



(12) **EUROPEAN PATENT APPLICATION**  
published in accordance with Art. 153(4) EPC

(43) Date of publication:  
**09.01.2019 Bulletin 2019/02**

(51) Int Cl.:  
**C10L 3/08 (2006.01)**

(21) Application number: **17760064.0**

(86) International application number:  
**PCT/JP2017/008079**

(22) Date of filing: **01.03.2017**

(87) International publication number:  
**WO 2017/150600 (08.09.2017 Gazette 2017/36)**

(84) Designated Contracting States:  
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**  
Designated Extension States:  
**BA ME**  
Designated Validation States:  
**MA MD**

(72) Inventors:  
• **SHIMIZU, Tsubasa**  
**Osaka-shi**  
**Osaka 541-0046 (JP)**  
• **YOKOYAMA, Kota**  
**Osaka-shi**  
**Osaka 541-0046 (JP)**

(30) Priority: **01.03.2016 JP 2016039205**

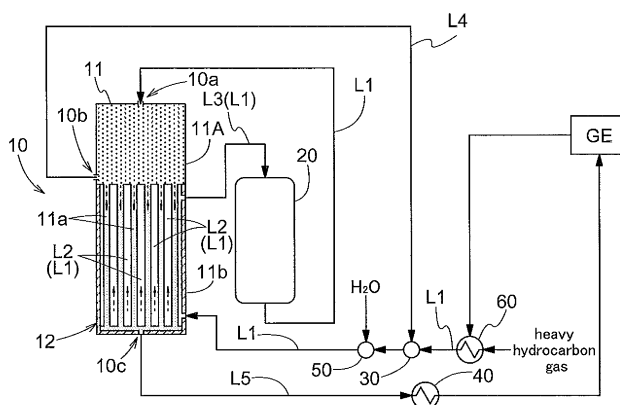
(74) Representative: **Lemcke, Brommer & Partner**  
**Patentanwälte Partnerschaft mbB**  
**Siegfried-Kühn-Straße 4**  
**76135 Karlsruhe (DE)**

(71) Applicant: **Osaka Gas Co., Ltd.**  
**Osaka-shi, Osaka 541-0046 (JP)**

(54) **FUEL GAS SUPPLY APPARATUS AND FUEL GAS SUPPLY METHOD**

(57) In order to provide a technique for supplying fuel gas obtained by reforming heavy hydrocarbon gas and containing methane gas at a high concentration, there are provided a reforming device 10 including a gas generating section 11 configured to effect a decomposing reaction in which the heavy hydrocarbon gas desulfurized by a desulfurizing device 20 is decomposed into methane through steam reforming thereof to generate methane-containing mixture gas and a resynthesizing section 12 for resynthesizing methane from carbon monoxide and hydrogen contained in the mixture gas by a catalyst. There are also provided a heavy hydrocarbon gas supplying passage L1 for supplying heavy hydrocarbon gas to the reforming device 10 via the desulfurizing device 20, a heat exchanging section for effecting, within the resynthesizing section 12, heat exchange between the mixture gas supplied from the gas generating section 11 and the heavy hydrocarbon gas before its desulfurization by the desulfurizing device 20 which flows in the heavy hydrocarbon gas supplying passage L1, a recycling passage L4 for recycling a portion of the mixture gas generated in the gas generating section 11 to the heavy hydrocarbon gas supplying passage L1, and a fuel gas supplying passage L5 for supplying the fuel gas discharged from the resynthesizing section 12 to a combustion device (gas engine GE).

Fig.1



**Description****Technical Field:**

**[0001]** This disclosure relates to an apparatus and a method for supplying fuel gas to a combustion device such as a gas engine, a gas turbine, etc., the fuel gas being obtained by reforming heavy hydrocarbon gas and containing methane as a principal component thereof.

**Related Art**

**[0002]** Conventionally, there is known a fuel gas supplying apparatus configured to obtain fuel gas containing methane as principal component thereof by reforming heavy hydrocarbon gas such as propane, butane, etc. with a reforming catalyst and to supply the obtained fuel gas to a combustion device. With such fuel gas supplying apparatus, mixture gas of heavy hydrocarbon gas and steam is supplied via a heavy hydrocarbon gas supplying passage to a reforming device, in which the supplied mixture gas is reformed by the reforming catalyst charged in the reforming device and the resultant fuel gas containing methane as principal component is supplied to the combustion device (see Patent Document 1 for example).

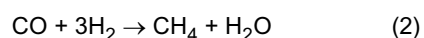
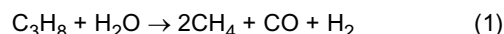
**Related Art Document****Patent Document**

**[0003]** Patent Document 1: detailed disclosure of U.S.P. No. 7866161

**Summary****Problem to be Solved by Invention**

**[0004]** Here, the produced fuel gas contains methane as its principal component. However, since the reforming reaction per se is an equilibrium reaction, it is inevitable for a certain amount of heavy hydrocarbon gas to be mixed into the fuel gas. However, since mixed presence of heavy hydrocarbon gas in the fuel gas tends to invite gas engine knocking phenomenon, it is desirable to minimize the mixing amount of heavy hydrocarbon gas. Minimization of mixing amount is desirable also for other components such as hydrogen, carbon monoxide which may be present in the produced gas, for the sake of stabilizing the caloric value of the produced fuel gas. Moreover, for a constant combustion device such as a gas turbine, variation in its fuel composition can lead to lift and reverse fire. Therefore, minimization of mixing amount of heavy hydrocarbon gas is again desirable. For this reason, Patent Document 1 proposes preheating heavy hydrocarbon gas fed to the reforming device with heat contained in the produced fuel gas, thereby to suppress generation of hydrogen or carbon monoxide due to cracking, while enhancing methanation efficiency at the same time.

reforming reaction:



**[0005]** In the above reaction part (2), the equilibrium reaction proceeds to the right side at a temperature lower than the reaction part (1). Thus, with the conventional reforming device, hydrogen content can be lowered by managing to a predetermined equilibrium temperature which will produce less hydrogen and less carbon monoxide and more methane. With this measure, however, the decomposing reaction of heavy hydrocarbon gas in the reaction part (1) is also suppressed. Therefore, there is a limit in the degree of improvement in the methanation efficiency possible through such temperature management. Thus, there remains a need for a technique that can supply fuel gas with high methane concentration in a more stable manner.

**[0006]** Further, the heavy hydrocarbon gas as feedstock gas often contains impurities such as sulfur, etc. If the reforming catalyst becomes poisoned with such impurities, this may result in reduction in the reforming reaction efficiency, shortening of its service life. Therefore, there is a need for a technique for supplying high methane content fuel gas, with possibility of removal of impurities.

**[0007]** Therefore, the present invention aims at providing a technique that can supply a fuel gas with high methane content, by reforming heavy hydrocarbon gas.

**Solution**

**[0008]** For accomplishing the above-noted object, according to characterizing feature of the present invention, there is provided a fuel gas supplying apparatus for supplying fuel gas to a combustion device, the fuel gas being obtained by reforming heavy hydrocarbon gas and containing methane as its principal component, the apparatus comprising:

a desulfurizing device for desulfurizing the heavy hydrocarbon gas;  
 a reforming device including a gas generating section configured to effect a decomposing reaction in which the heavy hydrocarbon gas desulfurized by the desulfurizing device is decomposed into methane through steam reforming thereof with a reforming catalyst, thereby to generate methane-containing mixture gas, and a resynthesizing section for resynthesizing methane from carbon monoxide and hydrogen contained in the mixture gas by a catalyst;  
 a heavy hydrocarbon gas supplying passage for supplying heavy hydrocarbon gas to the reforming device via the desulfurizing device;  
 a heat exchanging section for effecting, within the resynthesizing section, heat exchange between the mixture gas supplied from the gas generating section and the heavy hydrocarbon gas before its desulfurization by the desulfurizing device which flows in the heavy hydrocarbon gas supplying passage;  
 a recycling passage for recycling a portion of the mixture gas generated in the gas generating section to the heavy hydrocarbon gas supplying passage; and  
 a fuel gas supplying passage for supplying the fuel gas discharged from the resynthesizing section to the combustion device (e.g. a gas engine) .

**[0009]** Incidentally, the heavy hydrocarbon gas for use in the present disclosure refers to a gaseous hydrocarbon having a larger molecular weight than methane and including ethane, propane, butane, isobutene. Further, the term "principal component" as used herein means a component having a higher content among main effective components and it need not be contained by 50% or more, or it need not be a component having the highest content, either. However, as the principal component, a content exceeding 50% is more preferred. And, in case its content does not exceed 50%, it is preferably the component having the highest content.

**[0010]** With the above-described arrangement, since a desulfurizing device is provided and the reforming device includes a gas generating section and a resynthesizing section, the reaction at the gas generating section in which heavy hydrocarbon gas as the feedstock gas is desulfurized and then decomposed can be positively promoted and at the resynthesizing section, methane can be resynthesized from carbon monoxide and hydrogen contained in the mixture gas produced based on the decomposing reaction.

**[0011]** Specifically, at the gas generating section, of the reforming reaction described above, the reaction of decomposing heavy hydrocarbon gas is positively promoted, whereby the concentration of heavy hydrocarbon gas present in the produced gas can be significantly reduced. In this, since the produced gas has reached a high temperature due to the reaction heat, the concentrations of hydrogen and carbon monoxide contained in the produced gas are rather high. Then, since hydrogen and carbon monoxide produced here are used in the reaction of methane resynthesis at the resynthesizing section, these concentrations of hydrogen and carbon monoxide contained in the mixture gas are lowered, which in turn increases the concentration of methane gas. As a result, a fuel gas having a high methane concentration can be obtained.

**[0012]** Namely, at the gas generating section, the decomposing reaction is effected more positively, thus decomposing heavy hydrocarbon more completely, so that the decomposing reaction of heavy hydrocarbon (reforming reaction part (1) described above) is promoted, and hydrogen and carbon monoxide produced are resynthesized (reforming reaction part (2) described above) for obtaining more methane at the resynthesizing section. Thus, the respective reaction conditions can be optimized easily, so that methane concentration can be enhanced in a more efficient manner.

**[0013]** Here, preferably, the heavy hydrocarbon gas supplied to the reforming device is preheated. This is because the subsequent reaction is to take place at a high temperature. Further, the reaction at the gas generating section is effected at a higher temperature than the reaction at the resynthesizing section. Thus, a desulfurizing device is provided for desulfurizing heavy hydrocarbon gas to be supplied to the gas generating section; and by providing a heavy hydrocarbon gas supplying passage for supplying heavy hydrocarbon desulfurized by the desulfurizing device to the reforming device and a heat exchanging section for effecting heat exchange between the mixture gas flowing at the resynthesizing section and the heavy hydrocarbon gas supplied from the heavy hydrocarbon gas supplying passage, the heavy hydrocarbon gas supplied to the reforming device before being desulfurized by the desulfurizing device is preheated by the heat of the resynthesizing section, so that the mixture gas at the resynthesizing section can be adjusted to a temperature suitable for resynthesis through discharge of its heat to the heavy hydrocarbon gas. As a result, the temperature conditions for allowing the reforming reaction to proceed in a more efficient manner can be realized easily.

**[0014]** Moreover, the mixture gas to be supplied to the resynthesizing section after the decomposing reaction at the gas generating section has a high hydrogen concentration. On the other hand, the sulfur component contained in the

heavy hydrocarbon gas is removed by the desulfurizing device. In this, by providing a recycling passage for recycling a portion of the mixture gas generated in the gas generating section to the heavy hydrocarbon gas supplying passage, the mixture gas generated at the gas generating section can be supplied into the heavy hydrocarbon gas to be supplied to the desulfurizing device. With this arrangement, hydrogen gas needed at the desulfurizing device for reducing removal of sulfur component can be supplied from the reforming device, without need to obtain it from the outside. Thus, in spite of provision of the desulfurizing device, there can be provided a simple arrangement that supplies hydrogen gas from the reforming device via the recycling passage. Moreover, thanks to the provision of the desulfurizing device, a reforming catalysis if any employed that can be easily poisoned by the decomposing reaction and/or the reforming reaction effected by the reforming device can be used for a long period of time with maintaining high activity.

**[0015]** Incidentally, the fuel gas obtained by the resynthesizing section is under a state where optimal reforming reaction has been completed upon completion of the heat exchange. Thus, in comparison with the conventional arrangement (the exemplary arrangement in Patent Document 1) in which heat exchange between fuel gas and heavy hydrocarbon gas is effected after reforming reaction, at the time of resynthesizing mixture gas to obtain product gas, the excess heat can be provided efficiently for the preheating of the heavy hydrocarbon gas.

**[0016]** The fuel gas thus obtained contains methane gas at a high concentration and will be supplied to a combustion device via a fuel gas supplying passage.

**[0017]** The above-described arrangement can be realized more specifically as follows.

**[0018]** Namely:

the reforming device includes the gas generating section at an upper section thereof and the resynthesizing section at a lower section thereof integrally;

the gas generating section includes an adiabatic reaction vessel configured to receive the heavy hydrocarbon gas desulfurized by the desulfurizing device and to effect a reforming reaction thereon by a reforming catalyst;

the resynthesizing section includes a tubular reacting portion that communicates the inside of the adiabatic reaction vessel to the fuel gas supplying passage and having a catalyst therein and a heat exchanging vessel formed to surround the tubular reacting portion; and

the heat exchanging section is configured to effect heat exchange between mixture gas flowing in the tubular reacting portion and heavy hydrocarbon gas flowing in the heavy hydrocarbon gas supplying passage which is a space formed between the tubular reacting portion and the heat exchanging vessel.

**[0019]** With the above-described arrangement, between the gas generating section and the resynthesizing section in the reforming device, at the adiabatic reaction vessel, there is effected the decomposing reaction for decomposing heavy hydrocarbon gas into methane through steam reforming thereof with a reforming catalyst, and methane is produced through resynthesis at the resynthesizing section on hydrogen and carbon monoxide contained in the mixture gas generated at the gas generating section and also the concentrations of hydrogen and carbon monoxide contained in the fuel gas can be reduced also. In this, the resynthesizing section includes a tubular reacting portion and a heat exchanging vessel and effects heat exchange between mixture gas supplied from the gas generating section and heavy hydrocarbon gas flowing through the heavy hydrocarbon gas supplying passage, prior to being desulfurized by the desulfurizing device. Thus, the reforming reaction conditions such as the component compositions among the supplied heavy hydrocarbon gas, the produced mixture gas and the discharged fuel gas, temperature, pressure, etc. can be easily adapted for higher efficiency and heat balance between the mixture gas and the heavy hydrocarbon gas can be optimized between the tubular reacting portion and the heat exchanging passage in the resynthesizing section and the composition of the mixture gas to be supplied to the recycling passage can be made suitable for the desulfurizing reaction at the desulfurizing device, so that the fuel gas to be supplied to the combustion device can be readily optimized to contain a higher concentration of methane gas in an efficient manner.

**[0020]** Further, an arrangement can be made such that the tubular reacting portion communicates the inside of the adiabatic reaction vessel to the fuel gas supplying passage in a vertical direction and at the heat exchanging section, the mixture gas flowing inside the tubular reacting section flows downwards whereas the heavy hydrocarbon gas flowing inside the heavy hydrocarbon gas supplying passage as the space between the tubular reacting portion and the heat exchanging vessel flows upwards, thus effecting the heat exchange in counter-flow manner.

**[0021]** With the above-described arrangement, as the heat exchange takes place between the mixture gas flowing inside the tubular reacting portion and the heavy hydrocarbon gas in the counter-flow manner, efficiency of the heat exchange can be improved.

**[0022]** Further, the recycling passage can be configured such that one side portion thereof is connected to a lower end portion of the gas generating section and the other end side thereof is connected to an upstream side of the reforming device in the heavy hydrocarbon gas supplying passage.

**[0023]** With the above-described arrangement, mixture gas generated at the gas generating section is recycled to the upstream side of the reforming device. Thus, with ensuring sufficient mixing between the mixture gas and the heavy

hydrocarbon gas, the mixture gas and the heavy hydrocarbon gas can be supplied to the reforming device.

**[0024]** Moreover, there can be provided a preheating section for preheating, in the heavy hydrocarbon gas supplying passage, the heavy hydrocarbon gas to be supplied to the reforming device with exhaust gas from the combustion device.

**[0025]** In the combustion device, power is obtained from the resultant fuel gas and also exhaust heat is generated therefrom. With provision of such preheating section, with effective utilization of this exhaust heat, the heavy hydrocarbon gas before being supplied to the reforming device is preheated, so that the reforming reaction can proceed in an more reaction efficient manner. As a whole, there can be configured a fuel gas supplying apparatus capable of supplying fuel gas with further enhanced heat efficiency.

**[0026]** For accomplishing the above-noted object, according to the characterizing feature of the present invention, there is provided a fuel gas supplying method as follows.

**[0027]** A fuel gas supplying method for supplying a combustion device with fuel gas obtained by reforming heavy hydrocarbon gas and containing methane as a principal component thereof;

wherein in the above-described fuel gas supplying apparatus, heavy hydrocarbon gas having an S/C (steam/carbon ratio) value of 0.4 or higher and 1.0 or lower and having a temperature of 300°C or higher and 450°C or lower is supplied to the gas generating section, so that at the gas generating section, a mixture gas having a temperature higher than 450°C and 520°C or lower is obtained, and at the resynthesizing section, a fuel gas having a temperature of 250°C or higher and 300°C or lower is obtained.

**[0028]** At the gas generating section, the reforming reaction part (1) proceeds with an S/C value of 0.4 to 1.0 and a temperature of from 300°C to 450°C and heat is generated. The mixture gas obtained thereby has a temperature exceeding 450 °C and 520 °C or lower and contains hydrogen by 10%. Incidentally, as to the S/C value, if this value is too low, carbon precipitation tends to occur due to thermal decomposition of feedstock gas. So, its value is 0.7 or higher preferably. Conversely, if it is too high, this will lead to reduction in the methane concentration in the reformed gas, which in turn may give adverse effect on engine combustion. Thus, its value is 1.0 or lower preferably. More preferably, its value ranges from 0.8 to 0.9. Therefore, the mixture gas obtained here can be used as desulfurized gas for sulfuric component reduction by the desulfurizing device, so that the desulfurizing reaction can proceed in an efficient manner. Further, the obtained mixture gas can be used in the reaction of the reforming reaction part (2) at the resynthesizing section. At the resynthesizing section, hydrogen contained in the mixture gas is reacted with carbon monoxide or carbon dioxide to resynthesize methane, so that it can be converted into a quality fuel gas having a high methane concentration and a low hydrogen concentration.

## Effects of Invention

**[0029]** Therefore, it has become possible to reform heavy hydrocarbon gas and to supply fuel gas having methane gas at a high concentration.

## Brief Description of Drawings

**[0030]**

[Fig. 1] is a flow diagram of a fuel gas supplying apparatus, and

[Fig. 2] is a flow diagram of a fuel gas supplying apparatus to be described in a further embodiment.

## Embodiments

**[0031]** Next, fuel gas supplying apparatuses relating to embodiments of the present invention will be explained. Incidentally, it is understood that preferred embodiments will be described next, but these respective embodiments are disclosed only for the sake of specific illustration of the present invention, so various modifications are possible within a range not departing from the essence of the present invention, so the present invention is not limited by the following description.

[Fuel Gas Supplying Apparatus]

**[0032]** A fuel gas supplying apparatus, as shown in Fig. 1, includes, in order to supply a gas engine GE as an example of "combustion device", with fuel gas obtained by reforming heavy hydrocarbon gas and containing methane as its principal component, a reforming device 10 including a gas generating section 11 for effecting a decomposing reaction of the heavy hydrocarbon gas to generate mixture gas containing methane and a resynthesizing section 12 for resynthesizing methane from carbon monoxide and hydrogen contained in the mixture gas generated based on the decomposing reaction. The apparatus further includes a desulfurizing device 20 for desulfurizing the heavy hydrocarbon gas

supplied to the gas generating section 11 of the reforming device 10.

**[0033]** Further, in this fuel gas supplying apparatus, there are provided a heavy hydrocarbon gas supplying passage L1 for supplying heavy hydrocarbon gas to the reforming device 10 via the desulfurizing device 20, a heat exchanging section for effecting heat exchange between the mixture gas supplied from the gas generating section 11 and the heavy hydrocarbon gas supplied from the gas generating section 11 and flowing through the heavy hydrocarbon gas supplying passage L1 before being desulfurized by the desulfurizing device 20, a recycling passage L4 for recycling a portion of the mixture gas generated at the gas generating section 11 to the heavy hydrocarbon gas supplying passage L1, and a fuel gas supplying passage L5 for supplying fuel gas discharged from the resynthesizing section 12 to the gas engine GE. Incidentally, in the fuel gas supplying passage L5, there is incorporated a cooling section 40 for cooling the fuel gas discharged from the resynthesizing section 12 and removing resultant condensate water.

[Reforming Device]

**[0034]** The reforming device 10 includes the gas generating section 11 at an upper section thereof and the resynthesizing section 12 at a lower section thereof integrally.

**[0035]** The gas generating section 11 includes an adiabatic reaction vessel 11A configured to receive the heavy hydrocarbon gas desulfurized by the desulfurizing device 20 and to effect a reforming reaction thereon by a reforming catalyst. Namely, inside the adiabatic reaction vessel 11A, there is charged the reforming catalyst and with management to a predetermined temperature and pressure and through a reforming reaction by liquefied petroleum gas (may be referred to as LPG containing propane as its principal component) as the "heavy hydrocarbon gas" and steam, a mixture gas containing methane as its principal component can be generated.

**[0036]** To an upstream end portion 10a (upper portion) of the adiabatic reaction vessel 11A of the gas generating section 11, the heavy hydrocarbon gas supplying passage L1 is connected and steam is supplied. And, the heavy hydrocarbon gas desulfurized by the desulfurizing device 20 is supplied via the heavy hydrocarbon gas supplying passage L1 from the upstream end portion 10a (upper portion) of the adiabatic reaction vessel 11A into this adiabatic reaction vessel 11A.

**[0037]** As the reforming catalyst, a nickel-based or noble-metal based low-temperature steam reforming catalyst can be employed for example. Specifically, a non-conductive porous body having fine pores with coating of its surface with membrane of one kind of metal selected from the group consisting of palladium, silver, nickel, cobalt and copper can be used advantageously.

**[0038]** Further, to the vicinity of a downstream end portion 10b of the gas generating section 11, there is connected the recycling passage L4 configured to take, from a lateral portion thereof, a portion of the mixture gas generated at the gas generating section 11 and then to guide it to a mixture gas adding portion 30 provided in the heavy hydrocarbon gas supplying passage L1. Namely, the recycling passage L4 has its one end side connected to the downstream end portion 10b (lower end portion) of the gas generating section 11 and has its other end side connected to the upstream side (between a steam supplying section 50 and a preheating section 60 to be described later) of the reforming device 10 in the heavy hydrocarbon gas supplying passage L1.

**[0039]** The mixture gas obtained at the gas generating section 11 is guided to the resynthesizing section 12 formed at the lower section of the gas generating section 11 in the reforming device 10.

**[0040]** The resynthesizing section 12 includes many tubular reacting portions 11a that communicate the inside of the adiabatic reaction vessel 11A to the fuel gas supplying passage L5 in a vertical direction and having therein a catalyst charging portion and a heat exchanging vessel 11b formed to surround the tubular reacting portions 11a. Therefore, the mixture gas generated at the gas generating section 11 will flow, from the inside of the adiabatic reaction vessel 11A, downwards inside the many tubular reacting portions 11a and will then be combined together at the lower end portion of the heat exchanging vessel 11b and then discharged into the fuel gas supplying passage L5 via a most downstream end portion 10c formed at the lower end of this heat exchanging vessel 11b.

**[0041]** Also, inside the resynthesizing section 12, between the respective tubular reacting portions 11a and the heat exchanging vessel 11b, a space is formed. Further, spaces are formed also between adjacent tubular reacting portions 11a. These spaces are arranged to communicate with each other inside the heat exchanging vessel 11b. Namely, these spaces, inside the resynthesizing section 12, are formed in a region from the approximate lower end portion to the upper end portion inside the heat exchanging vessel 11b, surrounding the circumference of each tubular reacting portion 11a. Incidentally, these spaces are arranged not to communicate with the inside of the adiabatic reaction vessel 11A.

**[0042]** And, the heat exchanging vessel 11b is configured such that heavy hydrocarbon gas (containing steam) which flows in the heavy hydrocarbon gas supplying passage L1 and before being desulfurized by the desulfurizing device 20 is received laterally and at the lower end portion of the heat exchanging vessel 11b and is caused to flow upwards from the lower end portion to the upper end portion of the space and subsequently discharged laterally and via the upper end portion of the heat exchanging vessel 11b into the heavy hydrocarbon gas supplying passage L1 to be eventually supplied to the desulfurizing device 20.

**[0043]** With the above, it can be configured such that heat exchange can be effected between the mixture gas having a relatively high temperature and flowing downwards in the tubular reacting portions 11a and the heavy hydrocarbon gas having a relatively low temperature and flowing upwards in the above-described space, in a counter-flow arrangement with each other. Namely, the above-described spaces function as heat exchanging passage L2. Incidentally, when the function of the heavy hydrocarbon gas supplying passage L1 for supplying heavy hydrocarbon gas to the reforming device 10 is considered, it is understood that the heat exchanging passage L2 functions as a part of this heavy hydrocarbon gas supplying passage L1.

**[0044]** Therefore, the heat exchanging section is configured to effect heat exchange between mixture gas flowing in the tubular reacting portion 11a and heavy hydrocarbon gas flowing through the heavy hydrocarbon gas supplying passage L1 which is the space between the tubular reacting portion 11a and the heat exchanging vessel 11b. That is, the heat exchanging vessel 11b functions as the "heat exchanging section".

**[0045]** Incidentally, in the catalyst charging portion of the resynthesizing section 12, there is charged low-temperature steam reforming catalyst based on nickel or noble metal. Specifically, for example, a reforming catalyst comprising a non-conductive porous body having fine pores with coating of its surface with membrane of one kind of metal selected from the group consisting of palladium, silver, nickel, cobalt and copper is charged.

**[0046]** On the other hand, on the upstream side of the reforming device 10 in the heavy hydrocarbon gas supplying passage L1, in the order from the upstream side thereof, there are disposed the preheating portion 60 for preheating heavy hydrocarbon gas with high-temperature exhaust gas from the gas engine GE, the mixture gas adding portion 30 for adding the mixture gas recycled via the recycling passage L4 as recycled gas, and the steam supplying section 50 for mixing steam further in the heavy hydrocarbon gas mixed with the recycled gas recycled via the recycling passage L4.

[Desulfurizing Device]

**[0047]** The heavy hydrocarbon gas containing steam discharged from the upper end side of the heat exchanging passage L2 inside the resynthesizing section 12 of the reforming device 10 is caused to flow to the desulfurizing device 20. Incidentally, the portion of the heavy hydrocarbon gas supplying passage L1 from the discharging from the heat exchanging passage L2 to the introduction to the desulfurizing device 20 may sometimes be referred to as a "desulfurizing passage L3" herein. The desulfurizing device 20 is comprised of a desulfurizing reaction vessel with a desulfurizing catalyst charged therein and the desulfurizing passage L3 is connected to the upper portion of the desulfurizing device 20. As a desulfurizing catalyst, there can be advantageously employed one capable of reducing mercaptans compound to hydrogen sulfide and adsorptively removing it, such as a combination of nickel-molybdenum based, cobalt-molybdenum based catalyst and zinc oxide. The steam-containing heavy hydrocarbon gas past the desulfurizing device 20 is introduced to the gas generating section 11 via the heavy hydrocarbon gas supplying passage L1.

**[0048]** With the above-described arrangement in operation, in the heavy hydrocarbon gas supplying passage L1, the heavy hydrocarbon gas is preheated by the preheating section 60 with the high-temperature exhaust gas from the gas engine GE and added with the recycled gas and steam and is caused to flow upwards in the heat exchanging passage L2 inside the resynthesizing section 12 from its lower end side to its upper end side. In this, the heavy hydrocarbon gas flowing in the heat exchanging passage L2 is preheated as receiving heat from the tubular reacting portions 11a and discharged under this state into the desulfurizing passage L3 from the upper portion of the resynthesizing section 12. And, after being desulfurizing by the desulfurizing device 20, the gas will flow into the gas generating section 11 from the most upstream side (upstream end portion 10a) of the gas generating section 11 of the reforming device 10.

**[0049]** With the above, of the above-described reforming reaction at the gas generating section, the reaction of decomposing heavy hydrocarbon gas is positively promoted, whereby the concentration of heavy hydrocarbon gas contained in the produced gas can be lowered largely. In the course of this, the produced gas has reached a high temperature (e.g. exceeding 450°C and 520°C or lower) due to the reaction heat, so that the concentrations of hydrogen and carbon monoxide contained in the produced gas are rather high.

**[0050]** Further, the mixture gas that flows in the gas generating section 11 and whose heavy hydrocarbon gas has been decomposed will flow inside the respective tubular reacting portions 11a of the resynthesizing section 12 downwards from the upper end side toward the lower end side. In the course of this, the mixture gas flowing in the heat exchanging passage L2 gives heat to the heavy hydrocarbon gas flowing in this heat exchanging passage L2 and having a relatively low temperature, thus being cooled thereby per se. And, methane resynthesis will proceed with carbon monoxide and hydrogen contained in this mixture gas by the catalyst inside the tubular reacting portions 11a. Thereafter, with progress of the methane resynthesis, the mixture gas becomes fuel gas, which is discharged from the resynthesizing section 12 into the fuel gas supplying passage L5 and then cooled by the cooling section 40 and eventually supplied to the gas engine GE.

**[0051]** With the above-described arrangement, since hydrogen and carbon monoxide generated in the gas generating section 11 are used in the reaction effected at the resynthesizing section 12 for resynthesis of methane, the concentrations of hydrogen and carbon monoxide contained in the mixture gas are lowered and the methane concentration is increased

at the same time. As a result, a fuel gas having a high methane concentration can be obtained.

**[0052]** Namely, at the gas generating section 11, the decomposing reaction is effected positively for decomposing heavy hydrocarbon more completely, so that the decomposing reaction of heavy hydrocarbon (the reforming reaction part (1) described above) is promoted and hydrogen and carbon monoxide produced are resynthesized (the reforming reaction part (2) described above) to obtain more methane at the resynthesizing section 12. Consequently, the respective reaction conditions can be readily optimized, so that the methane concentration can be increased in a more efficient manner.

**[0053]** Accordingly, the reforming reaction conditions such as the component composition among the supplied heavy hydrocarbon gas, the produced mixture gas and the discharged fuel gas, temperature, pressure, etc. can be readily optimized, whereby heat balance between the mixture gas and the heavy hydrocarbon gas can be made efficient between the tubular reacting portions 11a and the heat exchanging passage L2 at the resynthesizing section 12 and the composition of the mixture gas supplied to the recycling passage L4 can be made suitable for the desulfurizing reaction at the desulfurizing device 20, so optimization can be readily made for causing the fuel gas to be supplied to the combustion device to have a high concentration methane gas in a more efficient manner.

#### [Method of Supplying Fuel Gas]

**[0054]** In the fuel gas supplying apparatus having the above-described configuration, heavy hydrocarbon gas having an S/C (steam/carbon ratio) value of 0.4 or higher and 0.8 or lower and having a temperature of 300°C or higher and 450 °C or lower having passed the heat exchanging passage L2 and the desulfurizing passage L3 is supplied to the gas generating section 11. With this, at the gas generating section 11, the reforming reaction using the reforming catalyst is promoted, so that a mixture gas having a temperature higher than 450°C and 520°C or lower is obtained. This mixture gas contains methane as its principal component with presence of almost no heavy hydrocarbon gas therein and contains also hydrogen by about 10%. A portion of this mixture gas guided to the recycling passage L4 to be used in the desulfurizing reaction therein and the remaining portion of this mixture gas is used at the resynthesizing section 12 at which the resynthesizing reaction proceeds at from 250°C to 300°C, whereby a fuel gas containing methane as its principal component can be obtained.

#### [Example]

**[0055]** Feedstock gas (LPG + H<sub>2</sub>O + H<sub>2</sub>) having a gauge pressure of 0.90 MPaG was supplied at 370°C to the gas generating section 11 of the reforming device 10 described above and composition of mixture gas obtained at the terminal end (lower end) of the gas generating section 11 was studied (composition after removal of condensate water through cooling of recycling gas (parenthesized in the table) was also studied). Further, the recycled gas was supplied to the resynthesizing section 12 and composition of fuel gas obtained at the terminal end of the resynthesizing section 12 was studied.

**[0056]** As a result, the compositions of the respective gases were as shown in Table 1 below.

**[0057]** Incidentally, here, in the reforming device 10, a gas generating section 11 having an inside diameter of about 440 mm and a total length of about 1500 mm was charged with a reforming catalyst prepared by causing a substrate of alumina or the like to carry a nickel or noble metal such as ruthenium catalyst and the feedstock gas was flown at 9.5 Nm<sup>3</sup>/min. Also, the obtained mixture gas was introduced into 140 (one hundred forty) units of tubular reacting portions, each having an inside diameter of about 20 mm and a total length of about 600 mm and the exit of the resynthesizing section 12 was maintained at 278°C by cooling gas (heavy hydrocarbon gas having a relatively low temperature) flown to the heat exchanging passage L2. Under these condition, the reactions were effected.

[Table 1]

	feedstock gas	mixture gas	fuel gas	recycled gas
pressure: MPaG	0.90	0.90	0.90	0.90
temperature: °C	370	452	278 (40)	40



(continued)

		feedstock gas	mixture gas	fuel gas	recycled gas
composition mol%	CO <sub>2</sub>	0.76	12.66	11.45 (17)	17.07
	CO	0.03	0.47	0.01 (0)	0.64
	H <sub>2</sub>	0.55	9.14	0.98 (1)	12.33
	CH <sub>4</sub>	3.07	51.28	55.87 (82)	69.19
	H <sub>2</sub> O	68.21	26.44	31.68 (0)	0.77
	C <sub>2</sub> H <sub>6</sub>	0.27	0.00	0.00 (0)	0.00
	C <sub>3</sub> H <sub>8</sub>	26.83	0.00	0.00 (0)	0.00
	n-C <sub>4</sub> H <sub>10</sub>	0.14	0.00	0.00 (0)	0.00
	i-C <sub>4</sub> H <sub>10</sub>	0.14	0.00	0.00 (0)	0.00
	N <sub>2</sub>	0.00	0.00	0.00 (0)	0.00

**[0058]** From Table 1 above, it was made clear that with the fuel gas supplying apparatus, heavy hydrocarbon gas such as LPG, etc. can be reformed in an efficient manner and quality fuel gas almost free from LPG component or hydrogen can be manufactured easily.

[Further Embodiment]

**[0059]** Respecting the configuration of the resynthesizing section 12, in case e.g. the reaction heat in the resynthesizing reaction is high and there is heat in excess, as shown in Fig. 2, there can be further provided a waste heat recovering type heat exchanging section on the downstream side (lower side) of the resynthesizing section 12, so that the outlet temperature of the mixture gas from the resynthesizing section 12 may be maintained favorable and heat utilization efficiency can be further enhanced. Incidentally, in this case, the heavy hydrocarbon gas supplying passage L1 will be connected to the lateral side of the lower end side of the resynthesizing section 12 and the heat exchanging passage L2 will not be disposed at the waste heat recovering type heat exchanging section.

**[0060]** Further, the amount of steam to be supplied from the steam supplying section 50 will be controlled in accordance with the composition of the heavy hydrocarbon gas supplied to the heavy hydrocarbon gas supplying passage L1, so as to obtain an appropriate S/C ratio value. Specifically, with use of a caloric meter (from Azbil Corp.) which functions under the principle of estimating gas composition based on heat conductivity of gas supplied thereto, there can be provided a controlling section which adjusts the amount of steam to be supplied from the steam supplying section 50 according to its output.

**[0061]** Also, the size and the shape of the fuel gas supplying apparatus are not limited to those illustrated or disclosed with some specific sizes, etc., and the catalyst used is not limited to these disclosed above. Furthermore, the operational conditions of the fuel gas supplying apparatus such as the temperature, pressure, etc., too can be variably set according to the catalyst employed, etc., thus not being limited by the foregoing disclosures.

### Industrial Applicability

**[0062]** The present discloses can be utilized as a fuel gas supplying apparatus to a combustion device mounted on e.g. a ship which is to output various powers.

### Description of Reference Marks/Numerals

**[0063]**

- 10: reforming device
- 11: gas generating section
- 11a: tubular reacting portion
- 11b: heat exchanging vessel
- 11A: adiabatic reaction vessel
- 12: resynthesizing section (heat exchanging section)

20: desulfurizing device  
 60: preheating section  
 GE: gas engine  
 L1: heavy hydrocarbon gas supplying passage  
 5 L2: heat exchanging passage  
 L3: desulfurizing passage  
 L4: recycling passage  
 L5: fuel gas supplying passage

## Claims

1. A fuel gas supplying apparatus for supplying fuel gas to a combustion device, the fuel gas being obtained by reforming heavy hydrocarbon gas and containing methane as its principal component, the apparatus comprising:

a desulfurizing device for desulfurizing the heavy hydrocarbon gas;  
 a reforming device including a gas generating section configured to effect a decomposing reaction in which the heavy hydrocarbon gas desulfurized by the desulfurizing device is decomposed into methane through steam reforming thereof with a reforming catalyst, thereby to generate methane-containing mixture gas, and a resynthesizing section for resynthesizing methane from carbon monoxide and hydrogen contained in the mixture gas by a catalyst;  
 a heavy hydrocarbon gas supplying passage for supplying heavy hydrocarbon gas to the reforming device via the desulfurizing device;  
 a heat exchanging section for effecting, within the resynthesizing section, heat exchange between the mixture gas supplied from the gas generating section and the heavy hydrocarbon gas before its desulfurization by the desulfurizing device which flows in the heavy hydrocarbon gas supplying passage;  
 a recycling passage for recycling a portion of the mixture gas generated in the gas generating section to the heavy hydrocarbon gas supplying passage; and  
 a fuel gas supplying passage for supplying the fuel gas discharged from the resynthesizing section to the combustion device.

2. The fuel gas supplying apparatus of claim 1, wherein:

the reforming device includes the gas generating section at an upper section thereof and the resynthesizing section at a lower section thereof integrally;  
 the gas generating section includes an adiabatic reaction vessel configured to receive the heavy hydrocarbon gas desulfurized by the desulfurizing device and to effect a reforming reaction thereon by a reforming catalyst;  
 the resynthesizing section includes a tubular reacting portion that communicates the inside of the adiabatic reaction vessel to the fuel gas supplying passage and having a catalyst therein and a heat exchanging vessel formed to surround the tubular reacting portion; and  
 the heat exchanging section is configured to effect heat exchange between mixture gas flowing in the tubular reacting portion and heavy hydrocarbon gas flowing in the heavy hydrocarbon gas supplying passage which is a space formed between the tubular reacting portion and the heat exchanging vessel.

3. The fuel gas supplying apparatus of claim 2, wherein the tubular reacting portion communicates the inside of the adiabatic reaction vessel and the fuel gas supplying passage in a vertical direction and at the heat exchanging section, the mixture gas flowing inside the tubular reacting section flows downwards whereas the heavy hydrocarbon gas flowing inside the heavy hydrocarbon gas supplying passage as the space between the tubular reacting portion and the heat exchanging vessel flows upwards, thus effecting the heat exchange in counter-flow manner.

4. The fuel gas supplying apparatus of any one of claims 1-3, wherein the recycling passage is configured such that one side portion thereof is connected to a lower end portion of the gas generating section and the other end side thereof is connected to an upstream side of the reforming device in the heavy hydrocarbon gas supplying passage.

5. The fuel gas supplying apparatus of any one of claims 1-4, further comprising a preheating section for preheating, in the heavy hydrocarbon gas supplying passage, the heavy hydrocarbon gas to be supplied to the reforming device with exhaust gas from the combustion device.

6. A fuel gas supplying method for supplying a combustion device with fuel gas obtained by reforming heavy hydrocarbon gas and containing methane as a principal component thereof;  
wherein in the fuel gas supplying apparatus of any one of claims 1-5, heavy hydrocarbon gas having an S/C (steam/carbon ratio) value of 0.4 or higher and 1.0 or lower and having a temperature of 300°C or higher and 450°C or lower is supplied to the gas generating section, so that at the gas generating section, a mixture gas having a temperature higher than 450 °C and 520 °C or lower is obtained, and at the resynthesizing section, a fuel gas having a temperature of 250°C or higher and 300°C or lower is obtained.

5

10

15

20

25

30

35

40

45

50

55

Fig.1

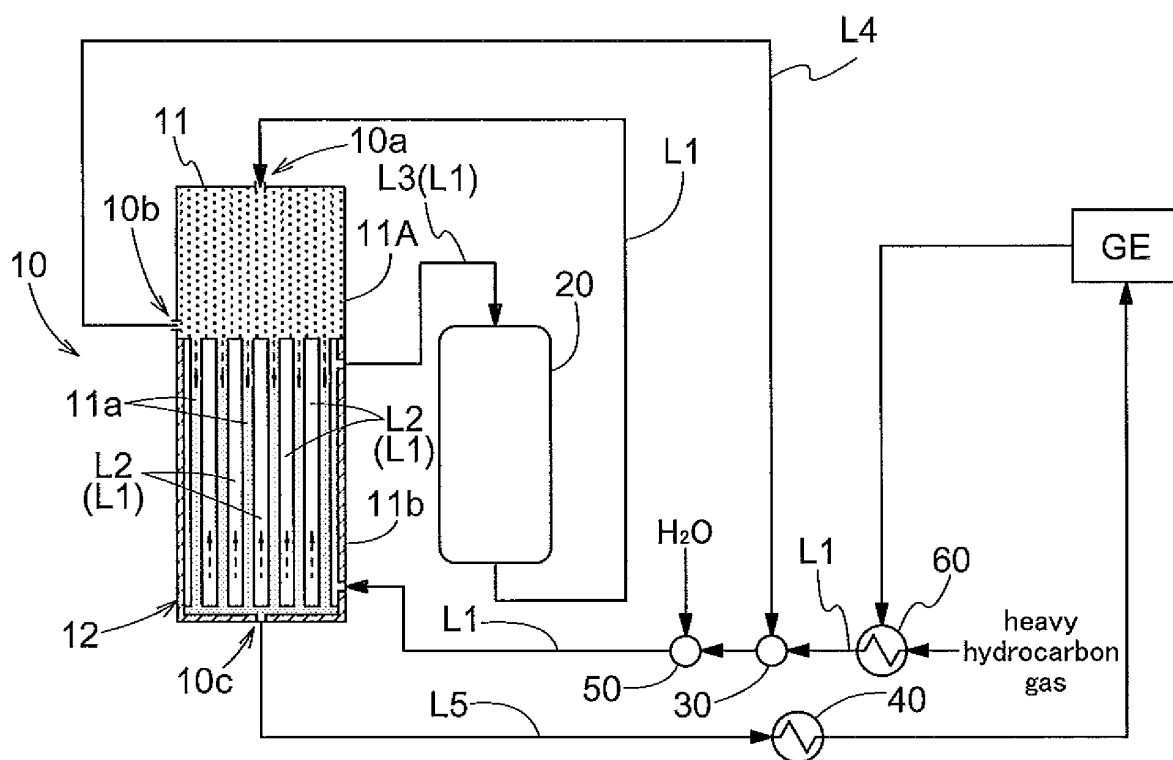
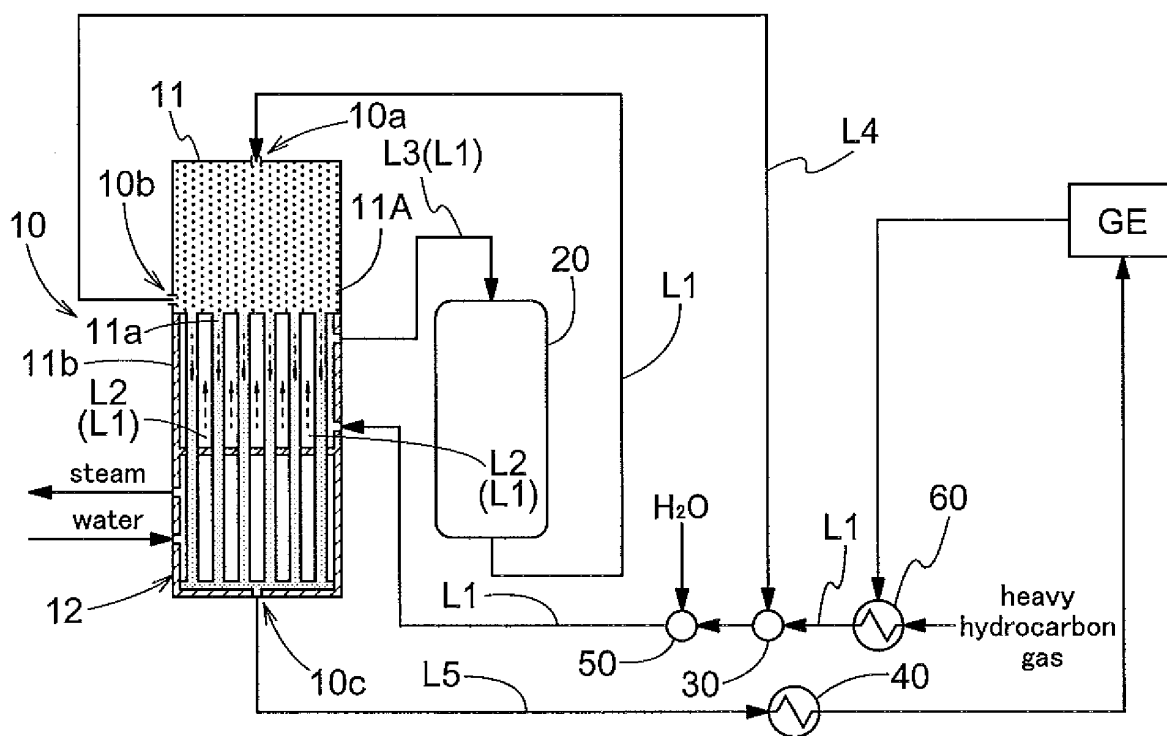


Fig.2



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/008079

A. CLASSIFICATION OF SUBJECT MATTER  
C10L3/08 (2006.01) i

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)  
C10L3/08

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched  
Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2017  
Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho 1994-2017

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 7-26271 A (Osaka Gas Co., Ltd.), 27 January 1995 (27.01.1995), examples; fig. 3 (Family: none)	1-6
A	JP 9-176663 A (Osaka Gas Co., Ltd.), 08 July 1997 (08.07.1997), (Family: none)	1-6
A	JP 48-78105 A (Japan Gasoline Co., Ltd.), 20 October 1973 (20.10.1973), & US 3870738 A	1-6

☐ Further documents are listed in the continuation of Box C.

☐ 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  
22 March 2017 (22.03.17)

Date of mailing of the international search report  
04 April 2017 (04.04.17)

Name and mailing address of the ISA/  
Japan Patent Office  
3-4-3, Kasumigaseki, Chiyoda-ku,  
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

**REFERENCES CITED IN THE DESCRIPTION**

*This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.*

**Patent documents cited in the description**

- US 7866161 B [0003]