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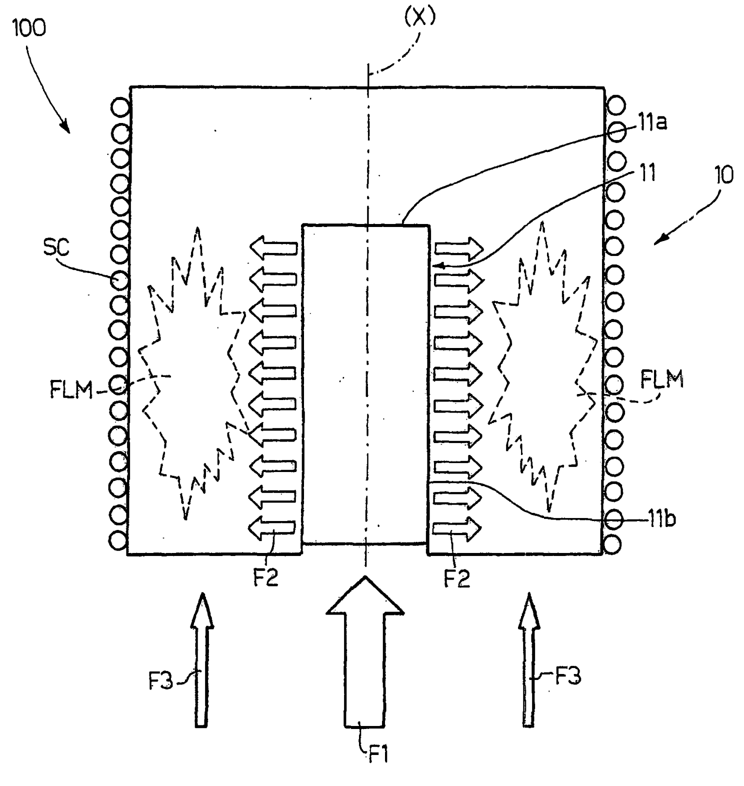
(54) Hybrid combustion boiler

(57) A hybrid combustion boiler (100). The boiler (100) is characterized in that it comprises a hybrid atmospheric burner (10) having a catalytic element (11) crossed by a fuel-rich mixture. Between the catalytic element (11) and a heat exchanger (SC) there is a secondary air flow (F3) introduction pipe, so as to obtain a flame (FLM) given by the ignition of the reformed gas produced when the fuel-rich mixture crosses the catalytic element (11), so that the heat transfer to the heat exchanger (SC) occurs mainly by radiation IR throughout the visible and in the near infrared spectrum.



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Description

[0001] The present invention relates to a hybrid combustion boiler comprising an atmospheric hybrid burner.

[0002] It is the specific object of the present invention to provide a high energy-efficient hybrid combustion boiler for domestic and industrial applications, in virtue of the combined and concurrent use of heat exchange mechanisms of both the radiant and the convective type. Furthermore, a considerable reduction of pollutant emissions (CO, unburned hydrocarbons, NOx) is obtained with the boiler which is the main object of the present invention.

[0003] A boiler made according to the principles of the method, a further object of the present invention, presents improved heat efficiency features with respect to the boilers of the known art, being at the same time less polluting and more stabile, quieter and safer during use.

[0004] As previously mentioned, in the hybrid burner used in the present hybrid combustion boiler, the treatment of gaseous or vaporized fuels occurs in two stages, wherein the first stage contemplates the partial catalytic oxidation of the fuel and the second stage the homogenous phase conversion of the partially oxidised and preheated charge, with intermediate removal of the partial oxidation heat and transfer to a heat exchanger.

[0005] An innovative element of this burner consists mainly in the hybrid operation with intermediate heat removal, which allows to improve the heat efficiency of the burner itself, reduce the level of emission of polluting substances, and makes operation during use more stable and safer.

[0006] In brief, the present invention relates to a hybrid combustion boiler characterized in that it comprises an atmospheric hybrid burner having a catalytic element crossed by a fuel-rich mixture; between the catalytic element and the heat exchanger there is a secondary air flow introduction pipe, so as to obtain a flame given by the ignition of the reformed gas produced when the fuel-rich mixture crosses the catalytic element, so that the transfer of heat towards the heat exchanger occurs mainly by radiation IR throughout the visible and in the near infrared spectrum.

[0007] The present invention will now be described with reference to the sole accompanying figure which illustrates a non-limitative embodiment.

[0008] In the sole accompanying figure, numeral 100 indicates as a whole a hybrid combustion boiler comprising a hybrid catalytic burner 10 and a heat exchanger SC.

[0009] The hybrid catalytic burner 10, in turn, comprises a preferably cylindrical catalytic element 11 comprising, in turn, a large gas-solid contact surface porous metallic substrate, on the surface of which there is deposited an active catalytic phase for the partial oxidation of a fuel-rich and primary air mixture. The combustion ratio between the fuel and the primary air is higher than the upper flammability limit, and thus in lack of oxidazing agent.

[0010] Advantageously, but not necessarily, the catalytic element 11 comprises a wire net, e.g. of the type described and claimed in European Patent Application EP 1 544 542 by the same applicant.

[0011] Incidentally, such European Patent Application EP 1 544 542 must be considered to all effects as an integral part of the present description.

[0012] The fuel/air mixture flows according to a direction and sense identified by an arrow F1 essentially aligned among a longitudinal axis of symmetry (X) of the catalytic element 11.

[0013] Essentially radial flows (arrow F2) of the gaseous mixture are formed within the catalytic element 11, the distal end 11a of which is preferably capped, such flows crossing the wire netting by which the catalytic element 11 itself is formed. In other words, flows are formed in the catalytic element 11 according to an arrow F2 perpendicular to the axis (X). Therefore, the outlet section of the gasses partially converted (reformed) by crossing through the meshes of the catalytic element 11 is constituted by the side surface of the catalytic element 11 itself in shape of thin cylindrical dome, being the gas flow passage at least partially inhibited in the upper part.

[0014] Furthermore, the wire netting on which the catalyzer is deposited also works as a stage of heat removal and direct transfer by radiation to a user, e.g. a heat exchanger SC.

[0015] In this manner, it is possible to reduce the adiabatic flame temperature of a fuel constituted by gaseous light hydrocarbons and/or pure or mixed pre-vaporized hydrocarbons, CO, H_2, or mixtures of these fuels.

[0016] Indeed, the mixture of gases partially converted by crossing of the catalyzer coated netting of the catalytic element 11 is characterized by a lower heat value in proportion to the removal of a share of reaction heat generated on the catalyzer which is transferred to the heat exchanger SC through an infrared radiation emission by the catalytic element 11 itself.

[0017] It is thus not possible to reduce the pollutant emissions of thermal NO_x in the exhaust gases of the burner 10 (of the partially premixed gas type) by reducing the adiabatic flame temperature of the mixture with the aid neither of excess air nor exhaust gas recirculation systems and without increasing the pollutant emissions of CO and unburned hydrocarbons.

[0018] Advantageously, the aforesaid combustion method also applies to fuels such as pure or mixed hydrogen characterized by very high adiabatic flame temperatures and subject to the formation of large amounts of NO_x if burned in traditional diffusion flame systems.

[0019] Advantageously, according to the present invention, the preheating of the partially oxidised fuel flow, output by the catalytic element 11 according to the arrows F2, and its high reactivity, mainly related to its high H2 content, make the homogenous phase secondary combustion particularly stable and promote the containment of unburned hydrocarbon emissions even at relatively low adiabatic flame temperatures.

[0020] The control of the relative weight between the catalytic combustion stage and the homogeneous combustion stage is efficiently obtained by adjusting the "feeding efficiency ratio" (λ), defined as the ratio between fuel and primary air actually fed to the burner 10 divided by the same ratio in stoichiometric conditions.

[0021] According to the method of the present invention, the temperature on the catalytic element 11, where a partial oxidation occurs, is controlled by adjusting the equivalence ratio (λ) so that the oxygen in the fuel/primary air mixture is always the limiting reactant, thus accurately determining in this manner the amount of heat generated on the surface of the catalytic element 11 itself, as well as that transferred by radiation to the heat exchanger SC.

[0022] Advantageously, in the boiler 100, which is the main object of the present invention, it is possible to preserve the durability and the performances of the partial oxidation catalyzer by accurately controlling its operating temperature so that it is constantly under the limit level of use determined by its specific chemical formula.

[0023] Again, according to the present invention, the "contact time" of the fuel/comburent mixture with the "active catalytic phase" present in the catalytic element 11 ("contact time" being defined as the ratio between the volumetric fuel gas and primary air flow rate, at standard temperature and pressure, and the void volume constituted by the pores of the catalytic element 11 itself) is comprised between 1 and 600 ms, and more advantageously between 3 and 100 ms.

[0024] Once the total heat value of the boiler 100 generated by the burner 10 is fixed, the distribution between the heat transmitted by radiation and the heat transmitted by convection by means of the burned gases may be simply controlled by varying the feeding ratio (λ), providing the constraint that the mixture is rich ((λ)>1) and that the temperature of the catalytic element 11 is not excessive so to avoid compromising functionality, durability, integrity and mechanical stability.

[0025] The feeding ratio (λ) to the burner 10 is maintained higher than 1 and preferably higher than the (λMax) value, which defines the upper flammability limit in air at ambient temperature and pressure of the specifically employed fuel.

[0026] According to the aforesaid method, the fuel mixture becomes progressively richer as the feeding ratio (λ) increases to values higher than 1, and specifically higher than (λMax); as a consequence, the partial catalytic oxidation of the fuel proceeds in lesser extent due to the decrease of the concentration of the limiting reagent reactant, constituted by the oxygen present in the primary air. Consequently, a lower fuel conversion in the catalytic stage determines the reduction of the temperature of the catalyzer, the reduction of the amount of heat transferred by radiation and/or by conduction towards the heat exchanger SC and, consequently, the increase of the share of secondary combustion in homogenous phase as well as the corresponding adiabatic flame temperature.

[0027] As the feeding ratio λ decreases, on the other hand, the adiabatic flame temperature of the secondary combustion decreases and consequently the heat formation of nitrogen oxides is gradually limited. Only in the case of hydrocarbon fuels, the CO emissions start to increase if the adiabatic flame temperature of the secondary combustion is excessively low.

[0028] Thanks to the particular configuration of the hybrid boiler 100, the start-up procedure may proceed by igniting a partially premixed flame FLM downstream of the catalytic element 11, which allows the preheating to temperatures higher than the temperature threshold of the partial oxidation reaction (typically between 200°and 400°C). The consequent beginning of the solid-catalyzed reactions causes the generation of heat inside the pores of the catalytic element 11 which is gradually heated and starts to transfer heat by radiation towards the heat exchanger SC, while the combustion continues to be completed by the diffusive or partially premixed flame FLM downstream of the catalytic element 11 until final stationary operation conditions are reached.

[0029] The catalytic element 11 comprises a metallic substrate, which presents a solid macro-porous structure with a high degree of void (preferably higher than 50%) with pores interconnected by tortuous channels without preferential directions so as to form an open mesh structure normally named as "foam" or "netting".

[0030] Truly surprising performances are obtained if the metallic substrate is made according to the teachings of European Patent Application EP 1 544 542. As mentioned, document EP 1 544 542 describes and claims a cover member for a gas burner having a tubular base structure formed by weaving further tubular structures having a much smaller diameter than that of the basic tubular structure, instead of weaving simple wires.

[0031] By using such a structure for making the catalytic element 11, there is an optimal contact of the fuel/ primary air mixture and the active catalytic phase.

[0032] This metallic substrate consists of a material which is not active in the concerned reactions and which has a high mechanical resistance to heat shocks and is preferably formed by a material resistant to temperatures of at least 1000°C, chemically and physically stabile, and free from oxidation, separation, volatility or phase transaction phenomena at said temperatures.

[0033] As previously mentioned, from the structural point of view, a netting of the type described in above mentioned European Patent Application EP 1 544 542 may be advantageously used.

[0034] Specifically, the monolithic metallic substrate consists of an alloy of high-temperature-resistant materials, preferably of a metallic alloy chosen between FeCrAlY, Nickel Cr, Nichrome, Hastelloy X, Inconel 600-625, and made in the shape of a netting.

[0035] The "active catalytic phase", deposited on the above-described macroporous substrate, is selected among those known in the field for the reaction and the production process of synthesis gas by means of partial oxidation of hydrocarbons, and is capable of supporting the conversion reaction of the hydrocarbon fraction of the fuel to H_2 and CO partial oxidation products, rather than to total oxidation of H_2O and CO_2, thus ensuring a high H_2 and CO conversion and selectivity also in autothermic operating conditions without preheating the input gaseous current. It is however apparent that, in presence of H_2 and/or CO in the fuel mixture fed to the burner 10, the active catalytic phase is capable of fully oxidizing these compounds to H_2O and CO_2 respectively, again restricted to the amount of oxygen contained in the primary air fed to the catalytic element in lack with respect to the stoichiometric value.

[0036] Specifically, the "active catalytic phase" is constituted by a dispersion of a metal chosen among the noble metals Pt, Pd, Rh, Ir, Re, Ru, Au, Ni, Ag and transition metals V, Cr, Mn, Fe, Co, or by a mixture thereof, preferably by a dispersion of Rh, Ni, Pt, Co, Fe, Cr, Mn.

[0037] The "catalytic active phase" is present in amount comprised between 0.01 and 10% of the total weight of the catalyzer. Alternatively, the "active catalytic phase" may be represented by a mixed transition metal oxide with perovskite structure and general formula AxA"1-xByB"1-yO3$\pm\delta$, wherein:

A is a cation of at least one element selected among the rare earth elements;
A' is a cation of at least one element selected from the groups Ia, IIa and VIa of the periodical element table;
B is a cation of at least one element selected from the groups IVb, Vb, VIb, VIIb or VIII of the periodical element table;
B' is a cation of at least one element selected from the groups IVb, Vb, VIb, VIIb or VIII of the periodical element table, Mg2+ or Al3+,
x is a number so that $0 \leq x \leq 1$,
y is a number so that $0 \leq y \leq 1$, and
δ is a number so that $0 \leq \delta \leq 0.5$.

[0038] Preferably, the "active catalytic phase" is finely dispersed on a large specific surface area support applied as a thin film onto the foam or wire netting substrate and preferably constituted by a refractory oxide with a low thermal expansion coefficient, provided with a good chemical affinity with the material by which said metallic substrate is formed.

[0039] Specifically, the large surface area support layer consists of MgO, MgAl2O4, ZrO2, γ-Al2O3 stabilized or not with La203, Ce02 or other stabilizer present in a total amount comprised between 1% and 10% by weight with respect to the total of the large surface area support layer.

[0040] During the initial step of starting up the boiler 100, the fuel-rich mixture crosses the meshes, or the pores of the catalytic element 11 at ambient temperature without being oxidised at all.

[0041] The fuel/primary air mixture being output from the holes, or the pores, of the catalytic element 11 is mixed with a flow of secondary air (indicated in the figure by the arrows F3) and ignited.

[0042] A flame front FLM is thus developed over the external cylindrical surface 11b of the catalytic element 11.

[0043] In turn, the flame front FML, by conduction and radiation, heats the catalytic element 11, which, having reached its threshold temperature starts to promote the partial oxidation reaction of the rich mixture. The heat generated by the partial oxidation will transform the catalytic element 11 into a radiating system throughout the visible and in the near infrared spectrum. An excellent percentage of the energy produced by the burner 10 will reach, in direct and/or indirect manner, the heat exchanger SC in which a heat conveying fluid, e.g. water, is heated.

[0044] The advantages of the combustion method and of the corresponding burner object of the present invention are:

- the possibility of radiating operation at any power;
- possibility of operating in low excess of air;
- possibility of modulating the load;
- possibility of operating with different gaseous or pre-vaporized fuels also with high H2 contents;
- low emission values of polluting substances; and
- safety of operation because "backfiring" is impossible.

Claims

1. A hybrid combustion boiler (100); the boiler (100) is **characterized in that** it comprises an atmospheric hybrid burner (10) having a catalytic element (11) crossed by a fuel-rich mixture; between said catalytic element (11) and a heat exchanger (SC) there is a secondary air flow (F3) introduction pipe, so as to obtain a flame (FLM) given by the ignition of the reformed gas produced when the fuel-rich mixture crosses the catalytic element (11), so that the transfer of heat towards the heat exchanger (SC) occurs mainly by radiation IR throughout the visible and in the near infrared spectrum.

2. A boiler (100) as claimed in claim 1, **characterized in that** the catalytic element (11) has a metallic substrate, which presents a solid macro-porous structure with a high degree of void, preferably higher than 50%, with pores interconnected by tortuous channels without preferential directions forming an open mesh structure normally named as "foam" or "netting".

3. A boiler (100), as claimed in claim 2, **characterized in that** said catalytic element (11) comprises a me-

tallic substrate having a tubular base structure made by weaving other tubular structures having a much smaller diameter than that of the tubular base structure itself.

4. A boiler (100), as claimed in claim 3, **characterized in that** the metallic substrate of the catalytic element (11) is coated with an "active catalytic phase" with which the fuel/comburent mixture comes into contact, the "active catalytic phase" supporting the conversion reaction of the hydrocarbon fraction of the fuel to H2 and CO partial oxidation products.

5. A boiler (100), as claimed in claim 4, **characterized in that** the "active catalytic phase" comprises a dispersion of a metal selected among the noble metals (Pt, Pd, Rh, Ir, Re, Ru, Au, Ni, Ag) and transition metals (V, Cr, Mn, Fe, Co), or a mixture thereof, preferably by a dispersion of (Rh, Ni, Pt, Co, Fe, Cr, Mn).

6. A boiler (100), as claimed in claim 4 or in claim 5, **characterized in that** the "active catalytic phase" is present in amounts comprised between 0.01 and 10% of the total weight of the catalyzer.

7. A boiler (100), as claimed in claim 14, **characterized in that** the "active catalytic phase" comprises a mixed transition metal oxide with perovskite structure and general formula (AxA"1-xByB"1-yO3±8), wherein:

    - A is a cation of at least one element selected among the rare earth elements;
    - A' is a cation of at least one element chosen from the groups Ia, IIa and VIa of the periodical element table;
    - B is a cation of at least one element selected from the groups IVb, Vb, VIb, VIIb or VIII of the periodical element table;
    - B' is a cation of at least one element selected from the groups IVb, Vb, VIb, VIIb or VIII of the periodical element table, Mg2+ or A13+;
    - x is a number so that $0 \leq x \leq 1$,
    - y is a number so that $0 \leq y \leq 1$, and
    - δ is a number so that $0 \leq \delta \leq 0.5$.

8. A boiler (100), as claimed in any of claims 4-7, **characterized in that** the "contact time" of the fuel/comburent mixture with the "active catalytic phase" present on the catalytic element (11) is comprised between 1 and 600 ms, specifically between 3 and 100 ms, having defined as "contact time" the ratio between the volumetric fuel and primary comburent flow rate at standard temperature and pressure and the void volume of the catalytic element itself.

9. A hybrid combustion method of pre-vaporized gas or liquids **characterized in that** it comprises:

    - a step of activating in which the fuel/comburent mixture, rich in fuel in excess of the upper flammability limit of the specific fuel, crosses the meshes, or the pores, of a catalytic element at ambient temperature without undergoing any appreciable oxidation;
    - a step in which the fuel/comburent mixture being output from the holes, or the pores, of the catalytic element is mixed with the flow of secondary comburent and is ignited thus developing a flame front over the external surface of the catalytic element;
    - a step in which the frame front, by conduction and radiation, heats the catalytic element which in turn having reached a threshold temperature normally comprised between 200 and 400°C, starts to promote the partial oxidation reaction of the rich mixture; and
    - a step in which the heat produced by the catalytic partial oxidation transforms the catalytic element into a radiating system throughout the visible and in the near infrared spectrum.

10. A method, as claimed in claim 9, **characterized in that** it comprises:

    - a first step in which the partial catalytic oxidation of the fuel occurs; and
    - a second step in which the homogenous phase conversion of the partially oxidised and preheated load occurs, with intermediate removal of the partial oxidation heat and transfer to a main user by radiation throughout the visible and in the near infrared spectrum.

11. A method, as claimed in claim 9 or in claim 10, **characterized in that:**

    - during operation, the temperature of the radiating catalytic element is comprised between 300°C and 1100°C and is however higher than the threshold temperature of the partial catalytic oxidation reaction and lower than the thermal stability limit of the materials; and
    - the temperature of the catalytic element, where the partial oxidation occurs, is controlled by adjusting the "equivalency feeding ratio" (λ), defined as the ratio between the fuel and the primary comburent actually fed to the burner divided by the same ratio in stoichiometric conditions, so that the oxygen present in the fuel/comburent is always the limiting reactant, thus accurately determining in this manner the amount of heat generated on the surface of the catalytic element itself, as well as that transferred by radiation to a user.

12. A method, as claimed in claim 11, **characterized in**

that the comburent is air oxygen and the feeding ratio (λ) is higher than 1 and preferably is higher than the value (λMax), which defines the upper flammability limit in air at ambient temperature and pressure of the specifically employed fuel.

13. A method, as claimed in any of claims 9-12, **characterized in that** the fuel/comburent mixture when crossing through the catalytic element is in contact with an "active catalytic phase", which supports the conversion reaction of the hydrocarbon fraction of the fuel to H2 and CO partial oxidation products.

14. A method as claimed in claim 13, **characterized in that** the "active catalytic phase" comprises a dispersion of a metal selected among the noble metals (Pt, Pd, Rh, Ir, Re, Ru, Au, Ni, Ag) and transition metals (V, Cr, Mn, Fe, Co), or a mixture thereof, preferably by a dispersion of (Rh, Ni, Pt, Co, Fe, Cr, Mn).

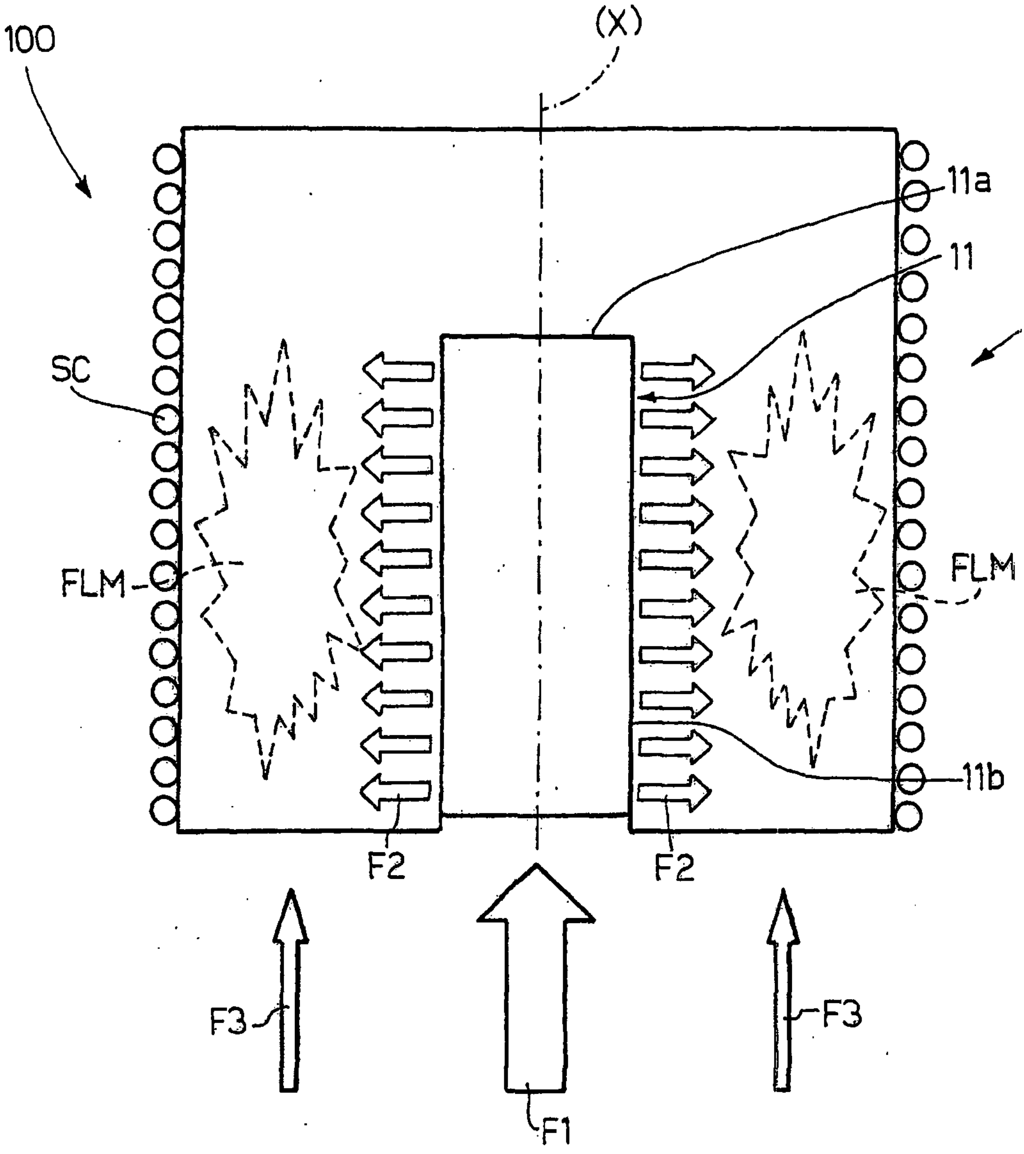
15. A method, as claimed in claim 13 or in claim 14, **characterized in that** the "active catalytic phase" is present in amounts comprised between 0.01 and 10% of the total weight of the catalyzer.

16. A method, as claimed in claim 13, **characterized in that** the "active catalytic phase" comprises a mixed transition metal oxide with perovskite structure and general formula (AxA’1-xByB’1-yO3$\pm\delta$), wherein:

- A is a cation of at least one element chosen among the rare earth elements;
- A’ is a cation of at least one element chosen from the groups Ia, IIa and VIa of the periodical element table;
- B is a cation of at least one element chosen from the groups IVb, Vb, VIb, VIIb or VIII of the periodical element table;
- B’ is a cation of at least one element chosen from the groups IVb, Vb, VIb, VIIb or VIII of the periodical element table, Mg2+ or A13+;
- x is a number so that $0 \leq x \leq 1$,
- y is a number so that $0 \leq y \leq 1$, and
- δ is a number so that $0 \leq \delta \leq 0.5$.

17. A method, as claimed in any of claims 13-16, **characterized in that** the "contact time" of the fuel/comburent mixture with the "active catalytic phase" present on the catalytic element (11) is comprised between 1 and 600 ms, specifically between 3 and 100 ms, having defined as "contact time" the ratio between the volumetric fuel and primary comburent flow rate at standard temperature and pressure and the void volume of the catalytic element itself.

18. A method, as claimed in any of claims 9-17, **characterized in that** the fuel is pure hydrogen.


100
(X)
11a
11
10
SC
FLM
FLM
11b
F2
F2
F3
F1
F3

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EUROPEAN SEARCH REPORT

Application Number
EP 07 42 5621

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
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TECHNICAL FIELDS SEARCHED (IPC)

F23D

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	1 April 2008	Theis, Gilbert

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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A : technological background
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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

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 07 42 5621

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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