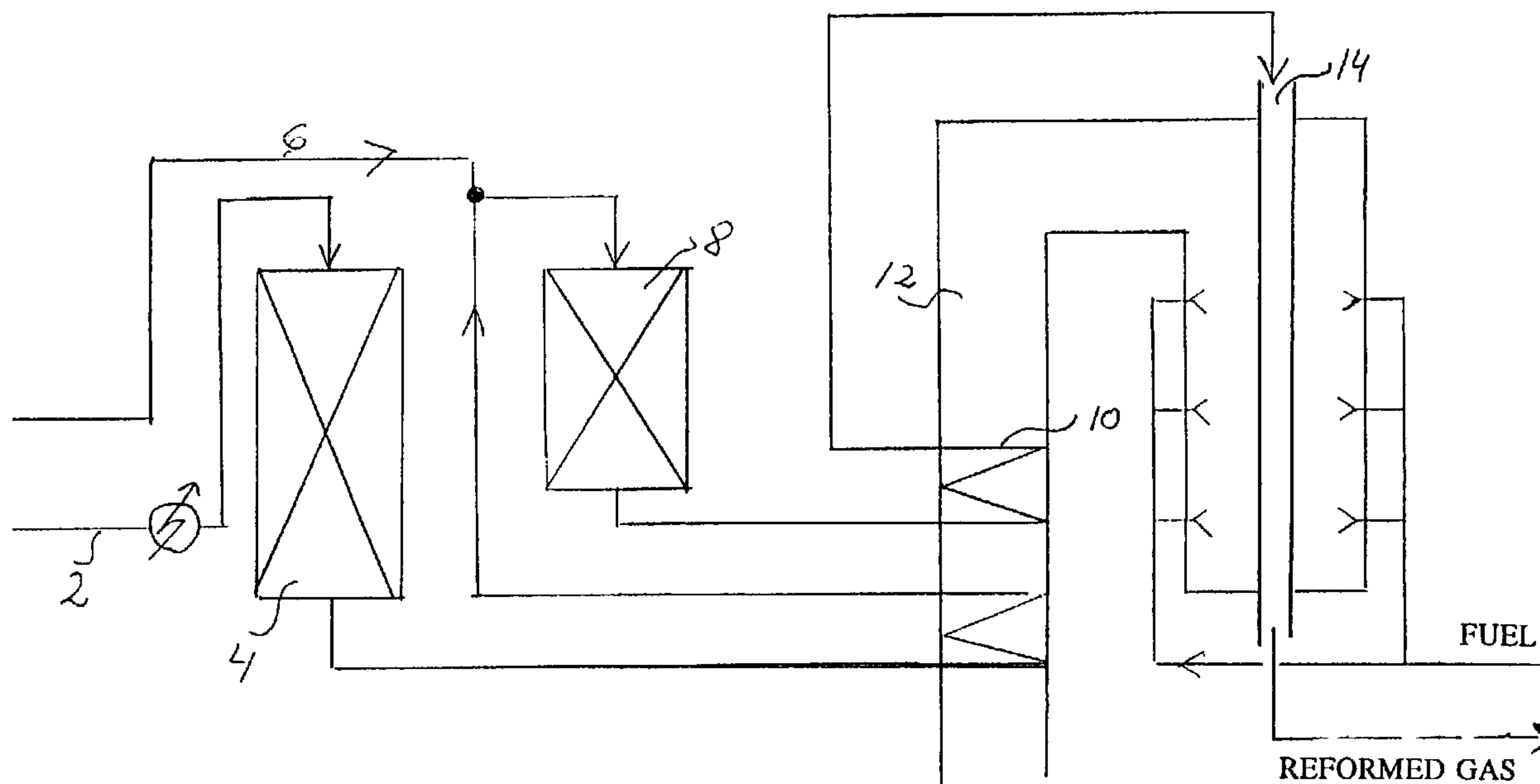




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(54) Titre : PRODUCTION DE GAZ DE SYNTHÈSE PAR REFORMAGE A LA VAPEUR EN PRESENCE DE MATERIEL CATALYTIQUE
 (54) Title: SYNTHESIS GAS PRODUCTION BY STEAM REFORMING USING CATALYZED HARDWARE



(57) Abrégé/Abstract:

The present invention provides an improvement in a process for the preparation of hydrogen and a carbon monoxide-rich gas by steam reforming of a hydrogen-rich gas in the presence of a steam reforming catalyst. The improvement comprising the essential steps of passing a heated, prereformed hydrogen feedstock through a second tubular reactor which is provided with a thin film of the steam reforming catalyst, and which is heated by the burning of fuel, thereby to obtain a partially-steam-reformed gas effluent and hot flue gas, passing the partially-steam-reformed gas effluent through a fixed bed, steam reforming catalyst, and withdrawing a product gas stream comprising hydrogen and a carbon monoxide-rich gas from the fixed bed.

ABSTRACT

The present invention provides an improvement in a process for the preparation of hydrogen and a carbon monoxide-rich gas by steam reforming of a hydrogen-rich gas in the presence of a steam reforming catalyst. The improvement comprising the essential steps of passing a heated, prereformed hydrogen feedstock through a second tubular reactor which is provided with a thin film of the steam reforming catalyst, and which is heated by the burning of fuel, thereby to obtain a partially-steam-reformed gas effluent and hot flue gas, passing the partially-steam-reformed gas effluent through a fixed bed, steam reforming catalyst, and withdrawing a product gas stream comprising hydrogen and a carbon monoxide-rich gas from the fixed bed.

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(a) TITLE OF THE INVENTION

Synthesis Gas Production By Steam Reforming Using Catalyzed Hardware

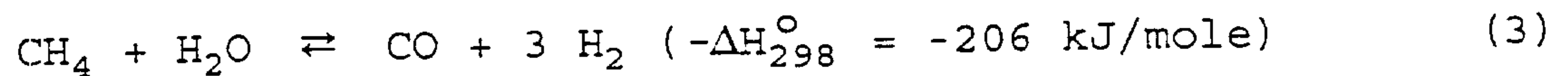
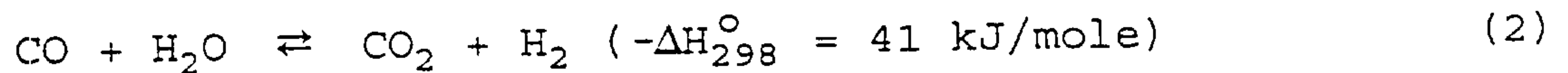
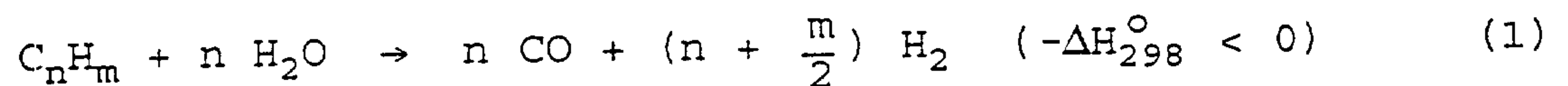
(b) TECHNICAL FIELD TO WHICH THE INVENTION BELONGS

The present invention relates to the production of synthesis gas by steam reforming of a hydrocarbon feedstock in contact with catalyzed hardware.

(c) BACKGROUND ART

The term catalyzed hardware is used for a catalyst system where a layer of catalyst is fixed on a surface of another material, e.g. metallic surfaces. The other material serves as the supporting structure giving strength to the system. This allows to design catalyst shapes which would not have sufficient mechanical strength in itself. The system herein consists of tubes on which a thin layer of reforming catalyst is placed on the inner wall.

Synthesis gas is produced from hydrocarbons by steam reforming by the reactions (1)-(3):



State of the art steam reforming technology makes use of reforming catalyst in the form of pellets of various sizes and shapes. The catalyst pellets are placed in fixed bed reactors (reformer tubes). The reforming reaction is endothermic. In conventional reformers, the necessary heat for the reaction is supplied from the environment outside the tubes usually by a combination of radiation and convection to the outer side of the reformer tube. The heat is transferred to the inner side of the tube by heat conduction through the tube wall, and is transferred to the gas

phase by convection. Finally, the heat is transferred from the gas phase to the catalyst pellet by convection. The catalyst temperature can be more than 100°C lower than the inner tube wall temperature at the same axial position of the reformer tube.

(d) DESCRIPTION OF THE INVENTION

By one broad aspect, the present invention provides an improvement in a process for the preparation of hydrogen and a carbon monoxide-rich gas by steam reforming of a hydrogen-rich gas in the presence of a steam reforming catalyst, the improvement comprising the essential steps of passing a heated, prereformed hydrogen feedstock through a second tubular reactor which is provided with a thin film of the steam reforming catalyst, and which is heated by the burning of fuel, thereby to obtain a partially-steam-reformed gas effluent and hot flue gas, passing the partially-steam-reformed gas effluent through a fixed bed, steam reforming catalyst, and withdrawing a product gas stream comprising hydrogen and a carbon monoxide-rich gas from the fixed bed.

By another broad aspect, the present invention provides a process for the preparation of hydrogen and a carbon monoxide-rich gas by steam reforming of a hydrogen-rich gas in the presence of a steam reforming catalyst, the essential steps of passing a process gas of prereformed hydrocarbon feedstock through a first tubular reactor which is provided with a thin film of the steam reforming catalyst which is supported on walls of the reactor in heat-conducting relationship with hot flue gas which has been recycled from a downstream second tubular steam reforming reactor, thereby to obtain a heated, prereformed hydrogen feedstock gas effluent, passing the heated, prereformed hydrogen feedstock from the first tubular reactor through a second tubular reactor which is provided with a thin film of the steam reforming catalyst, and which is heated by the burning of fuel, thereby to obtain a partially-steam-reformed gas effluent and the hot flue gas, passing the partially-steam-reformed gas effluent from the second tubular reactor to a fixed bed, steam reforming catalyst, and withdrawing a product gas stream comprising hydrogen and a carbon monoxide-rich gas from the fixed bed.

By one variant thereof, the fixed bed reforming catalyst is operated at adiabatic conditions. The fixed bed steam reforming catalyst may be arranged within the second tubular reactor.

By another variant thereof, the fixed bed steam reforming catalyst is arranged within the second tubular reactor.

By yet another variant thereof the steam reforming catalyst comprises at least one of nickel and ruthenium.

It has been found that heat transport is more efficient when catalyzed hardware is used in the steam reforming process. The heat transport to the catalyst occurs by conduction from the inner tube wall. This is a much more efficient transport mechanism than the transport by convection via the gas phase. The result is that the temperatures of the inner tube wall and the catalyst are almost identical (the difference below 5°C). Furthermore, the tube thickness can be reduced, see below, which makes the temperature difference between the inner and outer side of the reformer tube smaller. It is hence possible to have both a higher catalyst temperature and a lower tube temperature, all other conditions being the same when replacing the conventional reformer tubes with catalyzed hardware tubes. A low outer tube wall temperature is desirable since it prolongs the lifetime of the tube. A high catalyst temperature is advantageous since the reaction rate increases with temperature and since the equilibrium of reaction (3) is shifted to the right hand side resulting in a better utilisation of the feed.

Pressure drop in the catalyzed reformer tube is much lower than in the conventional case for the same tube diameter. This enables the use of reactor tubes with a smaller diameter and still maintaining an acceptable pressure drop. Smaller tube diameter results in an increased tube lifetime, tolerates higher temperatures and reduces the tube material consumption.

Finally, the catalyst amount is reduced when using catalyzed hardware reformer tubes compared to the conventional reformer with a fixed bed of reforming catalyst.

(e) DESCRIPTION OF THE FIGURES

In the accompanying drawings;

Fig. 1 is a schematic representation of the front end of a plant producing according to one aspect of the present invention;

Fig. 2 is a representation of process gas flow inside tubes showing the layout of one tube according to one aspect of the present invention; and

Fig. 3 is a flow scheme of a process according to one aspect of the present invention.

(f) AT LEAST ONE MODE FOR CARRYING OUT THE INVENTION

Fig. 1 shows the front-end of a plant producing syngas. Feed 2 is preheated, desulphurized in unit 4, mixed with process steam 6, and further heated before entering an adiabatic prereformer 8. The effluent stream from prereformer 8 is further heated in loop arranged in flue gas channel 12 and send to the tubular reformer 14, where conversion of methane to hydrogen, carbon monoxide, and carbon dioxide occurs. The processing of effluent gas downstream from the tubular reformer depends on the use of the product.

Catalyzed hardware can be used in two of the units shown in Fig. 1:

1. In the preheater coil 10 for heating the prereformer effluent gas before entering the tubular reformer 14.
2. In the tubular reformer 14.

Below is presented the results obtained for the plant in Fig. 1 when catalyzed hardware is used in the above two units. The catalyst used for the catalyzed hardware is the R-67R nickel steam reforming catalyst available from Haldor Topsoe A/S. The results are compared with the conventional case.

The purpose of the preheater coil is to use the heat content in the flue gas for preheating of the process gas before it enters the tubular reformer. The flue gas is used for preheating of process gas and for preheating of the combustion air for the tubular reformer (not shown in Fig. 1). However, the heat content of the flue gas is larger than what can be used for these purposes and the remaining heat is used for steam production. It will be an advantage, if a larger amount of the heat content in the flue gas can be transferred to the process gas. This will reduce the necessary amount of fuel in the tubular reformer, and it will reduce the size of the reformer since a smaller amount of heat is to be transferred in the unit.

The conventional preheater is limited by the risk of carbon formation by decomposition of methane. This sets an upper limit for the tube wall temperature, which can be accepted. Fixing a layer of catalyzed hardware on the inner tube wall of the preheater coil (as shown in Fig. 2) results in a decrease of both the tube wall temperature and the process gas temperature. This enables the transfer of a higher duty in the coil without having a higher tube temperature.

The preheater coil used in the calculation consists of 8 tubes in which the process gas flow inside the tubes. The flue gas flows on the outer side. The flow pattern is cross flow/co-current. Fig. 2 shows the layout for one tube. The two cases with and without catalyzed hardware are summarised in Table 1. It is apparent that the transferred

duty (heat energy) is 49% higher in the catalyzed hardware case compared to the conventional case. The catalyst layer thickness in the catalyst hardware case is 1.0 mm.

Table 1

| | Conventional case | Catalyzed hardware case |
|--------------------------------|---------------------------|---------------------------|
| Number of tubes | 8 | 8 |
| Total effective tube length | 51.6 m | 76.2 m |
| Flue gas in/out temperature | 1057°C/964°C | 1057°C/912°C |
| Process gas in/out temperature | 512°C/650°C | 512°C/631°C |
| Methane conversion | 0% | 8.7% |
| Transferred duty | 9.69×10^6 kcal/h | 1.44×10^7 kcal/h |

5 The effective tube length is the length of the tube inside the flue gas channel.

10 The conventional tubular reformer consists of a number of tubes which is filled with catalyst pellets. The process gas flows inside the tubes. The tubes are placed in a furnace which is heated by combustion of a fuel.

15 In the catalyzed hardware case the catalyst pellet filled tubes are replaced with a number of tubes with a layer of catalyzed hardware on the inner tube wall. The catalyst layer thickness is 0.25 mm. An additional adiabatic reforming fixed bed reactor is placed downstream

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from the tubular reactor since the conversion of methane in the catalyzed hardware tubular reformer is inferior to the conventional case. This reactor is called post reformer. The catalyst used in the post reformer is the RKS-2 nickel steam reforming catalyst available from Haldor Topsoe A/S.

The two cases are summarised below in Table 2. It is seen that catalyst consumption is decreased by a factor 11.5, and that material consumption for the tubes in the tubular reformer is decreased 24% in the catalyzed hardware case compared to the conventional case.

Table 2

| | Conventional case | Catalyzed hardware reformer | Catalyzed hardware case + post reformer |
|--|-------------------|-----------------------------|---|
| Number of tubes | 276 | 187 | |
| Tube length | 13 m | 55 m | |
| Catalyst consumption | 31.0 t | 0.63 t | 2.70 t |
| Tube material consumption for tubular reformer | 153.6 t | 116.0 t | |
| Methane conversion | 89.0 % | 80.7 % | 90.2 % |

A flow scheme of a process according to the invention is shown in Fig. 3. The numbers in the triangles refer to the table below in which the overall figures for the process are compared. The fuel consumption is decreased by 7.4% in the catalyzed hardware case compared to the conventional case.

Table 3

| Position | | Conventional case | Catalysed hardware case |
|----------|--|---|--|
| 1 | T (°C) P (kg/cm ² g) Total dry flow (Nm ³ /h) Total flow (Nm ³ /h) Composition (dry mole %) H ₂ CO CO ₂ CH ₄ | 512 28.5 57851 143168 23.78 0.74 21.14 54.34 | 512 28.5 57851 143168 23.78 0.74 21.14 54.34 |
| 2 | T (°C) P (kg/cm ² g) Total dry flow (Nm ³ /h) Total flow (Nm ³ /h) Composition (dry mole %) H ₂ CO CO ₂ CH ₄ | 650 27.5 57851 143168 23.78 0.74 21.14 54.34 | 631 27.4 67397 148720 34.58 2.67 20.16 42.59 |
| 3 | T (°C) P (kg/cm ² g) Total dry flow (Nm ³ /h) Total flow (Nm ³ /h) Composition (dry mole %) H ₂ CO CO ₂ CH ₄ | 925 24.1 141533 199121 68.85 20.24 8.47 2.44 | 1015 26.0 132653 194106 66.76 20.42 8.24 4.57 |
| 4 | T (°C) P (kg/cm ² g) Total dry flow (Nm ³ /h) Total flow (Nm ³ /h) Composition (dry mole %) H ₂ CO CO ₂ CH ₄ | No post reformer in this case | 930 24.4 142580 200003 69.08 20.35 8.40 2.17 |
| 5 | T (°C) Total flow (Nm ³ /h) | 1057 244672 | 1057 234677 |
| 6 | T (°C) | 964 | 912 |
| 7 | Total flow (Nm ³ /h) | 9524 | 8820 |

CLAIMS

1. In a process for the preparation of hydrogen and a carbon monoxide-rich gas by steam reforming of a hydrocarbon feedstock in the presence of a steam reforming catalyst, the essential steps of:

passing a heated, prereformed hydrocarbon feedstock through a tubular reactor which is provided with a thin film of said steam reforming catalyst, and which is heated by the burning of fuel, thereby to obtain a partially-steam-reformed gas effluent and hot flue gas;

passing said partially-steam-reformed gas effluent through a fixed bed, steam reforming catalyst; and

withdrawing a product gas stream comprising hydrogen and a carbon monoxide-rich gas from said fixed bed.

2. A process for the preparation of hydrogen and a carbon monoxide-rich gas by steam reforming of a hydrocarbon feedstock in the presence of a steam reforming catalyst, the essential steps of:

passing a process gas of prereformed hydrocarbon feedstock through a first tubular reactor which is provided with a thin film of said steam reforming catalyst supported on walls of said reactor in heat-conducting relationship with hot flue gas which has been recycled from a downstream second tubular steam reforming reactor, thereby to obtain a heated, prereformed hydrogen feedstock gas effluent;

passing said heated, prereformed hydrogen feedstock from said first reactor through the second tubular reactor which is provided with a thin film of said steam reforming catalyst, and which is heated by the burning of fuel, thereby to obtain a partially-steam-reformed gas effluent and said hot flue gas;

passing said partially-steam-reformed gas effluent from said second tubular reactor to a fixed bed, steam reforming catalyst; and

withdrawing a product gas stream comprising hydrogen and a carbon monoxide-rich gas from said fixed bed.

3. The process according to claim 1 or claim 2, wherein said fixed bed reforming catalyst is operated at adiabatic conditions.

4. The process according to claim 1, claim 2 or claim 3, wherein said fixed bed steam reforming catalyst is arranged within said second tubular reactor.

5. The process according to any one or more of claims 1 to 4, inclusive, wherein said steam reforming catalyst comprises at least one of nickel and ruthenium.

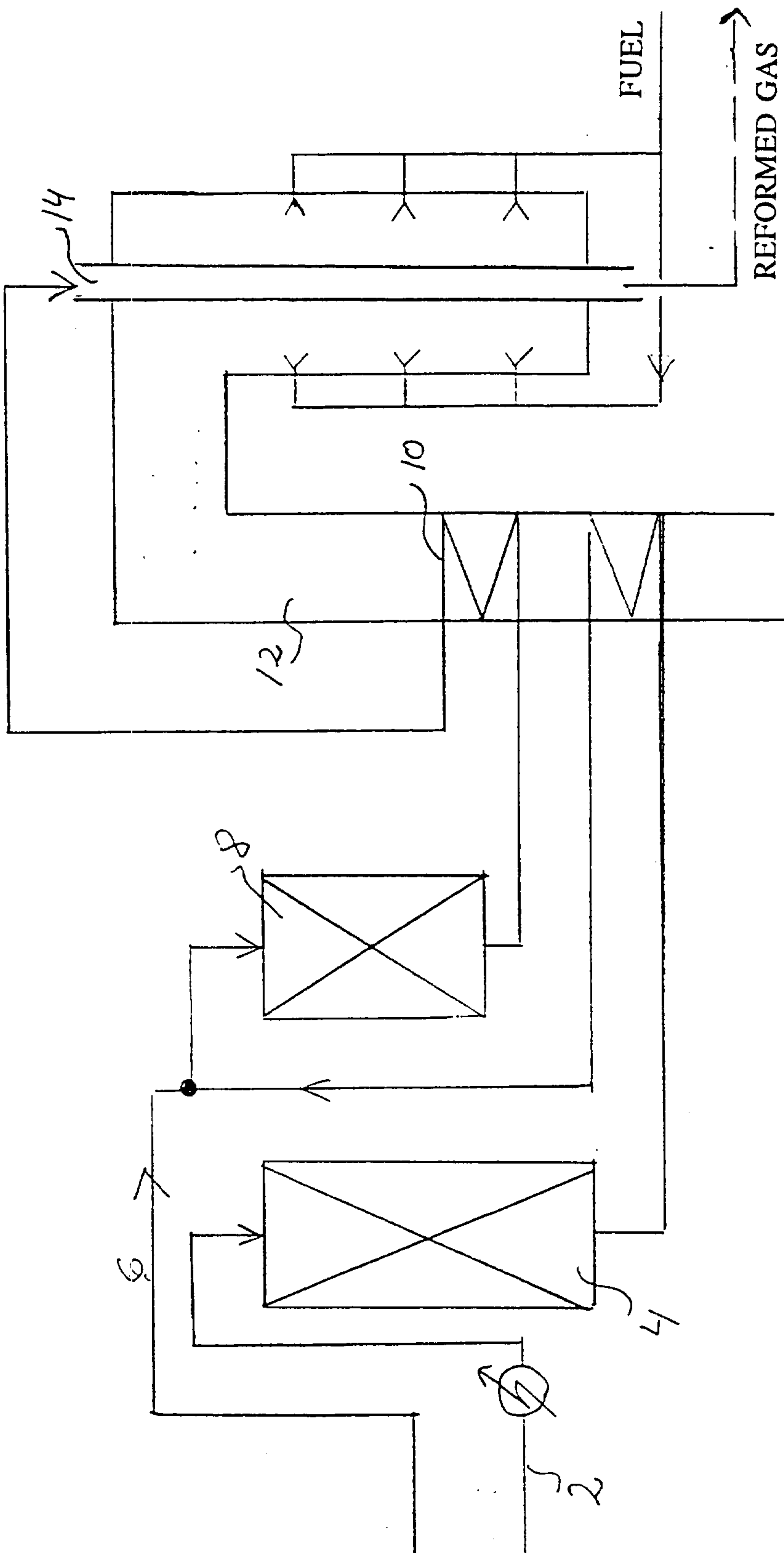


FIG. 1

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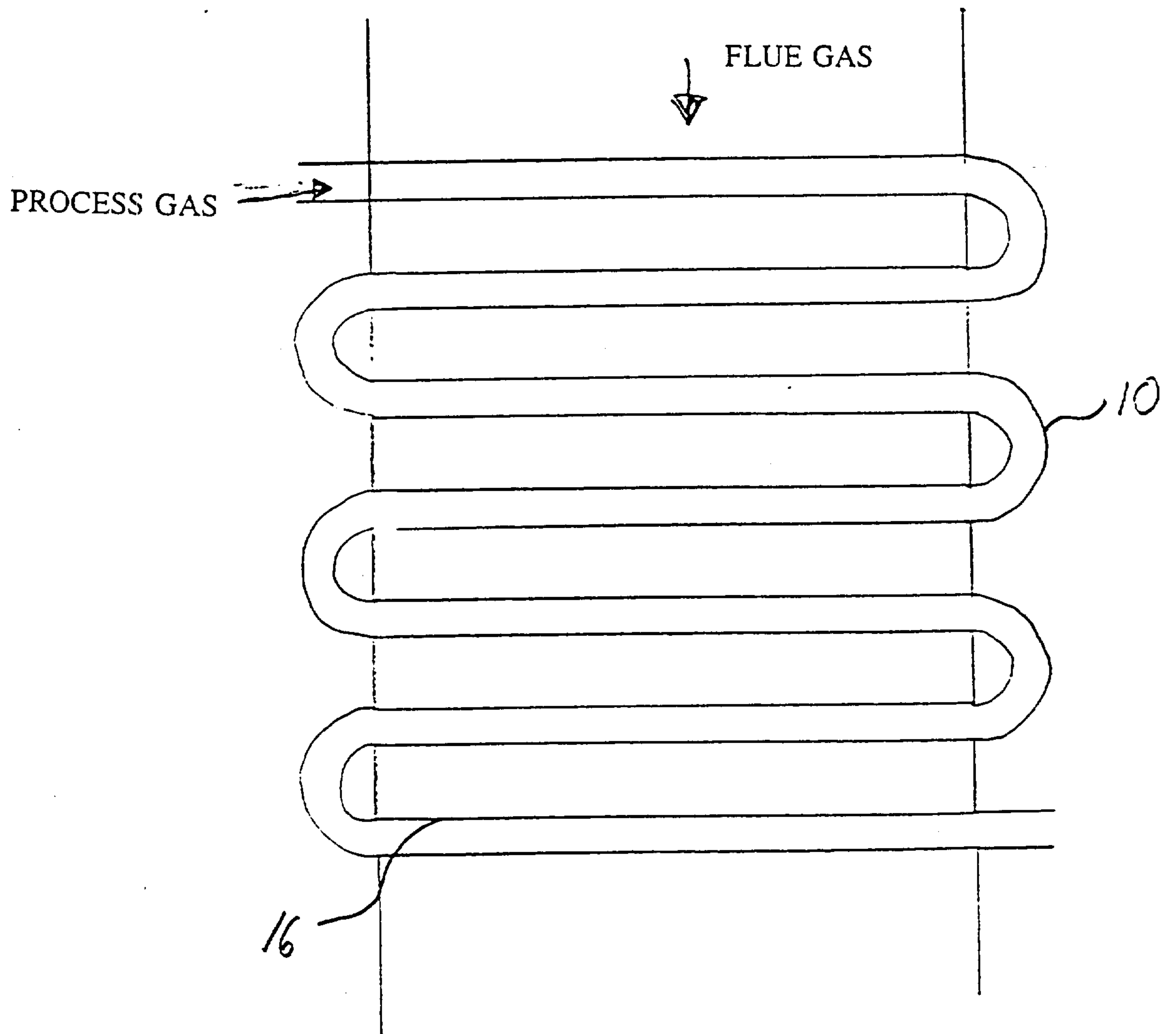


FIG. 2

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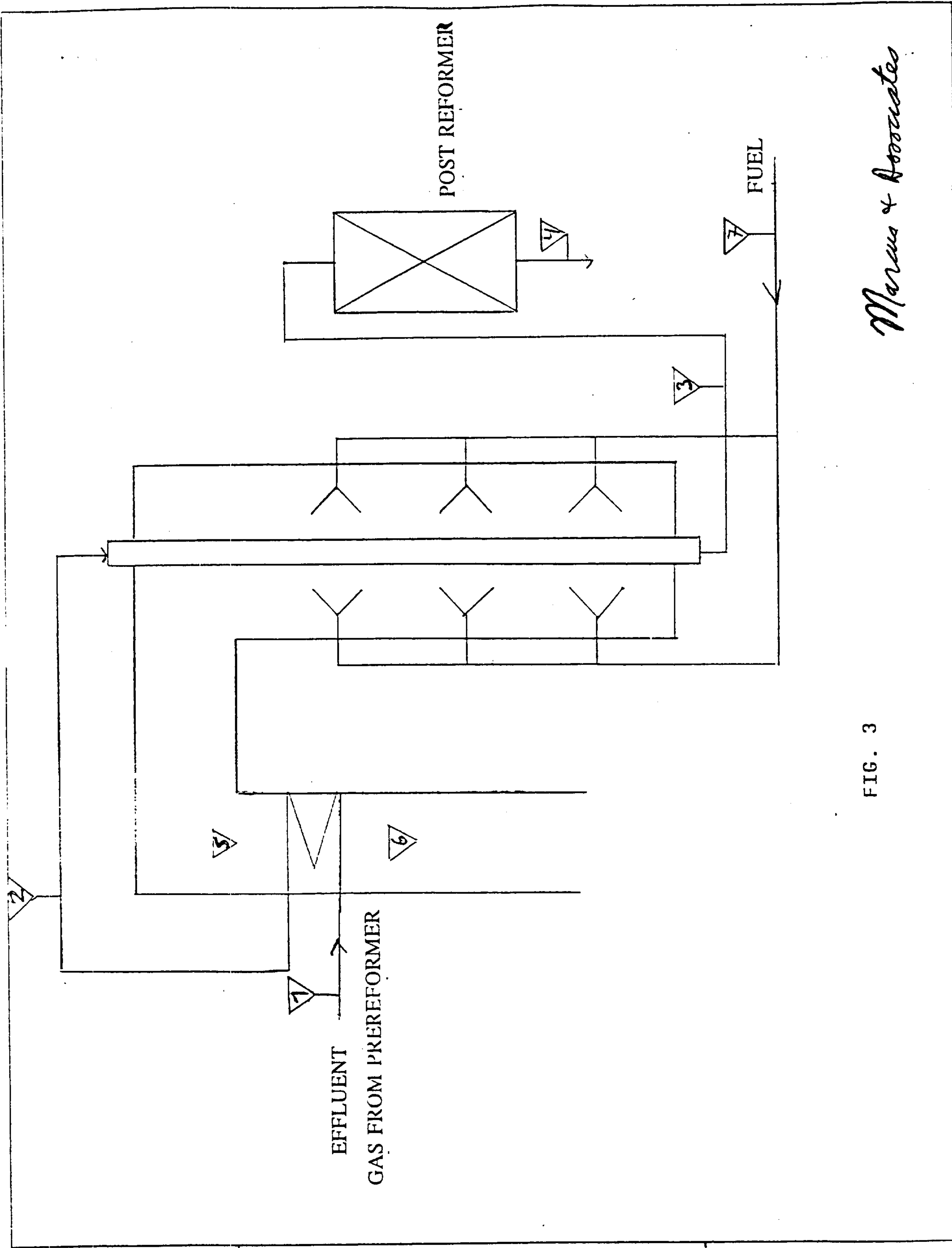


FIG. 3

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