United States Patent [19] [11] **3,788,281**
Van Lookeren Campagne [45] **Jan. 29, 1974**

[54] **PROCESS AND WASTE-HEAT BOILER FOR COOLING SOOT-CONTAINING SYNTHESIS GAS**

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[73] Assignee: **Shell Oil Company**, New York, N.Y.

[22] Filed: **Mar. 19, 1973**

[21] Appl. No.: **342,670**

[30] **Foreign Application Priority Data**
Mar. 27, 1972 Netherlands 7204070

[52] **U.S. Cl.** .... **122/7 R,** 165/163
[51] **Int. Cl.** **F22b 1/06**
[58] **Field of Search** .... 122/7 R, 32, 33; 165/163

[56] **References Cited**

UNITED STATES PATENTS

2,967,515	1/1961	Hofstede et al.	122/7
3,662,717	5/1972	Haar	122/7
3,712,371	1/1973	Haar et al.	165/163

FOREIGN PATENTS OR APPLICATIONS

634,687	1/1962	Canada	122/7

Primary Examiner—Kenneth W. Sprague

[57] **ABSTRACT**

Hot, soot-containing synthesis gas obtained by the incomplete combustion of carbonaceous fuels is cooled and heat abstracted therefrom in a waste-heat boiler containing one or more helically coiled tubes through which the hot gas is passed and one or more additional tubes through which steam is passed, said tubes being in external, heat-exchanging contact with a molten metal, metal alloy or metal salt coolant medium. The disclosed process and apparatus permit the generation of high pressure, superheated steam from synthesis gas while avoiding excessive pressure differences across the helically coiled gas tubes.

16 Claims, 2 Drawing Figures

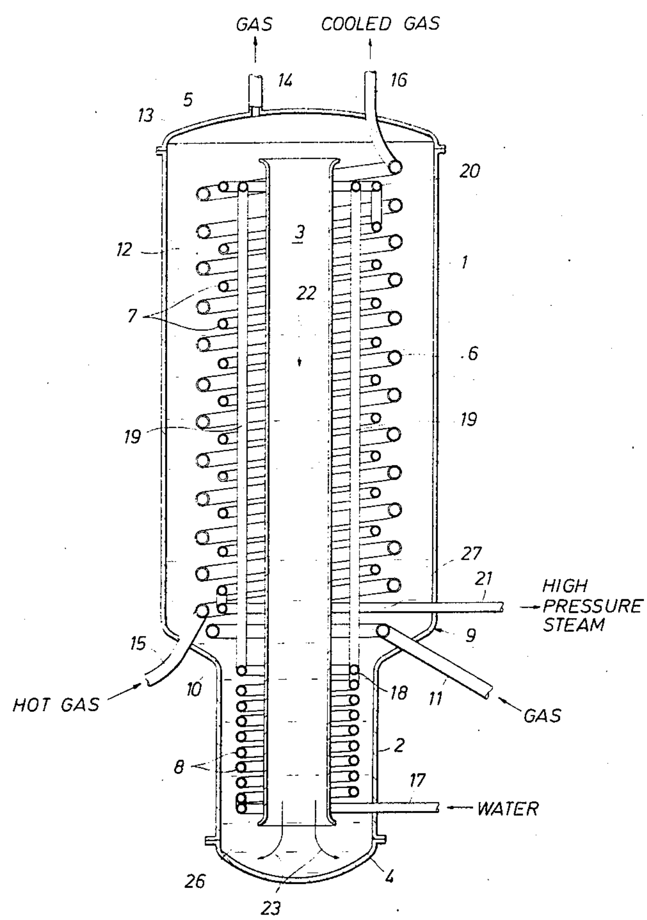
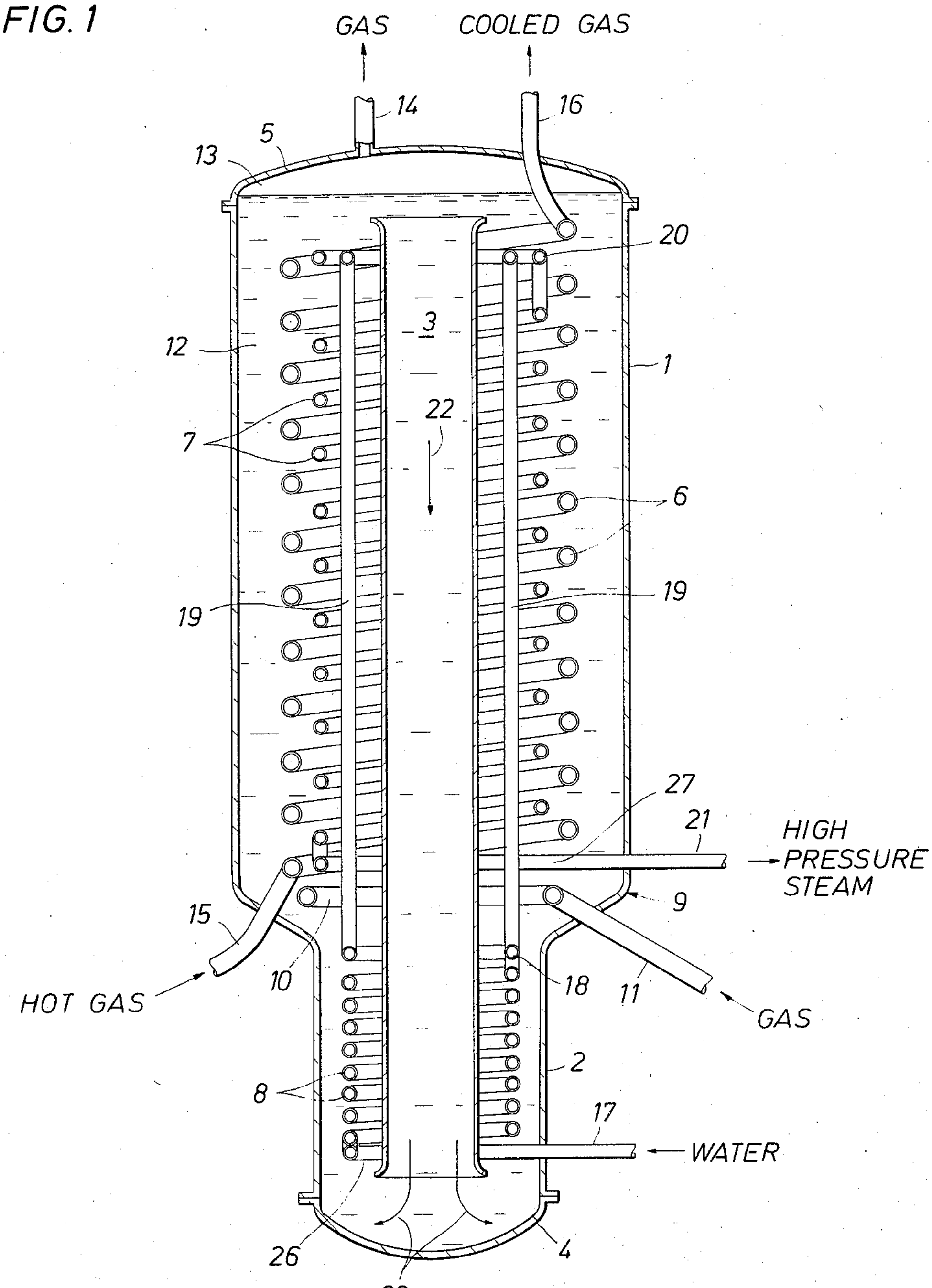


FIG. 1


GAS
COOLED GAS
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WATER
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4
23

PROCESS AND WASTE-HEAT BOILER FOR COOLING SOOT-CONTAINING SYNTHESIS GAS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to an improved process for cooling and abstracting heat from soot-containing synthesis gas obtained by the incomplete combustion of a fuel containing free and/or bound carbon with the simultaneous generation of high pressure steam. The invention also relates to a waste-heat boiler suitable for carrying out the process.

2. Description of Prior Art

Processes for the partial combustion of carbonaceous fuels to produce a hydrogen an carbon monoxide containing gas are well known. Fuels suitable for use in such processes include, for example, gaseous hydrocarbons, naphthas, heavy oils and solid fuels, e.g., coal in an aqueous slurry, and the like. The fuel may also contain process soot which has been separated from the synthesis gas.

The crude synthesis gas produced by partial combustion of the aforementioned fuels typically contains in addition to large quantities of hydrogen and carbon monoxide, a smaller quantity, up to 5% or more of suspended soot particles. Since the crude synthesis gas is generally discharged from the reactor at temperatures above 1,000° C, e.g., 1,200° to 1,400° C or more, it is an obvious source of potential energy. However, this thermal energy can be recovered only with great difficulty in conventional waste-heat boilers because of the presence of soot particles which tend to deposit on the inside of heat exchanger tubes. For this reason helically coiled waste-heat boilers, such as those described in U.S. Pat. No. 2,967,515, and Can. Pat. No. 634,687 to Hofstede et al. and U.S. Pat No. 3,712,371 to Ter Haar et al., are frequently used to cool and abstract heat from hot synthesis gas, since helically coiled tubes are less prone to soot deposition and in addition are less subject to dilatation problems resulting from temperature fluctuation because of the inherent resilience in the helical design.

While effective in overcoming the soot deposition problem, the use of helically coiled tubes place certain other limitations on the process with respect to permissible pipewall temperatures and the pressure differential between the cooling medium and the gases to be cooled. These limitations result from the lower mechanical strength of helically coiled tubes due to their method of manufacture. Generally, coiled tubes are formed by winding straight tubes which produces unroundness which in turn appreciably reduces the mechanical strength of the coiled tubes. Because of this decreased strength, helically coiled tubes are not well-suited for the generation of steam at high pressures, e.g., 50 to 150 atmospheres or higher, from hot gases having moderate or low pressures because of the excessive difference in pressure between the coolant (typically water or steam) on the outside of the coiled tube and the pressure of the hot gases flowing through the tube. Moreover, high tubewall temperatures are often experienced which also contribute to tube failures.

Previously mentioned U. S. Pat. No. 3,712,271 discloses one suitable method for cooling hot synthesis gas and generating high pressure steam in a coiled tube-type waste-heat boiler which involves utilizing a

straight tube of critical length in conjunction with the coiled tube, and controlling the velocity of the gases flowing through the tubes. The present invention is directed to a quite different approach to this problem which utilizes a molten coolant medium to indirectly transmit heat from the hot gases to the water/steam which permits the generation of superheated steam at very high pressures while avoiding excessive pressure differences across the helically-coiled tubes.

SUMMARY OF THE INVENTION

It has now been found that in a process for cooling and recovering heat from a hot, soot-containing gas synthesis gas obtained by the partial combustion of a carbonaceous fuel, by flowing the gas through a helically-coiled tube, which is in external contact with a coolant medium, that high pressure steam, above **50** atmospheres, e.g., 50 to 150 atmospheres or higher, can be generated with a substantially reduced risk of tube failure by employing as the coolant medium a metal metal, metal alloy, or metal salt, and effecting the cooling by indirect heat exchange with steam flowing through a separate tube which is also in external contact with the coolant medium. The coolant medium used in accordance with the invention has a high boiling point, e.g., higher than the temperature prevailing in the waste-heat boiler and thus remains in liquid phase. In practice, the temperature of the coolant medium will rise and fall in a range which is generally between 300° and 850° C. Preferably the pressure above the coolant medium is maintained at a pressure in the same order as that of the synthesis gas flowing through the helically coiled tube. This can be accomplished by use of an inert gas or a portion of the synthesis gas as hereinafter discussed. The inventive process and apparatus are eminently suitable for cooling synthesis gas obtained over a relatively wide range of pressures, e.g., 1 to 150 atm., more typically 25–60 atm.

DESCRIPTION OF EMBODIMENTS

The coolant medium employed in accordance with the invention can be any metal, metal alloy or metal salt or any other molten substance which has a sufficiently low melting point that it does not involve handling difficulties, e.g., a melting point or range below 420° C, and a sufficiently high boiling point that it remains substantially in liquid phase at the temperature prevailing in the waste-heat boiler, e.g., 350°–850° C. Examples of suitable metals include, lead, bismuth, cadmium, gallium, indium, mercury, selenium, thallium, tellurium and zinc. Alloys of these elements among themselves and/or with other elements can also possess the right properties for the coolant sought. Bismuth, indium, thallium, lead, gallium and tellurium have the advantage of a high boiling point (in the case of tellurium 1,390° C and in the other cases even higher) so that the vapor pressure at the operating temperatures in the waste-heat boiler will be low.

As is known, alloys do not have a solidification point, but a solidification range. Segregation phenomena, such as may occur in molten alloys, are obviated by circulation of the coolant as hereinafter described. Very attractive alloys include those in which the component elements are present in certain eutetic percentages so that intermetallic compounds are formed which have a lower melting point or melting range than the component metal. The alloys should preferably be completely miscible. Of the aforementioned metals and metal alloys, molten lead and molten lead alloys are particularly preferred.

Since the molten coolant medium employed in the present invention has a high boiling point (and corresponding low vapor pressure), there is no appreciable pressure buildup in the space above the coolant due to the evaporation of the coolant which is not the case when water alone is employed as coolant as in conventional waste-heat boilers. Since the coolant medium employed in the invention does not contribute to the pressure in the boiler, it is possible to regulate to control the pressure above the coolant at substantially the same pressure as that of the gas in helically coiled tubes as hereinafter described.

As previously discussed, in accordance with the invention the coolant medium in addition to being in external contact with one or more gas tubes, is also in external contact with one or more steam tubes, by means of which heat is transferred from the coolant to the steam. This in effect minimizes the temperature range through which the coolant passes and enables effective withdrawal of heat from the system, the heat being indirectly transmitted from the hot gases to the steam via the coolant medium.

The fact that the high pressure of the generated steam no longer affects the gas tubes is also significant because these tubes are generally exposed to the highest temperatures, particularly near the inlet side of the gas tubes where the gas arrives at a temperature of more than 1,000° C. The steam tubes, on the other hand, which the (high) steam pressure does affect, have a much lower temperature, which will generally be below 600° C. At such temperatures the strength of structural materials is much higher. The invention therefore permits the generation of steam in helical coil waste-heat boilers at much higher pressures and temperatures than was heretofore possible.

Good cooling of the gas tubes and good heat withdrawal are achieved by circulating the coolant between a first zone in which it comes into contact with the gas tube or tubes to be cooled, and a second zone in which it is out of contact with the gas tube or tubes.

For optimum protection, the gas tube or tubes are most intensively cooled at or near the inlet side where the temperature of the gas is highest, e.g., up to 1,400° C or higher. According to the invention, the coolant on coming into contact with the gas tube or tubes in the first zone, should on the whole preferably flow in the same direction as the gas in the gas tube or tubes.

Further cooling of the coolant in the above-mentioned second zone may be effected according to the invention by heat-exchanging contact with one or more water tubes through which water is flowed. Generally, steam will be formed in these tubes. Either straight or helically coiled tubes may be used for the steam or water tubes. If helically coiled tubes are employed, as the steam tubes, the coils are arranged coaxially between and/or inside one another.

The coolant preferably flows from the first to the second zone via a central- vertical - pipe which is arranged coaxially inside the coils of the helically coiled tubes for gas, steam and water, In this way natural circulation of the coolant is obtained, said coolant descending through the central pipe in cooling. This also implies that the coolant ascends in the space around the central pipe where the said tubes are situated in the various zones.

It is generally preferred that if both steam and water tubes are employed, that they be directly connected in order that the steam formed in the water tubes can be used as coolant in the steam tubes. The pressure of the steam in the water and steam tubes in this case will be identical. The temperature of the generated steam will-,of course, be much lower in the water tubes. While the steam in the steam tubes is generally superheated, in the water tubes it will be saturated. Thus, by proceeding in the above-mentioned manner, superheated steam is obtained from the saturated steam which is converted into superheated steam in the steam tubes.

The steam in the steam tube or tubes is preferably caused to flow countercurrently to the flow of gas in gas tube or tubes, In this way the steam immediately before leaving the waste-heat boiler, is in heat-exchanging contact with the gas while the latter is still hot.

As previously mentioned, the space above the coolant medium and outside the gas and steam tubes is preferably pressurized, e.g., by bubbling a gas directly through the coolant at an elevated pressure. It is obvious that for reasons of safety, a closed waste-heat boiler will never be entirely filled with liquid coolant because the coolant will expand upon heating. In general, an inert gas will be provided above the coolant, in which case it is possible according to the invention to keep the pressure of this inert gas at or near the value of the pressure of the synthesis gas in the gas tubes thereby minimizing the pressure difference across the tube-walls.

In this connection, it is very advantageous to utilize a portion of the synthesis gas (optionally after purification, i.e., soot removal) to maintain the pressure above the coolant medium at substantially the same pressure as that of the synthesis gas in the helically-coiled tubes. The use of synthesis gas for this purpose is attractive in that any fluctuations which occur in the pressure of the gas in the coiled tubes, will be reflected to the same degree in the space above the coolant medium. By operating in this manner the pressure inside and outside the gas tube will be virtually identical.

The present invention enables superheated steam to be produced having a temperature above 400° C and preferably above 500° C. This steam, which originates from the steam tube or tubes, has a relatively high energy content.

The present invention also relates to a waste-heat boiler for cooling and abstracting heat from high temperature gases containing solid particulate matter such as soot, which comprises (1) a closed vessel suitable for containing a coolant medium which is liquid at operating conditions, (2) a helically coiled tube extending through the vessel, said tube being in external heat-exchanging contact with the cooling medium and having an inlet end for receiving the high temperature gas and an outlet end through which the gas, at a lower temperature, is discharged from the boiler, (3) a second tube extending through said vessel, said tube also being in external heat-exchanging contact with the coolant medium and having an inlet end into which steam is introduced and an outlet end through which steam, at a higher temperature, is discharged from the vessel. If more than one gas tube and more than one steam tube, respectively, are used, a central inlet and-

/or outlet for gas and steam, respectively, may be used, or a separate inlet and/or outlet for gas and steam, respectively, may be used for each gas tube and each steam tube, respectively.

In practice, the above-described waste-heat boiler meets a secondary object of the invention, namely to provide a waste-heat boiler for cooling and abstracting heat from synthesis gas from a partial combustion process in which the gas tube or tubes are not subjected to an excessively high pressure at the prevailing high temperature of the gases. Moreover, it will be clear that this waste-heat boiler is filled with the coolant medium before use. If this coolant consists of lead, it may, for example, be poured into the vessel in the form of pellets, and heated and melted by means of the steam tube or tubes.

The vessel of this waste-heat boiler is preferably cylindrical with a central open-ended pipe mounted coaxially in the vessel through which the coolant is downwardly circulated. The central pipe is preferably located inside the coils of the helically coiled tube for gas and the tube for the steam which preferably is also a helically coiled tube, but may be straight tube. If a waste-heat boiler designed in this way is positioned vertically, a natural flow of the coolant downwardly in the central pipe will be achieved when the waste-heat boiler is in use. This ensures good cooling of the gas in the gas tube or tubes and good heat transmission to the steam in the steam tube or tubes.

In the elongated annular space between the vessel wall and the central pipe, one or more helically coiled water tubes may be provided in addition to the gas and steam tubes, the gas and steam tubes being mounted in a relatively wide upper part of the vessel, while the water tube or tubes are located in the relatively narrow lower part of the vessel. In this embodiment, the coolant is additionally cooled by the water tubes during circulation before coming into contact with the gas tube or tubes. It is also possible for the gas tube or tubes to be connected to the reactor for incomplete combustion via associated straight tubes which pass through the waste-heat boiler vessel. These straight tubes may then pass through the narrow lower part of the vessel, so that the gas in the tubes there is precooled by heat exchange with the coolant medium which will cause the temperature of the coolant in this narrow part of the vessel to rise. Precooling of the synthesis gas in straight sections of tube may under certain circumstances be advantageous.

The invention will be further illustrated and understood by reference to FIGS. 1 and 2 of the accompanying drawings which are diagrammatic vertical cross-sections of waste-heat boilers according to two embodiments of the invention.

DESCRIPTION OF THE DRAWINGS

The waste-heat boilers shown in FIG. 1 comprises a cylindrical vessel having a relatively wide upper part 1 and a relatively narrow lower part 2. The vessel contains along the greater part of its length a central vertical pipe 3, coaxially arranged within the vessel. The central pipe is secured to the wall of the vessel free from bottom closure 4 and top closure 5.

Arranged coaxially around pipe 3 in the upper part of the vessel, are helically coiled gas tube 6 for synthesis gas and helically coiled steam tube 7 for steam. Likewise arranged coaxially around the pipe 3 in the lower part of the vessel, is a helically coiled water tube 8 for cooling water.

At transition area 9 between parts 1 and 2 of the vessel and around central pipe 3, there is an annular tube 10 through which synthesis gas or ther inert gas can be passed under super-atmospheric pressure into the vessel via connection 11. The gas thus introduced serves to keep the coolant medium 12 e.g., lead, pressurized under gas cap 13. The synthesis gas bubbling through can be discharged via outlet 14 passing through top closure 5, by means of a tube (not shown) for maintaining the superatmospheric pressure inside the vessel. The pressure in the gas cap is preferably maintained at substantially the same pressure as the gas in gas tube 6.

The synthesis gas to be cooled — originating from a reactor (not shown) for the incomplete combustion of a carbonaceous fuel — is introduced into gas tube 6 via inlet 15 located in transition area 9, and after being cooled is discharged from the waste-heat boiler via outlet 16.

The required cooling water is introduced via inlet 17 into water tube 8 wherein it is partially vaporized and is discharged as low-pressure steam into annulus 18 and thence to risers 19, whereafter it is introduced into annular upper end 20 of steam tube 7. In steam tube 7 and in riser 19, the steam enters into indirect heat-exchange with the coolant medium which in turn cools gas tube 6. The steam is ultimately discharged from outlet 21 as high-pressure steam.

The steam which flows down through steam tube 7 and is discharged at 21 therefore moves countercurrently with the synthesis gas lowing in gas tube 6.

The synthesis gas supplied via annular tube 10 and subsequently bubbled through the coolant in the vessel 1, together with the gradual heating of the coolant, cause the latter to rise and flow up along tubes 6, 7 and 19 in the annular space between the central pipe and the vessel wall. This annular space is the above-mentioned first zone in which the coolant comes into contact with the gas tube and the steam tube.

The coolant descends in central pipe 3, gradually cooling as it descends. This is indicated by arrow 22. Incidentially, the interior of pipe 3 forms part of the above-mentioned second zone in which the coolant is not in direct contact with the gas tube.

Arrows 23 indicate the further cycle of the coolant, which now comes into heat-exchanging contact with water in tube 8 in the part 2 of the vessel. Here the coolant is in another part of the above-mentioned second zone, in which it is in contact with a water tube although it is not in contact with the gas tube.

In the waste-heat boiler shown in FIG. 2, functionally identical components are designated by the same reference numerals as in FIG. 1.

The waste-heat boiler shown in FIG. 2 comprises two helically coiled gas tubes 6 and 6′, which are arranged around central pipe 3 in part 1 of the vessel and which extend between lower ring 24 which is connected to inlet 15 for the hot gas, and upper ring 25 which is connected to the vertical pipe 16 for discharge of the cooled gas. In the part 2 of the vessel there are two helically coiled water tubes 8 and 8′, for cooling water. They are connected between lower annular line 26 and upper annular line 18 which is connected to stand-pipe 19 for passage of cooling water and/or generated steam to the upper ring 20 of helically coiled steam tubes 7 and 7′, which are arranged in the upper part of the vessel. These two steam tubes discharge at their lower ends into ring **27** which is connected to discharge **21** for high-pressure steam.

The gas cap **13'** above lead alloy coolant **12'** consists of an inert gas.

In a waste-heat boiler of the type shown in FIG. **2,** the following temperatures may, for example occur:

The hot synthesis gas enters the vessel through bottom closure **4,** via tube **15,** approximately at 1,400° C and is cooled to 1,100° C before entering ring **24.**

Halfway through part **1** of the vessel, the gas in helically-coiled tubes **6** and **6'** has a temperature of 750° C, while in ring **25** the temperature of the gas has fallen at 400° C. The cooled synthesis gas is discharged from the waste-heat boiler via vertical pipe **16.**

At the lower end of the central pipe **3,** i.e., near bottom closure **4,** the lead alloy coolant has a temperature of 330° C. At the highest coils of water tubes **8** and **8'** the temperature of the coolant is 600° C, and at the lowest coils of gas tubes **6** and **6'** its temperature is already 825° C. Halfway up the part **1** of the vessel the coolant has a temperature of 530° C, while immediately below gas cap **13'** the temperature of the coolant is **340**°C. This demonstrates the cooling function of the lead alloy.

Steam is discharged at a temperature of 270° C–280° C via tube **17** to lower ring **26.** By the time the steam has reached upper ring **18,** its temperature has risen to 310° C, whereas the steam has substantially the latter temperature after it has been passed up through riser **19** to upper ring **20.** After passing through steam tubes **7** and **7'** the steam in ring **27** and in discharge tube **21** has a temperature of 550° C. The pressure of this superheated steam is 120 atm. which is attractive for the generation of energy.

What is claimed is:

1. In a process for cooling and recovering heat from a hot, soot-containing synthesis gas obtained by the partial combustion of a carbonaceous fuel, by flowing said hot gas through a helically coiled tube which is in external contact with a coolant medium, the improvement which comprises employing as the coolant medium a molten metal, metal alloy or salt having a melting point below 420° C and a boiling point above the prevailing temperature in the reactor, and effecting the cooling by indirect heat exchange with steam flowing through a separate tube which is also in external contact with said coolant medium,whereby said hot gases are cooled and high pressure steam is generated.

2. The process of claim **1** wherein the coolant medium is lead or a lead alloy.

3. The process of claim **1** wherein the coolant medium is circulated between a first zone in which it comes into contact with the steam tube and helically coiled gas tube,and a second zone in which it is out of contact with said tubes.

4. The process of claim **3** wherein the coolant medium, on coming into contact with the helically coiled gas tube in the first zone, flows in substantially the same direction as the gas in said tube.

5. The process of claim **4** wherein the coolant medium is further cooled in the second zone by external contact with a tube through which water is flowed.

6. The process of claim **5** wherein steam in the steam tube flows countercurrently to the gas in the helically coiled gas tube.

7. The process of claim **6** wherein the water or generated steam in the water tube in the second zone is passed directly to the steam tube.

8. The process of claim **7** wherein a gas which is inert in respect to the coolant medium is bubbled directly through the coolant medium at a pressure substantially the same as the pressure of the gas flowing through the helically coiled tube.

9. The process of claim **8** wherein the gas bubbled directly through the coolant medium is synthesis gas which has been purified of soot.

10. The process of claim **9** wherein the coolant medium is lead or a lead alloy.

11. The process of claim **10** wherein superheated steam is produced having a temperature of more than 500° C.

12. A waste-heat boiler for cooling and abstracting heat from high temperature gases containing solid particulate matter, which comprises: (1) a closed vessel suitable for containing a coolant medium which is liquid at operating conditions, (2) a helically coiled tube extending through said vessel, said tube being in external,heat-exchanging contact with the coolant medium and having an inlet end for receiving the high-temperature gas and an outlet end through which the gas, at a lower temperature, is discharged from the boiler, (3) a second tube extending through said vessel, said tube also being in external, heat-exchanging contact with the coolant medium and having an inlet end into which steam is introduced and an outlet end through which steam, at a higher pressure, is discharged from the boiler.

13. The waste-heat boiler of claim **12** wherein the vessel is cylindrical and contains a central, open-ended, pipe through which the coolant medium is downwardly circulated, said pipe being coaxially mounted within said vessel and defining therewith an annular elongated space in which the helical coiled tube for the high temperature gas and the tube for the steam are located.

14. The waste-heat boiler of claim **13** wherein both the tube for the high temperature gas and the tube for the steam are helically coiled tubes, and the coils of said tubes surround the central pipe.

15. The waste-heat boiler of claim **14** wherein the vessel contains an additional helically coiled tube mounted coaxially in the lower part of the vessel, the coils of which surround the central pipe, said tube having an inlet end into which water is introduced and an outlet end connected to the helically coiled steam tube,which latter tube is located in an upper part of said vessel.

16. The waste-heat boiler of claim **15** wherein the vessel contains means for introducing a pressurized gas into the lower part thereof to maintain a pressure in said vessel substantially the same as the pressure of the high temperature gas in the helically coiled tube.

* * * * *

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,788,281 Dated January 29, 1974

Inventor(s) Nicolaas Van Lookeren

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

The sheet of drawing showing Figure 2 as shown on the attached sheet should be added.

Signed and Sealed this

ninth Day of *March 1976*

[SEAL]

Attest:

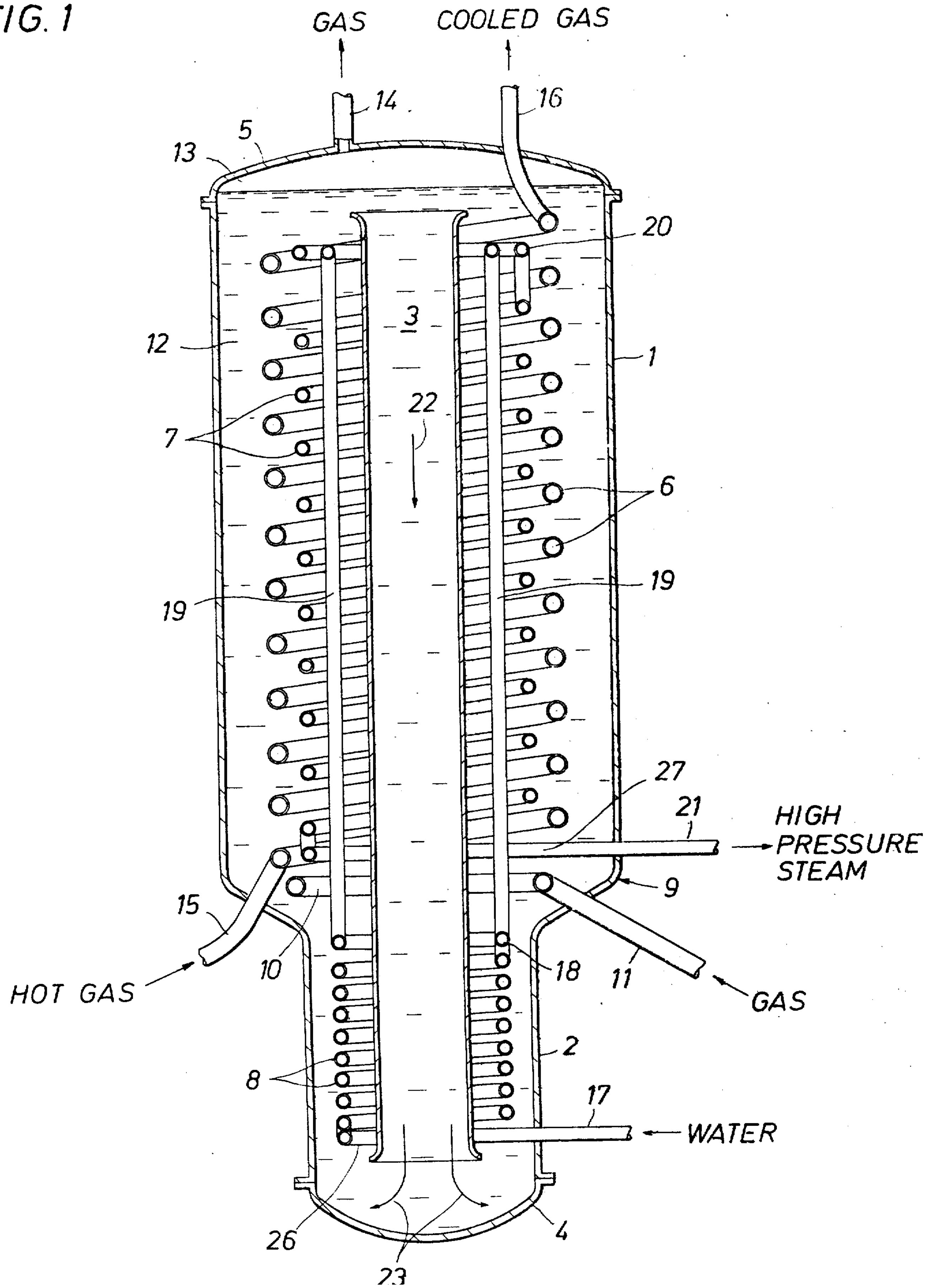
RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks

FORM PO-1050 (10-69)

USCOMM-DC 60376-P69
U.S. GOVERNMENT PRINTING OFFICE : 869-930

FIG. 1


GAS
COOLED GAS
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