

Formation of environmentally friendly chloroorganic compounds technology by sewage and by-products utilization

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The processes presented in the study enables the separation and disposal of the chloroorganic compounds as by-products from the vinyl chloride plant by using the dichloroethane method and also from the production of propylene oxide by the chlorohydrine method. The integrated purification method of steam stripping and adsorption onto activated carbon allows a complete removal and recovery of the chloroorganic compounds from waste water. Waste distillation fraction is formed during the production of vinyl chloride. 1,1,2-trichloroethane separated from the above fraction, can be processed to vinylidene chloride and further to 1,1,1-trichloroethane. 2,3-Dichloropropene, 2-chloroallyl alcohol, 2-chloroallylamine, 2-chlorothioallyl alcohol or bis(2-chloroallylamine) can be obtained from 1,2,3-trichloropropane. In the propylene oxide plant the waste 1,2-dichloropropane is formed, which can be ammonolysed to 1,2-diaminopropane or used for the production of β -methyltaurine. Other chloroorganic compounds are subjected to chlorinolysis which results in the following compounds: perchloroethylene, tetrachloromethane, hexachloroethane, hexachlorobutadiene and hexachlorobenzene. The substitution of the milk of lime by the soda lye solution during the saponification of chlorohydrine eliminates the formation of the CaCl_2 waste.

Keywords: recycling, chloroorganic compounds, vinyl chloride, propylene oxide.

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INTRODUCTION

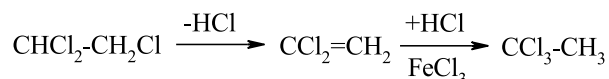
In the processes of the great organic synthesis next to the usable products a lot of by-products are formed. They are obtained from the system as the wastes or in the form of sewage. Those compounds in most cases are burnt or put to a destructive oxidation. Such action leads to the loss of the valuable raw materials and in the case of burning of the chloroorganic compounds to the emission of dangerous dioxins. This article presents the suggested methods of the separation and disposal of chloroorganic compounds from the sewage and wastes formed during the production of vinyl chloride by using the dichloroethane method, propylene oxide by using the chlorohydrin method and epichlorohydrin from allyl chloride.

BY-PRODUCTS AND SEWAGE UTILIZATION

By-products utilization

In order to develop new chemical technologies or to modify the existing ones, the elements of the green chemistry have been taken into consideration for many years. This way it is possible to create non-waste technologies. In the nowadays working industrial systems, even at their constant improvement, a large amount of sewage and wastes is produced. They are the processes of synthesis and the processing of the organic chloroderivatives which, for example, produce vinyl chloride by the pyrolysis of 1,2-dichloroethane obtained with the method of ethylene chlorination and oxychlorination. Waste streams of chloroderivatives constitute about 5% of the product weight and on average about 10000Mg/year¹. They are the distillation residues bottoms and the so-called light ends. Their main components are: 1,1,2-trichloroethane (112TCE), chloroform, tetrachloroethanes, perchloroethylene (PER),

pentachloroethane¹. It is possible to make their dehydrochlorination to vinylidene chloride (VDC) by the elimination of 112TCE and to obtain 1,1,1-trichloroethane (111TCE) as a result of hydrochlorination^{2,3}. The process proceeds in accordance with the reactions presented below:



The 112TCE dehydrochlorination is carried out in the flow reactor in the aqueous solution of NaOH. The basic technological parameters of those processes were presented in Table 1.

The directions of 123TCP processing to the usable compounds are shown in Fig.1. There is also a possibility to obtain 2-chloroallylamine and 2-chloroallyl alcohol from 2,3-dichloro-1-propene as a by-product. The optimal technological parameters of those carried out processes were presented in Table 2. The heavy distillation residue bottoms and fractional distillation residue bottoms of epichlorohydrin are the main source of obtaining 123TCP wastes. The standard composition (wt%) is as follows: epichlorohydrin (EPI) – 7,3; 1,3-dichloropropane-2-ol (13DCP2) – 1,7; 2,3-dichloropropane-1-ol (23DCP1) – 25,9; 1,2,3-trichloropropane (123TCP) – 59,5; bis(chloropropyl) ethers – 4,2; polymeric products – 1,4. The direction of the processing of heavy ends from the epichlorohydrin distillation is shown in Fig. 2. One of the usable products received from that waste is glycerine. It is obtained as a result of the alkaline hydrolysis of dichloropropanols and epichlorohydrin. It is possible to carry out the hydrolysis with the sodium carbonate or the mixture of carbonate and NaOH. The conditions of the process and the basic technological quantities are presented in Table 3.

Table 1. The technological parameters of the 1,1,2-trichloroethane (112TCE) dehydrochlorination to vinylidene chloride (VDC) and hydrochlorination of VDC to 1,1,1-trichloroethane (111TCE)

Parameter	Process	dehydrochlorination 112TCE to VDC	hydrochlorination VDC to 111TCE
Temperature, °C		70–80	20–25
Molar ratio, mol/mol		NaOH/112TCE 1,05–1,10	HCl/VDC 1,01
Concentration, wt%		NaOH - 10	FeCl ₃ - 0,3
Flow rate, g/(dm ³ ·h)		270	140

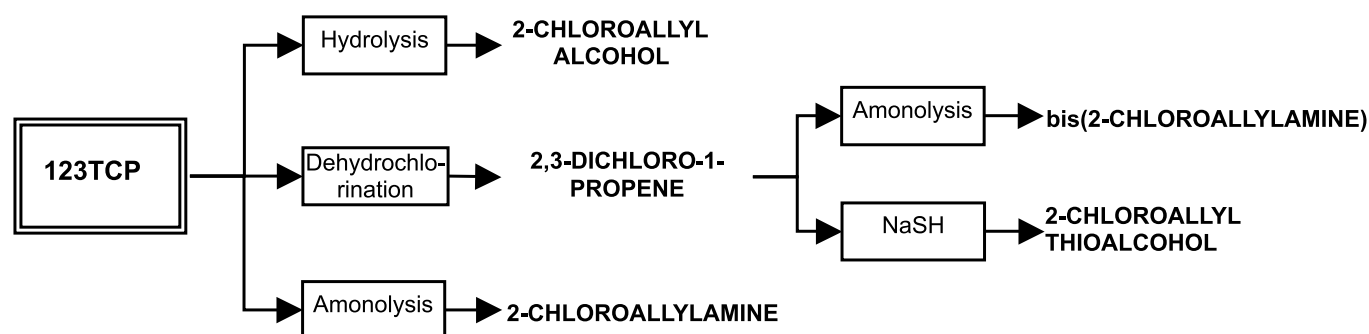
Table 2. The technological parameters of chloroallylamine, 2-chloroallyl alcohol and 2-chloroallyl thioalcohol production

Parameter	Product	2-chloroallyl Alcohol	2-Chloroallylamine	2-chloroallyl thioalcohol
Temperature, °C		80	58	58
Time, h		2,7	2,0	4,4
Molar ratio, mol/mol		NaOH/DCPen 20,0	NH ₃ /DCPen 17,8	NaSH/DCPen 2,2
Concentration, %w.		NaOH - 5,0	–	NaSH - 26,6
Conversion DCPen, %		100	100	97,6
Selectivity		84,3	97,4	59,2

DCPen = 2,3-dichloro-1-propene

Table 3. The condition of glycerol production from the epichlorohydrin distillation waste

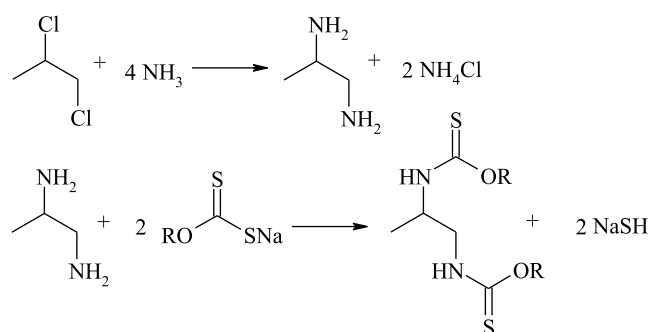
Parameter	Value
Temperature, °C	100
Molar ratio of the alkali to hydrolyzed chlorine, mol/mol	1,3:1
Time, min	105–150
Glycerol yield, mol%	92–94
Conversion of hydrolyzed chlorine	92–98
Glycerol concentration, wt%	20–30

**Figure 1.** The directions of 1,2,3-trichloropropane processing

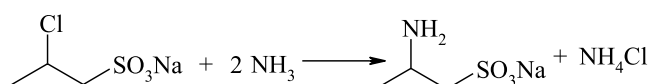
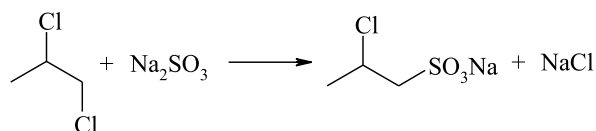
The chloroderivative wastes are also obtained in the systems producing the propylene oxide by chlorohydrin method. The main important ones are: 1,2-dichloropropane (12DCP) (5-7000Mg/year) and bis(1-chloropropyl) ether^{1,4}.

The possibilities of using the 1,2-dichloropropane usable compounds are presented in Diagram 3. The reactions proceeding in the processes are presented below:

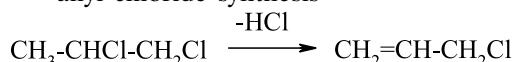
– thionourethane synthesis



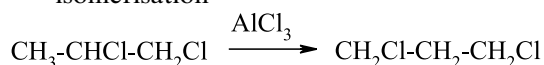
– β-methyltauryne synthesis



– allyl chloride synthesis



– isomerisation

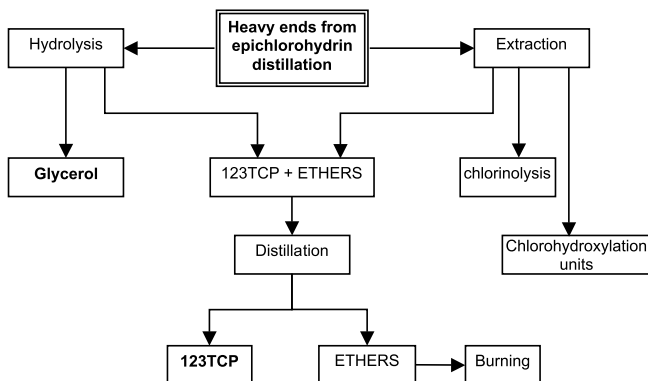


The optimal technological parameters of the 12DCP waste ammonolysis to 1,2-diaminopropane (12DAP) and polypropylenepolyamine (PPPA) were presented in Table 4.

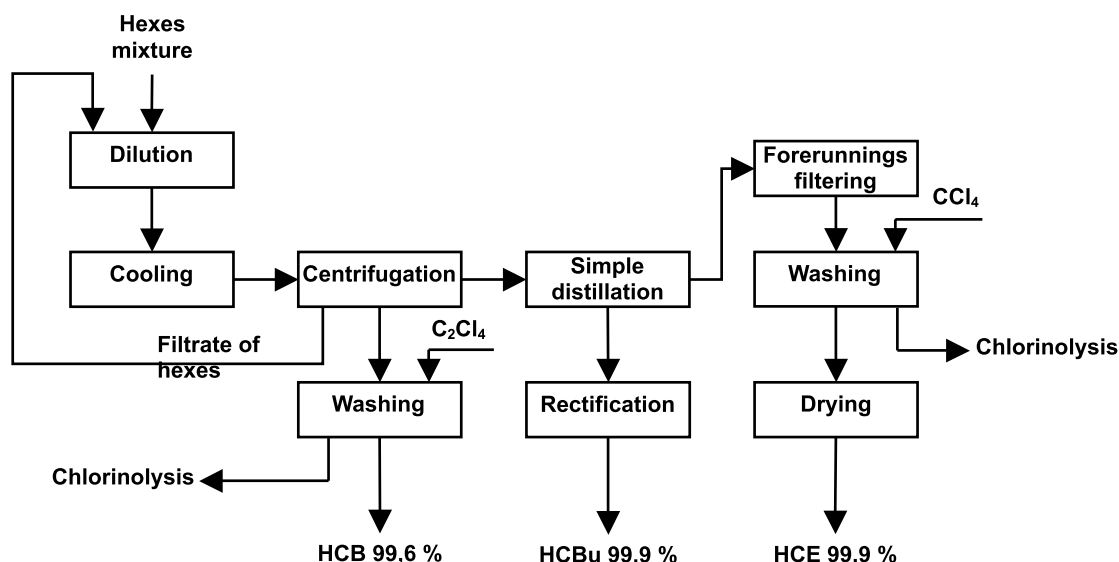
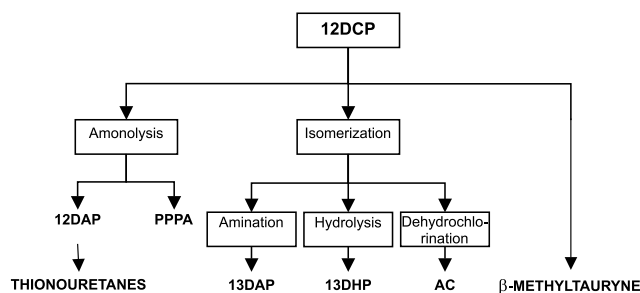
It is possible to subject the left wastes to chlorinolysis just to obtain tetrachloromethane and PER⁵. In recent years the demand for tetrachloromethane has been significantly decreased because of the discontinuation of the 11,12,13

Table 4. The optimal condition of 1,2-diaminopropane (12DAP) and polypropylenepolyamine (PPPA) production

Parameter \ Product	12DAP	PPPA
Temperature, °C	160–170	120–130
Time, h	3–4	3–4
Molar ratio (NH ₃ /12DCP), mol/mol	8–10	2–4
Emulsifier concentration, wt%	0,5	–
Selectivity 12DAP, mol%	74,4	55,0
Selectivity PPPA, mol%	22,5	40,0
Conversion of 12DCP, mol%	98,0	99,0

**Figure 2.** The directions of the heavy ends from epichlorohydrin distillation processing, 123TCP – 1,2,3-trichloropropane, ETHERS – mixture of bis(chloropropyl) ethers

Freon production. Nowadays the process is carried out towards PER. During the waste chloroderivatives chlorinolysis, the secondary wastes – „hexes” are formed. They are the mixture of hexachlorobenzene (HCB), hexachlorobutadiene (HCBu) and hexachloroethane (HCE)¹⁻⁵. It is possible to process HCBu to HCE, dichloromaleate anhydride or to use as a solvent. Applying HCE is connected with processing it into the 113 freon or with using it as antipirene, plasticizer or the component of fungicidal and insecticidal preparations. The diagram of HCB, HCBu and HCE separation from the post-reaction mixture is shown in Fig. 4. Pentachlorophenol (PCF) and sodium pentachlorophenate (PCFNa) obtained from HCB are the compounds of a great techni-

**Figure 4.** The diagram of the HCB, HCBu and HCE separation**Figure 3.** The directions of the waste 1,2-dichloropropane (12DCP) processing, 12DAP – 1,2-diaminopropane, PPPA – polypropylenepolyamines, 13DAP – 1,3-diaminopropane, 13DHP – 1,3-dihydroxypropane, CA – allyl chloride

cal matter. The HCB hydrolysis is carried out by using the sodium hydroxide in aqueous or methanol environments. The PCF synthesis is presented in Table 5 and Fig. 5 shows the diagram of the PCF production system. The HCB is mixed with the solution of sodium hydroxide in a mixer 1 and the formed suspension is forced through to the autoclave and led into direct steam heating of about 200°C. The aqueous suspension PCFNa, HCB, sodium chloride and the excess sodium chloride flows through the condenser 3 to the phase separator 4, where the unchanged HCB is separated. The aqueous solution is led to the batch refining kettle and acidified to the 3 – 5 pH. The PCF is separated in the form of small crystals which are filtered off and washed with hot water to eliminate sodium chloride on filter 7. The mother solution after the filtration and the water obtained during the washing are accumulated in container 8, separated from the rest of the crystals and led to the sodium chloride recovery.

Sewage utilization

During the vinyl chloride production, the stream of waste water, toxic for the environment, is produced as well¹. It contains chloroderivatives at about 4 – 5 kg/Mg of waste water. The application of the two-stage purification may lead to its total removal⁶. The first stage allows the removal of the chloroderivatives to the level 5 – 10g/Mg by using the method of steam stripping^{6 – 8}. Using the fixed bed adsorption in the form of activated carbon causes the decrease of the chloroderivatives concentration

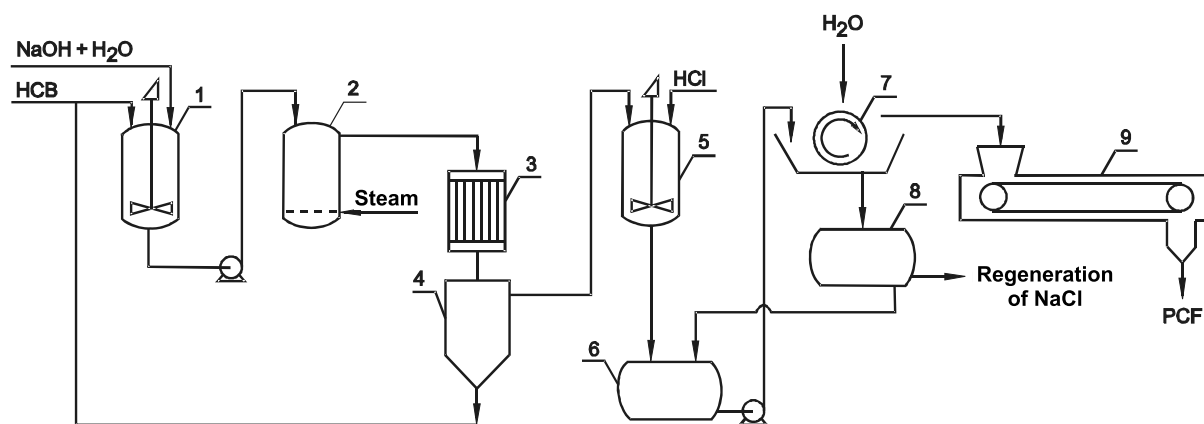


Figure 5. The PCF synthesis, 1 – agitator, 2 – reactor, 3 – cooler, 4 – separator, 5 – neutralizer, 6,8 – tanks, 7 – vacuum filter, 9 – dryer

Table 5. The condition of pentachlorophenol production

Reaction environment Parameter	water	methyl alcohol
Temperature, °C	200–210	130–150
Time, h		1,0–1,5
NaOH concentration, wt%		10–15
Molar ration of NaOH/HCB, mol/mol		2,5:1,0

below 1mg/Mg. The preservative way of those operations enables to recover and then to apply the chloroderivatives in about 900Mg/r^{9–11}.

The above method can be also used with the waste water obtained from the propylene oxide production^{12, 13}. The application of the integrated purification method of steam stripping and then adsorption onto the activated carbon allows to recover about 1920Mg/r of the usable chloroderivatives from the waste water from the system of epichlorohydrin productivity 25000Mg/r and about 820Mg/r of the usable chloroderivatives from the system of propylene oxide productivity 12000Mg/r^{1, 2, 14}.

Limitation of the waste water amount from the propylene oxide system is possible through the substitution of the milk of lime by the soda lye solution or catholyte. The produced brine is turned back to the electrolysis system after the removal of organic compounds and concentration^{15, 16}.

CONCLUSION

The suggested methods of the waste recycling and the waste water purification enable a recovery a large amount of chloroderivative compounds which can be used for the synthesis of valuable organic by-products and at the same time will lead to the reduction of toxic compounds emission into the environment.

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