

Description

Process and apparatus for preparing
1,2-dichloroethane by direct chlorination
with off-gas recycling

5 The invention relates to a process for preparing 1,2-dichloroethane, termed "EDC" below, by feeding chlorine and ethylene into circulated EDC which contains a catalyst system of iron(III) chloride and a halide of a metal of the first or second main group of the Periodic Table
10 of the Elements and small amounts of oxygen, a part-stream of the reaction mixture being fed to flash evaporation, the vaporized EDC being separated off from more readily volatile constituents and isolated, which comprises returning said more readily volatile constituents to the reaction, the combination of the following
15 process features being excepted: the metal chloride in the catalyst system is sodium chloride, the molar ratio of sodium chloride to iron(III) chloride remaining below 0.5 during the entire reaction, the flash evaporation
20 proceeds in a vessel under reduced pressure and ethylene-containing off-gas is recycled to the reaction by a compressor.

The process for preparing EDC by reaction of chlorine and ethylene is known under the term "direct chlorination".
25 Thus, for example, DE-A 41 33 810 relates to such a process in which the enthalpy of reaction is utilized with the aid of flash evaporation. This known process is carried out at a temperature of about 75 to 200°C and a pressure of about 1 to 15 bar.

30 A process has also already been proposed for preparing EDC by reaction of ethylene with chlorine over a sodium chloride/iron(III) chloride catalyst a feature of which is that the molar ratio of sodium chloride to iron(III) chloride remains below 0.5 during the entire reaction.
35 This process is preferably carried out at 50 to 105°C and

at a pressure of up to 1 bar gauge pressure. In a further preferred embodiment, all or part of the EDC is passed into a vessel under reduced pressure, the product distilling off being separated off and the remaining EDC
5 being recycled to the process. As an expedient design, it is further proposed, to decrease the ethylene losses, to recycle the ethylene-containing off-gas from the flash vessel downstream of the vacuum pump (which is necessary to maintain the reduced pressure in the flash vessel) to
10 the reaction by means of a suitable compressor, preferably a liquid-jet compressor, which is expediently mounted on the bottom of the reactor, and to react the ethylene with chlorine again. In this case, a part-stream of the EDC circulated by pumping advantageously serves as
15 motive jet for the preferred compressor (German Patent Application P 43 18 609.2 of 04.06.1993).

The process according to the invention is extraordinarily versatile: the reaction can proceed in a temperature range from about 50 to 200°C and at a pressure from about
20 1 to about 15 bar gauge pressure. The pressure in the flash vessel must be correspondingly lower and is in the range from 0.2 to 3.5 bar absolute. In one embodiment of the process, this pressure in the flash vessel is more than 0.7 bar absolute.

25 The metal halide in the catalyst system is preferably lithium chloride, potassium chloride or magnesium chloride and in particular sodium chloride. The molar ratio of metal halide and iron(III) chloride can vary within certain limits and in the known processes is between
30 0.5 : 1 and 2 : 1 (NL-A 6901398, DE-A 41 03 281).

The chlorine used can be fed in the liquid or gaseous state. It is not even necessary to use chlorine of the highest quality grade: as a result of a suitable choice of compressor, for example using the liquid-jet
35 compressor mentioned in the proposed process, a technical grade chlorine which contains small amounts of oxygen can

be used. Another possibility is the use of a compressor of a different type which is appropriately explosion-proof and resistant to pressure pulses.

5 If a liquid-jet compressor is selected, in the process according to the invention a part-stream of the EDC circulated by pumping also preferably serves as motive jet, in particular a part-stream of the EDC recycled to the reactor and preferably cooled.

10 The process according to the invention is advantageously carried out in an apparatus corresponding to the Figure. This apparatus contains
a reactor (1),
feed lines (2) and (3) for ethylene and chlorine respectively and preferably (4) for an inert gas,
15 a line (5) to the
flash vessel (6) which is under reduced pressure and has a line (7) to conduct away the vaporized product and a line (8) for recycling the nonvaporized product,
to which is preferably connected a dissolving vessel (9).
20 and which
preferably runs via a pump (10),
a line (11) for recycling a product part-stream, which preferably runs via a pump (12) and a cooler or heat exchanger (13).

25 The line (7) for the EDC vapor expediently runs via a cooler (14) to the vacuum pump (15). From the cooler (14), the line (16) runs to the receiving vessel (17) for the liquefied EDC.

30 The apparatus further contains a line (18) from the (pressure side of the) vacuum pump (15) via the compressor (19) to the reactor (1) for recycling residual amounts of unreacted ethylene. (20) and (21) are lines for off-gas disposal.

The invention is described in more detail in the example

below.

Example

For direct chlorination, a reactor (1) having a volume of 14.6 m³ was fed with 3000 m³ (S.T.P.)/h of ethylene via the line (2). Via the line (3), the equivalent chlorine stream was fed in. The pressure was kept at 0.8 bar gauge pressure via the line (4) with nitrogen and the temperature was kept at 90°C. Liquid EDC having an iron(III) chloride content of 780 ppm served as reaction medium.

10 Via the dissolving vessel (9), sufficient sodium chloride was metered into the reaction medium until the desired concentration of about 170 ppm was reached and remained constant.

15 A product part-stream was conducted via the line (5) into the downstream flash vessel (6) at a pressure of 0.7 to 0.8 bar absolute. Here, 13.3 t of EDC were vaporized per hour and taken off via the line (7). This EDC was free of catalyst and had a purity of 99.92%.

20 The EDC not vaporized in the flash vessel (6) was recycled into the reactor (1) via the line (8) and the pump (10). The main product stream was fed into the line (8) via the line (11) and the pump (12) and recycled to the reactor (1) via the cooler (13).

25 A stream of 50 m³ (S.T.P.)/h having an ethylene content of 6% by volume were fed to combustion via the off-gas line (21). This corresponds to an ethylene loss of 3 m³ (S.T.P.)/h. The off-gas line (20) was closed.

30 In contrast, if via the off-gas line (21) a stream of 28 m³ (S.T.P.)/h having an ethylene content of 6% by volume and via the off-gas line (20) a stream of 26 m³ (S.T.P.)/h having an ethylene content of 16% by volume is fed to combustion, that corresponds in total to an

ethylene loss of $5.9 \text{ m}^3 \text{ (S.T.P.)/h}$ or $2.9 \text{ m}^3 \text{ (S.T.P.)/h}$ more than by the procedure according to the invention. The process according to the invention with closed off-gas line (20) and recycling of the gas stream via the
5 line (18) thus virtually halves the ethylene loss to about 0.1% of the amount of ethylene used.

Claims

1. A process for preparing 1,2-dichloroethane (EDC) by feeding chlorine and ethylene into circulated EDC which contains a catalyst system of iron(III) chloride and a halide of a metal of the first or second main group of the Periodic Table of the Elements and small amounts of oxygen, a part-stream of the reaction mixture being fed to flash evaporation, the vaporized EDC being separated off from more readily volatile constituents and isolated, which comprises returning said more readily volatile constituents to the reaction, the combination of the following process features being excepted: the metal chloride in the catalyst system is sodium chloride, the molar ratio of sodium chloride to iron(III) chloride remaining below 0.5 during the entire reaction, the flash evaporation proceeds in a vessel under reduced pressure and ethylene-containing off-gas is recycled to the reaction by a compressor.
2. The process as claimed in claim 1, wherein the reaction proceeds at a temperature of about 50 to 200°C and at a pressure of about 1 to about 15 bar gauge pressure.
3. The process as claimed in claim 2, wherein the flash evaporation proceeds at a pressure of 0.2 to 3.5 bar absolute.

