

Apparatus and methods of dehydrochlorination of 1,3-dichloropropane-2-ol, reaction times in the pre-reactor and reactor

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Introduction

In 2010, the worldwide production of epichlorohydrin reached about 1.6 million Mg. The largest global manufacturers of epichlorohydrin by production capacity are as follows: Dow Chemical (31% of global production capacity), Hexion Specialty Chemicals (12%), Solvay (6%) and Nan Ya (6%). In 2012, the worldwide production of epichlorohydrin raised to about 2.0 million Mg [1]. This rise has been related to a launch of new installations of epichlorohydrin based on waste glycerol from biodiesel production. For this and other types of production, glycerol is isolated from the glycerol phase which is a side product of biodiesel production. The concentration of glycerol in the glycerol phase amounts to 50–60% [2].

The conversion of glycerol to epichlorohydrin requires a multi-step process of hydrochlorination and dehydrochlorination of the resulting 1,3-dichloropropane-2-ol. The dehydrochlorination process may be conducted in the reaction column with a continuous removal of epichlorohydrin in the stream of steam.

There are reports in the literature [3, 4] concerning a possibility to conduct the dehydrochlorination using aqueous solutions of sodium hydroxide. The steam improves the mixing of reaction components in the reaction-stripping section of the column and provides the epichlorohydrin distillation, in the course of its creation, in the form of an azeotrope with water (boiling temperature/101.3 kPa=88.0°C) together with by-products, to the zone of product collection. The instantaneous removal of epichlorohydrin from the reaction system generates smaller quantities of by-products, such as 3-chloropropane-1,2-diol, glycerol, glycidol, ethers and polyglycerols.

Experimental part

Materials

The compound used in the studies was 1,3-dichloropropane-2-ol with a purity of 98% containing 2% of 2,3-dichloropropane-1-ol purchased from Merck (Warsaw). The dehydrochlorination process was carried out using a 10–14% solution of milk of lime which was made by dissolving calcium hydroxide in water: 96 wt% of $\text{Ca}(\text{OH})_2$ and 3 wt% of CaCO_3 (Chempur, Piekary Śląskie).

An aqueous solution of cresol red was used to determine contact times of reagents (reaction times) in the pre-reactor and reactor (Chempur, Piekary Śląskie).

Apparatus

The dehydrochlorination of an 88% aqueous solution of 1,3-dichloropropane-2-ol (13DCP2OL) with a solution of milk of lime was carried out in the apparatus shown in Figure 1.

There are reports in the literature [5] concerning the apparatus for dehydrochlorination of 1,3-dichloropropane-2-ol, in which the epichlorohydrin-water azeotrope is collected at the top of reaction-stripping column. In this paper, the system for epichlorohydrin formation in which the distillate is collected from the re-boiler of the reaction-stripping column is described.

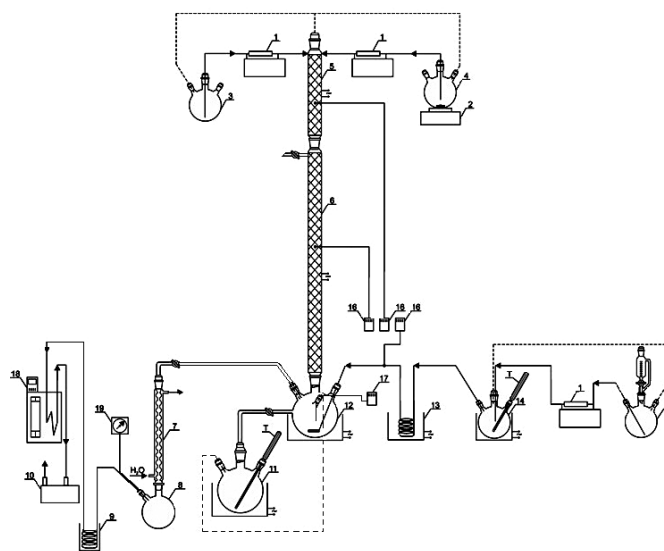


Fig. 1. Diagram of installation for dehydrochlorination of 1,3-dichloropropane-2-ol with a solution of milk of lime.
1 – metering pump; 2 – magnetic stirrer; 3 – tank for an aqueous solution of 1,3-dichloropropane-2-ol; 4 – tank for a solution of milk of lime; 5 – pre-reactor; 6 – reaction-stripping column; 7 – product condenser; 8 – tank for distillate of epichlorohydrin and water; 9 – freeze-dryer cooled with ice; 10 – vacuum pump; 11 – sewage tank; 12 – re-boiler; 13 – steam superheater; 14 – steam generator; 15 – water tank; 16 – temperature indicator; 17 – pH and temperature meter; 18 – cryostat; 19 – vacuum gauge; T – mercurial thermometer

The collection of distillate at the upper section of the reactor makes it possible to achieve almost a full conversion of 1,3-dichloropropane-2-ol, whereas, the selectivity of transformation to epichlorohydrin is low and depends to a high extent on the process technological parameters. The aim of a change in the reaction system was to increase the selectivity of the transformation to epichlorohydrin.

The important elements of the apparatus for dehydrochlorination of 1,3-dichloropropane-2-ol are as follows: pre-reactor, reactor, peristaltic pumps, re-boiler, system for product collection, steam generator, vacuum pump, cryostat and temperature and pH meters.

Pre-reactor and reactor

The pre-reactor 5 and reactor 6 were formed as glass tubes with the length of 260 mm and 760 mm, respectively. The inner diameter of both elements was equal and amounted to 36 mm. The tubes were filled with glass Raschig rings with dimension of 6 x 8 mm to provide a better contact of reagents. The pre-reactor and reactor were isolated with mineral wool, which minimises the amount of heat loss and makes the adjustment of predetermined temperature easier. Both segments were heated separately and each of them was equipped with the temperature meter. A connection

used for a single introduction of an aqueous solution of cresol red in experiments, in which the reaction time was measured in the reactor, was located at the upper section of the reactor.

Peristaltic pumps

Three peristaltic pumps model 7524–55 purchased from Masterflex were used to create the apparatus for dehydrochlorination. The first one was used to supply water from the tank 15 to the steam generator 14. Two other pumps were dispensing reagents – an 88% aqueous solution of 1,3-dichloropropane-2-ol and a 10–14% solution of milk of lime. As a result of the continuous use of the magnetic stirrer they were maintained in the suspension form.

Re-boiler

The re-boiler served as a distillation pot and enabled the epichlorohydrin and by-products of dehydrochlorination, volatile in steam, to be distilled off. The re-boiler was a four-neck round-bottom flask of 500 cm³ from which the tail fraction was removed by a siphon. A system for removal and condensation of products distillate was connected to one of the connection. An electrode for pH measurement was installed in the second connection. The third connection was used to supply the steam into the re-boiler via bubbler. Thus, the re-boiler worked in a continuous mode and the liquid level was maintained constant. The excess of sewage aqueous solution containing organic compounds: 3-chloropropane-1,2-diol, glycidol, glycerol, diglycidyl ether, polyglycerols, occasionally 1–3-dichloropropane-2-ol, epichlorohydrin and nonorganic compounds: calcium chloride, calcium hydroxide and calcium carbonate, was discharged to the sewage tank 11. Because the process was conducted at a reduced pressure, the re-boiler and the tank were connected with a common collecting pipe. Additionally, the re-boiler was heated in the electric bath.

System for product collection

The product in a form of the epichlorohydrin-water azeotrope and by-products, volatile in steam, flew from the re-boiler to the cooler 7 and were collected in the tank 8 upon condensation. At the same time, the distillate was split up into two layers – the organic one and water. Both layers contained: epichlorohydrin, uncreated form of 1,3-dichloropropane-2-ol and traces of 2,3-dichloropropane-1-ol. In some experiments, the water layer of distillate contained traces of 3-chloropropane-1, 2-diol. The composition of both layers was changing with the steam flow rate and technological parameters of dehydrochlorination. The composition of the water and organic layer, together with experiment parameters, is presented in Table 1. In some experiments, steams from the tank 8 condensed in the freeze-dryer 9. The vacuum gauge DVR 2 was connected to the tank 8. The vacuum was created using an oil vacuum pump TW-1A.

Cryostat

The cryostat 18 was used to freeze-dry the steams (-40°C) which did not condense in the water cooler 7 and in the freeze-dryer with the ice. The Julabo F83 cryostat was used.

Temperature and pH meters

The universal meters model UT33C purchased from UNI-T were used to measure the temperature in the pre-reactor, the reactor and the steam superheater. The temperature in the re-boiler and the sewage tank was measured with a mercurial thermometer. The measurements of pH in the re-boiler were conducted with the pH meter HI 991001 purchased from Hanna Instruments equipped with an pH electrode measuring the temperature.

Table 1

Composition of the water and organic layer, technological parameters and process indicators

SUBSTRATES	QUANTITY
88% solution of 1,3-dichloropropane-2-ol, g	410.0
10% solution of milk of lime, g	1 419.0
TECHNOLOGICAL PARAMETERS	
molar ratio Ca(OH) ₂ /13DCP2OL	0.68:1
temperature (°C) of	
pre-reactor	62.7
reactor	75.6
re-boiler	56.1
steam	97.1
flow rate of	
solution 13DCP2OL, cm ³ /min	2.9
milk of lime, cm ³ /min	11.2
steam, dm ³ /min	2.5
time of reaction, min	120
pH in the re-boiler	11.2
pressure in the reactor, kPa	56.2
PRODUCT	
organic layer, g	194.3
Composition, wt%	
epichlorohydrin	96.5
1,3-dichloropropane-2-ol	1.4
2,3-dichloropropane-1-ol	0.06
water	2.1
water layer, g	244.6
Composition, wt%	
epichlorohydrin	6.0
1,3-dichloropropane-2-ol	0.3
2,3-dichloropropane-1-ol	0.01
water	93.7
SEWAGE, g	1 621.3
Composition, wt%	
epichlorohydrin	0.6
1,3-dichloropropane-2-ol	0.03
2,3-dichloropropane-1-ol	0.01
3-chloropropane-1,2-diol	0.8
glycidol	0.5
diglycidyl ether	0.004
glycerol	0.2
CONVERSION OF DICHLOROPROPANOLS, %	98.8
Selectivity, %	
epichlorohydrin	82.2
3-chloropropane-1,2-diol	4.5
glycidol	3.7
diglycidyl ether	0.005
glycerol	0.9

The method of dehydrochlorination

Before the installation was initiated, the tanks were filled with substrates of the process. An 88% aqueous solution of 1,3-dichloropropane-2-ol was prepared and entered into the tank **3** in a known quantity. Similarly, a 10–14% solution of calcium hydroxide was prepared and placed in the tank **4**. The tank **15** was filled with a known quantity of water. The quantity of current flowing through electrical heating bands of: pre-reactor **5**, reactor **6**, steam superheater **13**, steam generator **14** and re-boiler **12** was controlled using autotransformers. The vacuum pump **10** was switched on, and an adequate pressure set up. The cooling of product condenser **7** and cryostat **18** was switched on. The freeze-dryer **9** was cooled down. The steam flow to the re-boiler was controlled by determination of dosing rate of water to the tank **15** and the water flow via the peristaltic pump. Once the steam flow was established, peristaltic pumps **1** which dose the raw materials were switched on. In the course of the process, all temperature values were controlled every 30 min and adjusted. The product distillate and the steam were collected in the tank **8**, whereas, the sewage – in the tank **11**. After two hours of running the installation, the experiment was stopped. The peristaltic pumps which dose the raw materials and settings of the autotransformers controlling the temperature in individual elements of the reaction-stripping system were switched off. After few minutes when the residue of epichlorohydrin was stripped from the column and re-boiler, the water supplying pump, the steam generator heater **14** and the steam superheater **13** were switched off. At the end the vacuum pump was switched off.

The distillate was split up into two layers. Each of them was weighted and assayed chromatographically for organic compounds concentrations. In the organic layer, the content of water was assayed coulometrically. The substance remaining in the re-boiler was treated as sewage. Thus, it was connected with the content of the sewage tank and analysed chromatographically. In all of mentioned products, the content of organically and non-organically bound chlorine was assayed potentiometrically.

The conversion of 1,3-dichloropropane-2-ol, the selectivity of its transformation to epichlorohydrin and by-products were calculated based on the chromatographic analyses. The results for one of the conducted experiments are presented in Table 1.

Discussion

Reaction times in the pre-reactor and reactor

Once the raw materials are mixed, the dehydrochlorination of 1,3-dichloropropane-2-ol is conducted initially in the pre-reactor. The aim of experiments was to determine the contact times of reagents in the pre-reactor and reactor. The contact time of reagents has an impact on by-products quantity, especially of 3-chloropropane-1,2-diol, glycerol, glycidol and diglycidyl ethers. Mainly, too long contact time increases the total quantity of by-products. The experiments were conducted with the reaction-stripping column running. The distillate of epichlorohydrin was collected from the re-boiler. Once the temperatures values presented in Table 2 and other technological parameters similar to those presented in Table 1 were reached and the column got stabilised, 1 cm³ of a solution of cresol red was entered once to the reaction system. The contact time of reagents has been measured since a solution of cresol red was entered to the column until the red dye reached the re-boiler. In experiments in which the reaction time was measured in the pre-reactor, a solution of cresol red was entered above the pre-reactor.

Table 3 presents results of the reaction time determined in the pre-reactor and reactor, by the flow rate of 1,3-dichloropropane-2-ol and a solution of milk of lime. The double increase of the flow rate of an 88% solution of 1,3-dichloropropane-2-ol (from 3 cm³/min

to 6 cm³/min) and, respectively, of a 10% solution of milk of lime (from 10 cm³/min to 20 cm³/min) shortens the contact time of reagents by 4 s, both in the pre-reactor and the reactor. However, increasing the flow rate of 1,3-dichloropropane-2-ol (from 3 cm³/min to 9 cm³/min) and a solution milk of lime (from 10 cm³/min to 27 cm³/min) three times shortens the contact time of reagents (reaction time) in the pre-reactor by 45% and in the reactor by 34%. The reaction time in the pre-reactor was always shorter than in the reactor. Mainly, this is the result of a greater length with the same diameter (36 mm).

The increase of milk of lime concentration above 10 wt% caused problems with dosage. Due to sedimentation of calcium hydroxide particles and contaminating calcium carbonate the flow of a solution was irregular.

Table 2

Technological parameters of the reaction-stripping column system during measurements of reaction times in the pre-reactor and reactor

Concentration of milk of lime wt%	Temperature, °C			Steam flow, dm ³ /min
	Pre-reactor	Reactor	Re-boiler	
10.0	45-60	60-75	60-77	2.5

Table 3

Reaction times in the reactor and pre-reactor with the steam flow of 2.5 dm³/min

Flow, cm ³ /min			Reaction time, s		
88% solution 13DCP2OL	10% solution of milk of lime	Reagents flow in total	Pre-reactor	Reactor	Column
3	10	13	20	32	52
6	20	26	16	28	44
9	27	36	11	21	33

The contact times of reagents were also measured upon increasing the steam flow rate to 4.3 dm³/min. With the reagents flow as in Table 3 and upon raising the temperature of the reactor to 78–85°C, the reaction times in the column were shortened, respectively to 42 s, 33 s and 25 s, with the increase of the flow rate of 1,3-dichloropropane-2-ol and milk of lime solutions.

Summary and conclusions

The dehydrochlorination of an 88% aqueous solution of 1,3-dichloropropane-2-ol with milk of lime results in almost a full conversion of 1,3-dichloropropane-2-ol when the epichlorohydrin is collected from the re-boiler of the reaction-stripping column. It is associated with the selectivity of transformation to epichlorohydrin which amounts to 83%. In this mode of the epichlorohydrin collection, it is possible to achieve higher selectivity of transformation. However, this requires reduction of the conversion of 1,3-dichloropropane-2-ol by minimising the molar ratio of Ca(OH)₂/13DCP2OL.

The contact times of reagents (reaction times) were determined experimentally at the upper section of the column, i.e. in the pre-reactor and reactor with the stable steam flow. The increase of the reagents flow, with the stable steam flow, shortens the reaction time in individual elements of the reaction-stripping column. The most preferable situation is to dose an 88% solution of 1,3-dichloropropane-2-ol with the speed of 3 cm³/min and a 10% solution of milk of lime with the speed of 10 cm³/min. These reagent flows and collecting the epichlorohydrin from the re-boiler assure the longest contact time of

reagents in the reaction-stripping column which amounts to 52 s. Thus, a high conversion of 1,3-dichloropropane-2-ol and a slightly lower selectivity of transformation to epichlorohydrin are achieved.

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A crystal of a different color (8/18/2013)

Chemists have unexpectedly made two differently colored crystals - one orange, the other blue - from one chemical in the same flask while studying a special kind of molecular connection called an agostic bond. The discovery is providing new insights into important industrial chemical reactions such as those that occur while making plastics and fuels.

Bonds come in many varieties in molecules. They string atoms together, sometimes forming a trunk and branches of atoms like a tree. But the trunk and branches of chemicals often fold up into a more compact shape, requiring additional weaker bonds to hold the shape in place. An agostic bond is one of these additional bonds, a shape-holder. They occur between a metal and a distant carbon-hydrogen bond along some chain, folding the chain back to the metal and pinning it there.

The metal in a catalyst is usually the reactive heart of the molecule. Morris Bullock and Edwin van der Eide knew an agostic bond in their catalyst would help protect the reactive metal from working at the wrong time: The carbon-hydrogen bond blocks the reactive metal until conditions were right, which in turn would help the scientists control the catalytic reactions better.

During the experiments, two types of crystals were formed from one solution. Orange crystals formed at the bottom of the flask and blue above. Either the orange or blue crystals were dissolved in a fresh flask of the original solvent, the original color of the solution returned, with the same properties. These results suggested that either molecule in the two colored solids could give rise to both structures in liquid, where they easily change back and forth.

(Source: http://www.chemistrytimes.com/research/A_crystal_of_a_different_color.asp, 18.08.2013)

Binding together repelling atoms

Basic chemistry tells us that a bond between atoms can form if it is energetically more favorable for the atoms to stick together than staying apart. This fundamentally requires an attractive force between the atoms. However, new theoretical predictions show that the combination of a repelling force and controlled noise from an environment can also have the surprising effect of leading to a bound state, although one with quite exotic properties. The research is carried by team consisting of Harvard postdoc Mikhail Lemeshko and former Harvard postdoc Hendrik Weimer.

How is it possible that repulsion and noise, both two effects countering the formation of a chemical bond, can lead to a bound state nevertheless? We have to take into account the quantum properties of the atoms: adding controlled noise to a quantum system can result in an interference phenomenon that traps the atoms in a well-defined quantum state. The repulsive force then ensures that this trapping occurs at a particular distance, which sets the length of the bond. The nature of the novel bound state is strikingly different from their chemical counterparts. For example, the bound state is remarkably robust and can hardly be broken by depositing a constant amount of energy to it.

Lemeshko and Weimer consider one of the most basic and universally available sources of noise: vacuum fluctuations of the electromagnetic field. Authors believe that the first applications of the discovered binding mechanism might be in the area of cooling of atomic quantum gases.

(Source: http://www.chemistrytimes.com/research/Binding_together_repelling_atoms.asp, 16.08.2013)