

Dehydrochlorination of Glycerol Dichlorohydrin to Epichlorohydrin

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The composition of the waste after the process of dehydrochlorination and after concentration of the organic and water layer was determined. The conversion of dichloropropanols and selectivity of the reaction to epichlorohydrin, glycerol, and glycidol were calculated. The influence of sodium hydroxide excess on the concentration of glycerol and dichloropropanols in the waste water was also determined.

Dehydrochlorination of glycerol dichlorohydrin in industry is carried out with lime milk. It creates many ecological problems caused by waste water containing calcium chloride. It is advisable to replace the lime milk by sodium hydroxide or catholyte. The waste water after the concentration and purification could be recycled to the electrolysis. As it is known from previous studies [1], the process of dehydrochlorination does not depend on the changes in composition of sodium hydroxide in the range of 10–33 mass % and occurs in identical way. The same yield of epichlorohydrin and glycerol (94 mole % and 2 mole %) is also obtained when performing the dehydrochlorination with catholyte consisting of 10 mass % NaOH and 16 mass % NaCl. The total mass fraction of organic compounds in the waste water from the reactor is also very similar.

In this work the composition of the waste water resulting from dehydrochlorination with sodium hydroxide or with catholyte and the composition of the waste water after its concentration to reach the sodium chloride content required for the electrolysis process were determined. Simultaneously, the composition of the distillate from the reactor was determined in the same experiments. Basing on the analyses the process was balanced and the conversion of glycerol dichlorohydrin, the selectivity of the transformation to epichlorohydrin in relation to the quantity of dichlorohydrin used and its yield in relation to dichlorohydrin introduced into the reactor were calculated.

EXPERIMENTAL

The aqueous solution of glycerol dichlorohydrin (Z. Ch. Zachem, Bydgoszcz, Poland) consisting of the following components (*w/mass %*): 2,3-dichloropropan-1-ol (2.06), 1,3-dichloropropan-2-ol (0.23), epichlorohydrin (0.05), 1,2,3-trichloropropane (0.04), 1,2-dichloropropane (0.004), allyl chloride (0.001), and hy-

drogen chloride (0.08), was used, as well as sodium hydroxide (40 mass %) and catholyte solution (NaOH 10 mass % + NaCl 14 mass %) (both from Z. Ch. Zachem, Bydgoszcz, Poland).

The experiments were carried out on semitechnical apparatus, the main part of which was a reaction-stripping column. The scheme of the apparatus and method of procedure were described in the previous paper [1].

Each experiment was performed under pressure of approximately 50 kPa and lasted 5 h. The chlorohydrin solution flow rate was 10 kg h⁻¹, the soda lye or catholyte flow rate was 0.2 to 1.9 kg h⁻¹ to secure a stable excess of sodium hydroxide of 5 mass %. Epichlorohydrin was stripped with steam: $\theta = 112^\circ\text{C}$, $p = 0.06$ MPa. The steam flow rate was 2.0 kg h⁻¹. The temperature at the bottom of the column was 88°C, the temperature of distillation 65°C.

The mass fraction of glycerol was determined by the periodate method [2]. Mass fractions of other organic compounds were determined by gas chromatography method. The analysis was carried out using a Chrom 5 type gas chromatography with flame-ionization detector. A 3 m × 4 mm stainless steel column packed with Chromosorb WAW DMCS (0.17–0.25 mm), coated with 10 mass % SE 32 was used. The temperature of the column was linearly programmed in the range 60–170°C (the temperature gradient was 10°C min⁻¹). The injection temperature was 180°C and the detection temperature 180°C. The carrier gas flow rate was 32 cm min⁻¹. The mass fractions of sodium hydroxide and sodium chloride were determined potentiometrically.

RESULTS AND DISCUSSION

In the dehydrochlorination of glycerol dichlorohydrin in the reaction-stripping column the prod-

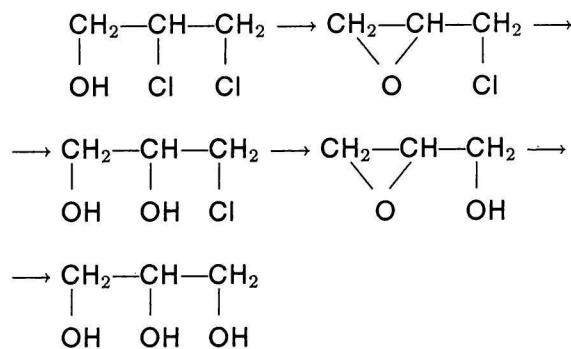
Table 1. Composition of Distillates after Dehydrochlorination of Glycerol Dichlorohydrin

Type of dehydrochlorinating factor	w (Sodium hydroxide)			w_i (Catholyte)	
	mass %			mass %	
	30	15	5	NaOH 5 NaCl 14	NaOH 10 NaCl 14
Organic layer			w_i /mass %		
Epichlorohydrin	89.12	91.80	82.17	82.83	84.00
2,3-Dichloropropan-1-ol	6.77	2.85	13.35	12.65	11.97
1,2,3-Trichloropropane	3.03	3.87	3.34	3.09	2.78
1,2-Dichloropropane	0.13	0.30	0.10	0.17	0.17
Allyl chloride	0.08	0.06	0.02	0.06	0.04
Water	0.87	1.12	1.02	1.20	1.14
Aqueous layer			w_i /mass %		
α -Monochlorohydrin	5.05	6.00	4.01	6.67	7.60
Glycidol	0.22	0.20	0.12	0.11	0.09
2,3-Dichloropropan-1-ol	0.06	0.04	0.24	0.08	0.02
Epichlorohydrin	0.01	0.02	0.22	0.10	0.10
1,2-Dichloropropane	0.07	0.15	0.08	0.07	0.10
Allyl chloride	0.06	0.05	0.02	0.04	0.02
Water	94.53	93.54	95.31	92.93	92.07

Ratio of aqueous layer mass to organic layer mass 1:1 to 3:1.

uct is obtained as the distillate. The distillate divides into organic and aqueous layers. The main compound of the organic layer is epichlorohydrin. Its mass fraction reaches 82–92 % and depends mainly on the level of dichlorohydrin conversion. The unchanged 2,3-dichloropropan-1-ol is also in this layer. The remaining components (1,2,3-trichloropropane, 1,2-dichloropropane, allyl chloride) are found in the organic layer in amounts depending on their mass fraction in the glycerol dichlorohydrin solution. The main compound of the aqueous layer is glycerol α -monochlorohydrin (approximately 6 mass %). The mass fractions of the remaining compounds are much lower: glycidol 0.1–0.2 mass %, epichlorohydrin 0.01–0.2 mass %, 2,3-dichloropropan-1-ol 0.02–0.2 mass %. The compositions of organic and aqueous layers obtained in respective tests are shown in Table 1. The amounts of organic compounds in the waste water from the reaction-stripping column do not change with sodium hydroxide or catholyte content. Maintaining the stable flow rates (see above) of steam, aqueous solution of dichlorohydrin and sodium hydroxide the waste water containing 0.01–0.04 mass % NaOH and 2.0–4.0 mass % NaCl is obtained. It is polluted with glycerol in quantity 0.02–0.04 mass % and by organic chloro derivatives. Among the chloro derivatives the major component is 2,3-dichloropropan-1-ol. In smaller quantities appear epichlorohydrin and glycerol α -monochlorohydrin. In some samples 1,2,3-trichloropropane was found. The precise compositions of the waste resulting from dehydrochlorination of glycerol dichlorohydrin with sodium hydroxide solutions and catholyte are shown in Table 2. The waste after dehydrochlorination was concentrated to 23 mass % of sodium chloride. The concentration was performed by simple distillation under pressure of 13.3

kPa. During the distillation a very small amount of chloro derivatives escaped into the vacuum. The main quantity remained in the brine solution. During the concentration the amount of glycerol in the brine solution increased with the simultaneous decrease in the amount of 2,3-dichloropropan-1-ol and epichlorohydrin and with a variation in the amount of α -monochlorohydrin. During the concentration the following reactions of dehydrochlorination and hydration take place



In the process of dehydrochlorination 1,3-dichloropropan-2-ol reacts in total quantity. The level of the conversion of dichlorohydrin (2,3-dichloropropan-1-ol + 1,3-dichloropropan-2-ol) is 95 mole % on the average. The selectivity of the synthesis of epichlorohydrin concerning reacted dichloropropanols used in the process is 90 mole %. Identically calculated selectivity of the synthesis of α -monochlorohydrin and glycerol is 6.7 mole % and 3.2 mole %, respectively. The yield of epichlorohydrin in relation to dichlorohydrin introduced is 85.2 mole %. These values are shown in

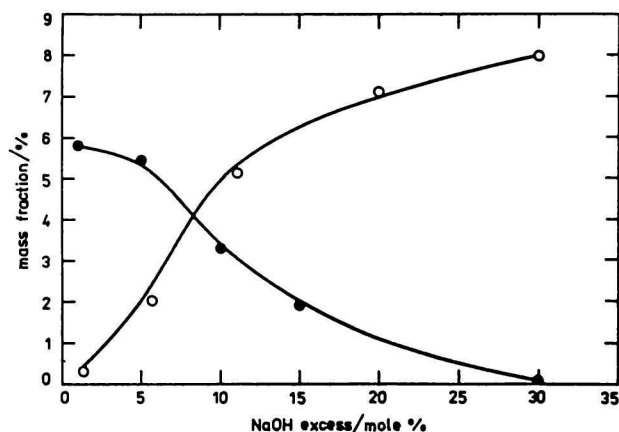
Table 2. Composition Waste and Brine after Dehydrochlorination and Concentration

Type of dehydrochlorinating factor	$w(\text{Sodium hydroxide})$			$w_i(\text{Catholyte})$	
	mass %			mass %	
	30	15	5	NaOH 5 NaCl 14	NaOH 10 NaCl 14
Waste from stripper			$w_i/\text{mass } \%$		
NaCl	2.31	2.18	1.97	3.08	3.82
NaOH	0.04	0.01	0.04	0.04	0.03
Glycerol	0.08	0.04	0.03	0.02	0.04
Organic chloro derivatives ppm					
2,3-Dichloropropan-1-ol	31	71	47	21	31
Epichlorohydrin	11	23	18	8	5
α -Monochlorohydrin	6	12	15	3	0
1,2,3-Trichloropropane	0	2	1	0	0
Brine after concentration			$w_i/\text{mass } \%$		
NaCl	22.31	21.10	23.04	24.52	24.81
NaOH	0.38	0.02	0.51	0.31	0.11
Glycerol	1.14	0.86	0.61	0.75	0.64
Glycidol ppm	11	6	10	12	0
Organic chloro derivatives ppm					
2,3-Dichloropropan-1-ol	62	540	602	27	113
Epichlorohydrin	43	13	23	0	5
α -Monochlorohydrin	226	33	162	62	26

Table 3. Technological Indices of Dehydrochlorination

Conversion of dichloropropanols/mole %	94.7
Selectivity σ_i to	$\sigma_i/\text{mole } \%$
epichlorohydrin	89.9
α -monochlorohydrin	6.7
glycerol	3.2
glycidol	0.3
Yield of epichlorohydrin/mole %	85.2

Table 3. From these investigations it results that constant excess of sodium hydroxide and thus constant flow rates of steam, aqueous solution of dichlorohydrin, and sodium hydroxide are of great importance for achieving the high yield of epichlorohydrin. The excess should be 5 mole %. Decreasing it to 1 mole % causes the decrease in conversion to dichlorohydrin from 95 to 88 mole %. The selectivity of the reaction to epichlorohydrin in relation to dichloropropanols used remains unchanged. The increase of hydroxide excess to 30 mole % lowers the selectivity of the reaction to epichlorohydrin to 82 mole % and raises the reaction to glycerol (6.0 mole %) and monochlorohydrin (12 mole %). Dichloropropanols (3 mass ppm) are not observed in the waste and glycerol mass fraction is the highest (0.08 mass %). The course of changes in mass fractions of dichloropropanols and glycerol in the waste as a function of sodium hydroxide excess is shown in Fig. 1. Achieving good results of dehydrochlorination requires precise control of flow rates of raw materials and steam. The decrease in steam flow rate or the increase in raw materials flow rate causes the increase in the content of dichloropropanols in the waste and


Fig. 1. Changes in mass fractions of dichloropropanols and glycerol in the waste as a function of sodium hydroxide excess. ○ Glycerol 10^{-2} , ● dichloropropanols 10^{-3}

lowers the epichlorohydrin yield. The decrease in flow rates of raw materials and steam causes the shift of the reaction sphere to the bottom of the column. The mass fraction of dichloropropanols in the waste increases. The yield of the synthesis of epichlorohydrin also decreases.

CONCLUSION

The high selectivity (90 mole %) of dehydrochlorination of glycerol dichlorohydrin is achieved using 10–33 mass % sodium hydroxide solution or catholyte (10 mass % NaOH + 14 mass % NaCl). The excess of sodium hydroxide should be 5 mole % in relation to

dichlorohydrin. The mass fraction of epichlorohydrin in organic layer of the distillate is 85—90 mass %. The main component of aqueous layer is monochlorohydrin (4—6 mass %). The ratio of aqueous layer mass to organic layer mass is 2—3:1. The waste from the column is 2.0—2.3 mass % NaCl solution contaminated mostly with glycerol. The distillation of the waste allows to obtain the brine of $w = 23$ mass %. In the best conditions the conversion of dichlorohydrin is 95 mole %.

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