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(71) Applicant(s)
Outotec (Finland) Oy

(72) Inventor(s)
Beyzavi, Ali-Naghi;Formanek, Lothar

(74) Agent / Attorney
Griffith Hack, GPO Box 1285, Melbourne, VIC, 3001

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(71) Applicant: **OUTOTEC OYJ** [FI/FI]; Riihitontuntie 7, FIN-02200 Espoo (FI).

(72) Inventors: **BEYZAVI, Ali-Naghi**; Peter-Henlein-Straße 22, 60435 Frankfurt am Main (DE). **FORMANEK, Lothar**; Libellenweg 67, 60529 Frankfurt am Main (DE).

(74) Agent: **KEIL & SCHAAFHAUSEN PATENT- UND RECHTSANWÄLTE**; Cronstettenstraße 66, 60322 Frankfurt am Main (DE).

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(54) **Title**: PROCESS AND APPARATUS FOR PRODUCING HARDENED GRANULES FROM IRON-CONTAINING PARTICLES

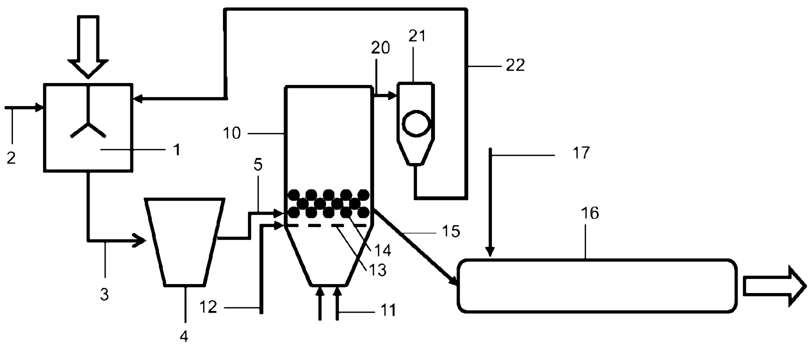

Fig. 1

(57) **Abstract**: In the production of hardened granules from iron-containing particles, the iron-containing particles are mixed with at least one binder and water to obtain a mix, the mix is formed to granules, and the granules are introduced into a fluidized-bed reactor for hardening. To reduce the abrasion in the downstream processing stages, the still moist granules are introduced into the fluidized-bed reactor at the hottest point of the fluidized bed.

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Process and Apparatus for Producing Hardened Granules from Iron-Containing Particles

The invention relates to the production of hardened granules from iron-containing dusts, wherein the iron-containing dusts are mixed with at least one binder and water to obtain a mix, the mix is formed to granules, the granules are introduced into a fluidized-bed reactor for hardening, and the hardened granules are subjected to a reduction.

In some reduction processes for obtaining metallized iron, the iron-containing material is introduced in the form of fine-grained particles. An example for such a process is the so-called SL/RN process, a combination of the Stelco-Lurgi process and the Republic Steel-National Lead process (RN). The Stelco-Lurgi process is a direct reduction process, which originally was directed to the production of sponge iron for steel furnaces and the use of ores rich in iron. The Republic Steel National-Lead process also is a direct reduction process, in which after the reduction iron ores are decomposed into their components metallic iron and gangue. In this connection, gangue is understood to be non-ferrous rocks which are present in iron ores. By combining the two processes, the SL/RN process was developed in 1964, in which iron oxides are reduced in the rotary kiln with solid reducing agents. In the furnace, ores or so-called green pellets together with coal, in particular lignite, are introduced in excess as reducing agent and dolomite is introduced for desulfurization. The furnace output is cooled indirectly in a tube cooler and thereafter is separated into sponge iron, excess, coal and ash by screening, magnetic separation and mineral coal separation.

In the SL/RN process, lump ores with a grain size of 5-18 mm or pellets with 9-16 mm usually are employed. What is also used are iron sands or ilmenites with a grain size preferably larger than 160 µm. Particles with a diameter < 63 µm are not suitable for use in an SL/RN process, since they lead to sticking and thus to the formation of crusts in the rotary kiln, which can lead to interruptions of operation.

To nevertheless render smaller particles suitable for this process, a number of processes are available for forming granules with the desired diameter. Due to the processing and additives, such as binders, the granules here can be designed such that the formation of dust during their production remains low (< 10 wt-%).

From WO 98/49352 A1 the granulation of fine-grained iron ore fractions is known, in which for example bentonite is used as binder material. Bentonite is a rock which contains a mixture of various clay minerals, with montmorillonite being the most important constituent (60 to 80 wt-%).

US 6,024,790 describes that it may be expedient to activate this binder material bentonite for its intended uses by ion exchange with the intercalated cations. An activated bentonite generally has a better swelling capacity as well as a higher thermal stability. The activation process described in US 6,024,790 must be carried out over a period of several hours to a few days, in order to ensure a sufficient ion exchange.

From JP 63103851 it is known to add small amounts of sodium hydroxide to the bentonite and thus activate the clay material.

DE 25 175 43 discloses a process for agglomerating metallurgical dusts, in which the metallurgical dust is mixed with 2 to 20 wt-% binder and about 0.5 to 5 wt-% silicon-containing material, this mixture is formed to pellets or granules and subsequently hardened. It is also known to add further additives to the binder, such as sodium hydroxide, sodium carbonate and sodium bicarbonate in quantities of about 3 wt-%.

From EP 1 290 232 B1, there is known a process for producing metallized iron agglomerates from fine iron-containing particles by means of a binder, wherein cellulose fibers are used as binder. When forming the particles, the cellulose fibers act as binder, but due to their high carbon content they can also be used as reducing agent in the downstream reduction process.

EP 0 916 742 also discloses a process in which the reducing agent is already incorporated in the iron-containing granules. For this purpose, the iron-oxide-containing raw material is mixed with a carbonaceous material, an organic binder and an inorganic coagulating agent and subsequently mixed with water. Provided with a dispersing agent, the pellets thus obtained are dried and subsequently reduced. As dispersing agent, sodium hydroxide solution can also be used, for example.

Due to the processing in a rotary kiln, together with the solid reducing agent and comparatively long retention times, an increased formation of fine abrasion is observed, however, in the further processing in all these processes, in particular in the SL/RN process, when using green pellets. A high abrasion requires a high processing expenditure, in order to be able to recover these dusts such that a valuable product can be produced from them. Otherwise, the material contained in the dusts gets lost.

Therefore, it is the object of the present invention to provide a process and an apparatus, in order to produce granules for the further processing, which have such a hardness that even in downstream processing steps no marked abrasion occurs.

In accordance with an embodiment of the invention, there is provided a process for producing hardened granules from iron-containing particles, wherein the iron-containing particles are mixed with at least one binder and water to obtain a mix, the mix is formed to granules, and the granules are introduced into a fluidized-bed reactor to harden in an oxidizing atmosphere, wherein the still moist granules have a water content of 8 to 14 wt-% and are introduced into the fluidized-bed reactor at the hottest point of the fluidized bed, wherein the hardened granules are supplied directly to a downstream reduction stage and wherein said reduction stage is a rotary kiln. The ultrafine-grained Fe concentrate is supplied to a mixing unit and mixed there with at least one binder and water. In addition, further aggregates can also be added in this mixing unit. The mix thus obtained then is formed to granules in a microcoagulator. Subsequently, the granules are introduced into a preferably circulating fluidized bed, with the introduction being effected at the hottest point of the fluidized bed. This sudden change in temperature leads to a rapid sintering of the small granules and hence to a sufficient strength of the grain for the subsequent reduction in a rotary kiln. In a circulating fluidized bed, the heat exchange is particularly good due to the high flow velocities, so that the sintering process is accelerated further.

This process contradicts the usual procedure, according to which the introduction of the material to be processed into the fluidized bed is effected in a region in which the material is not exposed to high temperature gradients, as in particular with larger particles a high temperature difference can lead to stresses in the material and consequently to cracks and deformations. In addition, due to the introduction at the hottest point, higher demands must be imposed on the material of the supply conduit. Dosing therefore also becomes more expensive.

The hottest point of the fluidized bed is located at the point where the combustion takes place or where the hot gases enter.

Furthermore, it was found to be favorable that the iron-containing particles have an iron content of at least 30 wt-%, preferably at least 50 to 80 wt-%, so that the processing expenditure remains economic.

An advantageous aspect of the invention provides that the Fe concentrate has a grain size of max. 5 wt-% coarser than 100 µm and about 55 to 60 wt-% smaller than 32 µm, as with diameters larger on average a direct processing may be economically more expedient.

The ultrafine-grained concentrate can be present as filter cake or as dry powdery bulk material. The specific surface of the particles lies between 1,600 and 4,000 cm²/g, depending on the mineralogy or the mineral composition of the iron concentrate used. A preprocessing, e.g. in the form of grinding, may be expedient for a more homogeneous grain size.

As binder, an inorganic binder such as e.g. bentonite is suited best, since undesired side reactions can thereby be excluded with the abrupt increase in temperature during hardening. According to the invention, the added quantity of this binder should lie between 0.25 and 1.5 wt-%, and in principle it is dependent on the mineral composition and the specific surface of the iron concentrate.

The mix formed to granules in the microgranulator favorably should have a grain size between 0.1 and 6 mm, as with this particle size it is ensured that during the introduction into the hottest stage of the reactor virtually the entire grain is homogeneously heated up and there are no significant temperature gradients within the individual particles.
Furthermore, a water content of 8 to 14 wt-% was found to be particularly favorable, with the same in principle depending on the respective mineral composition.

The optimum hardening temperature lies between 850 and 1,050 °C and within this range likewise has a dependence on the mineral composition. Experiments have shown that in the process according to the invention a maximum of about 5 wt-% of the granules are obtained as abrasion during the thermal hardening, wherein here the grain fraction < 100 μm was defined as abrasion.

As fuel for the hardening process natural gas or light fuel oil can be burnt directly in the fluidized-bed reactor or in a hot gas generator. If a hot gas generator is used, the hot gas is supplied to the fluidized-bed reactor.

Alternatively, coal can be used as fuel, wherein the coal is carbonized in a separate reactor at temperatures between 650 and 950 °C, the carbonization gases are introduced as fuel into the hardening reactor, and the hot carbonization coke is introduced as reducing agent into downstream process stages, preferably into a reduction taking place in a rotary kiln.

It also was found to be favorable to have the hardening take place in an oxidizing atmosphere, preferably with an oxygen content in the circulating fluidized bed between 2 and 10 wt-%. As a result, iron of oxidation stage 2 is oxidized up to iron of oxidation stage 3 and additional thermal energy is released. The heat input in the reactor can be reduced thereby.

During hardening in an oxygen-containing atmosphere, the following reactions take place:

$2\ Fe_3O_4 + \frac{1}{2}\ O_2 \rightarrow 3\ Fe_2O_3$ (oxidation of magnetite to hematite)

$Fe_2O_3\ x\ H_2O \rightarrow Fe_2O_3 + H_2O$ (elimination of the crystal water of e.g. goethite).

If no oxygen is contained in the atmosphere, only the second reaction, the elimination of the crystal water, takes place.

The hardened microgranules subsequently are subjected to a reducing treatment with coal in a rotary kiln, wherein the oxygen of the iron oxide is decomposed and the iron passes over into the metallic phase. The ratio between carbon and iron (C_{fix}: Fe) is 0.3 - 0.7 : 1. During the reduction, the following reactions take place:

$$Fe_2O_3 + CO \rightarrow 2\ FeO + CO_2$$

$$CO_2 + C \rightarrow 2\ CO$$

$$FeO + CO \rightarrow Fe_{met} + CO_2$$

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In the technical realization it seems to be particularly expedient to introduce the hardened hot granules from the fluidized-bed reactor into the rotary kiln without cooling. In this way, energy can be saved on the one hand and on the other hand the furnace volume can be reduced and thus its investment costs can be reduced. When charging the granules in the hot condition, the furnace length otherwise needed for the required heating of the granules in the rotary kiln is not necessary. The rotary kiln can be designed shorter or the throughput capacity can be increased in an existing rotary kiln. In existing rotary-tube systems, the throughput capacity can be increased by the hot introduction. The hot waste gases of the fluidized-bed reactor can be utilized for preheating the necessary process air or for steam generation.

To be able to supply the dusts generated in the fluidized bed and the reduction despite the improved hardening to an economic use, it was found to be favorable to separate these dusts from the fluidized bed and/or the reduction stage via a dust separation system and recirculate the same either into the mixing unit or into the granulation unit.

In particular with smaller scales, such as e.g. in laboratory and pilot experiments, it is expedient for safety reasons to cool the furnace output to a temperature below 30 °C, wherein this cooling preferably should be effected under an inert atmosphere, such as a nitrogen atmosphere. The cooled material, which is a mixture of sponge iron, char and ash, is charged into a magnetic separator, in order to separate the sponge iron from char and ash.

Another embodiment of the invention provides a plant for carrying out a process according to any of the preceding claims with a device for intermixing iron-containing particles with at least

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one binder and water to obtain a mix, a device for granulating the mix to obtain moist granules with a water content of 8 to 14 wt-%, and a fluidized-bed reactor to harden the granules in an oxidizing atmosphere, wherein the supply conduit of the granules opens into the lower region of the fluidized-bed reactor, wherein the hot output from the hardening furnace is charged directly into the reduction stage in the hot condition and wherein the reduction stage is a rotary kiln. Such plant includes an apparatus for intermixing iron-containing particles with at least one binder and water to obtain a mix. This apparatus is followed by an apparatus for granulating the mix to granules. This is followed by a reactor with a circulating fluidized bed for hardening the granules. The fluidized-bed reactor is designed such that the supply conduit of the granules opens into the lower region of the fluidized-bed reactor and hence the hottest point of the fluidized bed. For this purpose, in particular the material of this supply conduit and a dosing means provided there must be designed such that it permanently withstands these temperatures.

In a development of the invention, the fluidized bed is fed with hot gas and the supply conduit of the granules opens in the region of this feed conduit, since at this point the hot gases have not yet lost any thermal energy to the fluidized bed.

It is also favorable when at least one return conduit is provided from the fluidized-bed reactor and/or a downstream reduction apparatus into the apparatus for intermixing and/or the apparatus for microgranulation.

The advantages of the process according to the invention on the one hand consist in that so far there could only be used pellets which consist of magnetite and hematite concentrates and in addition have relatively large diameters (between 9 and 16 mm). With the process according to the invention there can also be used other ultrafine-grained concentrates and other grain sizes, without an unmanageable dust circuit being obtained.

In addition, the microgranules hardened according to the invention have a greater porosity as compared to lump ores and therefore can be reduced faster and better than lump ores and the classically burnt pellets, which have been hardened at over 1,300 °C.

In addition, by combining the hardening reactor according to the invention and an SL/RN furnace, the hot output from the hardening furnace can be charged directly into the rotary kiln in the hot condition. Thermal energy thereby is saved and the specific throughput capacity of the rotary kiln is increased.

Finally, the process according to the invention also allows that all dusts generated, wet or dry, are recirculated into the microgranulation process, whereby a completely closed material cycle is ensured.

The invention will subsequently be explained in detail with reference to the drawing and an exemplary embodiment. All features described and/or illustrated form the subject-matter of the invention per se or in any combination, independent of their inclusion in the claims or their back-reference.

The only Figure shows the flow diagram of a plant for carrying out the process according to the invention.

The fine-grained iron ore is introduced into a mixing device 1. Into this mixing device 1 at least one supply conduit 2 opens in addition, via which a mixture at least consisting of binder and water is introduced. It is of course also possible to provide separate supply conduits for each individual additive.

Via conduit 3, the mix thus produced is introduced from the mixing device 1 into the granulating device 4. From the mix, granules with a mean grain diameter of 0.1 to 6 mm are formed there (microgranulation), which are introduced into the fluidized-bed reactor 10 via conduit 5. Into the fluidized-bed reactor 10 preferably designed as circulating fluidized bed, fluidizing gas is injected via conduit 11, so that a circulating fluidized bed 14 is formed over a grate 13. Shortly above the grate 13 hot gas enters via conduit 12, by which the fluidized bed 14 is heated. Instead of supplying the hot gases in a reactor with internal combustion, fuel can also be introduced into the fluidized-bed reactor 10 via conduit 12 or an additional, non-illustrated conduit. The supply conduit 5 of the granules ends in direct vicinity of the supply conduit 12.

Via conduit 15, the hardened granules containing iron oxide are supplied to a reduction stage, in particular a rotary kiln 16, in which they are reduced for example by means of an SL/RN process. Via conduit 17, e.g. coal therefore is introduced into the rotary kiln 16 as reducing agent.

Via conduit 20, the dust generated in the fluidized-bed reactor 10 is guided into a cyclone 21, in which it is separated from the gas stream. Via conduit 22, the solids content is recirculated into the mixing device 1 and/or into the granulating device 4, in order to again be processed to granules.

Via conduit 30, the gas withdrawn from the fluidized-bed reactor 10 is supplied to a waste gas aftertreatment 31. The purified gas then can be discharged into the atmosphere via conduit 32 and/or be used as process gas.

Example

Granulation:

A magnetite concentrate with 69 wt-% iron, ground and processed to pelletizing fineness (< 100 µm), is mixed with 0.5 wt-% bentonite and the required amount of water, which is determined by the desired moisture content of the granules, and subsequently granulated. The moisture content of the granules thus obtained should be about 10 wt-%; the grain size of the granules is 0.1 to 3 mm.

Hardening:

The granules thus obtained subsequently are hardened in a fluidized-bed reactor in continuous operation at about 980 °C and then cooled to about 30 °C. The throughput capacity of the plant used is about 14 kg/h. During hardening, which takes place in an oxygen-containing gas atmosphere, magnetite is oxidized up to hematite, so that thermal energy is released in addition.

Reduction of the hardened microgranules in a short rotary furnace:
60 kg hardened microgranules and 40 kg coal are mixed and charged into the furnace. The ratio C_{fix} : Fe_{tot} is 0.60. The charge was treated at 1,020 to 1,050 °C for about 4 hours. After cooling under a nitrogen atmosphere, an average sample is taken and charged to a weak-field magnetic separator, in order to separate the residual coal and ash. The magnetic product, sponge iron, has the following analysis:

Fe_{total}: 80.0 wt-%
Fe^{2+}: 2.6 wt-%
Fe_{met}: 76.8 wt-%
Degree of metallization: 96 wt-%

The amount of particles with a diameter < 0.1 mm in the magnetic product was about 4.5 wt-%.

List of Reference Numerals

1	mixing device
2, 3	conduit
4	granulating device
5	conduit
10	fluidized-bed reactor
11, 12	conduit
13	grate
14	fluidized bed
15	conduit
16	reduction stage (rotary kiln)
17	conduit
20	conduit
21	cyclone
22	conduit
30	conduit
31	waste gas treatment
32	conduit

It is to be understood that, if any prior art publication is referred to herein, such reference does not constitute an admission that the publication forms a part of the common general knowledge in the art, in Australia or any other country.

Claims:

1. A process for producing hardened granules from iron-containing particles, wherein the iron-containing particles are mixed with at least one binder and water to obtain a mix, the mix is formed to granules, and the granules are introduced into a fluidized-bed reactor to harden in an oxidizing atmosphere, wherein the still moist granules have a water content of 8 to 14 wt-% and are introduced into the fluidized-bed reactor at the hottest point of the fluidized bed, wherein the hardened granules are supplied directly to a downstream reduction stage and wherein said reduction stage is a rotary kiln.

2. The process according to claim 1, **characterized in** that the moist granules are introduced into the lower region of the fluidized-bed reactor, into which hot gases are also introduced or in which the combustion of a fuel takes place.

3. The process according to claim 1 or 2, **characterized in** that the iron-containing particles have an iron content of at least 30 wt-% and/or a grain size of maximally 5 wt-% coarser than 0.1 mm.

4. The process according to any of the preceding claims, **characterized in** that the binder is an inorganic binding agent.

5. The process according to any of the preceding claims, **characterized in** that the granules have a grain size between 0.1 and 6 mm.

6. The process according to any of the preceding claims, **characterized in** that the temperature in the fluidized-bed reactor lies between 850 and 1,050 °C.

7. The process according to any of the preceding claims, **characterized in** that iron-containing dusts, which are generated in the fluidized-bed reactor and/or

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a reduction stage downstream of the fluidized-bed reactor, are recirculated for mixing and/or for granulating.

8. A plant for carrying out the process according to any one of the preceding claims with a device for intermixing iron-containing particles with at least one binder and water to obtain a mix, a device for granulating the mix to obtain moist granules with a water content of 8 to 14 wt-%, and a fluidized-bed reactor to harden the granules in an oxidizing atmosphere, wherein the supply conduit of the granules opens into the lower region of the fluidized-bed reactor, wherein the hot output from the hardening furnace is charged directly into the reduction stage in the hot condition and wherein the reduction stage is a rotary kiln.

9. The plant according to claim 8 with a supply conduit for hot gases or fuel, **characterized in** that the supply conduit of the granules opens in the region of the entry of the supply conduit of the hot gases or of the fuel into the fluidized-bed reactor.

10. The plant according to claim 8 or 9, **characterized in** that at least one return conduit leads from the fluidized-bed reactor and/or a downstream reduction stage into the device for intermixing and/or the device for granulating.

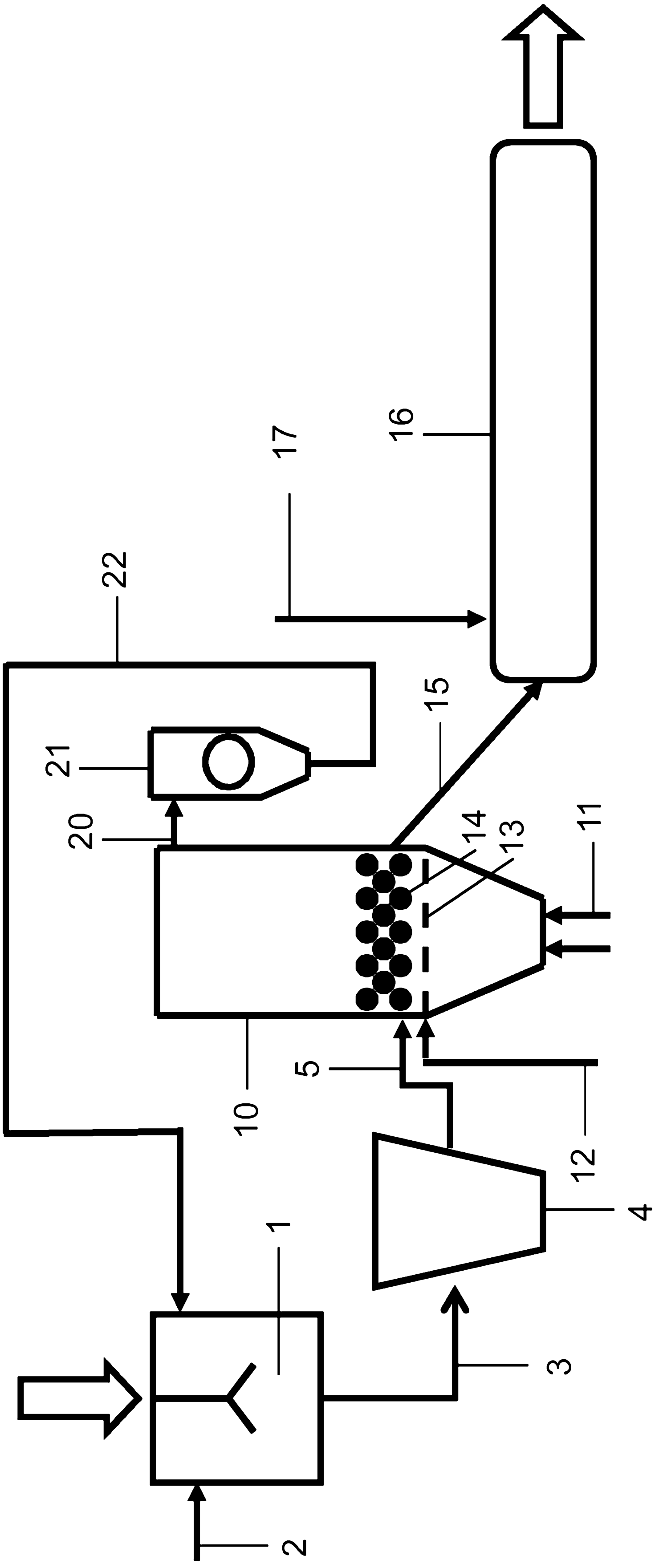

Fig. 1