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(54) **Title:** APPARATUS AND PROCESS FOR COOLING HOT GAS

(57) **Abstract:** The invention relates to an apparatus for cooling hot gas comprising a vertically oriented vessel (1) provided with a cooling medium compartment (2) comprising in use cooling medium, inlet means (3) to supply fresh cooling medium and outlet means (4) for discharge of used cooling medium, inlet means (5) for hot gas and outlet means (6) for cooled gas and one or more heat exchange tubes (7) positioned in the cooling medium compartment (2) and fluidly connecting the inlet (5) for hot gas and the outlet (6) for cooled gas, wherein at least part of at least one of the heat exchange tubes (7) is surrounded by a sheath tube (11) forming an annular space (12) between the heat exchange tube (7) and the sheath tube (11), and wherein the sheath tube (11) is open at its lower end and is provided with closing means (13) at its upper end. The invention also relates to a process for cooling hot gas to a temperature in a predefined temperature window using the above apparatus.



APPARATUS AND PROCESS FOR COOLING HOT GAS

Field of the Invention

The present invention relates to an apparatus for cooling hot gas which apparatus comprises a vessel provided with one or more heat exchanging tubes, the hot gas flowing through the said tube(s) and a cooling medium (e.g. water) flowing round the said tubes. The invention also relates to a process for cooling a hot gas using such apparatus.

Background of the Invention

Devices for cooling hot gas which comprise heat exchange tubes are well known in the art and widely used in industry. Such devices typically comprise a vessel with heat exchange tubes arranged therein. When in operation a cooling medium is present in the vessel and the outer wall of the heat exchange tubes are in direct contact with the cooling medium. The hot gas is then typically passed through heat exchange tubes. The tube walls absorb the heat from the hot gas and release this heat to the cooling medium. In order to find an optimum balance between size of the vessel and heat exchange surface provided by the outer walls of the heat exchange tubes, heat exchange tubes are often helically coiled.

When cooling hot gases, for example, hot gases obtained in the gasification of solid, liquid or even gaseous (hydro)carbon-containing fuels, the presence of small solid particles in the hot gas is inevitable. If not handled properly, such solid soot and/or ash particles could cause serious problems, such as fouling, erosion and corrosion of the heat exchange tubes. In case

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of fouling the solid particles will form a fouling layer at the inside of the tube, which will reduce the heat transfer and hence the heat exchange capacity of the cooling device. A consequence of such reduced heat exchange capacity is that the hot gas is insufficiently cooled which may have serious consequences for downstream treating and conversion processes, but also for equipment used. For example, the activity of a catalyst used in a downstream conversion processes may be adversely affected by temperatures which are too high. Likewise, materials used for downstream equipment should be able to withstand the often quite aggressive nature of the gas which could easily lead to corrosion. Corrosion-resistant materials are very expensive and to make the overall process economically viable, the use of such expensive materials should be limited as much as possible. Furthermore, even these expensive materials have their limitations: certain temperature limits cannot be exceeded, as this would lead to catastrophic metal dusting. High temperatures may also cause undesired side reactions. For example, in a synthesis gas manufacturing process high temperatures may cause methanation which is detrimental to the quality of the synthesis gas.

On the other hand, the temperature of the cooled gas leaving the cooling device should also not be too low, as this could go at the expense of heat recovery downstream of the cooling device. Typically the cooled gas at the outlet of the cooling device still contains sufficient heat to preheat other streams, e.g. the feed to the unit operation generating the hot gas upstream of the cooling device or any boiler feed water.

Accordingly, there typically is a certain operational window for the cooled gas outlet temperature which

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enables an optimum overall heat efficiency of the plant or process of which the cooling device forms part. The minimum temperature will be predominantly selected on the basis of process efficiency, in particular in relation to heat recovery, while the maximum temperature is determined mainly by mechanical design and material limits.

One way of mitigating the risk of too high outlet temperatures of the hot gas is to design additional heat exchange capacity into the heating device, typically by including additional heat exchange surface, that is, by means of additional heat exchange tubes or longer heat exchange tubes. However, the consequence of such additional heat exchange capacity is that during a substantial part of the lifetime of the heat exchange tubes - i.e. the period between two successive operations for cleaning or replacement of the heat exchange tubes - the outlet temperature of the cooled gas will be relatively low. This will result in less efficient heat integration and lower plant efficiency. Plant efficiency in this connection means heating value of the product compared with heating value of the feed. The difference is dissipated in the manufacturing process. When it concerns a (hydro)carbon feed, plant efficiency could also refer to the carbon number of the product relative to the carbon number of the feed. Finally, if the operational window of the outlet gas temperature is relatively small, the additional heat exchange capacity cannot be too high, as this would result in an outlet temperature below the lower limit of the operational window. As a result, the operation time of the cooling device may be limited, which in return would result in more frequent shutdowns of the cooling device and more

cleaning operations. Apart from the higher operating costs of such shutdowns and cleaning operations, the continuous operation of the plant in which the cooling device is used would necessitate that more cooling devices be arranged in parallel. This would also result in increased capital expenditure, which is economically unattractive.

An example of an industrial process in which an apparatus for cooling a hot gas by means of heat exchange is used, is the preparation of hot synthesis gas by partial oxidation of a (hydro)carbon-containing fuel. In such a process the hot raw synthesis gas from the partial oxidation reactor is typically cooled in a heat exchange cooling device located immediately after the partial oxidation reactor. The hot raw synthesis gas is cooled in such heat exchange cooling device with water as the cooling medium, thereby typically producing high pressure steam. An example of such device and partial oxidation process is disclosed in WO-2007/116045-A1. WO-2007/116045-A1 also discloses other prior art cooling devices.

Although the cooling device disclosed in WO-2007/116045-A1 adequately reduces fouling and ensures an effective heat transfer between the hot gas and the cooling medium in the main vessel, substantial additional heat exchange capacity in the form of additional and/or longer heat exchange tubes would still be required to ensure that the upper temperature limit of the cooled gas leaving the cooling device is not exceeded. As a consequence, the cooled gas outlet temperature, in particular in the early stages of operating the cooling device, will be at the low end of the operation window or even lower than desired. As indicated hereinbefore, this

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will result in a less optimal heat efficiency and lower overall plant efficiency.

The present invention aims to provide a cooling device which enables operation at a relatively small operational window, thus increasing the heat recovery efficiency, whilst at the same time providing the amount of additional heat exchange capacity required to avoid overshooting the upper temperature limit of the outlet cooled gas.

Summary of the Invention

The present invention relates to an apparatus for cooling hot gas comprising one or more heat exchange tubes located in a cooling medium compartment, wherein the heat exchange capacity is made variable by surrounding at least part of at least one of the heat exchange tubes by a sheath tube, thus forming an annular space between the heat exchange tube and said sheath tube, with the sheath tube being open at its lower end and being provided with closing means at its upper end. In this way the heat exchange capacity surface can be made variable by so called steam blanketing of part of the heat exchange tube when in operation and when using water as the cooling medium.

The present invention also relates to a process for cooling a hot gas by indirect heat exchange between the hot gas and a cooling medium using the cooling apparatus described above. In this process the annular space between the heat exchange tube and sheath tube is initially closed off by the closing means at the upper end of the sheath tube resulting in steam formation in said annular space. The steam expels the water out of the annular space through the open bottom end, thus forming a steam blanket in said annular space. Because of the low

heat conductivity and low heat absorption capacity of the stagnant steam in comparison with the heat conductivity and heat absorption capacity of flowing water, the overall heat transfer is reduced resulting in reduced heat exchange capacity of the cooling apparatus and hence in higher outlet temperatures of the cooled gas. When more heat exchange capacity is needed, the sheath tube is opened at its upper end, so that water can fill the annular space between the heat exchange tube and sheath tube, thereby increasing the surface of the heat exchange tube available for transferring heat from the hot gas inside the heat exchange tube to the water surrounding this tube and hence increasing the heat exchange capacity of the cooling apparatus. This will result in a lower outlet temperature of the cooled gas.

The apparatus and process of the present invention have as an important advantage that the heating surface (i.e. the surface of heat exchange tube available for exchanging heat between the hot gas inside the tube and the cooling medium surrounding the heat exchange tube) and thereby the heat exchange capacity is variable. As a result, the unit can be operated with a reduced heating surface to ensure high efficiency through maximum heat recuperation, while ensuring that the temperature of the outlet cooled gas will not exceed the upper limit of the operational window, thereby preventing damage to downstream equipment and possibly catalysts. And, finally, the flexibility in heat exchange capacity will also increase the lifetime of the internals of the cooling device.

Detailed description of the Invention

Accordingly, the present invention relates to an apparatus for cooling hot gas comprising a vertically

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oriented vessel (1) provided with a cooling medium compartment (2) comprising in use cooling medium, inlet means (3) to supply fresh cooling medium and outlet means (4) for discharge of used cooling medium, inlet means (5) for hot gas and outlet means (6) for cooled gas and one or more heat exchange tubes (7) positioned in the cooling medium compartment (2) and fluidly connecting the inlet (5) for hot gas and the outlet (6) for cooled gas, wherein at least part of at least one of the heat exchange tubes (7) is surrounded by a sheath tube (11) forming an annular space (12) between the heat exchange tube (7) and the sheath tube (11), and wherein the sheath tube (11) is open at its lower end and is provided with closing means (13) at its upper end.

When in operation there should be some circulation of cooling medium in cooling medium compartment (2) to ensure an effective heat exchange between the hot gas and the cooling medium. In one embodiment such circulation of cooling medium can be attained by separate means arranged externally of the cooling apparatus of the present invention. For example, when water is used as the cooling medium, such externally arranged means could comprise a steam drum having inlet means and outlet means fluidly connected with respectively a cooling medium outlet and a cooling medium inlet of the cooling apparatus. The water/steam mixture formed in the cooling apparatus is then passed via the cooling medium outlet of the cooling apparatus and inlet means of the steam drum into the steam drum where the steam is separated from the water. The resulting water is passed through cooling medium outlet of the steam drum and inlet means of the cooling apparatus into the cooling apparatus where it can again absorb heat from the hot gas via heat exchange. In this

way a circulation of the cooling medium can be effectively achieved. If the pressure differential between water and steam is sufficiently high, this differential will cause natural circulation of water between cooling device and steam drum. Otherwise a pump may be placed between the cooling device and steam drum to ensure that there is sufficient circulation of water inside the cooling device.

In a preferred embodiment of the present invention, however, the apparatus of the present invention comprises one or more downcomers (8) to ensure that, when in operation, there is an effective circulation of cooling medium inside the cooling medium compartment (2).

Typically from 1 to 6, suitably 1 to 3, downcomers (8) will be arranged inside the cooling compartment (2) in such embodiment. Those downcomers (8) will suitably be arranged symmetrically inside the cooling compartment (2). It was, however, found particularly effective to have the cooling medium compartment (2) comprise one single open ended downcomer (8) positioned vertically and centrally in cooling medium compartment (2) and one or more heat exchange tubes (7) positioned in the cooling medium compartment (2) in the space (9) between the downcomer (8) and the vessel wall (10). Although the use of multiple downcomers (8) is specifically included in the scope of this invention, the invention will be further described below with reference to the embodiment in which a single downcomer (8) is used.

The cooling medium most suitably used is water, although the use of an alternative cooling medium, for example water mixed with one or more other substances, is also possible. In further discussing and explaining the

cooling apparatus of the present invention, water will be referred to as the cooling medium.

The reference to "upper end" or "top end" in connection with the sheath tube (11) means the end part of the sheath tube closest to the top of the vertically oriented vessel (1). Likewise, the "lower end" of sheath tube (11) means the end part of the sheath tube (11) closest to the bottom of the vertically oriented vessel (1).

The hot gas to be cooled may be any hot gas. Applicant has found that the apparatus and process is particularly suited to cool hot synthesis gas, i.e. gases comprising carbon monoxide and hydrogen. Such synthesis gas is typically formed by reacting a (hydro)carbon feed, such as coal, residue oil, natural gas or biomass, with an oxidizing agent, such as oxygen, air or steam. It was found that the cooling apparatus according to the present invention is particularly suitable for cooling hot synthesis gas produced in a partial oxidation or POX process. In such POX process a methane comprising gas is reacted with an oxidizing gas, suitably oxygen or air, to form the hot synthesis gas.

Typically the hot gas to be cooled will have a temperature of up to 1500 °C. It was found that a hot gas of 1300 to 1500 °C can be effectively cooled to 250 to 500 °C, more suitably 330 to 450 °C, using the cooling apparatus of the present invention.

The heat exchange tubes (7) are suitably made of a material capable of resisting the high temperatures of the hot gas and, in the case of synthesis gas, the aggressive and acidic components that may be present in the synthesis gas. The tubes material may be low alloyed steel with 1 to 2.25 wt% chromium, chromium steel with 5

to 17 wt% chromium- or nickel-based alloys. When cooling synthesis gas, the skin temperature of the heat exchange tubes which come into contact with the hot gas, should suitably be maintained to a value of below 500 °C, more preferably below 450 °C. This is advantageous because by maintaining the skin temperature below these maximum values, the use of highly special and hence very expensive materials can be avoided. As is well known in the art, relevant parameters to control the skin temperature in addition to intensive cooling are tube diameter and velocity of the gas to be cooled: for a given hot gas mass flow larger diameter tubes result in lower velocities and hence in lower heat transfer. This, in return, will result in a lower skin temperature.

The hot gas inlet (5) and cooled gas outlet (6) are fluidly connected through at least one heat exchange tube (7). However, it is preferred to use two or more heat exchange tubes (7) which suitably run in parallel between inlet (5) and outlet (6). Generally between 2 and 24 tubes (7) run in parallel. If a downcomer (8) is present in cooling medium compartment (2), then these tubes (7) are preferably positioned around such downcomer (8) in parallel paths as ascending spirally shaped coils. Such spiral configuration could consist of one ascending cylinder of 1 to 10, preferably 3 to 8, spirally wound parallel heat exchange tubes (7) positioned around the downcomer (8). A configuration with two ascending cylinders, an outer cylinder and an inner cylinder, each consisting of 1 to 10, preferably 3 to 8, spirally wound heat exchange tubes (7), is also a suitable configuration. At the top end of such cylinder all heat exchange tubes (7) will suitably have a bend and become straight tubes extending vertically downwards in the

annular space between the (inner) cylinder of spirally shaped heat exchange tubes (7) and the downcomer (8) to the bottom part of vessel (1), where they will be fluidly connected to outlet (6).

5 Accordingly, in a preferred embodiment each heat exchange tube (7) comprises

(i) a spirally formed part (7a) fluidly connected to inlet means (5), and (ii) a further part (7b) fluidly connected to spirally formed part (7a) and outlet means
10 (6). If a downcomer (8) is present in the cooling medium compartment (2), then the spirally formed part (7a) is suitably positioned around downcomer (8) and the further part (7b) is suitably positioned in the annular space between the spirally formed part (7a) and such downcomer
15 (8). In this configuration it is preferred that the sheath tube (11) is positioned around at least part of the further part (7b) of at least one heat exchange tube (7). The further part (7b) may have any shape as long as it can extend downwardly in the annular space between the
20 spirally formed part (7a) and downcomer (8) and as long as sheath tube (11) can be positioned around at least part of it. For example, the further part (7b) can be curved or straight or have a curved part and straight part. Preferably, however, the further part (7b) is a
25 straight tube and extends vertically downward in said annular space. The length of the sheath tube (11) as well as the number of heat exchange tubes (7) around which such sheath tube is positioned may vary depending on the desired flexibility in heat transfer surface and heat
30 exchange capacity. The more sheath tubes used and the longer the sheath tubes are, the more the heat exchange capacity can be varied.

The length of a heat exchange tube (7) and total number of heat exchange tubes (7) used will depend on the heat exchange capacity needed to cool down the hot gas. The total heating surface is determined by the
5 temperature of the hot gas entering the cooling apparatus and the target temperature window of the cooled gas at outlet (6). Starting from the temperature ranges mentioned above for the hot gas and cooled gas a combination of 2 to 24, more preferably 6 to 17, heat
10 exchange tubes (7) each having a length of 30 to 90 metres, more preferably 40 to 60 metres, was found to be particularly suitable for the cooling apparatus of the present invention.

The inner diameter of the heat exchange tube (7) may
15 vary widely depending, for example, on gas velocity and heat transfer coefficient of the tube material used, but will typically be in the range of from 40 to 200 mm, more suitably 65 to 140 mm at inlet (5). An inner diameter of 90 to 130 mm at inlet (5) was found particularly
20 suitable. The inner diameter of tube (7) may be constant throughout the entire cooling device, but could also gradually decrease in the direction of outlet (6) to an inner diameter of between 1 and 0.4 times the inner diameter at inlet (5). Wall thickness of heat exchange
25 tube (7) may also vary and will, inter alia, depend on the type of material used, the length of the tube and the available space in cooling compartment (2). Typically a wall thickness of between 2 and 15 mm can be used, more suitably between 4 and 12 mm. A wall thickness of between
30 5 and 10 mm was found to be particularly suitable. Also the wall thickness may be constant throughout the entire cooling apparatus, but could also gradually decrease in the direction of outlet (6), particularly if the inner

diameter of the heat exchange tube (7) is also gradually decreasing.

When positioned in a cylinder configuration around the downcomer (8), the height of the cylinder will obviously be determined by number, outer diameter and length of the heat exchange tubes (7), which in return is determined by the total heating surface needed to cool the hot gas to the target temperature window.

In general, a cylinder of the spirally formed parts (7a) of heat exchange tubes (7) will have a height of between 2 and 12 metres, more suitably between 3 and 8 metres. The further part (7b) will, accordingly, be slightly longer and will typically have a length of between 3 and 11 metres, more suitably between 4 and 9 metres. However, different lengths may be used depending on the size of the vessel (1).

The sheath tubes (11), when positioned around the, preferably straight, further part (7b) of heat exchange tube (7), will obviously have a larger inner diameter than the outer diameter of heat exchange tube (7) to form the annular space (12). Typically the inner diameter of the sheath tube will be 16 to 80 mm wider than the outer diameter of the heat exchange tube (7) around which it is positioned, resulting in the annular space (12) having a width of from 8 to 40 mm. More suitably, the annular space (12) has a width between 10 and 25 mm. The length of the sheath tube (11) will depend on the length of the further part (7b) of heat exchange tube (7).

The sheath tube (11) may be fabricated from a lower grade material with lower wall thickness compared to the heat exchange tube (7) or be made of the same material with a lower or the same wall thickness.

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The sheath tubes (11) at their top end are provided with closing means (13). Such closing means (13) should be capable of closing the sheath tube (11) at the top end, thereby closing the annular space (12) between heat exchange tube (7) and sheath tube (11). As explained above, any liquid cooling medium present in such annular space will evaporate when the cooling device is in operation, thereby insulating the heating surface and hence reducing the heat exchange capacity resulting in higher gas outlet temperatures at outlet (6). In one preferred embodiment the closing means (13) consist of a closed metal disk (14) fixed to the outer wall of heat exchange tube (7) and top end of sheath tube (11), i.e. at the top end of the annular space (12). The closed metal disk (14) is suitably welded to the outer wall of heat exchange tube (7) and the top end of sheath tube (11), but could also be fixed in other ways, for example by clamps welded to the top end of sheath tube (11).

In another preferred embodiment of the present invention the closing means (13) consists of a metal disk (14) with at least one opening (16) fluidly connected to a vertical pipe (17) extending upwardly. If one or more downcomers (8) are present in the cooling compartment (2), the vertical pipe (17) will extend to above the top ends of all downcomers (8). This vertical pipe (17) would, however, remain below the water level in cooling medium compartment (2) when in operation. The vertical pipe (17) can be provided at its top end by closing means. For example, a suitable embodiment would be that the vertical pipe (17) ends in a welded neck flange, closed with a blind flange, thereby effectively closing off annular space (12) and creating a steam blanket in annular space (12) when in use. By removing this blind

flange the water/steam mixture from the annular space (12) can mix with the cooling water in cooling medium compartment (2), thereby creating an upward flow of water/steam and hence increasing the heat exchange capacity.

In a further preferred embodiment of the present invention the closing means (13) consist of a metal disk (14) with at least one opening (16) fluidly connected to an upwardly extending vertical pipe (17), the top end of which would, however, remain below the water level in cooling medium compartment (2) when in operation, wherein the upper end of said vertical pipe (17) can be closed and opened by a control valve. Such valve can suitably be controlled remotely in order to control the steam blanketing in the annular space (12) and hence the heat exchange capacity and outlet temperature of the cooled gas. In this embodiment the cooling apparatus does not have to be taken offline to adjust the heating surface.

The cooling apparatus will also suitably comprise means which make it possible to measure or otherwise determine the temperature. Such means are well known in the art and include, for example, thermocouples. Such means will typically be positioned just before or at hot gas inlet (5) and at or just after cooled gas outlet (6) to determine and monitor the temperature of the hot gas before and after cooling. Means for measuring and monitoring the temperature of the hot gas could also be installed inside the cooling device.

The present invention also relates to a process for cooling a hot gas to a temperature in a predefined temperature window by using the apparatus as described above comprising the steps of

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- (a) starting up the apparatus with annular space (12) of at least one heat exchange tube (7) being closed off by closing means (13) by filling the cooling medium compartment (2) with cooling water via inlet means (3) and starting to pass hot gas through all heat exchange tubes (7);
- (b) operating the apparatus by continuing to pass hot gas through all heat exchange tubes (7);
- (c) opening closing means (13) of at least one sheath tube (11), when the temperature of the cooled gas leaving the outlet means (6) reaches the upper limit of a predefined temperature window, to lower the temperature of the cooled gas to a temperature within the predefined temperature window;
- (d) repeating step (c) until all closing means (13) are opened; and
- (e) shutting down the apparatus by discontinuing the flow of hot gas through heat exchange tubes (7), when the temperature of the cooled gas leaving the outlet means (6) reaches the upper limit of the predefined temperature window.

In step (a) the cooling medium compartment (2) is filled with water. If one or more downcomers (8) are present in the cooling medium compartment (2), filling will take place until the water level is above the upper end of each downcomer (8). If no such downcomer (8) is present, then the water level will be such that the heat exchange tubes (7) are sufficiently immersed in water to provide the heat exchange capacity required. In step (a) the closing means (13) of all sheath tubes (11) are closed, so that all annular spaces (12) are filled with water. As soon as the hot gas starts to flow through heat exchange tubes (7), the water in the annular spaces (12)

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starts to heat up until it becomes steam. The steam thus formed expels the water from the annular spaces (12) at the bottom openings of the sheath tubes (11) and steam blankets are formed in the annular spaces (12). Whilst
5 operating the process in step (b) by continuing to pass hot gas through heat exchange tubes (7), the aforesaid steam blankets cause the heating surface and hence heat exchange capacity to be reduced. As the fouling in the heat exchange tubes (7) increases, the heat exchange
10 capacity is reduced and the temperature of the cooled gas at outlet (6) rises. When this temperature reaches the upper limit of the pre-defined operation temperature window, the heating surface needs to be increased to lower the cooled gas outlet temperature. This is attained
15 in step (c) by opening the closing means (13) of at least one sheath tube (11).

If the closing means (13) consist of a closed metal disk (14) welded to the heat exchange tube (7) and sheath tube (11) at the top end of the annular space (12), then
20 steps (c) and (d) are combined by taking the cooling apparatus offline. This is achieved by discontinuing the flow of hot gas. After the apparatus has sufficiently cooled down, the closed metal disks (14) are removed and the apparatus is put online again. The annular space (12)
25 is now open at both ends, so that no steam blanket is formed in annular space (12) and the heating surface remains at its maximum capacity, thereby lowering the temperature of the cooled gas at outlet (6). Likewise, if the closing means (13) consist of a metal disk (14) with
30 at least one opening (16) fluidly connected to a vertical pipe (17) extending upwardly to above the upper end of downcomer (8) with its top end remaining below the water level (18) in cooling compartment (2) when in operation

and closed off by a blind flange. By removing the blind flange after the apparatus has been taken offline and has cooled down, the annular space is effectively opened and filled with water. As a result, heating surface is increased and the temperature of the cooled gas at the outlet (6) decreases after the apparatus is put online again.

If the closing means (13) can be controlled remotely by a valve, then steps (c) and (d) can be distinct steps and involve opening valves to create additional heating surface to lower the cooled gas outlet temperature.

When all heat exchange surface is made available and the outlet temperature of the cooled gas reaches the upper limit of the predefined temperature window, then in step (e) the cooling apparatus is taken offline for cleaning the heat exchange tubes and suitably for closing the closing means (13) again.

The cooling apparatus and process of the invention as described above are particularly suitable for cooling hot synthesis gas. Such synthesis gas can be produced by processes known in the art, for example by partial oxidation of (hydro)carbon comprising feedstocks. Examples of such feedstocks include coal, oil residues, oil and methane-comprising gases, such as natural gas. For such synthesis gas, the predefined temperature window for the cooled gas leaving the cooling apparatus at outlet (6) is suitably in the range of from 250 to 500 °C, more suitably 330 to 450 °C.

Most suitably, however, the cooling apparatus and process of the invention as described above are used for cooling hot synthesis gas prepared by partial oxidation of a methane-comprising gas. Such partial oxidation (or POX) process is a well known process for producing

synthesis gas. Such POX process can take place in the presence of a suitable reforming catalyst or in the absence of a catalyst. Generally, in a POX process a methane comprising gas reacts with an oxidising gas in an exothermic reaction to form a gas comprising carbon monoxide and hydrogen (i.e. synthesis gas). Publications describing examples of POX processes are EP-A-291111, WO-A-97/22547, WO-A-96/39354 and WO-A-96/03345.

The methane comprising gas used as the feedstock to the POX process may be natural gas, associated gas or a mixture of C₁₋₄ hydrocarbons. The feed comprises mainly, i.e. more than 90 volume percent (% v/v), especially more than 94% v/v, C₁₋₄ hydrocarbons, and especially comprises at least 60% v/v methane, preferably at least 75% v/v, more preferably at least 90% v/v. Very suitably natural gas or associated gas is used.

The oxidising gas used may be oxygen or an oxygen-containing gas. Suitable gases include air (containing about 21 percent of oxygen) and oxygen enriched air, which may contain at least 60 volume percent oxygen, more suitably at least 80 volume percent and even at least 98 volume percent of oxygen. Such pure oxygen is preferably obtained in a cryogenic air separation process or by so-called ion transport membrane processes. The oxidising gas may also be steam.

The POX process is typically carried out in a partial oxidation reactor. This can be a catalytic or non-catalytic POX process. When carried out in the absence of a catalyst such partial oxidation reactor typically comprises a burner placed at the top in a reactor vessel with a refractory lining. The reactants are introduced at the top of the reactor. In the reactor a flame from the burner is maintained in which the methane comprising feed

gas reacts with the oxygen or oxygen-containing gas to form a syngas. Reactors for catalytic POX processes usually comprise a burner at the top and one or more fixed beds of suitable catalyst to react the methane in the feed with the oxygen added to the top of the reactor to form a syngas.

Non-catalytic POX processes are well known. The raw synthesis gas produced typically has a temperature of between 1100 and 1500 °C, suitably between 1200 and 1400 °C. The pressure at which the synthesis gas product is obtained may be between 3 and 10 MPa and suitably between 5 and 7 MPa. In addition to the oxygen-containing gas, steam may also be added.

The synthesis gas produced in a POX process and subsequently cooled in the cooling apparatus and process of the present invention may suitably be converted into methanol by well known processes. Alternatively, the synthesis gas can be converted into hydrocarbon products in a Fischer-Tropsch process. The Fischer-Tropsch (FT) process is well known in the art as a catalytic process for synthesizing longer chain hydrocarbons from carbon monoxide and hydrogen. It may be operated in a single pass mode ("once through") or in a recycle mode and could involve a multi-stage conversion process, which may involve, two, three, or more conversion stages.

Brief description of the drawings

Figure 1 shows a schematic drawing of an apparatus according to the present invention.

Figure 2 shows an embodiment for closing off a sheath tube (11).

Figure 3 shows a further embodiment for closing off a sheath tube (11).

Detailed description of the drawings

As shown in Figure 1 the hot gas enters the cooling vessel (1) via inlet (5) through heat exchange tubes (7) which are fixed in support plate (21). The hot gas passes through the heat exchange tube (7) into the spirally shaped part (7a) and subsequently through straight further part (7b) towards outlet (6), where the cooled gas leaves vessel (1). The spirally formed part (7a) of heat exchange tube (7) is positioned around the open-ended downcomer (8) which is centrally positioned in cooling medium compartment (2) and would typically be mounted to the inner wall (10) of vessel (1) via spacers (not shown). The downcomer (8) and heat exchange tube (7) are in use submersed in water (or another liquid cooling medium) present in cooling compartment (2). Saturated steam is collected above the water level (18) in saturated steam collection space (19). Figure 1 shows a demister (20). This is an optional feature. Demister (20) separates the saturated steam collection space (19) from a demisted steam collection space (21), from which the used cooling water is discharged via outlet (4) as demisted steam. Demister means (20) are well known in the art and may be used in the apparatus according to the present invention to remove any liquid water droplets from the saturated steam collected in saturated steam collection space (19). For example, the demister (20) may be a demister mesh, a vane pack or a swirl tube cyclone deck.

In use cooling medium having a relatively low temperature and thus high density (e.g. water) will flow downwards inside said downcomer (8). When passing the bottom end of downcomer (8) the cooling medium will again

start flowing upwards through the space (9) between the downcomer (8) and the vessel wall (10). In this, preferably annular, space (9) the cooling medium will contact the heat exchange tube (7) as positioned in said space (9) and absorb heat. The thus heated cooling medium which will also comprise bubbles of evaporated cooling medium, i.e. steam in case the heating medium is water, will have a relatively low density and will by consequence have an upwardly flow direction. Thus a circulation of cooling medium is created and enhanced because of the downcomer (8). Fresh cooling medium is added to cooling compartment (2) via inlet means (3).

In Figure 1 part of the straight further part (7b) of heat exchange tube (7) is surrounded by sheath tube (11) resulting in annular space (12) which is closed off by closing means (13) at the top end of sheath tube (11). As explained hereinbefore, when in use a steam blanket will form in said annular space (12) resulting in a reduced heating surface and higher temperature of the cooled gas at outlet (6). After opening of closing means (13), e.g. by removing it, the annular space (12) will be filled with liquid cooling medium and the heating surface will increase, resulting in lowering of the temperature of the cooled gas at outlet (6).

Figure 2 shows an embodiment, wherein closing means (13) consists of a closed metal disk (14) welded to the outer wall of the straight further part (7b) of a heat exchange tube (7) and top end of sheath tube (11), thus closing off the top end of the annular space (12).

Figure 3 shows an embodiment similar as in Figure 2, but wherein the metal disk (14) contains an opening (16) which is fluidly connected to a vertical pipe (17). This vertical pipe (17) will typically extend to above the

upper end of downcomer (8) but will remain below water level (18) when in operation (not shown in this figure).

Example

5 The effect of varying the heat surface length of heat exchange tubes (7) in a cooling device with a design as schematically shown in Figure 1 was determined. Starting point for the calculations was a design with heat exchange tubes (7) arranged around single downcomer (8),
10 each heat exchange tube consisting of a spirally formed part (7a) and a straight further part (7b) . The heat exchange tubes (7) were arranged such that the spirally formed parts (7a) formed a cylinder of six parallel syngas paths around the downcomer (8) and the straight
15 further parts (7b) were located in the annular space between downcomer (8) and said cylinder. Total length of each heat exchange tube (7), including inlet bend at inlet (5) and outlet connecting line at outlet (6), is 57.5 metres, total height of the cylinder is 5 metres. At
20 inlet (5) the outer diameter of each heat exchange tube (7) is 133 mm, which gradually decreases to 89 mm at outlet (6). Wall thickness is 6.3 mm.

 Syngas temperature when entering the heat exchange tube (7) at inlet (5) is 1350 °C.

25 Heat exchange capacity of the outer surface of heat exchange tube (7) is 30,000 W/m²K (evaporation cooling). This is reduced to 100 W/m²K, when using a sheath tube (11) closed at its top end in operation.

 Sheath tubes (11) (outer diameter 133 mm, wall
30 thickness 6.3 mm) of various lengths and closed at their top end were used. Table 1 shows the temperature of the cooled synthesis gas at outlet (6) at various lengths of sheath tube (11). The length of the sheath tube

corresponds with a reduction in available heating surface and hence a reduction in heat exchange capacity.

Table 1 - Effect of heating surface length variation

5

Sheath tube length (m)	0	3	5	7
Outlet temperature (°C)	400	414	423	434

As can be seen from Table 1 the outlet temperature of the synthesis gas can be effectively controlled by using sheath tubes of various lengths.

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C L A I M S

1. Apparatus for cooling hot gas comprising a vertically oriented vessel (1) provided with a cooling medium compartment (2) comprising in use cooling medium, inlet means (3) to supply fresh cooling medium and outlet means (4) for discharge of used cooling medium, inlet means (5) for hot gas and outlet means (6) for cooled gas and one or more heat exchange tubes (7) positioned in the cooling medium compartment (2) fluidly connecting the inlet (5) for hot gas and the outlet (6) for cooled gas, wherein at least part of at least one of the heat exchange tubes (7) is surrounded by a sheath tube (11) forming an annular space (12) between the heat exchange tube (7) and the sheath tube (11), and wherein the sheath tube (11) is open at its lower end and is provided with closing means (13) at its upper end.
2. Apparatus according to claim 1, wherein the cooling medium compartment (2) comprises one or more open ended downcomers (8) positioned vertically in cooling medium compartment (2).
3. Apparatus according to claim 2, wherein the cooling medium compartment (2) comprises one open ended downcomer (8) positioned vertically and centrally in cooling medium compartment (2) and wherein the one or more heat exchange tubes (7) are positioned around the downcomer (8) in the cooling medium compartment (2) in the space (9) between the downcomer (8) and the vessel wall (10).
4. Apparatus according to any one of claims 1-3, wherein at least one heat exchange tube (7) comprises
- (i) a spirally formed part (7a) fluidly connected to inlet means (5), and

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(ii) a further part (7b) fluidly connected to spirally formed part (7a) and outlet means (6).

5. Apparatus according to claim 4 and claim 2 or 3, wherein

5 the spirally formed part (7a) of each heat exchange tube (7) is positioned around a downcomer (8) and the further part (7b) is positioned in the annular space between the spirally formed part (7a) and the downcomer (8).

6. Apparatus according to any one of claims 2-5, wherein
10 the sheath tube (11) is positioned around at least part of the further part (7b) of at least one heat exchange tube (7).

7. Apparatus according to any one of claims 1-6, wherein the closing means (13) comprises a closed metal disk (14)
15 fixed to the outer wall of heat exchange tube (7) and top end of sheath tube (11).

8. Apparatus according to any one of claims 1-6, wherein the closing means (13) comprises a metal disk (14) with at least one opening (16) fluidly connected to an
20 upwardly extending pipe (17).

9. Apparatus according to claim 8, wherein the upper end of the upwardly extending pipe (17) comprises a remotely controllable valve for opening and closing said pipe (17).

25 10. Process for cooling a hot gas to a temperature in a predefined temperature window by using the apparatus according to any one of claims 1-9 comprising the steps of

(a) starting up the apparatus with annular space (12) of
30 at least one heat exchange tube (7) being closed off by closing means (13) by filling the cooling medium compartment (2) with cooling water via inlet means (3)

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and starting to pass hot gas through all heat exchange tubes (7);

(b) operating the apparatus by continuing to pass hot gas through all heat exchange tubes (7);

5 (c) opening closing means (13) of at least one sheath tube (11), when the temperature of the cooled gas leaving the outlet means (6) reaches the upper limit of a predefined temperature window;

10 (d) repeating step (c) until all closing means (13) are opened; and

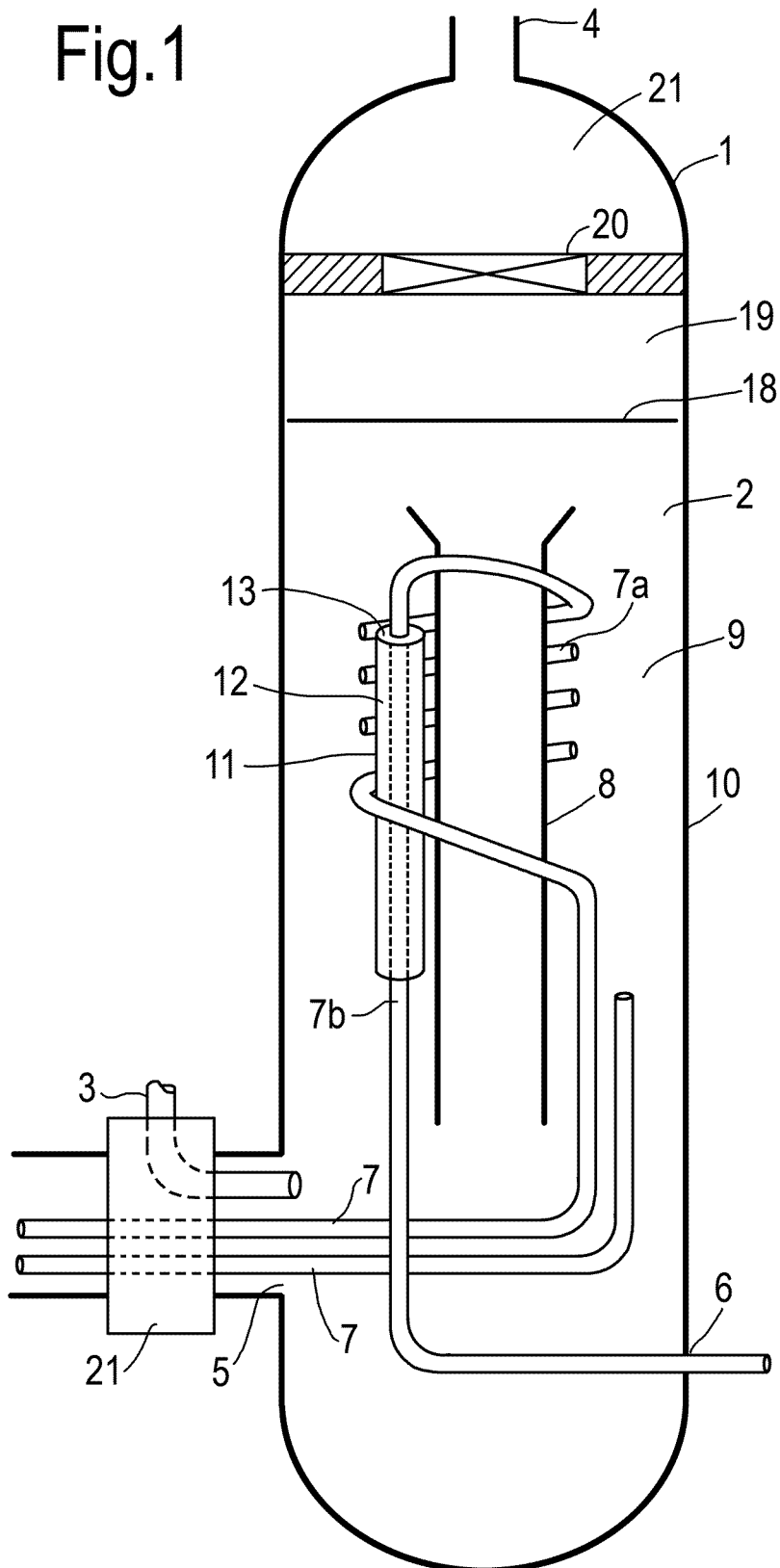
(e) shutting down the apparatus by discontinuing the flow of hot gas through heat exchange tubes (7), when the temperature of the cooled gas leaving the outlet means (6) reaches the upper limit of the predefined temperature window.

15 11. Process according to claim 10, wherein the hot gas is synthesis gas and the predefined temperature window is 330 to 450 °C.

20

1/2

Fig.1



2/2

Fig.2

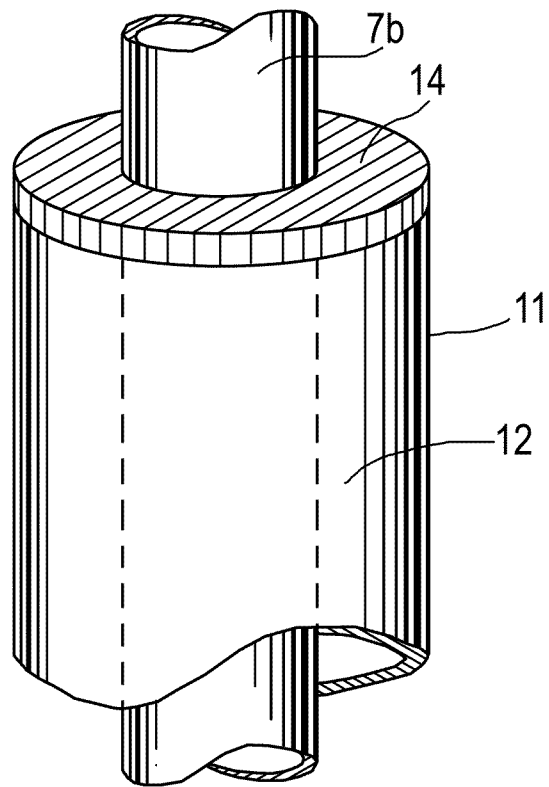
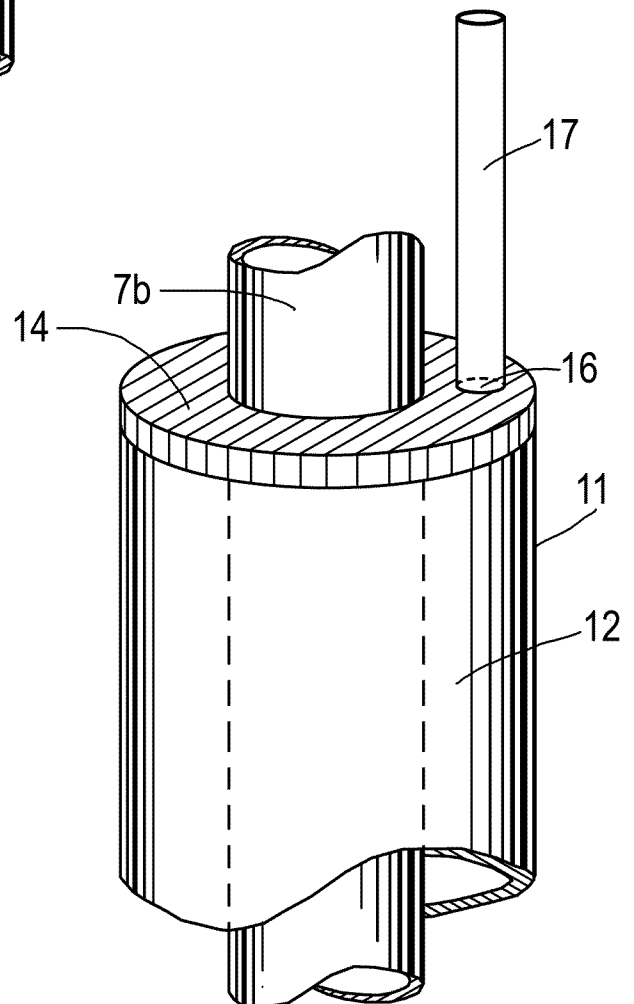


Fig.3



INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2015/064351

A. CLASSIFICATION OF SUBJECT MATTER
INV. C10J3/84 F28F13/14
ADD.

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)
C10J F28F F28D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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

EPO-Internal, WPI Data

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A	page 6, line 9 - page 8, line 22; claim 1; figure 1	10,11
Y	GB 2 053 444 A (WESTINGHOUSE ELECTRIC CORP) 4 February 1981 (1981-02-04)	1-9
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	-/--	



Further documents are listed in the continuation of Box C.



See patent family annex.

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INTERNATIONAL SEARCH REPORT

International application No

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
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