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(54) **Method and apparatus for adjusting the Wobbe-index of a gas mixture**

(57) Method for converting a first gas mixture comprising hydrocarbons to a product gas mixture with a lower Wobbe index than the first gas mixture, comprising the steps of (i) providing the first gas mixture, (ii) providing a second gas mixture comprising hydrocarbons, (iii) providing a third gas mixture comprising oxygen, (iv) carrying

the second and the third gas mixture into a chemical reactor configured to produce a fourth gas mixture comprising carbon dioxide gas, and (v) carrying the fourth gas mixture into the first gas mixture, thus obtaining the product gas mixture, and apparatus for converting a gas mixture comprising hydrocarbons in accordance with this method.

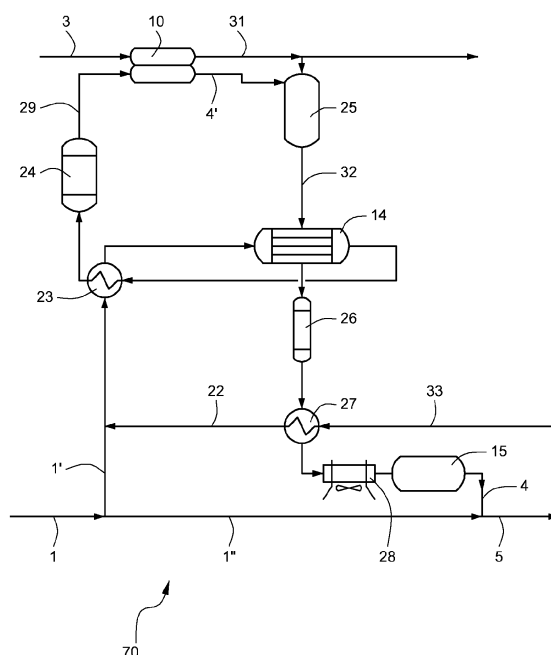


Fig. 7

Description

[0001] The invention relates to a method for adjusting the Wobbe index and reducing the calorific value of a gas mixture comprising hydrocarbons.

[0002] The Wobbe index W is a measure of the interchangeability of different gas mixtures on a burner, expressed in $[MJ/m^3]$, and is defined as

$$W = \frac{H}{\sqrt{\frac{\rho_{gas}}{\rho_{air}}}}$$

[0003] H is here the calorific value in $[MJ/m^3]$ of a gas mixture, ρ_{gas} is the density of the gas and ρ_{air} the density of air, both in $[kg/m^3]$.

[0004] The gas grid in the Netherlands is supplied with low-calorific gas comprising about 15% nitrogen, so-called Slochteren quality. Higher-calorific gas from other sources is at present diluted with nitrogen produced by means of gas separation from air, among other ways by means of pressure swing adsorption.

[0005] Dilution with nitrogen has the drawback that the production of nitrogen from gas separation from air requires much energy because the air has to be compressed in this process. For each quantity of nitrogen used it is usually necessary to compress a multiple of this quantity of air, as a result of which the efficiency of the gas separation typically lies in the region of 30%.

[0006] In order to stimulate the use of environmentally-friendly sources of methane it will become possible to supply gas from local sources, for instance locally obtained biogas, to the national gas grid. The calorific value and the Wobbe index in the national gas grid can hereby vary.

[0007] It is an object of the invention to provide a method for adjusting the Wobbe index of a gas mixture in order to thus be able to maintain a constant Wobbe index of a gas mixture to be supplied to an end user. It must be possible to perform this method in cost-saving manner, wherein it is for instance not required, other than in pressure swing adsorption, to compress a large quantity of diluent gas to a predetermined pressure.

[0008] This object is achieved, and other advantages realized, with a method for converting a first gas mixture comprising hydrocarbons to a product gas mixture with a lower Wobbe index than the first gas mixture, which according to the invention comprises the steps of (i) providing the first gas mixture, (ii) providing a second gas mixture comprising hydrocarbons, (iii) providing a third gas mixture comprising oxygen, (iv) carrying the second and the third gas mixture into a chemical reactor configured to produce a fourth gas mixture comprising carbon dioxide gas, and (v) carrying the fourth gas mixture into the first gas mixture, thus obtaining the product gas mixture.

[0009] Carrying the second and the third gas mixture into a chemical reactor as according to the step (iv) results in a significant saving compared to the known methods since it is not necessary to produce or compress nitrogen.

[0010] In a practically advantageous embodiment the second gas mixture is the first part of a first gas mixture separated into a first and a second part, and step (v) comprises of carrying the fourth gas mixture into the separated second part of the first gas mixture.

[0011] A method according to this embodiment is particularly suitable for converting a high-calorific gas comprising methane and having a Wobbe index higher than the Wobbe index of natural gas of Slochteren quality such that the Wobbe index becomes equal to that of the natural gas, so that after conversion this methane-comprising gas can be mixed with natural gas without the necessity for end users to adjust their burners or other natural gas appliances.

[0012] During application of the method according to this embodiment the high-calorific methane-comprising gas is supplied via a main conduit and a first part is carried via a parallel conduit to the chemical reactor. In the chemical reactor a fourth gas mixture comprising carbon dioxide gas is obtained from the gas and a third gas mixture comprising oxygen, and is carried into the separated second part of the first gas mixture, thus obtaining the product gas mixture, which has a lower Wobbe index than the initial high-calorific methane-comprising gas.

[0013] According to this method, distribution or local production of nitrogen is not necessary. The total quantity of diluent gas to be pressurized will further be smaller than in the prior art methods, thereby saving on costs of compressors and electricity.

[0014] In a practically advantageous embodiment the third gas mixture comprising oxygen to be provided as according to step (iii) is air. Air provides the advantage that the first gas mixture is also diluted with nitrogen as well as with carbon dioxide gas.

[0015] The invention further relates to an apparatus for converting as according to the above described method a first gas mixture, comprising hydrocarbons and carried through a transport conduit, to a product gas mixture with a lower Wobbe index than the first gas mixture, comprising a chemical reactor with a first inlet for admitting a second gas mixture comprising hydrocarbons and a second inlet for admitting a third gas mixture comprising oxygen, which reactor is configured to produce a fourth gas mixture comprising carbon dioxide gas, and with an outlet conduit for carrying the fourth gas mixture into the first gas mixture, thus obtaining the product gas mixture.

[0016] In a practically advantageous embodiment the first inlet of the reactor is coupled to a first branch of the transport conduit for the purpose of admitting a first part of the first gas mixture, and the outlet conduit of the reactor is coupled downstream of the first branch to a second branch of the transport conduit.

[0017] In an embodiment the chemical reactor com-

prises for instance a gas motor, and in a preferred embodiment a turbine.

[0018] A gas motor or a gas turbine as chemical reactor provides the advantage that the energy released during the reaction between the second and the third gas mixture can be utilized in efficient manner, for instance in a combined heat and power plant.

[0019] In the case of a gas motor or a gas turbine as chemical reactor the excess of supplied air is preferably minimal in order to achieve that the quantity of oxygen in the fourth gas mixture comprising carbon dioxide gas is minimal, or is at least below the permitted concentration.

[0020] In another embodiment the chemical reactor comprises a fuel cell, which is for instance provided with a reformer for the purpose of converting a first gas mixture comprising hydrocarbons to a gas mixture comprising hydrogen and carbon monoxide.

[0021] A reformer provides the option of converting the first gas mixture comprising hydrocarbons at least partially to a hydrogen-rich mixture prior to the reaction in the fuel cell.

[0022] The reformer is for instance an autothermal reformer, and the third gas mixture comprising oxygen to be provided as according to step (iii) for instance also comprises nitrogen, wherein cathode tailgas from the fuel cell is fed back to the autothermal reformer.

[0023] Cathode tailgas provides the advantage that the content of nitrogen therein is relatively high compared to that of oxygen, as a result of which the gas mixture coming from the autothermal reformer and to be carried into the fuel cell is enriched with nitrogen, whereby the Wobbe index of this gas mixture is reduced.

[0024] In an apparatus according to the invention the fuel cell is of any suitable type, for instance a solid polymer fuel cell (PEM FC).

[0025] In a subsequent embodiment the fuel cell is a solid oxide fuel cell (SOFC). With an SOFC it is possible to convert a gas mixture comprising hydrocarbons directly to carbon dioxide and water, i.e. without reformer, wherein electric power is generated.

[0026] In a subsequent embodiment the apparatus is provided with a measuring and control unit for determining the quantity of the fourth gas mixture to be produced comprising carbon dioxide gas.

[0027] The reactor is for instance a solid oxide fuel cell (SOFC) which converts the gas mixture of hydrogen and carbon monoxide to a flow of pure carbon dioxide and electric power.

[0028] A preferred embodiment of an apparatus according to the invention is provided with a drying unit for drying the fourth gas mixture comprising carbon dioxide gas.

[0029] This drying unit comprises for instance a gas refining unit on the basis of Pressure Swing Adsorption (PSA) technology for the purpose of further cleaning of the fourth gas mixture comprising carbon dioxide gas.

[0030] The invention will be elucidated hereinbelow on

the basis of exemplary embodiments, with reference to the drawings.

[0031] In the drawings in schematic view

5 Fig. 1 shows a prior art method and apparatus for reducing the calorific value of a gas mixture comprising hydrocarbons,

Fig. 2 shows a first embodiment of a method and apparatus according to the invention for reducing the calorific value of a gas mixture comprising hydrocarbons,

10 Fig. 3 shows a second embodiment of a method and apparatus according to the invention for reducing the calorific value of a gas mixture comprising hydrocarbons,

15 Fig. 4 shows a third embodiment of a method and apparatus according to the invention for reducing the calorific value of a gas mixture comprising hydrocarbons,

20 Fig. 5 shows a fourth embodiment of a method and apparatus according to the invention for reducing the calorific value of a gas mixture comprising hydrocarbons,

25 Fig. 6 shows a fifth embodiment of a method and apparatus according to the invention for reducing the calorific value of a gas mixture comprising hydrocarbons, and

30 Fig. 7 shows a sixth embodiment of a method and apparatus according to the invention for reducing the calorific value of a gas mixture comprising hydrocarbons.

[0032] Corresponding components are designated in the figures with the same reference numerals.

35 **[0033]** Fig. 1 is a schematic view of a prior art method for reducing the Wobbe index, wherein a gas mixture 1 comprising hydrocarbons, for instance pure methane (CH_4), with a pressure of for instance 66 bar and a Wobbe index $W_1 = 48 \text{ MJ/m}^3$, is mixed with nitrogen gas 6, wherein a product gas mixture 5 with a lower Wobbe index $W_5 = 40 \text{ MJ/m}^3$ is obtained. The nitrogen gas 6, which is likewise compressed to a pressure of 66 bar using a compressor 12, is obtained from an air separator 11 which is supplied with air 3 which is compressed to a pressure of for instance 7 bar using a compressor 13. A low-nitrogen residual air mixture 7 is released from air separator 11. The total compression energy required for this method amounts to about 0.6% of the energy content of the product gas mixture 5.

45 **[0034]** Fig. 2 is a schematic view of a method and apparatus 20 for reducing the Wobbe index W_1 of a first gas mixture 1 comprising hydrocarbons according to the invention, wherein a second gas mixture 2 comprising hydrocarbons is carried into a chemical reactor 10, for instance a fuel cell or a gas motor, to which a gas mixture 3 comprising oxygen is also supplied, wherein a fourth gas mixture 4 comprising carbon dioxide gas is obtained which is carried into the first gas mixture 1, thus obtaining

a product gas mixture 5 with a Wobbe index W_5 which is lower than W_1 .

[0035] Fig. 3 is a schematic view of a method and apparatus 30 for reducing the Wobbe index W_1 of a gas mixture 1 comprising hydrocarbons, for instance natural gas, wherein a first part 1' of the natural gas is carried into a chemical reactor 10, for instance a fuel cell or a gas motor, to which a gas mixture 3 comprising oxygen is also supplied, wherein a gas mixture 4 comprising carbon dioxide gas is obtained which is carried into the remaining, second part 1" of the natural gas, thus obtaining a product gas mixture 5 with a Wobbe index W_5 which is lower than W_1 .

[0036] Fig. 4 is a schematic view of a method and apparatus 40 for reducing the Wobbe index W_1 of a gas mixture 1 comprising hydrocarbons, for instance pure methane with a pressure of for instance 66 bar and a Wobbe index $W_1 = 48 \text{ MJ/m}^3$, wherein a first part 1' of the methane and air 3 is carried into an autothermal reformer 14, wherein the oxygen in the air 3 is wholly converted into a gas mixture 8 comprising substantially hydrogen in addition to methane, nitrogen, carbon monoxide and carbon dioxide. This gas mixture 8 is carried to a fuel cell 10, to which a gas mixture 3 comprising oxygen is also supplied, wherein a low-oxygen cathode tailgas 9 and a gas mixture 4' comprising carbon dioxide gas (the anode tailgas) is obtained. The anode tailgas 4' is successively cleaned and dried in a gas refining unit 15 with a catalytic burner, wherein water 16 is separated and the produced heat can be used in reformer 14 for the production of steam. The thus cleaned and dried anode tailgas 4 is carried via a compressor 12, wherein the gas is compressed to a pressure of 66 bar, into the remaining second part 1" of the methane, thus obtaining a product gas mixture 5 with a Wobbe index $W_5 = 40 \text{ MJ/m}^3$. About 4.5% of the supplied methane is consumed in the reformer in order to obtain this lower Wobbe index. The total required quantity of compression energy amounts to about half the energy required by the prior art method as described with reference to figure 1. Fuel cell 10 produces a surplus of about 1.3% electrical energy after subtraction of the energy required for compressor 12.

[0037] Fig. 5 is a schematic view of a method and apparatus 50 corresponding to apparatus 40 of Fig. 4, but wherein a part of the low-oxygen cathode tailgas 9 is fed back from fuel cell 10 to the autothermal reformer 14. According to this method, only 1.9% of the supplied methane is consumed in the reformer, but less electricity is obtained.

[0038] Fig. 6 is a schematic view of a method and apparatus 60 on the basis of a fuel cell 10, intended particularly for the purpose of reducing the Wobbe index W_1 of high-calorific natural gas 1.

[0039] High-calorific natural gas 1, 1' can be supplied, preferably at high pressure, to this apparatus 60 for the purpose of converting this natural gas to pure carbon dioxide 4 and electric power. The pure carbon dioxide 4

can then be fed back by means of a carbon dioxide mixing device 18 to the natural gas grid, preferably in a part 5 where the pressure has been reduced using a reducing device 19, so as to there reduce the Wobbe index W_5 to a value lower than the Wobbe index W_1 of the high-calorific natural gas 1, 1'. By thus reducing the Wobbe index it is not necessary to adjust the equipment downstream, for instance in a factory 21, to varying gas compositions.

[0040] Apparatus 60 is assembled from successively a measuring and control unit 17 for determining the quantity of carbon dioxide 4 to be admixed, a pre-reformer 14 for converting a gas mixture 1, 1' of varying composition to a gas mixture 8 of hydrogen and carbon monoxide, a solid oxide fuel cell 10 (SOFC) which converts the gas mixture 8 of hydrogen and carbon monoxide to a flow of pure carbon dioxide 4 and electric power, and a gas refining unit 15 on the basis of Pressure Swing Adsorption (PSA) technology for the purpose of further cleaning of the carbon dioxide. The dimensions of apparatus 60 are determined by the intended application thereof, and can vary from those of for instance a domestic refrigerator to a sea container.

[0041] Fig. 7 is a schematic view of a method and apparatus 70 on the basis of a PEM FC fuel cell 10, intended particularly for the purpose of reducing the Wobbe index W_1 of high-calorific natural gas 1.

[0042] Apparatus 70 is assembled from successively a heat exchanger, a heat exchanger/reformer 14, a CO reduction unit 24, the PEM FC fuel cell 10, a burner 25, a catalytic burner 26, a heat exchanger 27, a cooler 28 and a dryer 15.

[0043] The operation of apparatus 70 is as follows.

[0044] A part 1' of a mixture of high-calorific natural gas 1 is separated and admixed with steam 22 from water 33 which is heated in heat exchanger 23, and further heated in reformer/heat exchanger 14 and converted to a hot, hydrogen-rich mixture with carbon dioxide which is carried via heat exchanger 23 to the CO reduction unit 24. A cool, hydrogen-rich gas mixture is carried from the CO reduction unit 24 into the PEM FC fuel cell 10, from where a low-oxygen mixture 31 and the anode tailgas 4' are carried to burner 25, from where a very hot gas mixture 32 of nitrogen, carbon dioxide, steam and optionally small quantities of oxygen and carbon monoxide are added via the reformer/heat exchanger 14, catalytic burner 26, heat exchanger 27, cooler 28 and dryer 15 to the high-calorific natural gas 1", thus obtaining a product gas mixture 5 with a Wobbe index W_5 which is lower than W_1 .

Claims

1. Method for converting a first gas mixture (1) comprising hydrocarbons to a product gas mixture (5) with a lower Wobbe index than the first gas mixture (1), comprising the steps of

- (i) providing the first gas mixture (1),

- (ii) providing a second gas mixture (2) comprising hydrocarbons,
 (iii) providing a third gas mixture (3) comprising oxygen,
 (iv) carrying the second (2) and the third gas mixture (3) into a chemical reactor (10) configured to produce a fourth gas mixture (4) comprising carbon dioxide gas, and
 (v) carrying the fourth gas mixture (4) into the first gas mixture (1), thus obtaining the product gas mixture (5).
2. Method as claimed in claim 1, wherein the second gas mixture is the first part of a first gas mixture (1) separated into a first (1') and a second part (1''), and wherein step (v) comprises of carrying the fourth gas mixture (4) into the separated second part (1'') of the first gas mixture (1).
3. Method as claimed in any of the claims 1-2, wherein the third gas mixture (3) comprising oxygen to be provided as according to step (iii) is air.
4. Apparatus (20, 30, 40, 50, 60, 70) for converting a first gas mixture (1), comprising hydrocarbons and carried through a transport conduit, to a product gas mixture (5) with a lower Wobbe index than the first gas mixture (1), comprising a chemical reactor (10) with a first inlet for admitting a second gas mixture (2) comprising hydrocarbons and a second inlet for admitting a third gas mixture (3) comprising oxygen, which reactor (10) is configured to produce a fourth gas mixture (4) comprising carbon dioxide gas, and with an outlet conduit for carrying the fourth gas mixture (4) into the first gas mixture (1), thus obtaining the product gas mixture (5).
5. Apparatus (30, 40, 50, 60, 70) as claimed in claim 4, **characterized in that** the first inlet of the reactor (10) is coupled to a first branch of the transport conduit for the purpose of admitting a first part (1') of the first gas mixture (1), and the outlet conduit of the reactor (10) is coupled downstream of the first branch to a second branch of the transport conduit.
6. Apparatus as claimed in any of the claims 4-5, **characterized in that** the chemical reactor (10) comprises a gas motor.
7. Apparatus as claimed in any of the claims 4-5, **characterized in that** the chemical reactor (10) comprises a gas turbine.
8. Apparatus (40, 50, 60, 70) as claimed in any of the claims 4-5, **characterized in that** the chemical reactor (10) comprises a fuel cell.
9. Apparatus as claimed in claim 8, **characterized in that** the fuel cell is provided with a reformer (14) for converting a first gas mixture (1, 1') comprising hydrocarbons to a gas mixture (8) comprising hydrogen and carbon monoxide.
10. Apparatus (50) as claimed in claim 9, wherein the reformer (14) is an autothermal reformer, and the third gas mixture (3) comprising oxygen to be admitted into the second inlet also comprises nitrogen, **characterized in that** a conduit is provided for feedback of cathode tailgas (9) from the fuel cell to the autothermal reformer.
11. Apparatus (70) as claimed in any of the claims 8-10, **characterized in that** the fuel cell is a solid polymer fuel cell (PEM FC).
12. Apparatus as claimed in any of the claims 8-10, **characterized in that** the fuel cell is a solid oxide fuel cell (SOFC).
13. Apparatus (40, 50, 60, 70) as claimed in any of the claims 4-12, **characterized in that** it is provided with a drying unit (15) for drying the fourth gas mixture (4) comprising carbon dioxide gas.
14. Apparatus (60) as claimed in claim 13, **characterized in that** the drying unit (15) comprises a gas refining unit on the basis of Pressure Swing Adsorption (PSA) technology for the purpose of further cleaning of the fourth gas mixture (4) comprising carbon dioxide gas.
15. Apparatus (60) as claimed in any of the claims 4-13, **characterized in that** it is provided with a measuring and control unit (17) for determining the quantity of the fourth gas mixture (4) to be produced comprising carbon dioxide gas.

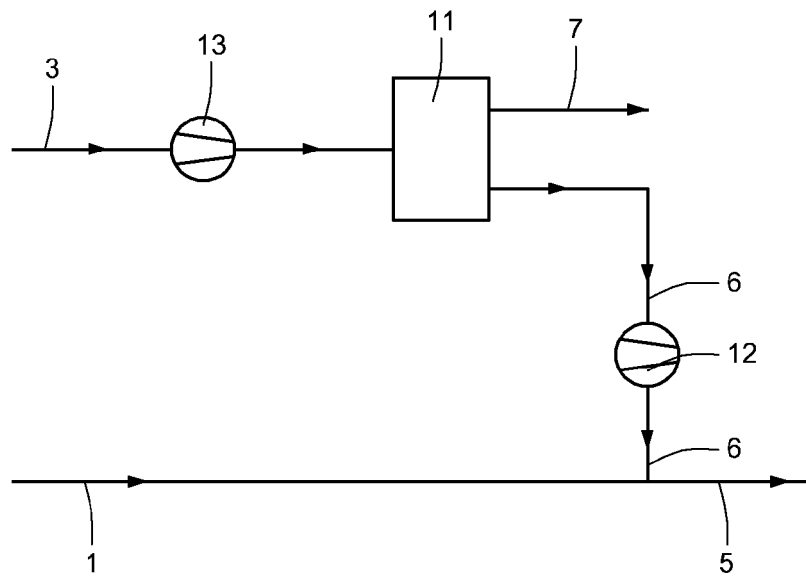


Fig. 1

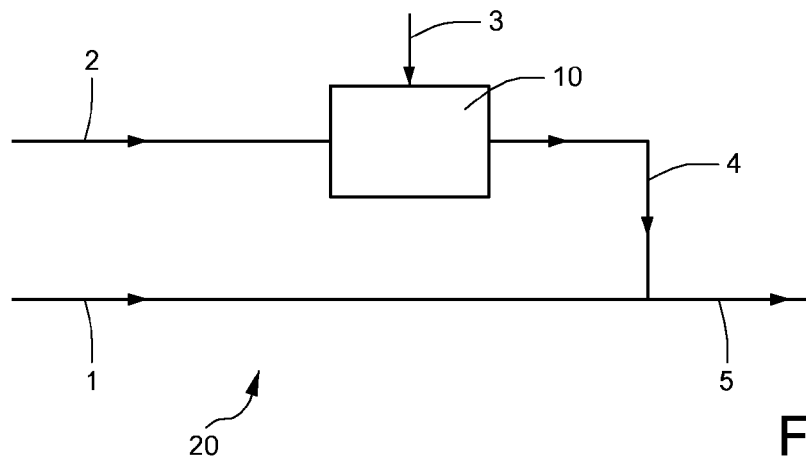


Fig. 2

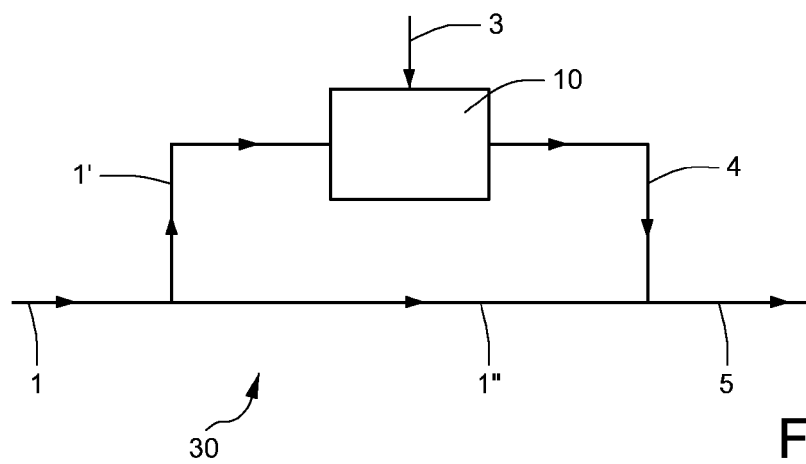


Fig. 3

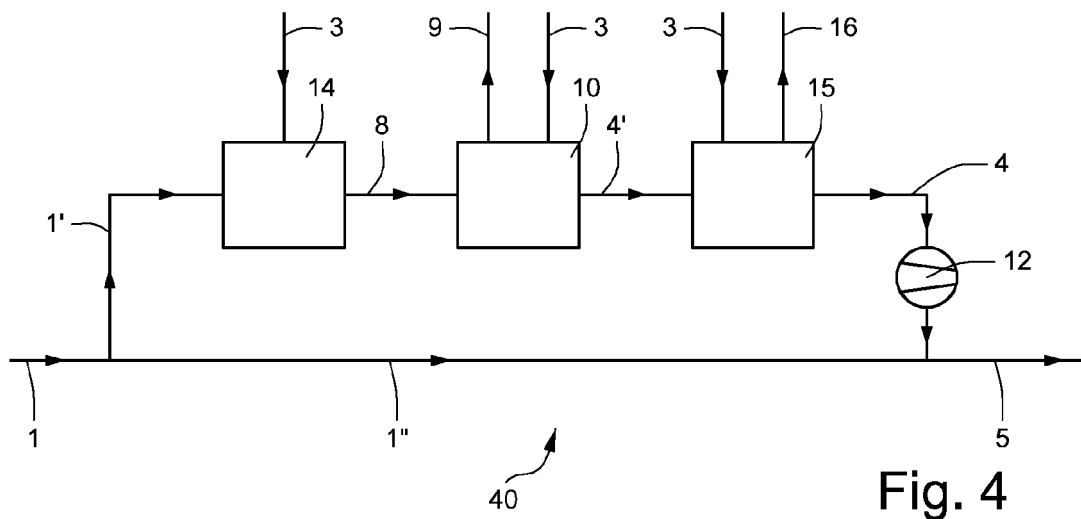


Fig. 4

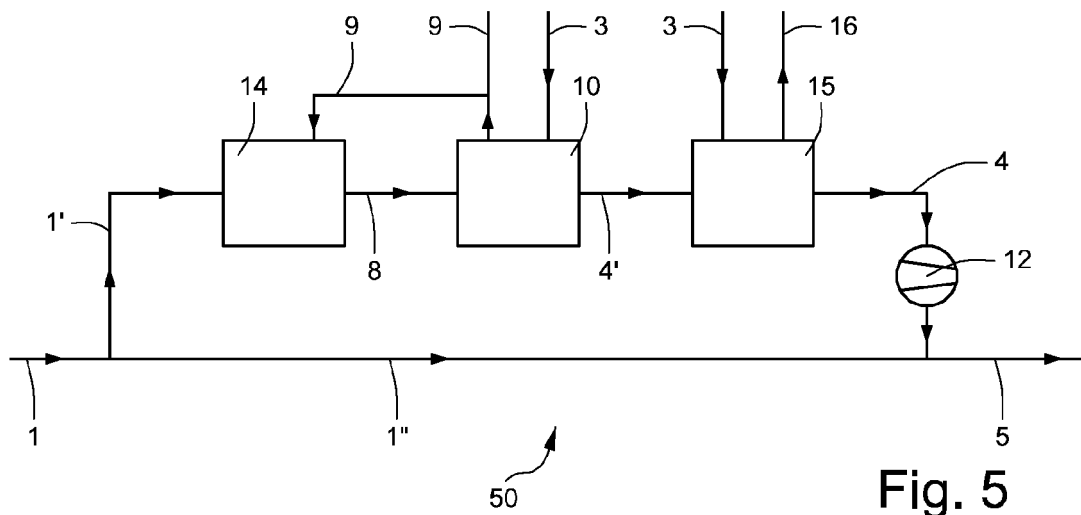


Fig. 5

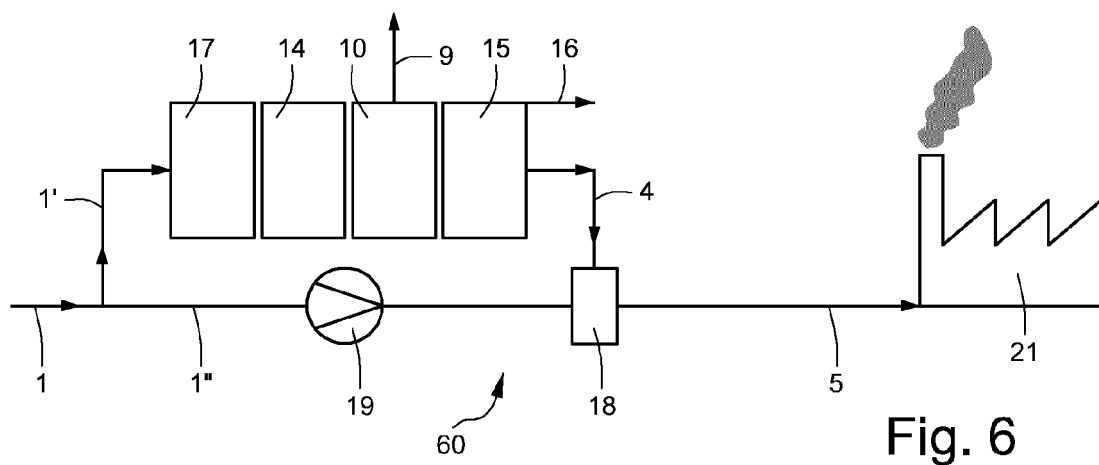


Fig. 6

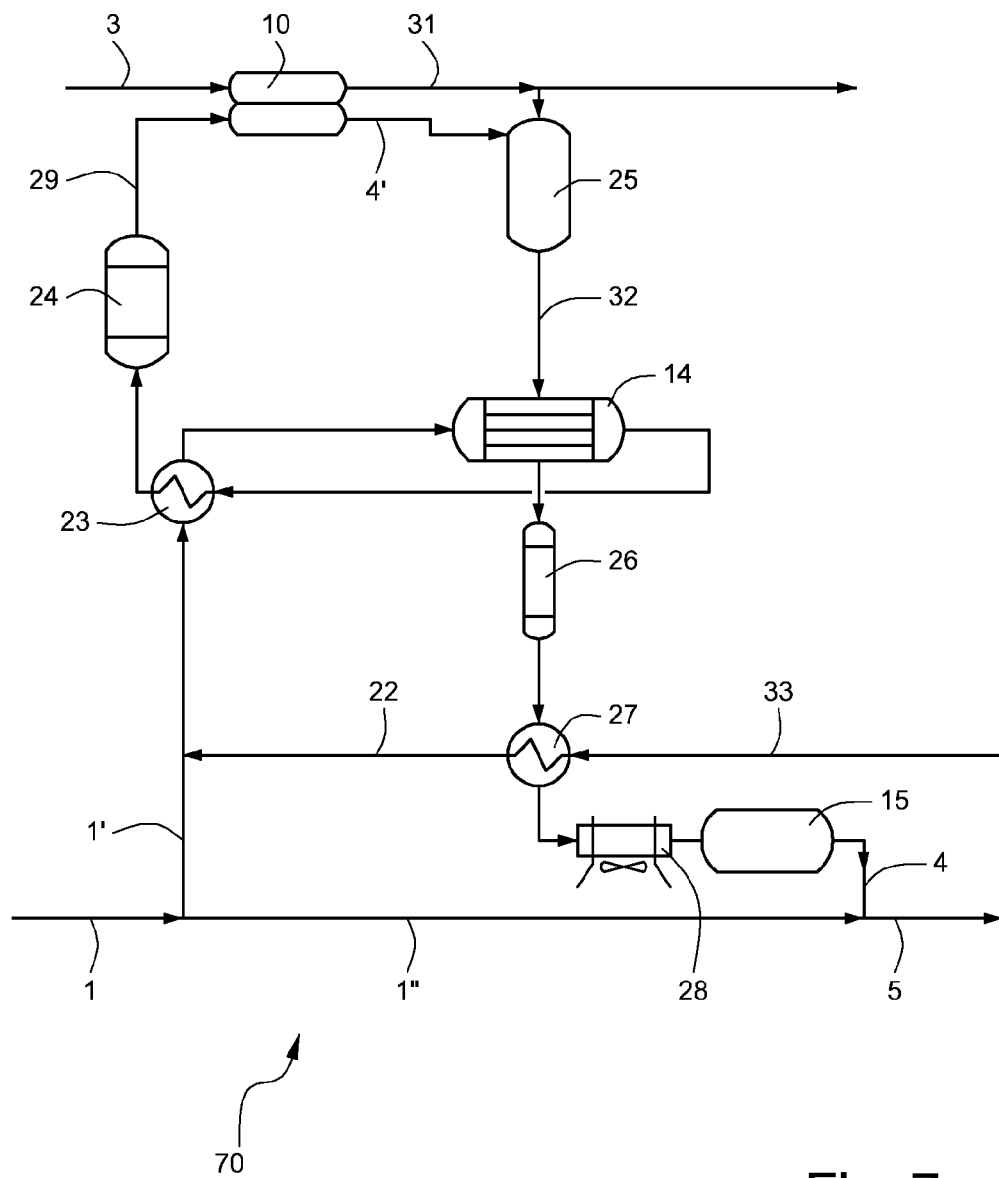


Fig. 7



EUROPEAN SEARCH REPORT

Application Number
EP 13 18 5369

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DE 21 12 447 A1 (BORSIG GMBH) 21 September 1972 (1972-09-21) * the whole document *	1-5, 13-15 6-12	INV. C10L3/10 C10L3/00
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			TECHNICAL FIELDS SEARCHED (IPC)
			C10L C10K
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 29 November 2013	Examiner Keipert, Olaf
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
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**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 13 18 5369

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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29-11-2013

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