

The invention relates to a process for indirectly heating a process gas stream in a reaction chamber for an endothermic, in particular catalytic, reaction in accordance with the preamble of Claim 1, and to an apparatus in particular for performing this process.

One preferred field of use of the invention is the catalytic steam reforming of hydrocarbons for producing a hydrogen-rich gas. A mixture of steam, hydrocarbon and/or carbon dioxide serves as the process gas. This gas mixture is fed at temperatures of about 400 to 600 degrees C and at pressures of up to 4 MPa to a reaction chamber, which may consist of a plurality of catalyst-filled tubes, and is heated therein to approximately 750 to 900 degrees C. This gas mixture then reacts endothermically over the catalyst to form a hydrogen-rich gas with contents of carbon monoxide, carbon dioxide and excesses of steam and hydrocarbon. The hydrogen content of the product gas produced depends, inter alia, on the excess of the steam used and on the temperature and the pressure in the catalyst-filled tube. An increase in the excess of steam and in the temperature in the catalyst-filled tube brings about an increase in the recovery of hydrogen, whereas an increase in pressure results in a reduction in the same.

An apparatus for performing an endothermic catalytic reaction of a process gas stream is known from EP 0 194 067 B1. Said apparatus has a housing with one or more catalyst-filled tubes, each with a blind end, arranged parallel to one another therein. In the housing, there are provided means for supplying and removing a flue gas for heating the outer surface of the catalyst-filled tubes, through the interior of which the process gas stream is passed, absorbing heat.

The catalyst-filled tubes are each surrounded by a tubular casing, which forms an annular gap with the tube. The casing extends over the majority of the length of the catalyst-filled tube. The feed line for the flue gas is directed directly at the blind end of the catalyst-filled tube. The direct inflow of the hot flue gas into the catalyst-filled tube which this brings about proves disadvantageous, since this means that the thermal stress on the blind end of the catalyst-filled tube is very high. At critical points in the casing of the catalyst-filled tube, temperatures occur which are so high that it is damaged after a relatively short time and has to be replaced, if provision has not previously been made for corresponding cooling of the flue gas. This could be effected, for example, by a preceding heat exchanger or by mixing with already-cooled flue gas. Both measures require corresponding additional construction-related expense.

Furthermore, a process is known from EP-A-195 688 in which the reaction mixture is passed through two annular, concentrically arranged catalyst beds, and in so doing is heated indirectly by flue gases. To this end the flue gases are produced in a cylindrical combustion chamber which is arranged in the axial direction within the inner annular catalyst bed. The combustion chamber in this case consists of a ceramic material having - as is known - poor thermal conductivity. The hot gas emerges at the upper end of the chamber, and in this case too strikes the heat exchanger walls at this high temperature.

In order to moderate the thermal stress on the catalyst-filled tubes, it is known to provide them on the outside with a ceramic protective shell in the region of direct exposure to the hot flue gas. One

disadvantage of such protective coatings resides in the susceptibility to thermal expansion stresses, which lead to damage to the ceramic and then after merely a time delay to damage to the catalyst-filled tubes themselves as well.

It is an object of the invention to improve the heating of the process gas stream in a reaction chamber, which may in particular be constructed in the form of catalyst-filled tubes, such that the thermal stress on the walls of the reaction chamber, i.e. in particular on the catalyst-filled tubes in the region of the entry of the flue gas, is evened out and is reduced to a harmless amount, without costly measures being required for this purpose. In so doing, as beneficial a utilisation of energy as possible should be ensured. Furthermore, an apparatus for performing the heating process according to the invention should be provided.

This object is achieved by a process having the features of patent claim 1 and is advantageously developed by the characterising features of patent claim 2. An apparatus for performing this process is given in Claim 3. The characterising features of sub-claims 4 to 13 represent advantageous forms of the apparatus according to the invention.

Owing to the preferred use of the invention in catalytic processes, the reaction chamber will be described each time as a catalyst-filled tube below. This is not intended to indicate any restriction, since it is of no significance for the performance of the heating according to the invention whether the process is catalytic or not.

The basic concept of the invention consists in not bringing the hot flue gas which is supplied for heating

the reaction chamber, i.e. the catalyst-filled tubes, into direct contact with these tubes while the flue gas is still at a temperature which might damage the catalyst-filled tubes. Rather, it is initially passed
5 along the outside of a tubular barrier made of a heat-conducting, thermally resistant material, preferably of metal, is cooled in so doing, and, after being deflected, is passed on along the inside of this barrier in the opposite direction of flow.

10 It is only the flue gas which flows along the inside of the barrier and has already been somewhat cooled which comes into direct contact with the catalyst-filled tube and gives off heat thereto, thus cooling further. At the same time, the inner-flowing flue gas may however
15 absorb heat, via the heat-conductive barrier, from the hotter flue gas which is flowing past in a counter-current on the outside. Up to the point of deflection, the outer-flowing flue gas is thereby cooled to such an extent that it can come into direct contact with the
20 catalyst-filled tube without the risk of heat damage. The concept of the invention can therefore be perceived in that the heat of the hot flue gas supplied which is at the highest temperature level is not transmitted to the catalyst-filled tube directly but indirectly by
25 means of an intermediate heat exchange with already partially cooled flue gas. Therefore a heat exchange takes place between two partial sections of one and the same stream of flue gas. In order to lower the temperature of the flue gas to a non-harmful level,
30 with the solution according to the invention neither mixing with a cooler heat transfer medium nor an intermediate heat accumulator nor a costly external heat exchange is required. Rather, the installation of an extremely simple tubular, heat-resistant and heat-
35 conducting barrier is sufficient for this purpose. The principle of the solution according to the invention

can also be applied to apparatus in which a plurality of catalyst-filled tubes are located in a common housing.

5 In principle, a reverse arrangement is also possible, in which the flow channels for the flue gas are provided in the middle region of the apparatus and the reaction chamber is located on the outside around the flow channels. The heating process according to the invention can then be applied correspondingly.

10 The invention will be explained in greater detail below with reference to the embodiment illustrated in the drawings.

Fig. 1 shows a longitudinal section through an apparatus according to the invention,

15 Fig. 2 shows various temperature curves in an apparatus according to the invention compared with a conventional apparatus.

Figure 1 shows a diagram of an apparatus according to the invention for performing an endothermic catalytic reaction, e.g. for steam reforming of hydrocarbons. The reaction takes place in a catalyst-filled tube 1, which is substantially enclosed on the outside by a housing 4 and has various fittings on the inside. These fittings include a heat-conducting tube 21 which is closed at the top and open at the bottom, and a flow displacement tube 2, likewise closed at the top and open at the bottom, which is located coaxially in said tube 21. The catalyst substance is enclosed between the wall of the tube 1 and the heat-conducting tube 21 in an outer annular chamber 19. The reaction gas enters the catalyst-filled tube 1 via the connection 18 and flows downwards through the outer annular chamber

19 filled with catalyst substance to the closed end 3 of the tube 1. The product gas which has been produced under the action of the catalyst then rises upwards through a further inner annular chamber 20 formed between the heat-conducting tube 21 and the flow displacement tube 2 and leaves the catalyst-filled tube 1 at the top through the outlet 17. A heat exchange between the reaction gas flowing through the annular chamber 19 and the hotter product gas flowing through the annular chamber 20 takes place via the wall of the heat-conducting tube 21 which is located therebetween.

The heat required for the endothermic catalytic reaction is fed to the catalyst-filled tube 1 from outside by means of a hot flue gas. The flue gas enters the housing 4 via a flue gas inlet port 14. It is first distributed in an annular gap 15 which is closed at the bottom, which is formed by the housing 4 and a cylindrical liner tube 16. The flue gas leaves this annular gap 15 at the top via a flue gas inlet 5 constructed as a ring duct 13, and flows with a flow which is already very evenly distributed across the periphery into a second annular gap 11. The second annular gap 11 is formed between the liner tube 16 and a tubular body 7 which acts as a barrier and which has at its upper end 9 a gastight connection 12 to the housing 4. The flue gas flows downwards through the annular gap 11 along the tubular body 7, and reverses its direction of flow at the free end 8 of the tubular body 7. There, it enters an annular gap 10 which is formed between the catalyst-filled tube 1 and the tubular body 7 or the wall of the housing 4 respectively. The flue gas then passes upwards past the catalyst-filled tube 1 in this annular gap 10 and leaves the former in a distinctly cooled form through the flue gas outlet 6. Then it passes through a

secondary heat recovery stage (not shown) to the chimney.

On its journey through the annular gap 10, the flue gas continuously gives off heat through the wall of the tube 1 to the reaction gas flowing in a counter-current through the catalyst-filled tube 1. A further heat exchange takes place between the hot flue gas flowing downwards in the annular gap 11 and the already somewhat cooled flue gas which is flowing upwards in the annular gap 10, since the tubular body 7 located therebetween, which acts as a barrier, is formed of a heat-resistant, heat-conductive material, preferably of metal. This heat exchange results firstly in the hot flue gas, during its passage through the annular gap 11, being able to be cooled even before its first contact with the catalyst-filled tube 1 to a temperature which does not involve any further impermissible thermal stress for the tube 1. Secondly, the heat absorption of the flue gas in the lower part of the annular gap 10 leads to the flue gas temperature remaining at a relatively high level despite the loss of heat to the reaction gas, so that for a substantial length of the catalyst-filled tube 1 extremely beneficial conditions for heating (high heat transfer rate) are provided.

It has proved expedient to select the axial length L of the tubular barrier 7 such that it is about 0.1 to 0.7 times the heatable length S of the tube 1.

The apparatus according to the invention is of very simple construction, which if necessary permits exchange of individual parts without difficulty, since the individual parts are predominantly detachably connected together. For instance, the housing 4 consists of an upper, a middle and a lower part, which

are held together by means of two flanged connections. The liner tube 16, which is comparatively highly stressed by the flue gas temperature and the impinging flue gas flow, is made of refractory material and can readily be replaced if damaged. The same applies to the tubular barrier 7, which is preferably made of heat-resistant steel and in itself is not subjected to any substantial mechanical stresses, since it can expand freely downwards under the action of the hot flue gases. Such thermal stress would not be permissible for the catalyst-filled tube 1, since it is additionally under a considerable internal pressure due to the catalytic process. The selection of different diameters of the tubular barrier 7 yields a good possibility of influencing the heat exchange between the annular gaps 10 and 11, since the ratio of the free flow cross-sections of the two annular gaps is also changed with the diameter of the barrier 7. An increase in diameter therefore leads to a more rapid flow through the annular gap 11 and to a slowing of the flow in the annular gap 10, i.e. to a corresponding change in the heat exchange. Correspondingly, the heat exchange between the product gas and the reaction gas can also be influenced, by using a flow displacement tube 2 of different diameter. The function of this flow displacement tube 2 is to reduce the free cross-section of the inner annular chamber 20 sufficiently to guide the product gas along the wall of the heat-conducting tube 21 so closely that the desired cooling is achieved over the given overall length of the apparatus each time. The flanged connection in the upper part of the heat-conducting tube 21 means that the flow displacement tube 2 can be replaced without difficulty.

The heating process according to the invention ensures a deliberate lowering of the flue gas temperatures to a

non-critical level for the catalyst-filled tube, and, by means of the guidance of the flue gas through the annular gap 15, the ring duct 13, the annular gap 11 and the annular gap 10 shown in Figure 1, avoids [sic] an extremely even temperature distribution over the periphery, so that localised excessive thermal stresses can also be ruled out.

The effectiveness of the solution according to the invention can be seen from the temperature curves shown in Figure 2, each of which were measured along the heatable length S of a catalyst-filled tube in an apparatus according to the invention and, in comparison therewith, in a conventional apparatus for producing hydrogen by steam reforming of natural gas on various components and the stream of flue gas. The curve A1 shows the temperature curve of the flue gas which flows at a starting temperature of about 1500°C in the annular gap 11 downwards along the tubular barrier 7 for an apparatus according to the invention. When the lower end 8 of the barrier 7 is reached, it has been cooled to about 1100°C, and then flows through the annular gap 10 in the opposite direction, whereby cooling in accordance with curve A2 takes place. It can clearly be seen that the compensating effect of the heat exchange via the barrier 7 means that the cooling of the flue gas takes place comparatively slowly. Curve B shows the temperature along the length L of the tubular barrier 7, which falls from about 1175°C in the upper portion to about 1110°C in the lower portion. Owing to the lack of mechanical stress, such thermal stresses can be perfectly withstood by current high-temperature-resistant steels. The temperature curve in the tube wall of the catalyst-filled tube 1 is shown in curve C. Over the length L, this temperature is almost constant at about 900°C, and then drops initially very sharply to about 750°C, and then drops continuously to

about 550°C over a longer section. This makes it clear that the tube wall temperature in the catalyst-filled tube 1 can be kept at non-critical values over the entire length S. This would not have been possible at the same initial flue gas temperature of about 1500°C for a conventional apparatus, i.e. without the metal barrier 7 according to the invention, as curve D shows, since the lower portion of the catalyst-filled tube 1 would then heat up to about 1000°C. The temperature curve of the process gas which flows into the catalyst-filled tube at about 500°C can be seen as curve E. The direction of flow is symbolised by an arrow. The temperature curve of the product gas which flows off after the catalytic reaction is shown as curve F. It can be seen from the temperature drop from about 840°C to about 600°C that a large part of the heat contained in the product gas passes over to the incoming process gas.

In addition to its simple, inexpensive construction and the ease of maintenance which results therefrom, which makes it suitable particularly for use in miniaturised hydrogen-generating plants, the apparatus according to the invention yields numerous other advantages:

- The tube wall temperature of the catalyst-filled tube is kept at non-critical values.
- Despite differing calorific values of the fuels used for heating, the same tube wall temperature can be set on the catalyst-filled tube owing to corresponding configuration of the tubular barrier.
- In the region of the tubular barrier an extremely effective heat exchange takes place between the flue gas and the reaction gas.

- The evening-out of the flue gas flow means that localised overheating is avoided.
- The cooling of the product gas can be set to a desired value by selecting the diameter of the readily exchangeable flow displacement tube.
- The good utilisation of the heat of the flue gas means that the fuel consumption is reduced.
- The flanged connection between the heat-conducting tube and the catalyst-filled tube means that the catalyst can readily be replaced, without the catalyst-filled tube having to be dismantled for this purpose.

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List of items

No.	Designation
	1 Reaction chamber (catalyst-filled tube)
	2 Flow displacement tube
5	3 Closed end of the catalyst-filled tube
	4 Housing
	5 Flue gas inlet
	6 Flue gas outlet
	7 Tubular body (barrier)
10	8 Free end of the tubular body 7
	9 Upper end of the tubular body 7
	10 Annular gap
	11 Annular gap
	12 Gastight connection
15	13 Ring duct
	14 Flue gas inlet port
	15 Annular gap
	16 Cylindrical liner tube
	17 Outlet for product gas
20	18 Connection for reaction gas
	19 Outer annular chamber with catalyst filling
	20 Inner annular chamber
	21 Heat-conducting tube
	L Length of the tubular body
25	S Length of the heated, catalyst-filled tube

Claims

1. A process for indirectly heating a process gas stream in a reaction chamber for an endothermic, in particular catalytic, reaction, in which a hot flue gas flows around the walls of the reaction chamber on the surface located outside the reaction chamber, and the heat absorbed is given off to the process gas, in which the hot flue gas is first guided along a barrier formed from a heat-conductive and heat-resistant material, the flue gas giving off heat to this barrier and being guided further in the opposite direction on the opposite side of the barrier and not until then is brought into contact with the outside of the walls of the reaction chamber, the flue gas which is guided further in the opposite direction on one hand absorbing heat from the barrier and on the other hand giving off heat to the reaction chamber, characterised in that the hot flue gas is passed along a metal barrier and in so doing is cooled from a starting temperature around 1500 degrees celsius to a temperature in the region of 1100 degrees celsius which is not harmful to the walls of the reaction chamber without mixing with a cooler heat-transfer medium until it is deflected on to the other side of the barrier.

2. A process according to Claim 1, characterised in that the product gas produced from the process gas by the endothermic reaction is guided out of the reaction chamber in a counter-current to the incoming process gas stream, the process gas stream and the product gas stream being separated from one another by a heat-conductive partition and the product gas stream, in order to intensify a heat exchange between these gas streams, being guided along the partition with a flat flow cross-section.



3. An apparatus in particular for performing the process according to Claim 1, with a reaction chamber (1) which is formed in particular from at least one catalyst-filled tube and which is provided with fittings (heat-conducting tube (21)), has a closed end (3) and can be heated externally by a flue gas, and with a housing (4) which is provided with a flue gas inlet (5) and a flue gas outlet (6) and surrounds the reaction chamber (1) in the region of the external heating means, and with a tubular body (7) which surrounds the reaction chamber (1) at least over a partial length and has a first free end (8) and a second end (9) connected in gastight fashion to the housing (4), the free end (8) facing the closed end (3) of the reaction chamber (1) and the tubular body (7) forming a first annular gap (10) with the wall of the reaction chamber (1) and forming a second annular gap (11) with the housing (4), characterised in that the flue gas inlet (5) is located directly on the second annular gap (11) at a distance from the free end (8) of the tubular body (7) which consists of heat-conductive material.

4. An apparatus according to Claim 3, characterised in that the flue gas inlet (5) is located in the immediate vicinity of the second end (9) of the tubular body (7).

5. An apparatus according to Claims 3 or 4, characterised in that the tubular body (7) is made of metal.

6. An apparatus according to one of Claims 3 to 5, characterised in that the length (L) of the tubular body (7) is between 0.1 and 0.7 times the length (S) of the reaction chamber (1) which is located in the region of the external heating means.



7. An apparatus according to one of Claims 3 to 6, characterised in that the gastight connection (12) of the tubular body (7) to the housing (4) is a connection which can be dismantled.

5 8. An apparatus according to one of Claims 3 to 7, characterised in that the flue gas inlet (5) is connected, via a ring duct (13) arranged concentrically to the tubular body (7) in the wall of the housing (4), to a flue gas inlet port (14).

10 9. An apparatus according to Claim 8, characterised in that the ring duct (13) is connected to the flue gas inlet port (14) via a third annular gap (15) located in the wall of the housing (4).

15 10. An apparatus according to Claim 9, characterised in that the third annular gap (15) is limited on the inside by a cylindrical liner tube (16) in the wall of the housing (4).

20 11. An apparatus according to Claim 10, characterised in that the cylindrical liner tube (16) can be dismantled and is made of refractory material.

12. An apparatus according to one of Claims 3 - 11, characterised in that the fittings in the reaction chamber (1) comprise a central, coaxially arranged flow displacement tube (2) which is open on one side.

25 13. An apparatus according to one of Claims 4 - 12, characterised in that the housing (4) is a combination of a metal casing with an inner refractory lining.