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(54) Benævnelse: **FREMGANGSMÅDE OG APPARAT TIL KATALYTISK METHANISERING AF GASSER**

(56) Fremdragne publikationer:
WO-A1-2014/154250
US-A1- 2012 063 963
STERNER MICHAEL ET AL: "Erneuerbares Methan", SOLARZEITALTER,, Bd. 1, 1. Januar 2010 (2010-01-01), Seiten 51-58, XP002676162,
BROOKS ET AL: "Methanation of carbon dioxide by hydrogen reduction using the Sabatier process in microchannel reactors", CHEMICAL ENGINEERING SCIENCE, OXFORD, GB, Bd. 62, Nr. 4, 4. Januar 2007 (2007-01-04) , Seiten 1161-1170, XP005822354, ISSN: 0009-2509, DOI: 10.1016/J.CES.2006.11.020

The invention relates to a method for the catalytic methanization of reactant gases, namely carbon dioxide and/or carbon monoxide, using hydrogen in a reactor, having a first step in which hydrogen gas is produced electrolytically from water, wherein in a second step the catalytic methanization of carbon dioxide and/or carbon monoxide is carried out using the obtained hydrogen, and a system for this purpose, wherein the necessary electrical energy is drawn from a renewable energy source, e.g. wind energy.

Renewable electricity, in particular from wind and photovoltaic systems, fluctuates greatly, both in terms of time and space. It is therefore necessary to strike a balance between supply and demand in the context of the expansion of renewable energy production. In this case, it may selectively be necessary to store large amounts of energy over several days or weeks. A suitable form of energy storage for this purpose is the so-called "power-to-gas" technology in which hydrogen is produced by means of water electrolysis, wherein the necessary electrical energy comes from a renewable energy source. The hydrogen thus produced is reacted in a heterogeneous gas-catalytic reaction with carbon dioxide in particular to methane, wherein the methane, optionally after appropriate treatment, is then fed into the existing natural gas infrastructure. In this way, the primary electrical energy is stored outside the grid in the form of natural gas. This natural gas can then be converted back into electrical energy as needed or used in the form of heat by combustion or as fuel, for example, to drive vehicles.

Such a "power-to-gas" method can be found in DE 10 2013 102 669 A1. The production of predominantly liquid hydrocarbons from carbon dioxide, water and regenerative electrical energy is described here. The publication STERNER Michael et al: "Renewable Methane", SOLARZEITALTER, Vol. 1, January 1, 2010 (2010-01-01), pages 51-58, XP002676162 also describes the storage of electricity from renewable sources by coupling the electricity and gas grids.

The methanization of carbon dioxide with hydrogen has usually been used commercially for years in the gasification of coal or biomass. Another area of

application is the purification of gas mixtures in production plants of the chemical industry, for example in the removal of small amounts of carbon monoxide and/or carbon dioxide from the synthesis gas of ammonia plants. These processes are usually carried out in fixed-bed or fluidized bed reactors, wherein these are usually operated continuously, so that no or only very small load changes are present. Such a method and a system for this purpose are disclosed in WO 2014/154250 A1.

Since the methanization is a highly exothermic reaction, the catalysts used, usually pellet-shaped bulk catalysts in the case of fixed-bed reactors, must be protected from excessive temperature increase in the bed. This is usually realized by product gas recirculation and intermediate cooling.

US 2012/0063963 A1 describes the preparation of a methanization catalyst, wherein honeycomb-like carrier structures are provided for the catalyst. This carrier structure may be either a ceramic oxide or also a metal. A similar catalyst is also described in EP 2 893 977 A1.

In the case of power-to-gas processes, the amount of the reaction gas produced by electrolysis, namely hydrogen gas, is obtained as a function of the available electrical current, namely a time-limited current surplus. Since this can of course vary greatly, the conventional methods for methanization are not or only poorly suited, because such load fluctuations can only be compensated for by means of very large hydrogen buffer stores.

It is therefore the object of the invention to provide a method which eliminates the disadvantages of the prior art and in particular allows continuous methanization of carbon dioxide and/or carbon monoxide with hydrogen largely independent of load fluctuations of the electrical energy used for the electrolysis of water. The invention is defined in the appended claims.

According to the invention, this object is achieved by a method for the catalytic methanization of reactant gases, namely carbon dioxide and/or carbon

monoxide, using hydrogen in a reactor, wherein in a first step hydrogen gas is produced electrolytically from water, and the electrical current required for the electrolysis is drawn from a renewable energy source, e.g. wind energy. The catalytic methanization itself takes place in a subsequent second step, wherein it is provided according to the invention that the catalyst used for the methanization is arranged on a carrier structure preferably designed as a honeycomb structure with a high heat storage capacity, preferably with a heat storage capacity greater than 700 J/(kgK), said carrier structure being used as a storage compound for the reaction heat produced during the methanization process.

Since the methanization represents an exothermic reaction, the resulting heat is stored in the carrier structure of the catalyst. As a result, the reactor space is kept at the reaction temperature through the catalyst arranged in the reactor for longer periods, even if the methanization is interrupted in the reactor due to load fluctuations and the resulting lack of hydrogen.

During methanization, at least one heat exchanger device ensures the removal of excess reaction heat, which can be used for controlling the temperature of further reaction chambers if required.

Particularly preferably, it is provided that the reactor has at least two chambers which are fed in series, in parallel or alternately with reactant gas. The chambers preferably contain at least two switchable compartments in which the catalysts are arranged. As already described above, this has the advantage that at partial load operation only at least one chamber and/or compartment is fed with reaction gas, namely hydrogen and carbon dioxide and/or carbon monoxide for carrying out the methanization reaction, while at least one second chamber is kept in standby mode, wherein the reaction heat stored in the carrier structure maintains that second chamber and/or compartment at reaction temperature.

For purposes of this disclosure, the terms "reactor chamber", "chamber" and "reactor space" are used interchangeably. The same applies to the terms "compartment" and "section".

To carry out the method according to the invention, it is particularly preferable to use a plant having at least one reactor in which the catalyst is arranged, wherein the at least one reactor has at least one gas feed line and preferably at least one heat exchanger device, wherein the catalyst used for the methanization has a carrier structure having a high heat storage capacity greater than 700 J/(kgK), wherein the carrier structure can be used as a storage mass for the reaction heat obtained during methanization, and the reaction heat stored in the carrier structure can be removed, if required, via at least one heat exchanger device.

In a particularly preferred embodiment of the invention, the carrier structure of the catalyst has a honeycomb structure with honeycomb-shaped base bodies, wherein advantageously the honeycomb-shaped base bodies have a rectangular, square, uniform triangular or uniform hexagonal cross-section. These cross-sections allow the construction of catalyst layers within a reactor space, wherein preferably the honeycombs are arranged along their side edges to each other. Honeycombs with a side length of 0.05 m to 0.3 m and a honeycomb height of 0.1 m to 0.6 m have proved to be particularly suitable for the construction of catalyst layers.

The carrier structure of the catalyst is advantageously made of a material selected from the group containing ceramic oxides such as silicon oxide, titanium oxide, aluminum oxide, cerium oxide, zirconium oxide, or mixtures thereof. Due to the reaction heat liberated during the methanization and the resulting high temperatures, carrier structures have proven their worth in particular which are made of cordierite, mullite or aluminum oxide compounds fired at 1300°C to 1600°C. In particular, these materials withstand the high temperature stresses and temperature changes associated with methanization.

In this case, it is provided according to the invention that a catalytically active material, preferably as a washcoat, is applied at least partially to the surface of the carrier structure, wherein the catalyst contains at least one element of the group VIII elements, selected in particular from the nickel group, the cobalt group and/or the iron group.

For the production of the washcoat, an acidic metal oxide suspension, for example aluminum oxide or zirconium oxide, is usually applied to the carrier structure, and the carrier structure coated in this way is subsequently dried and fired. Finally, this layer is impregnated with a salt solution of the chosen catalyst, and the catalyst is fixed on the carrier structure by further drying and optionally firing.

In a particularly preferred embodiment of the invention, a reactor system having at least two reactor chambers is provided, in which the catalyst, in particular ceramic honeycomb catalysts, are arranged, wherein advantageously each reactor chamber has at least one gas line and preferably at least one heat exchanger device. As a result, the partial load behavior of the reactor system, which is particularly preferably designed as a tray reactor system, is considerably improved.

In a further preferred embodiment, each chamber is additionally subdivided into at least two compartments or sections, wherein reactant gas can flow into each compartment independently. This provides an additionally higher load flexibility.

In the case of low reactant gas streams, in particular with regard to the hydrogen produced by electrolysis, only a first compartment of a first chamber can be provided with an inflow, for example, while the other compartments remain in the idle state. Due to the large ceramic mass of the carrier structure, in particular in honeycomb catalysts, the heat generated during the reaction is stored, wherein the compartment or compartments remain in the idle state at reaction temperature by the heat emitted from the carrier structure. The supply of reactant gas can be alternately controlled between the individual compartments or

sections of the tray reactor such that in all compartments alternately exothermic reaction heat is released and stored, and thus the compartments are each kept at reaction temperature. In continuous operation, the heat exchanger devices in the respective reaction chambers allow removal of excess heat, in order to avoid overheating of the catalyst and/or the reactor space.

The system according to the invention can be adapted in size to the respective throughputs, in particular in the case of tray reactors it is possible to provide an extension of the system when using honeycomb catalysts in a simple manner. In this case, only the number of honeycombs used has to be adapted to the maximum expected reactant gas flow.

In an alternative embodiment of the invention, a reactor system having at least two fixed-bed reactors is provided, in which the catalyst is arranged, wherein advantageously each reactor has at least one gas supply line and preferably at least one heat exchanger device.

Particularly preferably, it is provided that the carrier structure of the catalyst is arranged within the respective reactors or reaction chambers in layers, wherein the layer structure preferably has 4 to 30 channels per square centimeter, thus a cell density of 25 cpsi to 200 cpsi. These channels allow the respective reaction gases to flow through the respective layers without significant pressure drop while providing a sufficiently high contact area of the gases with the active centers of the catalyst.

The storage capacity in the respective reaction chamber can be improved by the layer structure having at least one catalytically active layer or area and additionally at least one catalytically inactive layer or area, wherein the inactive layer is preferably formed from the carrier structure for the catalyst. In this case, the respective layers particularly preferably have the honeycomb structure already described, wherein the honeycomb-shaped base bodies of the catalytically inactive layer have no catalytically active constituents and/or coating and are used exclusively for heat storage. It can likewise be provided that

catalytically active and catalytically inactive honeycomb bodies are mixed in any ratio within a layer.

The invention is explained in more detail below with reference to non-limiting exemplary embodiments with associated figures, wherein:

Fig. 1 shows a schematic view of a first embodiment of the device according to the invention;

Fig. 2 shows a schematic cross-section of a reaction chamber of the device from Fig. 1;

Fig. 3 shows a schematic view of a second embodiment of the device according to the invention; and

Fig. 4 shows a schematic view of a third embodiment of the device according to the invention.

Fig. 1 shows a schematic representation of a reactor 100 according to the invention, which is designed as a tray reactor in this embodiment of the invention. This tray reactor 100 has three reactor chambers 110a, 110b, 110c, each having a gas distribution layer 120a, 120b, 120c, usually of porous material, which serves to uniformly distribute the gas within the reactor chambers 110a, 110b, 110c.

In each reactor chamber 110a, 110b, 110c, in this embodiment of the invention, catalyst material 140 in the form of honeycomb catalysts is arranged in two compartments 131, 132 (Fig. 2).

The feed of reactant gases (arrow A) is carried out via a gas distribution system 150a, 150b, 150c, which is cyclically switchable, so that inflow into the respective compartments 131, 132 can occur independently of each other. This cyclic switching allows a time-staggered sequence of methanization reactions in the individual compartments 131, 132 or in the catalyst layers located therein. In this case, the temporal sequence is selected such that exothermic reaction heat is repeatedly released in the individual compartments 131, 132 in order to keep the compartments 131, 132 and, as a consequence, the reactor chambers 110a,

110b, 110c at the operating temperature. The reaction heat is stored here in the honeycomb base bodies of the carrier structure of the catalyst 140.

A bypass system 160 permits a cyclical switching of the reactant gas in the individual reactor chambers 110a, 110b, 110c, wherein shut-off valves 161 provided for this purpose in the gas distribution system 150a, 150b, 150c optionally prevent the gas supply into the gas distribution layers 120a, 120b, 120c. If the reactant gas streams are available in an insufficient quantity for operation of all reactor chambers 110a, 110b, 110c or compartments 131, 132, this cyclic switching permits a time-staggered sequence of methanization reactions in the individual reactor chambers 110a, 110b, 110c or compartments 131, 132.

Furthermore, each reactor chamber 110a, 110b, 110c is equipped with heat exchanger devices 170, which allow a dissipation of excess heat and/or temperature of the respective reactor chamber 110a, 110b, 110c.

The removal of the product gas, namely the raw methane, is preferably carried out at the top of the tray reactor 100 (arrow B).

Fig. 2 shows, by way of example, the reactor chamber 110a in a plan view, wherein catalyst material 140 is arranged in each of the two compartments 131, 132. The catalyst layer 140 consists of a plurality of honeycomb-shaped base bodies, which have a catalytically active salt, for example in the form of a washcoat, wherein the base bodies are arranged along their side edges to one another.

The honeycomb base bodies of this catalyst material 140 have channels (not shown) extending parallel to the longitudinal axis of the tray reactor 100, which allow a flow through the catalyst material 140 in the compartments 131, 132.

Fig. 3 shows a further embodiment of the invention, wherein the tray reactor 100 shown therein has substantially the same structure as shown in Fig. 1. In this

variant, the compartments 131, 132 are filled with catalyst material 140, wherein the catalyst material 140 is penetrated by heat storage layers 141. These heat storage layers 141 are catalytically inactive, and are particularly preferably formed from the honeycomb base bodies of the carrier structure of the catalytically active layer 140, but in contrast to this have no catalytically active equipment. The arrangement of these heat storage layers 141 may surround or pass through the catalyst layer 140.

A third embodiment of the device 200 according to the invention can be seen from Fig. 4. In this case, three fixed-bed reactors 210 are provided, which in turn are filled with catalyst material 140, which consists according to the invention of honeycomb base bodies. In turn, a gas distribution layer 220 is provided which effects a uniform distribution of the gas flowing in via a gas distribution system 250 (arrow A) within the reactor chamber. If necessary, the incoming gas can be temperature-controlled by means of a heat exchanger device 270.

Furthermore, shut-off valves 261 are provided in the gas distribution system 250, which allow a cyclic and/or alternating supply of reactant gases to the respective fixed-bed reactors 210.

It is understood that the present invention is not limited to the embodiments shown above. In particular, different types of fixed-bed reactors may be used, which are suitable for receiving the catalyst layers described above. It is essential to the invention that these catalyst layers have a high heat storage capacity and/or further catalytically inactive layers with a high heat storage capacity are provided. This heat storage capacity allows a partial load operation of the reactor or of a system comprising several reactors according to the invention, which has at least two independently operable reactor chambers and/or reactors, which can be operated either simultaneously or in a time-staggered manner depending on the load. An essential advantage of the system according to the invention is that it can be expanded as required by further reactor chambers and/or reactors with associated catalyst layer in a simple manner. Furthermore, this design allows a very flexible operation that tolerates highly fluctuating load changes due to the

coupling of the methanization method with the electrolysis used to produce the hydrogen gas with electrical energy from renewable energy sources.

Patentkrav

1. Fremgangsmåde til katalytisk methanisering af reaktantgasser, nemlig carbondioxid og/eller carbonmonoxid, under anvendelse af hydrogen i en reaktor (100, 200), hvilken fremgangsmåde har et første trin, i hvilket der elektrolytisk fremstilles hydrogengas ud fra vand, hvor den katalytiske methanisering af carbondioxid og/eller carbonmonoxid med det opnåede hydrogen udføres i et andet trin, hvor den elektriske energi, der er nødvendig til elektrolysen, opnås fra en fornyelig energikilde, for eksempel vindenergi, **kendetegnet ved, at** en katalysator (140), som anvendes til methanisering, anbringes på en bærerstruktur med en varmelagringskapacitet på over 700 J/(kgK), hvor bærerstrukturen fortrinsvis er udformet som en honeycomb-struktur, der anvendes som en lagringsforbindelse til den reaktionsvarme, som genereres under methanisering, hvor reaktionsvarmen, der lagres i bærerstrukturen, fjernes via mindst én varmevekslerindretning (170, 270).

2. Fremgangsmåde ifølge krav 1, **kendetegnet ved, at** reaktoren (100) omfatter mindst to reaktorkamre (110a, 110b, 110c), der serielt, parallelt eller skiftevis påfyldes med reaktantgas.

3. Fremgangsmåde ifølge krav 2, **kendetegnet ved, at** de mindst to reaktorkamre (110a, 110b, 110c) er underopdelt i mindst to kompartmenter (131, 132), der serielt, parallelt eller skiftevis påfyldes med reaktantgas.

4. Fremgangsmåde ifølge et af kravene 2 eller 3, **kendetegnet ved, at** hvert reaktionskammer (110a, 110b, 110c) er forsynet med varmevekslerindretninger (170), hvilket tillader overskudsvarme at blive fjernet og/eller temperaturstyring af det tilhørende reaktionskammer (110a, 110b, 110c).

5. System til udførelse af en fremgangsmåde til katalytisk methanisering af reaktantgasser, nemlig carbondioxid og/eller carbonmonoxid, med hydrogen, hvor der tilvejebringes en elektrolyse af vand til fremstilling af hydrogengas ved hjælp af elektrisk energi fra en fornyelig energikilde, hvilket system har mindst én reaktor, i hvilken katalysatoren (140) er anbragt, hvor den mindst ene reaktor (110a, 110b, 110c) omfatter mindst én gasforsyningsledning (150a, 150b, 150c) og mindst én varmevekslerindretning (170), **kendetegnet ved, at** katalysatoren (140), der anvendes til methanisering, har en bærerstruktur

med en varmelagringskapacitet på over 700 J/(kgK), hvor bærerstrukturen kan anvendes som en lagringsmasse til den reaktionsvarme, som opnås under methanisering, og reaktionsvarmen, der lagres i bærerstrukturen, kan fjernes via mindst én varmevekslerindretning (170, 270).

6. System (100, 200) ifølge krav 5, **kendetegnet ved, at** katalysatorens (140) bærerstruktur har en honeycomb-struktur med honeycomb-formede grundkroppe.

7. System (100, 200) ifølge krav 6, **kendetegnet ved, at** de honeycomb-formede grundkroppe har et rektangulært, kvadratisk, ensartet triangulært eller ensartet heksagonalt tværsnit, hvor honeycomb-strukturerne fortrinsvis har en sidelængde på 0,05 m til 0,3 m og en honeycomb-højde på 0,1 m til 0,6 m.

8. System (100, 200) ifølge et af kravene 5 til 7, **kendetegnet ved, at** katalysatorens (140) bærerstruktur er fremstillet af et materiale, der valgt fra en gruppe, som indeholder keramikoxider såsom siliciumoxid, titanoxid, aluminiumoxid, ceriumoxid, zirconiumoxid eller blandinger deraf, hvor bærerstrukturen særligt fortrinsvis er fremstillet ud fra cordierit-, mullit- eller aluminiumoxidforbindelser, der er brændt ved 1300 °C til 1600 °C.

9. System (100, 200) ifølge et af kravene 5 til 8, **kendetegnet ved, at** der anvendes et katalytisk aktivt materiale, fortrinsvis som washcoat, mindst delvist på bærerstrukturens overflade, hvor katalysatoren indeholder mindst ét grundstof fra gruppe VIII-grundstofferne, især fra nikkelgruppen, cobaltgruppen eller jerngruppen.

10. System (100) ifølge et af kravene 5 til 9, **kendetegnet ved, at** der tilvejebringes et reaktorsystem med mindst to reaktorkamre (110a, 110b, 110c), i hvilke katalysatoren (140) er anbragt.

11. System (100) ifølge krav 10, **kendetegnet ved, at** reaktorkamrene (110a, 110b, 110c) er underopdelt i mindst to kompartmenter (131, 132), hvor reaktantgas uafhængigt kan strømme ind i hvert kompartment (131, 132).

12. System (200) ifølge et af kravene 5 til 9, **kendetegnet ved, at** der tilvejebringes et reaktorsystem med mindst to fixed bed-reaktorer (210), i hvilke katalysatoren (140) er anbragt, hvor hver reaktor (210) med fordel omfatter mindst én gasforsyningsledning (250) og fortrinsvis mindst én varmevekslerindretning (270).

13. System (100, 200) ifølge et af kravene 5 til 12, **kendetegnet ved, at** katalysatorens (140) bærerstruktur er anbragt i lag inden i det tilhørende reaktorkammer (110a, 110b, 110c), hvor lagstrukturen fortrinsvis omfatter 4 til 30 kanaler pr. cm^2, altså med en celledensitet på 25 cpsi til 200 cpsi.

14. System (100, 200) ifølge krav 13, **kendetegnet ved, at** lagstrukturen omfatter mindst ét katalytisk aktivt lag (140) og mindst ét katalytisk inaktivt lag (141), der fortrinsvis er dannet ud fra bærerstrukturen for katalysatoren (140).

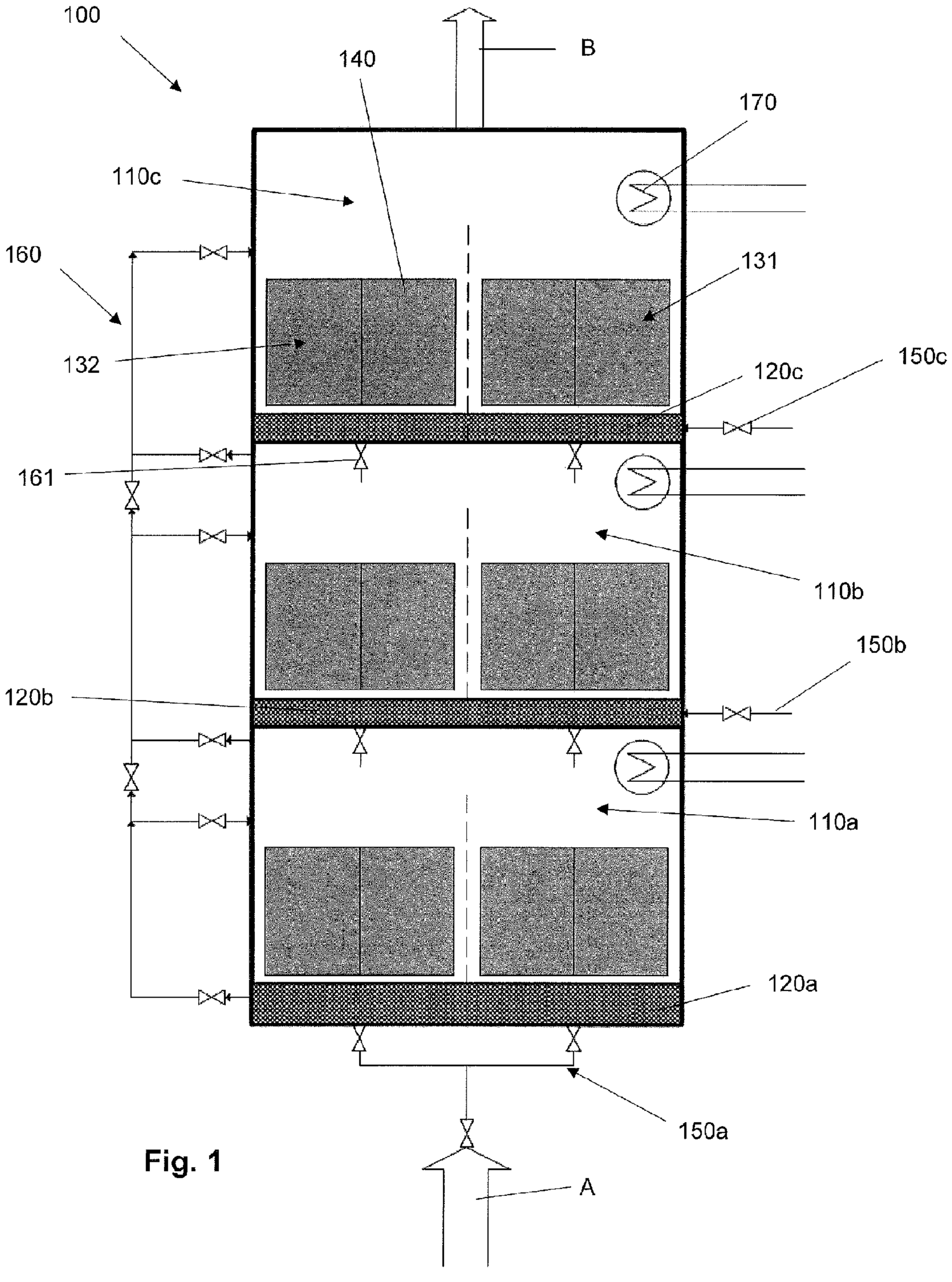
100
140
B
170
110c
160
131
132
150c
120c
161
110b
150b
120b
110a
120a
150a
A

Fig. 1

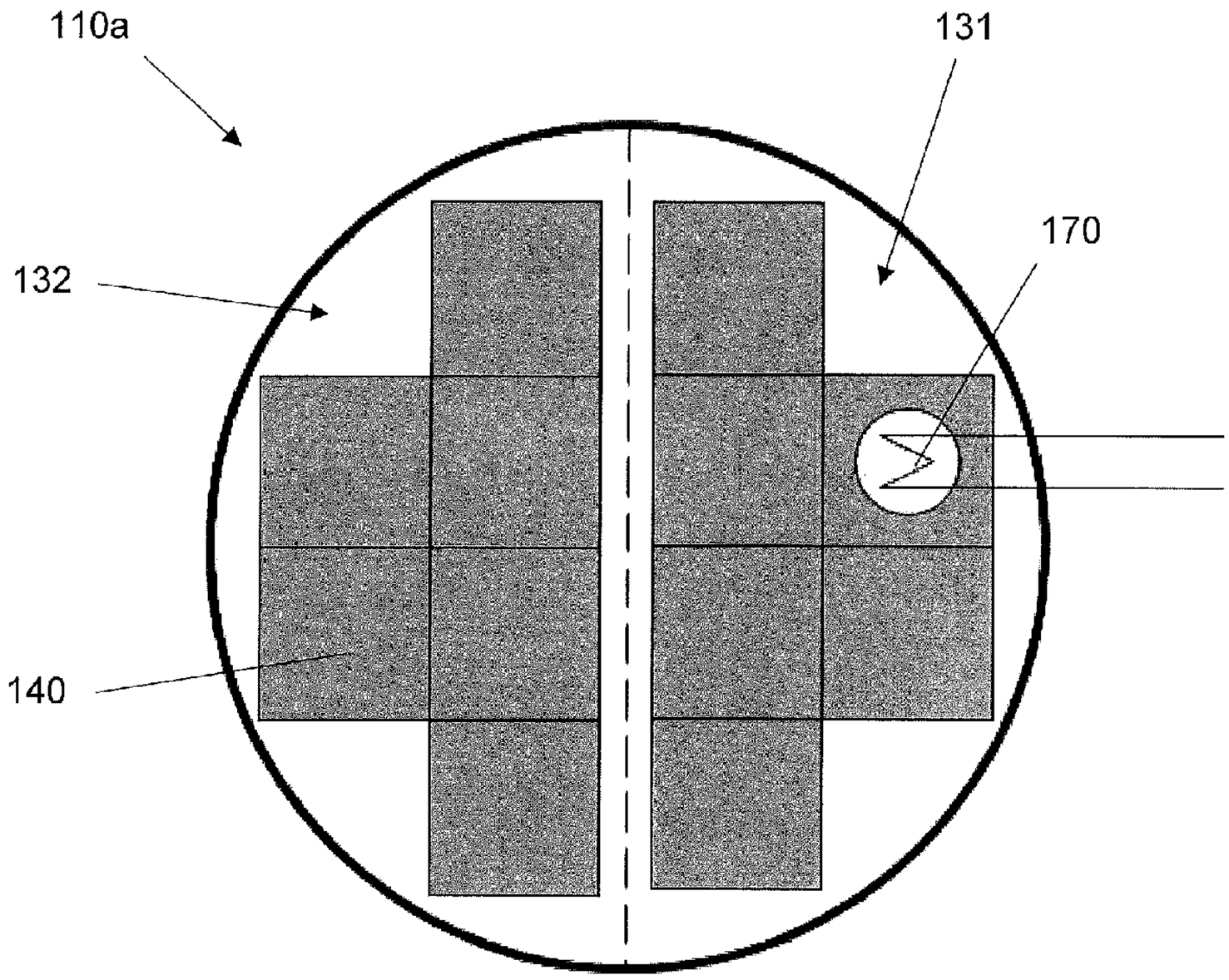

Fig. 2

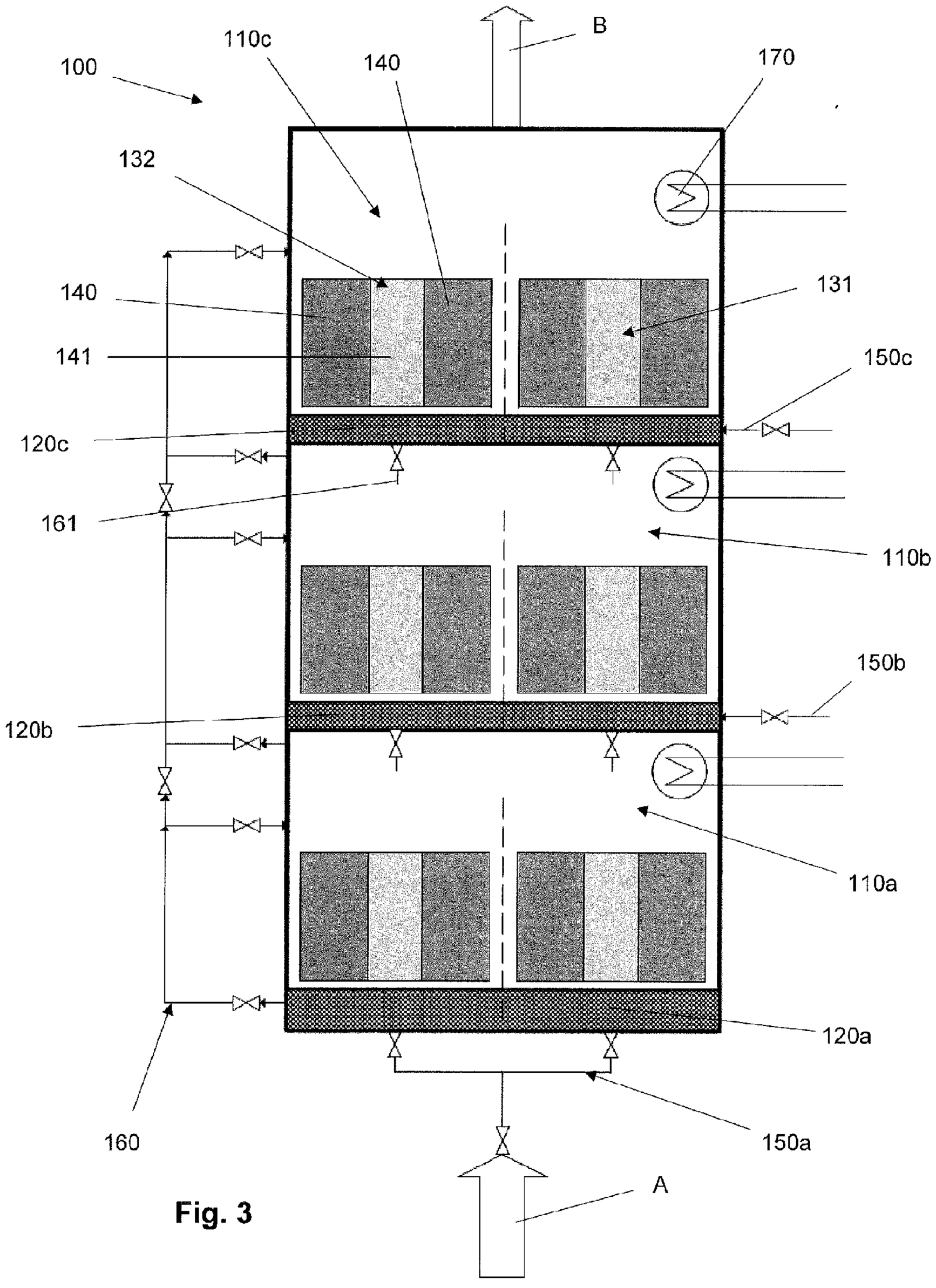
100
110c
140
B
170
132
131
140
141
150c
120c
161
110b
150b
120b
110a
120a
160
150a
A

Fig. 3

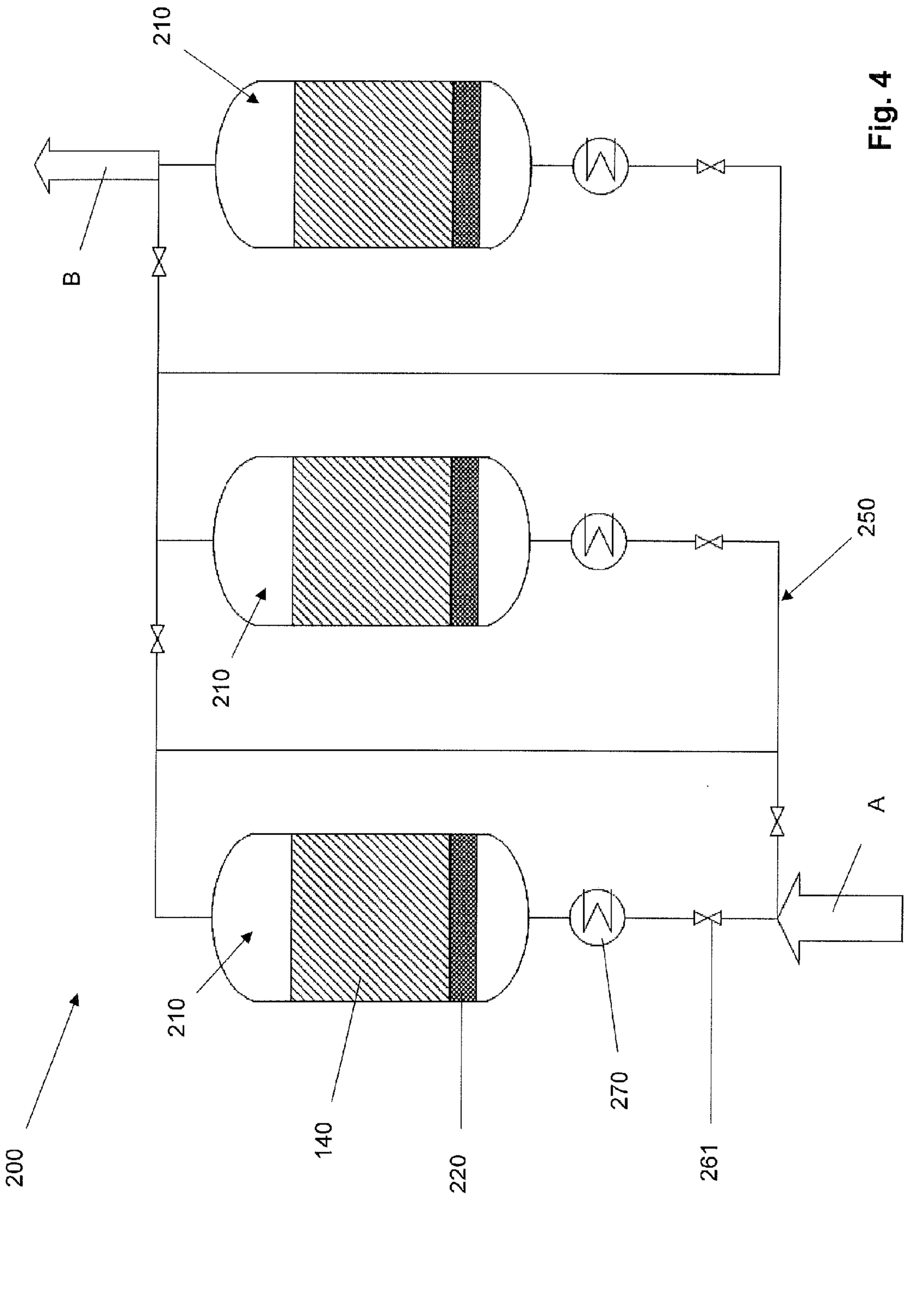

Fig. 4