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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
12 July 2012 (12.07.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/092980 A1

(51) International Patent Classification:
B01D 45/14 (2006.01) *B01D 53/22* (2006.01)
B01D 53/18 (2006.01) *C10L 3/10* (2006.01)

(21) International Application Number:
PCT/EP2011/050174

(22) International Filing Date:
7 January 2011 (07.01.2011)

(25) Filing Language: English

(26) Publication Language: English

(71) Applicant *(for all designated States except US)*: **STATOIL PETROLEUM AS** [NO/NO]; N-4035 Stavanger (NO).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **FIVELAND, Torbjørn** [NO/NO]; Svensjordet 9, N-3721 Skien (NO). **AASEN, Knut, Ingvar** [NO/NO]; Tiurvegen 22, N-3940 Porsgrunn (NO).

(74) Agent: **ZACCO NORWAY AS**; P.O. Box 2003 Vika, N-0125 Oslo (NO).

(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, 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, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, 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.

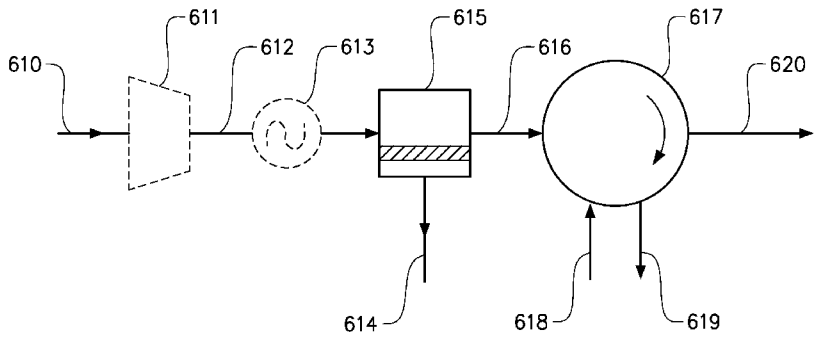
(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU,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

Published:

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

(54) **Title**: PROCESS FOR REMOVING ACID GAS FROM NATURAL GAS

FIG. 6



(57) **Abstract**: The invention relates to the treatment of natural gas and other gas streams containing methane and at least one acid gas, such as carbon dioxide. More particularly, the invention involves contacting the raw natural gas feed stream with a separation membrane to obtain a natural gas product stream rich in methane and having a carbon dioxide content reduced to a first level relative to the raw natural gas stream. Subsequently, the natural gas product stream is passed through a rotating absorption zone, in order to obtain a sweetened natural gas product having a carbon dioxide content reduced to a second level relative to the raw natural gas stream.

WO 2012/092980 A1

PROCESS FOR REMOVING ACID GAS FROM NATURAL GAS

TECHNICAL FIELD

The invention relates to the treatment of natural gas and other gas streams containing methane and at least one acid gas, such as carbon dioxide. More particularly, the invention relates to the use of gas separation membranes to remove at least excess carbon dioxide from the gas

BACKGROUND ART

Natural gas is an important fuel gas and is also used extensively as a basic raw material in the petrochemical and other chemical process industries. The composition of natural gas varies widely from field to field. For example, a raw gas stream may contain as much as 95 percent methane, with only minor amounts of other hydrocarbons, nitrogen, carbon dioxide (CO_2), hydrogen sulphide (H_2S) or water vapour. On the other hand, streams with large proportions of one or more of these contaminants are common. For example, gas that is extracted as a result of miscible flood enhanced oil recovery may be very rich in carbon dioxide, as well as being saturated with C3+ hydrocarbons.

The separation of carbon dioxide from the raw gas stream is important in natural gas processing because carbon dioxide reduces the energy content of natural gas. Some natural gas wells may contain high concentrations of carbon dioxide (as high as 70 percent), and most of this carbon dioxide must be removed before the natural gas is shipped and/or used.

Overall, about 10 percent of gas exceeds the typical gas pipeline specification for carbon dioxide which is usually less than 2,4 percent, preferably no more than 2 percent.

Before such gas can be sent to the supply pipeline, the carbon dioxide content must be reduced. Various techniques for acid gas removal, including

absorption into an amine solution, cryogenic separation and membrane separation, have been used in the industry. Each has its own advantages and disadvantages.

Membrane units, when compared with relatively large conventional treating processes such as amine absorption columns and associated regeneration columns, require a relatively small operational area, require small amounts of energy, and require only minor operational efforts. Also maintenance and inspection requirements are moderate.

If membrane separation is used, cellulose acetate membranes, which can provide a carbon dioxide/methane selectivity of about 10-20 in gas mixtures at pressure, have been the membranes of choice. Other types of membrane that may be considered are polyethylene oxide based membranes, such as polyethylene oxide based membranes comprising block-copolymers (especially PEO 600/5000 T6T6T or a cross linked PEO), polyimide or polyaramide based membranes, cellulose acetate based membranes, zeolite based membranes, such as silica-alumina phosphate based membranes, especially, SAPO-34, micro-porous silica membranes or carbon molecular sieve membranes, or nano-molecular sieve-polymer mixed matrix membranes (MMMS). The selection of a suitable membrane for the purpose of removing CO_2 is not part of the invention per se and will not be discussed in further detail.

It would be desirable in many more cases to use membrane separation, because membrane systems are relatively simple, have few moving parts, can operate under moderate temperature and pressure conditions and, unlike amine scrubbing, do not require a regeneration cycle. Also, the wellhead gas pressure may be high enough to provide the total driving force for trans-membrane permeation.

However, cellulose acetate, polymeric and other types of membranes are not without problems. Likewise, many membranes are irreparably damaged by

liquid hydrocarbons, and similar precautions must be taken to avoid the risk of condensation of C3+ hydrocarbons on the membranes at any time. The presence of more than modest ppm levels of hydrogen sulphide, especially in conjunction with water and heavy hydrocarbons, is also potentially damaging.

Furthermore, carbon dioxide readily sorbs into and interacts strongly with many polymers, and in the case of gas mixtures such as carbon dioxide/methane with other components, the carbon dioxide tends to have a swelling or plasticizing effect, thereby adversely changing the membrane permeation characteristics. Although some membrane materials, such as polyimide, exhibit a high ideal selectivity for carbon dioxide over methane when measured with pure gases at modest pressures in the laboratory, the selectivity obtained under mixed gas, high-pressure conditions is much lower. This means it is often very difficult under field conditions to meet target specifications for carbon dioxide content without resorting to impractically large amounts of membrane area and/or unacceptably complicated processing schemes.

Thus, although membranes have been, and are, used to remove carbon dioxide from natural gas, there are many situations where the composition of the gas, the size of the stream to be processed, the size of the membrane required, or the site geography renders a membrane-based process technically or economically unrealistic.

That membranes can separate C3+ hydrocarbons from gas mixtures, such as natural gas, is known, for example from US 4857078, US 5281255 and US 5501722.

In spite of the above knowledge and practices, technology that can process natural gas containing excess quantities of carbon dioxide in a cost-effective manner is still needed. The challenge of treating gas that contains relatively large amounts of carbon dioxide, such as more than about 10 percent, for example, is particularly difficult.

SUMMARY OF THE INVENTION

The above problems have been solved by a process and a production plant according to the appended claims.

The invention relates to a process for treatment of a raw natural gas and other gas streams containing methane and at least one acid gas, such as carbon dioxide, by removing said acid gas to produce a sweetened natural gas stream, the process comprising the steps of:

- contacting the raw natural gas feed stream with a separation membrane to obtain a natural gas product stream rich in methane and having a carbon dioxide content reduced to a first level relative to the raw natural gas stream;
- supplying the natural gas product stream and a lean absorption medium comprising a liquid diluent and at least one amine to an absorber;
- passing the natural gas product stream into cross-flow contact with the lean absorption medium within a rotating absorption zone in the absorber, wherein carbon dioxide is removed from the natural gas product stream by the lean absorption medium when passing through the rotating absorption zone, in order to obtain a sweetened natural gas product having a carbon dioxide content reduced to a second level relative to the raw natural gas stream.

Examples of suitable absorbent media comprise amine based absorbents such as primary, secondary and tertiary amines. One well known example of applicable amines is mono ethanol amine (MEA). The liquid diluent is selected among diluents that have a suitable boiling point, are stable and inert towards the absorbent in the suitable temperature and pressure interval. An example of an applicable diluent is water. Examples of suitable amines for use with a diluents such as water are aqueous solutions of monoethanolamine (MEA), methylaminopropylamine (MAPA), piperazine, diethanolamine (DEA), triethanolamine (TEA), diethylethanolamine (DEEA),

diisopropylamine (DIPA), aminoethoxyethanol (AEE), dimethylaminopropanol (DIMAP) and methyldiethanolamine (MDEA), methyldiisopropanolamine (MDIPA), 2-amino-1-butanol (2-AB) or mixtures thereof.

According to one example the raw natural gas feed stream can be contacted with a membrane to reduce the carbon dioxide content of the raw natural gas feed stream from at least 30 % CO_2 to a first level at or below 20 % CO_2. The reduction of CO2 is dependent on the CO2 content of the raw natural gas and/or the type and surface area of the membrane used. By using a membrane with a larger surface area or by using a raw natural gas with a lower CO2 content the raw natural gas feed stream can be contacted with a membrane to reduce the carbon dioxide content of the raw natural gas feed stream from at least 30 % CO_2 to a first level between 7 and 12 % CO_2.

The resulting natural gas product stream can be supplied to the further absorber to reduce the carbon dioxide content of the natural gas product stream from a first level of 20 % CO_2 or less, e.g from 7-12 % CO_2, to a second level of 2,4 % CO_2 or less. A typical gas pipeline specification for carbon dioxide which is usually less than 2,4 % CO_2, preferably no more than 2 % CO_2.

The reduction of the carbon dioxide content from the first level to the second level is achieved by supplying the lean absorption medium to an inner portion of at least one annular rotating absorber unit within the absorber, causing the lean absorption medium to flow radially outwards through the rotating absorption zone; and supplying the natural gas product stream to an outer portion of said annular rotating absorber unit, causing the natural gas product to flow radially inwards in order to create a radial cross-flow in the absorption zone. The lean absorption medium is preferably supplied to a pair of identical and mirrored annular rotating absorber units rotating about a common axis within the absorber.

The above process is particularly well suited for offshore applications, or in locations where space is an issue. Conventional processes often require multiple membrane steps to reduce the CO_2 content of the natural gas to acceptable levels. In practice this means that there is a cost or size dependent limit to the size and/or number of membranes used, as each percent reduction requires progressively larger membranes. By combining a membrane with a rotary wheel absorber, the membrane allows the CO_2 content of the raw natural gas to be reduced to a first level by a membrane having an acceptable size, whereby the reduction of CO_2 content to a gas pipeline specification can be performed by a compact rotary wheel absorber.

As stated above, many membranes can be damaged by the presence of more than modest ppm (parts per million) levels of hydrogen sulphide (H_2S). Should the raw natural gas feed stream also contain hydrogen sulphide, the process can comprise the further steps of;

- supplying the raw natural gas stream and an organic scrubbing agent specific to hydrogen sulphide to a further absorber prior to the separation membrane step; and
- passing the raw natural gas stream into cross-flow contact with the organic scrubbing agent within a rotating absorption zone in the further absorber, wherein the hydrogen sulphide is removed from the raw natural gas stream by the organic scrubbing agent when passing through the rotating absorption zone, in order to obtain a raw natural gas stream free from hydrogen sulphide.

Suitable organic scrubbing agents for this purpose are toluene, N-methylpyrrolidone, dimethylformamide, isopropanolamine and especially dialkyl ethers of diethylene glycols and especially the dimethyl ethers of di- to heptaethylene glycols are suitable. Highly effective results are also obtained with dimethylisopropyl ethers of ethylene glycols. Unless otherwise stated, the term "alkyl" will mean C1 to C18 straight or branched chain hydrocarbons and corresponding cycloalkyl compounds.

In principle, hydrogen sulfide-selective water-based solvents can also be used, for example aqueous solutions of aminoacid salts, although these scrubbing agents must be employed at temperatures above their respective freezing points and additional stages must be provided to dry the gas.

The elimination of the hydrogen sulfide content from the raw natural gas stream is achieved by supplying the organic scrubbing agent to an inner portion of at least one annular rotating absorber unit within the further absorber, causing the organic scrubbing agent to flow radially outwards through the rotating absorption zone; and supplying the raw natural gas stream to an outer portion of said annular rotating absorber unit, causing the raw natural gas stream to flow radially inwards in order to create a radial cross-flow in the absorption zone. The organic scrubbing agent is preferably supplied to a pair of identical and mirrored annular rotating absorber units rotating about a common axis within the absorber.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be described in detail with reference to the attached figures. It is to be understood that the drawings are designed solely for the purpose of illustration and are not intended as a definition of the limits of the invention, for which reference should be made to the appended claims. It should be further understood that the drawings are not necessarily drawn to scale and that, unless otherwise indicated, they are merely intended to schematically illustrate the structures and procedures described herein:

Figure 1 shows a schematic, partially cross-sectioned absorber for use in a process according to the invention;

Figure 2 shows a cross-section through a first alternative embodiment of an absorber for use in a process according to the invention;

Figure 3 shows a schematic diagram of the flow of absorbent and natural gas through the absorbers of Fig. 1 and Fig.2;

Figure 4 shows a cross-section through a second alternative embodiment of an absorber for use in a process according to the invention;

Figure 5 shows a schematic diagram of the flow of absorbent and natural gas through the absorber of Fig.4;

Figure 6 shows a schematic diagram of a process according to a first embodiment of the invention; and

Figure 7 shows a schematic diagram of a process according to a second embodiment of the invention.

DETAILED DESCRIPTION

Figure 6 shows a schematic diagram of a process according to a first embodiment of the invention.

As shown in Figure 6 a raw gas stream 610, which may be any natural gas, or hydrocarbon-containing gas, from which it is desired to remove carbon dioxide is directed into a production plant for carrying out the process. The gas may be from a natural gas well, may be associated gas produced in conjunction with oil, either spontaneously or as a result of carbon dioxide injection, may be gas gathered from a landfill, or may arise from any other source.

The raw gas stream 610 may be as-extracted from the ground or may have been subjected to pretreatment of any kind, including, but not limited to, filtration to remove particulates, entrained water or hydrocarbon liquids, separation by any means, including, but not limited to absorption, adsorption, condensation and other membrane or non-membrane separation, to remove gaseous contaminants, such as nitrogen or water vapor. The raw gas stream 610 is typically at above atmospheric pressure, such as at a few hundred psia (a few thousand kPa), and may or may not be at sufficiently high pressure for the desired process performance for the membrane.

The content of carbon dioxide in raw gas stream 610 may be any amount, ranging from, for example, 20-30 percent or more. Natural gas pipeline specification for carbon dioxide is usually no more than 2-2,4 percent. If the process is directed at treating carbon-dioxide-containing gas from a natural gas well, therefore, the raw gas stream 610 will contain at least 2 percent carbon dioxide. The process is particularly well suited to treat gas containing at least about 20 percent carbon dioxide or more.

Usually, the raw gas stream 610 also contains C3+ hydrocarbons and water vapor, and these also may be present in any quantities. Therefore, the partial pressures of both the hydrocarbons and the water in the feed may be close to the saturation vapor pressures of those components at the temperature of the raw gas stream 610.

For example, depending on the mix of hydrocarbons and the temperature of the gas, the aggregate partial pressure of all C3+ hydrocarbons in the gas might be as much as 30 psia, 50 psia, 75 psia, 100 psia or more. Expressed as a percentage of the saturation vapor pressure at that temperature, the partial pressure of hydrocarbons, particularly C3+ hydrocarbons, may be 20 percent, 50 percent, 80 percent or more of saturation, for example. The typical water content is up to about 1,200 ppm. Water can be removed in a separate dehydration process prior to the carbon dioxide removal. The other most significant component of the stream is methane, frequently, but not necessarily, the major component, and the stream may typically contain a number of other components, such as ethane, hydrogen sulfide and/or inert gases such as helium and argon in minor or trace amounts. However, the current invention is mainly directed to the removal of carbon dioxide.

The first embodiment relates to a process for treatment of a raw natural gas and other gas streams containing methane and carbon dioxide, by removing said carbon dioxide to produce a sweetened natural gas stream, the process comprising the initial steps of contacting the raw natural gas feed stream with a separation membrane to obtain a natural gas product stream rich in methane and having a carbon dioxide content reduced to a first level relative

to the raw natural gas stream; As mentioned above, the raw gas stream 610 is typically at elevated pressure. If it is at insufficiently high pressure to operate the process satisfactorily, the raw gas stream 610 may optionally be compressed, as shown in Figure 6. The raw gas stream 610 then passes into an optional compression step 611.

The compressor used in compression step 611 may be of any convenient type, such as centrifugal, screw or reciprocating, based on considerations of outlet pressure needed, gas flow rate and composition, and like issues familiar to those of skill in the art. Screw compressors are relatively inexpensive and are widely used to reach pressures up to about 300 or 400 psia; for higher pressures, piston compressors are more commonly used. Typically, but not necessarily, the compression step raises the pressure of the gas stream between 3 and 10 times. This may be done in a single-stage or multiple-stage compressor, as is well known in the art.

For most applications of the membrane separation process, it is neither necessary nor desirable to compress the feed gas to very high pressures. Most preferably, compression step 611 raises the pressure of the feed stream 612 to between about 500 psia and 1,500 psia, depending on the type of membrane used. It is possible to use fuel gas generated by the process to power a gas engine to drive the compressor. This provides a cost advantage that is an attractive feature of the process.

Gas emerges from compression step 611, if used, as compressed feed stream 612 and is passed to optional cooling step 613. If a compression step is used, the compressor exhaust gas is hot and an after-cooling step will be needed. If the compression step is not used, the cooling step 613 is optional.

The cooling step is carried out by any suitable means, for instance by air cooling. If a lower temperature than can be attained by air cooling is desired, the step may be carried out using cooling water, refrigerants and/or heat exchange against other plant streams, for example. Such techniques are well known in the art.

An optional phase separation step (not shown) can be used upstream of the membrane separation step 615 if the raw gas stream 610 is a two-phase mixture containing entrained hydrocarbon liquids as mist or droplets, or if a compression step 611 and/or cooling step 613 have been used.

The optional phase separation step can produce a single liquid phase and gas phase, as will be the case if a simple knock-out drum or two-phase separator is used. Alternatively, a three-phase separator may be used to produce discrete liquid water and natural gas liquid (NGL) streams.

The gas phase of the natural gas stream is withdrawn from the phase separation step, if used, and passed to the membrane separation step 615. This step 615 is carried out using a membrane separation unit equipped with a membrane that is selective in favor of carbon dioxide over methane and other hydrocarbons. The membrane material used in this step is preferably a glassy polymer with good carbon dioxide/methane selectivity under conditions of high carbon dioxide partial pressure. Representative membrane materials that can be used for this step include cellulose acetate, other cellulose derivatives, polyimide, and fluorinated dioxoles and dioxolanes.

Despite their susceptibility to water, hydrogen sulfide and heavy hydrocarbons, cellulose acetate membranes are still the most widely used membranes in industrial carbon dioxide separation units. They typically provide a carbon dioxide/methane selectivity of about 10 under real operating conditions. Such membranes are available commercially from Kvaerner Process Systems of Houston, Texas, or as Separex Membrane Systems from UOP of Des Plaines, Ill. As the raw gas has already been treated in cooling/phase separation steps the gas stream supplied to the membrane unit may be sufficiently dry, light and sweet that cellulose acetate membranes may be used. Alternative candidate membranes of this type include those made from different cellulose derivatives, such as ethyl cellulose, methyl cellulose, nitrocellulose, and particularly other cellulose esters.

Other preferred materials for membranes are modern polyimides that exhibit resistance to plasticization or swelling when exposed to high partial pressures of carbon dioxide and C3+ hydrocarbons, in conjunction with good carbon dioxide/methane selectivity and carbon dioxide permeability. As a non-limiting example, certain polyimides based on 6FDA may be used. For example, the polyimide 6FDA-MPDA has a carbon dioxide/methane selectivity of about 50 as measured in C3+ hydrocarbon-free gas mixtures, and may provide a selectivity of about 10 or above under real operating conditions. Polyimide membranes are available commercially from Ube Industries, of Ube City, Japan, or from Medal L P, of Newport, Del., a division of Air Liquide.

The most preferred membranes for use in said step are made from glassy polymers characterized by having repeating units of a fluorinated, non-aromatic cyclic structure, the ring having at least five members, and further characterized by a fractional free volume no greater than about 0.3. Preferred polymers in this group are formed from fluorinated monomers of (i) dioxoles that polymerize by opening of the double bond, or (ii) dioxolanes, similar five-member rings but without the double bond in the main ring, or (iii) aliphatic structures having an alkyl ether group, polymerizable into cyclic ether repeat units with five or six members in the ring. The polymers may take the form of homopolymers or copolymers. Such materials are discussed at length in e.g. US 6572680, entitled "Carbon Dioxide Gas Separation Using Organic-Vapor-Resistant Membranes", and in US 6361583.

Another highly preferred alternative, membranes suitable for use in the invention are characterized by a fractional free volume no greater than about 0.3, a glass transition temperature, Tg, of at least about 100[deg.] C., and a fluorine:carbon ratio of at least 1:1, but need not necessarily include a cyclic structure. Such materials are discussed at length in US 6572680, entitled "Carbon Dioxide Gas Separation Using Organic-Vapor-Resistant Membranes", and in US 6361582.

For carbon dioxide over methane, the most preferred membranes can provide a typical selectivity of 10, 15 or more under real operating conditions. Such selectivity is remarkable, in that it can be achieved even in the presence of significant concentrations of C3+ hydrocarbons and/or carbon dioxide, and at high feed pressure.

The membranes used for the membrane separation step may again take any convenient form known in the art. Preferably the membranes are asymmetric membranes, having a thin skin that is responsible for the separation properties and an underlying integral micro porous support layer, or composite membranes.

The membrane separation unit used in the membrane separation step 615 divides the gas stream into a carbon-dioxide-enriched permeate stream 614 and a carbon-dioxide-depleted, methane-rich residue stream 616. The residue stream is in this text also referred to as a natural gas product stream 616.

The natural gas product stream 616 has a carbon dioxide content reduced to a first level relative to the raw natural gas stream 610. If the principal goal of the process is to upgrade raw natural gas to pipeline specification, the natural gas product stream 616 may be the primary product of the process. Preferably, this stream contains no more than about 20 percent carbon dioxide and more preferably no more than 7-12 percent carbon dioxide. To meet pipeline specification, it is most preferable that this stream contains no more than about 2 percent carbon dioxide. This requires a further process step, which will be described in detail below.

If the raw gas contains relatively large amounts of carbon dioxide, it is not uncommon that the natural gas product stream 616 may still contain too much carbon dioxide to pass directly to the pipeline. In this case, the natural gas product stream 616 is passed to an amine absorption step 617 for further reducing the carbon dioxide content to a second level relative to the raw natural gas stream 610.

The amine absorption step 617 involves supplying the natural gas product stream and a lean absorption medium comprising a liquid diluent and at least one amine to an absorber unit (see Figures 1-5).

The natural gas product stream is passed into cross-flow contact with the lean absorption medium within a rotating absorption zone in the absorber, wherein carbon dioxide is removed from the natural gas product stream by the lean absorption medium when passing through the rotating absorption zone, in order to obtain a sweetened natural gas product 620 having a carbon dioxide content reduced to a second level relative to the raw natural gas stream. A lean amine stream 618 is supplied to the absorber from an amine regeneration unit (not shown). A rich amine stream 619 containing absorbed carbon dioxide is removed from the absorber and is supplied to said amine regeneration unit. The sweetened natural gas product 620 contains no more than about 2-2,4 percent carbon dioxide in order to meet pipeline specification standards.

Figure 1 shows a schematic, partially cross-sectioned absorber for use in a process according to the invention. The absorber in Figure 1 comprises a vessel 101 in the form of a cylindrical outer stator shell containing a first and a second annular absorber packing 102a, 102b rotatable about a longitudinal axis X within the vessel 101, which absorber packings have a predetermined axial extension with an inner radius r and an outer radius R (see Fig.3). The absorber further comprises an absorbent inlet 103, arranged for supplying lean absorbent to the absorber packing, and absorbent outlets 104a, 104b, arranged for removing rich absorbent on the vessel radially outside the outer perimeter 111 of the absorber packings at the lower section of the vessel 101. Lean absorbent is supplied to the vessel 101 from a conduit (not shown) connected to a rotary joint 105 attached to an inlet shaft 106 in the form of a hollow idle shaft comprising a central pipe for transport of lean absorbent through the inlet shaft 106 to a number of radial channels 107a, 107b for transport of lean absorbent to a number of longitudinal distribution tubes

108a, 108b, which distribution tubes adjacent the inner perimeter 112 of the absorber packings 102a, 102b is provided with nozzles (not shown) for even distribution of lean absorbent tangentially and axially on the inner perimeter of the absorber packings. The absorber also comprises natural gas inlets 109a, 109b for pressurized natural gas, arranged radially outside an outer perimeter of the absorber packing, and natural gas outlets 110, arranged on the vessel radially outside the outer perimeter of the absorber packing. In this example, the natural gas outlets 110 are arranged axially separated from the natural gas inlets 109a, 109b, and aligned with a radially open section 113 separating the absorber packings 102a, 102b. The arrangement in Figure 1 has four natural gas outlets 110 arranged in a radial plane through the vessel, which outlets are located equidistant around the circumference of the vessel. The radially open section 113 is separated from the natural gas inlets 109a, 109b and the facing end surfaces of the absorber packings 102a, 102b by first and second radial walls 114a, 114b. Each radial wall 114a, 114b extends from the inner perimeter of the annular absorber packing to a gas tight labyrinth seal 115a, 115b at the inner wall of the vessel. A third radial wall 114c is located between the first and second radial walls 114a, 114b and extends from the inlet shaft 106 to the outer perimeter of the absorber packings 102a, 102b. The third radial wall 114c is provided to guide the flow of sweet natural gas from the inner perimeter of the absorber packings towards the natural gas outlets 110.

The opposing end surfaces of the absorber packings 102a, 102b are sealed by a pair of rotor end plates 116a, 116b to form a an absorber packing assembly or rotor assembly. The rotor end plates 116a, 116b are each supported inside the vessel by a rotor shaft journalled at each end of the vessel. The rotor assembly is held together by means of multiple axial tension rods 117 (one shown) which extend through all the radial walls in the assembly outside the outer perimeter of each absorber packing and are bolted to the rotor end plates and the radial walls 114a, 114b adjacent the open section 113. The vessel 101 comprises a cylindrical outer stator shell

having a pair of end domes, wherein each dome is provided with a gas tight seal 118a, 118b around the respective rotor shaft. The entire absorber assembly located between these rotor shafts is rotated as a unit by a driving torque T applied to a driven rotor shaft 119 located on the opposite side of the vessel relative to the absorbent inlet 103. The absorber packing assembly comprises two absorber packings which are symmetrical on either side of a central plane at right angles to the rotational axis of the absorber packing. The central plane is, in this case, taken through a position half way between the facing ends of two absorber packings located end-to-end or with an axial separation along a common axis of rotation.

For the embodiment described in Figure 1, an example of a suitable size for the absorber arrangement is a pair of absorber packings each having an inner diameter of 1 m, an outer diameter of 2,5 m and a length of 2,2 m. Using a suitable metal foam having a surface area of 2500 m2/m3, theses dimensions give surface area of 223 m3 and a volume of 18 m3 of metal foam. Four natural gas inlets with a diameter of 200-250 mm will give a gas velocity of up to 20 m/s. A lean absorbent inlet with a diameter of 169 mm at the idle rotor shaft will give an absorber velocity of 10 m/s. In order to rotate the assembly at 450 rpm to achieve 400 G on the absorbent in the absorber packing, 1250 kW is required for transport of the lean absorbent alone. The power consumption for the gas will be lower because momentum is exchanged from the lean absorbent.

Figure 2 shows a cross-section through a first alternative embodiment of an absorber for use in a process according to the invention. The absorber in Figure 2 differs from that of Figure 1 in that it comprises an absorber provided with means for recuperating energy from the gas flow through the absorber. The recuperating means is placed within the open section 113 between the absorber packings 102a, 102b, as shown in Figure 1, and comprises a radial discharge fan 201 with curved radial vanes, as shown in Figure 2. In Figure 2, the radially open section 113 is separated from the natural gas inlets (not shown) and the facing end surfaces of the absorber

packings 102a, 102b by first and second radial walls 114a, 114b. A third radial wall 114c is located between the first and second radial walls 114a, 114b and extends from the inlet shaft 106 to the outer perimeter of the absorber packings 102a, 102b. The third radial wall 114c is provided to guide the flow of sweet natural gas from the inner perimeter of the absorber packings towards the natural gas outlets (not shown).

The radial discharge fan 201 comprises a first and a second set of radial vanes 202a, 202b, wherein the first set of radial vanes 202a is attached between the first radial wall 114a and the third radial wall 114c. Similarly, the second set of radial vanes 202b is attached between the second radial wall 114b and the third radial wall 114c.

The radial vanes have several functions, such as acting as a mechanical, torque transmitting connection between the two absorber sections, assisting in transport of sweet gas from centre to periphery while recovering some of the momentum to rotational power, and assisting in separating rich absorbent droplets from the sweet natural gas. The latter function requires droplet traps to be integrated in the design, as described for the embodiment according to Figure 1 above.

The energy recovery is achieved by guiding sweet natural gas through the radial vanes 202a, 202b in the radially open section 113, whereby some of the momentum from the pressurized sweet natural gas flowing towards the outlet is transferred to the vanes of the discharge fan 201. The recovered momentum causes a driving torque applied to the rotor shaft and assists in rotating the absorber assembly.

Figure 3 shows a schematic illustration of the flow patterns of fluids in the rotated absorber assembly in the rotational symmetric radial-axial plane of the units shown in Figures 1 and 2. Absorbent medium is supplied from an inlet a_1 through a central rotor shaft and is distributed on the inner perimeter a_2 of the absorber packing. The lean absorbent is distributed and transported a_3 to the outer perimeter a_4 by the high centrifugal forces (high G) in the

rotating absorber assembly. The rich absorbent is then removed via an outlet a_5 for processing and re-use. The sour gas is supplied from inlets A_1 at the outer periphery of the absorber packing and is forced towards the centre of the assembly in the opposite direction A_2 allowing efficient cross flow for mass transfer of CO_2 to the lean absorbent. The sweet gas is guided along the inner perimeter A_3 and then outwards A_4 through an open section from the axial centre of the assembly. This open section can have vanes allowing recovery of kinetic energy from the gas as well as droplet traps to remove absorbent droplets carried over in the gas. Finally, the sweet gas is removed form the assembly through an outlet A_5.

Figure 4 shows a cross-section through a second alternative embodiment of an absorber for use in a process according to the invention. The absorber in Figure 4 differs from that of Figure 2 in that it comprises an absorber provided with means for recuperating energy from the gas flow through the absorber placed within a first and a second open section 413a, 413b at either end of an absorber packing 400. Each open section 413a, 413b comprises a radial discharge fan 401a, 401b with curved radial vanes, similar to the arrangement shown in Figure 2. In Figure 4, the radially open sections 413a, 413b are separated from the natural gas inlets (not shown) and the opposite end surfaces of the absorber packing 400 by first and second radial walls 414a, 414b. A third radial wall 414c is located in a position equidistant from the first and second radial walls 414a, 414b and extends from the inlet shaft 406 to the inner perimeter 412 of the absorber packing 400. The third radial wall 414c is provided to guide the flow of sweet natural gas from the inner perimeter of the absorber packing towards the natural gas outlets 410a, 410b. This arrangement also ensures that the flow of natural gas is distributed so that each radial discharge fan 401a, 401b will receive approximately the same gas flow.

The radial discharge fans 401a, 401b comprise a first and a second set of radial vanes 402a, 402b, wherein the first set of radial vanes 402a is

attached between the first radial wall 416a and a first rotor end plate 412a. Similarly, the second set of radial vanes 402b is attached between the second radial wall 414b and a second rotor end plate 416b, in order to form a an absorber packing assembly or rotor assembly. The rotor assembly is held together by means of multiple axial tension rods 417 (schematically indicated in Fig.4) which extend through all the radial walls in the assembly outside the outer perimeter 411 of the absorber packing and are bolted to the rotor end plates. The absorber packing assembly comprises a single absorber packing which is symmetrical on either side of a central plane at right angles to the rotational axis of the absorber packing. The central plane is, in this case, taken through a position located at the mid-point of the single absorber packing along the axis of rotation.

As stated above, the radial vanes have several functions, such as acting as a mechanical, torque transmitting connection between the two absorber sections, assisting in transport of sweet gas from centre to periphery while recovering some of the momentum to rotational power, and assisting in separating rich absorbent droplets from the sweet natural gas. The latter function requires droplet traps to be integrated in the design, as described for the embodiment according to Figure 1 above. In the embodiment of Figure 4, the radial walls 414a, 414b extends from the inner perimeter of the annular absorber packing to a gas tight labyrinth seal 415a, 415b at the inner wall of the vessel.

The energy recovery is achieved by guiding sweet natural gas through the radial vanes 402a, 402b in the radially open section 413a, 413b, whereby some of the momentum from the pressurized sweet natural gas flowing towards the outlet is transferred to the vanes of the discharge fans 401a, 401b. The recovered momentum causes a driving torque applied to the rotor shaft 119 and assists in rotating the absorber assembly.

Figure 5 shows a schematic illustration of the flow patterns of fluids in the rotated absorber assembly in the rotational symmetric radial-axial plane of

the unit shown in Figure 4. Absorbent medium is supplied from an inlet a_1 through a central rotor shaft and is distributed on the inner perimeter a_2 of the absorber packing. The lean absorbent is distributed and transported a_3 to the outer perimeter a_4 by the high centrifugal forces (high G) in the rotating absorber assembly. The rich absorbent is then removed via an outlet a_5 for processing and re-use. The sour gas is supplied from inlets A_1 at the outer periphery of the absorber packing and is forced towards the centre of the assembly in the opposite direction A_2 allowing efficient cross flow for mass transfer of CO_2 to the lean absorbent. The sweet gas is guided along the inner perimeter A_3 and then outwards A'_4 from the axial centre of the assembly through open sections at each end of the assembly. The open sections can have vanes allowing recovery of kinetic energy from the gas as well as droplet traps to remove absorbent droplets carried over in the gas. Finally, the sweet gas is removed form the assembly through outlets A'_5 at each end of the assembly.

Figure 7 shows a schematic diagram of a process according to a second embodiment of the invention. The second embodiment is substantially the same as the embodiment described in connection with Figure 6, with the difference that a further absorption step 702 for eliminating hydrogen sulphide has been introduced prior to the steps 611, 613, 615, 617 shown in Figure 6.

The process according to the second embodiment comprises the further step of supplying a raw natural gas stream 701 comprising , for instance, up to 5 percent hydrogen sulphide and an organic scrubbing agent 704 specific to hydrogen sulphide to a further absorber prior to a separation membrane step 715. Suitable organic scrubbing agents for this purpose have already been discussed in the text of the description.

The raw natural gas stream 701 is passed into cross-flow contact with the lean organic scrubbing agent 704 within a rotating absorption zone in the further absorber, wherein the hydrogen sulphide is removed from the raw

natural gas stream by the organic scrubbing agent when passing through the rotating absorption zone, in order to obtain a raw natural gas stream 710 free from hydrogen sulphide.

The hydrogen sulphide removal process involves supplying the organic scrubbing agent to an inner portion of at least one annular rotating absorber unit within the further absorber, causing the organic scrubbing agent to flow radially outwards through the rotating absorption zone; and supplying the raw natural gas stream to an outer portion of said annular rotating absorber unit, causing the raw natural gas stream to flow radially inwards in order to create a radial cross-flow in the absorption zone. The organic scrubbing agent is supplied to a pair of identical and mirrored annular rotating absorber units rotating about a common axis within the absorber. The absorber units described in connection with Figures 1-5 above are suitable for this purpose.

The raw natural gas stream 710 free from hydrogen sulphide is then directed into a production plant for carrying out the process for removal of carbon dioxide. As mentioned in connection with Figure 6 above, the raw gas stream 710 is typically at elevated pressure. If it is at insufficiently high pressure to operate the process satisfactorily, the raw gas stream 710 may optionally be compressed, as shown in Figure 7. The raw gas stream 710 then passes into an optional compression step 711.

Gas emerges from compression step 711, if used, as compressed feed stream 712 and is passed to optional cooling step 713. If a compression step is used, the compressor exhaust gas is hot and an after-cooling step will be needed. If the compression step is not used, the cooling step 713 is optional.

An optional phase separation step (not shown) can be used upstream of the membrane separation step 715 if the raw gas stream 710 is a two-phase mixture containing entrained hydrocarbon liquids as mist or droplets, or if a compression step 711 and/or cooling step 713 have been used.

This step 715 is carried out using a membrane separation unit equipped with a membrane that is selective in favour of carbon dioxide over methane and other hydrocarbons. The membrane separation unit used in the membrane separation step 715 divides the gas stream into a carbon-dioxide-enriched permeate stream 714 and a carbon-dioxide-depleted, methane-rich residue stream 716. The residue stream is in this text also referred to as a natural gas product stream 716.

The natural gas product stream 716 has a carbon dioxide content reduced to a first level relative to the raw natural gas stream 710. If the principal goal of the process is to upgrade raw natural gas to pipeline specification, the natural gas product stream 716 may be the primary product of the process. Preferably, this stream contains no more than about 20 percent carbon dioxide and more preferably no more than 7-12 percent carbon dioxide. To meet pipeline specification, it is most preferable that this stream contains no more than about 2 percent carbon dioxide. This requires a further process step, which has been described in detail above.

The natural gas product stream 716 is passed to an amine absorption step 717 for further reducing the carbon dioxide content to a second level relative to the raw natural gas stream 710. The amine absorption step 717 involves supplying the natural gas product stream and a lean absorption medium comprising a liquid diluent and at least one amine to an absorber unit (see Figures 1-5).

The natural gas product stream is passed into cross-flow contact with the lean absorption medium within a rotating absorption zone in the absorber, wherein carbon dioxide is removed from the natural gas product stream by the lean absorption medium when passing through the rotating absorption zone, in order to obtain a sweetened natural gas product 720 having a carbon dioxide content reduced to a second level relative to the raw natural gas stream. This process has been described in detail in connection with Figures 1-5 above. A lean amine stream 718 is supplied to the absorber from

an amine regeneration unit (not shown). A rich amine stream 719 containing absorbed carbon dioxide is removed from the absorber and is supplied to said amine regeneration unit. The sweetened natural gas product 720 contains no more than about 2-2,4 percent carbon dioxide in order to meet pipeline specification standards.

The invention is not limited to the above embodiments, but may be varied freely within the scope of the appended claims.

CLAIMS

1. A process for treatment of a raw natural gas and other gas streams containing methane and at least one acid gas, such as carbon dioxide, by removing said acid gas to produce a sweetened natural gas stream, the process comprising the steps of:

- contacting the raw natural gas feed stream with a separation membrane to obtain a natural gas product stream rich in methane and having a carbon dioxide content reduced to a first level relative to the raw natural gas stream;
- supplying the natural gas product stream and a lean absorption medium comprising a liquid diluent and at least one amine to an absorber;
- passing the natural gas product stream into cross-flow contact with the lean absorption medium within a rotating absorption zone in the absorber, wherein carbon dioxide is removed from the natural gas product stream by the lean absorption medium when passing through the rotating absorption zone, in order to obtain a sweetened natural gas product having a carbon dioxide content reduced to a second level relative to the raw natural gas stream.

2. A process according to claim 1, *characterized by* contacting the raw natural gas feed stream with a membrane to reduce the carbon dioxide content of the raw natural gas feed stream from at least 30 % CO_2 to a first level at or below 20 % CO_2.

3. A process according to claim 2, *characterized by* contacting the raw natural gas feed stream with a membrane to reduce the carbon dioxide content of the raw natural gas feed stream from at least 30 % CO_2 to a first level between 7 and 12 % CO_2.

4. A process according to any one of claims 1-3, *characterized by* supplying the natural gas product stream to the further absorber to reduce the carbon dioxide content of the natural gas product stream from 20 % CO_2 or less, to a second level of 2,4 % CO_2 or less.

5. A process according to any one of claims 1-4, *characterized by* supplying the lean absorption medium to an inner portion of at least one annular rotating absorber unit within the absorber, causing the lean absorption medium to flow radially outwards through the rotating absorption zone; and supplying the natural gas product stream to an outer portion of said annular rotating absorber unit, causing the natural gas product to flow radially inwards in order to create a radial cross-flow in the absorption zone.

6. Process according to claim 5, characterized by supplying the lean absorption medium to a pair of identical and mirrored annular rotating absorber units rotating about a common axis within the absorber.

7. A process according to any one of the above claims, *characterized by* the further steps of;

- supplying the raw natural gas stream and an organic scrubbing agent specific to hydrogen sulphide to a further absorber prior to the separation membrane step; and
- passing the raw natural gas stream into cross-flow contact with the organic scrubbing agent within a rotating absorption zone in the further absorber, wherein the hydrogen sulphide is removed from the raw natural gas stream by the organic scrubbing agent when passing through the rotating absorption zone, in order to obtain a raw natural gas stream free from hydrogen sulphide.

8. A process according to claim 7, *characterized by* supplying the organic scrubbing agent to an inner portion of at least one annular rotating absorber unit within the further absorber, causing the organic scrubbing agent to flow radially outwards through the rotating absorption zone; and

supplying the raw natural gas stream to an outer portion of said annular rotating absorber unit, causing the raw natural gas stream to flow radially inwards in order to create a radial cross-flow in the absorption zone.

9. Process according to claim 8, *characterized by* supplying the organic scrubbing agent to a pair of identical and mirrored annular rotating absorber units rotating about a common axis within the absorber.

10. A production plant for treatment of a raw natural gas and other gas streams containing methane and at least one acid gas, such as carbon dioxide, by removing said acid gas to produce a sweetened natural gas stream, the production plant comprising:

- a separation membrane, wherein the raw natural gas feed stream is brought into contact with said separation membrane to obtain a natural gas product stream rich in methane and where the carbon dioxide content is reduced to a first level relative to the raw natural gas stream;

- an absorber, which is supplied with the natural gas product stream and a lean absorption medium comprising a liquid diluent and at least one amine; where said absorber comprises a rotating absorption zone through which the natural gas product stream is arranged to pass in a cross-flow contact with the lean absorption medium;

wherein carbon dioxide is removed from the natural gas product stream by the lean absorption medium when passing through the rotating absorption zone to obtain a sweetened natural gas product having a carbon dioxide content reduced to a second level relative to the raw natural gas stream.

11. A process according to claim 10, *characterized in* that the raw natural gas feed stream is arranged to contact the membrane to reduce the carbon dioxide content of the raw natural gas feed stream from at least 30 % CO_2 to a first level at or below 20 % CO_2.

12. A process according to claim 12, *characterized in* that the raw natural gas feed stream is arranged to contact the membrane to reduce the carbon dioxide content of the raw natural gas feed stream from at least 30 % CO_2 to a first level between 7 and 12 % CO_2.

13. A process according to any one of claims 10-12, *characterized in* that the natural gas product stream is arranged to be supplied to the further absorber to reduce the carbon dioxide content of the natural gas product stream from 20 % CO_2 or less, to a second level of 2,4 % CO_2 or less.

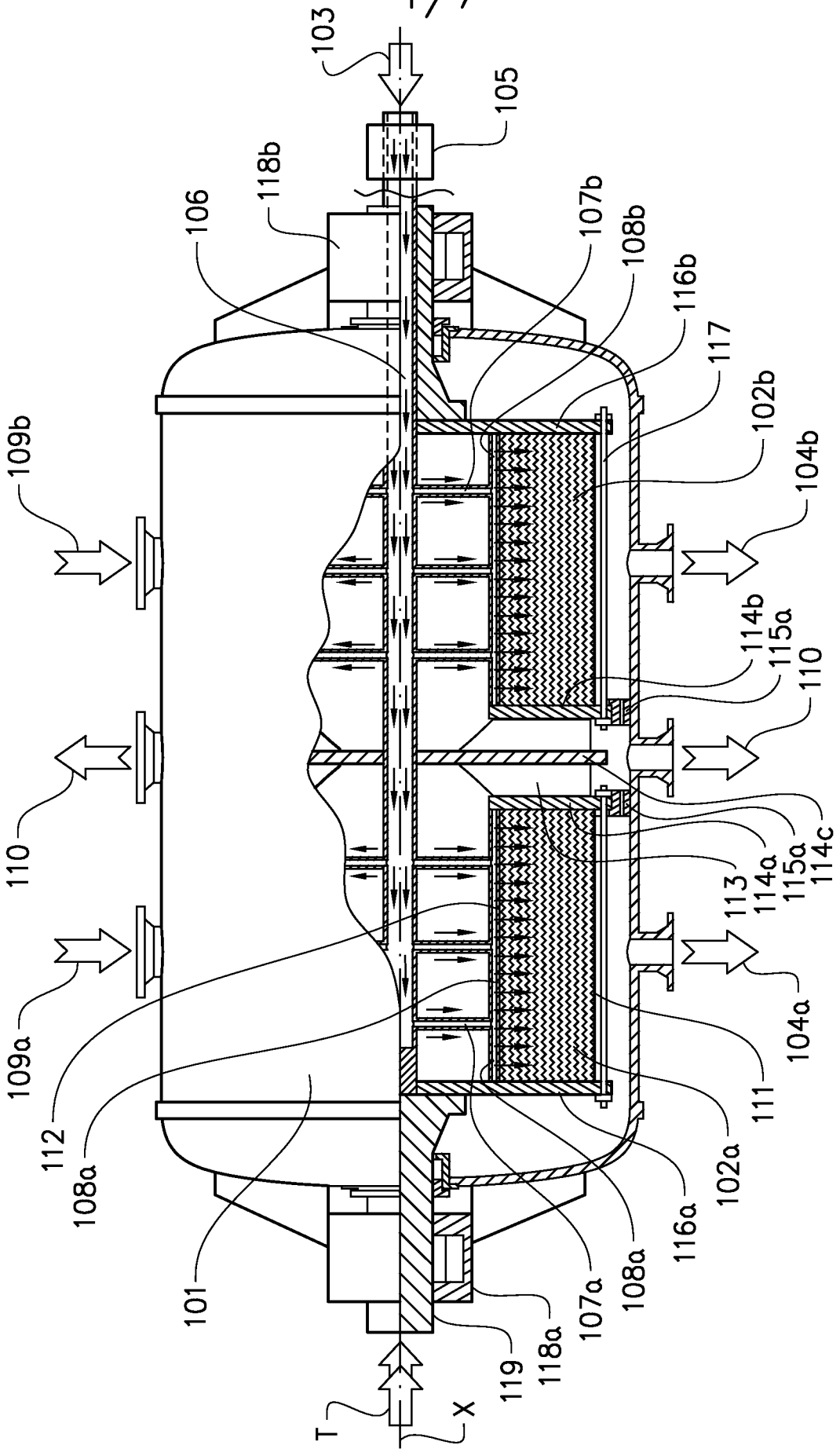

103
105
118b
106
107b
108b
116b
117
102b
104b
109b
110
114b
115a
110
114c
115a
114a
113
104a
109a
112
108a
111
102a
116a
108a
107a
118a
119
101
T
X

FIG. 1

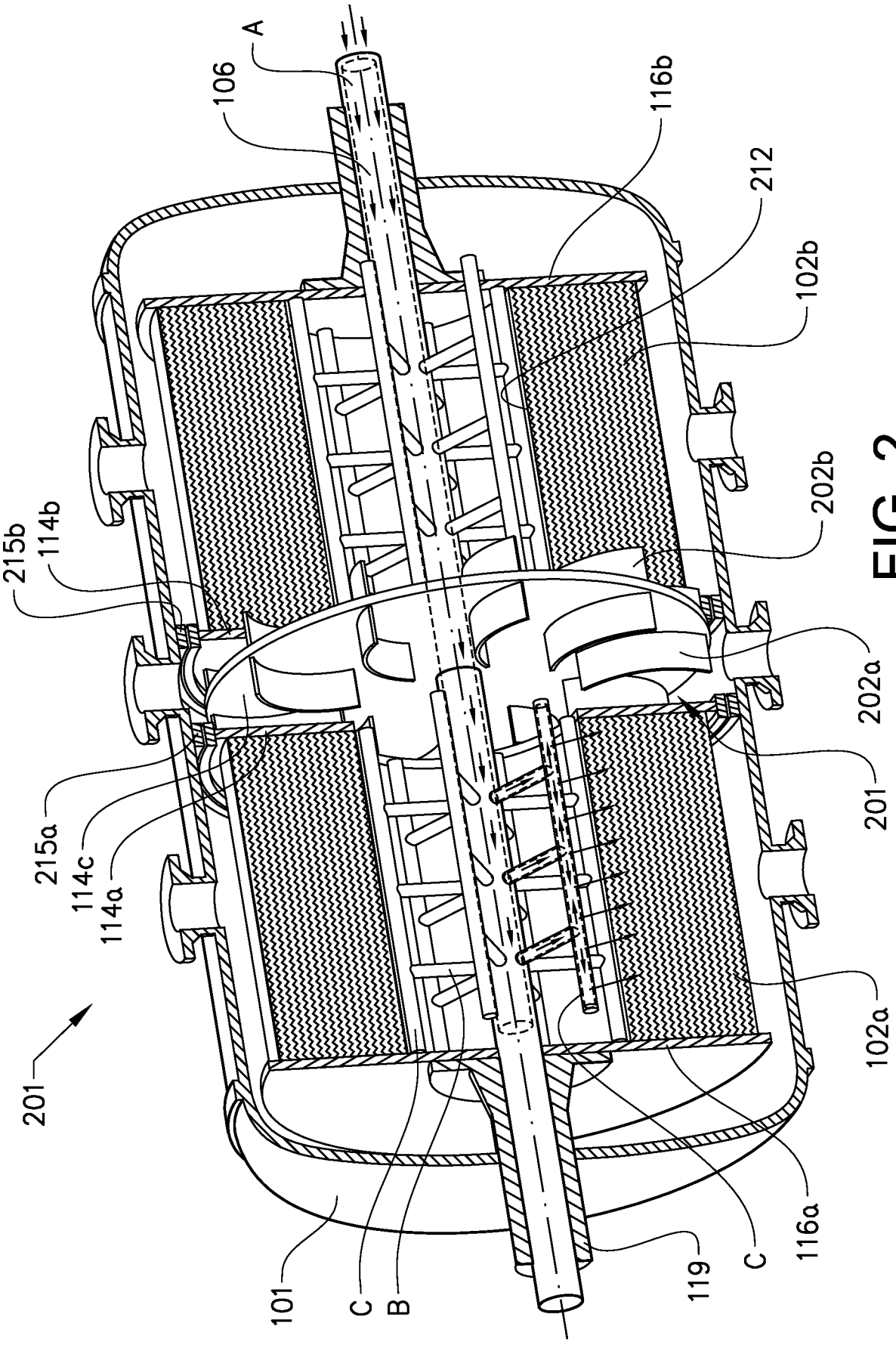

A
106
116b
212
102b
202b
215b
114b
202a
215a
114c
114a
201
201
102a
116a
C
119
C
B
101

FIG. 2

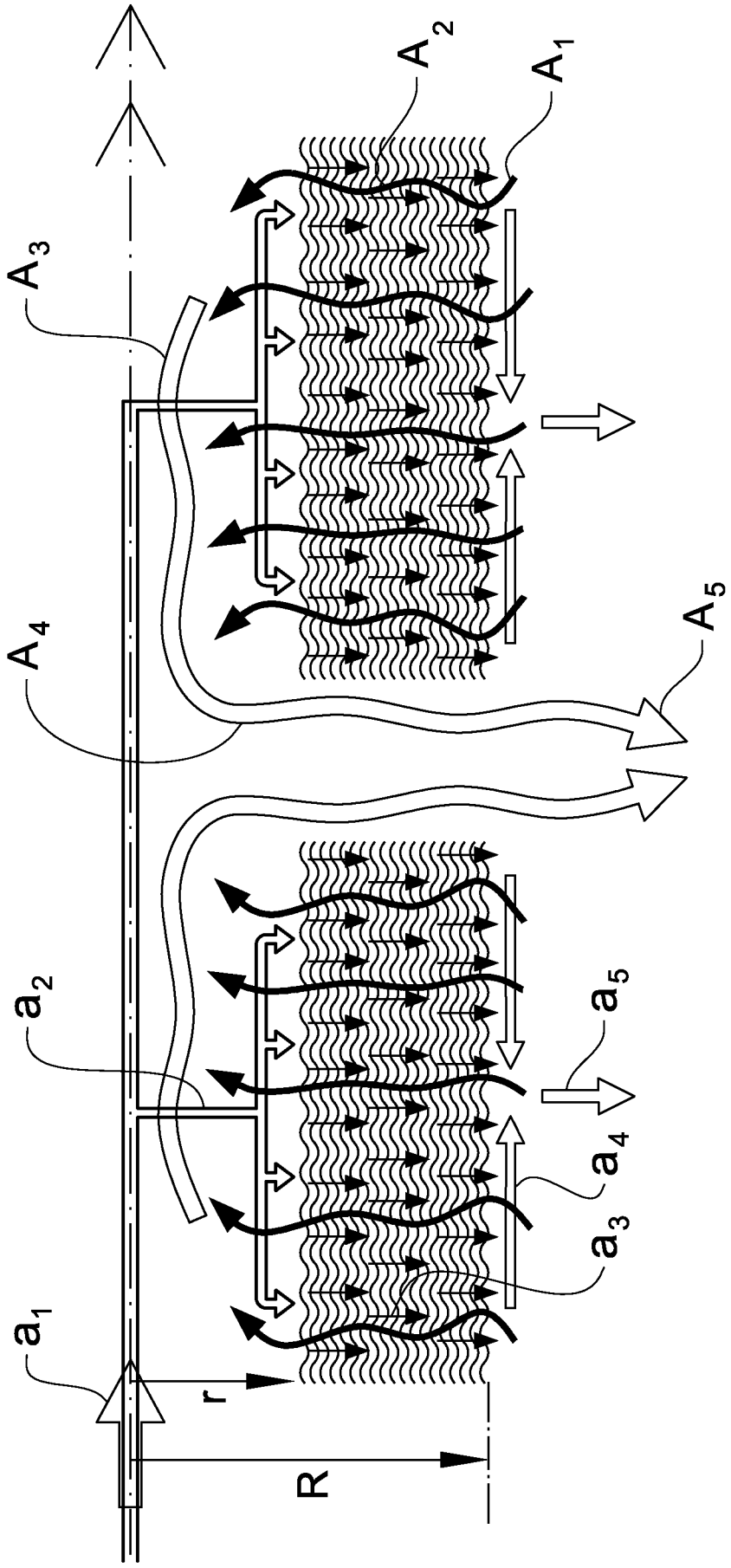


FIG. 3

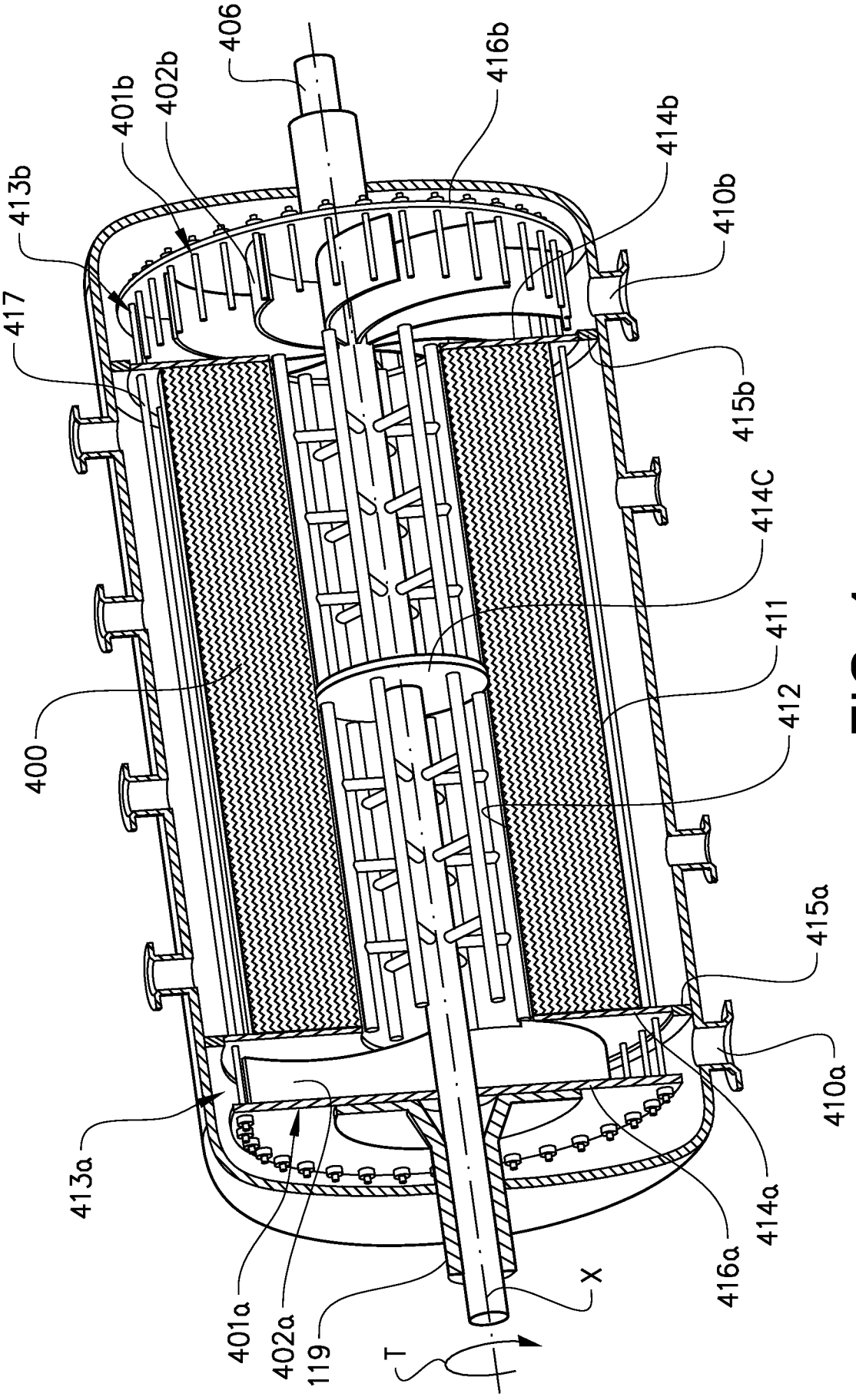

406
401b
402b
413b
416b
414b
410b
417
415b
414C
411
400
412
415a
410a
413a
414a
416a
401a
402a
119
X
T

FIG. 4

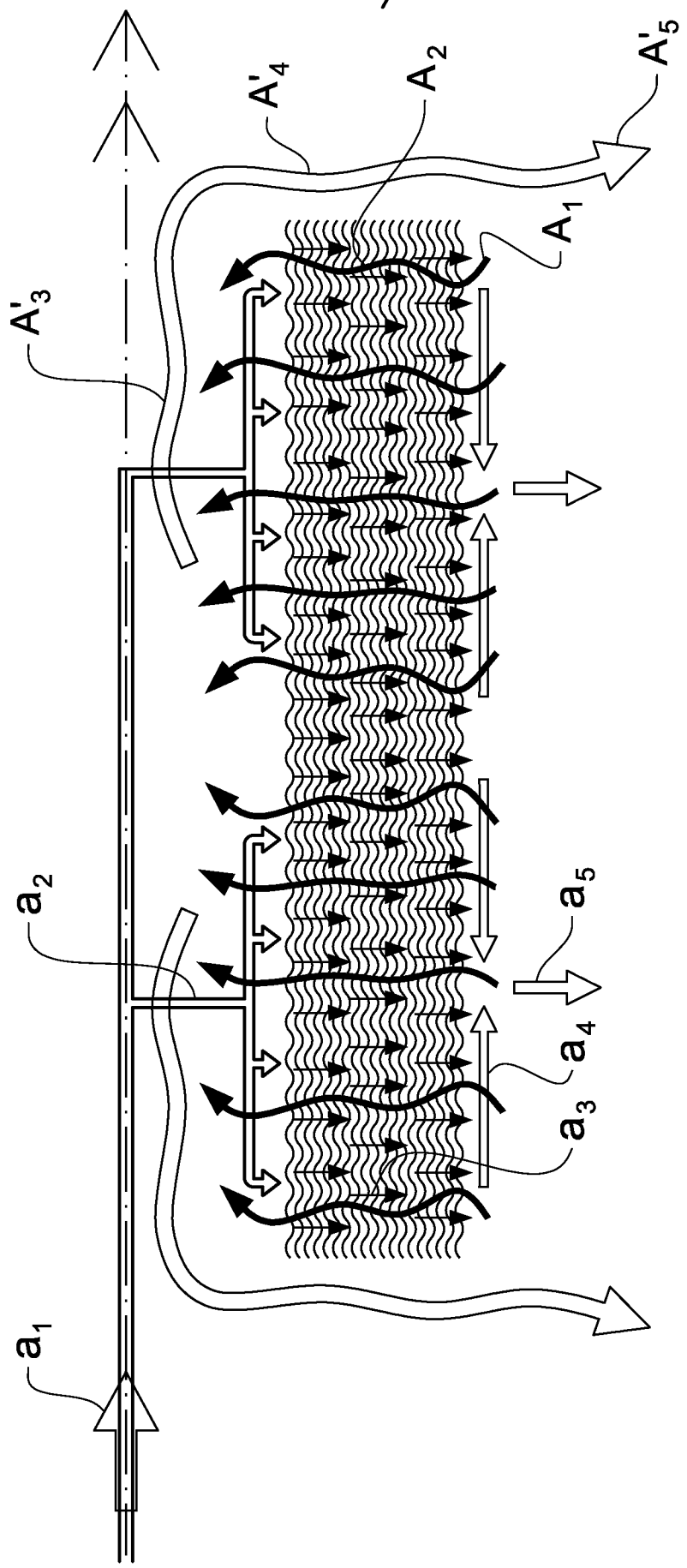


FIG. 5

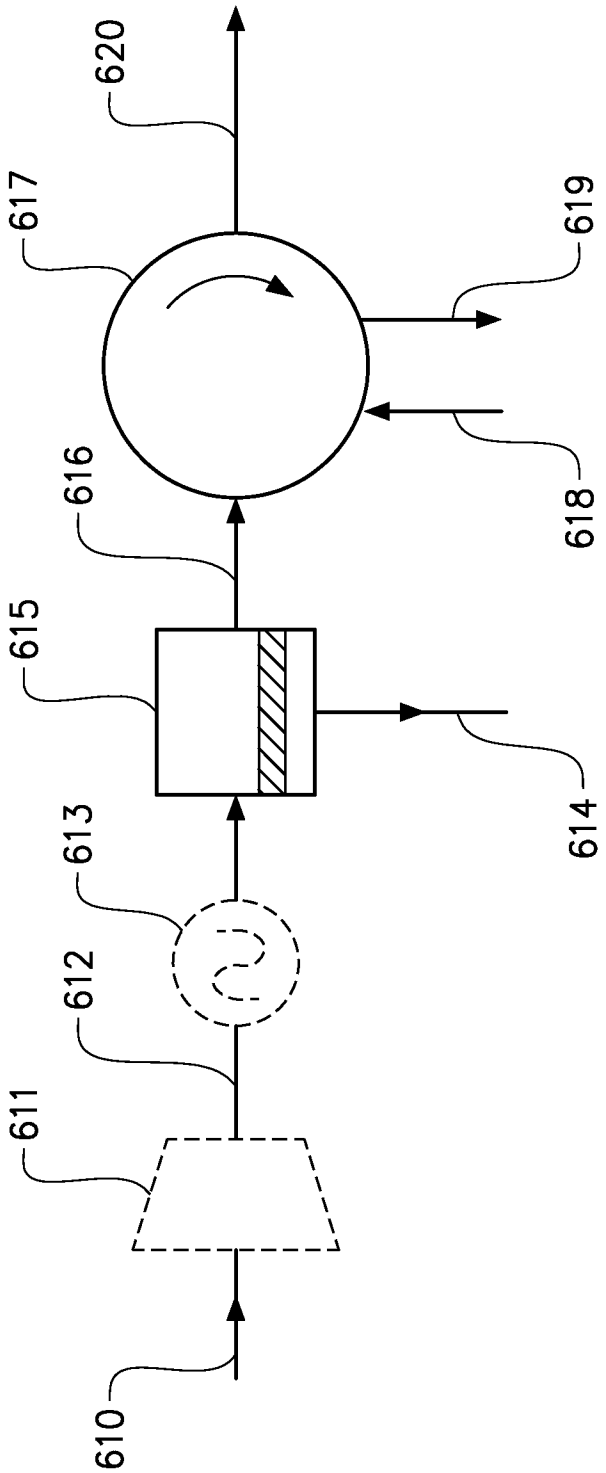


FIG. 6

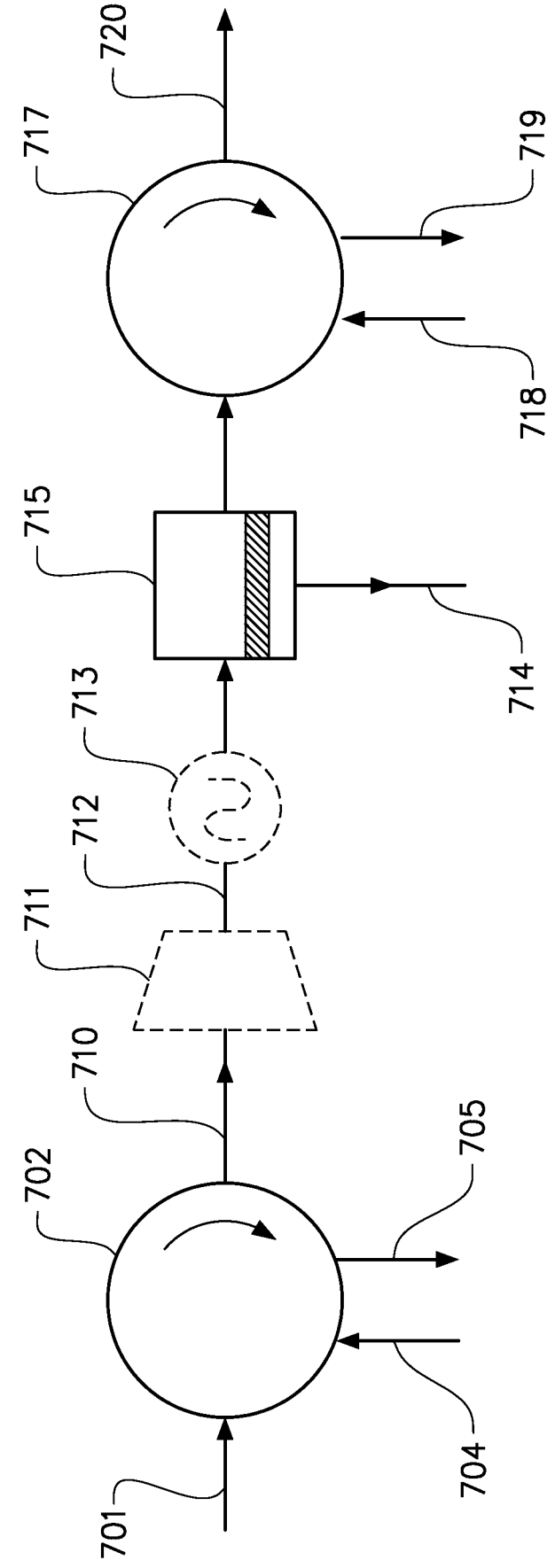


FIG. 7

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/050174

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D45/14 B01D53/18 B01D53/22 C10L3/10
ADD.

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01D C10L

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 practical, 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.
X	JP 2005 290151 A (TOYO ENGINEERING CORP) 20 October 2005 (2005-10-20)	11-13
Y	abstract -& DATABASE WPI Week 200577 Thomson Scientific, London, GB; AN 2005-752938 XP002659654, -& JP 2005 290151 A (TOYO ENG CORP) 20 October 2005 (2005-10-20) abstract	1-10

Y	EP 0 204 193 A2 (MAN TECHNOLOGIE GMBH [DE]) 10 December 1986 (1986-12-10) figure 2 the whole document	1-10

	-/--	

[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 document 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
29 September 2011	10/10/2011

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	Gruber, Marco

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

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2011/050174

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 2 210 656 A1 (GEN ELECTRIC [US]) 28 July 2010 (2010-07-28) the whole document	1-13
A	WO 95/21683 A1 (KVAERNER ENG [NO]; ROENNING SVEIN O [NO]; BJERVE YNGVIL [NO]; FALK PED) 17 August 1995 (1995-08-17) figure 4	1-13
A	US 3 486 743 A (TODD DAVID B) 30 December 1969 (1969-12-30) the whole document	1-13
A	US 3 653 187 A (PETERSEN GERD HUGO) 4 April 1972 (1972-04-04) the whole document	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2011/050174

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
JP 2005290151 A	20-10-2005	NONE	
EP 0204193 A2	10-12-1986	DE 3519661 A1	04-12-1986
		JP 61278336 A	09-12-1986
EP 2210656 A1	28-07-2010	CA 2749787 A1	05-08-2010
		WO 2010088054 A2	05-08-2010
WO 9521683 A1	17-08-1995	AT 167408 T	15-07-1998
		AU 687171 B2	19-02-1998
		AU 1826095 A	29-08-1995
		AU 5637798 A	30-04-1998
		CA 2183374 A1	17-08-1995
		DE 69503036 D1	23-07-1998
		DE 69503036 T2	22-10-1998
		DK 744987 T3	01-02-1999
		EP 0744987 A1	04-12-1996
		ES 2118574 T3	16-09-1998
		HK 1012835 A1	06-08-1999
		JP 3659970 B2	15-06-2005
		JP 9509608 T	30-09-1997
		NO 940527 A	16-08-1995
		US 5832712 A	10-11-1998
US 3486743 A	30-12-1969	NONE	
US 3653187 A	04-04-1972	BE 750690 A1	03-11-1970
		CA 954037 A1	03-09-1974
		CH 526983 A	31-08-1972
		ES 379943 A1	01-04-1973
		FR 2048604 A5	19-03-1971
		GB 1320164 A	13-06-1973
		NL 7006874 A	26-11-1970