

Process and apparatus for preparing high-purity
1,2-dichloroethane with heat recovery

The invention relates to a process for preparing high-purity 1,2-dichloroethane with heat recovery by reacting ethylene and chlorine in liquid 1,2-dichloroethane in the presence of a special catalyst, other undesired chlorinated products only being formed in negligible amounts, so that the resulting 1,2-EDC does not have to be purified by distillation. An apparatus for carrying out the process is described.

The catalytic addition reaction of chlorine with ethylene in 1,2-dichloroethane as solvent proceeds in 3 steps:

1. dissolution of the gaseous chlorine in 1,2-dichloroethane
2. dissolution of the gaseous ethylene in 1,2-dichloroethane
3. reaction of the dissolved reactants to give 1,2-dichloroethane.

While steps 1 and 3 proceed rapidly, step 2 is slow, probably due to the only slight solubility of ethylene in 1,2-dichloroethane, and is therefore the rate-determining reaction step. For this reason, 1,2-dichloroethane preparation has hitherto been carried out in industry in reactors comprising a main reactor of sufficient residence time and an after-reactor for complete conversion of the ethylene.

According to the suggestion of EP-0,080,098 B1 (CA-1,221,708), chlorine and ethylene are reacted in gaseous form in 1,2-dichloroethane as solvent in a double-loop reactor with after-reactor. A mixing zone charged with packing is arranged in the main reactor in order to finely divide the reaction gases. The reaction

time stated is 1 to 15 hours. The 1,2-dichloroethane is purified in downstream distillation columns.

5 In DE-C-3,445,896, a static mixer or an ejector nozzle for dispensing gaseous ethylene in the liquid 1,2-dichloroethane circulation is proposed for the preparation of 1,2-dichloroethane.

10 For preparing 1,2-dichloroethane, a special catalyst is mentioned in EP-0,111,203 A1 (US-A-4,774,373), the use of which results in only a low corrosion rate of the steel surfaces of the apparatus parts. This special catalyst comprises anhydrous tetrachloroferrate(1⁻), the cation of which is an alkali metal ion, alkaline earth metal ion or an ammonium ion.

15 Accordingly, the object was to modify the known procedures and apparatuses such that the entire chlorinated by-products formed in 1,2-dichloroethane are present at less than 500 ppm and not only installation of a large main and secondary reactor but also separation of the by-products by distillation are unnecessary and the enthalpy of reaction is completely available for other processes
20 in a variable manner.

25 Accordingly, the invention relates to a process for preparing high-purity 1,2-dichloroethane with heat recovery from equimolar amounts of ethylene and chlorine in 1,2-dichloroethane as solvent in the presence of a tetrachloroferrate(1⁻) catalyst at a temperature of 75 to 200°C and a pressure of 1 to 15 bar in a reaction zone, which process comprises dissolving the chlorine gas in
30 recirculating 1,2-dichloroethane in an upstream mixing zone, reacting the ethylene gas in finely disperse liquid phase having a bubble diameter of at most 2.0 mm in the downstream reaction zone, allowing this finely disperse liquid phase to flow through the reaction zone at a velocity of 0.3 to 1 m/s with a residence time of 2.5 to
35 25 seconds, calculated relative to the liquid phase, and

then removing the high-purity 1,2-dichloroethane formed, which contains less than 500 ppm of chlorinated by-products, in gaseous form by flash evaporation.

5 The process can have the additional feature that the bubble diameter of the ethylene gas optionally is less than 1.5 mm.

10 By means of the process according to the invention, a very simple process for preparing high-purity 1,2-dichloroethane is now available. After flash evaporation, the gaseous 1,2-dichloroethane is condensed and obtained in a purity of more than 99.95% by weight. It contains 1,1,2-trichloroethane as the main secondary component. The heat liberated during condensation can be utilized, for example, for distilling the 1,2-dichloroethane
15 obtained by the oxychlorination process. The distillation columns usually required for 1,2-dichloroethane preparation by the direct chlorination process in order to separate off low-boiling and high-boiling components are completely unnecessary in the process according to the
20 invention. This saves not only the corresponding investment costs but also operating costs. The 1,2-dichloroethane yields are 99.7%, relative to C_2H_4 , and 99.7%, relative to Cl_2 .

25 For the process according to the invention, it is of crucial importance that the ethylene gas be finely divided. It is not sufficient to inject the ethylene gas in finely divided form into the 1,2-dichloroethane, since the ethylene gas bubbles rapidly combine to form large bubbles, which then greatly reduce the reaction rate.
30 Care must therefore be taken that their combination, which gives fairly large ethylene gas bubbles, is prevented. This fine dispersion of the ethylene gas is achieved in so-called "static mixers", such as described in Chemie-Ingenieur-Technik 52 (1980), No. 4, pages 285
35 to 291.

Furthermore, an apparatus for carrying out the process is described, which comprises a mixer 1 with chlorine inlet 11, a "static mixer" 2 with ethylene inlet 5, a let-down vessel 3, a recirculating pump 6 and a heat exchanger 7, the mixer 1, the "static mixer" 2, the let-down vessel 3, the recirculating pump 6 and the heat exchanger 7 being connected to one another in terms of flow, the let-down vessel 3 being connected to a condenser 8 via a control valve 4, and a product discharge line 9 and a waste-gas line 10 leaving condenser 8.

The apparatus can optionally have the further features that

- a) a "static mixer" 2 with flow obliquely around the web is used,
- b) the blades in the "static mixer" 2 are perforated, slotted, serrated and/or corrugated,
- c) the blades form meandering channels or channels crossing each other,
- d) a pressure-holding device 12 is arranged between the "static mixer" 2 and the let-down vessel 3,
- e) instead of the pressure-holding device 12, the let-down vessel 3 is arranged 8 to 12 m above the "static mixer" 2.

The pressure in the "static mixer" 2 increased in this manner prevents the 1,2-dichloroethane from boiling in the reaction zone, which would cause a decrease in the reaction rate.

The process and the apparatus for preparing high-purity 1,2-dichloroethane are illustrated in more detail below with reference to the accompanying drawing.

Let-down vessel 3, heat exchanger 7, mixing zone 1 and "static mixer" 2 are filled with 1,2-dichloroethane and the 1,2-dichloroethane is set to a flow rate of 200 m³/h by means of recirculating pump 6. 2867 kg/h of chlorine gas are metered into mixing zone 1 via the line 11.

Mixing zone 1 has been designed in the form of a mixing nozzle. The chlorine-charged 1,2-dichloroethane contains 0.2% by weight of NaFeCl_4 as catalyst and flows into the "static mixer" 2, into which 1134 kg/h of ethylene gas are metered in via line 5. The "static mixer" 2 used is an SMV mixer, 3 m in length, from Sulzer, Winterthur/Switzerland, containing corrugated blades forming open channels crossing each other.

The diameter of the ethylene gas bubbles was 1.0 to 1.5 mm; the 1,2-dichloroethane flows through the "static mixer" at a rate of 0.4 m/s.

After a stationary state has been reached in condenser 8, 7.5 m³/m of water are heated to 60°C; another 20.0 m³/h of water are heated to 96°C in heat exchanger 7. The 1,2-dichloroethane cycle is operated at 125°C and at a pressure of 4 bar. The 1,2-dichloroethane formed is passed from the let-down vessel 3 via a level control through control valve 4 in gaseous form into condenser 8. 3997 kg of 1,2-dichloroethane are discharged per hour through dichloroethane outlet 9. Non-condensable gases are passed through waste-gas line 10 to an incineration plant.

The 1,2-dichloroethane produced additionally contains the following chlorinated impurities:

400 ppm of 1,1,2-trichloroethane
50 ppm of 1,1-dichloroethane
5 ppm of 1,2-trans-dichloroethylene

The yield is 99.7%, relative to C_2H_4 ,
99.7%, relative to Cl_2 .

Process and apparatus for preparing high-purity
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Patent Claims

- 5 1. A process for preparing high-purity 1,2-dichloroethane with heat recovery from equimolar amounts of ethylene and chlorine in 1,2-dichloroethane as solvent in the presence of a tetrachloroferrate(1⁻) catalyst at a temperature of 75 to 200°C and a pressure of 1 to 15 bar in a reaction zone, which process comprises dissolving
10 the chlorine gas in recirculating 1,2-dichloroethane in an upstream mixing zone, reacting the ethylene gas in finely disperse liquid phase having a bubble diameter of at most 2.0 mm in the downstream reaction zone, allowing this finely disperse liquid phase to flow through the
15 reaction zone at a velocity of 0.3 to 1 m/s with a residence time of 2.5 to 25 seconds, calculated relative to the liquid phase, and then removing the high-purity 1,2-dichloroethane formed, which contains less than 500 ppm of chlorinated byproducts, in gaseous form by flash
20 evaporation.
2. The process as claimed in claim 1, wherein the bubble diameter of the ethylene gas is less than 1.5 mm.
- 25 3. An apparatus for carrying out the process as claimed in one of claims 1 or 2, which apparatus comprises a mixer (1) with chlorine inlet (11), a "static mixer" (2) with ethylene inlet (5), a let-down vessel (3), a recirculating pump (6) and a heat exchanger (7), the mixer (1), the "static mixer" (2), the let-down vessel (3), the recirculating pump (6) and the heat exchanger
30 (7) being connected to each other in terms of flow, and the let-down vessel (3) being connected to a condenser (8) in terms of flow via a control valve (4), and a product discharge line (9) and a waste gas line (10)



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Patent Claims

1. A process for preparing high-purity 1,2-dichloroethane with heat recovery from equimolar amounts of ethylene and chlorine in 1,2-dichloroethane as solvent in the presence of a tetrachloroferrate(1⁻) catalyst at a temperature of 75 to 200°C and a pressure of 1 to 15 bar in a reaction zone, which process comprises dissolving the chlorine gas in recirculating 1,2-dichloroethane in an upstream mixing zone, reacting the ethylene gas in finely disperse liquid phase having a bubble diameter of at most 2.0 mm in the downstream reaction zone, allowing this finely disperse liquid phase to flow through the reaction zone at a velocity of 0.3 to 1 m/s with a residence time of 2.5 to 25 seconds, calculated relative to the liquid phase, and then removing the high-purity 1,2-dichloroethane formed, which contains less than 500 ppm of chlorinated byproducts, in gaseous form by flash evaporation.

2. The process as claimed in claim 1, wherein the bubble diameter of the ethylene gas is less than 1.5 mm.

3. An apparatus for carrying out the process as claimed in one of claims 1 or 2, which apparatus comprises a mixer (1) with chlorine inlet (11), a "static mixer" (2) with ethylene inlet (5), a let-down vessel (3), a recirculating pump (6) and a heat exchanger (7), the mixer (1), the "static mixer" (2), the let-down vessel (3), the recirculating pump (6) and the heat exchanger (7) being connected to each other in terms of flow, and the let-down vessel (3) being connected to a condenser (8) in terms of flow via a control valve (4), and a product discharge line (9) and a waste gas line (10)



leaving the condenser (8).

4. The apparatus as claimed in claim 3, wherein a "static mixer" (2) with a flow obliquely around the web is used.

5 5. The apparatus as claimed in claim 4, wherein the blades in the "static mixer" (2) are perforated, slotted, serrated and/or corrugated.

6. The apparatus as claimed in claim 5, wherein the blades form meandering channels.

10 7. The apparatus as claimed in claim 5, wherein the blades form channels crossing each other.

8. The apparatus as claimed in claim 3, wherein a pressure-holding device (12) is arranged between the "static mixer" (2) and the let-down vessel (3).

15 9. The apparatus as claimed in claim 3, wherein the let-down vessel (3) is arranged 8 to 12 m above the "static mixer" (2).