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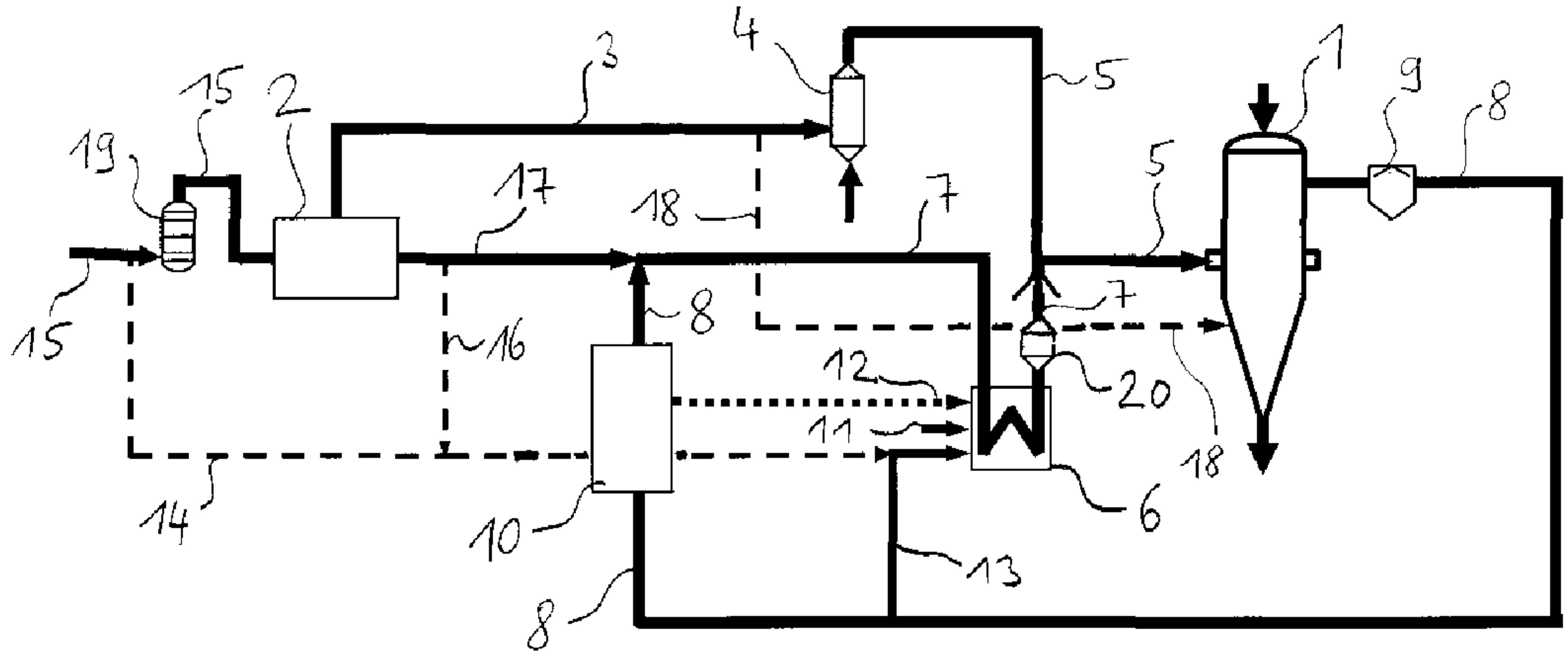
(54) Titre : REDUCTION D'OXYDES METALLIQUES A L'AIDE D'UN FLUX DE GAZ CONTENANT UN HYDROCARBURE ET DE L'HYDROGENE

(54) Title: REDUCTION OF METAL OXIDES USING A GAS STREAM CONTAINING BOTH HYDROCARBON AND HYDROGEN

Figur 1



(57) Abrégé/Abstract:
The invention relates to a process for reducing metal oxides using a gas stream containing both hydrocarbon and hydrogen. In the process the gas stream containing both hydrocarbon and hydrogen is separated into a hydrogen-rich fraction and a hydrocarbon-rich fraction. Then at least one sub-quantity of the hydrocarbon-rich fraction is subjected to at least one operation from the group - oxidation using technically pure oxygen, - reforming using CO_2 and H_2O. Then, it is introduced at least as a component of a reduction gas into a reduction unit containing the metal oxides. In this process the hydrocarbon content is set by the at least one operation from said group in such a manner that the hydrocarbon content in the reduction gas on entry into the reduction unit is below 12% by volume. The invention also relates to a device for carrying out such a process.

Abstract

The invention relates to a process for reducing metal oxides using a gas stream containing both hydrocarbon and hydrogen. In the process the gas stream containing both hydrocarbon and hydrogen is separated into a hydrogen-rich fraction and a hydrocarbon-rich fraction. Then at least on sub-quantity of the hydrocarbon-rich fraction is subjected to at least one operation from the group – oxidation using technically pure oxygen, - reforming using CO_2 and H_2O. Then, it is introduced at least as a component of a reduction gas into a reduction unit containing the metal oxides. In this process the hydrocarbon content is set by the at least one operation from said group in such a manner that the hydrocarbon content in the reduction gas on entry into the reduction unit is below 12% by volume. The invention also relates to a device for carrying out such a process.

Reduction of metal oxides using a gas stream containing both hydrocarbon and hydrogen

Technical field

The present invention relates to a process for reducing metal oxides, preferably iron oxides, using a gas stream containing both hydrocarbon and hydrogen. The invention also relates to a device for carrying out such a process.

Prior art

Coke oven gas is formed when coke is generated in integrated smelting works or stand-alone production plants and is used to date, for example, for reinforcing the heating value of the blast furnace top gases before use thereof in recuperators, as fuel gas in slab reheating furnaces or roller hearth furnaces, and for electricity generation in power plants. As main components it contains not only hydrocarbon - for example one or more hydrocarbons C_nH_{2n+2}, wherein n can be 1 or 2 or 3 or 4; but chiefly methane, that is to say n = 1 - but also hydrogen. In some integrated smelting works, coke oven gas is also used for generating technically pure hydrogen, for example for use in annealing furnaces. Typical coke oven gas compositions formed in integrated smelting works are as follows

COG analysis (dry):			
H_2	[% by volume]	65	62.1
N_2	[% by volume]	2.5	Included in remainder
CO	[% by volume]	6	6.2
CH_4	[% by volume]	22	21.4
C_nH_m	[% by volume]	3	Included in remainder
CO_2	[% by volume]	1.5	Included in remainder
H_2O	[% by volume]	Saturated	Included in remainder
H_2S	[g/Nm^3 (S.T.P)]	0.35	n.a.
Tar	[g/Nm^3 (S.T.P)]	5	n.a.
Dust	[g/Nm^3 (S.T.P)]	5	n.a.
Remainder	[% by volume]	-	10.3

Although the coke oven gas contains components such as hydrogen and carbon monoxide which are readily usable for reducing metal oxides in general, and iron oxides in particular, on account of the hydrocarbon content, it can only be used with restrictions for reducing metal oxides, especially iron oxides, in a reducing unit, since, as a consequence of highly endothermic reactions of the hydrocarbons proceeding on the introduction of coke oven gas into the reducing unit,

for example hydrocarbon CH_4

$CH_4 \rightarrow 2\ H_2 + C$ Cracking $\Delta H_{298} = +\ 74.86$ [kJ/mol]

$3\ Fe + CH_4 \rightarrow Fe_3C + 2\ H_2$ Carbonizing $\Delta H_{298} = +\ 99.7$ [kJ/mol]

the reduction temperature would decrease too greatly, which in turn would greatly restrict the productivity of the reducing unit.

Brief description of the invention

Technical object

It is an object of the present invention to provide a process which permits the use of a gas stream containing hydrocarbon and hydrogen for reducing metal oxides. It is likewise an object to provide a device for carrying out such a process.

Technical solution

This object is achieved according to the invention by a process for reducing metal oxides using a gas stream containing not only hydrocarbon but also hydrogen,
which is characterized in that
the gas stream containing not only hydrocarbon but also hydrogen
is separated
into a hydrogen-rich fraction
and a hydrocarbon-rich fraction,
and subsequently
at least a subquantity of the hydrocarbon-rich fraction
is subjected
to at least one operation of the group
- oxidation using technically pure oxygen,
- reformation using CO_2 and H_2O,
and then it is introduced at least as a component of a reducing gas into a reducing unit containing the metal oxides,
wherein the hydrocarbon content is adjusted by the at least one operation of the aforementioned group,
in such a manner that the hydrocarbon content in the reducing gas is, on entry into the reducing unit, less than 12% by volume, preferably less than 10% by volume, particularly preferably less than 8% by volume.

Metal oxides can be, for example, iron oxides, or oxides of nickel, copper, lead, cobalt.

The reduction of the metal oxides preferably proceeds to form extensively metalized metal - that is to say the degree of metalization is greater than or equal to 90%, preferably greater than or equal to 92%, for example sponge iron.

Advantageous effects of the invention

The gas stream containing not only hydrocarbon but also hydrogen can contain one or two or more types of hydrocarbon. For example, it contains relatively low-saturated hydrocarbons C_nH_{2n+2}, wherein n = 1, that is to say methane, or n = 2, that is to say ethane, or n = 3, that is to say propane, or n = 4, that is to say butane or isobutane. It can also contain relatively low-monounsaturated or polyunsaturated hydrocarbons, wherein, for example, C_nH_{2n} applies, for example ethene. It can also contain aromatic hydrocarbons, such as benzene or toluene. In the gas stream containing not only hydrocarbon but also hydrogen, one or more types of hydrocarbon having the general formula C_nH_m can also be present, wherein m can be
$m = n$,
$m = 2n$,
$m = 2n+2$.

According to the invention, the gas stream containing not only hydrocarbon but also hydrogen is separated into a hydrogen-rich fraction and a hydrocarbon-rich fraction. In this case the hydrocarbon-rich fraction contains not only hydrocarbons, but also further components such as argon, nitrogen, carbon monoxide, carbon dioxide and steam. The term hydrocarbon-rich relates to the fact that this fraction, compared with the gas stream containing not only hydrocarbon but also hydrogen, has a higher content of hydrocarbon.
The hydrogen-rich fraction contains not only hydrogen.
The term hydrogen-rich relates to the fact that this fraction, compared with the gas stream containing not only hydrocarbon but also hydrogen, has a higher content of hydrogen.

Subsequently for the separation, at least a subquantity of the hydrocarbon-rich fraction obtained in the separation is subjected to at least one operation of the group

- oxidation using technically pure oxygen,
- reforming using CO_2 and H_2O.

It can also be subjected to a combination of these two operations.

In the case of a combination, partial oxidation is preferably performed first using technically pure oxygen for the purpose of temperature elevation, and subsequently reforming is performed using CO_2 and H_2O, for example in an autothermal reformer. In an autothermal reformer, the reformer does not need to be fired, because no feed line of fuel gas to the autothermal reformer is necessary. This saves expenditure on construction and reduces the exhaust gases of the reformer.

In this case, in the oxidation, the total amount of hydrocarbons is not oxidized, but only a part of the amount of hydrocarbons - in the context of this application, this is also termed partial oxidation.

In this case, in the reforming, the total amount of hydrocarbons is not reformed, but a predominant part of the amount of hydrocarbons.

Via said operations, alone or in combination, the content of hydrocarbons decreases.

After at least a subquantity of the hydrocarbon-rich fraction obtained in the separation has been subjected to at least one operation of said group, it is introduced at least as a component of a reducing gas into a reducing unit containing the metal oxides - this means of course that the product obtained in the operation or operations is introduced.

At least as a component of a reducing gas means that the reducing gas can also contain other components which may optionally be added before a mixture obtained in the addition is introduced as reducing gas into the reducing unit.

According to the invention, the hydrocarbon content of the subquantity is set by the at least one operation of said group in such a manner that the hydrocarbon content in the reducing gas, on entry into the reducing unit, is less than 12% by volume, preferably less than 10% by volume, particularly preferably less than 8% by volume, but greater than 1% by volume, preferably greater than 2% by volume, particularly preferably greater than 3% by volume. Said limits are comprised herein. The higher the hydrocarbon content is in the reducing gas on entry into the reducing unit, the higher the reduction temperature must be set - in reducing shafts as reducing unit, also termed - gas temperature bustle or the lower is the productivity of the plant. At a hydrocarbon content set according to the invention, the reduction temperature owing to a lower endothermic reactions of the hydrocarbons does not fall so greatly that the productivity of the reducing unit decreases below an economically acceptable level.

The lower limit of the hydrocarbon content is determined, for example, in the reduction of iron oxides, by the required carbon content - carbon bound as Fe_3C or elemental carbon - in the reduced product for the steelworks - there, for example, an electric arc furnace. With increasing carbon content in the reduced product, the energy requirement in the subsequent treatment in the electric arc furnace decreases. A hydrocarbon content in the reducing gas on entry into the reducing unit in the range of the lower limit is used, for example, for generating a minimum content of carbon in a sponge iron, in particular in the form of Fe_3C, or such a hydrocarbon content is necessary optionally for controlling the temperature in the reducing unit.

In addition, for example in the production of sponge iron, hot briquetted iron (HBI) plants - as are customary in direct reduction (DR) plants - also require certain minimum briquetting temperatures - preferably > 650°C for avoidance of increased maintenance costs and to achieve product densities > 5 g/cm^3 - which, in the event of excessive cooling of the DRI in the reducing unit, cannot be achieved owing to endothermal reactions.

According to a preferred embodiment, the gas stream containing not only hydrocarbon but also hydrogen is coke oven gas.

The latter embodiment is preferred because coke oven gas, in an integrated smelting works, is usually formed in any case, or, in a stand-alone coking plant, is only used for electricity generation, or is flared off without being used. Using the process according to the invention, it can be utilized for efficient iron production; the material utilization thereof achieved in this case has a higher efficiency than, for example, utilization for electricity generation. An integrated smelting works is taken to mean a steel generation route which consists, inter alia, of coking plant, sintering plant and blast furnace. The gas stream containing not only hydrocarbon but also hydrogen can also be gas generated in a coal gasifier.

According to a preferred embodiment, the gas stream containing not only hydrocarbon but also hydrogen
is separated
into a hydrogen-rich fraction
and a hydrocarbon-rich fraction
by at least one operation of the group
- pressure-swing adsorption,
- membrane separation.

The pressure-swing adsorption proceeds, for example, in a PSA or VPSA plant, wherein PSA means Pressure Swing Adsorption and VPSA means Vacuum Pressure Swing Adsorption. More preferably, a prepurification of the gas stream proceeds before the pressure-swing adsorption, for example in a prepurification appliance for separating off tar and dust using tar filters made of fibers or adsorption materials. Owing to the differing adsorption forces, a gas stream containing not only hydrocarbon but also hydrogen, for example coke oven gas, in the case of an appropriate design of the plant size of pressure-swing adsorption plants and by operation using correspondingly designed cycle times using a PSA plant or a VPSA plant can be separated into a hydrogen-rich fraction and a hydrocarbon-rich fraction. The hydrogen is formed on the product side virtually without a significant pressure drop. The hydrocarbon-rich fraction is formed at very low pressure or a vacuum and is then compressed to the required pressure in the subsequent process steps.

In the case of membrane separation, the separation proceeds on the basis of the differing permeability of a membrane. Hydrogen is produced in this case in the concentrated state on the low-pressure side of the membrane.

According to a preferred embodiment, at least a proportion of the
at least one subquantity of the hydrocarbon-rich fraction which was subjected to at least one operation of the group
- oxidation using technically pure oxygen,
- reforming using CO_2 and H_2O,
is mixed
with an auxiliary reducing gas,
before the resultant mixture of these two components is introduced
as reducing gas into the reducing unit containing the metal oxides.

In this case the reducing gas introduced into the reducing unit containing the metal oxides is generated by mixing two components, wherein the one component is obtained by oxidizing and/or reforming at least one subquantity of the hydrocarbon-rich fraction.

In such a procedure, other gases having a reduction potential can also be materially utilized for the reduction of metal oxides by adding them as auxiliary reducing gas.

In a device for carrying out such a process according to the invention, corresponding feed lines are present for introducing auxiliary reducing gases to the proportion of the hydrocarbon-rich fraction, or optionally to the total amount of the hydrocarbon-rich fraction,
which has been subjected to at least one operation of the group

- oxidation using technically pure oxygen,
- reforming using CO_2 and H_2O.

According to a preferred embodiment, the mixing ratio of the two components is set in dependence on a preset temperature for the mixture. In this manner, it is ensured that the reducing gas is in the temperature region which is favorable in terms of the process and economics for reducing metal oxides. By setting the temperature, the reaction rate in the reducing reactor - kinetics, can be set optimally. In addition, the efficiency of the reducing gas preheating can be optimized.

Corresponding devices for controlling the mixing ratio and also temperature measuring devices for measuring the temperature of the mixture and/or for measuring the temperatures of the components are present in a device for carrying out the process according to the invention.

According to a preferred embodiment, the two components are mixed after the auxiliary reducing gas has been heated in a gas furnace. This makes possible an improved temperature setting of the reducing gas. The temperature of the reducing gas should preferably be in the range 780 - 1050°C, according to the H_2/CO ratio in the reducing gas.

According to a preferred embodiment, top gas is taken off from the reducing unit, and the auxiliary reducing gas is obtained at least in part by mixing top gas that is dedusted and substantially freed from CO_2, and at least one further gas. In this manner, the reductants (CO and H_2) still present in the top gas are utilized again for reducing the metal oxides.

Advantageously, the at least one further gas comprises the hydrogen-rich fraction obtained in the separation of the gas stream, preferably coke oven gas, containing not only hydrocarbon but also hydrogen.

In this manner, the reduction potential present in this fraction is also utilized for reducing metal oxide; utilized, especially in that the reduction rate - kinetics - is generally more rapid via hydrogen:

$$3\ Fe_2O_3+H_2 \rightarrow 2\ Fe_3O_4+H_2O \qquad \Delta\ H_{298} = -2.72\ [kJ/mol]$$
$$Fe_3O_4+H_2 \rightarrow 3FeO+H_2O \qquad \Delta\ H_{298} = +59.83\ [kJ/mol]$$
$$FeO+3H_2 \rightarrow Fe + 2H_2+H_2O \qquad \Delta\ H_{298} = +29.60\ [kJ/mol]$$

Advantageously, the gas furnace is operated with a fuel gas which at least in part comprises at least one gas of the group
- tail gas formed in the removal of CO_2 from the top gas,
- top gas,
- gas stream, preferably coke oven gas, containing not only hydrocarbon but also hydrogen,
- hydrogen-rich fraction obtained by separation of the gas stream, preferably coke oven gas, containing not only hydrocarbon but also hydrogen,
- hydrocarbon-rich fraction obtained by separation of the gas stream, preferably coke oven gas, containing not only hydrocarbon but also hydrogen.

In this manner, these gases are utilized in the process for reducing metal oxides, which increases the efficiency thereof. When hydrogen-rich gases are used for firing the gas furnace from below, the CO_2 emission can be kept correspondingly low.

Single, a plurality of, or all of the corresponding fuel gas feed line(s) to the gas furnace is/are present in a device for carrying out the process according to the invention:
- a tail gas feed line for feeding tail gas produced in the removal of CO_2 from the top gas, which tail gas feed line exits from the CO_2 removal plant.

- A top gas feed line for feeding top gas, which top gas feed line exits from a top gas outlet line withdrawing top gas from the reducing unit.

- A fuel gas feed line for feeding gas stream containing not only hydrocarbon but also hydrogen, which fuel gas feed line exits from a feed line for a gas stream containing not only hydrocarbon but also hydrogen and which itself opens out into a device for separating a gas stream containing not only hydrocarbon but also hydrogen into a hydrogen-rich fraction and a hydrocarbon-rich fraction.

- A fuel gas feed line for feeding a hydrogen-rich fraction obtained by separation of the gas stream, preferably coke oven gas, containing not only hydrocarbon but also hydrogen,
which fuel gas feed line exits

from a device for separating a gas stream containing not only hydrocarbon but also hydrogen into a hydrogen-rich fraction and a hydrocarbon-rich fraction,

or from an outlet line for the hydrogen-rich fraction which itself arises from

a device for separating a gas stream containing not only hydrocarbon but also hydrogen into a hydrogen-rich fraction and a hydrocarbon-rich fraction,

- a fuel gas feed line for feeding a hydrocarbon-rich, hydrogen-rich fraction obtained by separation of the gas stream, preferably coke oven gas, containing not only hydrocarbon but also hydrogen, which fuel gas feed line exits

from a feed line for the hydrocarbon-rich, hydrogen-rich fraction which itself

arises from a device for separating a gas stream containing not only hydrocarbon but also hydrogen into a hydrogen-rich fraction and a hydrocarbon-rich fraction,

or a device for separating a gas stream containing not only hydrocarbon but also hydrogen into a hydrogen-rich fraction and a hydrocarbon-rich fraction.

Advantageously,
the reducing unit is a reducing shaft and
a first subquantity
of the hydrocarbon-rich fraction
is introduced directly into the reducing shaft,
and
a second subquantity
of the hydrocarbon-rich fraction
before introduction thereof into the reducing shaft
is subjected to at least one operation of the group
- oxidation using technically pure oxygen
- reforming using CO_2 and H_2O,
and then is introduced at least as component of a reducing gas into a reducing unit containing the metal oxides,
and the hydrocarbon content
is set by the at least one operation of said group, in such a manner
that the hydrocarbon content in the reducing gas, on entry into the reducing unit, is less than 12% by volume, preferably less than 10% by volume, particularly preferably less than 8% by volume.

The first subquantity can thus be utilized for carbonization of the metal generated in the reducing unit; for example, it can be utilized for carbonization of metallic iron.

Advantageously, the at least one gas stream containing CO_2 and/or H_2O is added to the hydrocarbon-rich fraction before reforming using CO_2 and H_2O. In this process, this can be, for example, steam, tail gas from a CO_2 removal process - for example from the removal of CO_2 from the top gas - top gas from the reducing shaft, or converter gas. Water can also be added.

In this manner, these gases are utilized in the process for reducing metal oxides, which increases the efficiency thereof, and reduces the environmental emissions, since CO_2 is converted back to CO.

Corresponding feed lines for feeding one or more of these gases which exit from devices producing such gases or lines bearing such gases are present in a device for carrying out the process according to the invention.

In the hydrocarbon-rich fraction, H_2S is also enriched. According to a preferred embodiment, therefore, desulfurization of the hydrocarbon-rich fraction is carried out before it is subjected to at least one operation of the group

- oxidation with technically pure oxygen,
- reforming using CO_2 and H_2O or.

The sulfur content can thereby be reduced in the largely metalized metal.

In a device for carrying out a process according to the invention, then, in a feed line for the hydrocarbon-rich fraction 3, a desulfurization device is present, before - seen in the direction of flow - the feed line opens out into a unit for carrying out an operation of the group

- oxidation with technically pure oxygen,
- reforming using CO_2 and H_2O.

The process according to the invention has the following advantages:
- efficient material utilization of coke oven gas for reducing metal oxides, especially for reducing iron oxides for sponge iron production - advantage in comparison with the thermal utilization of coke oven gas proceeding to date according to the prior art,
- in comparison with utilization of natural gas for reducing metal oxides, especially for the reduction of iron oxides for sponge iron production, high economic advantages in comparison with natural gas, since the coke oven gas is produced at lower costs
- very environmentally friendly process, in particular owing to low CO_2 and NO_x emissions, since firstly in some embodiments a very hydrogen-rich gas can be used for the reduction and secondly by utilization of low-carbon gases in the reformer and/or gas furnace, emissions thereof can further be reduced.
- Furthermore, in the reformer, some of the CO_2 emissions can be converted back to CO and subsequently utilized for the reduction.
The specific carbon emission factor in the case of coke oven gas is 43.7 kg of CO_2/GJ of fuel, while in the case of natural gas it is 55.7 kg of CO_2/GJ of fuel. The use of coke oven gas is therefore considerably more environmentally friendly than the use of natural gas.

A further subject matter of the present application is a device for carrying out the process according to the invention
having a reducing unit for reducing metal oxides,
having a device for separating a gas stream containing not only hydrocarbon but also hydrogen into a hydrogen-rich fraction and a hydrocarbon-rich fraction,
having, arising therefrom, a
feed line for the hydrocarbon-rich fraction which
opens out
into a unit for

carrying out an operation of the group
- oxidation using technically pure oxygen
- reforming using CO_2 and H_2O,

and having one or more introduction lines for introducing at least one gas stream from the group

- hydrocarbon-rich fraction,
- gas stream obtained in the unit for carrying out oxidation using technically pure oxygen,
- gas stream obtained in the unit for carrying out reforming using CO_2 and H_2O,

into the reducing unit.

Preferably, the device for separating a gas stream containing not only hydrocarbon but also hydrogen into a hydrogen-rich fraction and a hydrocarbon-rich
hydrogen-rich fraction is
a device for separating coke oven gas into a hydrogen-rich fraction and a hydrocarbon-rich fraction.

Preferably, the device for separating a gas stream containing not only hydrocarbon but also hydrogen into a hydrogen-rich fraction and a hydrocarbon-rich fraction is
a device of the group

- device for pressure-swing adsorption,
- device for membrane separation.

Preferably, the one or more introduction lines open out into the reducing unit, wherein upstream of the opening of at least one of the introduction lines into the reducing unit, an auxiliary reducing gas line for feeding auxiliary reducing gas to the reducing unit opens out into this introduction line.

Preferably, upstream of the opening of the auxiliary reducing gas line into the introduction line, a gas furnace is present in the auxiliary reducing gas line.

Preferably, x introduction lines are present, wherein x is greater than 2 or is equal to 2, of the at most x-1 introduction lines it is true that, upstream of the opening of at least one of the introduction lines into the reducing unit, an auxiliary reducing gas line, for feeding auxiliary reducing gas to the reducing unit, opens out into this introduction line.
In this manner, at least one introduction line is present into which no auxiliary reducing gas line opens out. Therefore, a subquantity of the hydrocarbon-rich fraction can be introduced directly into the reducing shaft without being mixed with auxiliary reducing gas; this subquantity can be used, for example, for carbonizing the metal generated in the reducing unit; for example it can be used for carbonizing metallic iron.

According to one embodiment, the reducing unit is a reducing shaft, for example a fixed-bed reducing shaft for carrying out a MIDREX® or HYL® reduction process.

According to one embodiment, the reducing unit is a fluidized-bed cascade.

Brief description of the drawings

With reference to the schematic and exemplary figures hereinafter, the invention will be described with reference to embodiments.

Figure 1 shows a device for carrying out a process according to the invention, in which coke oven gas is separated into a hydrogen-rich fraction and a hydrocarbon-rich fraction and the latter is subjected to an oxidation before it is introduced into a reducing shaft as part of a reducing gas.

Figure 2 shows a device and procedure similar to figure 1, with the difference that the hydrocarbon-rich fraction is subjected to reforming using CO_2 and H_2O before it is introduced as part of a reducing gas into a reducing shaft.

Figure 3 shows a device and procedure according to the invention which chiefly differs from figure 1 in that a fluidized-bed cascade is present as reducing unit, and the device present for separating coke oven gas, instead of a device for pressure-swing adsorption, is a device for membrane separation.

Figure 4 shows a device and procedure according to the invention which chiefly differs from figure 1 in that a fluidized-bed cascade is present as reducing unit, and the device for separating coke oven gas, instead of a device for pressure-swing adsorption, is a device for membrane separation.

Description of the embodiments

Figure 1 shows a device for carrying out a process according to the invention. This comprises, as reducing unit for reducing metal oxides, a reducing shaft 1 which contains iron ore, that is to say iron oxides. It likewise comprises a device for separating a gas stream containing not only hydrocarbon but also hydrogen, in this case a PSA or a VPSA plant 2 using pressure-swing adsorption, into a hydrogen-rich fraction and a hydrocarbon-rich fraction. In the present example, the gas stream containing not only hydrocarbon but also hydrogen is coke oven gas. From the PSA or VPSA plant 2 there arises a feed line for the hydrocarbon-rich fraction 3 which opens out into a unit for carrying out an oxidation using technically pure oxygen 4. In this unit for carrying out an oxidation using technically pure oxygen 4, the hydrocarbon-rich fraction is partially oxidized; that is, the entire amount of substance is not oxidized, but only a part of the amount of substance of the hydrocarbon-rich fraction. Via an introduction line 5 for introducing the gas stream obtained in the unit for carrying out oxidation using technically pure oxygen 4, this gas stream is introduced as a component of a reducing gas into the reducing shaft 1. In the partial oxidation the hydrocarbon content is set in such a manner that the hydrocarbon content in the reducing gas is less than 12% by volume on entry into the reducing shaft.

The gas stream obtained in the unit for carrying out oxidation using technically pure oxygen 4 is mixed with an auxiliary reducing gas, the resultant mixture is introduced as reducing gas into the reducing shaft 1. The two components of the reducing gas are mixed after the auxiliary reducing gas has been heated in a gas furnace 6. The auxiliary reducing gas is added via an auxiliary reducing gas line 7 for feeding auxiliary reducing gas to the reducing unit 1, which reducing gas line 7 opens out into the introduction line 5. Via the introduction line 5, therefore, not only the gas stream obtained in the unit for carrying out oxidation using technically pure oxygen 4, but also the auxiliary reducing gas is introduced into the reducing shaft 1, specifically as a mixture termed reducing gas. The temperature preset of the auxiliary reducing gas which is heated in the gas furnace 6 is set in dependence on a temperature preset for the mixture. The gas furnace 6 is arranged in the auxiliary reducing gas line 7.

From the reducing shaft 1, top gas is conducted away via a top gas outlet line 8. The auxiliary reducing gas, in the example shown, is formed by mixing dedusted - a gas scrubber 9 is present in the top gas outlet line 8 - top gas that is largely freed from CO_2 - a CO_2 removal plant 10 is present in the top gas outlet line 8 - and a further gas. The further gas is the hydrogen-rich fraction obtained in the separation of the coke oven gas.

The gas furnace 6 is operated using a fuel gas. The fuel gas is burnt with feed of air through an air feed line 11 opening out into the gas burner. The fuel gas consists of gases of the group

- tail gas formed in the removal of CO_2 from the top gas,

- top gas,
- coke oven gas,
- hydrogen-rich fraction obtained by separation of coke oven gas.

For feeding these gases into the gas burner 6, there are present

- a tail gas feed line 12 for feeding tail gas formed in the removal of CO_2 from the top gas which exits from the CO_2 removal plant 10 and opens out into the gas burner,
- a top gas feed line 13 for feeding top gas which exits from the top gas outlet line 8 conducting away top gas from the reducing unit and opens out into the gas burner,
- a coke oven gas feed line 14 for feeding coke oven gas, which exits from a feed line for coke oven gas 15 and opens out into the top gas feed line 13,
- a hydrogen fraction feed line 16 which branches off from a hydrogen fraction outlet line 17 exiting from the PSA or VPSA plant 2 and opens out into the coke oven gas feed line 14.

In order that auxiliary reducing gas can be obtained by mixing top gas that is dedusted and largely freed from CO_2 and the hydrogen-rich fraction obtained in the separation of the coke oven gas, not only the hydrogen fraction outlet line 17 but also the top gas outlet line 8 open out into the auxiliary reducing gas line 7.

The feed line for coke oven gas 15 exits from a coke oven gas source that is not shown and opens out into the PSA or VPSA plant 2.

In the device shown in figure 1, two introduction lines opening out into the reducing shaft 1 are present. The introduction line 5, called first introduction line, has already been described. A further introduction line, called second introduction line 18, branches off from the feed line for the hydrocarbon-rich fraction 3 and opens out into the reducing shaft. Via this second introduction line 18, a subquantity of the hydrocarbon-rich fraction can be introduced directly into the reducing shaft. This subquantity can thus be used for carbonizing the metallic iron, in this case sponge iron, generated in the reducing shaft 1. A cooling gas line for feeding cooling gas into the reducing shaft 1 is not shown for reasons of clarity; in principle, for the purpose of carbonization, a subquantity of the hydrocarbon-rich fraction could also be added to the cooling gas via a corresponding branch from the feed line for the hydrocarbon-rich fraction 3 which opens out into the cooling gas line.

In the tar filter appliance 19 arranged in the feed line for coke oven gas 15, tar is removed from the coke oven gas.

In the burner 20, the auxiliary reducing gas can be partially oxidized with feed of technically pure oxygen, if this is wanted for temperature elevation.

For reasons of clarity, depiction of device parts which are not essential to the present invention has been dispensed with, for example the depiction of diverse compressors, bypass lines, gas holders, gas coolers, flare stacks.

In figure 2, in an otherwise similar device and procedure, the hydrocarbon-rich fraction, instead of a partial oxidation, is subjected to reforming using CO_2 and H_2O before it is introduced as part of a reducing gas into a reducing shaft. Plant parts and process steps which are identical to figure 1 are not described again here for the most part, and the reference signs for the same plant parts, for better clarity, are not entered into the drawing. The reforming takes place in a unit for carrying out reforming using CO_2 and H_2O, here a reformer 21, into which the feed line for the hydrocarbon-rich fraction 3 opens out. Off-gas from the reformer 21 is used via a heat exchanger 22 for heating the hydrocarbon-rich fraction before entering into the reformer 21.
Via a plurality of feed lines 23a, 23b, which open out into the feed line for the hydrocarbon-rich fraction 3, before entry into the reformer 21, a plurality of CO_2-containing gas streams are added to the hydrocarbon-rich fraction. Via feed line 23a, tail gas from the CO_2

removal plant 10 is added; the feed line 23a arises from the tail gas feed line 12. Via feed line 23b, top gas is added. Via a water feed line 24 which opens out into the feed line for the hydrocarbon-rich fraction 3, before entry into the reformer 21, steam and/or water is added to the hydrocarbon-rich fraction. The reformer 21 can be fired using top gas, coke oven gas or with the hydrocarbon-rich fraction; corresponding lines opening out into the reformer 21, for the sake of clarity, are not shown.

Via a branch line 29 which branches off from the second introduction line 18 and opens out into the first introduction line 5, the hydrocarbon content in the reducing gas on entry into the reducing shaft 1 can be influenced via the feed of hydrocarbon-rich fraction.

In figure 3, the reducing unit is a fluidized-bed cascade 25, from the last fluidized-bed reactor 26 of which, seen in the direction of flow of the reducing gas, top gas is taken off; the top gas line is given the reference sign 8, as is the top gas line in figure 1. The introduction line 5, which in figure 1 is shown opening out into the reducing shaft 1, is, in figure 3, shown opening out into the first fluidized-bed reactor 27, similarly seen in the direction of flow of the reducing gas. As a device for separating coke oven gas, - instead of, as in figure 1, a device for pressure-swing adsorption - there is a device for membrane separation 28. Via a branch from the feed line for the hydrocarbon-rich fraction 3, hydrocarbon-rich fraction can be fed into the first introduction line 5, which offers a possibility for influencing the hydrocarbon content in the reducing gas.

Figure 4 differs from figure 2 by the same modifications by which figure 3 differs from figure 1. In addition, in figure 1, in contrast to figure 2, no heat exchanger 22 is present.

List of reference signs

1	Reducing shaft
2	PSA or VPSA plant
3	Feed line for the hydrocarbon-rich fraction
4	Unit for carrying out an oxidation using technically pure oxygen
5	(First) introduction line
6	Gas furnace
7	Auxiliary reducing gas line for feeding auxiliary reducing gas to the reducing unit 1
8	Top gas outlet line
9	Gas scrubber
10	CO_2 removal plant
11	Air feed line
12	Tail gas feed line
13	Top gas feed line
14	Coke oven gas feed line
15	Supply line for coke oven gas
16	Hydrogen fraction feed line
17	Hydrogen fraction outlet line
18	Second introduction line
19	Tar filter appliance
20	Burner
21	Reformer
22	Heat exchanger
23a, 23b	Feed line
24	Water feed line
25	Fluidized-bed cascade
26	Last fluidized-bed reactor

27	First fluidized-bed reactor
28	Device for membrane separation
29	Branch line

Claims

1. A process for reducing metal oxides using a coke oven gas, **characterized in that**
the coke oven gas
is separated
into a hydrogen-rich fraction
and a hydrocarbon-rich fraction,
and subsequently
at least a subquantity of the hydrocarbon-rich fraction
is subjected
to at least one operation of the group
- oxidation using technically pure oxygen,
- reforming using CO_2 and H_2O,
and then it is introduced at least as a component of a reducing gas into a reducing unit containing the metal oxides,
wherein the hydrocarbon content is adjusted by the at least one operation of the aforementioned group,
in such a manner that the hydrocarbon content in the reducing gas is, on entry into the reducing unit, less than 12% by volume, preferably less than 10% by volume, particularly preferably less than 8% by volume, but greater than 1% by volume, preferably greater than 2% by volume, particularly preferably greater than 3% by volume,
and wherein
at least a proportion of the

at least one subquantity of the hydrocarbon-rich fraction which was subjected to at least one operation of the group
- oxidation using technically pure oxygen,
- reforming using CO_2 and H_2O,

is mixed

with an auxiliary reducing gas,

before the resultant mixture of these two components is introduced as reducing gas into the reducing unit containing the metal oxides,

wherein the auxiliary reducing gas is obtained at least in part by mixing top gas that is dedusted and substantially freed from CO_2, and at least one further gas, wherein the at least one further gas comprises the hydrogen-rich fraction obtained in the separation of the coke oven gas.

2. The process as claimed in any one of claims 1 to 3, **characterized in that** the gas stream containing not only hydrocarbon but also hydrogen is separated into a hydrogen-rich fraction and a hydrocarbon-rich fraction by at least one operation of the group
- pressure-swing adsorption,
- membrane separation.

3. The process as claimed in claim 1 or 2, **characterized in that** the two components are mixed after the auxiliary reducing gas has been heated in a gas furnace.

4. The process as claimed in claim 3, **characterized in that** the gas furnace is operated with a fuel gas which at least in part comprises at least one gas of the group
- tail gas formed in the removal of CO_2 from the top gas,
- top gas,
- coke oven gas,
- hydrogen-rich fraction obtained by separation of the coke oven gas,
- hydrocarbon-rich fraction obtained by separation of the coke oven gas.

5. The process as claimed in any one of claims 1 to 4, wherein the reducing unit is a reducing shaft, **characterized in that**

a first subquantity
of the hydrocarbon-rich fraction
is introduced directly into the reducing shaft,

and
a second subquantity
of the hydrocarbon-rich fraction
before introduction thereof into the reducing shaft
is subjected
to at least one operation of the group
- oxidation using technically pure oxygen
- reforming using CO_2 and H_2O,
and then is introduced at least as component of a reducing gas into a reducing unit containing the metal oxides,
wherein the hydrocarbon content
is set by the at least one operation of said group, in such a manner

that the hydrocarbon content in the reducing gas, on entry into the reducing unit, is less than 12% by volume, preferably less than 10% by volume, particularly preferably less than 8% by volume.

6. The process as claimed in any one of claims 1 to 5, **characterized in that**
at least one gas stream containing CO_2 and/or H_2O is added to the hydrocarbon-rich fraction before reforming using CO_2 and H_2O.

7. A device for carrying out a process as claimed in any one of claims 1 to 6,
having a reducing unit (1, 25) for reducing metal oxides,
having a device (2, 28) for separating coke oven gas into a hydrogen-rich fraction and a hydrocarbon-rich fraction,

having, arising therefrom, a
feed line for the hydrocarbon-rich fraction which
opens out
into a unit (21) for
carrying out an operation of the group
- oxidation using technically pure oxygen
- reforming using CO_2 and H_2O,

and having one or more introduction lines (5, 18) for introducing at least one gas stream from the group
- hydrocarbon-rich fraction,
- gas stream obtained in the unit for carrying out oxidation using technically pure oxygen,
- gas stream obtained in the unit for carrying out reforming using CO_2 and H_2O,
into the reducing unit (1, 25),

wherein the

one or more introduction lines (5, 18) open out into the reducing unit, and

upstream of the opening of at least one of the introduction lines (5) into the
reducing unit, an
auxiliary reducing gas line (7) for feeding auxiliary reducing gas to the
reducing unit opens out into this introduction line.

8. The device as claimed in claim 7, **characterized in that** the device (2, 28) for separating coke oven gas into a hydrogen-rich fraction and a hydrocarbon fraction is
a device of the group
- device for pressure-swing adsorption (2),
- device for membrane separation (28).

9. The device as claimed in claim 7 or 8, **characterized in that** upstream of the opening of the auxiliary reducing gas line (7) into the introduction line (5), a
gas furnace (6) is present in the auxiliary reducing gas line (7).

10. The device as claimed in any one of claims 7 to 9, **characterized in that** x introduction lines (5, 18) are present, wherein x is greater than 2 or is equal to 2, of the at most x-1 introduction lines (5) it is true that, upstream of the opening of at least one of the introduction lines (5) into the reducing unit, an auxiliary reducing gas line (7), for feeding auxiliary reducing gas to the reducing unit, opens out into this introduction line (5).

11. The device as claimed in any one of claims 7 to 10, **characterized in that** the reducing unit (1, 25) is a reduction shaft (1).

12. The device for carrying out the process as claimed in any one of claims 7 to 11, **characterized in that** the reducing unit (1, 25) is a fluidized-bed cascade (25).

Figure 1

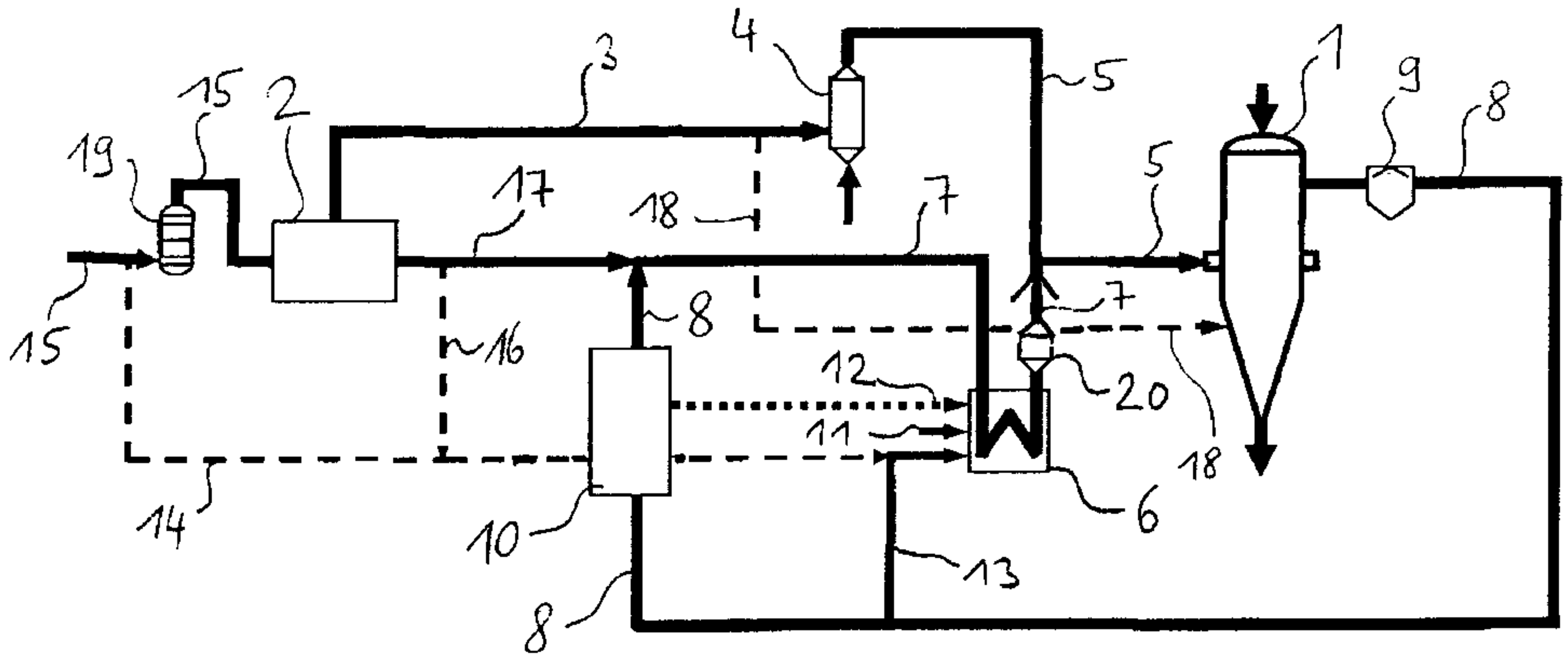


Figure 2

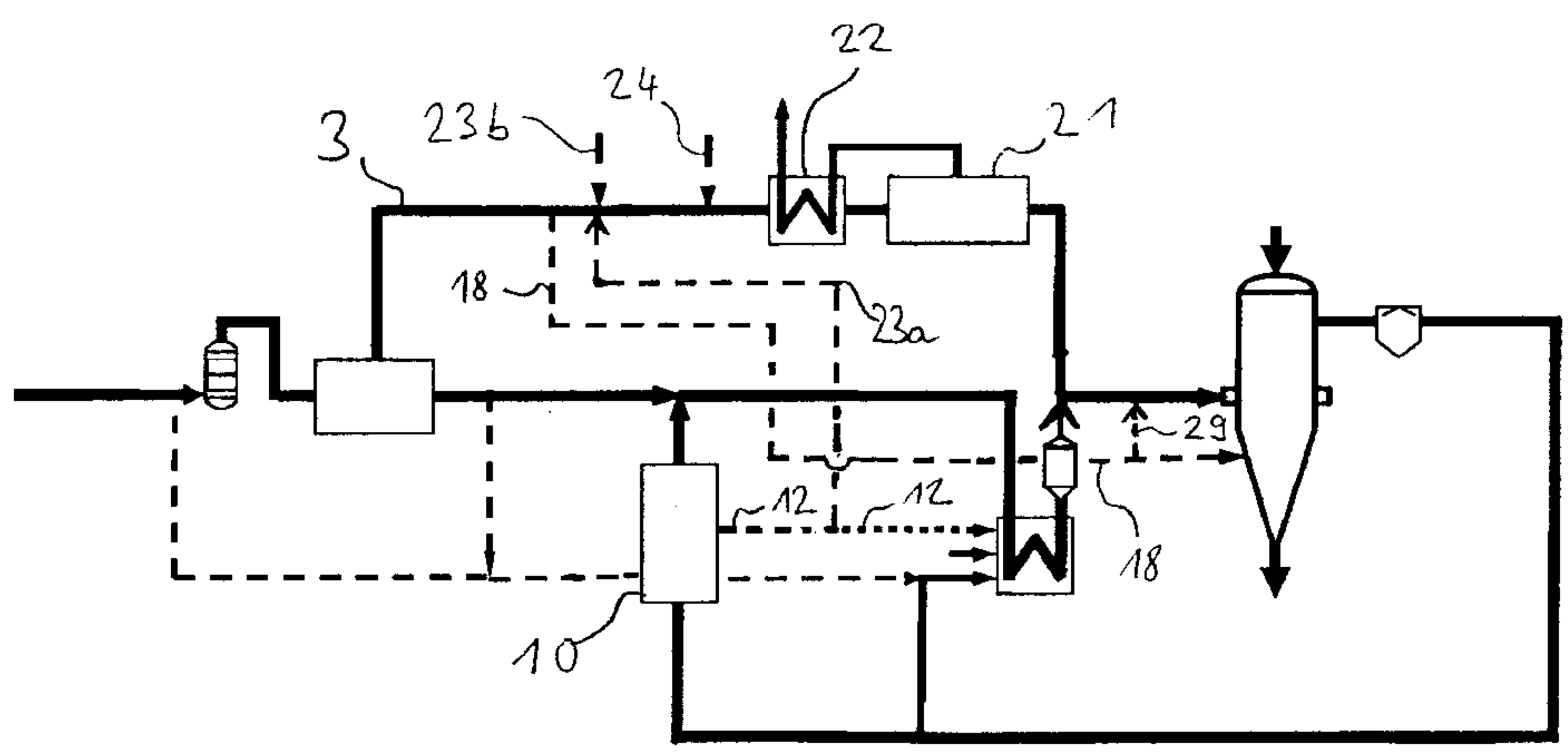


Figure 3

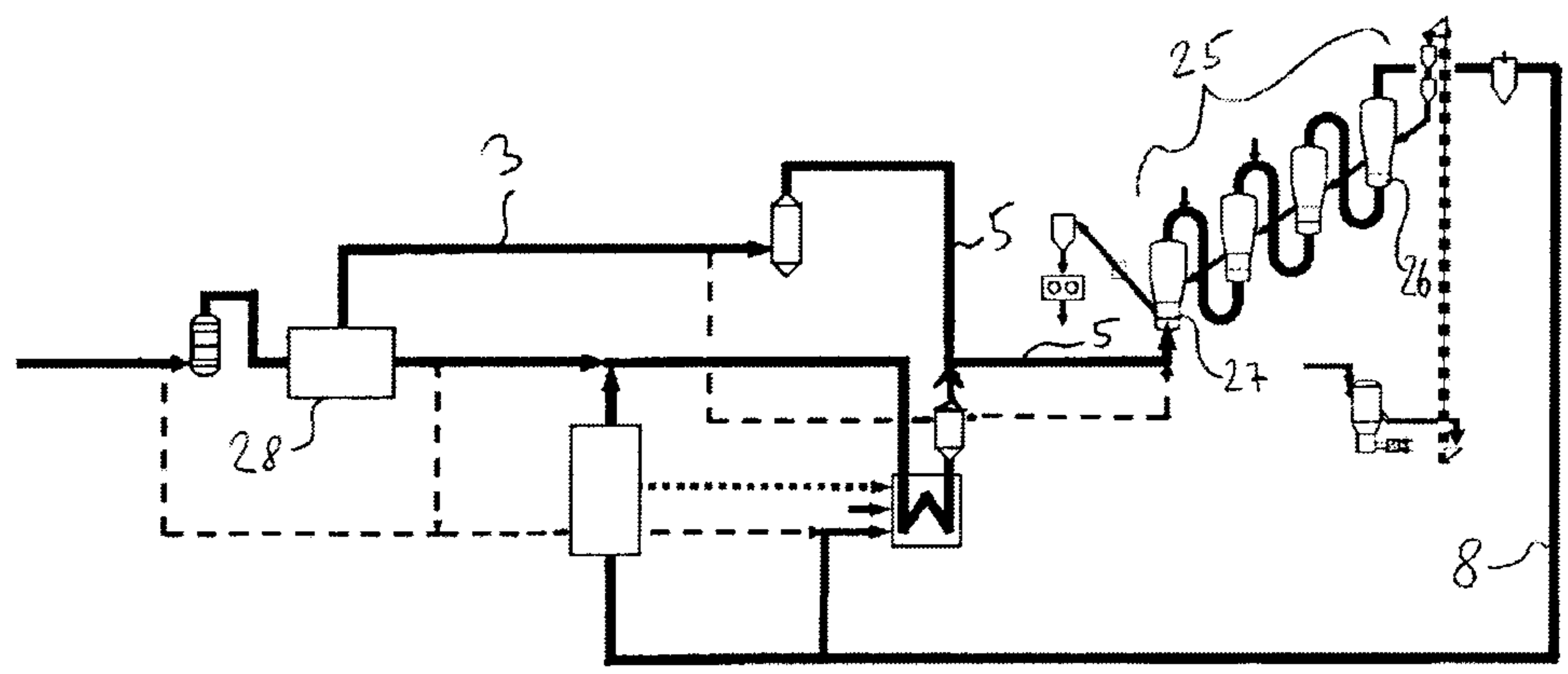
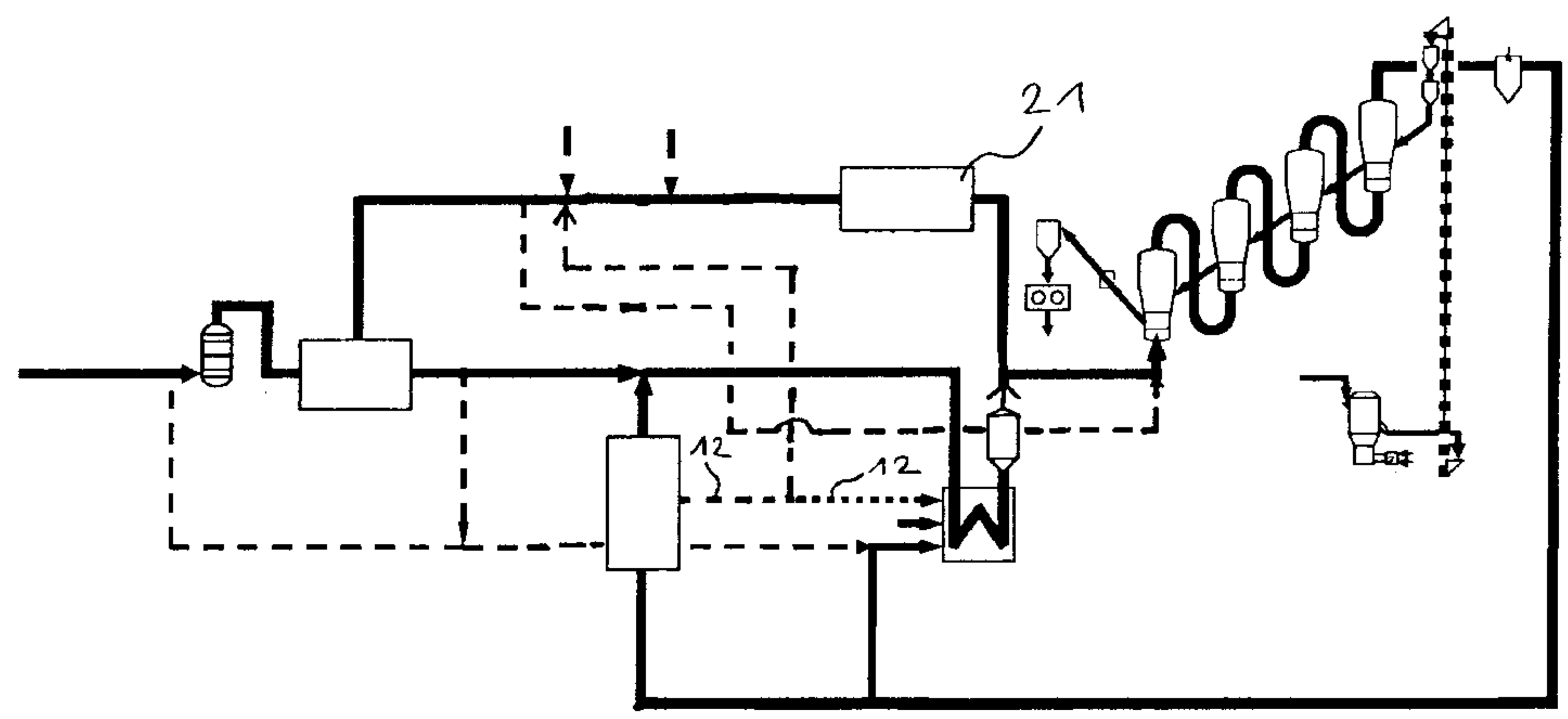


Figure 4



Figur 1