Description

Apparatus and its use for oxychlorination

Description

"Oxychlorination" is taken to mean the reaction of ethylene with hydrogen chloride and oxygen or an oxygen-containing gas, 1,2-dichloroethane (EDC) being formed. The hydrogen chloride used in this case is customarily the hydrogen chloride produced in the thermal cracking of EDC to give vinylchloride.

For the oxychlorination use is made, inter alia, of catalysts which contain metal halides, preferably copper chloride, on dust-fine supports such as alumina. The catalyst particles in this case have a mean diameter of about 50 μm and form a fluid bed, which is either supported only by the reaction gas streams, if appropriate with portions of inert gas, or is additionally supported by a circulated gas stream. In this process, the heat of reaction is distributed in the fluid bed and removed at cooling surfaces, which achieves a uniform temperature distribution in the fluid-bed reactor. In this case, the catalyst particles must have a high abrasion resistance. This property is given essentially by the support material, for which, in addition to the alumina already mentioned, silica, kieselguhr or pumice are also used. If the abrasion resistance is inadequate, the catalyst particles are crushed, in particular by the gas jets of the gas inlet apparatus, and the catalyst support dust thus arising is discharged from the oxychlorination reactor by the upwards-directed gas stream. This not only causes a catalyst loss, but also produces increased abrasion in the apparatus.

The use of an abrasion-resistant support material, on the other hand, is accompanied by an increased wear of the

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

gas inlet apparatuses, which leads to their frequent exchange, this signifying considerable outlay and additional costs owing to the interruption in production.

In addition to the necessary balance between the stability of the catalyst particles and the abrasion caused thereby, it must also be further ensured that the catalyst particles do not agglomerate, since agglomerates caused by this lead to disturbance of the fluid bed. The consequences would be a nonuniform temperature distribution in the fluid bed with a correspondingly less favorable reaction course, and, possibly, blockages at points of constriction in the apparatus, for example in cyclones for dust separation above the fluid bed or in descender pipes for returning the dust from these cyclones to the fluid bed. This tendency to agglomeration depends, in particular, on the concentration of the reaction gases in the fluid bed, in addition to the properties of the catalyst and its distribution on the catalyst support.

WO 94/19099 discloses an apparatus for oxychlorination which comprises a reactor 1, a lower delimitation 2 for a fluid-bed catalyst 3, a gas inlet (distributor tube) 4 which contains nozzles 5, the nozzles 5 opening into tubes 6 which impart a horizontal component in the direction of flow to the exiting gas stream, and a gas inlet 9 beneath the delimitation 2.

Preferred embodiments are focused on said tubes, into which the nozzles open out, containing at the end guiding apparatuses having outlet orifices, or these tubes pointing at an angle upwards or in a horizontal direction or at an angle downwards and these tubes ending open in the catalyst bed, or these tubes or the outlet orifices of adjacent tubes being arranged in such a way that the effluent gas jets do not meet one another frontally and/or do not meet an adjacent tube. Other preferred embodiments are focused on tubes being run through the

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

delimitation, in which tubes nozzles are arranged beneath the delimitation, but above the lower end of the tubes which have been run through, these nozzles preferably being installed in the lower half of the tubes in question, in particular at a distance of about one tube diameter from the lower end.

It has now been found that this known apparatus, in long-term operation and with high throughputs, that is at high gas velocities, exhibits a certain abrasion in the gas inlet apparatuses. Surprisingly, it has further been found that this abrasion does not occur, or occurs only to a considerably reduced extent, if the tubes into which the nozzles open conduct the exiting gas stream essentially in the opposite direction to the gas stream which keeps the catalyst in the form of a fluid bed.

The invention thus relates to an apparatus for oxychlorination, which comprises

- a reactor 1,
- a lower delimitation 2 for a catalyst fluid bed 3,
- a gas inlet (distributor tubes) 4 above the delimitation 2 and within the catalyst fluid bed 3, which gas inlet contains nozzles 5 distributed over the entire cross section of the reactor 1,
- the nozzles 5 opening into tubes 6 which conduct the exiting gas stream essentially in countercurrent to the gas stream which fluidizes the catalyst, and
- a gas inlet 7 beneath the delimitation 2.

The apparatus of the invention is advantageously designed so that there are arranged opposite the number of tubes 8 the same number of tubes 6, uniformly distributed over the cross section of a reactor 1. The alignment of the respective tubes 8 and 6 gives particularly a correspondence of the amounts of gases reacting with one another from the tubes 8 and 6.

In another embodiment of the apparatus of the invention,

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

an identical number of tubes 8 and 6 are situated opposite each other in a staggered manner. This geometry produces the lowest possible erosion of the tubes 6 due to the gas stream ascending from the tubes 8. Furthermore, this arrangement enables the reactants entering into the catalyst fluid bed 3 from the tubes 8 and 6 to be immediately exposed to an intimate contact with the catalyst. By this means, the desired reaction in the direction of the formation of EDC is promoted, and side reactions, for example the combustion of ethylene with oxygen, are suppressed.

A further embodiment of this apparatus permits greater freedom for its design and construction. In this case, the number of tubes 6 is different from the number of tubes 8. However, in this case also, the most uniform distribution possible of these tubes over the cross section of the reactor 1 is important. This form makes it possible to change the number of tubes 6 in an existing reactor, without at the same time adapting the tubes 8, which would signify a high expenditure.

The invention is described in more detail in the following example.

Example

An apparatus according to Figure 1 is used. The reactants preheated to 160°C are introduced in the gaseous state into a reactor 1 of diameter 2.8 m and height 26 m. A mixture of 5974 kg/h of hydrogen chloride and 1417 kg/h of oxygen flows through the gas inlet 4 via the nozzles 5 and the tubes 6 into the catalyst fluid bed 3. The nozzles 5 have different diameters, so that as uniform a gas distribution as possible is achieved at all nozzles 5 and thus over the cross section of the reactor 1. The diameter of the nozzles 5 increases in the downstream direction of the gas inlet 4 from 8.6 mm to 9.3 mm and

THIS SHEET HAS BEEN REPLACED

further to 10 mm, in order to compensate for the various pressure drops along the gas inlet up to the individual nozzles 5. The tubes 6 of an internal diameter of 40 mm have a length of 300 mm. 2380 kg/h of ethylene flow through the lower delimitation 2 via the gas inlet 7 and the tubes 8 containing the nozzles 9. In the reactor 1, there is situated as catalyst copper(II) chloride on an alumina support in the form of a catalyst fluid bed 3. The abovementioned reactants are introduced into this fluid bed. To fluidize the fluid bed, a circulated gas stream of 8780 kg/h additionally flows via the gas inlet 7 and the tubes 8 through the lower delimitation 2 into the reactor 1. The upper ends of the tubes 8 are flush with the lower delimitation 2. The distance between this lower delimitation and the lower ends of the tubes 6 is 400 mm. In this section, the reactants are distributed over the reactor cross section, and mixing zones between the individual reactants and the catalyst form. Ethylene and circulated gas flow from bottom to top in the reactor. On this path, they meet the hydrogen chloride and oxygen and react with interaction of the catalyst present to form EDC and water. The heat of reaction of 238.5 kJ/mol arising in this case is taken off via the catalyst fluid bed 3 to the cooling coil 12 in which water vaporizes at 183°C. The reaction temperature is 225°C at a gauge pressure of 3.2 bar in the reactor. The gas stream at the reactor top, comprising the reaction products and the circulated gas, leaves the reactor 1 via three cyclones for further processing (not depicted in the figure). The three cyclones connected in series serve for separating off the entrained catalyst dust from the gas stream at the reactor top above the catalyst fluid bed.

This Sheet Has Been Replaced

This Sheet Has Been Replaced



THIS SHEET HAS BEEN REPLACED

Claims

1. An apparatus for oxychlorination, which comprises
   - a reactor (1),
   - a lower delimitation (2) for a catalyst fluid bed (3),
   - a gas inlet (distributor tubes) (4) above the delimitation (2) and within the catalyst fluid bed (3), which gas inlet contains nozzles (5) distributed over the entire cross section of the reactor (1),
   - the nozzles (5) opening into tubes (6) which conduct the exiting gas stream essentially in countercurrent to the gas stream which fluidizes the catalyst, and
   - a gas inlet (7) beneath the delimitation (2).

2. The apparatus as claimed in claim 1, which comprises tubes (8) leading through the delimitation (2), in which tubes nozzles (9) are arranged beneath the delimitation (2), but above the lower end of (8).

3. The apparatus as claimed in claim 2, wherein the nozzles (9) are installed at such a distance from the upper end of the tubes (8) that the upwards-directed flow velocity of the gas jets from the nozzles (9) has become uniform over the respective cross section of a tube (8) by the upper end of the tubes (8).

4. The apparatus as claimed in claim 3, wherein the nozzles (9) are installed at a distance of about one diameter of the tubes (8) from the lower end of the tubes (8).

5. The apparatus as claimed in claim 1, wherein the length of the tubes (6) is such that the downwards-directed flow velocity of the gas jets from the nozzles (5) has become uniform over the respective



This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

cross section of a tube (6) by the lower end of the tubes (6).

6. The apparatus as claimed in claims 1 and 5, wherein the nozzles (5) have different diameters, so that the gas conducted via the gas inlet (4) is uniformly distributed over the cross section of the reactor (1).

7. The apparatus as claimed in claims 1 to 6, wherein the space between the upper ends of the tubes (8) and the lower ends of the tubes (6) forms a mixing zone which is dimensioned so large that, on the one hand, the mixing of the reactants with the catalyst can occur as early as here and that, on the other hand, a high mutual erosive stress of the tubes (4, 6, 8) and of the lower delimitation (2) no longer results.

8. Use of the apparatuses as claimed in claims 1 to 7 for the reaction of ethylene with hydrogen chloride and oxygen or an oxygen-containing gas to give 1,2-dichloroethane.

* C L M S *

This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

AMENDED CLAIMS

[filed at the International Bureau on December 4, 1995 (4.12.95)
original claims 1 and 7 amended;
all other claims unchanged (2 pages)]

1. An apparatus for oxychlorination, which comprises
   - a reactor (1),
   - a lower delimitation (2) for a catalyst fluid bed (3),
   - a gas inlet (distributor tubes) (4) above the delimitation (2) and within the catalyst fluid bed (3), which gas inlet contains nozzles (5) distributed over the entire cross section of the reactor (1),
   - the nozzles (5) opening into tubes (6) which conduct the exiting gas stream essentially in countercurrent to the gas stream which fluidizes the catalyst,
   - a gas inlet (7) beneath the delimitation (2) and
   - tubes (8) leading through the delimitation (2),
   - the space between the upper ends of the tubes (8) and the lower ends of the tubes (6) forming a mixing zone which is dimensioned so large that the mixing of the reactants each exiting from these tubes with the catalyst can occur as early as here.

2. The apparatus as claimed in claim 1, which comprises tubes (8) leading through the delimitation (2), in which tubes nozzles (9) are arranged beneath the delimitation (2), but above the lower end of (8).

3. The apparatus as claimed in claim 2, wherein the nozzles (9) are installed at such a distance from the upper end of the tubes (8) that the upwards-directed flow velocity of the gas jets from the nozzles (9) has become uniform over the respective cross section of a tube (8) by the upper end of the

* C L M S *

This Sheet Has Been Replaced

THIS SHEET HAS BEEN REPLACED

tubes (8).

4. The apparatus as claimed in claim 3, wherein the nozzles (9) are installed at a distance of about one diameter of the tubes (8) from the lower end of the tubes (8).

5. The apparatus as claimed in claim 1, wherein the length of the tubes (6) is such that the downwards-directed flow velocity of the gas jets from the nozzles (5) has become uniform over the respective cross section of a tube (6) by the lower end of the tubes (6).

6. The apparatus as claimed in claims 1 and 5, wherein the nozzles (5) have different diameters, so that the gas conducted via the gas inlet (4) is uniformly distributed over the cross section of the reactor (1).

7. The apparatus as claimed in claims 1 to 6, wherein the space between the upper ends of the tubes (8) and the lower ends of the tubes (6) is dimensioned so that a high mutual erosive stress of the tubes (4, 6, 8) and of the lower delimitation (2) does not result.

8. Use of the apparatuses as claimed in claims 1 to 7 for the reaction of ethylene with hydrogen chloride and oxygen or an oxygen-containing gas to give 1,2-dichloroethane.

* C L M S *