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| <p><b>(51) International Patent Classification:</b><br/> <b>C22B 1/00</b> (2006.01)      <b>C01D 15/08</b> (2006.01)<br/> <b>B01J 8/26</b> (2006.01)      <b>C22B 1/10</b> (2006.01)</p>                                | <p><b>(74) Agent: KEIL &amp; SCHAAFHAUSEN PATENT- UND RECHTSANWÄLTE PARTGMBB;</b> Friedrichstraße 2-6, 60323 Frankfurt am Main (DE).</p>                                                                                                                                                                                                                                                                                                                                                                                                                                                                                   |
| <p><b>(21) International Application Number:</b><br/> PCT/EP2017/055937</p>                                                                                                                                             | <p><b>(81) Designated States</b> <i>(unless otherwise indicated, for every kind of national protection available):</i> AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.</p> |
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*[Continued on next page]*

- (54) Title:** PROCESS AND FACILITY FOR THERMAL TREATMENT OF GRANULAR SOL

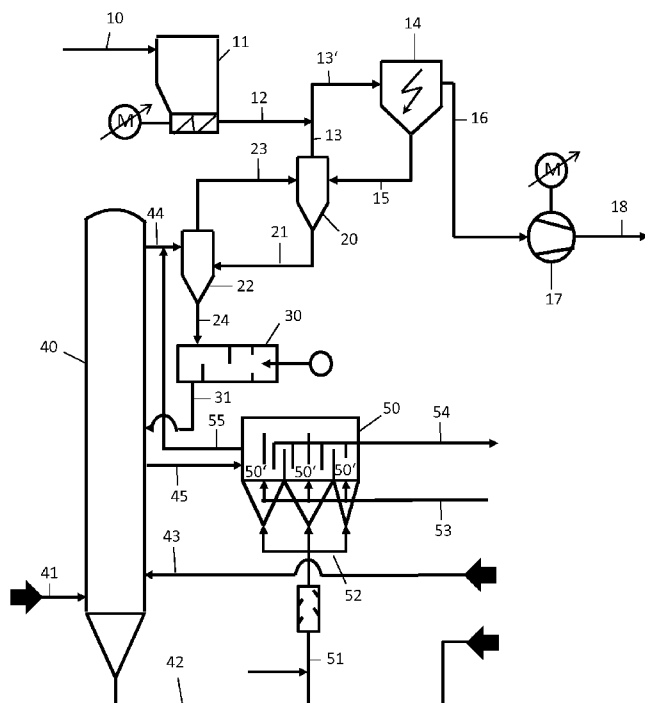


Fig. 1

- (57) Abstract:** The invention relates to a process for thermal treatment of granular solids, wherein the solids at first are fed into a first reactor being designed as a flash reactor or a fluidized-bed reactor, where they are, in the case of a fluidized-bed reactor at a temperature of between 500 and 1500 °C or in the case of a flash reactor at a flame temperature of between 500 and 1500°C, brought into contact with hot gases. Subsequently, the solids are guided through a residence time reactor, in which they are present in fluidized form and from which they are drawn off after a residence time of 10 to 600 min. Into the residence time reactor an additional fuel is introduced, whereby the temperature in the residence time reactor is at least as high as in the first reactor.



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**Declarations under Rule 4.17:**

— *of inventorship (Rule 4.17(iv))*

### Process and facility for thermal treatment of granular solids

The invention relates to a process for thermal treatment of granular solids, wherein the solids at first are fed into a first reactor being designed as a flash reactor or a fluidized-bed reactor, where they are, at temperatures of between 500 and 1500 °C, brought into contact with hot gases, wherein the solids are subsequently guided through a residence time reactor, in which they are present in fluidized form and from which they are drawn off after a residence time of 10 to 600 min. The residence time in the residence time reactor is variable due to a number of compartments, which are in operation or not. Furthermore, the invention comprises also a facility for conducting the process.

A series of thermal processes for treating solids require very exact temperatures for achieving the desired conversion. Examples for such a reaction are the thermal reactions required for the recovery of lithium carbonate by phase conversions of lithium-bearing ores such as  $\alpha$ -spodumene, petalite, zinnwaldite and lepidolite. This reaction is required for the phase transition in the lithium bearing mineral to enable an acid respectively soda leaching in the downstream hydro metallurgical section. Another example is calcination of phosphate rock

In this context it was shown to be advantageous to carry out the thermal treatment in reactors in which it is guaranteed that the required narrow temperature window is neither fallen below of nor exceeded. This, in the first instance, is a circulating fluid bed reactor which, together with its features, is known from DE 36 22 105 A1.

However, both, the circulating fluid bed and also the flash reactor, are characterized by the disadvantage that with them the residence time can only be adjusted in a limited manner, in the case of the flash reactor in the range of seconds and

in the case of the circulating fluid bed in the low single-digit range of minutes. In a fluid bed the residence time is a consequence of the feed of solids into the reactor and the solid stock which is proportional to the pressure loss between the reactor bottom and the upper level of the reactor. When the residence time  
5 in the reactor is increased and at the same time the feed rate is remained constant, then due to the higher stock of the reactor a higher pressure loss results from this higher load. In this case, the increase of the pressure loss across the reactor, normally, is limited by the maximum pressure increase of the fans used. At the same time, also a certain minimum load and minimum feed rate are re-  
10 quired for generating a homogenous fluid bed. Thus, in summary, as shown in DE 36 22 105 A1, a residence time window results which is strongly limited and which for the circulating fluid bed in large industrial plants is typically between about 3 and 10 minutes.

15 Therefore, it is an object of the invention to provide a process with which the thermal treatment of granular solids within a small temperature window is possible without any limitation with respect to the residence time.

This object is solved by an invention with the features of patent claim 1.

20 Such a process, in a first step, comprises a flash reactor or a fluidized-bed reactor into which granular solids are fed and in which they are brought into contact with hot gases having a temperature of between 500 and 1500 °C (or in the case of using a flash reactor, a flame temperature of between 500 and  
25 1500 °C). Subsequently, the solids are guided through a residence time reactor in which they are also present in fluidized form. The residence time in the residence time reactor is between 10 and 600 min, and the residence time is variable. The variable residence time is achieved by dividing the residence time reactor vessel into a number of compartments. The number of compartments in  
30 operation or not may be selected according to the requirements of the process.

The subject matter of the invention is that the temperature in the residence time reactor is at least as high as the temperature in the flash reactor and/or the fluidized-bed reactor and thus in both consecutive reactors comparable process conditions prevail. This is achieved by introducing additional fuel into the residence time reactor, which in the residence time reactor due to the temperatures prevailing there burns and also provides energy. So, cooling effects which, for example, emerge due to lines respectively ducts between both reactors and also temperature losses within the residence time reactor can be compensated. As a result it is possible to initiate, in a first step, the desired reaction and to virtually exclude undesired side reactions and sintering due to the small temperature window by which the first reactor is characterized. At the same time, with the subsequent treatment in the residence time reactor it can be guaranteed that the reaction in deed completely proceeds.

In a preferable embodiment of the invention the residence time in the flash reactor is between 0.1 and 10 sec, preferably 1 and 5 sec or in the fluidized-bed reactor between 10 sec and 10 min, preferably between 1 min and 10 min. So the advantages of this first type of reactor with respect to the homogeneity of the temperature distribution can be utilized fully without any disadvantages in this step by an artificially prolonged residence time.

Basically, it is also possible to use an inert fluidization gas with respective temperature which is generated e.g. in an external combustion chamber. A further possibility is to feed the fuel and the oxygen which is required for burning into the residence time reactor via separate nozzle systems. Also in this case the fuel feed is not limited by the explosive limit.

Preferably, air is used as a fluidization gas in the residence time reactor, particularly preferably also in an upstream circulating fluid bed furnace. Air has the

advantage that it is abundant, available everywhere and in addition contains oxygen which is required for burning the additional fuel and thus for the generation of further energy.

5 In addition, it is preferable to feed the fuel in gaseous form and according to the required amount either together with the fluidization gas or as described via a separate nozzle system. This has the advantage that it can be dosed very easily and in addition guarantees a complete combustion. Particularly preferable is a gas which contains at least 80 % by volume of methane. Especially preferable is  
10 natural gas.

One embodiment of the invention is characterized by feeding the additional fuel jointly together with the fluidization gas into the residence time reactor. So it will be possible to save further equipment for this additional fuel injection and instead of that to use the present fluidization gas feed o. In addition, in this way a  
15 uniform continuous feed of the fuel and a thorough mixing with the fluidization gas can be achieved.

In another embodiment of the invention the gaseous fuel is fed into the residence time reactor separately from the fluidization gas. This is required in particularly in the case, when the fluidization gas contains oxygen, because in this case the added amount of fuel is limited by the explosive limit. When natural gas is used as a fuel and air is used as a fluidization gas, depending on the temperature and other conditions this limit is between 3 and 4 % by volume. A separate feed of the fuel can be realized by a second nozzle system in the lower  
20 area of the residence time reactor. Another option is feeding via the side walls.

According to the use, it may be favorable to feed the fuel in such an amount that the residence time reactor is running either under reducing or oxidizing conditions. Oxidizing conditions mean a small excess of oxygen, typically a Lambda  
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(ratio of the used amount of air to the stoichiometrically required amount of air being required for exactly oxidizing all oxidizable constituents) of 1.1 – 1.3. Reducing conditions mean a deficit amount of oxygen below the stoichiometric amount of oxygen, typically a Lambda of 0.6 – 0.9. So a change between the first reactor and the second reactor from oxidizing conditions to reducing conditions or vice versa can be realized, resulting in expanding the spectrum of possible applications.

In a preferable embodiment of the invention the fluidized-bed reactor as the first reactor comprises a circulating fluid bed furnace. The advantage of a circulating fluid bed is that it allows adjusting the temperature prevailing in the reactor in a particularly homogenous and targeted manner. At the same time, however, it is in particular characterized by the disadvantage that residence times of maximum 10 minutes are possible.

For the example of calcining a spodumene concentrate to produce lithium bearing intermediates, like lithium carbonate or lithium hydroxide, the temperature in both reactors, the first reactor and the second residence time reactor, is between 1060 and 1090 °C, which corresponds to the temperature for the conversion of alpha-spodumene to beta-spodumene during the recovery of lithium carbonate from lithium-containing ores.

The feedstock from the concentration plant will be calcined having a moisture content in the range of typically 4 – 10 wt-%. Calcination of the concentrates includes drying, pre-heating, calcination and cooling of the calcine to a temperature defined by the downstream process. The temperature in the furnace should be as high as possible to accelerate the conversion reaction, and to reduce or limit residence time. This limitation of the residence time is mainly driven by reducing the size of the reactor. On the other hand, there is a limitation in reaction temperature as sintering at the particle surface will start at temperatures

above 1100°C, which will reduce conversion efficiency of the calcination process, but also will lead to sticking inside the reactor.

In summary, the furnace temperature needs to be limited. This limitation of temperature needs to be compensated by a higher residence time in the reactor. The residence time corresponding to a furnace temperature of 1060 and 1090 °C is preferably between 20 -30 minutes. This residence time cannot be reached with a circulating fluidized bed reactor or flash reactor alone. Therefore an additional residence time reactor is installed downstream of one of these reactors to ensure that a sufficient residence time will be achieved.

In addition, the invention also comprises an apparatus with the features of patent claim 10. Such an apparatus is preferably designed such that a process with any of the features of claims 1 to 9 can be operated therein.

Such an apparatus comprises a first reactor being designed as a flash reactor or a fluidized-bed reactor. In addition, it comprises a second reactor, the so-called residence time reactor, being designed such that in it the solid is present in fluidized form. Via a first line granular solid is fed into the first reactor and via at least one second line it is transferred from the first reactor into the residence time reactor. Subject matter of the invention is that the residence time reactor comprises facilities for feeding in additional fuel so that it is possible through this additional burning to add energy to the system in a manner that the temperature in the residence time reactor is just about as high as the temperature in the first reactor.

The residence time in the residence time reactor is variable. This is accomplished by a residence time reactor vessel capable to incrementally reduce its active volume. This is achieved by providing a residence time reactor subdivided

into a number of compartments which provide for a defined solids flow, thus ensuring a technically uniform residence time for all solids.

Preferably, the number of compartments in operation can be chosen so as to best suit any preferred process conditions flexibly, thereby allowing the regulation of residence time within the residence time reactor to flexibly vary between 10 to 600 minutes in one apparatus. So, the claimed reactor can be flexible switch to a residence time in dependence of the used starting material(s).

In one embodiment, at least one, or several of the compartments, preferably however all of the compartments of the residence time reactor vessel are tapped and preferably the tapping points are connected to a mutually shared conveying device which transports the discharged hot solids to the next process step. This enables withdrawing of the product from each compartment simultaneously and, thereby, with achieving products as a result of different residence times in one apparatus.

Moreover, the invention is directed to the use of an apparatus to with the features on any claim 10 to 14, preferably to produce/recover lithium-bearing intermediates, like lithium carbonate or lithium hydroxide from lithium-containing ores due to the process requirements discussed above.

Further objectives, features, advantages and possible applications of the invention also follow from the description of the enclosed figures below. Here, all described and/or depicted features form on its own or in arbitrary combination the subject matter of the invention, independently from their summary in the single patent claims or their back references.

Shown is:

In Fig. 1 a process flow diagram of the process according to the present invention.

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Via line 10 the solid is charged into a storage vessel 11, from which it is mixed via line 12 into line 13 and is fed into an electrical precipitator 14 via line 13'. From the electrical precipitator 14 the granular solid is transported into the first preheater stage 20 via line 15.

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From the first preheater stage 20 hot gas is drawn off via line 13 and is fed into the electrical precipitator 14' via line 13' together with the solid in known manner, in which a first preheating and a separation of the solid from the gas is realized. Subsequently, the gas is fed into a compressor 17 via line 16 and then into a facility for after-treatment of exhaust gases for purification (not shown) via line 18.

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The solid is transported from the first preheater stage 20 via line 21 into the second preheater stage 22. For optimizing the energy efficiency of the process, the hot gas is returned back in a counter-flow manner from the preheater stage 22 into the first preheater stage 20 via line 23.

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Via line 24 the solid is fed into a discharging device 30 from which either via line 31 it is fed into the first reactor 40 being designed as a circulating fluid bed or via line 32 it is discharged from the furnace system and fed into the downstream residence time reactor 50. The residence time reactor vessel is subdivided into a number of compartments 50' which provide for a defined solids flow, thus ensuring a technically uniform residence time for all solids. The number of compartments in operation may be flexibly changed according to process requirements, therefore allowing for variable residence time of 10 to 600 minutes within

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the residence time reactor. At least one compartment, or several compartments, preferably however all of the compartments of said vessel are tapped, and the tapping points are connected to a mutually shared conveying device which transports the discharged hot solids to the next process step..

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This first reactor 40 is charged with fuel via line 41. Furthermore, for the fluidization the so-called primary air is fed at the bottom of reactor 40 via line 42, 42'. For forming a circulating fluid bed, in addition, secondary air is required which is introduced via line 43.

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Via line 44 the hot exhaust is drawn off from the first reactor and is fed into the return cyclone 22 for separating the solid particles from the hot gas and for returning them again back into reactor 40 via the furnace seal pot 30. The solid is discharged via the discharging device 30 from which it is guided into the residence time reactor 50. For the fluidization of the solid, from the feed line of the primary air 42 a line 51 branches off and it is transported as fluidization air into the residence time reactor 50. Line 52 is the first possibility for introducing the additional fuel which is then mixed with the fluidization air already in line 51'. In addition or as an alternative, the fuel can also be fed directly into the residence time reactor 50 via a separate system, as is suggested with line 53. Also possible is the fluidization via an inert gas with respective temperature being generated in a separate firing chamber.

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Then the solid is discharged via line 54. Subsequently, here it is imaginable to use for example a seal pot, as shown in DE 10 2009 0326785. The hot air from the residence time reactor 50 is mixed into line 44 via line 55 and then it is returned back into the second preheater stage 22.

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One example for the use of the process is the calcination of spodumene ores for achieving a phase conversion of alpha-spodumene into beta-spodumene. The

reaction proceeds at 1050 °C. The conversion depends on the residence time, namely, the longer the residence time, the higher the conversion. For achieving a conversion of higher than 90 %, a residence time of at least 30 minutes is required. Therefore, the use of a flash reactor or a circulating fluid bed (ZWS) is  
5 only possible, when downstream to these reactors a residence time reactor is provided.

**List of reference signs**

|    |            |                                    |
|----|------------|------------------------------------|
|    | 10         | line                               |
| 5  | 11         | solid stock                        |
|    | 12,13, 13' | line                               |
|    | 14         | electrical precipitator            |
|    | 15, 16     | line                               |
|    | 17         | compressor                         |
| 10 | 18         | line                               |
|    | 20         | first preheater stage              |
|    | 21         | line                               |
|    | 22         | second preheater stage             |
|    | 23-25      | line                               |
| 15 | 30         | dosing facility                    |
|    | 31         | line                               |
|    | 40         | reactor with circulating fluid bed |
|    | 41-45      | line                               |
|    | 50         | residence time reactor             |
| 20 | 50'        | residence time reactor compartment |
|    | 51-55      | line                               |

**Patent claims:**

1. A process for thermal treatment of granular solids, wherein the solids at first are fed into a first reactor being designed as a flash reactor or a fluidized-bed reactor, where they are, in the case of a fluidized-bed reactor at temperatures of between 500 and 1500 °C and in the case of a flash reactor at a flame temperature of between 500 and 1500 °C, brought into contact with hot gases, wherein the solids are subsequently guided through a residence time reactor, in which they are present in fluidized form and from which they are drawn off after a residence time of 10 to 600 min, **characterized in** that into the residence time reactor an additional fuel is introduced, whereby the temperature in the residence time reactor is at least as high as in the first reactor.
2. The process according to claim 1, **characterized in** that the residence time in the flash reactor is between 0.1 and 10 sec or in the fluidized-bed reactor between 10 sec and 30 min and or the residence time in the residence time reactor is between 20 and 30 minutes.
3. The process according to claim 1 or 2, **characterized in** that the fluidization gas in the residence time reactor is air.
4. The process according to one of the preceding claims, **characterized in** that the additional fuel is introduced in gaseous state.
5. The process according to one of the preceding claims, **characterized in** that the additional fuel together with the fluidization gas is introduced into the residence time reactor.
6. The process according to one of the preceding claims, **characterized in** that the additional fuel is introduced separately from the fluidization gas.

7. The process according to one of the preceding claims, **characterized in** that the fuel is introduced in an amount which results in oxidizing or reducing conditions in the residence time reactor.

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8. The process according to one of the preceding claims, **characterized in** that the fluidized-bed reactor is a fluidized-bed reactor with circulating fluid bed.

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9. The process according to one of the preceding claims, **characterized in** that beta-spodumene is produced and/or the temperature in both reactors is between 1060 and 1090 °C.

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10. An apparatus for thermal treatment of granular solids, comprising a first reactor (40) being designed as a flash reactor or a fluidized-bed reactor and a second residence time reactor (50), wherein the residence time reactor (50) is designed such that in it the solid is also present in fluidized form, **characterized in** that the residence time reactor (50) comprises facilities (52, 53) with which additional fuel can be introduced into the residence time reactor (50).

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11. The apparatus according to claim 10, characterized in that the residence time reactor (50) is subdivided into at least two compartments (50').

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12. The apparatus according to claim 11, characterized in that the number of compartments (50') in operation is variable.

13. The apparatus according to claims 11 or 12, characterized in that at least one of the compartments (50') is tapped.

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14. The apparatus according to claim 13, characterized in that at least two compartments (50') are tapped, and that the tapping points are connected to a

mutually shared conveying device which transports the discharged hot solids to a next process step.

15. Use of the apparatus according any one of the claims 10-14 to produce/recover lithium-bearing intermediates.
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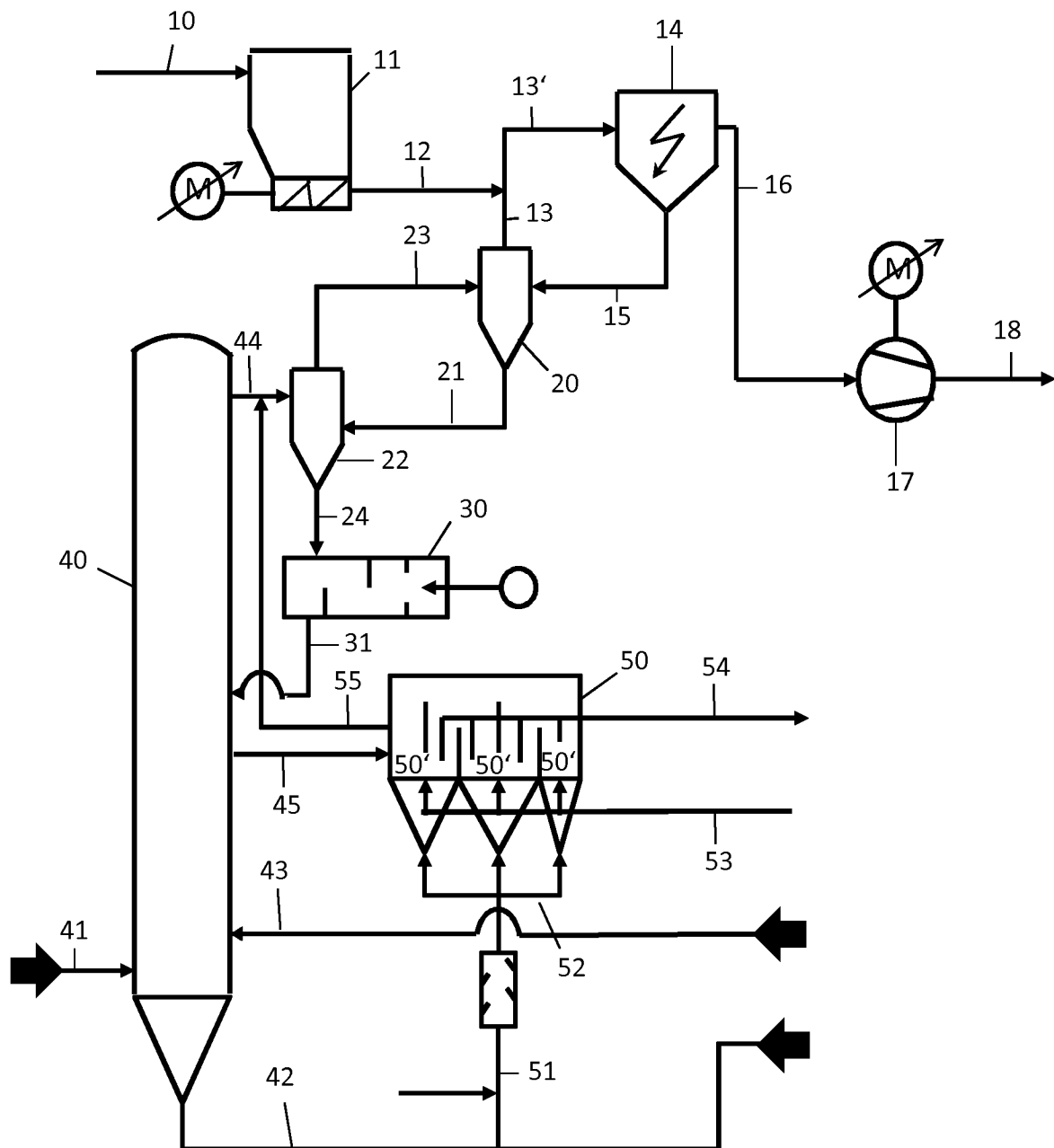


Fig. 1

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2017/055937

A. CLASSIFICATION OF SUBJECT MATTER  
INV. C22B1/00 B01J8/26 C01D15/08 C22B1/10  
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)  
C22B B01J C01D

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, COMPENDEX, WPI Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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☒ Further documents are listed in the continuation of Box C.

☒ 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

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"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

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26/05/2017

Name and mailing address of the ISA/

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## INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2017/055937

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Information on patent family members

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