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(54) **Titre : PROCEDE DE DECARBONATATION DE MATIERES CARBONEES DANS UN FOUR VERTICAL A PLUSIEURS ARBRES**
(54) **Title: DECARBONATION PROCESS OF CARBONATED MATERIALS IN A MULTI-SHAFT VERTICAL KILN**

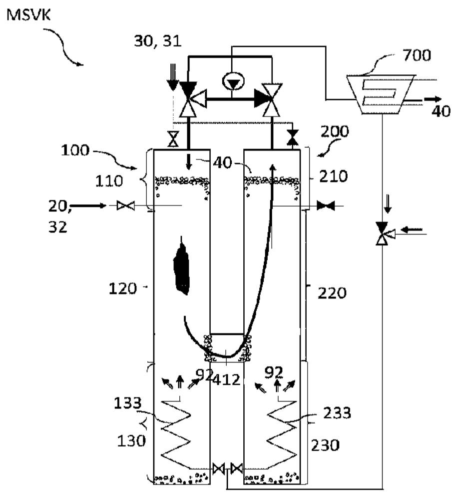

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Fig. 8

(57) **Abrégé/Abstract:**
The present invention relates to a decarbonation process of carbonated materials, in particular limestone and dolomitic limestone, with CO_2 recovery in a multi-shaft vertical kiln (MSVK) comprising a first and a second shaft with preheating, heating and cooling zones and a cross-over channel between each shaft, alternately heating carbonated materials by a combustion of at least one fuel with at least one comburent, up to a temperature range in which carbon dioxide of the carbonated materials is released, the combustion of the fuel and the decarbonatation generating an exhaust gas, wherein decarbonated materials are cooled in the cooling zones with one or more cooling streams, said process further comprising cooling the decarbonated materials with the one or more cooling streams comprising a water steam stream, said stream being fed in the cooling zone of at least the first and/or the

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(54) **Title:** DECARBONATION PROCESS OF CARBONATED MATERIALS IN A MULTI-SHAFT VERTICAL KILN

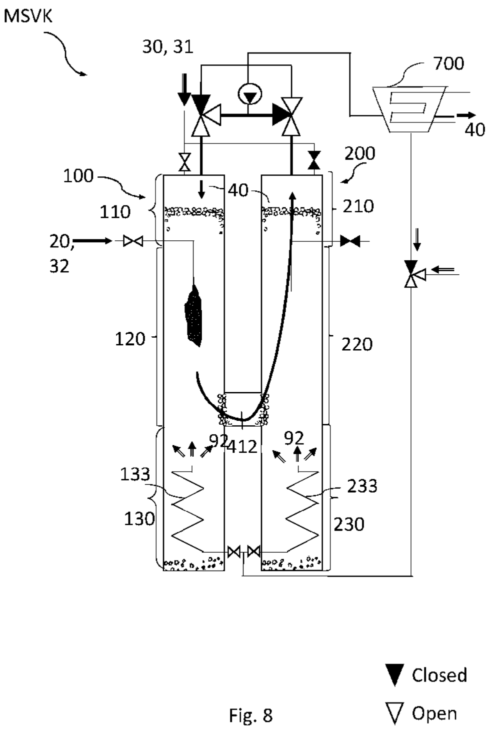

Fig. 8

(57) Abstract: The present invention relates to a decarbonation process of carbonated materials, in particular limestone and dolomitic limestone, with CO_2 recovery in a multi-shaft vertical kiln (MSVK) comprising a first and a second shaft with preheating, heating and cooling zones and a cross-over channel between each shaft, alternately heating carbonated materials by a combustion of at least one fuel with at least one comburent, up to a temperature range in which carbon dioxide of the carbonated materials is released, the combustion of the fuel and the decarbonatation generating an exhaust gas, wherein decarbonated materials are cooled in the cooling zones with one or more cooling streams, said process further comprising cooling the decarbonated materials with the one or more cooling streams comprising a water steam stream, said stream being fed in the cooling zone of at least the first and/or the second shaft.

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DECARBONATION PROCESS OF CARBONATED MATERIALS IN A MULTI-SHAFT VERTICAL KILN

Technical Field

[0001] The present invention relates to a decarbonation process of carbonated materials and to a multi-shaft vertical kiln for carrying said process.

Background Art

[0002] The increasing concentration of carbon dioxide in the atmosphere is recognized as one of the causes of global warming, which is one of the greatest concerns of present days. This increase is largely owed to human actions and particularly to the combustion of carbon-containing fossil fuel, for instance for transportation, household heating, power generation and in energy-intensive industries such as steel, cement and lime manufacturing.

[0003] Within the lime-production process, natural limestone (mainly composed of calcium carbonate) is heated to a temperature above 900°C in order to cause its calcination into quicklime (calcium oxide) and carbon dioxide according to the following reversible reaction :

$$CaCO_3 \leftrightarrow CaO + CO_2 \ \Delta H = 178 \text{ kJ/mol} : \text{Equation 1}$$

[0004] Calcium oxide is considered as one of the most important raw materials and is used in a multitude of applications such as steel manufacturing, construction, agriculture, flue gas and water treatment as well as in glass, paper and food industry. The global annual production is estimated to be above 250 million tons.

[0005] As indicated in Equation 1, CO_2 is a co-product of the lime-production process meaning that approximately 760 to 790 kg of CO_2 is unavoidably generated when producing 1 ton of lime. Moreover, the heat required for heating limestone and for conducting the reaction is usually provided by the combustion of a carbonaceous fuel, which results in additional production of CO_2 (ranging between 200 and more than 700 kg per ton of lime depending on the nature of the fuel and efficiency of the kiln).

[0006] The use of vertical shaft kiln prevails in the lime industry as they are particularly suitable for the production of lumpy quicklime compared to other types of furnaces, such as rotary kiln, and because they have the advantage of lower specific energy input.

[0007] In a single shaft vertical kiln, limestone or dolomitic limestone is fed through the top of the shaft and the produced lime is discharged at its bottom. In the pre-heating zone, the limestone is heated by hot gases flowing upward from the combustion zone. In the combustion zone, heat is produced through the direct firing of a fuel to reach a temperature above 900°C and consequently causing the decomposition of the limestone into quicklime and CO_2. The lime then enters the cooling zone where it is cooled by air fed from the bottom of the shaft. The produced lime is finally discharged, ground and sieved into the desired particle size. Flue gas leaves the shaft at the top of the pre-heating zone and is fed to a filter system before it is vented to the atmosphere. Specific energy consumption for such single-shaft vertical kilns ranges between 4 and 5 GJ per ton of lime.

[0008] Parallel flow regenerative kilns (PFRK) are a variant of vertical shafts that are considered as the best available technology for lime production with design capacity up to 800 tons per day. They consist in several vertical shafts (usually 2 or 3) connected by a cross-over channel. Each shaft operates alternately according to a defined sequence. Initially, fuel is burnt in one of the shaft ("in combustion") with combustion air flowing downwards ("parallel flow" with the limestone). Hot gases are then transferred to the other shafts ("in regeneration") through the cross-over channel in order to pre-heat limestone in said other shafts. A reversal between combustion and regeneration shafts occurs typically every 15 minutes.

[0009] This operational mode enables optimal recovery of the heat contained in product and hot gases bringing the specific energy consumption down to 3.6 GJ per ton of lime. The combustion of the fuels required to bring this heat results in the production of approximately 200 kg of CO_2 per ton of lime when natural gas is used.

[0010] The lime industry is making efforts for reducing its CO_2 emissions by improving energy efficiency (including investment in more efficient kilns), using lower-carbon energy sources (e.g. replacing coal by natural gas or biomass) or supplying lime plants with renewable electricity. The CO_2 related to energy can thus be reduced to some extent. Nevertheless, none of these actions impacts the CO_2 which is inherently produced during decarbonation of limestone.

[0011] A route for further reducing emission consists in capturing CO_2 from the lime kiln flue gas for permanent sequestration (typically in underground geological formation) or recycling for further usage (e.g. for the production of synthetic fuels). Those processes are known under the generic term CCUS (Carbon Capture, Utilization and Storage).

[0012] Combustion air used in conventional lime kilns contains approximately 79 vol% nitrogen resulting in CO_2 concentration in flue gas not higher than 15-20 vol%. Additional measures are thus required to obtain a CO_2 stream sufficiently concentrated to be compatible with transportation, sequestration and/or utilization.

[0013] Several technologies have been investigated for concentrating CO_2 in particular for the power, steel and cement industry.

[0014] The reference technology for CO_2 capture is a post-combustion technology based on absorption with aqueous amine solvents. A typical process includes an absorption unit, a regeneration unit and additional accessory equipment. In the absorption unit, CO_2-containing flue gas is contacted with amine solution to produce a CO_2-free gas stream and an amine solution rich in CO_2. The rich solution is then pumped to the regeneration unit where it is heated with steam to produce a concentrated stream of CO_2 and a lean amine that can be recycled to the absorber. The CO_2 stream is then cleaned and liquefied for storage and transportation.

[0015] The energy requirements for regenerating an amine solvent (e.g. mono-ethanolamin (MEA)) is substantial (approx. 3.5 GJ per ton of CO_2 for MEA). While recovering waste heat to produce low temperature steam is often possible in other industrial processes, almost no waste heat is available from a PFRK (as a consequence of the high energy efficiency of PFRK). Fuel must thus be burnt for the purpose of generating steam, resulting in additional CO_2 production.

[0016] As described above, limestone calcination in a PFRK is an intermittent process in terms of gas flow rate (e.g. absence of flow during reversal) and in term of flue gas composition (CO_2 concentration varies during a cycle). However, amine scrubbers optimally operate with continuous and relatively steady flue gas. In other words, adapting the process to PFR kilns could only be achieved at the expense of a negative impact on the overall efficiency and a complex control of the process.

[0017] It is estimated that amine-based CO_2 capture would approximately more than double the production cost of lime or dolime. Those costs are mostly owed to fuel consumption for generating steam, electrical consumption for amine scrubbing and compression, and capital cost for equipment.

[0018] Other post-combustion technologies have been proposed for capturing CO_2 from flue gas (e.g. chilled ammonia, adsorption, cryogenic distillation, membranes). All these options show with varying degrees identical drawbacks to those of amines regarding capital cost, energy penalty and adaptability to intermittent processes.

[0019] Oxy-combustion is an alternative to post-combustion capture which consists in burning fuel with technical oxygen instead of conventional combustion air in order to increase CO_2 concentration in the flue gas. Within this process, downstream purification is eased at the expense of requiring a source of substantially pure oxygen. For instance, patent CN 105000811 B discloses the use of oxy-combustion for PFRK.

[0020] Oxygen is industrially produced using an air separation unit (based on cryogenic distillation of air) or by pressure swing adsorption. An amount of 200-230 kWh of electricity is required to produce one ton of oxygen with an air separation unit.

Aims of the Invention

[0021] The invention aims to provide a solution to overcome at least one drawback of the teaching provided by the prior art.

[0022] More specifically, the invention aims to provide a process and a device for simultaneously allowing a decarbonation with a high production throughput of a product (e.g. quicklime, dolime) with a high decarbonation grade while producing a CO_2-rich stream that is suitable for sequestration or use.

Summary of the Invention

[0023] For the above purpose, the invention is directed to a decarbonation process of carbonated materials, in particular limestone and dolomitic limestone, preferably with CO_2 recovery, in a multi-shaft vertical kiln comprising a first, a second, and optionally a third shaft with preheating, heating and cooling zones and a cross-over channel between each shaft, alternately heating carbonated materials by a combustion of at least one fuel with at least one comburent, preferably said comburent comprising less than 70% N_2, more preferably less than 50% of N_2, in particular said comburent being oxygen-enriched air or substantially pure oxygen, up to a temperature range in which carbon dioxide of the carbonated materials is released, the combustion of the fuel and the decarbonatation generating an exhaust gas, the decarbonated materials being cooled in the cooling zones with one or more cooling streams, said process further comprising at least one of the following steps:

(a) cooling the decarbonated materials with the one or more cooling streams comprising a water steam stream, said stream being fed in the cooling zone of at least the first, the second and/or the third shaft;

(b) providing a heat exchanger in the cooling zone of at least the first, the second and/or the third shaft for the cooling of the decarbonated materials, said heat exchangers being fed by the one or more cooling streams;

(c) separating each shaft with a selective separation means arranged in an upper portion of the corresponding cooling zone, said selective separation means dividing the inner space of the corresponding shaft into an upper and lower space, said selective separation means being arranged so as to allow the transfer of the decarbonated materials between the upper and the lower space while substantially preventing the passage of the one or more cooling streams and/or the exhaust gas;

(d) recirculating at least a portion of the exhaust gas alternately exiting the second or the first shaft, injecting the recirculated exhaust gas in a lower portion of the preheating zone of at least one of the second and/or first shaft or at least one of the first and/or second shaft, respectively, more preferably the second shaft or the first shaft, respectively, feeding the cooling zone of at least one of the first and/or the second shaft with the one or more cooling streams, heating the recirculated exhaust gas with the one or more heated cooling streams extracted from the upper portion of the cooling zone of the at least one of the first and/or the second shaft;

(e) separating air with an air separation unit forming an Oxygen-enriched composition comprising at least 70% (dry volume) O_2, preferably at least 90% (dry volume), in particular 95% (dry volume) and a Nitrogen-enriched composition comprising at least 80% (dry volume) N_2 preferably at least 90% (dry volume), in particular at least 95% (dry volume) and less than 19% (dry volume) O_2, preferably less than 15 % (dry volume), in particular less than 10% (dry volume) and feeding the at least one comburent comprising the Oxygen-enriched composition in the preheating zones and/or heating zones, wherein the air separation unit is within a radius of 2 km, preferably 500 m from the multi-shaft vertical kiln; and/or

(f) heating the exhaust gas extracted from the multi-shaft vertical kiln using a heater, in particular, in particular an electric heater, a oxyfuel burner or a indirect burner, and/or a heat exchanger transferring heat with the one or more heated cooling streams extracted from said kiln MSVK, in particular at an upper portion of said cooling zone.

[0024] Preferred embodiments of the process disclose one or more of the following features:

- providing water for the water steam stream in step 1a) via : cooling the exhaust gas extracted from at least the first, the second and/or the third shaft in a separate condensation unit and/or an external water source; boiling the water in at least one boiler and/or at least one of the heat exchangers, into the water steam stream that is fed in at least the first, second and/or third shaft;
- the one or more cooling streams comprise the water steam stream in step a), and an

additional cooling stream comprising at least 95% of air (dry volume) or the Nitrogen-enriched composition in step 1e) (dry volume) and optionally less than or equal to 5 % of CO_2 (dry volume), said process further comprising feeding the additional cooling stream in the cooling zone of at least the first, the second and/or the third shaft, in particular at the lower portion thereof, and extracting the heated additional cooling stream from said shafts, wherein an inlet opening in the first, the second or the third shaft cooling zone, through which the water steam stream is fed, is positioned above an outlet opening in the same shaft, through which the heated additional cooling is extracted;

- feeding the cooling zone of at least the first, the second and/or the third shaft with at least one of the cooling streams, in particular the additional cooling stream, and extracting the at least one of the heated cooling streams at an upper portion of said cooling zone;
- providing at least one hopper for conditioning the carbonated materials before they are fed to at least one of the first and/or the second shaft, and supplying the at least one hopper with the one or more of the heated cooling streams extracted from the upper portion and/or the heat exchanger of the cooling zone of the first and/or second shafts ;
- feeding a buffer or a storage tank with the exhaust gas extracted from the multi-shaft vertical kiln, said buffer or storage tank can be connected to a CO_2 purification unit which can be fed at any time with the exhaust gas;
- feeding the carbonated materials into at least one of the first, second or third shaft, via a feeding system, each system comprising a lock chamber delimited by an upstream valve assembly and a downstream valve assembly, said feeding system being configured to collect the carbonated materials in the lock chamber, while the upstream valve assembly is open and the downstream valve assembly is closed, to store in a substantially gas tight manner the carbonated materials, while both the upstream and downstream valve assemblies are closed, and to release the carbonated materials, while the upstream valve assembly is closed and the downstream valve assembly is open;
- discharging the decarbonated materials from at least one of the first, second or third shaft, via a discharging system, each system comprising a lock chamber delimited by an upstream valve assembly and a downstream valve assembly, said discharging being configured to collect the decarbonated materials, while the upstream valve assembly is open and the downstream valve assembly is closed, to store in a

substantially gas tight manner the decarbonated materials, while both the upstream and downstream valve assemblies are closed, and to release the decarbonated materials, while the upstream valve assembly is closed and the downstream valve assembly is open;

- the upstream or downstream valve assembly comprising a single or multiple flap valve, a table feeder, a rotary valve, a cone valve, a J valve, a L valve, a trickle valve, preferably a single or multiple flap valve;
- boiling liquid CO_2 stored in the storage tank to form a substantially pure CO_2 gas and transferring said gas to the multi-shaft vertical kiln;
- providing one or more additional kilns to the multi-shaft vertical kiln forming a plurality of kilns generating an aggregated exhaust gas stream, so as to minimize flow variation of the aggregated exhaust gas stream entering a CO_2 purification unit, in particular coordinating the plurality of kilns by selecting at least one cycle phasing and duration of said kilns;
- the CO_2 purification unit is continuously fed with either the exhaust gas from the buffer, the exhaust gas from the storage tank, the exhaust gas from the multi-shaft vertical kiln, the one or more additional or a combination of them;
- the fuel used is either carbon-containing fuel or dihydrogen-containing fuel or a mixture of them;
- recirculating the exhaust gas alternately exiting the second or the first shaft, to the first or second shaft, respectively, preferably by means of a positive displacement fan or blower;
- the recirculated exhaust gas is mixed with the at least one comburent before (the resulting mixture) being fed to the correspond shaft;
- transferring the CO_2 from the storage tank to the buffer;
- the at least one comburent supplied in the preheating zones and/or heating zones during a given heating cycle in the first shaft and a subsequent heating cycle in the second or third shaft comprises at least 40% (dry volume), preferably at least 70% (dry volume), in particular at least 90% (dry volume) of the Oxygen-enriched composition of step 1e);
- feeding the Oxygen-enriched composition of step 1e) alone or mixed with the recycled exhaust gas in the preheating zones and/or heating zones;
- mixing feeding the Oxygen-enriched composition of step 1e) with another comburent, such as air and optionally the recycled exhaust gas; before feeding said mixture in

the preheating zones and/or heating zones;

- the one or more cooling streams fed during the or a given heating cycle in the first shaft and the or a subsequent heating cycle in the second or third comprise at least 80% (dry volume), preferably at least 90% (dry volume), in particular at least 95% of said Nitrogen-enriched composition of step 1e).
- feeding Nitrogen-enriched composition of step 1e) in the one or more cooling streams.

The invention is also directed to a multi-shaft vertical kiln comprising a first, a second, and optionally a third shaft with preheating, heating and cooling zones and a cross-over channel between each shaft, said kiln being arranged for being cooled with one or more cooling streams, said kiln being adapted for carrying out the process according to the invention, said kiln comprising at least one of the following elements:

(a) at least one injection means for carrying out step 1a), in use, said streams comprising a water steam stream, said injection means being arranged in the cooling zone of at least the first, the second and/or the third shaft;

(b) a heat exchanger arranged in each cooling zone for carrying out step b);

(c) a selective separation means for carrying out step c) arranged in an upper portion of the cooling zone, said selective separation means comprising: a wall separating the inner space of corresponding shaft into an upper and lower space, and at least one passage arranged in said wall, said passage being arranged so as to allow the transfer of the decarbonated materials between the upper and the lower space while substantially preventing the passage of the one or more cooling streams and/or the exhaust gas.

[0025] Preferred embodiments of the multi-shaft vertical kiln disclose one or more of the following features:

- each heat exchanger comprises a plurality of passages arranged in the corresponding cooling zone, said passages being delimited by walls, in which the one or more cooling streams circulates;
- the buffer and/or the storage tank, being arranged downstream form said kiln for storing the exhaust gas generated in said kiln in a gasified or liquid form, respectively, said storage tank comprising a blow-off valve for cooling liquid CO_2 stored in said tank, an outlet of said blow-off valve being fluidly connected to said kiln via a recirculation passage for transferring boiled substantially pure CO_2 gas to said kiln.

[0026] The invention is moreover directed to a system for carbon capture and utilization or carbon capture and storage application comprising a multi-shaft vertical kiln according to the invention, comprising a CO_2 purification unit for purifying the exhaust gas exiting said kiln, preferably comprising one or more additional kilns generating an exhaust gas stream, the CO_2 purification unit being selectively connected to the one or more additional kilns and/or to the multi-shaft vertical kiln according to the invention.

[0027] Preferably, said system comprises a CO_2 purification unit for purifying the exhaust gas exiting said kiln, preferably comprising one or more additional kilns generating an exhaust gas stream, the CO_2 purification unit being selectively connected to the one or more additional kilns and/or to said kiln.

Brief Description of Drawings

[0028] Aspects of the invention will now be described in more detail with reference to the appended drawings, wherein same reference numerals illustrate same features.

[0029] Figures 1 to 14 show the first to the fourteenth embodiment according to the invention.

[0030] Figures 15 to 20 show further embodiments according to the invention.

[0031] List of reference symbols

MSVK	multi-shaft vertical kiln
CPU	CO_2 purification unit
10	carbonated materials
14	exhaust gas from combustion chamber 600
20	Fuel
30,31,32	Comburent
40	exhaust gas (from fuel + decarbonation)
41	exhaust gas (from auxiliary combustion chamber 600) to be injected in the shaft via the cross-over channel
42	exhaust gas mixture (from combustion chambers 180, 280 or mixing chambers 190, 290) to be injected in the shaft via the cross-over channel
50	decarbonated materials
91,92	cooling streams: 91 = at least air and/or CO_2 92 = water steam
100,200,300	1st, 2nd, 3rd shafts

110,210,310	preheating zones
111,211	upper end of preheating zones
120,220,320	heating zones
130,230,330	cooling zones
131,231,331	upper end of cooling zone
132,232,332	lower end of cooling zone
133,233,333	heat exchanger
140,240,340	partition wall separating cooling & heating zone
141,241,341	selective separation means connecting heating/cooling zones
170,171,270, 271,370,371	cross over channel portions
180,280	combustion chamber
190,290	mixing chamber
412,423,431	cross over channels
600	auxiliary combustion chamber
700	condensation unit
800	Boiler
900	Hopper
1100	Feeding system for the carbonated material feeding
1200	Discharge system for the decarbonated material discharge
1300	Discharge table

Detailed description

[0032] The present invention will now be described more fully hereinafter with reference to the accompanying drawings, in which embodiments of the invention are shown. This invention may however be embodied in many different forms and should not be construed as limited to the embodiments set forth herein; rather, these embodiments are provided for thoroughness and completeness.

[0033] Figure 1 shows a multi-shaft vertical kiln MSVK according to a first embodiment of the present invention. The multi-shaft vertical kiln MSVK in Figure 1 is based on a traditional parallel-flow regenerative kiln which is a specific case of multi-shaft vertical kiln. The multi-shaft vertical kiln, also designated kiln MSVK comprises a first 100 and a second 200 shaft with preheating zones 110, 210, heating zones 120, 220 and cooling zones 130, 230, 330, as well as a cross-over channel 412 arranged between the first 100 and second 200 shafts. In use, the carbonated materials 10 are introduced at an upper portion 111, 211 of each shaft 100, 200. The carbonated materials 10 slowly move to the bottom. In the preheating zones 110, 210, the carbonated materials 10 are essentially preheated with the alternating regenerative exhaust gas 40. In the combustion zones 210, 220, the carbonated materials 10 are alternately heated by a combustion of fuel 20 with at least one comburent 30, 31, 32, preferably depleted in nitrogen, in particular oxygen-enriched air or substantially pure oxygen, up to a temperature range in which carbon dioxide of the carbonated materials 10 is released. Both the combustion of the fuel 20 with the at least one comburent 30, 31, 32 and the decarbonatation generate the exhaust gas 40.

[0034] The present disclosure defines the at least one comburent as an oxidizing agent such as either air, air enriched with oxygen (i.e. oxygen-enriched air) or substantially pure oxygen, alone or in combination with the exhaust gas 40 or substantially pure CO_2. Preferably, the comburent is an oxygen-enriched air or substantially pure oxygen. One or more comburents are foreseen, in particular:

- a comburent 30, or

- a first 31 and a second comburent 32.

[0035] Figure 1 schematically shows a multi-shaft vertical shaft MSVK with three separate supply passages per shaft:

- a first passage is arranged at an upper portion of the multi-shaft vertical kiln (e.g. PFRK) traditionally supplying a (first) comburent 30, 31 (e.g. primary air supply). Even if Figure 1 shows one first supply passage, the multi-shaft vertical kiln MSVK may comprise more than one first supply passage per shaft 100, 200, 300. The one or more first passage outlet openings are arranged in the corresponding shaft 100, 200, 300. In the present disclosure, the comburent 30 or the first comburent 31 is preferably oxygen-enriched air or substantially pure oxygen.

- a second passage (e.g. fuel lance) is traditionally supplying fuel 20 (e.g. natural gas, oil) and optionally the second comburent 32 (e.g. air). Even if Figure 1 shows only one second supply passage, the multi-shaft vertical kiln comprises one or more second supply passage per shaft 100, 200, 300, generally under the form of fuel/air lances. For instance, a mixture of fuel 20 and the second comburent 32 (e.g. coke with the conveying second comburent such as air) can be supplied through at least a part of the lances. Alternatively, a group of lances supplies the second comburent 32 (e.g. air) while another group of lances supplies the fuel 20 (natural gas or oil). In the present disclosure, the second comburent 32 is preferably oxygen-enriched air or substantially pure oxygen.

- a third passage is shown in Figure 1. Such a passage is traditionally not present on a multi-shaft vertical kiln MSVK, in particular a parallel flow regenerative kiln PFRK. Said third passage is dedicated to the supply of the recycled exhaust gas 40. The present disclosure is not limited to a single third passage. Indeed, it can be foreseen that one or more third passages are in fluid connection with the corresponding shaft 100, 200, 300.

In an alternative preferred form (shown schematically in a “window” arranged above the MSVK in Fig. 1), a downstream end of the third passage is connected to the first passage. The present disclosure is not limited to a single third passage connected to a single first passage. Indeed, it can be foreseen that one or more downstream ends of the third passage(s) are connected to one or more first passages. The one or more first passages can feed the corresponding shaft 100, 200, 300 with:

- a gas mixture comprising the recycled exhaust gas 40 and the first comburent 31 (e.g. oxygen-enriched air or substantially pure oxygen) according to the first preferred alternative, or
- the recycled exhaust gas 40 according to the second preferred alternative.

In the above-mentioned first preferred alternative, the fuel 20 (e.g. natural gas or oil, dihydrogen) is supplied via the one or more second passages.

In the above-mentioned second preferred alternative, the one or more second passages supply both the second comburent 32 (e.g. oxygen-enriched air or substantially pure oxygen) and the fuel 20 (e.g. natural gas, oil, coke or dihydrogen). For instance, a group of lances supply the second comburent 32 (e.g. oxygen-enriched air or substantially pure oxygen) while another group supplies the fuel 20 (e.g. natural gas, oil or dihydrogen).

The first, second and third passages can be found in other embodiments of the present disclosure.

[0036] The decarbonated materials 50 formed after the release of the CO_2 from the carbonated materials 10 are indirectly cooled in the cooling zones 130, 230 by an air stream 91 circulating in heat exchangers 133, 233. This solution minimizes the mixing between the exhaust gas 40 and the air of the cooling stream 91. Owing to these measures, the exhaust gas 40 exits the kiln MVSK with a high content of CO_2 of at least 45 % (dry volume), even 60% or more.

[0037] Figure 2 shows a multi-shaft vertical kiln MSVK according to a second embodiment of the present invention. The second embodiment differs from the first embodiment in a specific design of heat exchanger, namely a plurality of passages is provided in the cooling zones of the first 100 and the second 200 shafts. The passages extending preferably vertically are delimited by walls, in which the cooling stream, in particular an air stream, circulates. Air is presented as a preferred cooling medium because of its accessibility but other fluid can be used depending on the circumstances.

[0038] Figure 3 shows a multi-shaft vertical kiln MSVK according to a third embodiment of the present invention. The third embodiment differs from the first embodiment in that the cooling of the decarbonated materials 50 is a direct cooling instead of indirect cooling for the first embodiment, to the extent that a cooling stream of for instance air or a mix of air and cooled CO_2, is fed into the cooling zones 130, 230, in particular at a lower portion 132, 232 thereof, more preferably at the bottom thereof. The stream of air or a mix of air and CO_2 91 fed to the cooling zones 130, 230 is then extracted at an upper portion of the cooling zones 130, 230 through one or more apertures arranged in a wall of each shaft 100, 200.

[0039] Figure 4 shows a multi-shaft vertical kiln MSVK according to a fourth embodiment of the present invention. The fourth embodiment differs from the third embodiment in that the one or more apertures (in Fig. 4, only one aperture is shown per shaft), through which the heated cooling stream 91 is extracted, are formed in a pipe assembly preferably centrally arranged in each shaft 100, 200. The one or more apertures are covered by a screen assembly preventing the intrusion of solid material into the cooling extraction system.

[0040] In a fifth embodiment of the present invention (shown in Fig. 5), it is envisaged to combine a direct cooling (e.g. Fig. 3 or 4) and an indirect cooling (e.g. Fig. 1 or 2) so as to enhance the cooling and/or use two different cooling media (e.g. air and water).

[0041] Figure 6 shows a multi-shaft vertical kiln MSVK according to a sixth embodiment of the present invention. The sixth embodiment differs from any of the previous embodiments in that a selective separation means 141, 241 is provided in each shaft 100, 200. Each selective separation means 141, 241 is arranged in an upper portion of the cooling zone 130, 230, 330 and is arranged so as to allow the transfer of the decarbonated materials 50 downwards while substantially preventing the passage of the one or more cooling streams comprising air 91 and/or the exhaust gas 40. Each separation means 141, 241 can be suspended by a partition wall extending from the corresponding inner shaft wall to the center of said shaft. Typically, the wall can present a funnel shape. Alternatively, a plurality of selective separation means 141, 241 can be provided. In comparison to the solutions presented in Figure 3 or 4, the presence of selective separation means 141, 241 substantially prevents any mixing of the cooling medium and the exhaust gas 40. As shown in Figure 6, the heated cooling stream 91 can be extracted at an upper portion of the cooling zones 130, 230 though one or more apertures formed in a wall section of the corresponding shaft. In such a case, the one or more apertures are positioned below the partition wall outer circumferential end that connects the inner wall of the corresponding shaft. The lock assembly can comprise a rotary valve, a double flap sluice or any other suitable means.

[0042] Figure 7 shows the seventh embodiment of the present invention. The seventh embodiment differs from the first embodiment (Fig. 1) in that the cooling of the decarbonated materials 50 is performed with a water steam stream 92 fed in the cooling zones 130, 230, instead of providing a heat exchanger 133, 233.

[0043] We understand by water steam stream, a stream comprising at least 50% by weight water, preferably at least 80% by weight water, more preferably at least 90% by weight water.

[0044] The water used to generate the water steam can originate from either condensed water from the exhaust gas 40 exiting the kiln MVSK Another water source can be river water, rain water, industrial water, tap water, or a combination of them. The water is heated in a boiler 800 before it is fed to the cooling zones 130, 230. The supply of water steam 92 in the shafts 100, 200 is an efficient way to cool the decarbonated materials 50. Moreover, the water steam will occupy the cooling zone inner space 130, 230 and thereby forming a “barrier” against air penetration. Furthermore, the presence of water in the exhaust gas 40 following the mixing of water steam with the exhaust gas 40 can be easily removed in a condenser 700. However, the use of water steam as a cooling medium presents some limitations. Indeed, the temperature of the carbonated materials 50 should be maintained at a temperature above around 450°C in order to avoid a dry slaking of the decarbonated materials 50. Therefore, the water steam should be introduced via one or more nozzles arranged in a middle or upper portion of the cooling zone to minimize any hydration on the decarbonated materials 50 in the cooling zones 130, 230.

[0045] Figure 8 shows the eighth embodiment of the present invention. The eighth embodiment differs from the seventh embodiment in that heat exchangers 133, 233 arranged inside the cooling zones 130, 300 are provided to vaporize the liquid water and then superheat the water vapor instead of an external boiler 800. Heat exchangers 133, 233 arranged inside the cooling zones 130, 230 can also be combined with one or more external boiler 800.

[0046] Figure 9 shows the ninth embodiment of the present invention. The ninth embodiment differs from the eight embodiment in that external boilers 800 replace the heat exchangers 133, 233 and a further cooling cold stream is provided (compared to the relatively hot cooling stream of the water steam), said stream comprising essentially air or CO_2 or a combination of them. Using cold CO_2, preferably CO_2 at ambient temperature presents the advantage of depleting the cooling stream from nitrogen. However, the presence of CO_2 at low temperature would lead to negligible carbonation of the decarbonated materials 50. The position of the openings of the nozzle(s) of the relatively "hot" cooling stream (water steam) 92 are preferably arranged above the aperture(s) through which the relatively "cold" cooling stream (air or CO_2 or a combination of them) to minimize the mixing of the "hot" cooling stream 92 with "cold" cooling stream 91. Furthermore, the openings of the "hot" cooling stream 92 should be positioned close to the openings aperture(s) of the cold cooling streams so as to extend the zone in which the decarbonated materials 50 are cooled with "cold" cooling stream 91. The heated "cold" cooling streams 91 are extracted and collected in collectors (for instance encircling the shafts) and then supplied to the respective boilers 800 so as to vaporize and superheat the "hot" cooling streams 92.

[0047] Figure 10 shows the tenth embodiment of the present invention. The tenth embodiment differs from any of the previous embodiments in that a buffer 910 and a CO_2 purification unit CPU are provided in the exhaust line connected to the kiln MSVK. The buffer 910 ensures that the CO_2 purification unit CPU can be fed at any time with the exhaust gas 40. The CO_2 purification unit CPU is configured to remove at least one of the following elements: acid gases, O_2, Ar, CO, H_2O, NOx, sulfur compounds, heavy metals, in particular Hg, Cd, and/or organic compounds, in particular CH_4, benzene, hydrocarbons. Preferably, the CO_2 purification unit CPU is adapted to adjust the composition of the exhaust gas 40 to the specification required by a carbon capture and utilization or carbon capture and storage application, preferably with a CO_2 content above 80% (dry volume) and more preferably above 95% (dry volume).

[0048] Figure 11 shows the eleventh embodiment of the present invention. The eleventh embodiment differs from the tenth embodiment in the provision of a condensation unit 700 arranged in the exhaust line. The condensation unit 700 allows to increase the concentration of CO_2 by removing water. The water separated could be recycled for the cooling of the cooling zones 130, 230, 230 of the kiln MSVK.

[0049] Figure 12 shows the twelfth embodiment of the present invention. The twelfth embodiment differs from the eleventh embodiment in a recycling passage connecting the buffer 910 to the kiln MSVK. The buffer 910 allows to supply the kiln MSVK with exhaust gas 40 enriched with CO_2.

[0050] Figure 13 shows the thirteenth embodiment of the present invention. The thirteenth embodiment differs from the tenth embodiment in the provision of a storage tank 920 positioned downstream from the CO_2 purification unit CPU. The storage tank 920 is filled with purified CO_2, in particular in liquid form for the carbon capture and utilization or carbon capture and storage application. Furthermore, a recycling passage is provided for connecting the storage tank 920 to the kiln MSVK. The storage tank 920 allows to supply the kiln MSVK with exhaust gas 40 enriched with CO_2. The storage tank 920 can comprise a blow-off valve for cooling liquid CO_2 stored in said tank 920. The boiled CO_2 can be recycled to the kiln MVSK or any kiln of any type. The cooled CO_2 extracted from the storage tank can be used a cooling stream (91) before it is fed to the shafts of the kiln MSVK to enrich the exhaust gas in CO_2.

[0051] Figure 14 shows the fourteenth embodiment of the present invention. The fourteenth embodiment differs from the thirteen embodiment in that one or more multi-shaft vertical kilns according to any previous embodiments MSVK _1, MSVK _2, MSVK _N or either one or more traditional limestone kilns K_1, K_N are connected to the CO_2 purification unit CPU. These kilns MSVK, MSVK _1, MSVK _2, MSVK _N, K_1, K_N generate an aggregated exhaust gas stream, thereby minimizing flow variation of the aggregated exhaust gas stream entering the CO_2 purification unit CPU. In particular, the kilns MSVK, MSVK _1, MSVK _2, MSVK _N, K_1, K_N can be coordinated by selecting appropriate cycle phasing and duration of said kilns MSVK, MSVK _1, MSVK _2, MSVK _N, K_1, K_N. Advantageously, the purification unit CPU is continuously fed with either the exhaust gas 40 from one or more of the buffers 910, the exhaust gas 40 from the storage tank 920, the exhaust gas 40 from the kiln MSVK, the one or more additional kilns MSVK _1, MSVK _2, MSVK _N, K_1, K_N or a combination of them.

[0052] Figure 15 shows a further embodiment according to the invention, which differs from the first embodiment in that the MSVK comprises feeding and discharging systems 1100, 1200, respectively, for the feeding of carbonated materials 10 and the discharge of the decarbonated material 50, in order to minimize the idle time between cycles (reversal time) and to reduce or even eliminate the need for exhaust gas buffering before the CO2 purification unit (CPU). The feeding and discharge systems 1100, 1200, with for instance an upstream gas-tight flap valve and a downstream gas-tight flap valve can be integrated to anyone of the previously mentioned embodiment. A lock chamber of the feeding 1100 or discharging system 1200 is delimited by the upstream gas-tight flap valve and a downstream gas-tight flap valve. The lock chamber presents a working volume adapted to store the material batches to be fed into or discharged from the corresponding shaft 100, 200. By gas tight, is meant a valve assembly that substantially limits the gas exchanges to as to ensure an efficient usage of the MSVK and to minimise combustion gas leakage into the atmosphere.

[0053] In order to recover the energy of the heated cooling stream 91, 92, a hopper 900 (see Figure 16) can be provided between both shaft 100, 200. The hopper is used to condition (e.g. heat) the carbonated materials 10 before they are fed to the shafts 100, 200. For this purpose, the hopper 900 is supplied with the heated cooling streams 91, 92 extracted from the upper portion 131, 231 (not shown) or from heat exchangers 133, 233 (as shown) of the cooling zone 130, 230 of the shafts 100, 200. Alternatively, a dedicated hopper can be used for each shaft 100, 200. Other configurations of hoppers can be foreseen such as a serial arrangement.

[0054] Alternatively or complementary to the measure proposed in the previous embodiments, the heated cooling streams 91 extracted from the upper portion 111, 211 of the cooling zone 130, 230 of the shafts 100, 200 are used to heat the recycled exhaust gas 40 (comprising CO_2) extracted alternately from the second shaft 200 or first shaft 100 and then injected in the second shaft (shown in Figure 18) or first shaft (not shown), respectively. The reinjection is performed in the lower portion 112 of the preheating zone 110 of the shaft 100 in regeneration by means of a collecting ring.

[0055] Figure 18 shows a modified version of the thirteenth embodiment of the present invention. In Figure 18, the buffer 910 is directly supplied with CO_2 stored in the storage tank 920. With this measure, any pressure loss in the buffer 910 can be rapidly compensated. In Figures 19 and 20, the exhaust gas 40 exiting the MSVK is heated so as to remain above the dew point with an heat exchanger and a heater (electric heater), respectively. As an alternative to the electric heater, a oxyfuel burner or indirect burner can be foreseen.

[0056] Complementary or alternatively to any of the previous embodiment, at least one air separation unit ASU is provided in the proximity of the MSVK and optionally one or more additional kilns. The one or more ASU generate an Oxygen-enriched composition that can be fed in the MSVK and optionally in at least one another kiln as comburent 30, 31, 32. An ASU also produces a Nitrogen-enriched composition that can be released in the atmosphere.

[0057] Typically, an ASU produces both an Oxygen-enriched composition comprising at least 70% (dry volume) O_2, preferably at least 90% (dry volume), in particular at least 95% and a Nitrogen-enriched composition comprising at least 80% (dry volume) N_2 preferably at least 90% (dry volume), particular at least 95% (dry volume) and less than 19% (dry volume) O_2, preferably less than 15% (dry volume), in particular less than 10% (dry volume).

[0058] Preferably, the comburent 30, 31, 32 fed in the MSVK comprises at least 40% (dry volume), preferably at least 70% (dry volume), in particular at least 90% (dry volume), in particular at least 95% (dry volume) of the Oxygen-enriched composition.

[0059] The Nitrogen-enriched composition can be advantageously used to cool the MSVK during the heating cycles. Indeed, on one hand, the supply of comburent 30, 31, 32 fed in the pre-heating 110, 210 and combustions 120, 220 zones is adjusted so that a near stoichiometric combustion is achieved in the MSVK in the combustion zones 120, 220 of the MSVK, on the other, the cooling stream 91 comprising at least 80% (dry volume), preferably at least 90% (dry volume), in particular at least 95% (dry volume) of said Nitrogen-enriched composition is expected to dilute the exhaust gas 40. The amount of residual Oxygen present in the nitrogen-enriched composition is however sufficiently low to the extent that it dilutes the exhaust gas 40 without changing significantly the overall stoichiometric balance. A reduction in the amount of Oxygen introduced via the cooling stream 91 will improve the purification efficiency of the CPU.

[0060] Advantageously, the at least one fuel 20 used in a kiln MSVK according to the invention, in particular in any of the previous embodiments is either carbon-containing fuel or dihydrogen-containing fuel or a mixture of them. A typical fuel can be either wood, coal, peat, dung, coke, charcoal, petroleum, diesel, gasoline, kerosene, LPG, coal tar, naphtha, ethanol, natural gas, hydrogen, propane, methane, coal gas, water gas, blast furnace gas, coke oven gas, CNG or any combination of them. Furthermore, the kiln MVSK can use, for instance, two sources of fuel with different compositions.

[0061] Advantageously, the decarbonated materials 50 produced in a kiln MSVK according to the invention, in particular in any of the previous embodiments have a residual CO_2 <5%, preferably <2%, resulting from the rapid cooling of the decarbonated materials 50.

[0062] Preferably, measures are undertaken to recover heat from the one or more cooling streams 91, 92, and/or the recirculated exhaust gas 40.

[0063] Advantageously, the combustion of at least one fuel 20 with the at least one comburent 30 is under an oxygen-to-fuel equivalence ratio greater or equal to 0.9.

[0064] The comburent comprises less than 70% N_2 (dry volume), in particular less than 50% of N_2 (dry volume), in particular oxygen-enriched air. In particular, the comburent used in the invention, is a mixture of air with a substantially pure oxygen, the comburent comprising at least 50% O2 (dry volume), preferably more that 80% O_2 (dry volume).

[0065] The meaning of "substantially pure oxygen" in the present disclosure is an oxygen gas comprising at least 90 % (dry volume) dioxygen (i.e. O_2), preferably at least 95% (dry volume) dioxygen(i.e. O_2).

[0066] The meaning of "multi vertical-shaft kiln" in the present disclosure is a kiln comprising at least two shafts 100, 200, 300. The shafts 100, 200, 300 are not coaxial and are disposed side by side to the extent that any shaft of a group consisting of the first, second and optimally the third shaft 100, 200, 300 is not encircled by the other or another shaft 100, 200, 300 of said group. In other words, the cross-over channel(s) 412, 423, 431 are arranged outside the shafts 100, 200, 300. This definition excludes a annular-shaft kiln being interpreted as a multi vertical-shaft kiln. A parallel-flow regenerative kiln is a specific form of a multi vertical-shaft kiln in the present definition. The multi vertical-shaft kiln of the first to the fourteenth embodiment falls in the definition of a parallel-flow regenerative kiln (in German: "*Gleich Gegenstrom Regernativ Ofen*"). According to the invention, the term "vertical" in "multi vertical-shaft kiln" does not necessarily require that the longitudinal axes of the shafts 100, 200, 300 have an exact vertical orientation. Rather, an exact vertical directional component of the alignment should be sufficient, with regard to an advantageous gravity-related transport of the material in the shafts, an angle between the actual alignment and the exact vertical alignment amounts to at most 30°, preferably at most 15° and particularly preferably of 0° (exactly vertical alignment).

[0067] Each shaft 100, 200, 300 of the multi-shaft vertical kiln comprises a preheating zone 110, 210, 310, a heating zone 120, 220, 320 and a cooling zone 130, 230, 330. A cross-over channel 412, 423, 431 is disposed between each shaft 100, 200, 200. According to the present disclosure, the junction between the heating zones 120, 220, 320 and the cooling zones 130, 230, 330 is substantially aligned with the lower end of the cross-over channel(s) 412, 423, 431.

[0068] The technical features of the claimed invention improve the purity of the exhaust gas 40 extracted from the multi-shaft vertical kiln MSVK as shown in the following table:

	with REG (6)	w/o REG	kiln capacity tpd	heat input kcal/kg	Ratio stoech. %	cooling stream Nm3/kg CaO	fumes flow Nm3/h	fumes T° °C	[CO2] dry basis %	Embodiement/ figure
normal kiln operation (comparative example(ex.))		X	300	900	105 %	0.65	30700	106	24%	
normal kiln operation with FGR (comparative ex.)	x		300	900	105 %	0.65	30700	106	46%	
cooling with steam water (ex. acc. to 7th embodiment)	x		300	900	105 %	0.4	27300	50	96%	Fig. 7
cooling with steam water		X	300	900	105 %	0.4	27300	50	35%	
indirect cooling (example acc. to 1st/2nd embodiment)	x		300	900	105 %	NA	22300	< 50 (1)	96%	Fig. 1, 2, 16
indirect cooling (ex. acc. to 1st/2nd embodiment)		X	300	900	105 %	NA	22300	< 50 (1)	34%	Fig. 1, 2, 16
physical separation btw burning zone and cooling zone (ex. acc. to 6th embodiment)	x		300	900	105 %	0.65	22300	< 50 (1)	96%	Fig. 6
cooling air extraction w/o heat recovery (ex. acc. to 3rd/4th embodiment)	x		300	900	105 %	0.65	22300	< 50 (1)	96%	Fig. 3, 4
cooling air extraction with CO2 loop preheating (ex. acc. to further embodiment)	x		300	900	105 %	0.65	30700 (3)	> 60 (2)	96%	Fig.18
air at bottom (extracted), water on top of cooling zone (4) (ex. acc. to 9th embodiment)	x		300	900	105 %	0.5	24600	<50 (1)	96%	Fig. 9
air at bottom (not extracted), water on top of cooling zone (4) (ex. acc. to 8th embodiment)	x		300	900	105 %	0.5	28600	70	80%	Fig. 8

<u>Comments:</u>

(1) not enough energy in the exhaust gas - additional burner needed to reheat the exhaust gas and stay above dew point
(2) assuming we can recover 75% of energy from cooling air stream (via heat exchanger)
(3) assuming same flow for part of REG being recirculated/preheated and flow of cooling air being extracted
(4) assuming 50% steam and 50% cooling air
(5) including Lance cooling)
REG = Recycled Exhaust Gas

[0069] The simulations of flow, temperature and CO_2 concentration (volume dry basis) in exhaust gas for a multi-shaft vertical kiln MSVK at 300 tons per day (tpd), fired with natural gas show that the features proposed to reduce the mixing of air with the exhaust gas 40 considerably improve the CO_2 concentration in the exhaust gas 40 extracted from a multi-shaft vertical kiln, especially when the exhaust gas is recirculated. Additionally, the temperature of the exhaust gas 40 extracted from a multi-shaft vertical kiln MSVK drops with regard to the comparative example corresponding to a traditional parallel flow regenerative kiln, as the heated cooling gas 40 exiting the cooling zones 130, 230 of a multi-shaft vertical kiln MSVK according to the invention is not or slightly mixed with the exhaust gas 40. However, an additional burner or heat exchanger may be needed to reheat the exhaust gas so that it stays above dew point.

[0070] The present disclosure presents a multi-shaft vertical kiln with two or three shafts. The present teaching applies to multi-shaft vertical kiln with four and more shafts.

CLAIMS

1. Decarbonation process of carbonated materials (10), in particular limestone and dolomitic limestone, preferably with CO_2 recovery, in a multi-shaft vertical kiln (MSVK) comprising a first (100), a second (200), and optionally a third (300) shaft with preheating zones (110, 210, 310), heating zones (120, 220, 320) and cooling zones (130, 230, 330) and a cross-over (412, 423, 431) channel between each shaft (100, 200, 300), alternately heating carbonated materials (10) by a combustion of at least one fuel (20) with at least one comburent (30, 31, 32), preferably said comburent comprising less than 70% N_2 (dry volume), more preferably less than 50% of N_2 (dry volume), in particular said comburent being oxygen-enriched air or substantially pure oxygen, up to a temperature range in which carbon dioxide of the carbonated materials (10) is released, the combustion of the fuel (20) and the decarbonatation generating an exhaust gas (40), the decarbonated materials (50) being cooled in the cooling zones (130, 230, 330) with one or more cooling streams (91, 92), said process further comprising at least one of the following steps:

1a) cooling the decarbonated materials (50) with the one or more cooling streams (92) comprising a water steam stream, said stream being fed in the cooling zone (130, 230, 330) of at least the first (100), the second (200) and/or the third (300) shaft;

1b) providing a heat exchanger (133, 233, 333) in the cooling zone (130, 230, 330) of at least the first, the second and/or the third shaft (100, 200, 300) for the cooling of the decarbonated materials (50), said heat exchangers (133, 233, 333) being fed by the one or more cooling streams (91, 92);

1c) separating each shaft (100, 200, 300) with a selective separation means (141, 241, 341) arranged in an upper portion of the corresponding cooling zone (130, 230, 330), said selective separation means (141, 241, 341) dividing the inner space of the corresponding shaft (100, 200, 300) into an upper space and a lower space, said selective separation means (141, 241, 341) being arranged so as to allow the transfer of the decarbonated materials (50) between the upper and the lower spaces while substantially preventing the passage of the one or more cooling streams (91, 92) and/or the exhaust gas (40);

1d) recirculating at least a portion of the exhaust gas (40) alternately exiting the second (200) or the first shaft (100), injecting the recirculated exhaust gas (40) in a lower portion of the preheating zone (112, 212) of the second shaft (200) or the first shaft (100), respectively, in particular by means of a collecting ring encircling said shaft (100, 200), feeding the cooling zone (130, 230) of at least one of the first (100) and/or the second (200) shaft with the one or more cooling streams (91), heating the recirculated exhaust gas (40) with the one or more heated cooling streams (91) extracted from the upper portion (131, 231) of the cooling zone (130, 230) of the at least one of the first (100) and/or the second (200) shaft;

1e) separating air with an air separation unit (ASU) forming an Oxygen-enriched composition comprising at least 70% (dry volume) O_2, preferably at least 90% (dry volume), in particular at least 95% (dry volume) and a Nitrogen-enriched composition comprising at least 80% (dry volume) N_2 preferably at least 90% (dry volume), in particular at least 95% (dry volume) and less than 19% (dry volume) O_2, preferably less than 15 % (dry volume), in particular less than 10% (dry volume) and feeding the at least one comburent (30, 31, 32) comprising the Oxygen-enriched composition in the preheating zones (110, 210, 310) and/or heating zones (120, 220, 320), wherein the air separation unit (ASU) is within a radius of 2 km, preferably 500 m from the multi-shaft vertical kiln (MSVK); and/or

1f) heating the exhaust gas extracted from the multi-shaft vertical kiln (MSVK) using a heater, in particular an electric heater, a oxyfuel burner or a indirect burner, and/or a heat exchanger transferring heat with the one or more heated cooling streams (91, 92) extracted from said kiln MSVK, in particular at an upper portion (131, 231) of said cooling zone (130, 230).

2. Process according to any of the preceding claims, further comprising:

- providing water for the water steam stream (92) in step 1a) via :
  - cooling the exhaust gas (40) extracted from at least the first (100), the second (200) and/or the third (300) shaft in a separate condensation (700) unit ; and/or
  - an external water source;
- boiling the water in :
  - at least one boiler (800); and/or
  - at least one of the heat exchangers (133, 233, 333),

into the water steam stream (92) that is fed in at least the first (100), second (200) and/or third (300) shaft.

3. Process according to any preceding claims, wherein the one or more cooling streams (91, 92) comprise:

- the water steam stream (92) in step 1a); and
- an additional cooling stream (91) comprising at least 95% of air (dry volume) or the

Nitrogen-enriched composition in step 1e) and optionally less than or equal to 5 % of CO_2 (dry volume);

said process further comprising feeding the additional cooling stream (91) in the cooling zone (130, 230, 330) of at least the first (100), the second (200) and/or the third (300) shaft, in particular at the lower portion (132, 232, 332) thereof, and extracting the heated additional cooling stream (91) from said shafts (100, 200, 300), wherein an inlet opening in the first, the second or the third shaft cooling zone (130,230,330), through which the water steam stream (92) is fed, is positioned above an outlet opening in the same shaft (100, 200, 300), through which the heated additional cooling (91) is extracted.

4. Process according to any of the preceding claims, comprising feeding the cooling zone (130, 230, 330) of at least the first, the second and/or the third shaft with at least one of the cooling streams (91), in particular the additional cooling stream (91), and extracting the at least one of the heated cooling streams (91, 92) at an upper portion (131, 231, 331) of said cooling zone (130, 230, 330).

5. Process according to any of the preceding claims, further providing at least one hopper (900) for conditioning the carbonated materials (10) before they are fed to at least one of the first (100) and/or the second shaft (200), and supplying the at least one hopper (900) with the one or more of the heated cooling streams (91) extracted from the upper portion (111, 211) and/or the heat exchanger (133, 233) of the cooling zone (130, 230) of the first and/or second shafts (100, 200)

6. Process according to any of the preceding claims, comprising feeding a buffer (910) or a storage tank (920) with the exhaust gas (40) extracted from the multi-shaft vertical kiln (MSVK), said buffer or storage tank (920) being connectable to a CO_2 purification unit (CPU) which can be fed at any time with the exhaust gas (40).

7. Process according to any of the preceding claims, comprising feeding the carbonated materials (10) into and/or discharging the decarbonated materials (50) form at least one of the first, second and/or third shaft (100, 200, 300), via a feeding and/or discharging system (1100, 1200), respectively, each system (1100, 200) comprising a lock chamber delimited by an upstream valve assembly and a downstream valve assembly, said feeding or discharging system (1100, 1200) being configured to collect the carbonated (10) or decarbonated materials (50), respectively, while the upstream valve assembly is open and the downstream valve assembly is closed, to store in a substantially gas tight manner the carbonated (10) or decarbonated materials (50), respectively, while both the upstream and downstream valve assemblies are closed, and to release the carbonated (10) or decarbonated materials (50), respectively, while the upstream valve assembly is closed and the downstream valve assembly is open.

8. Process according to any of the preceding claims, comprising boiling liquid CO_2 stored in the storage tank (920) to form recycled exhaust gas (40) and transferring said gas (40) to the multi-shaft vertical kiln (MSVK).

9. Process according to any of the preceding claims, comprising providing one or more additional kilns (MSVK _1, MSVK _2, MSVK _N, K_1, K_N) to the multi-shaft vertical kiln (MSVK) forming a plurality of kilns generating an aggregated exhaust gas stream, so as to minimize flow variation of the aggregated exhaust gas stream entering a CO_2 purification unit (CPU), in particular coordinating the plurality of kilns by selecting at least one cycle phasing and duration of said kilns.

10. Process according to any of the preceding claims, wherein the CO_2 purification unit (CPU) is continuously fed with either the exhaust gas (40) from the buffer (910), the exhaust gas (40) from the storage tank (920), the exhaust gas (40) from the multi-shaft vertical kiln (MSVK), the one or more additional kilns (MSVK _1, MSVK _2, MSVK _N, K_1, K_N) or a combination of them.

11. Process according to any of the preceding claims, wherein the fuel (20) used is either carbon-containing fuel or dihydrogen-containing fuel or a mixture of them.

12. Process according to any of the preceding claims, comprising recirculating the exhaust gas (40) alternately exiting the second (200) or the first (100) shaft, to the first (100) or second (200) shaft, respectively, preferably by means of a positive displacement fan or blower, in particular the recirculated exhaust gas (40) being mixed with the at least one comburent (30, 31, 32) before being fed to the correspond shaft (100, 200).

13. Process according to any of the preceding claims, wherein the at least one comburent (30, 31, 32) supplied in the preheating zones (110, 210, 310) and/or heating zones (120, 220, 320) during a given heating cycle in the first shaft (100) and a subsequent heating cycle in the second (200) or third shaft (200) comprises at least 40% (dry volume), preferably at least 70% (dry volume), in particular at least 90% (dry volume) of the Oxygen-enriched composition of step 1e).

14. Process according to any of the preceding claims, further comprising feeding the Oxygen-enriched composition of step 1e) alone or mixed with the recycled exhaust gas, in the preheating zones (110, 210, 310) and/or heating zones (120, 220, 320).

15. Process according to any of the preceding claims, further comprising mixing the Oxygen-enriched composition of step 1e) with another comburent such as air and optionally the recycled exhaust gas before feeding said mixture in the preheating zones (110, 210, 310) and/or heating zones (120, 220, 30).

16. Process according to any of the preceding claims, further comprising feeding Nitrogen-enriched composition of step 1e) in the one or more cooling streams (91, 92).

17. Process according to any of the preceding claims, wherein the one or more cooling streams (91, 92) fed during the given heating cycle in the first shaft and the subsequent heating cycle in the second or third comprise at least 80% (dry volume), preferably at least 90% (dry volume), in particular at least 95% of said Nitrogen-enriched composition of step 1e).

18. Multi-shaft vertical kiln (MSVK) comprising a first (100), a second (200), and optionally a third (300) shaft with preheating zones (110, 210, 310), heating zones (120, 220, 320) and cooling zones (130, 230, 330) and a cross-over (412, 423, 431) channel between each shaft (100, 200, 300), said kiln (MSVK) being arranged for being cooled with one or more cooling streams (91, 92), said kiln (MSVK) being adapted for carrying out the process according to any of the preceding Claims 1 to 17, said kiln (MSVK) comprising at least one of the following elements:

- at least one injection means for carrying out step 1a), in use said streams comprising a water steam stream, said injection means being arranged in the cooling zone (130, 230, 330) of at least the first (100), the second (200) and/or the third (300) shaft;
- a heat exchanger (133, 233, 333) arranged in each cooling zone(130, 230, 330) for carrying out step 1b);
- a selective separation means (141, 241) for carrying out step 1c) arranged in an upper portion of the cooling zone (130, 230, 330), said selective separation means (141, 241) comprising:
  - a wall separating the inner space of corresponding shaft (100, 200, 300) into an upper and lower space, and
  - at least one passage arranged in said wall, said passage being arranged so as to allow the transfer of the decarbonated materials (50) between the upper and the lower space while substantially preventing the passage of the one or more cooling streams (91, 92) and/or the exhaust gas (40).

19. Multi-shaft vertical kiln (MSVK) according to the previous claim, comprising:

- at least one first aperture for extracting the one or more cooling streams (91), said aperture being arranged in a wall section of at least the first, the second and/or the third shaft (100, 200, 300) at an upper portion (131, 231, 331) of the corresponding cooling zone (130, 230; 330), and/or

- at least one second aperture for extracting the one or more cooling streams (91), said first aperture being arranged in a pipe assembly centrally arranged in at least the first, the second and/or the third shaft (100, 200, 300), said aperture being vertically positioned in an upper portion (131, 231, 331) of the corresponding cooling zone (130, 230; 330).

20. Multi-shaft vertical kiln (MSVK) according to any of the previous Claims 18 to 19, wherein each heat exchanger (133, 233, 333) comprises a plurality of passages arranged in the corresponding cooling zone (130, 230, 330), said passages being delimited by walls, in which the one or more cooling streams (91) circulates.

21. Multi-shaft vertical kiln (MSVK) according to any of the Claims 18 to 20, comprising the buffer (910) and/or the storage tank (920), said tank (920) being arranged downstream form said kiln (MSVK) for storing the exhaust gas (40) generated in said kiln (MSVK) in a gasified or liquid form, respectively, said storage tank (920) comprising a blow-off valve for cooling liquid CO_2 stored in said tank (920), an outlet of said blow-off valve being fluidly connected to said kiln (MSVK) via a recirculation passage for transferring boiled substantially pure CO_2 gas to said kiln (MSVK).

22. A system for carbon capture and utilization or carbon capture and storage application comprising a multi-shaft vertical kiln (MSVK) according to any of the Claims 18 to 21, comprising a CO_2 purification unit (CPU) for purifying the exhaust gas (40) exiting said kiln (MSVK), preferably comprising one or more additional kilns (K_1, K_N, MSVK_1, MSVK_N) generating an exhaust gas stream, the CO_2 purification unit (CPU) being selectively connected to the one or more additional kilns (K_1, K_N, MSVK_1, MSVK_N) and/or to said kiln (MSVK).

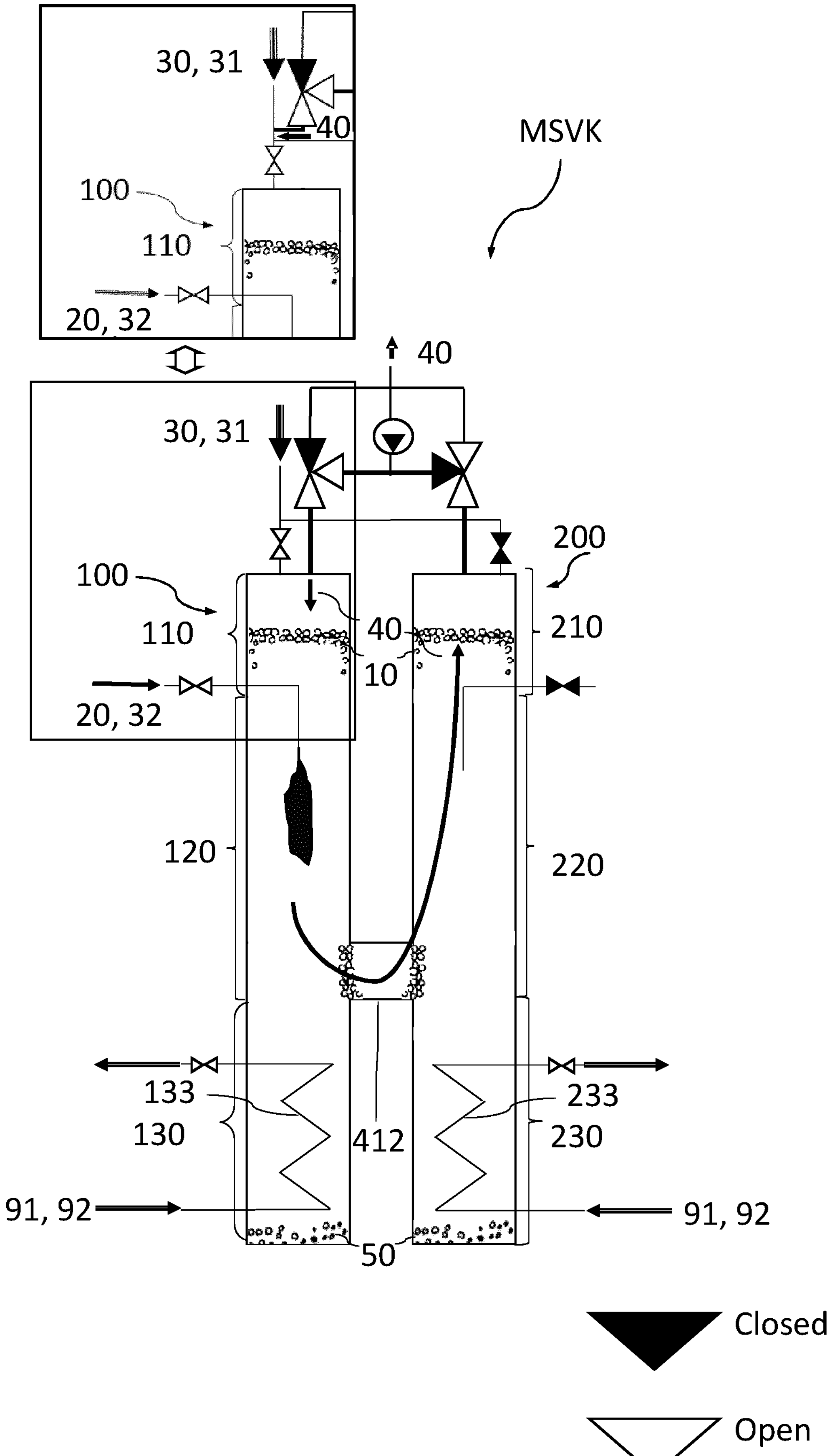

30, 31
40
MSVK
100
110
20, 32
40
30, 31
200
100
110
40
210
10
20, 32
120
220
133
233
130
412
230
91, 92
91, 92
50
Closed
Open

Fig. 1

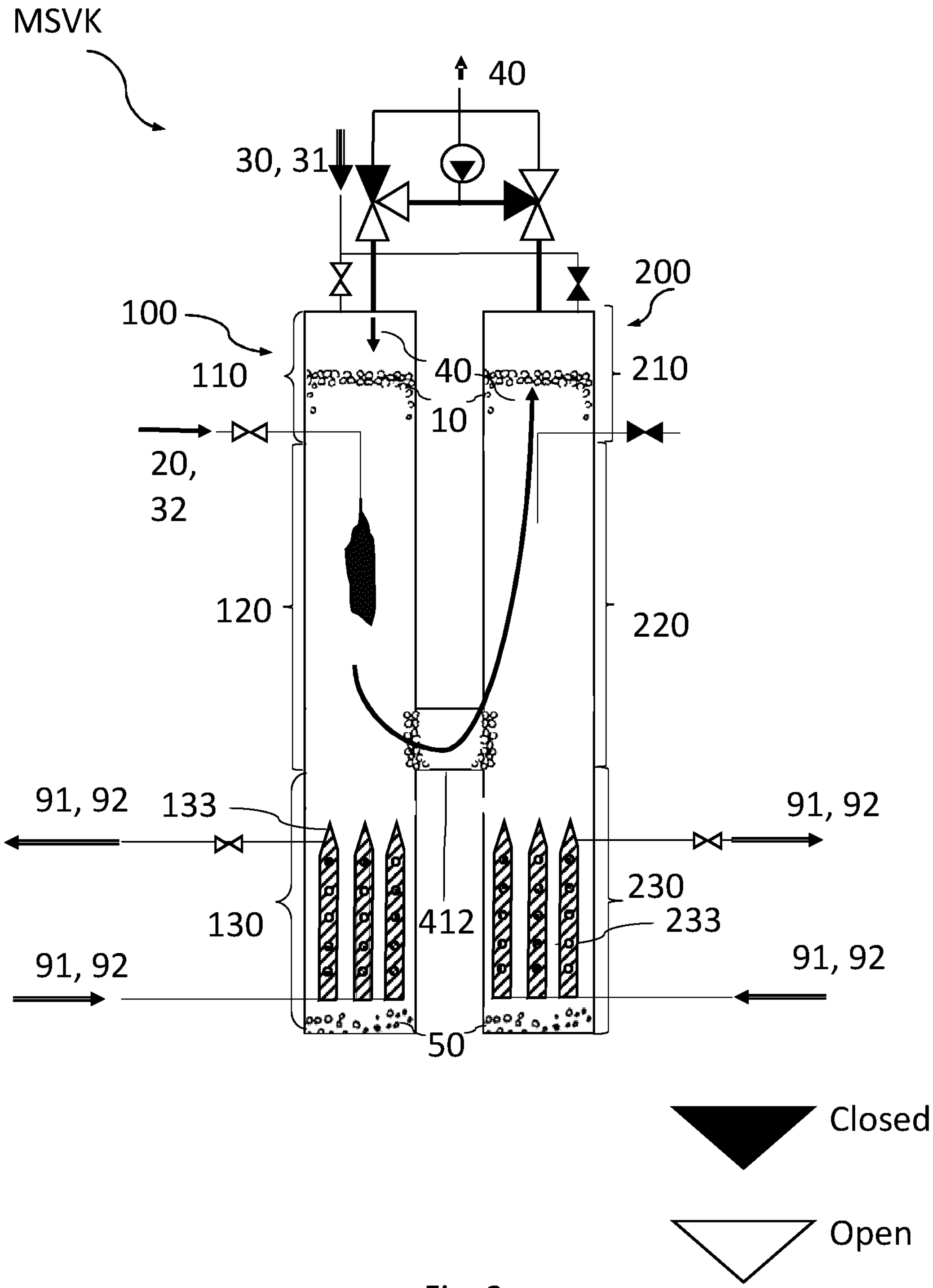

MSVK
40
30, 31
200
100
110
40
210
10
20,
32
120
220
91, 92
133
91, 92
230
130
412
233
91, 92
91, 92
50
Closed
Open

Fig. 2

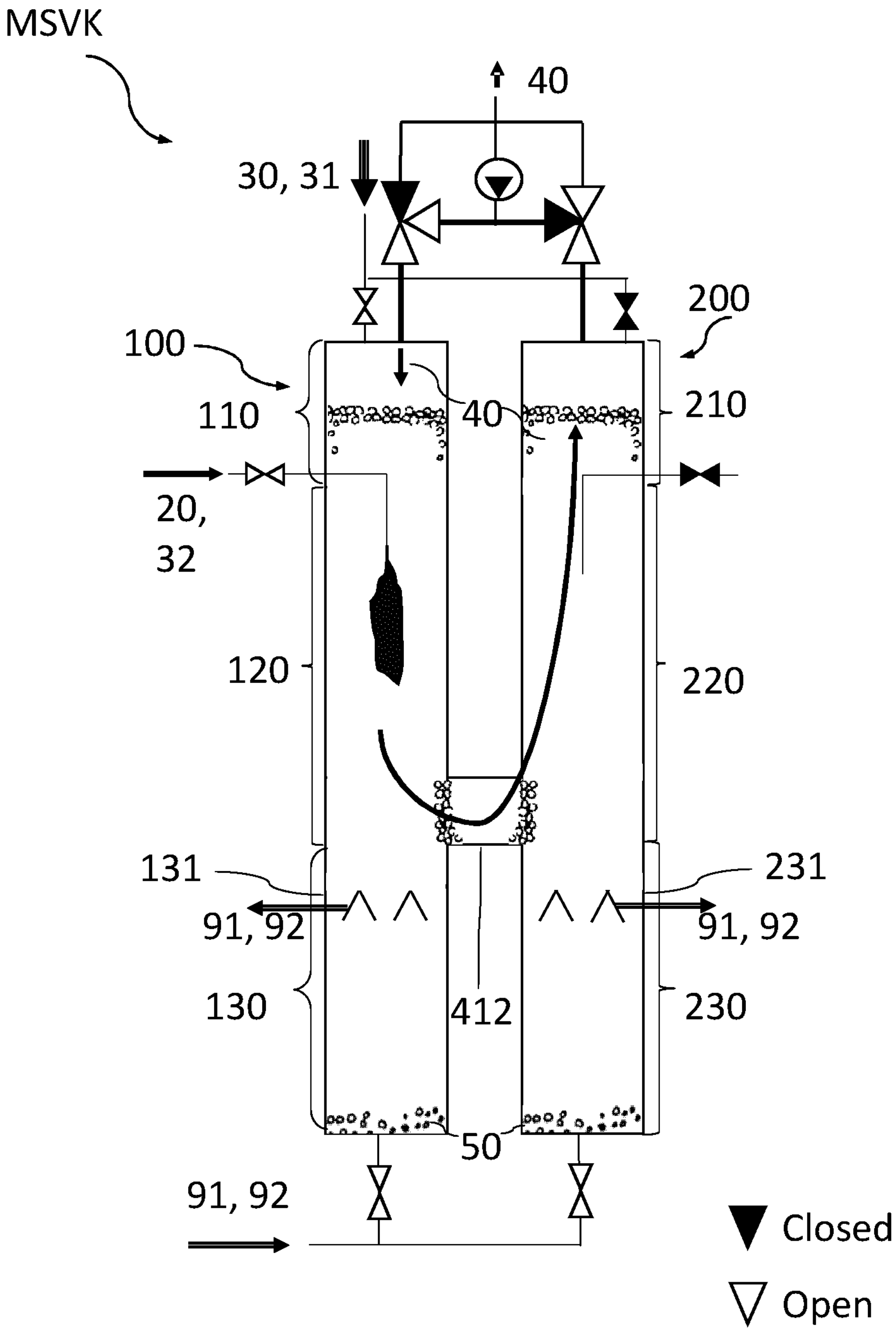

MSVK
40
30, 31
200
100
110
40
210
20,
32
120
220
131
231
91, 92
91, 92
130
412
230
50
91, 92
Closed
Open

Fig. 3

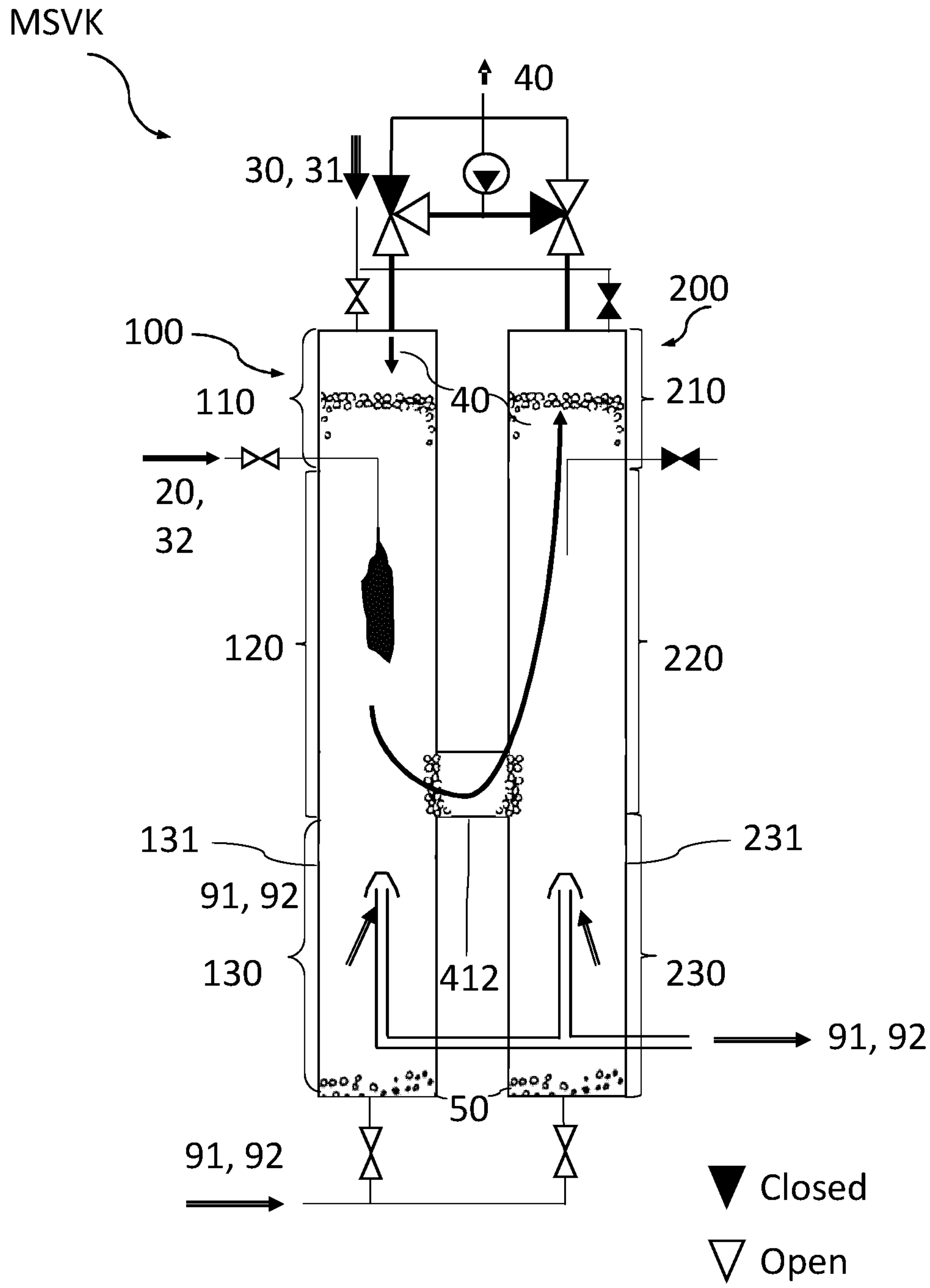

MSVK
40
30, 31
200
100
40
110
210
20,
32
120
220
131
231
91, 92
130
412
230
91, 92
50
91, 92
Closed
Open

Fig. 4

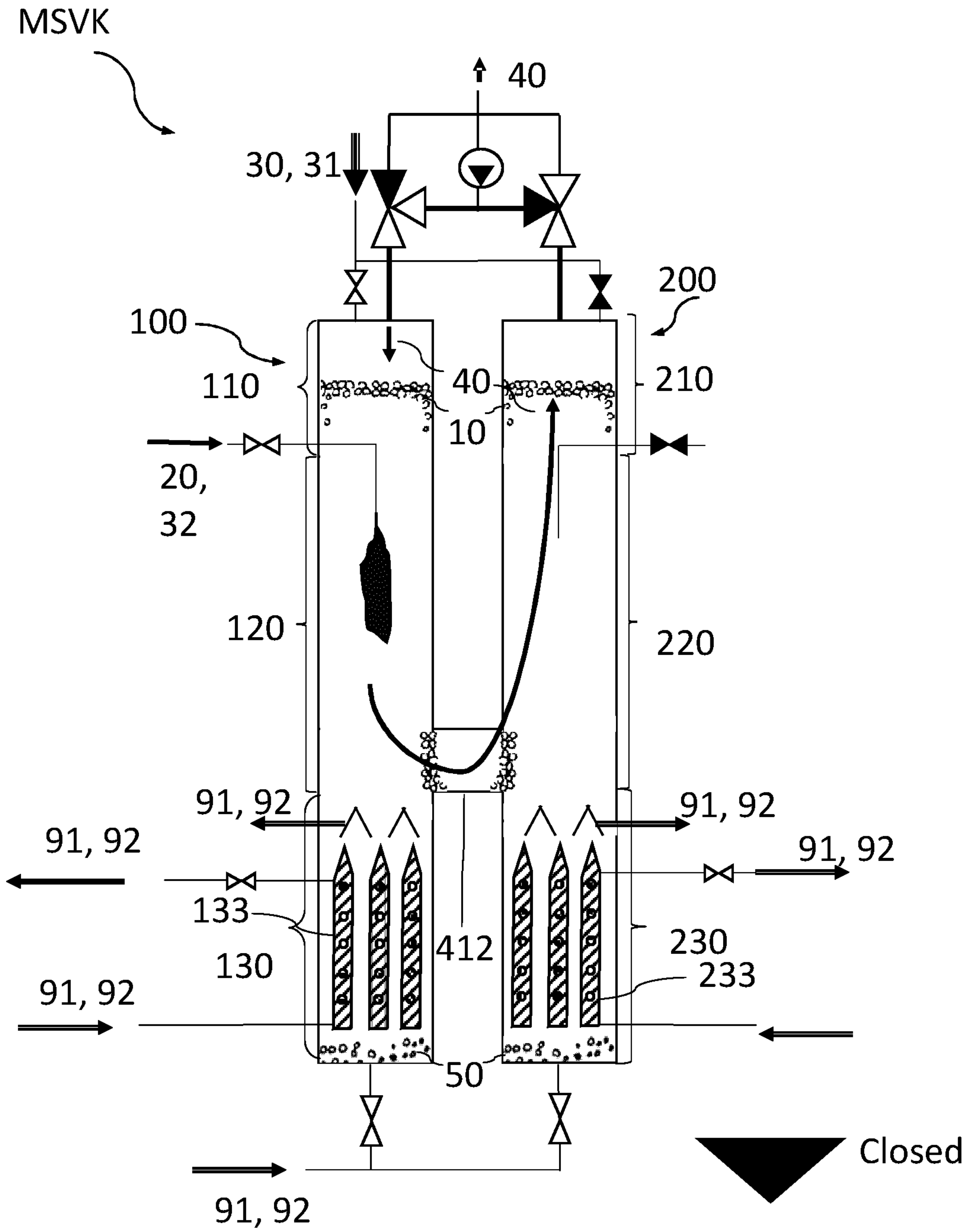
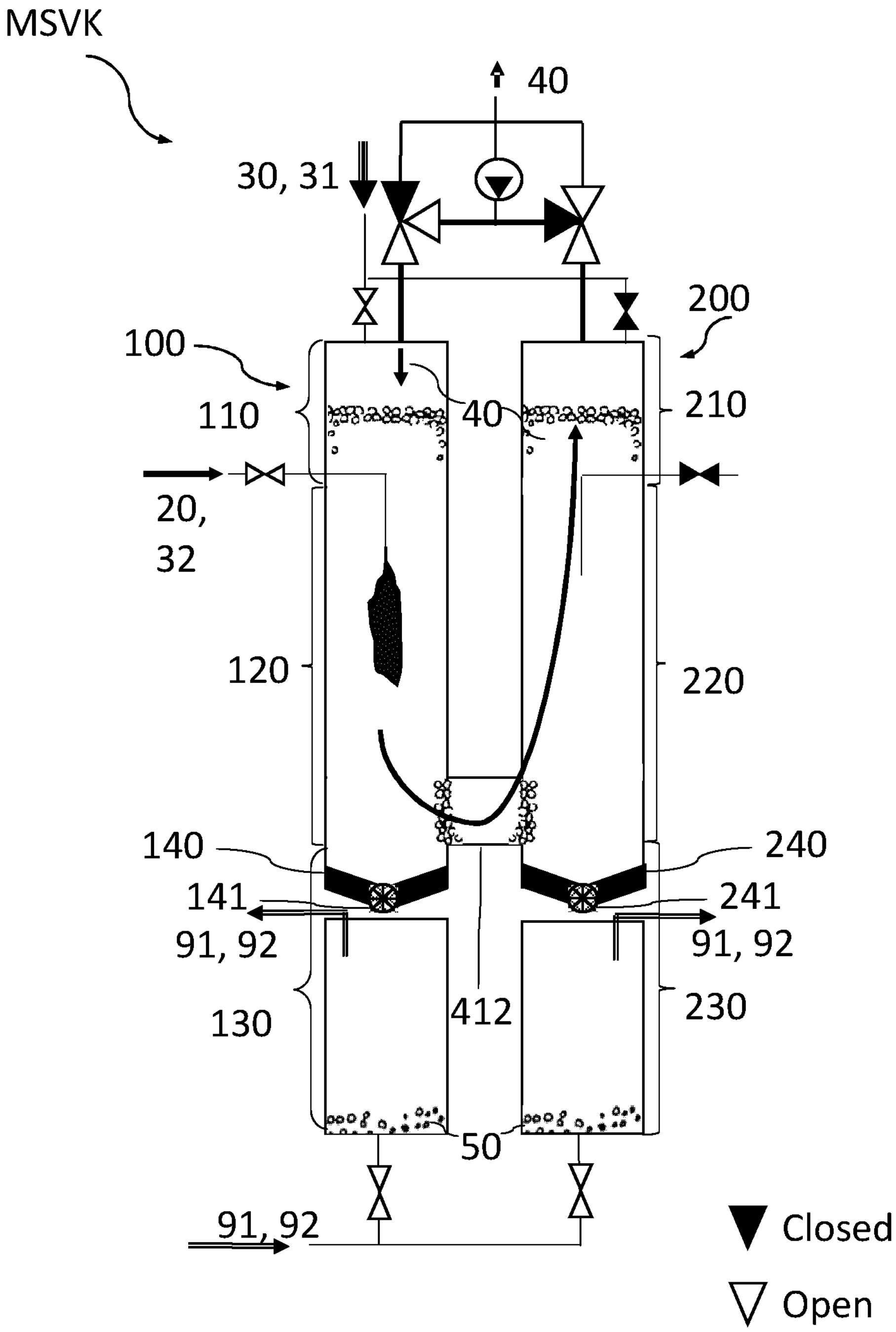

MSVK
40
30, 31
200
100
110
40
210
10
20,
32
120
220
91, 92
91, 92
91, 92
91, 92
133
412
230
130
233
91, 92
50
91, 92
Closed
Open

Fig. 5


MSVK
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30, 31
200
100
110
40
210
20,
32
120
220
140
240
141
241
91, 92
91, 92
130
412
230
50
91, 92
Closed
Open

Fig. 6

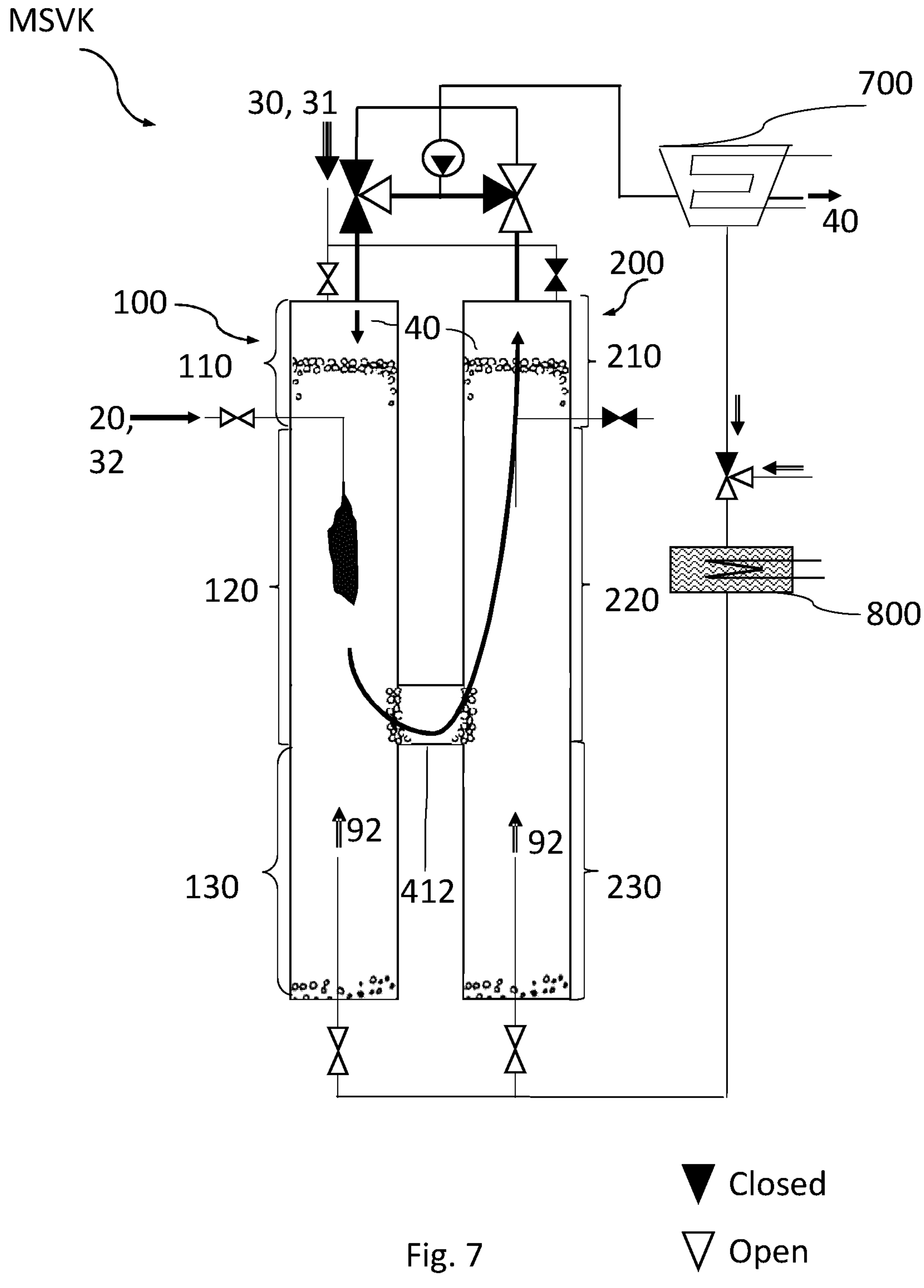

MSVK
30, 31
700
40
200
100
40
110
210
20,
32
120
220
800
130
92
412
92
230
Closed
Open

Fig. 7

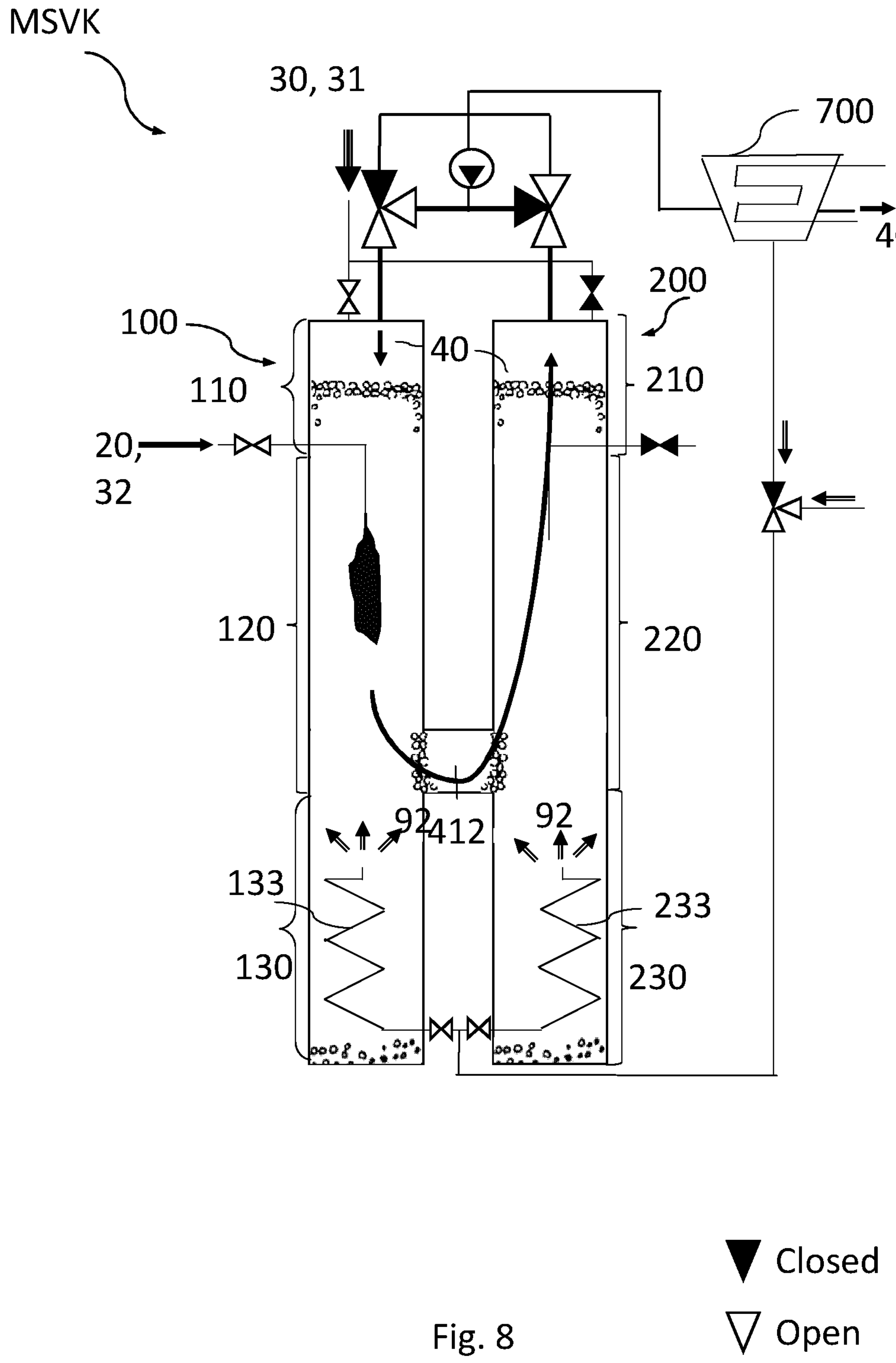

MSVK
30, 31
700
40
200
100
40
110
210
20,
32
120
220
92
412
92
133
233
130
230
Closed
Open

Fig. 8

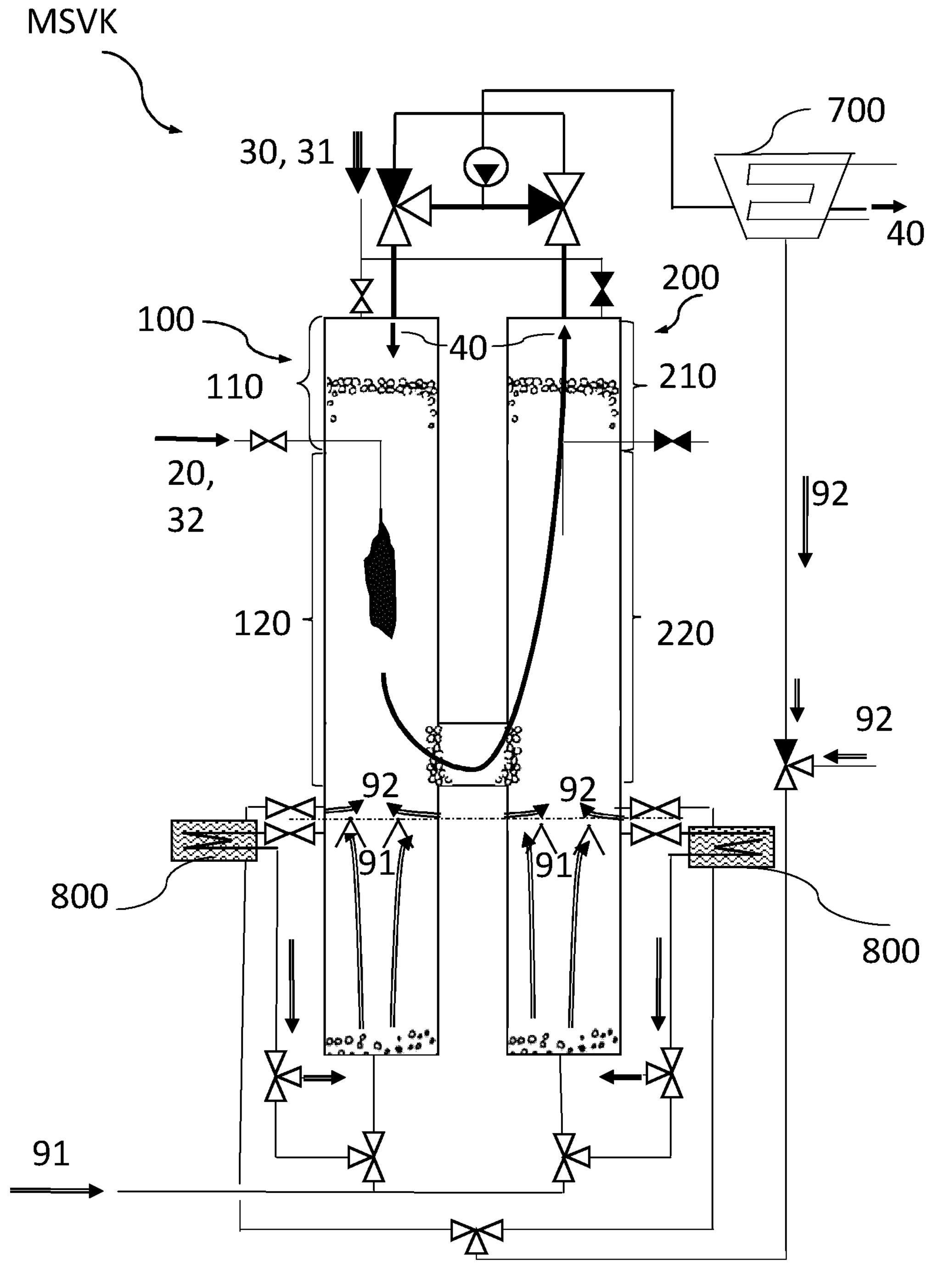

MSVK
700
30, 31
40
200
100
40
110
210
20,
32
92
120
220
92
92
92
91
91
800
800
91
Closed
Open

Fig. 9

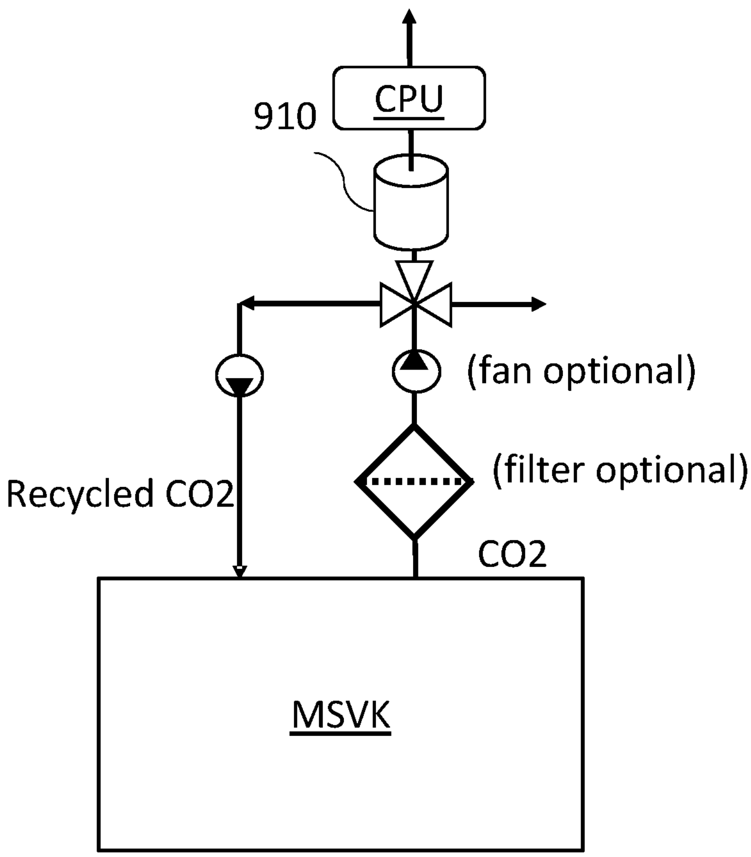


Fig. 10

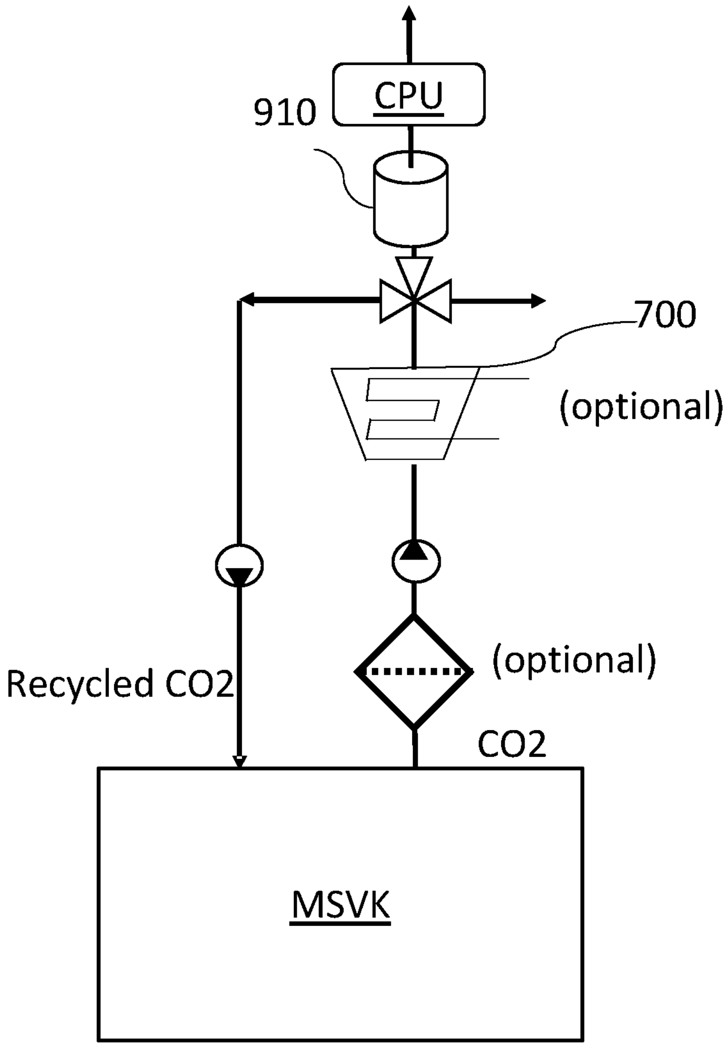


Fig. 11

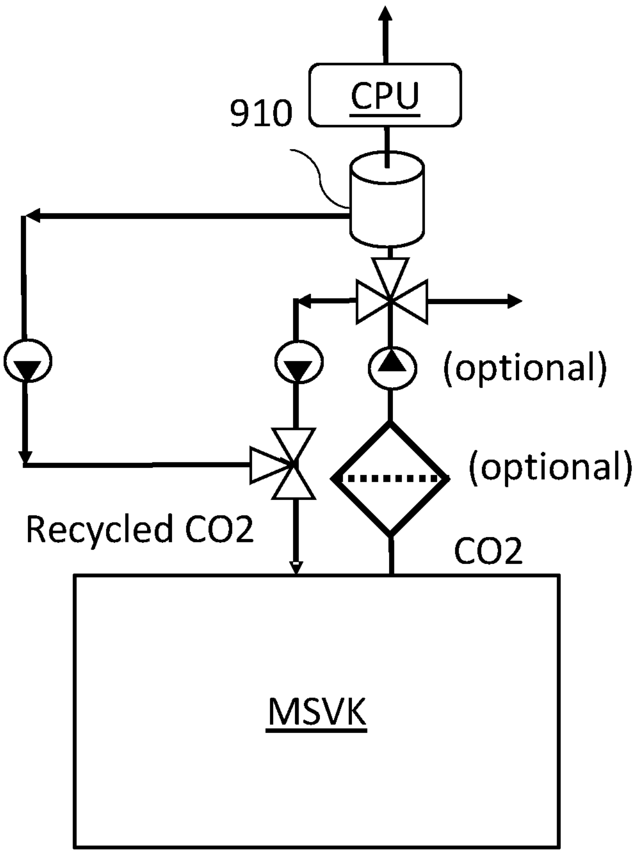


Fig. 12

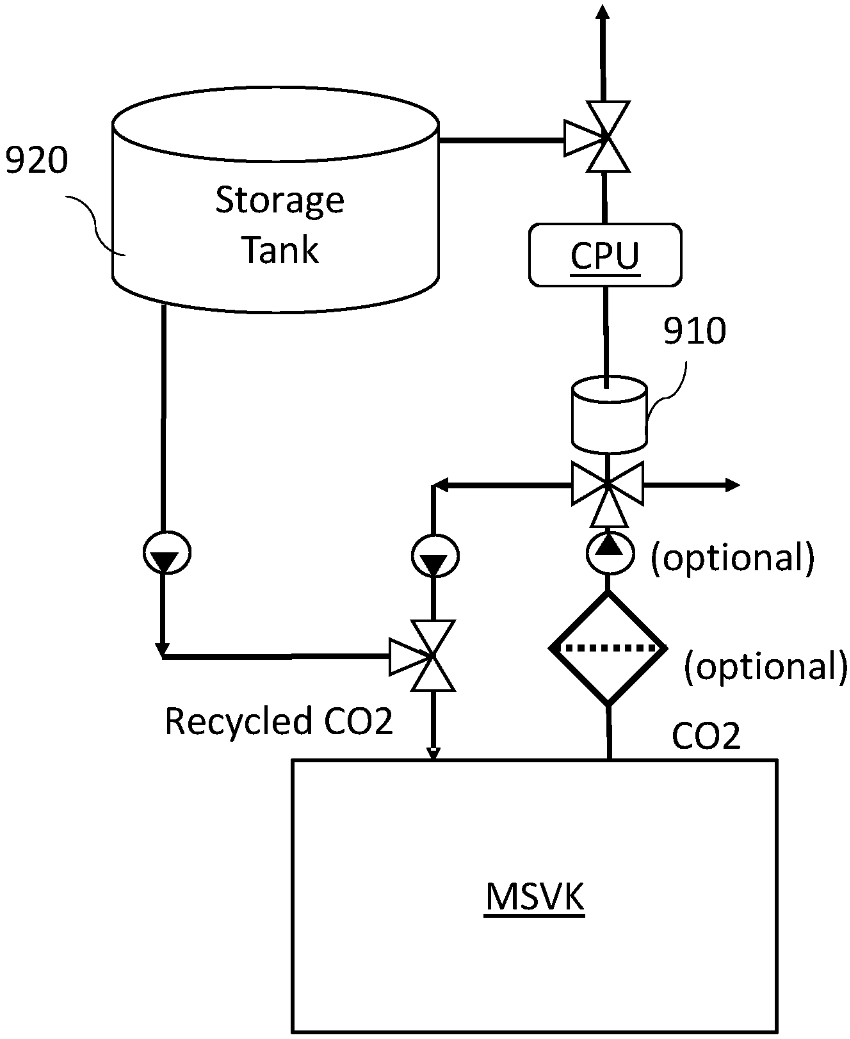

920
Storage
Tank
CPU
910
(optional)
(optional)
Recycled CO2
CO2
MSVK

Fig. 13

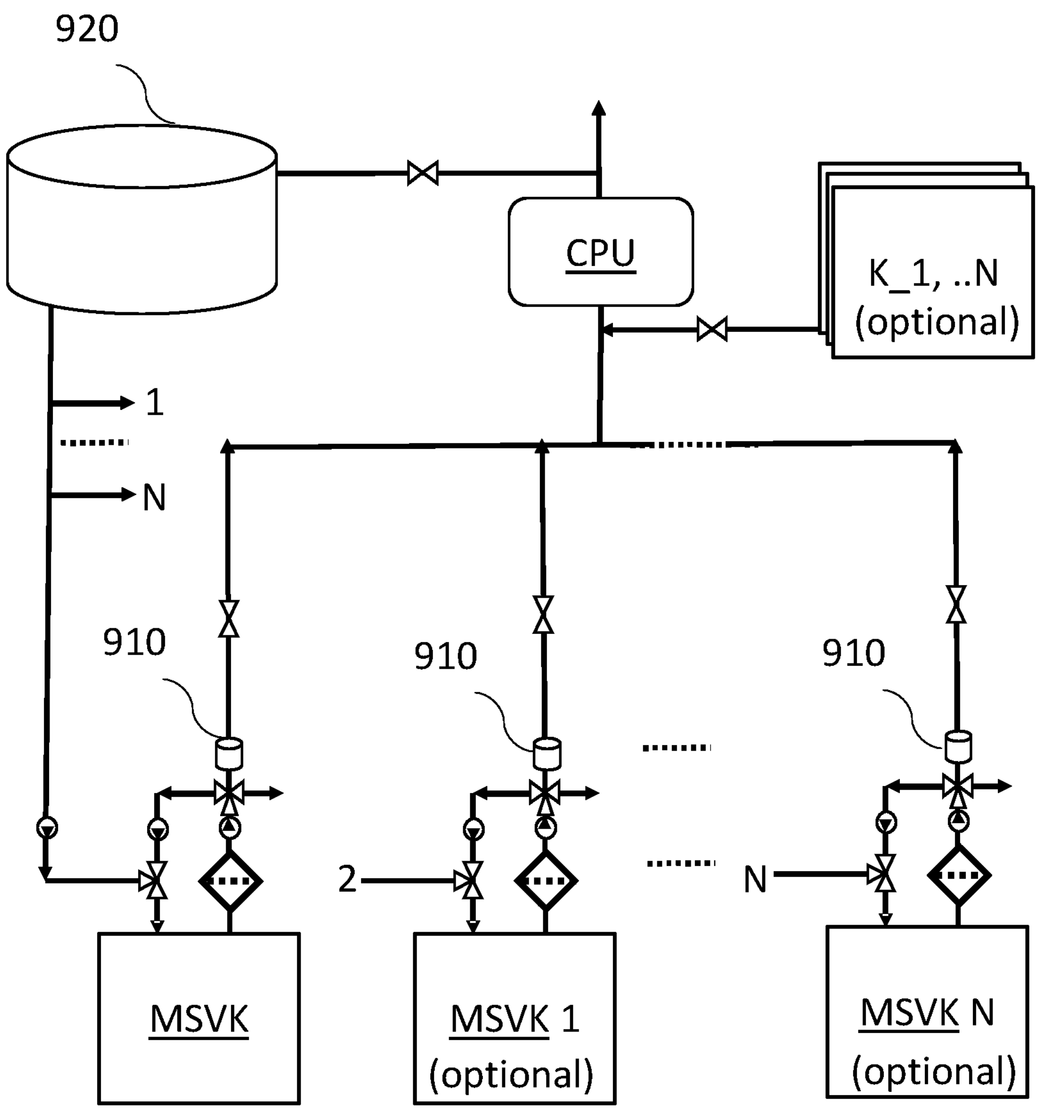
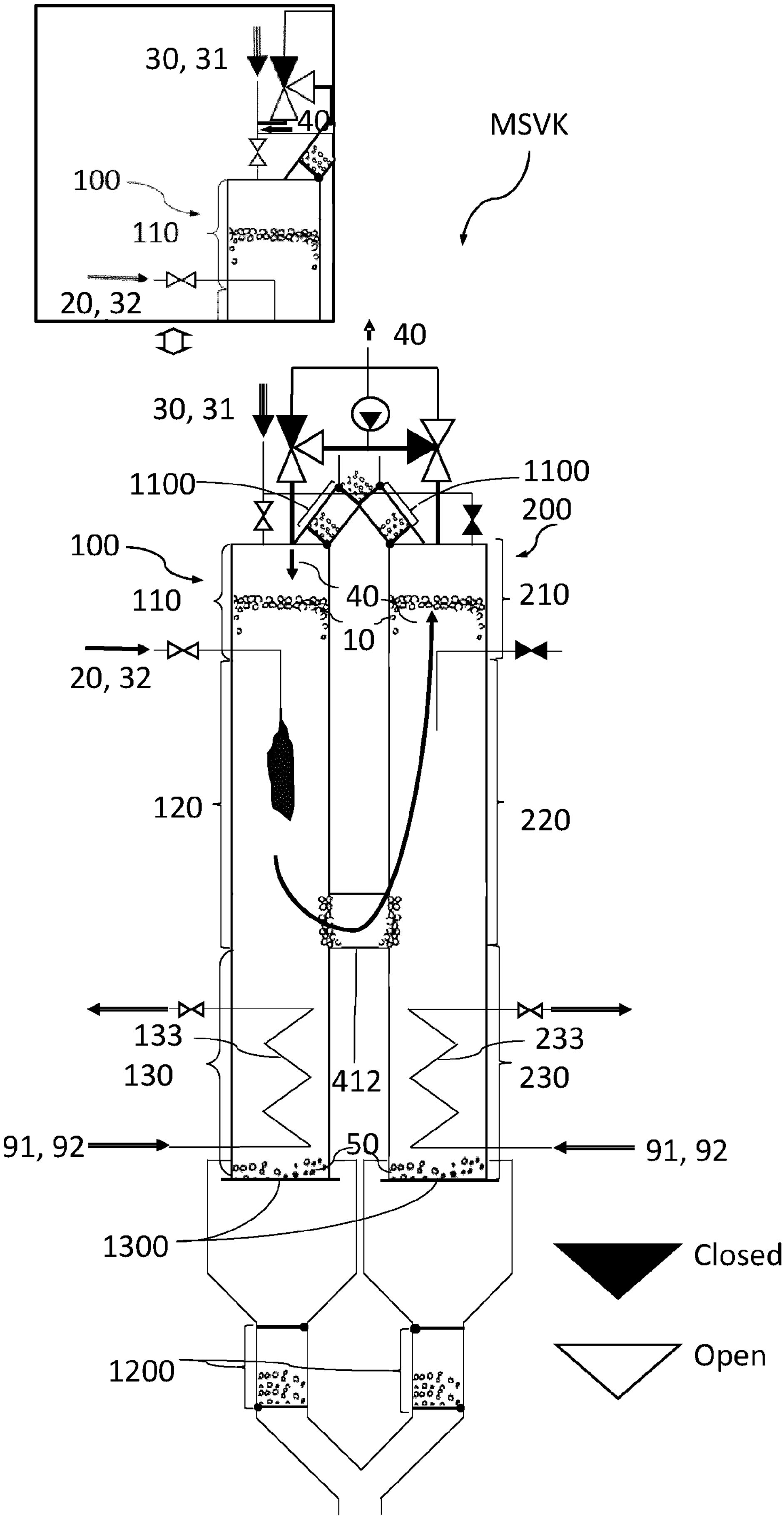

920
CPU
K_1, ..N
(optional)
1
N
910
910
910
2
N
MSVK
MSVK 1
(optional)
MSVK N
(optional)

Fig. 14


30, 31
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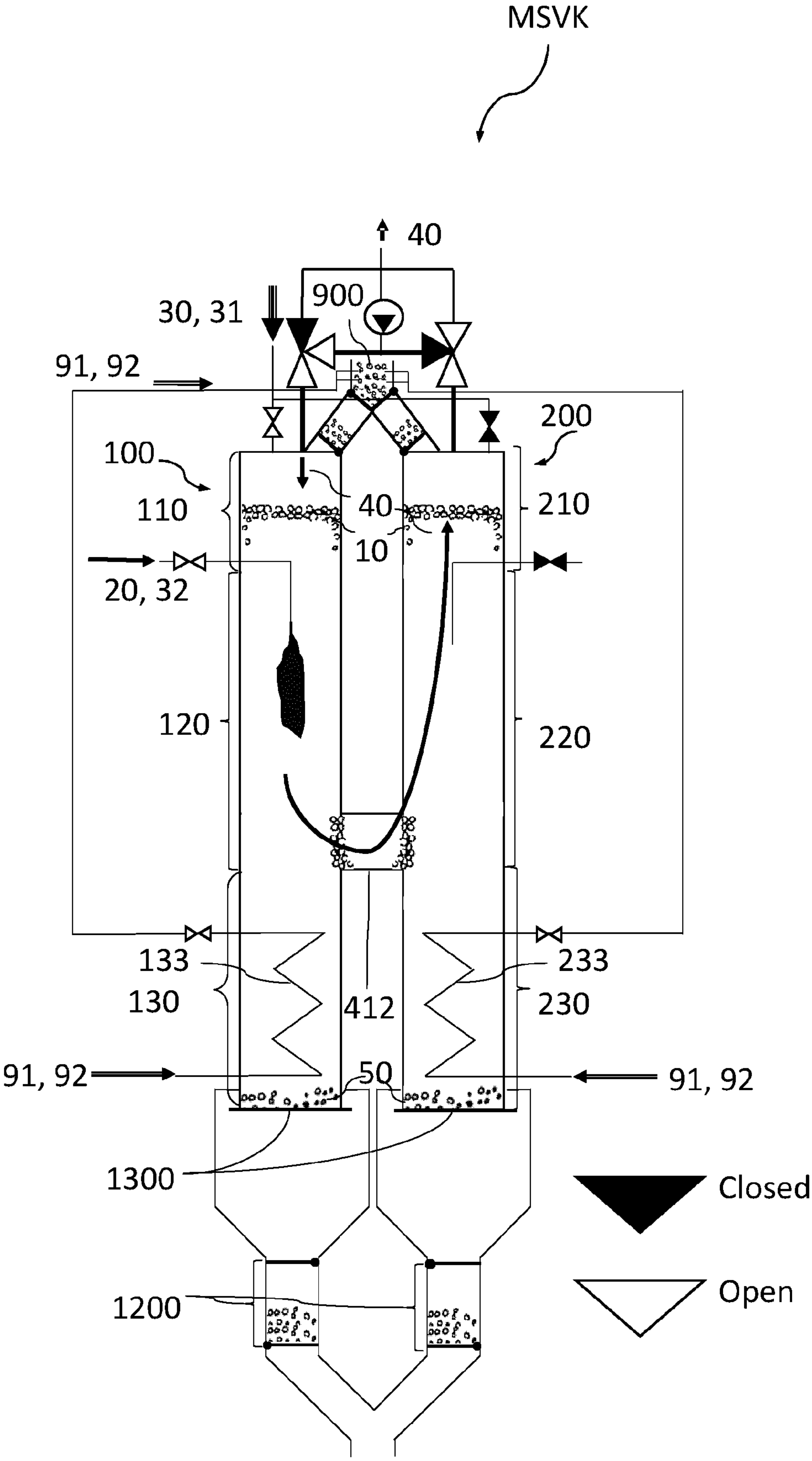
100
110
20, 32
MSVK
40
30, 31
1100
1100
200
100
110
40
210
10
20, 32
120
220
133
233
130
412
230
91, 92
50
91, 92
1300
Closed
1200
Open

Fig. 15


MSVK
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900
30, 31
91, 92
200
100
110
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210
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233
130
412
230
91, 92
50
91, 92
1300
Closed
Open
1200

Fig. 16

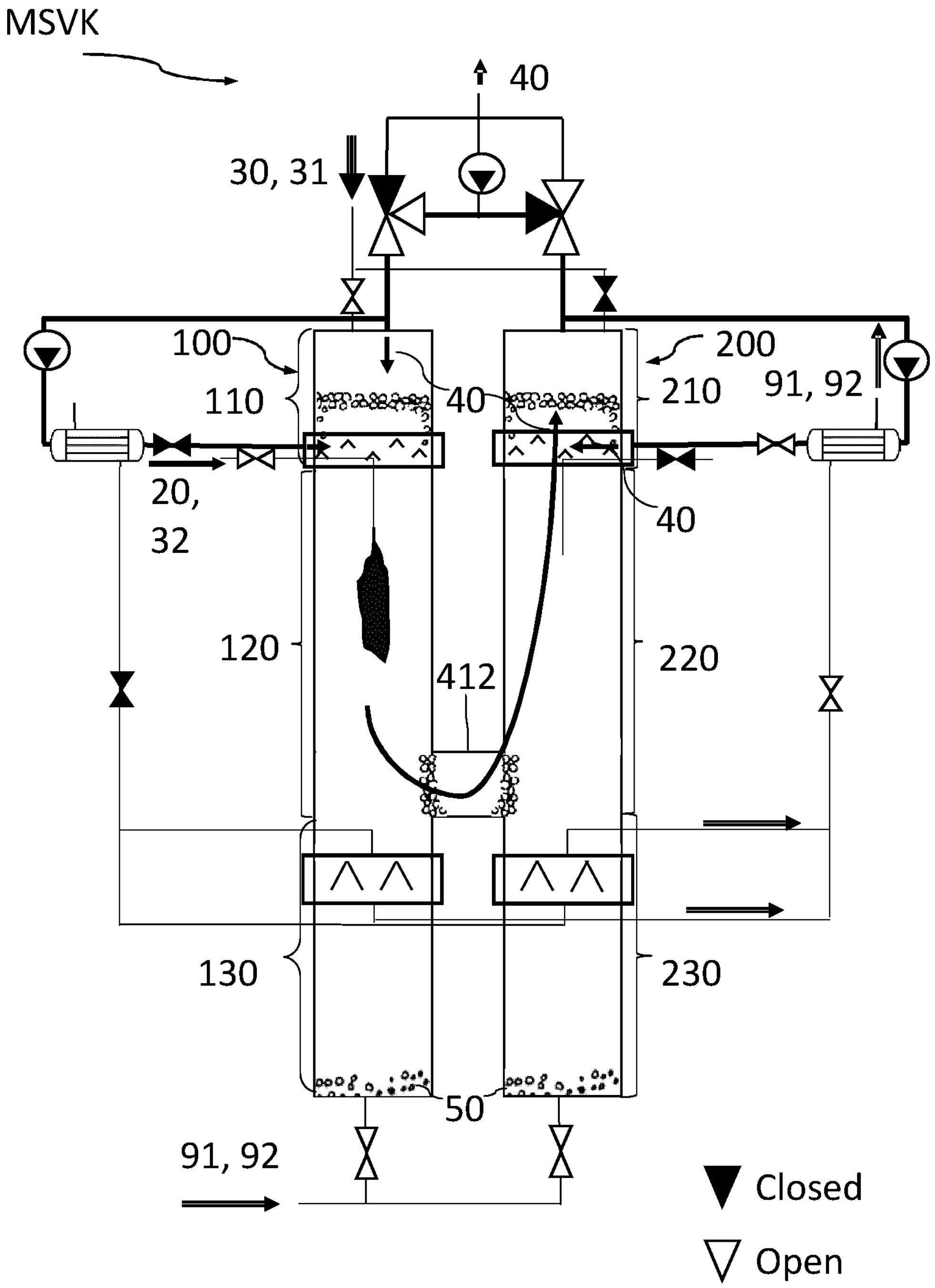

MSVK
40
30, 31
100
200
110
40
210
91, 92
20,
32
40
120
412
220
130
230
50
91, 92
Closed
Open

Fig. 17

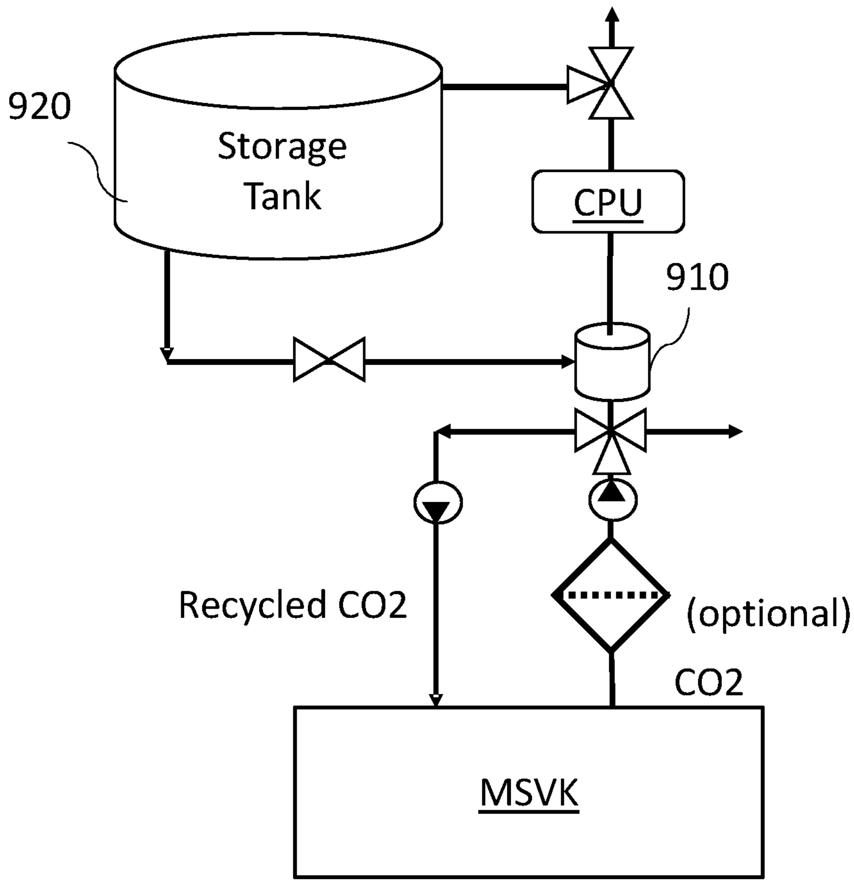


Fig. 18

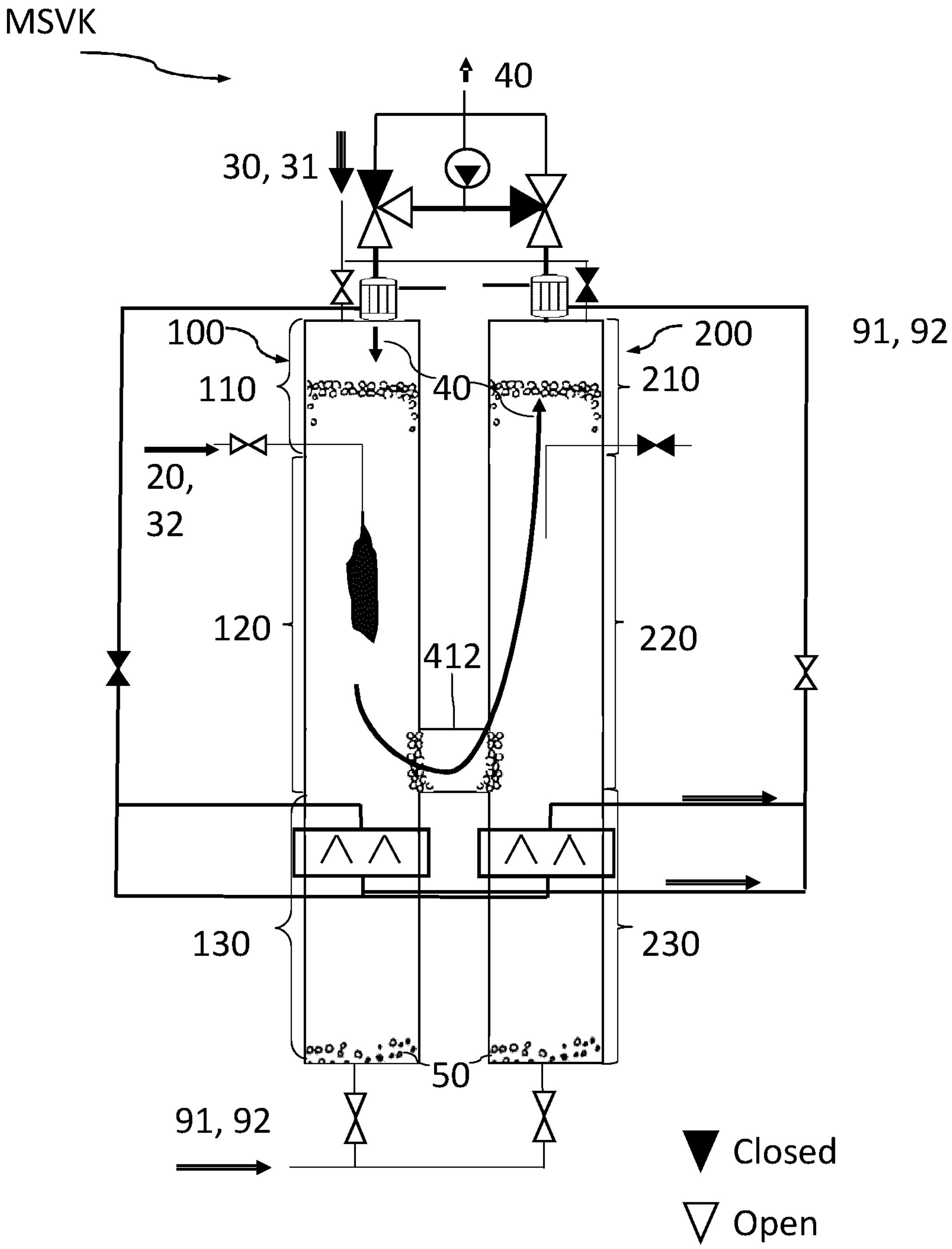
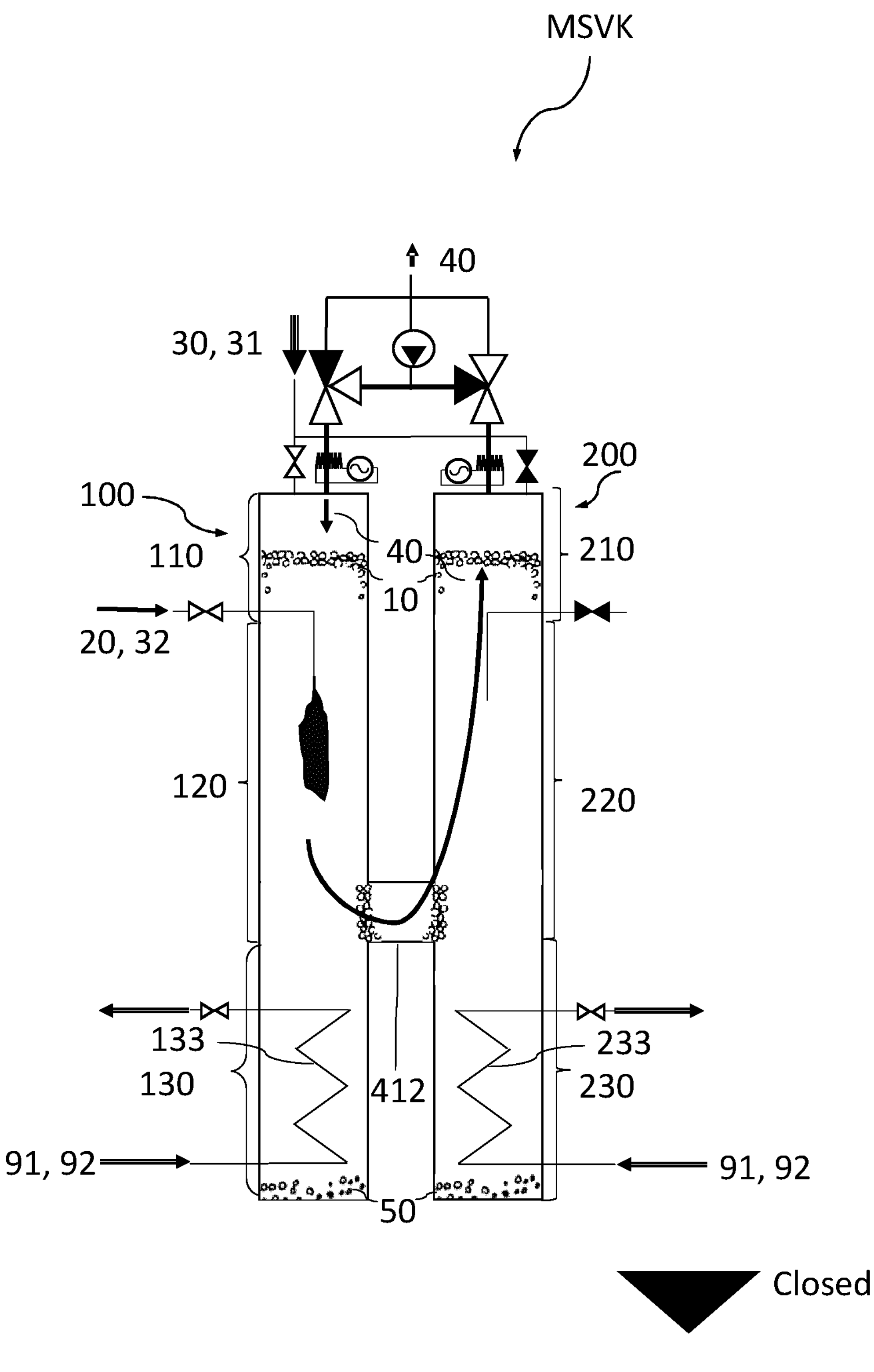

MSVK
40
30, 31
100
200
91, 92
110
40
210
20,
32
120
412
220
130
230
50
91, 92
Closed
Open

Fig. 19


MSVK
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30, 31
200
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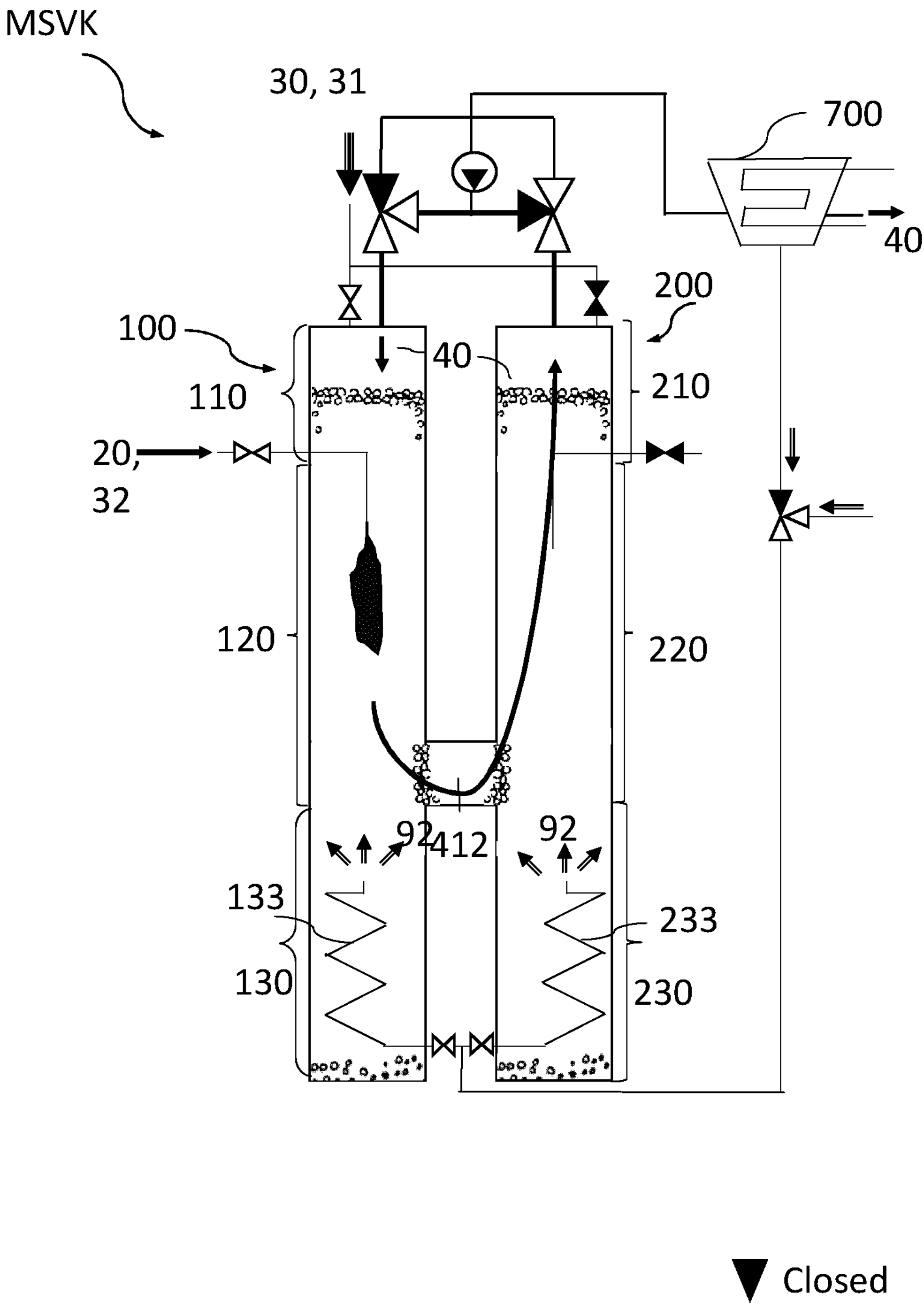
91, 92
50
Closed
Open

Fig. 20



MSVK
30, 31
700
40
200
100
40
110
210
20,
32
120
220
92
412
92
133
233
130
230
Closed
Open

Fig. 8