(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
04 July 2024 (04.07.2024)

WIPO | PCT

(10) International Publication Number
WO 2024/141398 A1

(51) International Patent Classification:
C04B 2/12 (2006.01) *F27B 1/08* (2006.01)
F27B 1/00 (2006.01) *F27B 1/10* (2006.01)
C04B 28/02 (2006.01) *F27D 99/00* (2010.01)

(21) International Application Number:
PCT/EP2023/087209

(22) International Filing Date:
21 December 2023 (21.12.2023)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
22217332.0 30 December 2022 (30.12.2022) EP
23170424.8 27 April 2023 (27.04.2023) EP

(71) Applicant: **S.A. LHOIST RECHERCHE ET DEVELOPPEMENT** [BE/BE]; Rue Charles Dubois 28, 1342 Ottignies Louvain-la-Neuve (BE).

(72) Inventor: **HABIB, Ziad**; Rue Arthur Van Dormael 10, 1630 Linkebeek (BE).

(74) Agent: **CALYSTA NV**; Lambroekstraat 5A, 1831 Diegem (BE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO,

(54) Title: PROCESS FOR CALCINING CARBONATED MINERAL STONES IN AN ANNULAR VERTICAL KILN AND IMPLEMENTED KILN

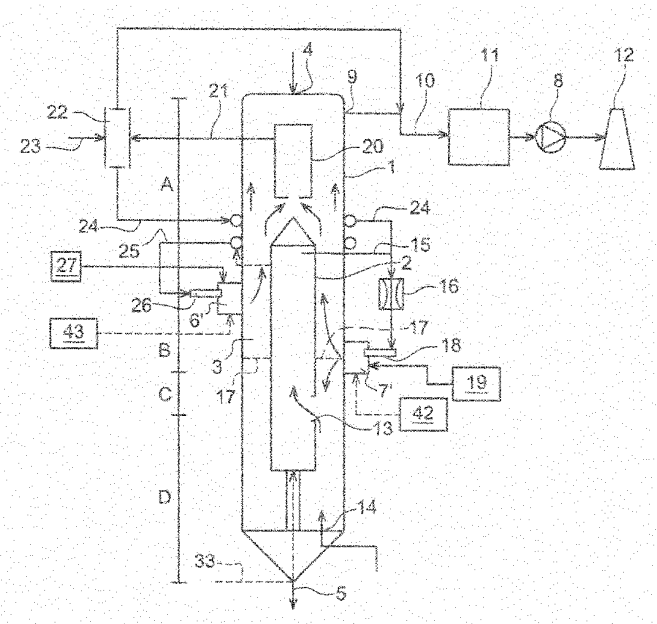


Fig. 2

(57) Abstract: Annular shaft kiln for calcining carbonated mineral stones, comprising an outer cylinder (1), an inner cylinder (2), forming an annular space (3) with the outer cylinder (1), material inlet means (4) for feeding said carbonated mineral stones at the top of the kiln into the annular space (3), material discharge means (5) at the bottom of the kiln for discharging the decarbonated calcined material, upper gas injection means at a first level of the annular space, provided for injecting an upper hot gas, lower gas injection means at a second level of the annular space lower than the level of the first gas injection means, provided for injecting a lower hot gas, said kiln being equipped with at least one plasma torch (18) for heating a gas and with, as lower gas injection means, at least one lower mixing chamber (7') wherein the heated gas is mixed with a control gas for providing a gaseous mixture which is said lower hot gas to inject having a controlled temperature equal or higher than the temperature of calcination of the loaded mineral stones, and

WO 2024/141398 A1

[Continued on next page]

RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report (Art. 21(3))*

— *in black and white; the international application as filed contained color or greyscale and is available for download from PATENTSCOPE*

process implemented in such a kiln.

Process for calcining carbonated mineral stones in an annular vertical kiln and implemented kiln.

The present invention relates to a process for calcining carbonated mineral stones in an annular shaft kiln (ASK), having an outer cylinder and an inner cylinder forming an annular space between them. Such a process is known and comprises

- a loading step of carbonated mineral stones at the top of the kiln,
- an injection of an upper hot gas into the annular space at a first level thereof,
- an injection of a lower hot gas into the annular space at a second level lower than the first level,
- a preheating step in a preheating zone of said loaded carbonated mineral stones flowing downwardly in the annular space,
- a calcining step of said preheated carbonated mineral stones in a calcination zone located in the annular space below the preheating zone, said preheating and calcining steps of said carbonated mineral stones flowing downwardly in the annular space taking place successively in contact with the upper hot gas and the lower hot gas which are at least partially submitted to an upwards draft in counter-current of the carbonated mineral stones and exhausted from the top of the kiln under the form of a gaseous effluent,
- an introduction of cooling air at the bottom of the kiln,
- a cooling step in a cooling zone below the calcination zone of decarbonated calcined material flowing downwardly, with cooling air flowing in counter-current through said decarbonated calcined material and forming a heated cooling air,
- an aspiration step of said heated cooling air into the inner cylinder at a third level lower than said second level, under the form of a gaseous stream containing said heated cooling air,
-a recirculation of the gaseous stream containing said heated cooling air from the inner cylinder to said injection step of a lower hot gas, and
- a discharging step of the decarbonated calcined material from the bottom of the kiln.

According to the invention, carbonated mineral stones particularly mean calcareous stones (limestones), dolomitic stones (dolostones or unburnt dolomites) and/or magnesite stones which are calcined into quicklime, quick dolime and/or magnesia.

The calcination reaction of limestone into quicklime is :

$CaCO_3$ (solid) + heat $\leftarrow\rightarrow$ CaO (solid)+ CO_2 (gas)

This reaction is endothermic and reversible. Below 900°C lime and CO_2 will easily recombine. But from a temperature of the order of 900°C the starting stones give off a significative volume of CO_2 during their decarbonation. In order to obtain such a decarbonation, the temperature must consequently be significatively increased in the calcining zone. Today this increase is mainly obtained by combustion of a fuel, frequently fossil, in presence of an oxidizer as air. In turn this fuel combustion contributes also to an important release of CO_2. Globally the current calcination methods actively participate in increasing the greenhouse effect.

During the fuel combustion a direct contact of the flame with the preheated carbonated mineral stones also results in possible local overheat in the calcination zone and the possibility that the flue gas would contaminate the calcined material. A prior careful selection of the fuel is required to maintain a high quality of the calcined material, notably while avoiding high sulphur fuels. Even with selected fossil fuels, the calcined material reactivity will be affected by the fuel ash and some minor pollutants.

The object of the present invention is to remedy the problems of fuel combustions, particularly fossil fuels, of ASK kilns, without modifying substantially their functioning and by making little or no changes to their structure. Another object is to avoid as much as possible overheat of the calcined material and introduction of impurities in this material and in the gaseous effluent exiting from the kiln. The main object of the calcination kilns must obviously be maintained, i.e. the production of a calcined material of high quality and purity.

In order to solve these problems, according to the invention a method as above indicated further comprises a first heating step of a gas by means of at least one plasma torch for producing a lower heated gas, and a first step of mixing in a lower mixing chamber said lower heated gas with a control gas which is not heated by the at least one plasma torch for controlling a temperature of a first gaseous mixture which is said lower hot gas injected into the kiln at the second level of the annular space, the controlled temperature allowing a calcining of the carbonated mineral stones. The at least one plasma torch according to the invention may also be qualified as “lower plasma torch”.

The invention relies mostly on externalizing the energy supply while heating a gas with a plasma torch, particularly at the second level of the kiln. The heated gas is partially broken down at high temperature in an electric arc, but mostly recombined in the process.

No fuel is still necessary for a combustion inside the kiln at the lower level. Consequently, no additional pollutant from a combustion will be emitted apart the minor ones

contained in the stones. No ash will be produced resulting to a pure decarbonated material. No more direct contact of the stones with a flame is to fear. The appropriate temperature of the heated gas from the plasma torch is controlled very easily by means of the step of mixing, leading to a high quality of lime.

For the sake of clarity, due to the configuration of the annular vertical kiln of the invention, the at least one plasma torch and the lower mixing chamber are arranged outside of the outer cylinder.

According to particular embodiments of the process of the invention, a) the lower heated gas which is heated by at least one plasma torch is selected among the group consisting of air, N_2, CO_2, steam, noble gas and their mixtures and the control gas is comprised of recirculated gaseous stream containing said heated cooling air or b) the lower heated gas which is heated by at least one plasma torch is comprised of recirculated gaseous stream containing said heated cooling air and the control gas is selected among the group consisting of air, N_2, CO_2, steam, and their mixtures or c) the lower heated gas which is heated by at least one plasma torch as well as the control gas are comprised of recirculated gaseous stream containing said heated cooling air.

Advantageously, during the first heating step, air and/or water is additionally introduced in the at least one plasma torch and /or mixed in the first gaseous mixture.

According to an embodiment of the present invention, the process comprises a second heating step of a gas by means of at least one additional plasma torch for producing an upper heated gas, and a second step of mixing in an upper mixing chamber said upper heated gas with an adjusting gas which is not heated by the at least one additional plasma torch for adjusting a temperature of a second gaseous mixture which is said upper hot gas introduced at the first level of the annular space, the adjusted temperature allowing a calcining of the carbonated mineral stones. No fuel is still necessary for a combustion inside the kiln. The process does not more necessitate any consumption of fossil fuel. The at least one additional plasma torch according to the invention may also be qualified as “upper plasma torch”. For the sake of clarity, due to the configuration of the annular vertical kiln of the invention, the at least one additional plasma torch and the upper mixing chamber are arranged outside of the outer cylinder.

Advantageously, the internal cylinder of the kiln has a shell and the process comprises a step of cooling said shell by secondary air and extracting an heated secondary air from the kiln.

According to particular embodiments of the process of the invention, a) the upper heated gas which is heated by at least one additional plasma torch in the second heating step is selected among the group consisting of air, N_2, CO_2, steam, noble gas and their mixtures and the adjusting gas is comprised of said heated secondary air or b) the upper heated gas which is heated by at least one additional plasma torch is comprised of said heated secondary air and the adjusting gas is selected among the group consisting of air, N_2, CO_2, steam, and their mixtures or c) the upper heated gas which is heated by at least one additional plasma torch as well as the adjusting gas are comprised of said heated secondary air.

In a preferential embodiment of the process according to the invention, in the at least one additional plasma torch, a gas selected among the group consisting of air, N_2, CO_2, steam, noble gas and their mixtures is heated in presence of said heated secondary air and an adjusting gas is additionally injected in said upper mixing chamber. Preferably, during the second heating step, air and/or water is additionally introduced in the at least one plasma torch and /or mixed in the second gaseous mixture.

According to an embodiment of the invention, said upwards draft and said aspiration of the aspiration step are equilibrated so that a first part of the lower hot gas introduced into the annular space is upwards drawn in counter-current of the stones to calcine and a second part of the lower hot gas is supplied downward the bottom of the annular space, in co-current with the mineral stones to calcine, and thereafter aspired inside the inner cylinder, while forming with said cooling air and CO_2 from the decarbonation in the co-current calcination zone said gaseous stream containing said heated cooling air. According to another embodiment of the invention, said upwards draft and said aspiration of the aspiration step are equilibrated so that the totality of the lower hot gas introduced into the annular space is submitted to the upwards draft, the gaseous stream aspired in the inner cylinder comprising only cooling air.

According to a preferential embodiment of the process according to the invention, said lower and upper hot gas which are drawn toward the top of the kiln form a gaseous stream which is partially recovered out of the kiln before the exhaust of the gaseous

effluent at the top of the kiln and the process further comprises a heat exchange between this recovered gaseous stream and a gas to recirculate towards said first heating step.

The present invention concerns also an annular shaft kiln for calcining carbonated mineral stones. Currently such a kiln comprises

- an outer cylinder,
- an inner cylinder, forming an annular space with the outer cylinder,
- material inlet means for feeding said carbonated mineral stones at the top of the kiln into the annular space,
- upper gas injection means at a first level of the annular space, provided for injecting an upper hot gas,
- lower gas injection means at a second level of the annular space lower than the level of the first gas injection means, provided for injecting a lower hot gas,
- a cooling air inlet, provided at the bottom of the annular space for cooling a decarbonated calcined material,
- material discharge means at the bottom of the kiln for discharging the decarbonated calcined material out of the kiln,
- upper gas outlet means at the top of the kiln for exhausting a gaseous effluent into a removal duct,
- return vents in the inner cylinder at a third level lower than said second level, through which a gaseous stream containing the cooling air heated in contact with the decarbonated calcined material is sucked from the annular space into the inner cylinder, and
-means for recirculating said gaseous stream containing the heated cooling air from the inner cylinder at least partially to the lower gas injection means.

According to the invention, at said second level, such a kiln is equipped with at least one plasma torch for heating a gas and with, as lower gas injection means, at least one lower mixing chamber which is connected to the at least one plasma torch for mixing the heated gas with a control gas for providing a gaseous mixture which is said lower hot gas to inject having a controlled temperature equal or higher than the temperature of calcination of the loaded mineral stones.

According to particular embodiments of the kiln according to the invention, a) the at least one lower mixing chamber is connected to the at least one plasma torch which is supplied from an external gas source and to said means for recirculating said gaseous stream containing

the heated cooling air, said gas heated by said at least one plasma torch being mixed in said at least one lower mixing chamber with recirculated gaseous stream containing the heated cooling air as control gas, for providing said lower hot gas to inject having a controlled temperature equal or higher than the temperature of calcination of the loaded mineral stones or b) the at least one lower mixing chamber is connected to an external gas source, for providing control gas, and to the at least one plasma torch which is connected to said means for recirculating said gaseous stream containing heated cooling air, said control gas being mixed in said at least one lower mixing chamber with said recirculated gaseous stream heated by the at least plasma torch, for providing said lower hot gas to inject having a controlled temperature equal or higher than the temperature of calcination of the loaded mineral stones or c) the at least one lower mixing chamber is connected to the at least one plasma torch and to said means for recirculating said gaseous stream containing the heated cooling air, the at least one plasma torch being also connected to the means for recirculating said gaseous stream containing the heated cooling air, a part of the recirculated gaseous stream containing the heated cooling air which has been heated by the at least one plasma torch being mixed in said at least one lower mixing chamber with, as control gas, another part of said recirculated gaseous stream which has not been heated by the at least one plasma torch.

In a typical embodiment of the invention, there will be 4 to 6 lower plasma torches and 4 to 6 lower mixing chambers.

According to a preferential embodiment, at the first level, the kiln of the invention is equipped with at least one additional plasma torch for heating a gas and with, as upper gas injection means, at least one upper mixing chamber which is connected to the at least one additional plasma torch for mixing the heated gas with an adjusting gas which has not been heated by the at least one additional plasma torch and thereby providing a gaseous mixture which is said upper hot gas to inject having an adjusted temperature allowing a calcining of the loaded mineral stones.

In such a kiln a plasma torch will replace each burner of a classical annular shaft kiln and a mixing chamber will replace each combustion chamber of said standard kiln. There is no structural modification of the kiln and such an adaptation is very easy and economic.

In a typical embodiment of the invention, there will be 4 to 6 upper/additional plasma torches and 4 to 6 upper mixing chambers.

Advantageously, the kiln comprises inlet means for secondary cooling air which are connected with the interior of a shell of the inner cylinder, and outlet means able to extract the heated secondary cooling air out of the kiln.

According to an advantageous embodiment of the kiln of the invention a) the at least one upper mixing chamber is connected to the at least one additional plasma torch which is supplied from an external gas source and to said outlet means able to extract said heated secondary cooling air, said gas heated by said at least one additional plasma torch being mixed in said at least one upper mixing chamber with said heated secondary cooling air as adjusting gas, for providing said upper hot gas to inject having an adjusted temperature equal or higher than the temperature of calcining of the loaded mineral stones or b) the at least one upper mixing chamber is connected to an external gas source, for providing an adjusting gas, and to the at least one additional plasma torch which is connected to said outlet means able to extract the heated secondary cooling air, said adjusting gas being mixed in said at least one upper mixing chamber with said heated secondary cooling air heated by the at least one additional plasma torch, for providing said upper hot gas to inject having an adjusted temperature equal or higher than the temperature of preheating of the loaded mineral stones or c) the at least one upper mixing chamber is connected to the at least one additional plasma torch and to said outlet means able to extract the heated secondary cooling air, the at least one additional plasma torch being also connected to the said outlet means able to extract the heated secondary cooling air, a part of the extracted heated secondary cooling air which has been heated by the at least one additional plasma torch being mixed in said at least one upper mixing chamber with, as adjusting gas, another part of said extracted heated secondary cooling air which has not been heated by the at least one additional plasma torch.

According to a preferential embodiment of the kiln of the invention the at least one upper mixing chamber is connected, on the one hand, to the at least one additional plasma torch which is supplied with a gas to heat from an external gas source in presence of the heated secondary cooling air extracted by means of said outlet means and, on the other hand, to an external gas source for providing an adjustment of the temperature of the heated gas issuing from the at least one additional plasma torch.

The invention concerns also a method for revamping a conventional annular shaft kiln for manufacturing an annular shaft kiln according to the present invention. Such a method comprises the following steps :

- removing burners in each combustion chambers arranged as upper gas injection means at a first level of the annular space of said conventional annular shaft kiln,

- removing burners in each combustion chambers arranged as lower gas injection means at a second level of the annular space of said conventional annular shaft kiln, which is lower than said first level,

-replacing each of said removed burners by a plasma torch able to heat a gas, in such a manner that the so heated gas be introduced into said combustion chambers,

- connecting each plasma torch with a source of gas to heat and each combustion chamber with a source of control or adjusting gas so that each combustion chamber of said classical annular shaft kiln becomes a mixing chamber wherein said heated gas is mixed with the control or adjusting gas for providing a gaseous mixture to inject into the annular space which has a controlled temperature equal or higher than the temperature of calcination of the loaded mineral stones, at the lower level, and an adjusted temperature allowing a calcining of the stones, at the upper level.

As it is to remark, only a replacement of burners by plasma torches within chambers already provided as combustion chambers and now used as mixing chambers is sufficient and necessary for modifying a classical kiln in a kiln which does not need combustion of fuel, particularly of fossil fuel.

Other features and details of the method and kiln according to the invention are indicated in the appended claims. Other particularities of the invention will also result from the non-limiting description given below, with reference to the drawings.

Figure 1 illustrates schematically a classical annular shaft kiln according to the prior art.

Figure 2 illustrates schematically an embodiment of a kiln according to the invention.

Figure 3 illustrates schematically another embodiment of the second level of a kiln according to the invention.

Figure 4 illustrates schematically another embodiment of the first level of a kiln according to the invention.

Figure 5 illustrates schematically an advantageous embodiment of a kiln according to the invention.

In the figures, identical or similar elements have the same references.

The kiln illustrated on Fig. 1 comprises an outer cylinder 1 and an inner cylinder 2 which form an annular space 3 wherein carbonated mineral stones descend by gravity. The stones

are introduced at the top of the kiln at the material inlet 4 and a decarbonated calcined material is collected by the discharge 5.

The fuel fumes are injected at two levels by means of burners arranged in combustion chambers 6 and 7 (4 to 6 combustion chambers at each level according to the kiln capacity). In the kiln of Fig.1 the totality of the fumes of the chambers 6 and a part of the fumes of the chambers 7 are drawn upwards by a fan 8, i.e. in countercurrent of the displacement of the material to calcine. They form of a gaseous effluent which is exhausted from the kiln by the upper outlet 9 , the removal duct 10, a treatment unit 11 and a stack 12. So the descending stones are preheated by heat exchange in the preheating zone A and calcined in a countercurrent calcination zone B. The other part of the hot gas issued from the lower combustion chambers 7 is aspired toward the bottom of the kiln by a reduced pressure provided at return vents 13 arranged in the inner cylinder at a level lower than the combustion chambers 7. In this zone C a co-current calcination of the stones takes place.

A cooling air inlet 14 is provided at the bottom of the annular space. The cooling air flows in counter-current of the decarbonated calcined material in a cooling zone D wherein it is so progressively heated. In the kiln of Fig.1, through the return vents 13, a gaseous stream containing the cooling air heated in contact with the decarbonated calcined material and the part of the lower hot gas aspired toward the bottom is sucked from the annular space 3 to the inner cylinder 2.

Via several recirculation ducts 15 the gaseous stream containing the heated cooling air is extracted from the inner cylinder 2 by means of aspiration means, such as eductors 16 (one eductor for each lower combustion chamber) and is recirculated at the level of the lower combustion chambers 7. The equilibrium between the draft toward the top and the aspiration toward the bottom is represented by the broken line 17.

This kiln further comprises an upper cylinder 20 which takes off a fraction of the gaseous effluent flowing to the top. Via a recovering duct 21 this gaseous fraction is introduced in a heat recovering means 22 wherein an heat exchange takes place between the recovered gaseous fraction and a driving air supplied by a feeding duct 23. The heated driving air is supplied via transfer ducts 24 to the eductors 16 in order to allow their functioning. The cooled fraction of gaseous effluent is removed toward the top of the kiln and the stack.

The fuel introduced in the combustion chambers 6 and 7 may be a solid fuel, as coke, coal, or a biomass, or a fluidic fuel such as natural gas, hydrogen, and so on. The fuel is

transferred to the burners 45 of the chambers 6 via supplying ducts 40 and to the burners 44 of the chambers 7 via supplying ducts 41.

In the upper combustion chambers 6, the oxidizer is air. Here this air is the cooling air extracted from the shell of the inner cylinder 2 which is supplied by the feeding duct 33 and is progressively heated during its climb in said shell while being recycled as oxidizer to the burners of the combustion chambers 6 and/or 7 via the recycling ducts 34 and/or 35. In the lower combustion chambers the oxidizer may be comprised of a mixture of the downwards sucked fumes and of the heated cooling air. By means of the eductors 16 this mixture is extracted from the inner cylinder 2 and recirculated into the combustion chambers 7 via recirculation ducts 15.

Each eductor 16 works by means of the driving air which is supplied by the feeding duct 23, heated in the heat recovering unit 22 and thereafter furnished to the eductors 16 by means of the transfer ducts 24.

The kiln according to the invention illustrated on Fig.2 is very similar to the kiln of the Fig.1. Here the main difference is that there is no more combustion of fuel, and particularly in the chambers 6 and 7. These chambers are now simply provided for mixing gas which are injected in the kiln under the form of a gas mixture at a controlled temperature for allowing a calcining of the stones. Here no more burners are necessary. These chambers (combustion chambers 6 and 7 in the kiln of Fig.1) become now mixing chambers 6' and 7' in the kiln according to the invention.

Upper gas injection means under the form of upper mixing chambers 6' are provided at a first level of the annular space for injecting into the annular space an upper hot gas.

Lower gas injection means under the form of lower mixing chambers 7' are provided at a second level of the annular space lower than the level of the chambers 6' for injecting a lower hot gas.

Hot gas is thus injected at two levels by means of several mixing chambers 6' and 7' (4 to 6 chambers at each level according the capacity of the kiln). In a general manner 1/3 of the hot gas is injected in the annular space by means of the mixing chambers 6' and 2/3 by means of the mixing chambers 7'.

The kiln of Fig.2 is divided in the same zones A, B, C, D and the displacement of the material to calcine and of the gaseous streams is identical to the kiln of Fig.1 at the difference that the gaseous streams do not contain any fuel combustion fumes.

Here also cooling air inlet 14 is provided at the bottom of the annular space. The cooling air flows in the same manner in counter-current of the decarbonated calcined material in a cooling zone D wherein it is so progressively heated. As in the kiln of Fig.1, through the return vents 13, a gaseous stream containing the cooling air heated in contact with the decarbonated calcined material and the part of the lower hot gas aspired toward the bottom is sucked from the annular space 3 to the inner cylinder 2.

Via the same recirculation ducts 15 the gaseous stream containing the heated cooling air is extracted from the inner cylinder 2 by means of aspiration means, such as eductors 16 (one eductor for each lower mixing chamber), and is recirculated at the level of the lower mixing chambers 7'.

At the difference of the kiln of Fig.1, the kiln of the invention is equipped with several lower plasma torches 18 (4 to 6 according to the capacity of the kiln) able to heat a gas. In the lower mixing chambers 7' the heated gas is mixed with a control gas for providing a gaseous mixture having a controlled temperature equal or higher than the temperature of calcination of the loaded mineral stones. The gas to heat may be comprised of the recirculated gaseous stream containing heated cooling air which has been extracted by the ducts 15 and the eductors 16. In the chambers 7' the heated gas is mixed with a control gas issued from a gas source 19 which has not been heated by a plasma torch 18 for providing a gaseous mixture having a controlled temperature which is injected into the annular space. Other arrangements may be conceived. For example, as illustrated on Fig. 3, the recirculated gaseous stream may be driven from the eductors directly into the chambers 7', as control gas, and the plasma torch is then supplied from a source 19 of a gas such as air, steam, CO_2, N_2. Another possibility is to heat a part of the recirculated gaseous stream and to use as control gas another part of the same recirculated stream which has not been heated.

A supply of water or air may be necessary and is injected in the mixing chamber 7'and/or directly in the plasma torch 18 from a separated source 42 (see Fig.2 and Fig.3).

This kiln further comprises an upper cylinder 20 which takes off a fraction of the gaseous effluent flowing to the top. Via a recovering duct 21 this gaseous fraction is introduced in an heat recovering means 22 wherein an heat exchange takes place between the recovered gaseous fraction and a driving air supplied by a feeding duct 23. The heated driving air is supplied via transfer ducts 24 to the eductors 16 in order to allow their functioning. The cooled fraction of gaseous effluent is removed toward the stack.

The kiln of Fig.2 is provided with several recirculation ducts 25. By means of these recirculation ducts, heated secondary cooling air is extracted from the shell of the inner cylinder 2 and is recirculated at the level of the upper mixing chambers 6'.

The kiln of Fig.2 is equipped with several upper plasma torches 26 (4 to 6 according to the capacity of the kiln) able to heat a gas and with the upper mixing chambers 6' wherein the heated gas is mixed with an adjusting gas for providing a gaseous mixture having an adjusted temperature appropriate for calcining the loaded mineral stones. The gas to heat may be comprised of heated secondary cooling air which, after being heated, is injected into the upper mixing chambers 6'. In these chambers the heated gas is mixed with an adjusting gas issued from a gas source 27, for example an air source, which has not been heated by a plasma torch 26. Other arrangements may be conceived. For example, as illustrated on Fig.4, the heated secondary cooling air may be introduced directly into the mixing chambers, as adjusting gas, and the gas to heat by the plasma torches may be supplied from the external gas source 27. Another possibility may also be to heat a part of the heated secondary cooling air, as gas to heat by the plasma torches, and to use another part of the heated secondary cooling air, as adjusting gas.

A supply of water or air may be necessary and is injected in the mixing chamber 6' and/or in the plasma torch 26 from a separated source 43.

In the kiln of Fig.2 the relative positions of the lower mixing chambers 7' and the return vents 13 in the inner shaft are the same as in the kiln of Fig.1. However it is possible to conceive another arrangement wherein the relative position of the mixing chambers 7' which inject lower hot gas into the annular space and the return vents 13 through which the cooling gas is aspired is so provided that the equilibrium illustrated by the broken line 17 is located just under the mixing chambers 7' (see Fig. 3). In this case the totality of the injected hot gas is drawn toward the top of the kiln, there is no co-current calcination and the heated gaseous stream aspired into the inner cylinder consists only of heated cooling air.

It results from the present comparison between a classical annular shaft kiln and a kiln of the invention that the structural differences are little and do not request expensive measures to revamp a known kiln to a kiln according to the invention and to profit of the very interesting advantages of the invention.

Example 1

In the following examples the different rates are expressed in Nm^3/t of produced lime.

In this example an embodiment of kiln as illustrated on Fig.1 is implemented as in the prior art. Above the working of such a kiln was already disclosed in detail. The kiln of this example allows a production of 150 t/day of lime. Limestone is introduced in the kiln by the material inlet 4 and is calcined under the form of quicklime which is collected by the discharge 5.

Standard burners 45 and 44 are provided on combustion chambers 6 and 7 arranged at two levels of the kiln. As fuel they are supplied with natural gas which is transferred to the burners via supplying ducts 40 and respectively 41. 67 vol % of the fuel are injected in the lower burners 44 and 33 vol% of the fuel in the upper burners 45.

800 Nm^3/t of cooling air are introduced in the kiln by the inlet 14 for cooling the calcined lime in counter-current. Through the return vents 13 the heated cooling air is sucked into the inner cylinder 2 with a portion of the fumes issuing from the lower combustion chambers 7 and this gaseous mixture is extracted from the top of the inner cylinder 2 by means of eductors 16. 1600 Nm^3/t of the extracted mixture containing the heated cooling air is so recirculated into the lower combustion chambers 7 at a temperature of 850°C. In order to allow a correct working of the eductors 16, 320 Nm^3/t of driving air are supplied via transfer ducts 24 to the eductors 16.

In the lower burners 44 the fuel is burned in presence of 175 Nm^3/t of an oxidizer which is the secondary air used for cooling the shell of the internal cylinder 2 and is extracted from the kiln by the recycling ducts 35.. In the lower combustion chambers 7 the temperature of the fumes reaches 1550°C.

In the upper burners 45 the fuel is burned in presence of 175 Nm^3/t of an oxidizer which is the secondary air used for cooling the shell of the internal cylinder 2 and is extracted from the kiln by the recycling ducts 34. In the upper combustion chambers 6 the temperature of the fumes reaches 1500°C.

The kiln has a thermal power of 7,5 MWth, i.e. 5 MWth from the lower burners 44 and 2,5 MWth from the upper burners 45.

After heat exchange with the calcareous stones descending by gravity in the kiln 2000 Nm^3/t of a gaseous effluent are exhausted from the upper outlet 9 of the kiln at a temperature of 250°C.

Example 2

In this example the classical ASK kiln according to Example 1 is revamped in a kiln according to the invention, illustrated on Figure 5, which is also able to produce 150 t/ day of quicklime.

The burners 45 and 44 are removed from each combustion chambers 6 and 7. Each upper burner 45 is replaced by an upper plasma torch 26 and each lower burner 44 is replaced by a lower plasma torch 18. Consequently, there is no more combustion of fuel in the chambers 6 and 7 and now they are called mixing chambers 6' and 7' wherein a gas heated by a plasma torch is mixed with a gas which controls or adjusts the temperature of a gaseous mixture to inject into the kiln.

As illustrated on Fig.5, in the lower plasma torches 18, 350 Nm^3/t of a gas, such as air or CO_2, issuing from the gas source 19 are heated in presence of 175 Nm^3/t of air issuing from the air source 42.

In the upper plasma torches 26, 175 Nm^3/t of a gas, such as air or CO_2, issuing from the external gas source 27, are heated in presence of 175 Nm^3/t of secondary air which was used for cooling the shell of the internal cylinder 2 and extracted from the kiln by the recycling ducts 25.

800 Nm^3/t of cooling air are introduced in the kiln by the inlet 14 for cooling the calcined lime in counter-current. Through the return vents 13 the heated cooling air is sucked into the inner cylinder 2 with a portion of the hot gas issuing from the lower mixing chambers 7' and this gaseous mixture is extracted from the top of the inner cylinder 2 by means of eductors 16. 1770 Nm^3/t of the extracted mixture containing the heated cooling air is so recirculated into the lower mixing chambers 7' at a temperature of 775°C. In order to allow a correct working of the eductors 16, 320 Nm^3/t of driving air are supplied via transfer ducts 24 to the eductors 16. In the lower mixing chambers the mean temperature of the mixture of the hot gas heated by the plasma torch 18 and of the recirculated gas is of 1420°C. If a higher temperature is necessary in the lower mixing chambers 7', for example of 1550°C, it is possible to reduce the flow of the air issuing from the air source 42 or to adapt the flow of cooling air in the kiln or to apply both solutions.

385 Nm^3/t of additional air are supplied to the upper mixing chambers 6' from the external gas source 43. This additional air is used for adjusting the temperature of the hot gaseous mixture issuing from the plasma torches 26 to an appropriate mean value of 1500°C.

Without this addition, the temperature would be close to 3000°C, such a value being not appropriate.

The kiln has a thermal power of 8,2 MWth, i.e. 5,5 MWth from the lower plasma torches 18 and 2,7 MWth from the upper plasma torches 26.

After heat exchange with the calcareous stones descending by gravity in the kiln 3000 Nm^3/t of a gaseous effluent are exhausted from the upper outlet 9 of the kiln at a temperature of 300°C.

In conclusion a classical kiln, such as disclosed in Example 1, may be transformed in a kiln of the invention, as disclosed in Example 2, in an extremely simple manner, kiln wherein no fossil fuel has to be burned.

Obviously, the present invention is not limited to the disclosed embodiments and several modifications may be provided without being outside the scope of the appended claims.

CLAIMS

1. A process for calcining carbonated mineral stones in an annular vertical kiln having an outer cylinder and an inner cylinder forming an annular space, comprising:

- a loading step of carbonated mineral stones at the top of the kiln,
- an injection of an upper hot gas into the annular space at a first level thereof,
- an injection of a lower hot gas into the annular space at a second level lower than the first level,
- a preheating step in a preheating zone of said loaded carbonated mineral stones flowing downwardly in the annular space,
- a calcining step of said preheated carbonated mineral stones in a calcination zone located in the annular space below the preheating zone, said preheating and calcining steps of said carbonated mineral stones flowing downwardly in the annular space taking place successively in contact with the upper hot gas and the lower hot gas which are at least partially submitted to an upwards draft in counter-current of the carbonated mineral stones and exhausted from the top of the kiln under the form of a gaseous effluent,
- an introduction of cooling air at the bottom of the kiln,
- a cooling step in a cooling zone below the calcination zone of decarbonated calcined material flowing downwardly, with cooling air flowing in counter-current through said decarbonated calcined material and forming a heated cooling air,
- an aspiration step of said heated cooling air into the inner cylinder at a third level lower than said second level, under the form of a gaseous stream containing said heated cooling air,
-a recirculation of the gaseous stream containing said heated cooling air from the inner cylinder to said injection step of a lower hot gas, and
- a discharging step of the decarbonated calcined material from the bottom of the kiln,

characterized in that said process further comprises a first heating step of a gas by means of at least one plasma torch for producing a lower heated gas, and a first step of mixing in a lower mixing chamber said lower heated gas with a control gas which is not heated by the at least one plasma torch for controlling a temperature of a first gaseous mixture which is said lower hot gas injected into the kiln at the second level of the annular space, the controlled temperature allowing a calcining of the carbonated mineral stones.

2. Process according to claim 1, characterized in that a) the lower heated gas which is heated by at least one plasma torch is selected among the group consisting of air,

N_2, CO_2, steam, noble gas and their mixtures and the control gas is comprised of recirculated gaseous stream containing said heated cooling air or b) the lower heated gas which is heated by at least one plasma torch is comprised of recirculated gaseous stream containing said heated cooling air and the control gas is selected among the group consisting of air, N_2, CO_2, steam, and their mixtures or c) the lower heated gas which is heated by at least one plasma torch as well as the control gas are comprised of recirculated gaseous stream containing said heated cooling air.

3. Process according to claim 2, wherein, during the first heating step, air and/or water is additionally introduced in the at least one plasma torch and/or mixed in the first gaseous mixture.

4. Process according to anyone of claims 1 to 3, comprising a second heating step of a gas by means of at least one additional plasma torch for producing an upper heated gas, and a step of mixing in an upper mixing chamber said upper heated gas with an adjusting gas which is not heated by the at least one additional plasma torch for adjusting a temperature of a second gaseous mixture which is said upper hot gas introduced at the first level of the annular space, the adjusted temperature allowing a calcining of the carbonated mineral stones.

5. Process according to anyone of claims 1 to 4 comprising cooling of the internal cylinder by secondary air and extracting an heated secondary air from the kiln.

6. Process according to claim 5, characterized in that a) the upper heated gas which is heated by said at least one additional plasma torch in the second heating step is selected among the group consisting of air, N_2, CO_2, steam, noble gas and their mixtures and the adjusting gas is comprised of said heated secondary air or b) the upper heated gas which is heated by said at least one additional plasma torch is comprised of said heated secondary air and the adjusting gas is selected among the group consisting of air, N_2, CO_2, steam, and their mixtures or c) the upper heated gas which is heated by said at least one additional plasma torch as well as the adjusting gas are comprised of said heated secondary air.

7. Process according to claim 5, characterized in that, in said at least one additional plasma torch, a gas selected among the group consisting of air, N_2, CO_2, steam, noble gas and their mixtures is heated in presence of said heated secondary air and an adjusting gas is additionally injected in said upper mixing chamber.

8. Process according to claim 6 or 7, wherein, during the second heating step, air and/or water is additionally introduced in said at least one additional plasma torch and/or mixed in said second gaseous mixture.

9. Process according to anyone of claims 1 to 8, wherein said upwards draft and said aspiration of the aspiration step are equilibrated so that a first part of the lower hot gas introduced into the annular space is upwards drawn in counter-current of the stones to calcine and a second part of the lower hot gas is supplied downward the bottom of the annular space, in co-current with the mineral stones to calcine, and thereafter aspired inside the inner cylinder, while forming with said cooling air and CO_2 from the decarbonation in the co-current calcination zone said gaseous stream containing said heated cooling air.

10. Process according to anyone of claims 1 to 8, wherein said upwards draft and said aspiration of the aspiration step are equilibrated so that the totality of the lower hot gas introduced into the annular space is submitted to the upwards draft, the gaseous stream aspired in the inner cylinder comprising only cooling air.

11. Process according to any one of claims 1 to 10, characterized in that said lower and upper hot gas which are drawn toward the top of the kiln form a gaseous stream which is partially recovered out of the kiln before the exhaust of the gaseous effluent at the top of the kiln and in that the process further comprises a heat exchange between this recovered gaseous stream and a gas to recirculate toward said first heating step.

12 . Annular shaft kiln for calcining carbonated mineral stones, comprising

- an outer cylinder (1),
- an inner cylinder (2), forming an annular space (3) with the outer cylinder (1),
- material inlet means (4) for feeding said carbonated mineral stones at the top of the kiln into the annular space (3),
- upper gas injection means at a first level of the annular space, provided for injecting an upper hot gas,
- lower gas injection means at a second level of the annular space lower than the level of the first gas injection means, provided for injecting a lower hot gas,
- a cooling air inlet (14), provided at the bottom of the annular space for cooling a decarbonated calcined material,
- material discharge means (5) at the bottom of the kiln for discharging the decarbonated calcined material out of the kiln,

- upper gas outlet means (9) at the top of the kiln for exhausting a gaseous effluent into a removal duct (10),

- return vents (13) in the inner cylinder (2) at a third level lower than said second level, through which a gaseous stream containing the cooling air heated in contact with the decarbonated calcined material is sucked from the annular space (3) into the inner cylinder (2), and

-means for recirculating said gaseous stream containing the heated cooling air from the inner cylinder (2) at least partially to the lower gas injection means,

characterized in that, at said second level, said kiln is equipped with at least one plasma torch (18) for heating a gas and with, as lower gas injection means, at least one lower mixing chamber (7') which is connected to the at least one plasma torch (18) for mixing the heated gas with a control gas and thereby providing a gaseous mixture which is said lower hot gas to inject having a controlled temperature equal or higher than the temperature of calcination of the loaded mineral stones.

13. Annular shaft kiln according to claim 12, wherein a) the at least one lower mixing chamber (7') is connected to the at least one plasma torch (18) which is supplied from an external gas source (19) and to said means for recirculating said gaseous stream containing the heated cooling air, said gas heated by said at least one plasma torch (18) being mixed in said at least one lower mixing chamber (7') with recirculated gaseous stream containing the heated cooling air as control gas, for providing said lower hot gas to inject having a controlled temperature equal or higher than the temperature of calcination of the loaded mineral stones, or b) the at least one lower mixing chamber (7') is connected to an external gas source (19), for providing control gas, and to the at least one plasma torch (18) which is connected to said means for recirculating said gaseous stream containing heated cooling air, said control gas being mixed in said at least one lower mixing chamber (7') with said recirculated gaseous stream heated by the at least plasma torch (18), for providing said lower hot gas to inject having a controlled temperature equal or higher than the temperature of calcination of the loaded mineral stones or c) the at least one lower mixing chamber (7') is connected to the at least one plasma torch (18) and to said means for recirculating said gaseous stream containing the heated cooling air, the at least one plasma torch being also connected to the means for recirculating said gaseous stream containing the heated cooling air, a part of the recirculated gaseous stream containing the heated cooling air which has been heated by the at least one plasma torch being mixed in said at least one lower mixing chamber

with, as control gas, another part of said recirculated gaseous stream which has not been heated by the at least one plasma torch.

14. Annular shaft kiln according to claim 12 or 13, characterized in that, at said first level, said kiln is equipped with at least one additional plasma torch (26) for heating a gas and with, as upper gas injection means, at least one upper mixing chamber (6') which is connected to the at least one additional plasma torch (26) for mixing the heated gas with an adjusting gas which has not been heated by the at least one additional plasma torch and thereby providing a gaseous mixture which is said upper hot gas to inject and having an adjusted temperature allowing a calcining of the loaded mineral stones.

15. Annular shaft kiln according to anyone of claims 12 to 14 further comprising inlet means (33) for secondary cooling air which are connected with the interior of the shell of the inner cylinder (2), and outlet means (25) able to extract the heated secondary cooling air out of the kiln.

16. Annular shaft kiln according to claim 15, wherein a) the at least one upper mixing chamber (6') is connected to the at least one additional plasma torch (26) which is supplied from an external gas source (27), and to said outlet means able to extract said heated secondary cooling air (25), said gas heated by said at least one additional plasma torch (26) being mixed in said at least one upper mixing chamber with said heated secondary cooling air as control gas, for providing said upper hot gas to inject having an adjusted temperature equal or higher than the temperature of calcining of the loaded mineral stones or b) the at least one upper mixing chamber (6') is connected to an external gas source (27), for providing a control gas, and to the at least one additional plasma torch (26) which is connected to said outlet means able to extract the heated secondary cooling air (25), said control gas being mixed in said at least one upper mixing chamber with said heated secondary cooling air heated by the at least one additional plasma torch, for providing said upper hot gas to inject having an adjusted temperature equal or higher than the temperature of calcining of the loaded mineral stones or c) the at least one upper mixing chambers (6') is connected to the at least one additional plasma torch (26) and to said outlet means able to extract the heated secondary cooling air (25), the at least one additional plasma torch being also connected to the said outlet means able to extract the heated secondary cooling air, a part of the extracted heated secondary air which has been heated by the at least one additional plasma torch being mixed in said at least one upper mixing chamber (6') with, as control gas, another part of said

extracted heated secondary cooling air which has not been heated by the at least one additional plasma torch (26).

17. Annular shaft kiln according to anyone of claims 14 to 16, characterized in that the at least one upper mixing chamber (6') is connected, on the one hand, to the at least one additional plasma torch (26) which is supplied with a gas to heat from an external gas source (27) in presence of the heated secondary cooling air extracted by means of said outlet means (25) and, on the other hand, to an external gas source (43) for providing an adjustment of the temperature of the heated gas issuing from the at least one additional plasma torch.

18. Method for revamping a conventional annular shaft kiln to manufacture an annular shaft kiln according to any of the claims 12 to 17, comprising the following steps :

- removing burners in each combustion chambers arranged as upper gas injection means at a first level of the annular space of said conventional annular shaft kiln,

- removing burners in each combustion chambers arranged as lower gas injection means at a second level of the annular space of said conventional annular shaft kiln, which is lower than said first level,

-replacing each of said removed burners by a plasma torch able to heat a gas, in such a manner that the so heated gas be introduced into said combustion chambers,

- connecting each plasma torch with a source of gas to heat and each combustion chamber with a source of control or adjusting gas so that each combustion chamber of said classical annular shaft kiln becomes a mixing chamber wherein said heated gas is mixed with the control or adjusting gas for providing a gaseous mixture to inject into the annular space which has a controlled temperature equal or higher than the temperature of calcination of the loaded mineral stones, at the lower level, and an adjusted temperature allowing a calcining of the stones at the upper level, at the upper level.

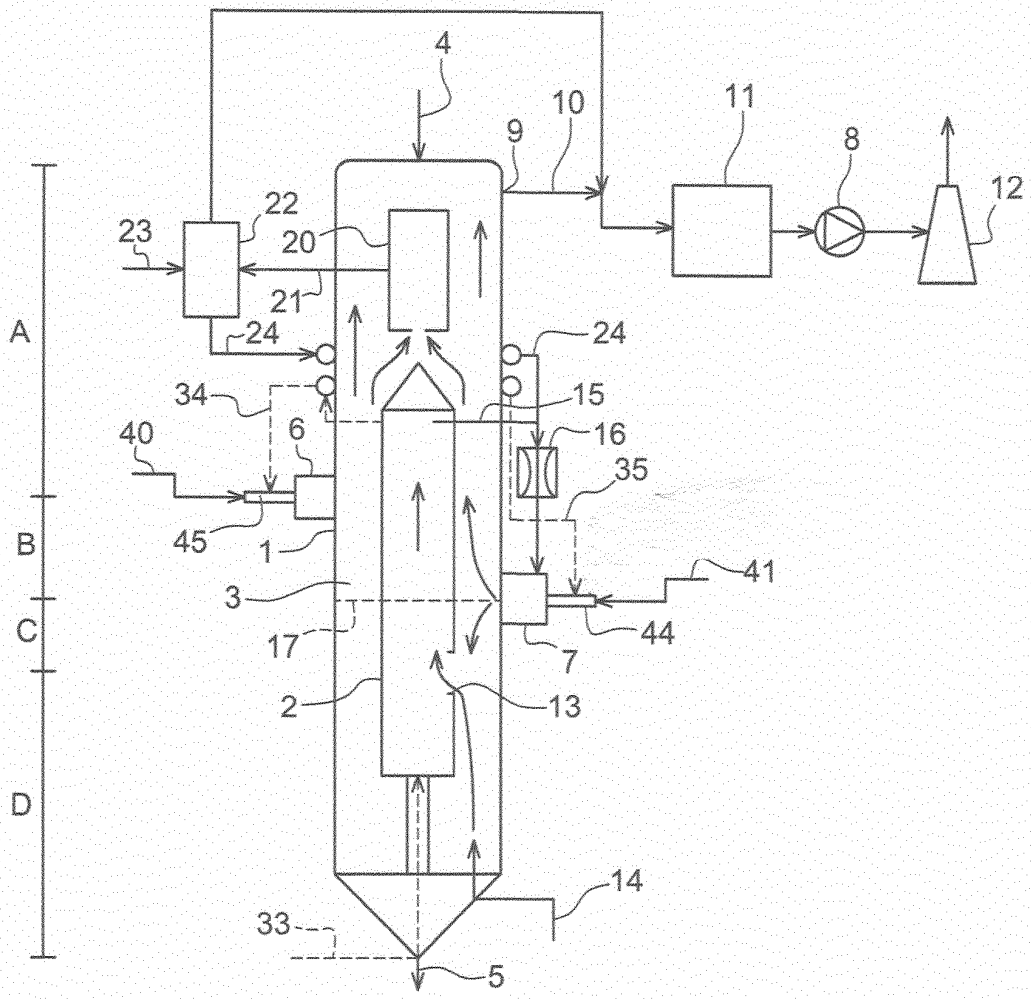

4
10
11
9
8
12
22
23
20
21
24
24
34
15
40
6
16
35
45
1
41
3
44
17
7
2
13
14
33
5
A
B
C
D

Fig. 1

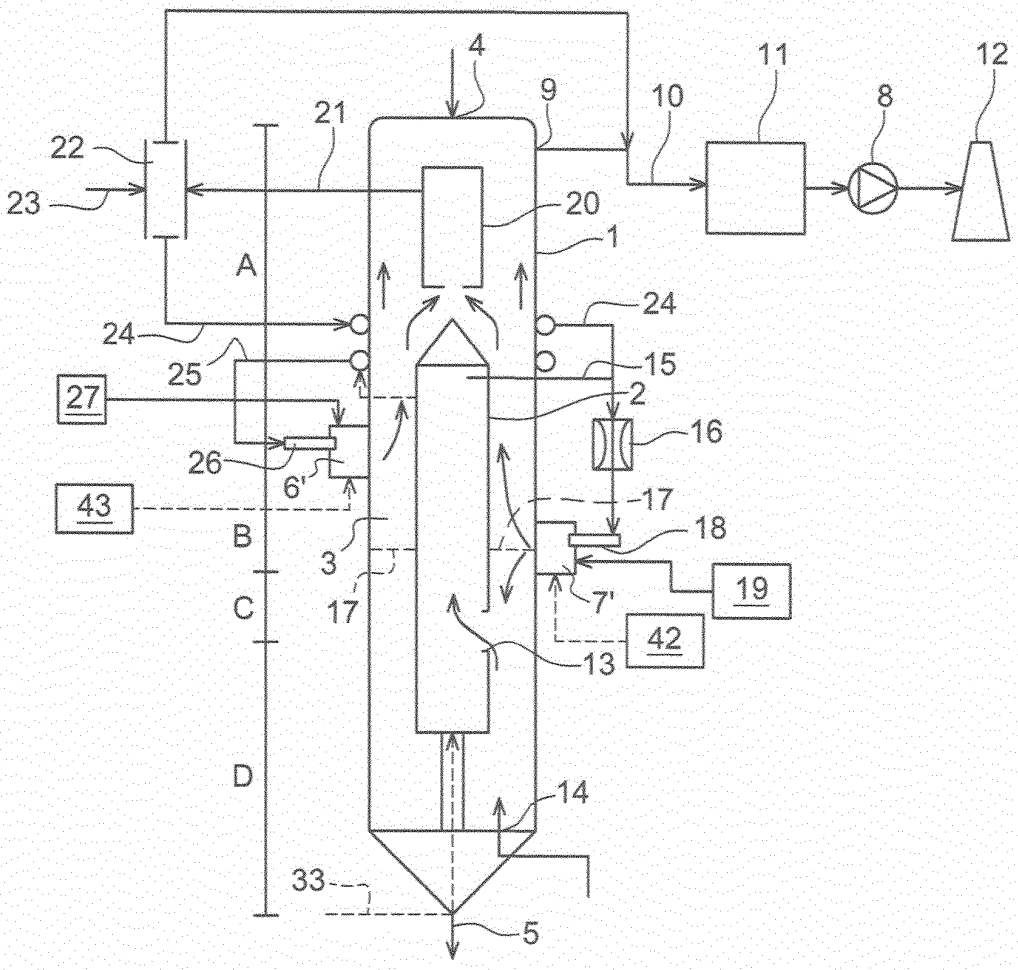

4
11
12
9
10
8
21
22
23
20
1
A
24
24
25
15
27
2
16
26
6'
17
43
B
18
3
19
17
7'
C
42
13
D
14
33
5

Fig. 2

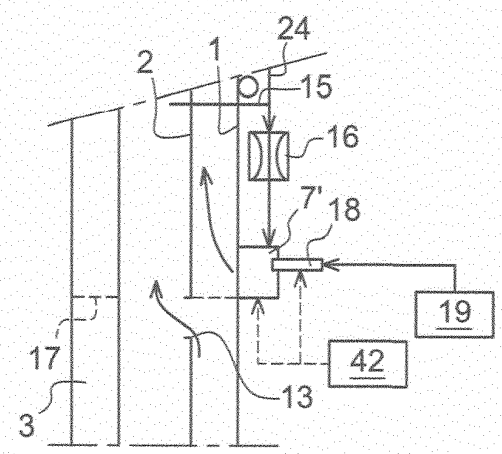


Fig. 3

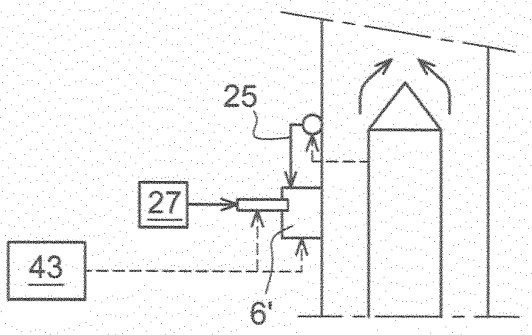


Fig. 4

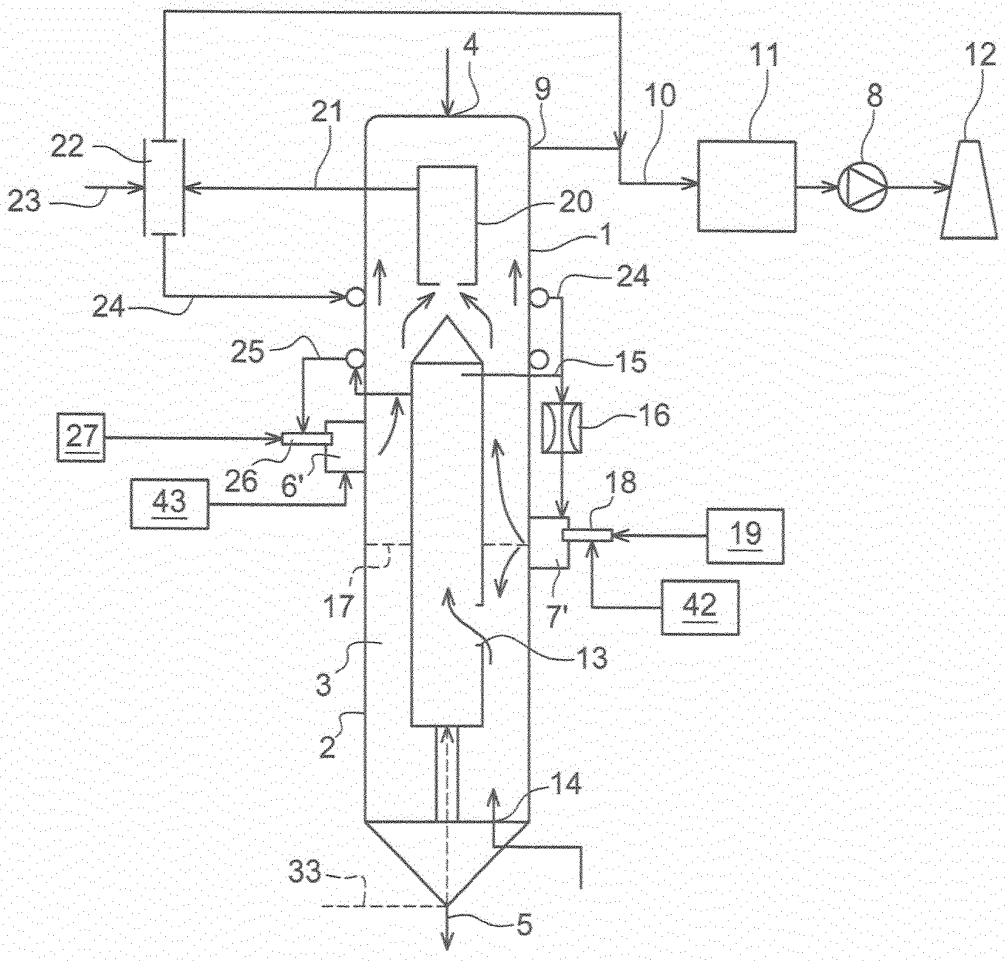

4
11
12
9
10
8
21
22
23
20
1
24
24
25
15
27
16
26
6'
43
18
19
17
7'
42
13
3
2
14
33
5

Fig. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/087209

A. CLASSIFICATION OF SUBJECT MATTER
INV. C04B2/12 F27B1/00 C04B28/02 F27B1/08 F27B1/10
F27D99/00
ADD.
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C04B F27B F27D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 452 584 A (BECKENBACH ULRICH [DE] ET AL) 5 June 1984 (1984-06-05) figures 1-10 column 2, line 5 - column 3, line 55 column 4, line 20 - column 6, line 61	1-18
Y	CN 204 125 380 U (SHIJIAZHUANG XINHUA ENERGY ENVIRONMENTAL TECHNOLOGY CO LTD) 28 January 2015 (2015-01-28) figure 1 paragraph [0001] paragraph [0005] - paragraph [0010] paragraph [0014] - paragraph [0017]	1-18
A	US 4 332 641 A (MCCONAGHY JAMES R ET AL) 1 June 1982 (1982-06-01) the whole document	1-18

-/--

[x] Further documents are listed in the continuation of Box C.

[x] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
7 March 2024	15/03/2024

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Jung, Régis

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/087209

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 626 200 A (COHEN SIDNEY M [US]) 2 December 1986 (1986-12-02) the whole document -----	1-18

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2023/087209

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 4452584 A	05-06-1984	AT E14110 T1	15-07-1985
		CA 1173239 A	28-08-1984
		EP 0082886 A1	06-07-1983
		US 4452584 A	05-06-1984
		ZA 821428 B	23-02-1983
CN 204125380 U	28-01-2015	NONE	
US 4332641 A	01-06-1982	NONE	
US 4626200 A	02-12-1986	NONE	