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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
29 August 2024 (29.08.2024)

WIPO | PCT

(10) International Publication Number
WO 2024/175322 A1

(51) International Patent Classification:
B01J 8/06 (2006.01)

(21) International Application Number:
PCT/EP2024/052458

(22) International Filing Date:
01 February 2024 (01.02.2024)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
23158120.8 23 February 2023 (23.02.2023) EP

(71) Applicant: **L' AIR LIQUIDE, SOCIETE ANONYME POUR L' ETUDE ET L' EXPLOITATION DES PROCEDES GEORGES CLAUDE** [FR/FR]; 75, quai d' Orsay, 75007 PARIS (FR).

(72) Inventors: **COSCIA, Antonio**; An der Höhle 44, 65589 Hadamar (DE). **KAISER, Tobias**; c/o Olof-Palme-Str. 35, 60439 Frankfurt am Main (DE).

(74) Agent: **DROPSCH, Holger**; Gwinnerstr. 27 - 33, 60388 Frankfurt am Main (DE).

(81) **Designated States** *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

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

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

(54) **Title:** BEARING ARRANGEMENT FOR A REFORMER TUBE

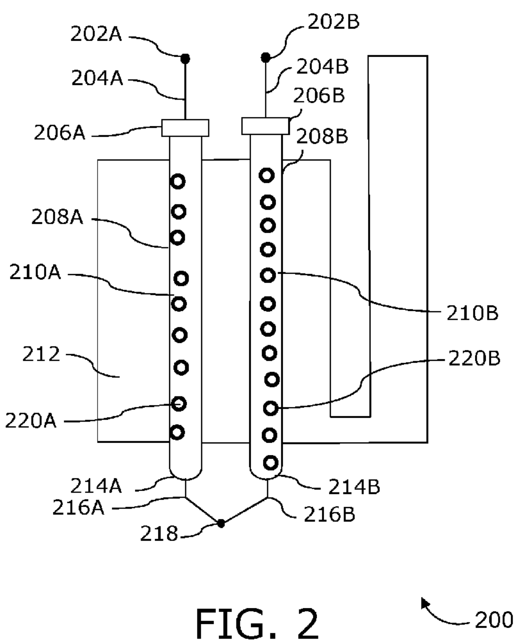

FIG. 2

(57) Abstract: A reformer tube (208A, 208B, 308A, 308B) for a steam reformer or ammonia cracker is provided. The reformer tube includes a pressure-bearing cylindrical jacket tube (210A, 210B, 310A, 310B) arranged to contain a catalyst (220A, 220B, 320A, 320B), an inlet end of the jacket tube connectable to a reactant feed line (204A, 204B, 304A, 304B), the reactant feed line connectable to a reactant feed system (202A, 202B, 302), an outlet end of the jacket tube connectable to a product discharge line (216A, 216B, 316A, 316B), and the product discharge line connectable to a product gas manifold (218, 318). The jacket tube is supported in the direction of its longitudinal axis by means of a fixed-floating bearing arrangement to allow thermal expansion of the jacket tube in longitudinal direction. The fixed bearing (214A, 214B, 314A, 314B) is located at the outlet end of the outer jacket tube and the floating bearing (206A, 206B, 306A, 306B) is located at the inlet end of the outer jacket tube.

WO 2024/175322 A1

BEARING ARRANGEMENT FOR A REFORMER TUBE

TECHNICAL FIELD

The present invention relates generally to a reformer tube and piping system for a steam reformer or ammonia cracker; more specifically, the present invention relates to a reformer tube for a steam reformer or ammonia cracker with a bearing arrangement to absorb thermal expansions. The present invention also relates to a process for steam reforming a hydrocarbonaceous feed stream with steam to form a synthesis gas stream containing carbon monoxide and hydrogen, and to a process of cracking an ammonia feed stream to form a product gas stream containing hydrogen and nitrogen.

BACKGROUND

In steam-methane based synthesis gas production, the previously superheated mixture of natural gas and steam is fed to individual cracking tubes, which are arranged in a cracking tube furnace, via a piping system for feed distribution. The operating temperatures of the piping system can be up to 650 °C resulting in considerable thermal expansion. The reactant feed line or manifold has an outlet for each connected reformer tube also referred to as a hairpin or a pigtail to absorb thermal expansions. Typically, the reformer tube is connected to the respective outlet via a pipe of the same or also smaller diameter than the reactant feed line or distributor itself. During operation, the reactant feed line and the reformer tube undergo elongation in the vertical direction due to thermal expansion, which also changes the position of the reactant feed line or manifold in the vertical direction. During operation, the reformer tubes experience a thermal expansion (dA) of up to 300 millimeters (mm) (e.g. upward thermal linear expansion). Due to the arrangement as described above, this upward expansion may be absorbed by a reactant distributor.

The stresses resulting from the thermal expansion, and resulting elongation (d_{comp}) are generally absorbed or compensated for by a flexible design of the outlets (i.e. hairpins or pigtails). The resultant elongation (d_{comp}) is the difference between the elongation of the reactant feed line (dB) and the elongation of the reformer tube, and the equation is as follows:

$$d_{comp} = dA - dB$$

The resulting elongation (d_{comp}) can be approximately 70 to 30 % of the elongation of the reformer tubes, depending on the steam reformer size.

Thermal linear expansions and displacements of the reactant feed line and/or manifold, resulting from the operating temperature of the system, and the thermal linear expansions and displacements of the feeders, resulting from the operating temperature of the system and the thermal linear expansion of the reformer tubes, are addressed by existing systems separately. One of the existing systems includes a combination of floating and fixed bearings in the reactant feed line/distributor. The floating bearings may be guides and cantilever hangers or similar pipeline supports. Another existing solution provides outlets as soft as possible with pipe routing with correspondingly large expansion bends. Short pipe routing, however, minimizes heat losses of the system and reduces the necessary material input. The outlets (e.g. a reactant distribution system) is one of the main sources of heat loss in the entire synthesis gas plant. Due to the necessary expansion bends or loops at the outlets, a high overall height and/or width depending on the configuration of the piping system results, which is usually housed in the "penthouse" (i. e. the upper, roofed part) of the reformer furnace generally provided for weather protection and reduction of heat losses due to wind effects. As a result, in addition to the steel structure, other piping such as for fuel gases, and combustion air must also be made longer in accordance with the resulting distances. This also increases heat losses of the other distribution systems and the construction costs of the entire structure.

Therefore, there is a need to address the aforementioned technical drawbacks in existing known technologies for providing reformer tubes for a reformer with efficient thermal expansion absorption capabilities.

In addition, since ammonia cracking is discussed as a way to provide hydrogen in vicinity of potential consumers, there is a need to propose respective apparatuses and processes. It has been found that apparatuses classically used for steam reforming, for example reformer tubes and/or reformer furnaces, can be operated as ammonia crackers after minor modifications. Thus, for the purposes of the present description, the terms reformer, reformer furnace, reformer tube are also to be understood as apparatuses and/or devices that can be used also in the context of ammonia cracking.

SUMMARY

The present invention seeks to provide a reformer tube for a steam reformer or ammonia cracker where capital costs are dominant in determining the overall economics. The present invention aims to provide a solution that overcomes, at least partially, the problems encountered in the prior art by using a rigid connection in combination with a floating bearing for absorbing stress forces due to the thermal expansion of a pressure-bearing cylindrical jacket tube of the reformer tube in a radial direction. The thermal linear expansion of the reformer tube is completely transferred from a product discharge line to a connected reactant feed line and compensated by the reactant feed line by means of the floating bearing. Thus, the additional expansion bends in the reactant feed line are avoided, thereby reducing the pipe length of the reformer tube in a synthesis gas plant.

The object of the present invention is achieved by the solutions provided in the enclosed independent claims. Advantageous implementations of the present invention are further defined in the dependent claims.

According to a first aspect, the reformer tube for a steam reformer or ammonia cracker according to the present invention comprises:

(a) a pressure-bearing cylindrical jacket tube arranged to contain a catalyst as a bulk catalyst, a catalyst bed of catalyst particles, structured packing, honeycomb catalyst, or combinations thereof;

(b) an inlet end of the pressure-bearing cylindrical jacket tube connectable to a reactant feed line;

(c) the reactant feed line connectable to a reactant feed system;

(d) an outlet end of the pressure-bearing cylindrical jacket tube connectable to a product discharge line;

(e) the product discharge line connectable to a product gas manifold;

wherein

(f) the pressure-bearing cylindrical jacket tube is supported in the direction of its longitudinal axis by means of a fixed-floating bearing arrangement to allow thermal expansion of the pressure-bearing cylindrical jacket tube in longitudinal direction,

wherein

(g) the fixed bearing is located at the outlet end of the outer pressure-bearing cylindrical jacket tube and the floating bearing is located at the inlet end of the outer pressure-bearing cylindrical jacket tube.

The reformer tube and the bearing arrangement of the reformer tube according to the present invention are of advantage in that a rigid connection in combination with the floating bearing is used for absorbing stress forces due to the thermal expansion of the pressure-bearing cylindrical jacket tube of the reformer tube in an axial (longitudinal) and/or radial direction. The thermal linear expansion of the reformer tube is completely transferred from the product discharge line to the connected reactant feed line and compensated by the reactant feed line by means of the floating bearing. Thus, the additional expansion bends in the reactant feed line (i.e. hairpins, pigtails) are avoided, thereby reducing the overall height or size of an entire synthesis gas plant system, and also reducing heat losses by shortening the transfer lines, namely the reactant feed line, and the product discharge line. Moreover, due to the large vertical transmission of forces via the product discharge line into the reactant feed line, the bending forces, loads, and stresses acting on the product discharge line are reduced which results in an increase in the expected service life and an increase in the operational reliability of the reformer furnace.

According to a second aspect, the present invention provides a reformer furnace comprising a floor, a ceiling and side walls forming a furnace interior, wherein a plurality of reformer tubes as described above are arranged within the furnace interior and are heated by burners.

According to a third aspect, the present invention provides a process for steam reforming a hydrocarbonaceous feed stream with steam to form a synthesis gas stream containing carbon monoxide and hydrogen, comprising the steps of:

(a) providing a plurality of reformer tubes as described above in a reformer furnace;

(b) connecting the reactant feed lines of the reformer tubes to a common reactant feed system;

(c) connecting the product discharge lines of the reformer tubes to a common product gas manifold;

(d) injecting the hydrocarbonaceous feed stream through the reactant feed system and the reactant feed lines of the reformer tubes;

(e) reacting the hydrocarbonaceous feed stream with steam in the reformer tubes under steam reforming conditions to form a crude synthesis gas stream;

(f) discharging the crude synthesis gas stream from the reformer tubes via the product discharge lines and the common product gas manifold;

(g) feeding the crude synthesis gas stream to at least one further work-up, separation, purification or conditioning step, and discharging a purified or conditioned synthesis gas stream and/or its constituents hydrogen and/or carbon monoxide.

According to a fourth aspect, the present invention provides a process for cracking an ammonia feed stream with steam to form a product gas stream containing hydrogen and nitrogen, comprising the steps of:

(a) providing a plurality of reformer tubes according to claims 1 to 7 in a reformer furnace (200, 300) according to claims 8 to 9;

(b) connecting the reactant feed lines (204A, 204B, 304A, 304B) of the reformer tubes (208A, 208B, 308A, 308B) to a common reactant feed system;

(c) connecting the product discharge lines (216A, 216B, 316A, 316B) of the reformer tubes (208A, 208B, 308A, 308B) to a common product gas manifold;

(d) injecting the ammonia feed stream through the reactant feed system (202A, 202B, 302) and the reactant feed lines (204A, 204B, 304A, 304B) of the reformer tubes (208A, 208B, 308A, 308B);

(e) reacting the ammonia feed stream in the reformer tubes (208A, 208B, 308A, 308B) under ammonia cracking conditions to form a product gas gas stream containing hydrogen and nitrogen;

(f) discharging the product gas gas stream from the reformer tubes (208A, 208B, 308A, 308B) via the product discharge lines (216A, 216B, 316A, 316B) and the common product gas manifold; and

(g) feeding the product gas gas stream to at least one further work-up, separation, purification or conditioning step, discharging a purified product gas gas stream and/or its constituents hydrogen and/or nitrogen.

The reformer tube and the bearing arrangement of the reformer tube according to the present invention are of advantage in that a rigid connection in combination with the floating bearing is used for absorbing stress forces due to the thermal expansion of the pressure-bearing cylindrical jacket tube of the reformer tube in an axial (longitudinal) and/or radial direction. The thermal linear expansion of the reformer tube is completely transferred from the product discharge line to the connected reactant feed line and compensated by the reactant feed line by means of the floating bearing. Thus, the additional expansion bends in the reactant feed line (i.e. hairpins, pigtails) are avoided, thereby reducing the overall height or size of an entire synthesis gas plant system, and also reducing heat losses by shortening the transfer lines, namely the reactant feed line, and the product discharge line. Moreover, due to the large vertical transmission of forces via the product discharge line into the reactant feed line, the bending forces, loads, and stresses acting on the product discharge line are reduced which results in an increase in the expected service life and an increase in the operational reliability of the reformer furnace.

Embodiments of the present invention eliminate the aforementioned drawbacks in existing known approaches by providing a rigid connection in combination with the fixed-floating bearing arrangement in the reformer tube for absorbing stress forces due to thermal expansion in the reformer tube.

Additional aspects, advantages, features, and objects of the present invention are made apparent from the drawings and the detailed description of the illustrative embodiments construed in conjunction with the appended claims that follow. It will be appreciated that features of the present invention are susceptible to being combined in various combinations without departing from the scope of the present invention as defined by the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

The summary above, as well as the following detailed description of illustrative embodiments, is better understood when read in conjunction with the appended drawings. To illustrate the present invention, exemplary constructions of the invention are shown in the drawings. However, the present invention is not limited to specific methods and instrumentalities disclosed herein. Moreover, those in the art will understand that the drawings are not to scale. Wherever possible, the same elements have been indicated by identical numbers. Embodiments of the present invention will now be described, by way of example only, with reference to the following diagrams wherein:

FIGS. 1A-1D are schematic illustrations of arrangements and configurations of reformed tubes in a reformer furnace according to the prior art;

FIG. 2 is a schematic illustration a reformer furnace with a double reactant feed system according to an embodiment of the present invention;

FIG. 3 is a schematic illustration a reformer furnace with a single reactant feed system according to an embodiment of the present invention.

DETAILED DESCRIPTION OF EMBODIMENTS

The following detailed description illustrates embodiments of the present invention and ways in which they can be implemented. Although some modes of carrying out the present invention have been disclosed, those skilled in the art would recognize that other embodiments for carrying out or practicing the present invention are also possible.

Steam reforming conditions or ammonia cracking conditions are known to those skilled in the art from the prior art. These are the physicochemical conditions under which a measurable, preferably industrially relevant, conversion of hydrocarbons to synthesis gas products, or conversion of ammonia to a product gas containing hydrogen and nitrogen is achieved. For example, in the context of steam reforming, important parameters include adjustment of a suitable steam reforming entry temperature of typically about 1000 °C and addition of steam to the input gas containing hydrocarbons and thus adjustment of a steam/carbon ratio (S/C ratio). Typical values for the S/C ratio are between 1.5 and 3.5 mol/mol. Typical steam reforming inlet temperatures are up to 700 °C and typically range between 550 and 650 °C. Necessary adjustments of these conditions to the respective operational requirements will be made by those skilled in the art on the basis of routine experiments. Any specific reaction conditions disclosed may serve here as a guide, but they should not be regarded as limiting in relation to the scope of the invention.

A fluid connection between two regions of an apparatus or a plant or a reformer furnace according to the invention is to be understood as meaning any type of connection whatsoever which makes it possible for a fluid, for example a gas stream, to flow from one to the other of the two regions, neglecting any interposed regions or components. In particular a direct fluid connection is to be understood as meaning any type of connection whatsoever which makes it possible for a fluid, for example a gas stream, to flow directly from one to the other of the two regions, wherein no further regions or components are interposed with the exception of purely transportation operations and the means required therefor, for example pipelines, valves, pumps, compressors, reservoirs. One example would be a pipeline leading directly from one to the other of the two regions.

A means is to be understood as meaning something that enables or is helpful in the achievement of a goal. In particular, means for performing a particular process step are to be understood as meaning any physical articles that would be considered by a person skilled in the art in order to be able to perform this process step. For example, a person skilled in the art will consider means of introducing or discharging a material stream to include any transporting and conveying apparatuses, i.e., for example pipelines, pumps, compressors, valves, which seem necessary or sensible to said skilled person for performance of this process step on the basis of his knowledge of the art.

For the purposes of this description steam is to be understood as being synonymous with water vapor unless the opposite is indicated in an individual case. By contrast, the term “water” refers to water in the liquid state of matter unless otherwise stated in an individual case.

In the context of the present invention, the reactant feed line or distributor is connected to one or more series or rows of reformer tubes through an individual outlet, by having a maximum of change of direction in 90°. The thermal linear expansion of the reformer tube is transferred from the outlets to the connected reactant feed line and is compensated by the reactant feed line of a corresponding floating bearing. The reactant feed line or distributor has only one fixed bearing in the axial (longitudinal) direction of the distributor.

According to a first aspect, the present invention provides a reformer tube for a reformer or ammonia cracker, comprising:

(a) a pressure-bearing cylindrical jacket tube arranged to contain a catalyst as a bulk catalyst, a catalyst bed of catalyst particles, structured packing, honeycomb catalyst, or combinations thereof;

(b) an inlet end of the pressure-bearing cylindrical jacket tube connectable to a reactant feed line;

(c) the reactant feed line connectable to a reactant feed system;

(d) an outlet end of the pressure-bearing cylindrical jacket tube connectable to a product discharge line;

(e) the product discharge line connectable to a product gas manifold;

wherein

(f) the pressure-bearing cylindrical jacket tube is supported in the direction of its longitudinal axis by means of a fixed-floating bearing arrangement to allow thermal expansion of the pressure-bearing cylindrical jacket tube in longitudinal direction,

wherein

(g) the fixed bearing is located at the outlet end of the outer pressure-bearing cylindrical jacket tube and the floating bearing is located at the inlet end of the outer pressure-bearing cylindrical jacket tube.

The reformer tube and the bearing arrangement of the reformer tube according to the present invention are of advantage in that a rigid connection in combination with the floating bearing is used for absorbing stress forces due to the thermal expansion of the pressure-bearing cylindrical jacket tube of the reformer tube in an axial (longitudinal) and/or radial direction. The thermal linear expansion of the reformer tube is completely transferred from the product discharge line to the connected reactant feed line and compensated by the reactant feed line by means of the floating bearing. Thus, the additional expansion bends in the reactant feed line (i.e. hairpins, pigtails) are avoided, thereby reducing the overall height or size of an entire synthesis gas plant system, and also reducing heat losses by shortening the transfer lines, namely the reactant feed line, and the product discharge line. Moreover, due to the large vertical transmission of forces via the product discharge line into the reactant feed line, the bending forces, loads, and stresses acting on the product discharge line are reduced which results in an increase in the expected service life and an increase in the operational reliability of the reformer furnace.

Optionally, the reactant feed line has only one single change of direction, preferably only one single change of direction of 90°. While this increases the number of expansion bends by one as compared to a entirely straight connection, the arrangement is still robust and serves to decrease the building height of the steam reformer or ammonia cracker, and reduces the length of the connection lines and the heat losses related thereto.

Optionally, the product discharge line has no change of direction and its longitudinal axis coincides with or is aligned with the longitudinal axis of the pressure-bearing cylindrical jacket tube. In this way, expansion stresses occur predominantly one-dimensional in the direction of the longitudinal axis of the pressure-bearing cylindrical jacket tube, and can be accounted for in the construction of the reformer furnace and its framework in a simple manner.

Optionally, the floating bearing is designed as a rolling bearing, ball bearing, plain bearing or floating support bearing.

Optionally, the floating bearing and the fixed bearing are designed such that they can absorb stress forces due to thermal expansion of the pressure-bearing cylindrical jacket tube in the radial direction. While the longitudinal length increase of the reformer tubes during heat-up of the reformer furnace dominates, the length increase in the radial direction is much smaller but may be still significant. Thus, this embodiment has special advantages in coping with thermal stresses in both the longitudinal as well as the radial direction.

Optionally, the inlet ends of several jacket tubes can be connected to a common reactant feed line. This further reduces the length of the connection lines and the heat losses related thereto.

Optionally, the product discharge line forms a right angle with the product gas manifold in the connected state. While this increases the number of expansion bends by one as compared to a entirely straight connection, the arrangement is still robust and serves to decrease the building height of the steam reformer or ammonia cracker, and reduces the length of the connection lines and the heat losses related thereto.

According to a second aspect, the present invention provides a reformer furnace comprising a floor, a ceiling and side walls forming a furnace interior, wherein a plurality of reformer tubes as described above are arranged within the furnace interior and are heated by burners.

Optionally, the plurality of reformer tubes are arranged in rows, preferably in parallel rows, wherein each two reformer tubes adjacent in a row are connected to a common reactant feed line. This further reduces the length of the connection lines and the heat losses related thereto.

Optionally, the present invention provides a use of a reformer tube and/or a reformer furnace as described above for steam reforming a hydrocarbonaceous feed stream with steam to a crude synthesis gas stream or for cracking an ammonia feed stream to a product gas stream containing hydrogen and nitrogen.

According to a third aspect, the present invention provides a process for steam reforming a hydrocarbonaceous feed stream with steam to form a synthesis gas stream containing carbon monoxide and hydrogen, comprising the steps of:

(a) providing a plurality of reformer tubes as described above in a reformer furnace;

(b) connecting the reactant feed lines of the reformer tubes to a common reactant feed system;

(c) connecting the product discharge lines of the reformer tubes to a common product gas manifold;

(d) injecting the hydrocarbonaceous feed stream through the reactant feed system and the reactant feed lines of the reformer tubes;

(e) reacting the hydrocarbonaceous feed stream with steam in the reformer tubes under steam reforming conditions to form a crude synthesis gas stream;

(f) discharging the crude synthesis gas stream from the reformer tubes via the product discharge lines and the common product gas manifold; and

(g) feeding the crude synthesis gas stream to at least one further work-up, separation, purification or conditioning step, and discharging a purified or conditioned synthesis gas stream and/or its constituents hydrogen and/or carbon monoxide.

According to a fourth aspect, the present invention provides a process for cracking an ammonia feed stream with steam to form a product gas stream containing hydrogen and nitrogen, comprising the steps of:

(a) providing a plurality of reformer tubes according to claims 1 to 7 in a reformer furnace (200, 300) according to claims 8 to 9;

(b) connecting the reactant feed lines (204A, 204B, 304A, 304B) of the reformer tubes (208A, 208B, 308A, 308B) to a common reactant feed system;

(c) connecting the product discharge lines (216A, 216B, 316A, 316B) of the reformer tubes (208A, 208B, 308A, 308B) to a common product gas manifold;

(d) injecting the ammonia feed stream through the reactant feed system (202A, 202B, 302) and the reactant feed lines (204A, 204B, 304A, 304B) of the reformer tubes (208A, 208B, 308A, 308B);

(e) reacting the ammonia feed stream in the reformer tubes (208A, 208B, 308A, 308B) under ammonia cracking conditions to form a product gas gas stream containing hydrogen and nitrogen;

(f) discharging the product gas gas stream from the reformer tubes (208A, 208B, 308A, 308B) via the product discharge lines (216A, 216B, 316A, 316B) and the common product gas manifold; and

(g) feeding the product gas gas stream to at least one further work-up, separation, purification or conditioning step, discharging a purified product gas gas stream and/or its constituents hydrogen and/or nitrogen.

The reformer tube with the fixed-floating bearing arrangement that is provided in the process according to the present invention are of advantage in that a rigid connection in combination with the floating bearing is used for absorbing stress forces due to the thermal expansion of the pressure-bearing cylindrical jacket tube of the reformer tube in an axial (longitudinal) and/or radial direction. The thermal linear expansion of the reformer tube is completely transferred from the product discharge line to the connected reactant feed line and compensated by the reactant feed line by means of the floating bearing. Thus, the additional expansion bends in the reactant feed line (i.e. hairpins, pigtails) are avoided, thereby reducing the overall height or size of an entire synthesis gas plant system, and also reducing heat losses by shortening the transfer lines, namely the reactant feed line, and the product discharge line. Moreover, due to the large vertical transmission of forces via the product discharge line into the reactant feed line, the bending forces, loads, and stresses acting on the product discharge line are reduced which results in an increase in the expected service life and an increase in the operational reliability of the reformer furnace.

Embodiments of the present invention substantially eliminate or at least partially address the aforementioned technical drawbacks in existing technologies by providing a rigid connection in combination with a floating bearing arrangement in the reformer tube for absorbing stress forces due to thermal expansion in the reformer tube.

DETAILED DESCRIPTION OF THE DRAWINGS

FIGS. 1A-1D are schematic illustrations of arrangements and configurations of reformer tubes in a reformer furnace **100** according to the prior art. The reformer furnace **100** may be arranged in different arrangements such as a radiant wall arrangement, a top–fired arrangement, a bottom fired arrangement and a terrace–wall arrangement.

FIG. 1A shows a reformer furnace **100** with exemplary two reformer tubes, arranged in a radiant wall arrangement including feed distribution systems **102A** and **102B**, feed lines **104A** and **104B**, reformer tubes **106A** and **106B**, product collector lines **110A** and **110B,** and a feed manifold **112**. The feed lines **104A** and **104B** are connected to an inlet of each reformer tubes **106A** and **106B**. The feed lines **104A** and **104B** are arranged at an angle to the reformer tubes **106A** and **106B**. The feed distribution systems **102A** and **102B** are connected to the feed lines **104A** and **104B** through a pipe of a smaller diameter than the feed lines **104A** and **104B** to transmit to the reformer tubes **106A** and **106B**. The reformer tubes **106A** and **106B** are connected to the product collector lines **110A** and **110B** via a pipe of a smaller diameter than the product collector lines **110A** and **110B**. The product collector lines **110A** and **110B** have an outlet and are connected to the product manifold **112**.

FIG. 1B shows a reformer furnace **100** with exemplary two reformer tubes, arranged in a top-fired arrangement, including feed distribution systems **102A** and **102B**, feed lines **114A** and **114B**, reformer tubes **106A** and **106B**, product collector lines **110A** and **110B**, and a feed manifold **112**. The feed lines **114A** and **114B** are connected to an inlet of each reformer tubes **106A** and **106B**. The feed lines **114A** and **114B** include one or more bends. The feed distribution systems **102A** and **102B** are connected to the feed lines **114A** and **114B** through a pipe of a smaller diameter than the feed lines **114A** and **114B** to transmit to the reformer tubes **106A** and **106B**. The reformer tubes **106A** and **106B** are connected to the product collector lines **110A** and **110B** via a pipe of a smaller diameter than the product collector lines **110A** and **110B**. The product collector lines **110A** and **110B** have an outlet and are connected to the product manifold **112**.

FIG. 1C shows a reformer furnace **100** with exemplary two reformer tubes, arranged in a bottom–fired arrangement, including a feed distribution system **116A**, feed lines **118A** and **118B**, reformer tubes **106A** and **106B**, product collector lines **110A** and **110B,** and feed manifolds **120A** and **120B**. The feed lines **118A** and **118B** are connected to an inlet of each reformer tubes **106A** and **106B**. The feed lines **118A** and **118B** include a bend. The feed distribution system **116A** is connected to the feed lines **118A** and **118B** through a pipe of a smaller diameter than the feed lines **118A** and **118B**. The reformer tubes **106A** and **106B** are connected to the product collector lines **110A** and **110B** via a pipe of a smaller diameter than the product collector lines **110A** and **110B.** The product collector lines **110A** and **110B** are in an example U-shaped and have an outlet and are connected to the product manifolds **120A** and **120B**.

FIG. 1D shows a reformer furnace **100** with exemplary two reformer tubes, arranged in a terrace wall arrangement, including feed distribution systems **122A** and **122B**, feed lines **124A** and **124B**, which are in an example U-shaped, reformer tubes **106A** and **106B**, product collector lines **110A** and **110B**, and a feed manifold **126A.** The feed lines **124A** and **124B** are connected to an inlet of each reformer tube **106A** and **106B**. The feed lines **124A** and **124B** include a hairpin or a pigtail bend. The reformer tubes **106A** and **106B** are connected to the feed lines **124A** and **124B** through a pipe of a smaller diameter than the feed lines **124A** and **124B**. The reformer tubes **106A** and **106B** are connected to the product collector lines **110A** and **110B** via a pipe of a smaller diameter than the product collector lines **110A** and **110B**. The product collector lines **110A** and **110B** have an outlet and are connected to the product manifold **126A**.

In an example, the superheated mixture of natural gas or methane and steam is fed to the individual reformer tubes **106A** and **106B** that are arranged in the reformer furnace **100** using the feed distribution system (e.g. **102A** and **102B**, **116A**, **122A** and **122B**). The operating temperature of the feed lines may be up to 650 °C, which results in considerable thermal expansion. The piping system (i.e. feed lines and product collector lines) may absorb the thermal expansions.

During operation, the feed lines (e.g. **104A** and **104B, 114A** and **114B, 118A** and **118B,** and **124A** and **124B**) of various arrangements (i.e. a radiant wall, a top–fired wall, a bottom fired wall and a terrace–wall) in the reformer furnace **100** undergo elongation in the vertical direction due to thermal expansion. The reformer tubes **106A** and **106B** change the position of the product collector lines **110A** and **110B** in the vertical direction. The reformer tubes **106A** and **106B** experience a thermal expansion of up to 300 millimeters (mm) (i.e. upward thermal linear expansion). Due to this arrangement, the product collector lines **110A** and **110B** absorb upward thermal expansion. The operating temperature of the reformer furnace **100** results in thermal linear expansions of the reactant feed lines (e.g. **104A** and **104B, 114A** and **114B, 118A** and **118B,** and **124A** and **124B**) and displacements of the feed and/or product manifolds (e.g. **112, 120A** and **120B,** and **126A**) of various arrangements of the reformer furnace **100**.

FIG. 2 is a schematic illustration of a reformer furnace **200** with a double reactant feed system according to an embodiment of the present invention. The reformer furnace **200** includes reactant feed systems **202A** and **202B,** reactant feed lines **204A** and **204B**, floating bearings **206A** and **206B**, reformer tubes **208A** and **208B** comprising pressure-bearing cylindrical jacket tubes **210A** and **210B**, a furnace interior **212**, fixed bearings **214A** and **214B**, product discharge lines **216A** and **216B**, and a product gas manifold **218**.

The reformer furnace **200** may include a floor, a ceiling or side walls to form the furnace interior **212**, which arranges the reactant feed systems **202A** and **202B,** the reactant feed lines **204A** and **204B**, the floating bearings **206A** and **206B**, the reformer tubes **208A** and **208B**, the pressure-bearing cylindrical jacket tubes **210A** and **210B**, the fixed bearings **214A** and **214B**, the product discharge lines **216A** and **216B**, and the product gas manifold **218** in the furnace interior **212**. Optionally, the reformer furnace **200** has one or more reformer tubes that are arranged within the furnace interior **212** and are heated by burners.

The pressure-bearing cylindrical jacket tube **210A** and **210B** is arranged to contain a catalyst **220A** and **220B** as a bulk catalyst, a catalyst bed of catalyst particles, structured packing, honeycomb catalyst, or combinations thereof. An inlet end of the pressure-bearing cylindrical jacket tube (**210A** and **210B**) is connectable to the reactant feed lines **204A** and **204B**. The reactant feed lines **204A** and **204B** are connectable to the reactant feed systems **202A** and **202B**. The fixed bearings **214A** and **214B** are located at an outlet end of the pressure-bearing cylindrical jacket tubes **210A** and **210B** and the floating bearings **206A** and **206B** are located at an inlet end of the pressure-bearing cylindrical jacket tubes **210A** and **210B**. The floating bearings **206A** and **206B** may be designed as a rolling bearing, a ball bearing, a plain bearing or a floating support bearing. The outlet end of the pressure-bearing cylindrical jacket tubes **210A** and **210B** is connectable to the product discharge lines **216A** and **216B**. The product discharge lines **216A** and **216B** are connectable to the product gas manifold **218**. Optionally, the product discharge lines **216A** and **216B** form a right angle with the product gas manifold **218** in a connected state.

The pressure-bearing cylindrical jacket tubes **210A** and **210B** are supported in a direction of their longitudinal axis using a fixed-floating bearing arrangement (i.e. the floating bearings **206A** and **206B**, and the fixed bearings **214A** and **214B**) to allow thermal expansion of the pressure-bearing cylindrical jacket tubes **210A** and **210B** in a longitudinal direction. Optionally, the floating bearings **206A** and **206B** and the fixed bearings **214A** and **214B** absorb stress forces due to the thermal expansion of the pressure-bearing cylindrical jacket tubes **210A** and **210B** in a radial direction. The thermal linear expansion of the reformer tubes **208A** and **208B** is transferred to the reactant feed systems **202A** and **202B** and is compensated using the floating bearing **206A** and **206B**.

Optionally, the reactant feed lines **204A** and **204B** are connected to one or more series or rows of reformer tubes through one or more individual outlets of the reactant feed systems **202A** and **202B**. Optionally, the reactant feed lines **204A** and **204B** include only one single change of direction. The only one single change of direction may be 90°.

Optionally, the product discharge line (e.g. **216A** and **216B**) has no change of direction and its longitudinal axis coincides with or is aligned with the longitudinal axis of the pressure-bearing cylindrical jacket tubes **210A** and **210B**. Optionally, inlet ends of one or more jacket tubes can be connected to a common reactant feed line. Optionally, the one or more reformer tubes are arranged in rows, preferably in parallel rows. Optionally, each of the one or more reformer tubes adjacent in a row are connected to the common reactant feed line. The reformer furnace **200** steam reforms a hydrocarbonaceous feed stream with steam to form a crude synthesis gas stream.

The bearing arrangement of the reformer tube (**208A**, **208B**) according to the present invention is of advantage in that a rigid connection in combination with the floating bearing (**206A**, **206B**) is used for absorbing stress forces due to the thermal expansion of the pressure-bearing cylindrical jacket tube (**210A**, **210B**) of the reformer tube (**208A**, **208B**) in an axial (longitudinal) and/or radial direction. The thermal linear expansion of the reformer tube (**208A**, **208B**) is completely transferred from the product discharge line (**216A**, **216B**) to the connected reactant feed line and compensated by the reactant feed line (**204A**, **204B**) by means of the floating bearing (**206A**, **206B**). Thus, the additional expansion bends in the reactant feed line (i.e. hairpins, pigtails) (**204A**, **204B**) are avoided, thereby reducing the overall height or size of an entire plant, and also reducing heat losses by shortening the transfer lines, namely the reactant feed line, and the product discharge line. Moreover, due to the large vertical transmission of forces via the product discharge line (**216A**, **216B**) into the reactant feed line, the bending moments, loads, and stresses acting on the product discharge line (**216A**, **216B**) are reduced which results in an increase in the expected service life and an increase in the operational reliability of the reformer furnace **200**.

FIG. 3 is a schematic illustration a reformer furnace **300** with a single reactant feed system according to an embodiment of the present invention. The reformer furnace **300** includes a reactant feed system **302,** reactant feed lines **304A** and **304B**, floating bearings **306A** and **306B**, reformer tubes **308A** and **308B** comprising pressure-bearing cylindrical jacket tubes **310A** and **310B**, a furnace interior **312**, fixed bearings **314A** and **314B**, product discharge lines **316A** and **316B**, and a product gas manifold **318**.

The pressure-bearing cylindrical jacket tube **310A** and **310B** is arranged to contain a catalyst **320A** and **320B** as a bulk catalyst, a catalyst bed of catalyst particles, structured packing, honeycomb catalyst, or combinations thereof. An inlet end of the pressure-bearing cylindrical jacket tube (e.g. **310A** and **310B**) is connectable to the reactant feed lines **304A** and **304B**. The reactant feed lines **304A** and **304B** are connectable to the reactant feed system **302**. The fixed bearings **314A** and **314B** are located at an outlet end of the pressure-bearing cylindrical jacket tubes **310A** and **310B** and the floating bearings **306A** and **306B** are located at an inlet end of the pressure-bearing cylindrical jacket tubes **310A** and **310B**. The floating bearings **306A** and **306B** may be designed as a rolling bearing, a ball bearing, a plain bearing or a floating support bearing. The outlet end of the pressure-bearing cylindrical jacket tubes **310A** and **310B** is connectable to the product discharge lines **316A** and **316B**. The product discharge lines **316A** and **316B** are connectable to the product gas manifold **318**. Optionally, the product discharge lines **316A** and **316B** form a right angle with the product gas manifold **318** in a connected state.

The pressure-bearing cylindrical jacket tubes **310A** and **310B** are supported in a direction of their longitudinal axis using a fixed-floating bearing arrangement (i.e. the floating bearings **306A** and **306B**, and the fixed bearings **314A** and **314B**) to allow thermal expansion of the pressure-bearing cylindrical jacket tubes **310A** and **310B** in a longitudinal direction. Optionally, the floating bearings **306A** and **306B** and the fixed bearings **314A** and **314B** absorb stress forces due to the thermal expansion of the pressure-bearing cylindrical jacket tubes **310A** and **310B** in a radial direction. The thermal linear expansion of the reformer tubes **308A** and **308B** is transferred to the reactant feed system **302** and is compensated using the floating bearing **306A** and **306B**.

The reformer tube with the fixed-floating bearing arrangement that is provided in the process is of advantage in that a rigid connection in combination with the floating bearing is used for absorbing stress forces due to the thermal expansion of the pressure-bearing cylindrical jacket tube of the reformer tube in an axial (longitudinal) and/or radial direction. The thermal linear expansion of the reformer tube is completely transferred from the product discharge line to the connected reactant feed line and compensated by the reactant feed line by means of the floating bearing. Thus, the additional expansion bends in the reactant feed line (i.e. hairpins, pigtails) are avoided, thereby reducing the overall height or size of an entire plant, and also reducing heat losses by shortening the transfer lines, namely the reactant feed line, and the product discharge line. Moreover, due to the large vertical transmission of forces via the product discharge line into the reactant feed line, the bending moments, loads, and stresses acting on the product discharge line are reduced which results in an increase in the expected service life and an increase in the operational reliability of the reformer furnace.

Modifications to embodiments of the present invention described in the foregoing are possible without departing from the scope of the present invention as defined by the accompanying claims. Expressions such as “including”, “comprising”, “incorporating”, “have”, “is” used to describe, and claim the present invention are intended to be construed in a non-exclusive manner, namely allowing for items, components or elements not explicitly described also to be present. Reference to the singular is also to be construed to relate to the plural.

CLAIMS

1. Reformer tube (208A, 208B, 308A, 308B) for a steam reformer or ammonia cracker, comprising:

(a) a pressure-bearing cylindrical jacket tube (210A, 210B, 310A, 310B) arranged to contain a catalyst (220A, 220B, 320A, 320B) as a bulk catalyst, a catalyst bed of catalyst particles, structured packing, honeycomb catalyst, or combinations thereof;

(b) an inlet end of the pressure-bearing cylindrical jacket tube (210A, 210B, 310A, 310B) connectable to a reactant feed line (204A, 204B, 304A, 304B);

(c) the reactant feed line (204A, 204B, 304A, 304B) connectable to a reactant feed system (202A, 202B, 302);

(d) an outlet end of the pressure-bearing cylindrical jacket tube (210A, 210B, 310A, 310B) connectable to a product discharge line (216A, 216B, 316A, 316B);

(e) the product discharge line (216A, 216B, 316A, 316B) connectable to a product gas manifold (218, 318);

wherein

(f) the pressure-bearing cylindrical jacket tube (210A, 210B, 310A, 310B) is supported in the direction of its longitudinal axis by means of a fixed-floating bearing arrangement to allow thermal expansion of the pressure-bearing cylindrical jacket tube (210A, 210B, 310A, 310B) in longitudinal direction,

wherein

(g) the fixed bearing (214A, 214B, 314A, 314B) is located at the outlet end of the outer pressure-bearing cylindrical jacket tube (210A, 210B, 310A, 310B) and the floating bearing (206A, 206B, 306A, 306B) is located at the inlet end of the outer pressure-bearing cylindrical jacket tube (210A, 210B, 310A, 310B).

2. Reformer tube (208A, 208B, 308A, 308B) according to claim 1, characterized in that the reactant feed line (204A, 204B, 304A, 304B) has only one single change of direction, preferably only one single change of direction of 90°.

3. Reformer tube (208A, 208B, 308A, 308B) according to claim 1 or 2, characterized in that the product discharge line (216A, 216B, 316A, 316B) has no change of direction and its longitudinal axis coincides with or is aligned with the longitudinal axis of the pressure-bearing cylindrical jacket tube (210A, 210B, 310A, 310B).

4. Reformer tube (208A, 208B, 308A, 308B) according to one of the preceding claims, characterized in that the floating bearing (206A, 206B, 306A, 306B) is designed as a rolling bearing, ball bearing, plain bearing or floating support bearing.

5. Reformer tube (208A, 208B, 308A, 308B) according to one of the preceding claims, characterized in that the floating bearing (206A, 206B, 306A, 306B) and the fixed bearing (214A, 214B, 314A, 314B) are designed such that they can absorb stress forces due to thermal expansion of the pressure-bearing cylindrical jacket tube (210A, 210B, 310A, 310B) in the radial direction.

6. Reformer tube (208A, 208B, 308A, 308B) according to one of the preceding claims, characterized in that the inlet ends of several jacket tubes can be connected to a common reactant feed line.

7. Reformer tube (208A, 208B, 308A, 308B) according to any of the preceding claims, characterized in that the product discharge line (216A, 216B, 316A, 316B) forms a right angle with the product gas manifold (218, 318) in the connected state.

8. Reformer furnace (200, 300) comprising a floor, a ceiling and side walls forming a furnace interior, wherein a plurality of reformer tubes according to any one of claims 1 to 7 are arranged within the furnace interior and are heated by burners.

9. Reformer furnace (200, 300) according to claim 8, characterized in that the plurality of reformer tubes are arranged in rows, preferably in parallel rows, wherein each two reformer tubes adjacent in a row are connected to a common reactant feed line.

10. Use of a reformer tube (208A, 208B, 308A, 308B) according to claim 1 to 7 and/or a reformer furnace (200, 300) according to claim 8 to 9 for steam reforming a hydrocarbonaceous feed stream with steam to a crude synthesis gas stream.

11. Use of a reformer tube (208A, 208B, 308A, 308B) according to claim 1 to 7 and/or a reformer furnace (200, 300) according to claim 8 to 9 for cracking an ammonia feed stream into a hydrogen and nitrogen containing product gas stream.

12. Process for steam reforming a hydrocarbonaceous feed stream with steam to form a synthesis gas stream containing carbon monoxide and hydrogen, comprising the steps of:

(a) providing a plurality of reformer tubes according to claims 1 to 7 in a reformer furnace (200, 300) according to claims 8 to 9;

(b) connecting the reactant feed lines (204A, 204B, 304A, 304B) of the reformer tubes (208A, 208B, 308A, 308B) to a common reactant feed system;

(c) connecting the product discharge lines (216A, 216B, 316A, 316B) of the reformer tubes (208A, 208B, 308A, 308B) to a common product gas manifold;

(d) injecting the hydrocarbonaceous feed stream through the reactant feed system (202A, 202B, 302) and the reactant feed lines (204A, 204B, 304A, 304B) of the reformer tubes (208A, 208B, 308A, 308B);

(e) reacting the hydrocarbonaceous feed stream with steam in the reformer tubes (208A, 208B, 308A, 308B) under steam reforming conditions to form a crude synthesis gas stream;

(f) discharging the crude synthesis gas stream from the reformer tubes (208A, 208B, 308A, 308B) via the product discharge lines (216A, 216B, 316A, 316B) and the common product gas manifold; and

(g) feeding the crude synthesis gas stream to at least one further work-up, separation, purification or conditioning step, discharging a purified or conditioned synthesis gas stream and/or its constituents hydrogen and/or carbon monoxide.

13. Process for cracking an ammonia feed stream with steam to form a product gas stream containing hydrogen and nitrogen, comprising the steps of:

(a) providing a plurality of reformer tubes according to claims 1 to 7 in a reformer furnace (200, 300) according to claims 8 to 9;

(b) connecting the reactant feed lines (204A, 204B, 304A, 304B) of the reformer tubes (208A, 208B, 308A, 308B) to a common reactant feed system;

(c) connecting the product discharge lines (216A, 216B, 316A, 316B) of the reformer tubes (208A, 208B, 308A, 308B) to a common product gas manifold;

(d) injecting the ammonia feed stream through the reactant feed system (202A, 202B, 302) and the reactant feed lines (204A, 204B, 304A, 304B) of the reformer tubes (208A, 208B, 308A, 308B);

(e) reacting the ammonia feed stream in the reformer tubes (208A, 208B, 308A, 308B) under ammonia cracking conditions to form a product gas gas stream containing hydrogen and nitrogen;

(f) discharging the product gas gas stream from the reformer tubes (208A, 208B, 308A, 308B) via the product discharge lines (216A, 216B, 316A, 316B) and the common product gas manifold; and

(g) feeding the product gas gas stream to at least one further work-up, separation, purification or conditioning step, discharging a purified product gas gas stream and/or its constituents hydrogen and/or nitrogen.

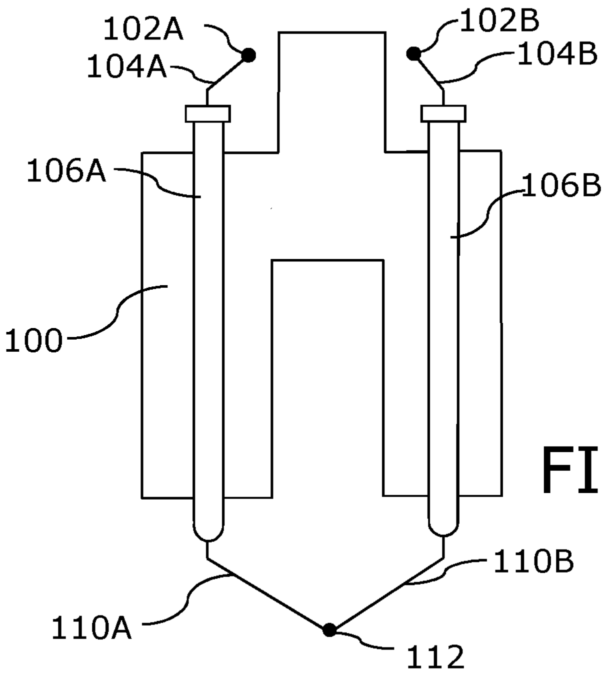
102A
104A
102B
104B
106A
106B
100
110A
110B
112

FIG. 1A

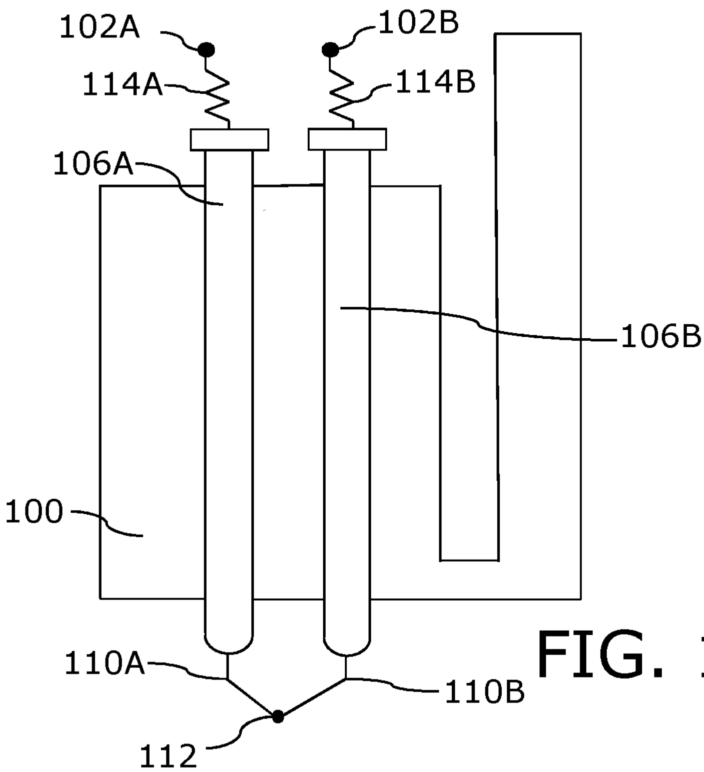
102A
114A
102B
114B
106A
106B
100
110A
110B
112

FIG. 1B

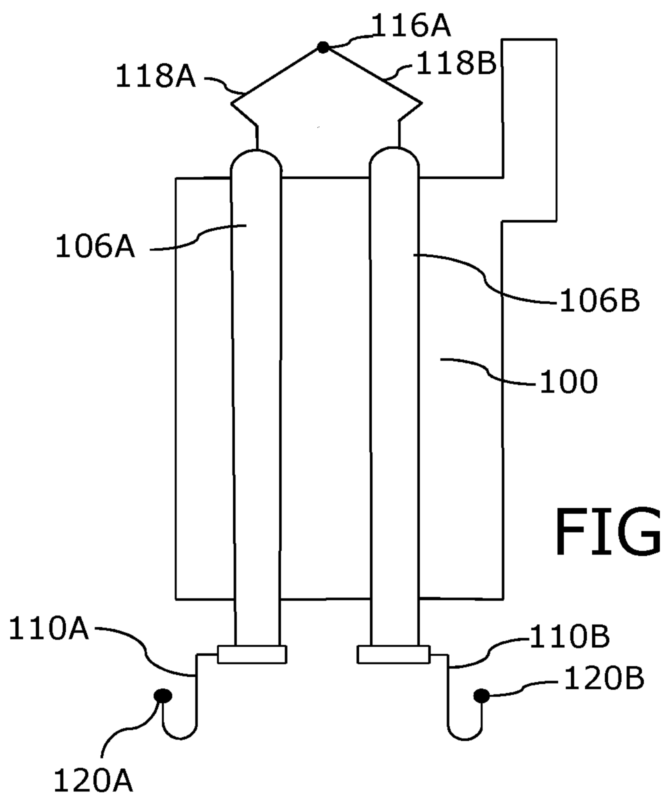
116A
118A
118B
106A
106B
100
110A
110B
120B
120A

FIG. 1C

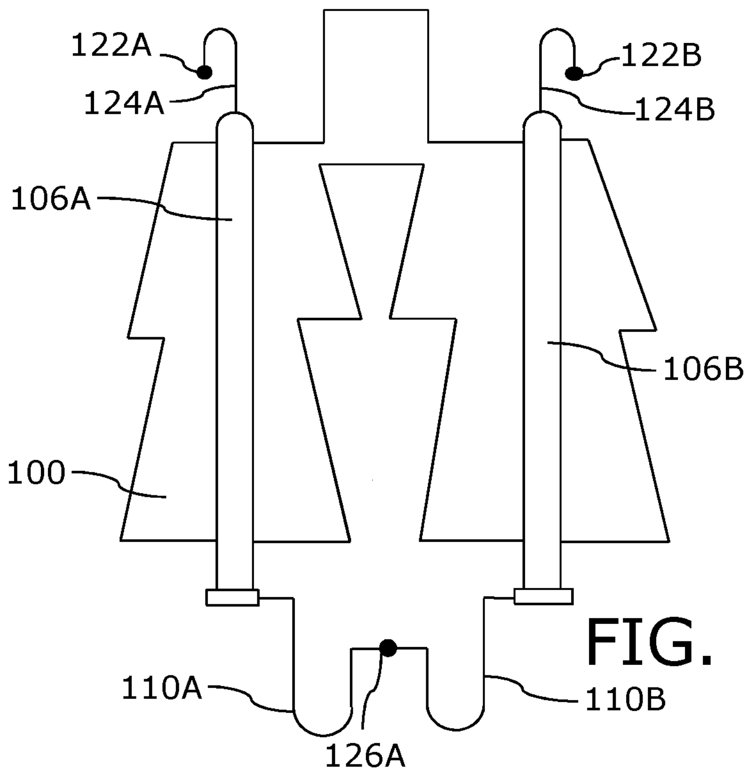
122A
122B
124A
124B
106A
106B
100
110A
110B
126A

FIG. 1D

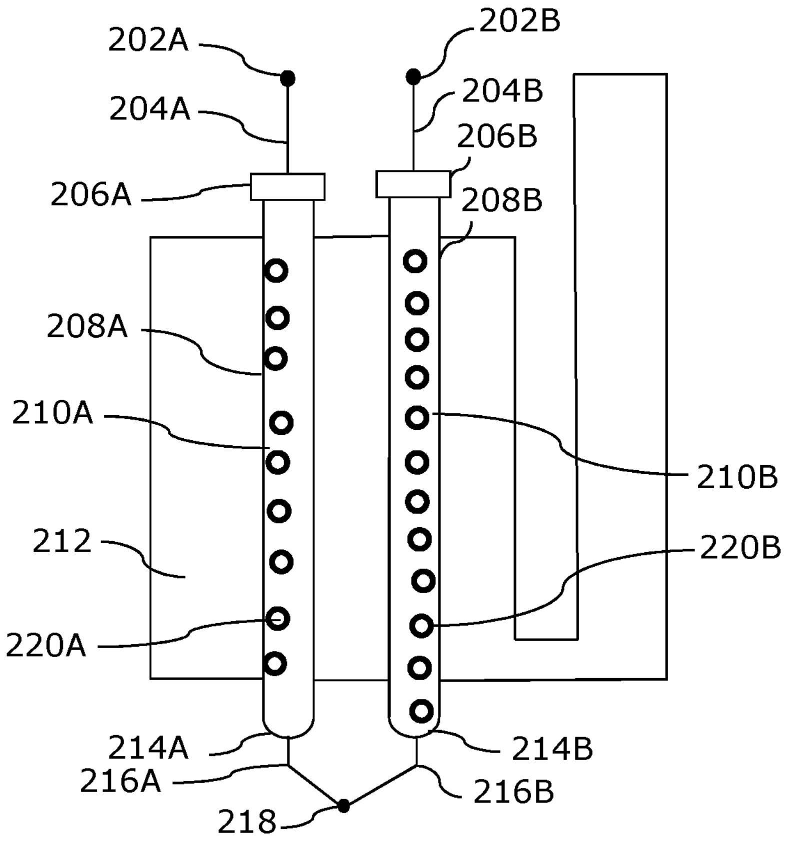
202A
202B
204A
204B
206B
206A
208B
208A
210A
210B
212
220B
220A
214A
214B
216A
216B
218
200

FIG. 2

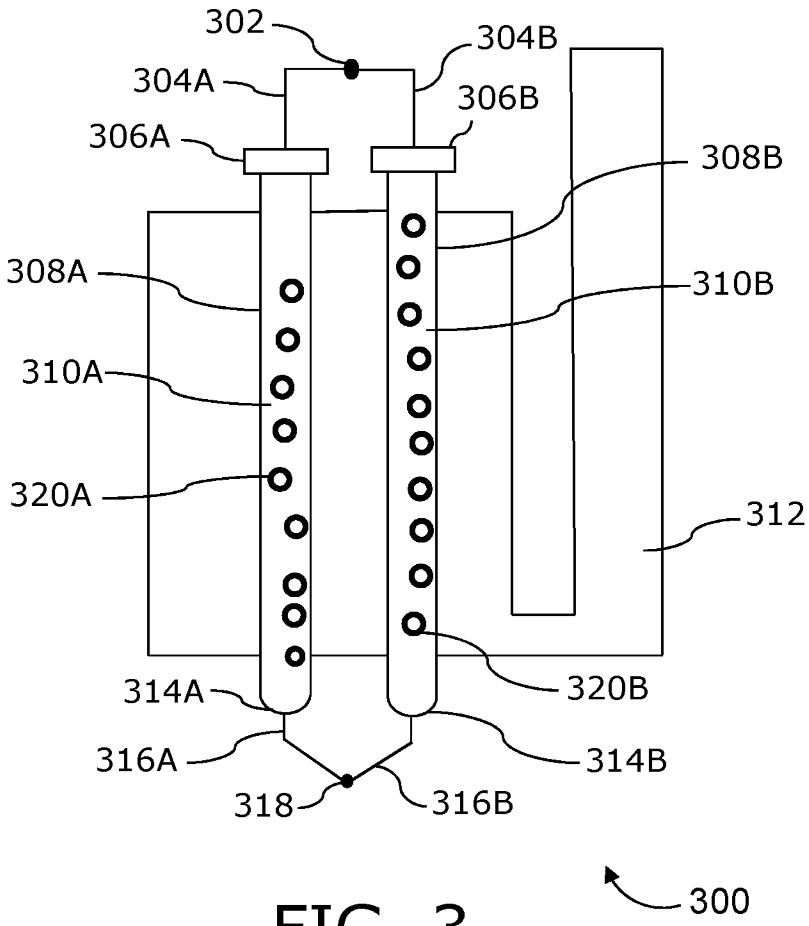
302
304B
304A
306B
306A
308B
308A
310B
310A
320A
312
320B
314A
316A
314B
318
316B
300

FIG. 3

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2024/052458

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J8/06
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2005/287053 A1 (SAKAI KENJI [JP] ET AL) 29 December 2005 (2005-12-29) paragraph [0035]; claim 1; figure 1 paragraph [0058]; figure 2 -----	1-13
A	CN 113 559 793 A (SHANGHAI INT ENGINEERING CONSULTING COMPANY) 29 October 2021 (2021-10-29) the whole document -----	1-13
A	WO 94/29013 A1 (STANDARD OIL CO OHIO [US]) 22 December 1994 (1994-12-22) abstract page 10 - page 11; figure 1 page 12, line 17 - page 13, line 9; figure 1D -----	1-13
	-/--	

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

[x] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
3 April 2024	29/04/2024

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

1

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

International application No
PCT/EP2024/052458

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2014/069612 A1 (CHEN LIEN-YAN [US] ET AL) 13 March 2014 (2014-03-13) abstract paragraph [0026] -----	1-13
A	US 3 713 784 A (POHL K ET AL) 30 January 1973 (1973-01-30) page 1; claim 1; figure 2 -----	1-11

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2024/052458

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 2005287053	A1	29-12-2005	JP	4477432	B2	09-06-2010
			JP	2006008480	A	12-01-2006
			US	2005287053	A1	29-12-2005
CN 113559793	A	29-10-2021	NONE			
WO 9429013	A1	22-12-1994	AU	699464	B2	03-12-1998
			CA	2165449	A1	22-12-1994
			CN	1127997	A	31-07-1996
			CZ	292204	B6	13-08-2003
			DE	69419921	T2	02-12-1999
			DE	69432233	T2	20-11-2003
			DK	0703823	T3	06-12-1999
			DK	0895806	T3	07-07-2003
			EP	0703823	A1	03-04-1996
			EP	0895806	A2	10-02-1999
			FI	955977	A	13-02-1996
			JP	3583780	B2	04-11-2004
			JP	H08511503	A	03-12-1996
			KR	100323275	B1	22-06-2002
			MY	138879	A	28-08-2009
			NO	308725	B1	23-10-2000
			NZ	267919	A	26-08-1998
			RU	2136360	C1	10-09-1999
			SA	94150129	B1	11-06-2005
			US	5567398	A	22-10-1996
			WO	9429013	A1	22-12-1994
			ZA	944027	B	08-12-1995
US 2014069612	A1	13-03-2014	CN	103666581	A	26-03-2014
			US	2014069612	A1	13-03-2014
US 3713784	A	30-01-1973	DE	1901758	A1	13-08-1970
			ES	183753	U	01-08-1973
			GB	1296193	A	15-11-1972
			SE	366771	B	06-05-1974
			US	3713784	A	30-01-1973