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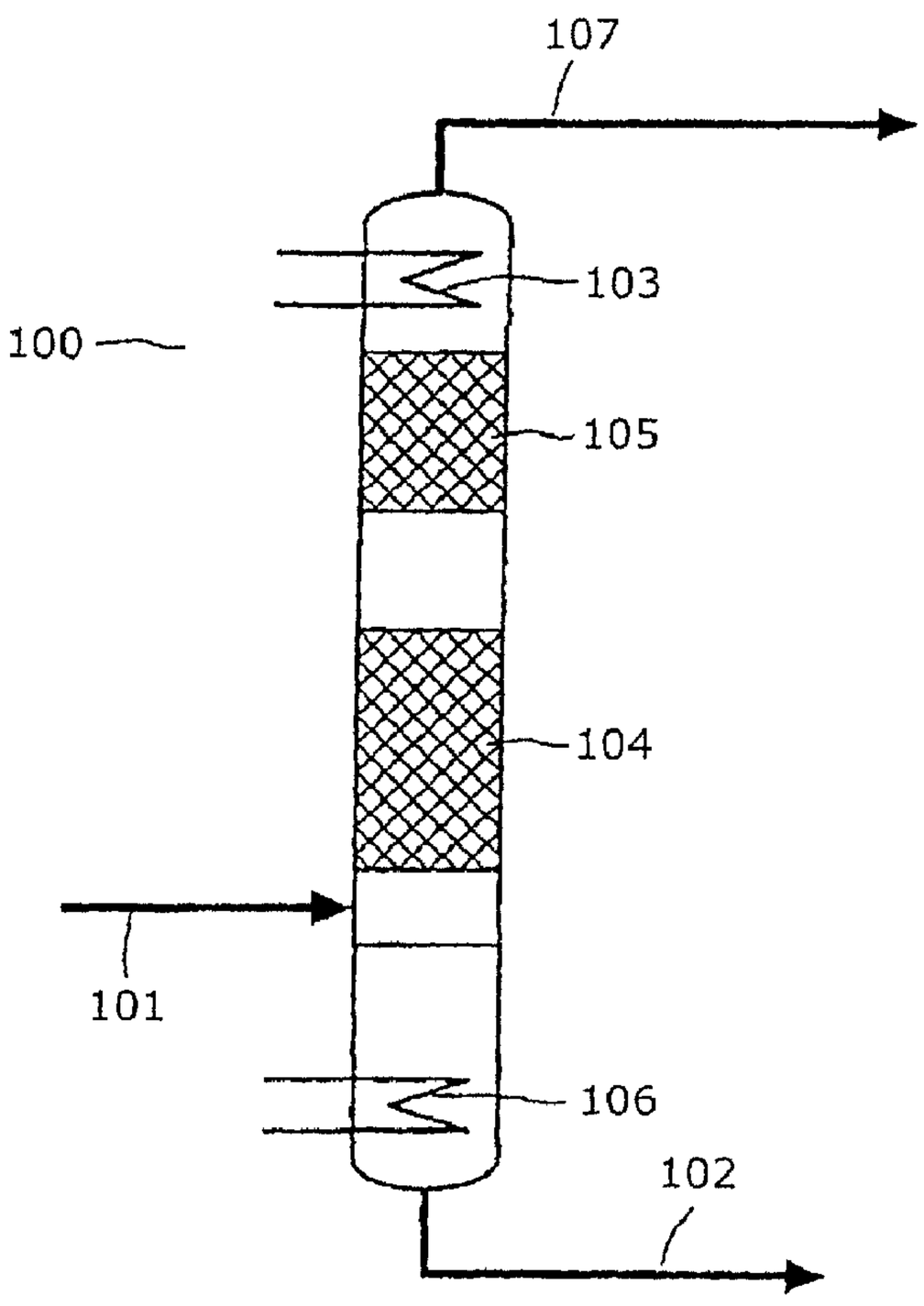
(72) **Inventeurs/Inventors:**
PETRIK, ADOLF, DE;
SCHMID, CHRISTIAN, DE;
HAHN, JOCHEM, DE

(73) **Propriétaire/Owner:**
SCHMID SILICON TECHNOLOGY GMBH, DE

(74) **Agent:** NORTON ROSE FULBRIGHT CANADA LLP/S.E.N.C.R.L., S.R.L.

(54) **Titre : PROCEDE ET INSTALLATION POUR LA FABRICATION DE MONOSILANE**
(54) **Title: METHOD AND SYSTEM FOR PRODUCING MONOSILANE**



(57) **Abrégé/Abstract:**
A description is given of a plant for preparing monosilane, which comprises a reaction column (100) having a feed line (101) for trichlorosilane and a discharge line (102) for silicon tetrachloride formed and also at least one condenser (103) via which the

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(57) **Abrégé(suite)/Abstract(continued):**
monosilane produced can be discharged from the reaction column, wherein the reaction column has at least two reactive/distillative reaction regions (104, 105) which are operated at different temperatures and contain different catalytically active solids. Furthermore, a process for preparing monosilane by catalytic disproportionation of trichlorosilane, in which the disproportionation is carried out in at least two reactive/distillative reaction regions (104, 105) which are operated at different temperatures and contain different catalytically active solids, is described.

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Abstract

A description is given of a plant for preparing monosilane, which comprises a reaction column (100) having a feed line (101) for trichlorosilane and a discharge line (102) for silicon tetrachloride formed and also at least one condenser (103) via which the monosilane produced can be discharged from the reaction column, wherein the reaction column has at least two reactive/distillative reaction regions (104, 105) which are operated at different temperatures and contain different catalytically active solids. Furthermore, a process for preparing monosilane by catalytic disproportionation of trichlorosilane, in which the disproportionation is carried out in at least two reactive/distillative reaction regions (104, 105) which are operated at different temperatures and contain different catalytically active solids, is described.

Description

Method and system for producing monosilane

[0001] The present invention relates to a plant for preparing monosilane (SiH_4), which comprises a reaction column having a feed line for trichlorosilane and a discharge line for silicon tetrachloride ($SiCl_4$) formed and also at least one condenser via which the monosilane produced can be discharged from the reaction column. Furthermore, the present invention relates to a process for preparing monosilane by catalytic disproportionation of trichlorosilane.

[0002] High-purity silicon is generally produced in a multistage process starting from metallurgical silicon which can have a relatively high proportion of impurities. To purify the metallurgical silicon, this can, for example, be converted into a trihalosilane such as trichlorosilane ($SiHCl_3$) which is subsequently thermally decomposed to give high-purity silicon. Such a procedure is known, for example, from DE 29 19 086. As an alternative thereto, high-purity silicon can also be obtained by thermal decomposition of monosilane, as described, for example, in DE 33 11 650. Monosilane can be obtained, in particular, by disproportionation of trichlorosilane. The latter can in turn be prepared, for example, by reaction of metallurgical silicon with silicon tetrachloride and hydrogen.

[0003] To accelerate the disproportionation, it is possible to use catalysts. Basic catalysts such as the amine compounds known from DE 25 07 864 and derivatives have been found to be particularly useful. These are preferably used in bound form, as described, for example, in DE 33 11 650. Catalysts bound to solid supports can be separated in a simple manner from liquid or gaseous reaction mixtures. In the case of

amine compounds, introduction of contaminated amines into the silane/chlorosilane mixture can be avoided in this way. Owing to the associated advantage, virtually only amine catalysts immobilized on supports or amine catalysts incorporated into crosslinked polymers are nowadays used in the industrial disproportionation of trichlorosilane.

[0004] It is known from, inter alia, DE 198 60 146 that the disproportionation of trichlorosilane can be allowed to proceed according to the principle of reactive distillation. Reactive distillation is characterized by a combination of reaction and separation by distillation in one apparatus, in particular in a column. In this apparatus, the lowest-boiling component is continually removed by distillation, with maintenance of an optimal difference between equilibrium state and actual content of low-boiling components or lowest-boiling component always being strived for in each volume element of the apparatus.

[0005] The advantages of reactive distillation can be combined with the advantages of catalysed reaction of trichlorosilane. This can be achieved by carrying out the disproportionation, for example of trichlorosilane into silicon tetrachloride and monosilane, in a column in which the packings (packing elements, internals, etc.) which make mass transfer possible are combined with catalytically active solids. In particular, such a column can contain a catalytically active solid as packing elements.

[0006] It is naturally necessary to take into account the thermal stability of the catalytically active packing elements used. In general, these are based on polystyrene-divinylbenzene resins which are commer-

cially available and relatively inexpensive but become unstable at temperatures just above 100°C. In principle, the disproportionation of trichlorosilane can be accelerated to a greater degree the higher the reaction temperature set. In practice, however, a compromise has to be made because of the limited thermal stability of the catalyst.

SUMMARY

[0007] It was an object of the invention described in the present patent application to develop and improve the known processes for the disproportionation of trichlorosilane, in particular in respect of the rate of the reaction of trichlorosilane.

[0008] In accordance with one aspect of the present invention, there is provided a plant for preparing monosilane (SiH_4) by catalytic disproportionation of trichlorosilane ($SiHCl_3$), which comprises a reaction column having a feed line for trichlorosilane and a discharge line for silicon tetrachloride ($SiCl_4$) formed and also at least one condenser via which the monosilane produced can be discharged from the reaction column, wherein the reaction column has at least two reactive/distillative reaction regions which are operated at different temperatures and contain different catalytically active solids, wherein at least one of the reaction regions contains a catalytically active solid based on vinylpyridine and at least one of the reaction regions contains a catalytically active solid based on styrene, wherein the reaction column is aligned vertically so that the reaction regions operated at different temperatures are arranged one above the other, and the at least one reaction region containing the catalytically active solid based on vinylpyridine, is arranged below the at least one

reaction region containing the catalytically active solid based on styrene.

[0008a] In accordance with another aspect of the present invention, there is provided a system for preparing monosilane (SiH_4) by catalytic disproportionation of trichlorosilane ($SiHCl_3$), wherein the disproportionation is carried out in at least two reactive/distillative reaction regions which are operated at different temperatures and contain different catalytically active solids wherein at least one of the reaction regions contains a catalytically active solid based on vinylpyridine and at least one of the reaction regions contains a catalytically active solid based on styrene, wherein the reaction regions are arranged one above another and the at least one reaction region containing the catalytically active solid based on vinylpyridine, is arranged below the at least one reaction region containing the catalytically active solid based on styrene.

[0009] In a plant according to the invention for preparing monosilane, monosilane is prepared by catalytic disproportionation of trichlorosilane as in almost all plants of this type. The plant of the invention always comprises at least one reaction column which has a feed line for trichlorosilane and a discharge line for the silicon tetrachloride formed in the disproportionation. The plant further comprises at least one condenser via which the monosilane or monosilane-containing product mixture produced can be discharged from the reaction column.

[0010] The at least one reaction column is particularly preferably characterized in that it has at least two reactive/distillative reaction regions which are operated at different temperatures and contain different catalytically active solids.

[0011] The principle of reactive distillation has already been mentioned at the outset. This principle is also used in the reaction column of a plant according to the invention for preparing monosilane. Thus, a reaction proceeds in each of the reactive/distillative reaction regions with continual discharge of the low boilers. These can then be transferred to a downstream reactive/distillative reaction region for further reaction or else they are fed directly to the at least one condenser mentioned (whose function will be described in more detail below).

[0012] A plant according to the invention can comprise one or more of the reaction columns mentioned. It is completely conceivable that, for example, two or more of the reaction columns are connected in parallel within a plant in order to multiply the speed of the disproportionation accordingly.

[0013] In general, the at least one reaction column in a plant according to the invention is aligned vertically so that the reactive/distillative reaction regions operated at different temperatures are arranged one above the other. Within the reaction column, the temperature preferably decreases in an upward direction, so that a reactive/distillative reaction region located higher up is generally operated at a lower temperature than a region underneath. In general, the reaction column is heated only at its lower end. The lowest reactive/distillative reaction region in a

reaction column accordingly usually has the highest operating temperature.

[0014] A decisive advantage of the plant of the invention compared to the procedure known from the prior art is that, as mentioned above, not only one catalytically active solid but at least two different catalytically active solids are used. Each of the solids can be selected so that it is matched to a very particular operating temperature. Preference is thus given according to the invention to a thermally more stable solid to be used as catalyst in a reactive/distillative reaction region located lower down than in a reaction region located higher up. The reaction column in a plant according to the invention can accordingly all be operated at a higher temperature than is known from the prior art. The disproportionation rate may correspondingly be significantly higher.

[0015] Particular preference is given to at least one of the reactive/distillative reaction regions of the reaction column of a plant according to the invention having a catalytically active solid based on vinylpyridine or a vinylpyridine derivative. The solid is particularly preferably based on a copolymer with divinylbenzene, i.e. in particular on a vinylpyridine-divinylbenzene copolymer. A suitable catalytically active vinylpyridine-divinylbenzene copolymer is described, for example, in US 4,613,489.

[0016] However, as an alternative to vinylpyridine, it is also possible to use other nitrogen-containing heterocycles, including, in particular, polyvinylpyrrolidone, polyvinylpyrrolidine, copolymers of vinylpyrrolidone and vinylpyrrolidine with divinylbenzene and derivatives thereof.

[0017] All these compounds have a multiply bonded nitrogen atom and generally remain thermally stable even at temperatures of up to 200°C.

[0018] At least one of the reactive/distillative reaction regions of the reaction column of a plant according to the invention preferably contains a catalytically active solid based on styrene or a styrene derivative, in particular based on a styrene-divinylbenzene copolymer. As mentioned at the outset, such resins are commercially available and relatively inexpensive but can be used only at limited temperatures. In a reaction column according to the invention, they are therefore preferably used in a reaction region preceded by a further reaction region filled with a comparatively more heat-resistant resin.

[0019] The catalytic activity of the resins based on styrene or based on styrene-divinylbenzene copolymers is due to the presence of amine groups, in particular tertiary and quaternary amine groups, in the resins. Polystyrene-divinylbenzene resins having tertiary amine groups can be obtained by various methods which in each case lead to products having identical formulae (see Ullmanns Enzyklopädie der technischen Chemie, 4th edition, volume 13, Weinheim 1997, pages 301-303). Purely by way of example, mention may be made of the phthalimide process in this context. In this, a divinylbenzene-crosslinked polystyrene resin is reacted with phthalimide or a phthalimide derivative. After hydrolysis of the product obtained, viz. a primary polyvinylbenzylamine, this is reacted with formaldehyde and formic acid. Thus, the desired catalyst is obtained in the form of a polystyrene resin having tertiary amino groups.

[0020] In particularly preferred embodiments, a plant according to the invention has, in accordance with what has been said above, a reaction column which

- has at least one reaction region which is at least partly filled with a catalytically active solid based on vinylpyridine or a vinylpyridine derivative, in particular a vinylpyridine-divinylbenzene copolymer, and

- has at least one reaction region which is filled with a catalytically active solid based on styrene or a styrene derivative, in particular on the basis of a styrene-divinylbenzene copolymer,

wherein the at least one reaction region containing the catalytically active solid based on vinylpyridine or the vinylpyridine derivative is arranged below the at least one reaction region containing the catalytically active solid based on styrene or the styrene derivative.

[0021] The lower reaction regions of the column are accordingly able to withstand higher temperatures than the upper reaction regions. The temperature decreases towards the top and here it is possible to use the cheap ion-exchange resins based on the styrene-divinylbenzene copolymer mentioned.

[0022] As mentioned above, both a reaction and a continuous removal of low boilers (i.e. the monosilane-containing fraction) by distillation takes place in each of the reaction regions. The low boilers can then be transferred to downstream reactive/distillative reaction regions, so that the concentration of monosilane in a column generally increases in an upward direction. From the last or uppermost reaction region

in a column, the silane-containing product mixture is then fed to a condenser which is generally operated so that either only monosilane or a monosilane-containing fraction having very low proportions of further volatile components can pass through. Chlorine-containing silanes should if possible be held back in the reaction column by the condenser. For this reason, the condenser is, in preferred embodiments, integrated into the top of the reaction column. However, it is also possible in principle to use a separate condenser located downstream of the column. The chlorosilanes separated off in such a condenser can be returned to the reaction column via a return line.

[0023] A plant according to the invention can naturally also have a plurality of condensers connected in parallel and/or in series.

[0024] In a manner analogous to what has been said above, trichlorosilane is also catalytically disproportionated in the process of the invention for preparing monosilane, with the disproportionation being carried out in at least two reactive/distillative reaction regions which are operated at different temperatures and contain different catalytically active solids. The process of the invention is particularly preferably carried out in a plant as has been described above.

[0025] As mentioned above, the catalysts based on vinylpyridine can generally be used at higher temperatures than the catalysts based on styrene. In a process according to the invention, the reaction regions containing the catalytically active solid based

on vinylpyridine or the vinylpyridine derivative, in particular the vinylpyridine-divinylbenzene copolymer, are preferably operated at temperatures in the range from 50°C to 100°C.

[0026] Analogously, the reaction region or regions containing the catalytically active solid based on styrene or a styrene derivative, in particular, a solid based on a styrene-divinylbenzene copolymer, is/are preferably operated at temperatures in the range from 50°C to 100°C.

[0027] The pressure in the reaction regions is generally set to a pressure in the range from 0.1 bar to 20 bar.

[0028] The operating temperature of the condenser mentioned is preferably in the range from -20°C to -100°C.

[0029] Further features of the invention may be derived from the following description of preferred embodiments in conjunction with the dependent claims. Here, individual features can in each case be realized on their own or as a combination of a plurality thereof, in an embodiment of the invention. The preferred embodiments described serve merely for the purposes of illustration and for better understanding of the invention and are not to be construed as having any limiting effect.

Description of figure:

[0030]

Fig. 1 schematically shows the reaction column of a plant according to the invention for preparing monosilane.

[0031] The figure shows the reaction column **100** in which trichlorosilane can be reacted under disproportionating conditions. Trichlorosilane can be fed in via the feed line **101**. The reaction column has a heated region **106** in which the energy required for disproportionation of the trichlorosilane is provided. The actual reaction occurs in the reaction regions **104** and **105**. Catalytically active solids are present in each of the two reaction regions. The reaction region **104** is filled with catalytically active particles composed of a vinylpyridine-divinylbenzene copolymer, while the reaction region **105** is filled with a commercially available ion-exchange resin based on a styrene-divinylbenzene copolymer having tertiary amino groups (Amberlyst™ 21 from Rohm & Haas). Trichlorosilane introduced into the column via the feed line **101** is thus reacted in a first step in the reaction region **104** to form a monosilane-containing product mixture which can go into the reaction region **105**. Conversely, disproportionation products having a greater density and a higher boiling point (tetrachlorosilane) travel downwards. A second, further disproportionation can occur in the reaction region **105**, resulting in the proportion of monosilane in the reacted reaction mixture increasing further. The condenser **103** which is integrated into the top of the reaction column **100** is operated at a temperature below the condensation point of monochlorosilane, so that essentially only monosilane can pass through the condenser. The condenser accordingly acts as a partial condenser which in the ideal case only allows monosilane to pass through. Chlorine-containing silanes are generally held back in the reaction column by the condenser.

Monosilane can be discharged via the discharge line **107**. At the lower end of the column, tetrachlorosilane which accumulates can be discharged via the discharge line **102**.

CLAIMS:

1. System for preparing monosilane (SiH_4) by catalytic disproportionation of trichlorosilane ($SiHCl_3$), which comprises a reaction column (100) having a feed line (101) for trichlorosilane and a discharge line (102) for silicon tetrachloride ($SiCl_4$) formed and also at least one condenser (103) via which the monosilane produced can be discharged from the reaction column, wherein the reaction column has at least two reactive/distillative reaction regions (104; 105) which are operated at different temperatures and contain different catalytically active solids, wherein at least one of the reaction regions contains a catalytically active solid based on vinylpyridine and at least one of the reaction regions contains a catalytically active solid based on styrene, wherein the reaction column (100) is aligned vertically so that the reaction regions (104; 105) operated at different temperatures are arranged one above the other, and the at least one reaction region containing the catalytically active solid based on vinylpyridine, is arranged below the at least one reaction region containing the catalytically active solid based on styrene.

2. System according to claim 1, characterized in that within the column (100) the temperature decreases in an upward direction so that a reaction region (105) located higher up is generally operated at a lower temperature than a reaction region located underneath (104).

3. System according to claim 1 or 2, characterized in that at least one reaction region contains a catalytically active solid based on a vinylpyridine-divinylbenzene copolymer.

4. System according to any one of claims 1 to 3, characterized in that at least one reaction region contains a catalytically active solid based on a styrene-divinylbenzene copolymer.

5. System according to any one of claims 1 to 4, characterized in that the condenser (103) is integrated into the top of the reaction column (100).

6. Process for preparing monosilane (SiH_4) by catalytic disproportionation of trichlorosilane ($SiHCl_3$), wherein the disproportionation is carried out in at least two reactive/distillative reaction regions (104; 105) which are operated at different temperatures and contain different catalytically active solids wherein at least one of the reaction regions contains a catalytically active solid based on vinylpyridine and at least one of the reaction regions contains a catalytically active solid based on styrene, wherein the reaction regions (104,105) are arranged one above another and the at least one reaction region containing the catalytically active solid based on vinylpyridine, is arranged below the at least one reaction region containing the catalytically active solid based on styrene.

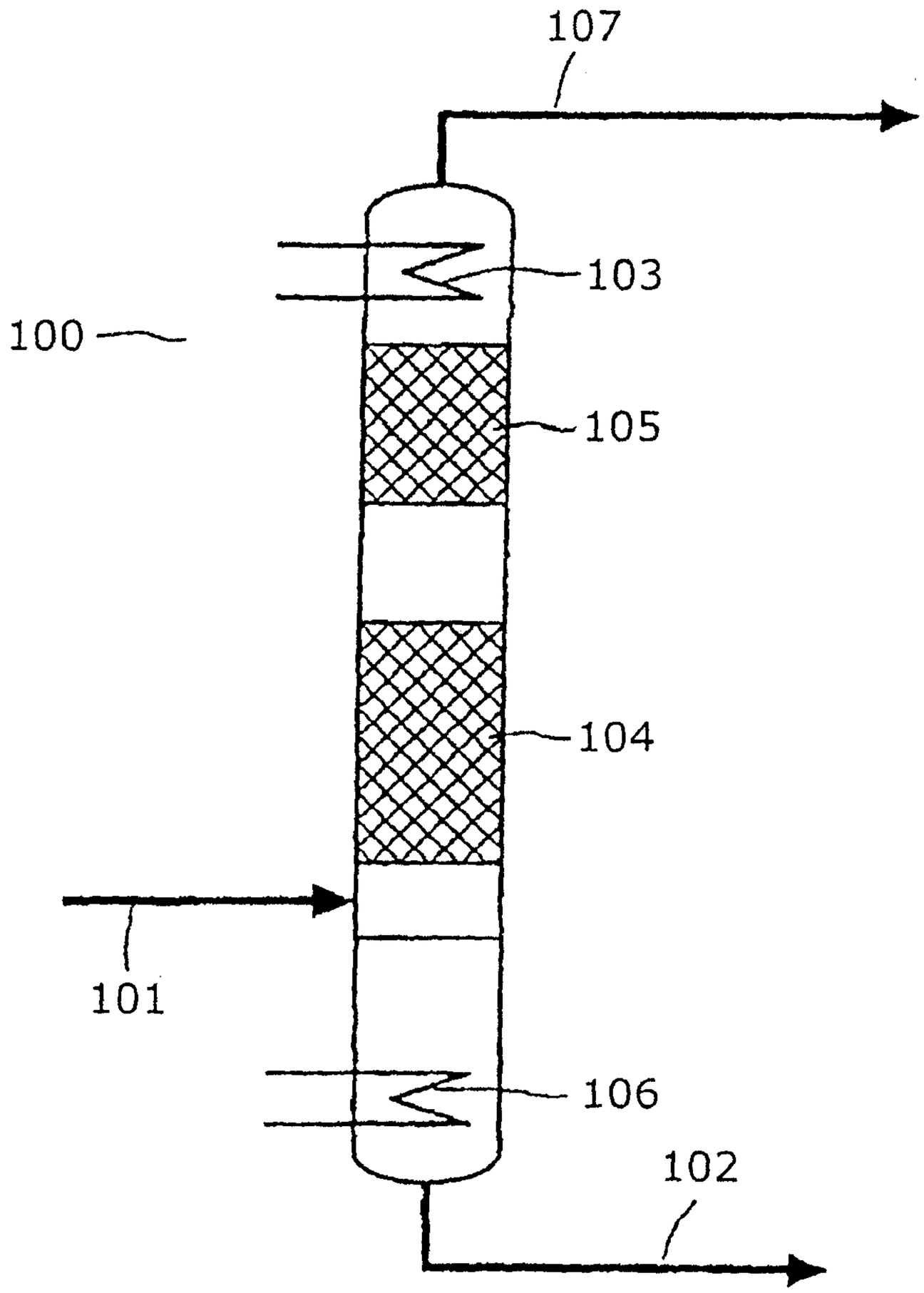
7. Process according to claim 6, characterized in that it is carried out in a system according to any one of claims 1 to 5.

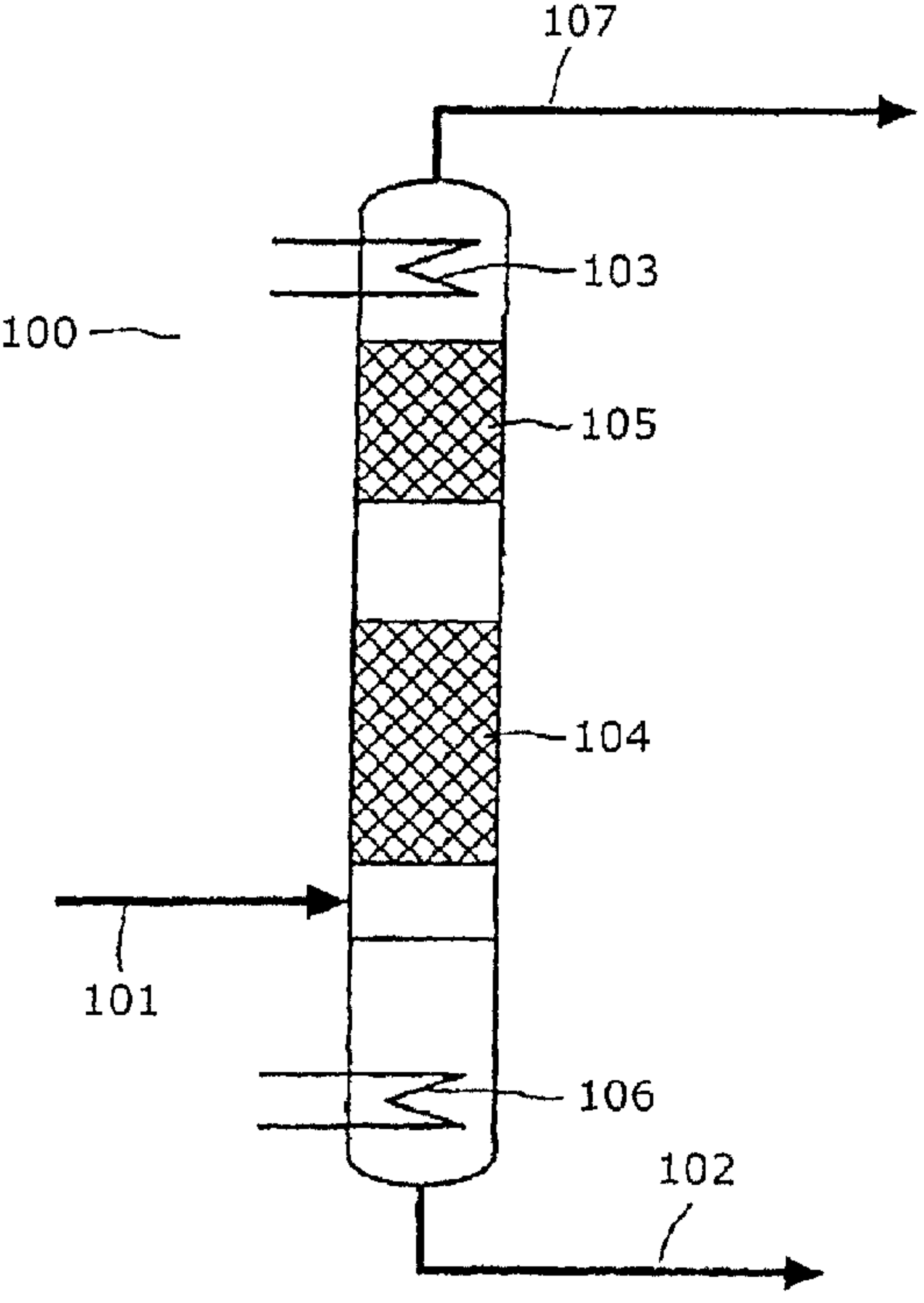
8. Process according to claim 7, characterized in that the reaction region containing the catalytically active solid based on styrene is operated at temperatures in the range from 50°C to 100°C.

9. Process according to any one of claims 6 to 8, characterized in that the pressure in the reaction regions (104; 105) is set to a pressure in the range from 0.1 bar to 20 bar.

10. Process according to any one of claims 7 to 9, characterized in that the condenser (103) is operated at a temperature in the range from -20°C to -100°C.

Fig. 1

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