

(12) STANDARD PATENT
(19) AUSTRALIAN PATENT OFFICE

(11) Application No. AU 2014350603 B2

(54) Title
Method and device for steam reforming and for steam cracking of hydrocarbons

(51) International Patent Classification(s)
B01J 8/04 (2006.01) **C01B 3/38** (2006.01)
B01J 8/06 (2006.01) **F23C 6/04** (2006.01)

(21) Application No: **2014350603** (22) Date of Filing: **2014.11.07**

(87) WIPO No: **WO15/070963**

(30) Priority Data

(31) Number	(32) Date	(33) Country
10 2013 019 148.3	2013.11.15	DE
10 2014 007 470.6	2014.05.20	DE

(43) Publication Date: **2015.05.21**

(44) Accepted Journal Date: **2017.11.09**

(71) Applicant(s)
Linde Aktiengesellschaft

(72) Inventor(s)
Nold, Michael

(74) Agent / Attorney
Shelston IP Pty Ltd., Level 21, 60 Margaret Street, Sydney, NSW, 2000, AU

(56) Related Art
US 20120259147 A1
US 2101485 A
US 20090094894 A1
US 3573012 A
DE 2007012 A1

(12) NACH DEM VERTRAG ÜBER DIE INTERNATIONALE ZUSAMMENARBEIT AUF DEM GEBIET DES
PATENTWESENS (PCT) VERÖFFENTLICHTE INTERNATIONALE ANMELDUNG

(19) Weltorganisation für geistiges

Eigentum

Internationales Büro



(43) Internationales

Veröffentlichungsdatum

21. Mai 2015 (21.05.2015)

(10) Internationale Veröffentlichungsnummer

WO 2015/070963 A1

(51) Internationale Patentklassifikation:

B01J 8/04 (2006.01) C01B 3/38 (2006.01)
B01J 8/06 (2006.01) F23C 6/04 (2006.01)

(74) Anwalt: FISCHER, Werner; Linde AG, Legal Services
Intellectual Property, Dr.-Carl-von-Linde-Str. 6-14, 82049
Pullach (DE).

(21) Internationales Aktenzeichen: PCT/EP2014/002986

(81) Bestimmungsstaaten (soweit nicht anders angegeben, für

(22) Internationales Anmeldedatum:

7. November 2014 (07.11.2014)

jede verfügbare nationale Schutzrechtsart): 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, 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, KN, KP, KR, 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.

(25) Einreichungssprache:

Deutsch

(26) Veröffentlichungssprache:

Deutsch

(30) Angaben zur Priorität:

10 2013 019 148.3

(84) Bestimmungsstaaten (soweit nicht anders angegeben, für
jede verfügbare regionale Schutzrechtsart): ARIPO (BW,
GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST,
SZ, TZ, UG, ZM, ZW), eurasisches (AM, AZ, BY, KG,
KZ, RU, TJ, TM), europäisches (AL, AT, BE, BG, CH,
CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE,
IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO,

15. November 2013 (15.11.2013)

DE

10 2014 007 470.6 20. Mai 2014 (20.05.2014)

DE

(71) Anmelder: LINDE AKTIENGESELLSCHAFT
[DE/DE]; Klosterhofstr. 1, 80331 München (DE).

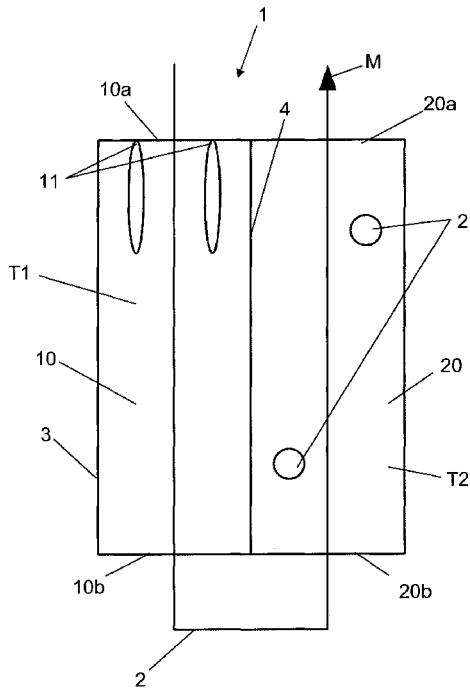
(72) Erfinder: NOLD, Michael; Am Loisachbogen 9B, 82515
Wolfratshausen (DE).

[Fortsetzung auf der nächsten Seite]

(54) Title: METHOD AND DEVICE FOR STEAM REFORMING AND FOR STEAM CRACKING OF HYDROCARBONS

(54) Bezeichnung : VERFAHREN UND VORRICHTUNG ZUR DAMPFREFORMIERUNG SOWIE ZUR DAMPFSPALTUNG
VON KOHLENWASSERSTOFFEN

Figur 1



(57) Abstract: The invention relates to a furnace (1) and to a method for adjusting a material flow (M) to an appropriate temperature, wherein the furnace (1) has a first combustion chamber (10), at least one reactor pipe (2) which serves for receiving a material flow (M) to be heated and which is led through the first combustion chamber (10), and at least one second combustion chamber (20), wherein the at least one reactor pipe (2) is also led through the at least one second combustion chamber (20), wherein the furnace (1) is designed for respectively separately setting a first temperature (T1), which can be generated in the first combustion chamber (10), and a second temperature (T2), which can be generated in the at least one second combustion chamber (20).

(57) Zusammenfassung: Die Erfindung betrifft einen Ofen (1) sowie ein Verfahren zur Temperierung eines Stoffstroms (M), wobei der Ofen (1) eine erste Brennkammer (10), zumindest ein Reaktorrohr (2) zur Aufnahme eines zu erhitzenden Stoffstromes (M), das durch die erste Brennkammer (10) geführt ist, sowie zumindest eine zweite Brennkammer (20) aufweist, wobei das mindestens eine Reaktorrohr (2) auch durch die mindestens eine zweite Brennkammer (20) geführt ist, wobei der Ofen (1) dazu ausgebildet ist, eine in der ersten Brennkammer (10) erzeugbare erste Temperatur (T1) und eine in der mindestens einen zweiten Brennkammer (20) erzeugbare zweite Temperatur (T2) jeweils separat einzustellen.



RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, **Veröffentlicht:**
CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, — *mit internationalem Recherchenbericht (Artikel 21 Absatz
3)*
TG).

06 Oct 2017

2014350603

Process and device for the steam reforming and steam cracking of hydrocarbonsDescription

The invention relates to a furnace, in particular for the cracking of hydrocarbons for producing olefins, and also to a reformer for hydrogen generation via the steam reforming of methane, and also a process for bringing a material stream flowing in a furnace to, and maintaining it at, a temperature.

5 Steam reforming of methane for hydrogen generation is a known process. In such a process, a warmed material stream is passed through a bundle of reactor tubes, which 10 bundle is situated in a fire box (also termed firing chamber) of a furnace. The material stream in this case contains the methane-containing feed, and also steam. The introduction of the material stream into such a furnace proceeds preferably by conducting into the fire box the reactor tubes via the ceiling of a vertically extending fire box, and passing them out again from the fire box at the opposite base. In order to heat 15 the material stream, on the ceiling of the fire box, generally burners are provided which generate very high temperatures (for example up to 1800°C in the flame) locally in the furnace. The reactor tubes of the tube bundle therefore consist of a correspondingly heat-resistant material in order that they can withstand these extreme radiation 20 conditions. The gas burners are operated usually in flame operation, which leads to an inhomogeneous temperature distribution developing in the fire box, wherein the temperature decreases downwards from the ceiling of the fire box.

25 The steam cracking of hydrocarbons is likewise a known process. In such a process, a warmed material stream is passed through a bundle of reactor tubes which are situated in a fire box of a furnace. The material stream in this case contains the gaseous hydrocarbon-containing feed, and also steam. The material stream is introduced into such a furnace preferably by conducting the reactor tubes through the ceiling of a vertically extending fire box into the fire box and conducting them upwards again in a bend tightly above the opposite base, and passing them out of the fire box. For heating 30 the material stream, on the base and/or on the side wall of the fire box, burners are generally provided which generate very high temperatures (for example up to 2000°C in the flame) locally in the furnace. The reactor tubes of the tube bundle therefore consist of a correspondingly heat-resistant material in order that they can withstand these extreme radiation conditions.

2014350603 06 Oct 2017

On entry of the material stream into the fire box, the reactor tubes are first protected against overheating by the comparatively cold material stream. In the further course, the material stream heats up so intensely that it can no longer cool the tubes sufficiently, in such a manner that the temperature of the firing must be restricted in order not to overheat the tubes. The temperature course in the material stream is, inter alia, dependent on the flow velocity of the material stream, the temperature profile in the fire box and other factors, such as, for example, the type and amount of catalyst material arranged in the tubes. Reaction conditions, in particular with respect to the temperature course in the fire box, are variable only to a limited extent as a result of these factors, inter alia, also because the reactor tubes must not be overheated. The result, moreover, is that the efficiency of the energy transfer owing to the given temperature differences between firing and material stream is limited at the tubes. For both processes, a high degree of energetic efficiency is of great importance for economic reasons, for which reason some effort is made in order to utilize the waste heat of burnt fuel.

Any discussion of the prior art throughout the specification should in no way be considered as an admission that such prior art is widely known or forms part of common general knowledge in the field.

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

It is an object of a preferred embodiment of the present invention to specify a device and a process to permit more flexible handling of the reaction dynamics in the material stream with simultaneously high energetic efficiency, and at the same time ensure sufficient protection of the reactor tubes against overheating.

According to a first aspect, the present invention provides furnace having a first and at least one second combustion chamber and also at least one reactor tube which is likewise conducted through the first and at least second combustion chamber for receiving a material stream that is to be heated, thereby flowing first through the first combustion chamber, and then through the at least one second combustion chamber, at least one first burner in the first combustion chamber, for burning a fuel and generating a flame to heat the material stream, wherein the furnace is designed in such a manner that a first temperature which can be generated in the first combustion

chamber and a second temperature which can be generated in the at least one second combustion chamber are each adjustable separately, wherein the furnace has at least one second burner, which is designed to oxidise flamelessly a fuel in the at least one second combustion chamber.

5

According to a second aspect, the present invention provides process for bringing to, and holding at, a temperature of a material stream flowing in a flow direction in at least one reactor tube of a furnace, wherein the material stream flowing in the at least one reactor tube is exposed in a first combustion chamber to a separately adjustable first

10

temperature and subsequently in at least one second combustion chamber for protection of the at least one reactor tube against overheating is exposed to a separately adjustable second temperature, wherein a homogeneous second temperature is set in the at least one second combustion chamber.

15

It is provided according to the invention that the furnace has at least one second combustion chamber, wherein the at least one reactor tube is also conducted through the at least one second combustion chamber, wherein the furnace is designed to adjust, in each case separately, a first temperature which can be generated in the first combustion chamber and a second temperature which can be generated in the at least one second combustion chamber.

20

Via this multichamber principle, in particular the temperature courses in the material stream may be adjusted better, since the ambient temperature in the at least one second combustion chamber is separately adjustable, and therefore a temperature difference between a reactor tube and the at least one further combustion chamber is

5 presetable. As a result, in particular the protection of the reactor tube against overheating can be ensured. At the same time, the possibility of temperature control of the material stream in a reactor tube is obtained. The furnace can of course have a plurality of reactor tubes for conducting/heating the material stream, which reactor tubes can form a tube bundle.

10

In a preferred variant of the invention, it is provided that the at least one reactor tube is conducted through the combustion chambers in such a manner that a material stream flowing therein is conducted first through the first, and then through the at least one second, combustion chamber and possibly further combustion chambers.

15

In a preferred embodiment of the invention, the furnace has at least one first burner which is designed for heating a material stream flowing in the at least one reactor tube to burn a fuel, generating a flame in the first combustion chamber. The furnace can also have a plurality of such first burners in the first combustion chamber.

20

In a preferred variant of the invention, the furnace has at least one second burner, which is designed to oxidize flamelessly a fuel in the at least one second combustion chamber (what is termed an FLX burner).

25 Here also, optionally a plurality of such second burners can be provided in the second combustion chamber (or optionally further combustion chambers).

Such a flameless oxidation (FLX) is distinguished, for example, by the reduction of the formation of nitrogen oxides. By means of such second burners, via a high entry impulse of the air stream, a good flue gas mixing is generated, which leads to a 30 homogeneous temperature distribution in the corresponding combustion chamber.

35 In a preferred embodiment of the invention, it is provided that the at least one first burner is arranged in particular on a ceiling or on a base of the first combustion chamber, wherein, in particular, the entry of the at least one reactor tube into the first combustion chamber is made on that side of the first combustion chamber on which the

2014350603 06 Oct 2017

at least one first burner is also arranged, and wherein, in particular, the at least one reactor tube exits from the first combustion chamber on that side which is opposite the at least one first burner.

- 5 In a further preferred embodiment of the invention, the furnace has a fire box which is subdivided via at least one wall of the fire box into the first and the at least one second combustion chamber. Alternatively, there is of course also the possibility of providing completely separate combustion chambers in the form of separate fire boxes.
- 10 Preferably, the first and the at least one further combustion chamber share, in particular, a common wall. In the case of a plurality of combustion chambers in the form of separate units, the combustion chambers are connected by the reactor tubes which run between the units.
- 15 In a preferred variant of the invention, the furnace is designed in such a manner that the first temperature that can be generated in the first combustion chamber is higher than the second temperature that can be generated in the at least one second combustion chamber. Since the temperature distribution in the first combustion chamber, owing to the arrangement of the first burner, generally turns out in a
- 20 heterogeneous manner, the first temperature relates in particular to the region of the flame of the at least first burner.

Preferably, the furnace is in addition designed in such a manner that a homogeneous second temperature is adjustable in the at least one second combustion chamber. This
25 is the case in particular when the at least one second combustion chamber is heated by the abovedescribed FLX process.

As mentioned above, in particular second burners in the form of FLX burners are suitable for developing a spatially homogeneous temperature profile which need not be
30 the case with a burner operated in flame mode.

In addition, a process is provided for bringing to, and holding at, a temperature of a material stream flowing in a flow direction in at least one reactor tube of a furnace, in particular using a furnace according to the invention, wherein the material stream
35 flowing in the at least one reactor tube is exposed in a first combustion

chamber to a separately adjustable first temperature and subsequently in at least one second combustion chamber for protection of the at least one reactor tube against overheating is exposed to a separately adjustable second temperature.

5 In a preferred embodiment of the invention, a homogeneous second temperature is set in the at least one second combustion chamber. In this case, in particular in the first combustion chamber, the material stream flowing in the at least one reactor tube is exposed to a first temperature decreasing in the direction of flow, wherein the maximum of the first temperature is in particular markedly higher (several 100 K) than
10 the second temperature.

The process according to the invention may be applied to various processes in furnaces.

15 For instance, in a preferred embodiment of the invention it is provided that the material stream hydrocarbon compounds and steam, optionally with the use of suitable catalysts, are reacted in the furnace to form hydrogen and carbon oxides. This chemical reaction is widely known summarized under the expression steam reforming. As catalysts, preferably nickel- or noble metal-based catalyst materials are used.

20 In a further preferred variant of the invention it is provided that the material stream contains relatively long-chain hydrocarbon compounds, in particular naphtha, propane, butane and or ethane, and water, wherein the hydrocarbon compounds are reacted with the water in the furnace to form olefins such as ethene and propene. This
25 chemical reaction is widely known summarized under the expression steam cracking.

30 In a further preferred variant of the invention, the material stream contains propane and, in particular, steam, wherein the propane, optionally in the presence of corresponding catalysts, is reacted in the furnace to form propene in the context of a propane dehydrogenation reaction.

Further features and advantages of the invention are described in the exemplary embodiments shown schematically hereinafter in Figures 1 and 2. In the drawings:

35 Fig. 1 shows a schematic image of a furnace according to the invention; and

Fig. 2 shows a further embodiment of a furnace according to the invention.

Figure 1 shows a schematic depiction of a furnace 1 according to the invention. A material stream M in this case, in at least one reactor tube 2, or a reactor tube bundle 2, is introduced into the first combustion chamber 10 through the ceiling 10a of a first combustion chamber 10. On the ceiling 10a of the first combustion chamber 10, at least one first burner 11 is provided which, in this example, oxidizes a fuel with formation of a flame. In the first combustion chamber 10, the material stream M heats up. The at least one reactor tube 2 leaves the first combustion chamber 10 through the base 10b of the first combustion chamber 10 that is opposite along the vertical the ceiling 10a and enters, through the base 20b of a second combustion chamber 20, into said second combustion chamber 20. In this second combustion chamber 20, two second burners in the form of FLX burners 21 are arranged, in particular, diagonally opposite one another, which burners are preferably designed to generate a comparatively homogeneous spatial temperature profile in the second combustion chamber 20. The material stream M which, in this section, may consist partly of reagent and product (see also the abovedescribed uses of the process), exits from the furnace 1 through the ceiling 20b of the second combustion chamber 20 and is passed on further from there in order possibly to be further processed. It should be noted that in this example, the first and the second combustion chambers 10, 20 are formed by one fire box 3 which is subdivided into the two combustion chambers 10, 20 by a central, vertically running wall 4 of the fire box 3, in such a manner that the two combustion chambers 10, 20 are laterally adjacent to one another. Further combustion chambers in the form of the second combustion chamber 20 can be provided which can be connected, e.g. laterally, to the one second combustion chamber 20.

In Figure 2, as in Figure 1, the material stream M is first conducted through a first combustion chamber 10 of the type of Figure 1, which is likewise heated in the flame-oxidation mode, before the material stream M enters a second combustion chamber 20 which is heated in the FLX process. However, in this case, the material stream M (and the at least one reactor tube 2) enters the second combustion chamber 20 through the ceiling 20a of the second separate combustion chamber 20 and exits again at the base 20b thereof. The dotted depiction of the at least one reactor tube 2 indicates a region or a module 100 of the furnace 1, which can be serially connected as often as desired at

this point. This module 100 has a section of the at least one reactor tube 2 (which is shown dotted) and the said second combustion chamber 20. In each further module, the temperature can be controlled separately. After passing through a last combustion chamber 50, the material stream M exits therefrom and can be appropriately further

5 processed. This system is an optimization of conventional furnaces. A modification of the arrangement according to Figure 2 can provide that the combustion chambers 10, 20, 50 again proceed from a single fire box by subdivision of the fire box by means of walls of the fire box.

List of reference signs

1	Furnace
2	Reactor tube/tube bundle
3	Fire box
4	Dividing wall of two combustion chambers
10	First combustion chamber
10a	Ceiling of the first combustion chamber
10b	Base of the first combustion chamber
11	Burner of the first combustion chamber
20	Second combustion chamber
20a	Ceiling of the second combustion chamber
20b	Base of the second combustion chamber
21	FLX burner of the second combustion chamber
50	A last combustion chamber
100	Combustion chamber module
M	Material stream
T1	First temperature
T2	Second temperature

Claims

2014350603 06 Oct 2017

1. Furnace having a first and at least one second combustion chamber and also at least one reactor tube which is likewise conducted through the first and at least second combustion chamber for receiving a material stream that is to be heated, thereby flowing first through the first combustion chamber, and then through the at least one second combustion chamber, at least one first burner in the first combustion chamber, for burning a fuel and generating a flame to heat the material stream, wherein the furnace is designed in such a manner that a first temperature which can be generated in the first combustion chamber and a second temperature which can be generated in the at least one second combustion chamber are each adjustable separately, wherein the furnace has at least one second burner, which is designed to oxidise flamelessly a fuel in the at least one second combustion chamber.
- 15 2. Furnace according to claim 1, wherein the at least one first burner is arranged on a ceiling or on a base of the first combustion chamber.
- 20 3. Furnace according to claim 1 or 2, wherein the entry of the reactor tube into the first combustion chamber is made on that side of the first combustion chamber on which the at least one first burner is also arranged.
- 25 4. Furnace according to any one of claims 1 to 3, wherein the at least one reactor tube exits from the first combustion chamber on that side which is opposite the at least one first burner.
- 30 5. Furnace according to any one of claims 1 to 4, wherein the furnace has a fire box which is subdivided via at least one wall of the fire box into the first and the at least one second combustion chamber, or wherein the combustion chambers are formed by separate fire boxes.
- 35 6. Furnace according to any one of claims 1 to 5, wherein the furnace is designed in such a manner that the first temperature that can be generated in the first combustion chamber is higher than the second temperature that can be generated in the at least one second combustion chamber.
7. Furnace according to claim 6, wherein the difference between the first temperature and the second temperature is several 100 K.

2014350603
06 Oct 2017

8. Furnace according to any one of claims 1 to 7, wherein the furnace is designed in such a manner that a homogeneous second temperature is adjustable in the at least one second combustion chamber.

5

9. Process for bringing to, and holding at, a temperature of a material stream flowing in a flow direction in at least one reactor tube of a furnace, wherein the material stream flowing in the at least one reactor tube is exposed in a first combustion chamber to a separately adjustable first temperature and subsequently in at least one second combustion chamber for protection of the at least one reactor tube against overheating is exposed to a separately adjustable second temperature, wherein a homogeneous second temperature is set in the at least one second combustion chamber.

10

15 10. Process according to claim 9, wherein the furnace is a furnace according to any one of claims 1 to 8.

11. Process according to claim 9 or 10, wherein the material stream contains hydrocarbon compounds and steam, wherein the hydrocarbons are reacted with 20 the water optionally with a catalyst in the furnace to form hydrogen and the corresponding oxidized carbon compounds.

25 12. Process according to any one of claims 9 to 11, wherein the material stream contains hydrocarbon compounds and steam, wherein the hydrocarbon compounds are reacted with the water in the furnace to form olefins.

13. Process according to claim 12, wherein the hydrocarbon compounds are naphtha, propane, butane and/or ethane.

30 14. Process according to claim 12 or 13, wherein the olefins are ethene and/or propene.

15. Process according to claim 9 or 10, wherein the material stream contains propane and steam, wherein the propane is reacted in the furnace to form propene.

35

16. Process according to claim 15, wherein the propane is reacted in the furnace to form propene in the presence of a catalyst.

1/2

Figure 1

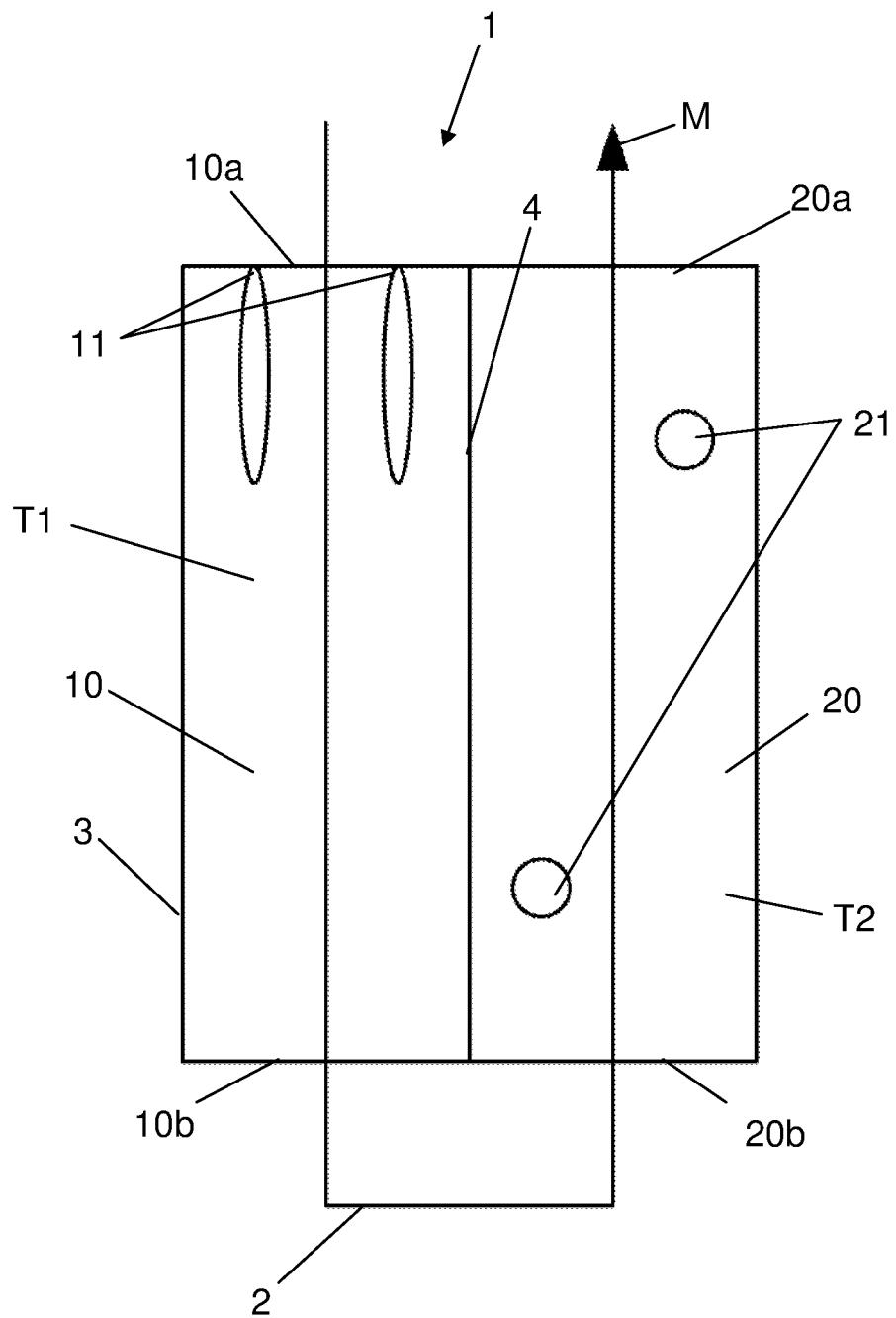


Figure 2

