohydrin production reduces the need for utilization of waste fractions containing organic chlorine derivatives, including high boiling chloropropyl ethers. Moreover there is no need to build an incineration plant for chlorine derivatives. This technology also allows the use of waste hydrogen chloride at the hydrochlorination stage.

Dichloropropanols prepared by both methods differ significantly in the composition which causes the need to use different technological parameters. In the chlorine method realized commercially, calcium hydroxide solutions are used. It results from literature that in a new glycerol technology sodium hydroxide at the concentration range 20–50 wt%^{4–8} can be used for the dehydrochlorination of dichloropropanols. This creates the possibility of separation of sodium chloride and its utilization for production of sodium hydroxide and chlorine by membrane electrolysis method. However, this solution has not yet been implemented in the industrial realization, with regard to the significant costs of purifying sodium chloride. The dehydrochlorination of dichloropropanols has previously been investigated in several other papers. The kinetic aspects of the dehydrochlorination process⁹, kinetic parameters of reaction carried out in the microreactor¹⁰, dehydrochlorination in the continuous flow stirred tank reactor¹¹ were investigated. The Solvay Company had obtained more than 30 patents for solutions applied in the hydrochlorination process of glycerol and dehydrochlorination of dichloropropanols.

A consumption of raw materials and energy media in both methods, calculated on the basis of the mass and energy balances are shown in Table 1.

Table 1. The consumption of raw materials and energy media in the chlorine and glycerol methods in relation to 1 Mg of epichlorohydrin

Raw material		Chlorine method	Glycerol method
Propylene	[kg]	645	–
Chlorine		2100	–
Calcium hydroxide (as $\text{Ca}(\text{OH})_2$)		1060	581
Glycerol		–	1061
Hydrogen chloride (as HCl)		–	970
Steam	[kg]	7000	4800
Process water	[kg]	58	1,8
Electric energy	[kWh]	600	110

A comparison of parameters of the dehydrochlorination process of 13DCP2OL with a solution of calcium and sodium hydroxide in a pilot plant scale has not been presented in the literature. A kind of dehydrochlorination agent, method of process running and the technological parameters have an essential influence on the course of dehydrochlorination, moreover, they determine the conversion of raw materials and the selectivity of transformation to epichlorohydrin.

The objective of this work was to investigate the effect of the type and concentration of hydroxide on the conversion of 13DCP2OL and selectivity of transformation to epichlorohydrin and by-products in the reaction-stripping column. In this study was compared the course of dehydrochlorination of 88 wt% aqueous solution of 13DCP2OL with the use of calcium and sodium hydroxide solutions (3–10 wt%). The best technological parameters were determined for the dehydrochlorination process by calcium hydroxide solution in the reaction-stripping column.

EXPERIMENTAL

Material

In the study 13DCP2OL of 98% purity, containing 2 wt% of 2,3-dichloropropan-1-ol (Merck, Warsaw) was used. The dehydrochlorination was performed with calcium hydroxide (96 wt% $\text{Ca}(\text{OH})_2$ and 3 wt% CaCO_3 , Chempur, Piekary Śląskie) and sodium hydroxide (98.8 wt% NaOH and 0.7 wt% Na_2CO_3 , Chempur, Piekary Śląskie).

Analytical methods

After each synthesis, the wastewater and organic and aqueous layers of the distillate were subjected to quantitative chromatographic analyses performed. The organic layer was analyzed on an SRI 8610C apparatus, equipped with a flame ionization detector (FID) and a capillary column DB-WAX (30 m x 0.25 mm x 1.0 μm). The aqueous layer and wastewater were analyzed on a Trace GC Ultra Thermo apparatus with a flame-ionization detector (FID) fitted with an RTX Restek 1701 (30 m x 0.53 mm x 1.0 μm) capillary column.

The identification of peaks on the chromatograms was performed on the basis of retention times of the standards. A quantitative determination of compositions of the distillate and wastewater was made by means of the internal standard method, with octane.

The concentration of chlorine combined in the inorganic manner was determined by the argentometric method. Titrator TitroLine Easy module 3 (Schott) was used for

the determinations. The amount of water in the organic layer of the distillate was determined by a modified coulometric method on KF831 apparatus (Metrohm). The glycerol concentration in the wastewater from reboiler was determined by the periodate method.

Experimental procedure

Dehydrochlorination process was carried out in the reaction-stripping column system with a continuous removal of epichlorohydrin in the steam stream^{12, 13}. The distillate of epichlorohydrin was collected from the top of the reaction-stripping column as water-epichlorohydrin azeotrope. After condensation this azeotrope was separated into the organic and the aqueous layer.

RESULTS

Dehydrochlorination by calcium hydroxide solution

The dehydrochlorination was performed using 5 and 10 wt% aqueous solutions of calcium hydroxide, at the molar ratio equal to or very close to the reaction stoichiometry – $\text{Ca}(\text{OH})_2/13\text{DCP2OL} = 0.5:1$ (Table 2 and 3). A pre-reactor temperature was varied in the range of 38–47°C, the reactor from 63 to 72°C, reboiler 74–77°C. The values of remaining parameters were presented in the above tables.

The organic and aqueous layer of the distillate collected from the reaction-stripping column contained: epichlorohydrin, 13DCP2OL, 2,3-dichloropropan-1-ol, 3-chloropropane-1,2-diol and water, in the amounts presented in Table 2. The epichlorohydrin concentration in the organic layer of distillate amounted to 94–96 wt%, whereas in the aqueous layer from 0.5 to 6 wt%. In the case of disturbance in the flow rate of $\text{Ca}(\text{OH})_2$ solution, the 13DCP2OL concentration increased in both layers and the concentration of epichlorohydrin and 13DCP2OL in effluent stream was higher. Under presented conditions, the conversion of 13DCP2OL at least at the level of 92% is achieved regularly with the selectivity of transformation to epichlorohydrin equal to 98%.

Because of limited solubility, 10 wt% calcium hydroxide occurs in water in the form of suspension, with a constant value of $\text{pH} = 12.5$. The suspension was continuously stirred with a magnetic stirrer and dispensed onto the column using a peristaltic pump. Dosing this solution caused difficulties induced by sedimentation of calcium hydroxide and calcium carbonate (contained in the calcium hydroxide) in the feeding line and on the Raschig rings in the reaction-stripping column, which could lead to reduced efficiency of distillation. To prevent this, the

Table 2. The technological parameters and results of dehydrochlorination of 13DCP2OL by calcium and sodium hydroxide solution

Type of alkalis		Technological parameters					NaOH 10
		Ca(OH) ₂ 5	Ca(OH) ₂ 10	Ca(OH) ₂ 10	NaOH 3	NaOH 10	
Concentrations	[wt%]						
Molar ratio of alkalis /13DCP2OL	[mol/mol]	0.55:1	0.47:1	0.48:1	0.79:1	0.89:1	1.06:1
Temperature	[°C]						
– pre-reactor		47.2	41.7	38.0	46.8	44.6	45.6
– reactor		62.7	69.3	71.7	74.5	68.0	76.2
– reboiler		73.7	77.0	76.7	77.8	67.7	78.9
pH in reboiler		9.8	9.6	9.2	8.4	8.9	9.3
Pressure in the column	[kPa]	50.1	53.7	53.2	54.8	54.2	53.8
Flow rate of 88 wt% 13DCP2OL solution	[cm ³ /min]	6.4	13.0	20.0	4.5	14.0	14.0
Flow rate of alkalis solution	[cm ³ /min]	40.0	40.0	50.0	40.0	40.0	40.0
Flow rate of steam	[dm ³ /min]	6.1	6.0	6.3	5.6	6.2	6.1
Contact time of the reagents*	[s]	21	21	21	27	21	21
13DCP2OL conversion	[%]	Technological indicators					91.1
		91.4	89.3	84.3	86.5	88.7	
Selectivity to	[%]						
– epichlorohydrin		82.6	99.0	99.4	90.1	96.7	89.4
– 3-chloropropane-1,2-diol		2.5	0.5	0.0	0.03	0.0	0.6
– glycidol		0.0	0.0	0.0	1.9	0.8	0.8
– glycerol		3.7	0.5	0.6	0.6	0.3	1.2

* experimentally determined contact time of the reagents in the column

Table 3. The composition of distillate epichlorohydrin and wastewater

Type of alkalis		Ca(OH) ₂ 5	Ca(OH) ₂ 10	Ca(OH) ₂ 10	NaOH 3	NaOH 10
Concentrations	[wt%]					
Molar ratio of alkalis/13DCP2OL		0.50:1	0.46:1	0.45:1	0.91:1	0.93:1
pH in reboiler		9.2	9.1	9.0	9.2	9.3
Mass of organic layer	[g]	56.70	367.10	567.50	149.60	443.70
Composition:	[wt%]					
– epichlorohydrin		95.66	93.78	82.20	93.50	92.48
– 1,3-dichloropropan-2-ol		3.06	4.54	14.94	4.62	5.83
– 2,3-dichloropropan-1-ol		0.05	0.03	0.13	0.05	0.00
– water		1.23	1.65	2.73	1.83	1.69
Mass of aqueous layer	[g]	470.00	221.00	539.40	281.30	343.00
Composition:	[wt%]					
– epichlorohydrin		5.58	0.45	1.75	3.04	4.88
– 1,3-dichloropropan-2-ol		2.00	0.80	1.07	1.35	1.08
– 2,3-dichloropropan-1-ol		0.03	0.01	0.02	0.01	0.01
– 3-chloropropane-1,2-diol		0.28	0.00	0.00	0.02	0.00
– glycidol		0.00	0.00	0.00	0.14	0.14
– water		92.11	98.74	97.16	95.44	94.99
Wastewater	[g]	2336.60	2313.00	2001.60	2395.40	2201.00
Composition:	[wt%]					
– epichlorohydrin		0.12	0.16	0.53	0.01	0.15
– 1,3-dichloropropan-2-ol		0.26	1.52	1.23	1.03	6.03
– 2,3-dichloropropan-1-ol		0.02	0.06	0.06	0.02	0.04
– 3-chloropropane-1,2-diol		0.11	0.09	0.00	0.01	0.00
– glycidol		0.00	0.00	0.00	0.10	0.13
– glycerol		0.21	0.13	0.14	0.04	0.05
13DCP2OL conversion	%	93.1	90.5	91.7	89.5	90.6
Selectivity to epichlorohydrin	%	88.3	99.1	97.8	91.1	95.5

Average temperatures in the pre-reactor, reactor, reboiler, flow rates of reagents and steam were similar to those presented in Table 2.

* disturbances in the flow of solution.

reaction-stripping column was periodically washed (after 5 trials) by a 10 wt% nitric acid(V) solution and distilled water. The limited solubility of calcium hydroxide in water is beneficial since permits to maintain the pH at a constant level (nearly constant concentration of the OH⁻ ions), thereby too high alkalization of the medium is avoided which also prevents the formation of organic by-products in considerable amounts.

The wastewater contained organic compounds: epichlorohydrin, 13DCP2OL, 2,3-dichloropropan-1-ol, 3-chloropropane-1,2-diol, glycidol, glycerol, polyglycerols and inorganic ones: calcium carbonate, calcium hydrocarbonate, calcium chloride and unreacted calcium hydroxide.

Dehydrochlorination by sodium hydroxide solution

The dehydrochlorination was carried out with the use of 3 and 10 wt% aqueous solutions of sodium hydroxide, at the molar ratio of NaOH/13DCP2OL slightly below or above the equimolar ratio (Table 2 and 3). An average temperatures of pre-reactor, reactor, reboiler, as well as the flow rate of reagents and steam, pH in the reboiler and contact time of the reagents were similar to those applied during the dehydrochlorination with a calcium hydroxide solution. These studies indicated that the application of NaOH solution with the concentration of 10 wt% is more advantageous in a comparison with more diluted solution. In both cases the 13DCP2OL

conversion in the range 89–91% was obtained, while the selectivity of transformation to epichlorohydrin was equal to 97%, when a more concentrated solution of NaOH was used (Table 3). The effect of the molar ratio of NaOH/13DCP2OL is also noticeable. The conversion of 13DCP2OL is higher above the equimolar ratio, but the selectivity of transformation to epichlorohydrin was decreased (Table 2).

Dosing of sodium hydroxide did not cause any problems owing to its high solubility in water. The aqueous layer of the distillate and wastewater were found to contain glycidol, which was not identified in these media in the syntheses performed using calcium hydroxide. The total concentration of organic compounds discharged with the effluents amounts to 1.2–1.4 wt% (Table 3). The losses of 13DCP2OL and epichlorohydrin are the highest, whereas the compounds in the form of 2,3-dichloropropan-1-ol, 3-chloropropane-1,2-diol, glycidol and glycerol were lost in a smaller quantity. A spent solution (NaCl) from dehydrochlorination with sodium hydroxide after the concentration and removal of organic compounds can be used again in the electrolyzer for the production of chlorine, hydrogen and sodium hydroxide. This solution cannot be used in new electrolyzers using the ion exchange membranes or in mercury electrolyzers.

Comparison of dehydrochlorination with the use of calcium hydroxide and sodium hydroxide solution

As a result of dehydrochlorination of 88 wt% aqueous solution of 13DCP2OL with the use of sodium or calcium hydroxide solutions of 3 and 5 wt%, respectively, the conversion of 13DCP2OL in the range 87–93% was achieved. The selectivity of transformation to epichlorohydrin when sodium hydroxide is applied reaches 91%, and when lime milk is applied it is 88%. The dehydrochlorinations performed using these relatively diluted solutions of calcium hydroxides, leads to a larger quantity of 3-chloropropane-1,2-diol in the aqueous layer of the distillate and in wastewater. This compound was formed as a result of hydration of epichlorohydrin during its stripping in the flow of steam. 3-Chloropropane-1,2-diol does not form or it is formed in much less amounts when the dehydrochlorination is carried out by 10 wt% solutions of sodium or calcium hydroxide. Thus the use of diluted solutions leads to increased amount of aqueous layer of the distillate and wastewater.

In the process performed with a 5 wt% calcium hydroxide solution, the wastewater contained the greatest amount of glycerol. It results from a high rate of glycidol hydration to glycerol. As a result, glycidol does not occur in the distillate and effluent, however, the glycerol concentration in the effluent is higher.

At similar process parameters, with an increase of alkaline reagent concentration to 10 wt%, the selectivity of transformation to epichlorohydrin increases to 99% and to 96% respectively in the case of calcium and sodium hydroxide. A comparison of results demonstrates that the application of a 10 wt% calcium hydroxide solution leads to slightly better results than those with a 10 wt% sodium hydroxide solution (Table 3). A lower selectivity of transformation to epichlorohydrin can be caused by a higher alkalinity of sodium hydroxide ($\text{pH}_{10\text{wt}\%} = 14.4$). Despite a good stirring, the side-reactions can locally

proceed, with regard to their consecutive character and the alkalinity of the reaction medium.

Moreover the studies demonstrate other regularities. A decrease in the conversion of 13DCP2OL is accompanied by increased amount of this compound mainly in the organic layer of distillate and to a lesser degree in the aqueous layer. The concentration of 13DCP2OL in the effluent is at the same level. This results from higher solubility of 13DCP2OL in the epichlorohydrin in a comparison with its solubility in water. Simultaneously, this relationship confirms a sufficient flow rate of steam, ensuring distilling off the epichlorohydrin and less volatile components. Moreover, the unreacted 13DCP2OL is distilling off with steam relatively easily because it forms an azeotrope with steam with the boiling point lower than the boiling point of each of the components¹⁴. It was found that glycidol and 2,3-chloropropane-1-ol occurs in the effluent at a lower level of the concentrations, when glycidol and 3-chloropropane-1,2-diol is present in the trace amounts.

The molar ratio of the reactants also affects the course of dehydrochlorination. An interesting relationship was observed in the syntheses with calcium hydroxide. In the reactions in which the molar ratio of $\text{Ca}(\text{OH})_2/13\text{DCP2OL}$ amounted to 0.47–0.48:1, and hence, was smaller than the ratio resulting from the reaction stoichiometry (0.5:1), a lower conversion of 13DCP2OL was obtained, with a slightly higher selectivity of transformation to epichlorohydrin. As a consequence, the yield of epichlorohydrin, calculated as a product of conversion and the selectivity, was similar to that obtained during the application of a 10 wt% NaOH solution.

Using an excess of calcium hydroxide ($\text{Ca}(\text{OH})_2/13\text{DCP2OL} = 0.55:1$), the conversion was even higher, while the selectivity of transformation to epichlorohydrin was decreased. Similar relationships were observed in the presence of an excessive of 10 wt% solution of NaOH ($\text{NaOH}/13\text{DCP2OL} = 1.06:1$). However the epichlorohydrin yield was slightly lower. In the technological process under study, the achievement of the highest selectivity of transformation to epichlorohydrin takes on greater importance than the achievement of the highest conversion. The 13DCP2OL unreacted can be relatively easy recovered by the distillation method and recycled to the dehydrochlorination. Owing to the recirculation, the losses of 13DCP2OL as a result of the formation of by-products, are smaller.

Several syntheses were conducted with a 14 wt% calcium hydroxide solution in order to verify how a further increase in the concentration will affect the results of the dehydrochlorination. Simultaneously, it would allow to reduce the quantity of effluents. The values of technological parameters and the magnitudes of technological indicators are summarized in Table 4. The dehydrochlorination carried out with a 14 wt% calcium hydroxide solution gives less favorable results. Epichlorohydrin is formed with a lower selectivity at a similar conversion of 13DCP2OL. Epichlorohydrin undergoes the reaction to a greater degree to 3-chloropropane-1,2-diol and to consecutive by-products (glycidol, glycerol, polyglycerols). A higher concentration of calcium hydroxide also increases its deposition on the column packing material and in the feed lines.

Table 4. The technological parameters and results of dehydrochlorination of 13DCP2OL by 10 wt% and 14 wt% calcium hydroxide solutions

Concentration of calcium hydroxide solution	[wt%]	Technological parameters				
		10	10	10	14	14
Molar ratio of $\text{Ca}(\text{OH})_2$ /13DCP2OL	[mol/mol]	0.43:1	0.65:1	0.67:1	0.59:1	0.55:1
Temperature	[°C]					
– pre-reactor		76.1	45.7	67.1	48.6	53.9
– reactor		82.4	70.8	71.3	71.5	54.5
– reboiler		82.8	79.5	78.4	76.6	66.5
pH in reboiler		10.0	10.0	10.9	10.1	11.0
Pressure in the column	[kPa]	52.8	53.2	54.2	80.1	73.6
Flow rate of 88 wt% 13DCP2OL solution	[cm ³ /min]	3.0	13.0	3.0	3.0	3.0
Flow rate of calcium hydroxide solution	[cm ³ /min]	9.0	41.3	13.0	8.0	7.5
Flow rate of steam	[dm ³ /min]	2.0	4.3	2.0	2.0	2.0
Contact time of the reagents*	[s]	33	21	33	30	30
Technological indicators						
13DCP2OL conversion	[%]	87.6	97.1	99.7	92.8	97.0
Selectivity to	[%]					
– epichlorohydrin		98.4	98.2	93.1	91.2	84.4
– 3-chloropropane-1,2-diol		0.2	0.5	1.2	1.8	4.9
– 2-chloropropane-1,2-diol		0.3	0.0	0.0	0.0	2.8
– glycidol		0.0	0.0	2.2	0.0	1.0
– glycerol		0.6	0.9	2.6	2.0	1.5

* experimentally determined contact time of the reagents in the column.

CONCLUSION

A comparison of the dehydrochlorination results by aqueous solutions of calcium and sodium hydroxides, as well as the process course reveals that the use of calcium hydroxide is more preferable. The dehydrochlorination of 88 wt% of aqueous solution of 13DCP2OL in the reaction-stripping column with a continuous removal of distillate from the top of the column allows to obtain epichlorohydrin with nearly 99% product selectivity and the conversion of 13DCP2OL about 90%. This requires the application of a 10 wt% aqueous solution of calcium hydroxide, molar ratio of $\text{Ca}(\text{OH})_2$:13DCP2OL = 0.48-0.50:1, and the following, remaining process parameters: pre-reactor temperature 46°C, reactor 71 °C, reboiler 80°C, flow rate of 88 wt% aqueous solution of 13DCP2OL – 13 cm³/min, flow rate of 10 wt% aqueous solution of calcium hydroxide – 41 cm³/min, flow rate of steam 4.3 dm³/min, pressure in the reaction-stripping column about 53 kPa. A lower conversion of 13DCP2OL equal to 90%, with the selectivity of transformation to epichlorohydrin 96% are achieved during the dehydrochlorination by a 10 wt% sodium hydroxide solution.

ACKNOWLEDGMENT

Financial support from the Resources for Science in years 2011–2014 as a Ministry of Science and Higher Education research project (No. N N209 089940) is gratefully acknowledged.

LITERATURE CITED

1. Heathman, J.F., Covington, R.L. & Loughridge, B.W. (2000). U.S. Patent No. 6124246 A. High temperature epoxy resin compositions, additives and methods.
2. Grzywa, E. & Molenda, J. (2008). Technology of basic organic synthesis, WNT, Warsaw, 278–280. (in Polish).
3. Bell, B.M. & Briggs, J.R. et al. (2008). Glycerin as a Renewable Feedstock for Epichlorohydrin Production. The GTE

Process. Clean. Soil, Air, Water. 36, 657–661. DOI: 10.1002/clen.200800067.

4. Gilbeau, P. & Krafft, P. (2008). WO 101866 A2, Process for manufacturing epichlorohydrin.

5. Krafft, P. & Gilbeau, P. (2009). WO 000773 A1, Manufacture of dichloropropanol.

6. Hook, B., Briggs, J. Campbell, R., Kruper, W., Schreck, D., Varijan, R. & Hippler, J., (2008). US 015370 A1, Process for the conversion of a crude glycerol, crude mixtures of naturally derived multicomponent aliphatic hydrocarbons or esters thereof to chlorohydrins.

7. Kanzler, W. (2009). EP 2093221, Method for manufacturing epichlorohydrin from glycerine.

8. Krafft, P., Gilbeau, P., Balthasart, D. & Boulos, N. (2008). WO 152045 A1, Epichlorohydrin, manufacturing process and use.

9. Ma, L., Zhu, J.W., Yuan, X.Q. & Yue, Q. (2007). Synthesis of epichlorohydrin from dichloropropanols. Kinetic aspects of the process. Chem. Eng. Res. Des. 85 (A12), 1580–1585, DOI: 10.1016/S0263-8762(07)73202-1.

10. Zhang, J.S., Lu, Y.C., Jin, Q.R., Wang, K. & Luo, G.S. (2012). Determination of kinetic parameters of dehydrochlorination of dichloropropanol in a microreactor. Chem. Eng. J. 203, 142–147, DOI: 10.1016/j.cej.2012.07.061.

11. Spadło, M., Brzezicki, A., Iwański, L. & Forajter, M. (2012). Study on the synthesis of epichlorohydrin by dehydrochlorination of dichloropropanols from the glycerol hydrochlorination, Przem. Chem. 91, 1935–1940. (in Polish).

12. Krzyżanowska, A. & Milchert, E. (2013). Continuous dehydrochlorination of 13DCP2OL to epichlorohydrin: process parameters and by-products formation. Chem. Pap. 67, 1218–1224, DOI: 10.2478/s11696-012-0300-x.

13. Krzyżanowska, A., Milchert, E. & Paździoch, W. (2013). Technological parameters of dehydrochlorination of 1,3-dichloropropan-2-ol to epichlorohydrin. Ind. Eng. Chem. Res. 52, 10890–10895, dx.doi.org/10.1021/ie400924c.

14. Kraft, P., Gilbeau, P., Gosselin, B. & Claessens, S. (2007). EP 1752436 A1, Pseudo-azeotropic composition containing dichloropropanol and process for producing such composition.