March 18, 1941. J. R. GIER, JR 2,235,401

GAS GENERATOR FOR HEAT TREATING ATMOSPHERES

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Fig.1.

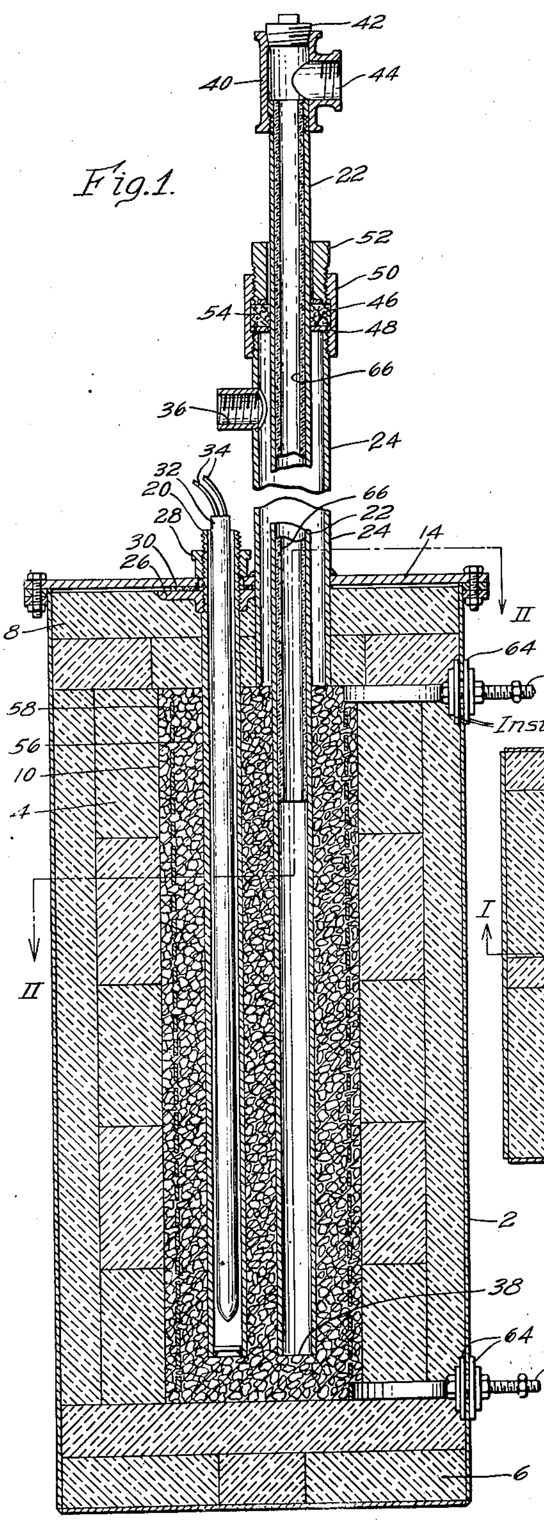
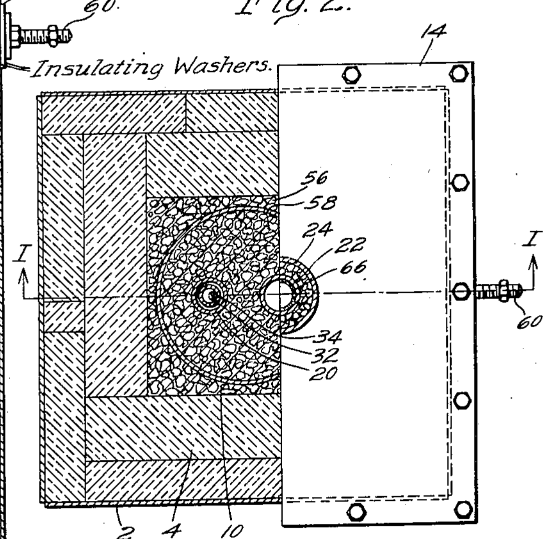


Fig.2.



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GAS GENERATOR FOR HEAT TREATING ATMOSPHERES

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9 Claims. (Cl. 23—288)

This invention relates generally to gas generators of the type in which protective gaseous atmospheres are produced to be employed for enveloping a charge, usually metallic, that is undergoing heat-treatment in a suitable furnace, it being understood in the art that heat-treatment may involve either heating or cooling, or both, and that the furnace may be a structure for heating or cooling, or both.

My invention relates more particularly to that type of generator in which a combustible hydrocarbon gas or fuel is partially or completely burned, or cracked, preferably in the presence of a catalyst, and from which the final gas products are led to the heat-treating furnace, with or without intermediate processing to remove undesired ingredients.

The atmospheres commonly produced by the reaction of hydrocarbon fuels with air consist of mixtures of nitrogen, hydrogen, carbon monoxide, carbon dioxide, water in the form of vapor, and methane with their respective proportions depending largely on the ratio of the amount of fuel gas and air admitted to the generator, and to some extent upon the temperature of the generator.

While protective gaseous atmospheres find application in the heat-treatment of various metals, its greatest use probably exists in the heat treatment of steel to control scaling or contamination of the surface of the steel, and also to control decarburization, or sometimes, carburization. Of the aforesaid constituents of protective atmospheres, carbon dioxide and water vapor have a strong tendency to oxidize hot steel under the usual heat-treating conditions, this tendency being opposed by the reducing action of carbon monoxide, hydrogen and methane. Carbon dioxide and water vapor also are active decarburizing agents while carbon monoxide and methane are carburizing. The nitrogen present is generally inert to steel. The net effect on any particular steel of a mixture of these various individual gases is the resultant of their combined reactions according to the chemical laws of mass action which, of course, depend upon the pressures and temperatures involved, and the percentages of the different individual components present.

Conventional gas generators which are of the self-heated type, will produce protective atmospheres which are non-scaling to ordinary steels but which are decarburizing to medium and high carbon steels, and particularly to the tool steels. Accordingly, it is usual to subject the reaction products coming from the conventional gas generators to further processing to remove carbon dioxide and water vapor, so that the ultimate protective atmosphere is rendered non-decarburizing, such processing being practically essential if the atmosphere is to be employed for enveloping high carbon steel. With known methods for the continuous removal of carbon dioxide and water vapor, this additional processing requires an elaborate and costly equipment having a high maintenance expense.

A purpose of my invention, therefore, is to devise a simple, inexpensive and commercially practical gas generator capable of producing protective gaseous atmospheres universally suitable for heat-treating substantially all kinds of tool steels without surface contamination, and particularly one capable of producing an atmosphere having no decarburizing effect on the tool steels. Since decarburizing and scaling are due primarily to the presence of carbon dioxide and water vapor, I prefer to operate my novel generator with a low ratio of combustible hydrocarbon fuel to air, so that a rich product is obtained, that is, one consisting substantially entirely of inert or reducing gases.

In accordance with the customary practice, my novel generator is filled with a catalyst whose function is to promote and complete the desired chemical reactions in the feed mixture which is best obtained by heating the catalyst, preferably through the medium of an electric heating element. Since the capacity of this generator is dependent chiefly on the catalyst temperature, and this, in turn, is limited by the maximum safe operating temperature of the heating element, it is desirable that the heat transfer from the heating element to the catalyst and to the gas be as direct and unimpeded as possible so as to minimize temperature differences between them and also to minimize heat losses. Accordingly, as a novel feature of my invention, I immerse or embed the electric heating element directly in the catalyst.

In the particular embodiment of my invention the gas generator is of the vertical type, and it is a further feature of my invention to so construct this type of gas generator that the gas inlet and outlet pipes extend therefrom through the top only.

From the foregoing, it should be apparent that my novel generator is primarily for, but not necessarily limited to, the production of a protective atmosphere rich in carbon monoxide and hydrogen, and that it is to be operated, preferably, at relatively high temperatures (actually between 900° C. and 1050° C., and even higher).

This rich gas coming from the generator at a high temperature is conveyed to the heat-treating furnace through some suitable pipes or conduit system, and on this journey the gas is cooled considerably. Frequently, in such conduit systems the catalytic action or chemical action of the elements of which the pipes are made upon the carbon-containing gases rich in carbon monoxide causes a deposition of soot inside the system with a formation of carbon dioxide. In the course of time, the soot deposit becomes so large that the conduit system clogs, and a shutdown of all the apparatus dependent upon the operation of the gas generator is required while the soot is cleaned out.

Outlet pipes in gas generators are most commonly made of either heat-resistant alloys or steel pipes, both of which contain substances chemically or catalytically active toward the carbon-containing gases through certain ranges of temperatures. While the product gases are conveyed from the hot generator to a point where it is to be employed at a much lower temperature, the gases are susceptible to such action. During the extent of piping when such action is possible, that is, to the point where the temperature is sufficiently low so that the aforesaid chemical or catalytic reactions might occur, I line the outlet pipes with a non-catalytic heat-resistance refractory preferably of a non-metallic substance, so that the carbon-containing gases, and particularly the carbon monoxide, pass through the conduit system intact, with the advantages that the composition of the gas produced in the generator remains unaltered, and the more particular advantage that no soot is deposited inside the pipes to clog the flow.

Additionally, in my generator I achieve a rapid cooling of the outflowing atmospheres so that the length of the pipes that need be lined is kept down. Of course, this could be accomplished by a water cooled jacket but such construction would be inefficient and result in a considerable waste of heat. Accordingly, I provide two concentric pipes for my gas generator, the inner of which is for outflowing gases while the outer is for the incoming gases. This construction, therefore, accomplishes the dual purpose of rapidly cooling the outflowing gases and also preheating the incoming gases.

It is an additional object of my invention to cool the gas produced in the generator immediately after it leaves to a temperature below the range at which the carbon-containing constituents may react with the material of the outlet pipes, or may be catalytically changed thereby.

Other objects, features and methods of my invention will be apparent from the following description thereof, taken in conjunction with the drawing, in which:

Figure 1 is a vertical sectional view on the line I—I of Fig. 2 of a gas generator built in accordance with my invention, and

Fig. 2 is a horizontal view partly in section and partly in elevation on the line II—II of Fig. 1.

The gas generator of a preferred form of my invention is adapted for vertical disposition and the drawing depicts this. The generator comprises an outer, gas-impervious metallic shell **2** of box-like form and suitable dimensions, the side walls of which are lined with a heat-resistant and insulating refractory **4** resting on a similar bottom wall **6**. Heat-resistant and insulating refractories **8** form a top wall which in conjunction with the side walls **4** and the bottom wall **6** form an internal reaction chamber indicated by the reference character **10**. A metallic top plate **14** completes the shell, and is provided with suitable apertures through which extend a thermocouple well **20**, and open-bottomed, gas passage pipes **22** and **24**, preferably of relatively inexpensive stainless steel.

The thermo-couple well **20** may take any usual form and is secured to the top plate **14** in such manner as to provide a lower portion extending into the chamber **10**. The upper end of the well **20** is suitably threaded so that it may be securely maintained in position through the medium of clamping nuts **26** and **28** threaded thereupon, the first below the top plate and the second above so that the plate is clamped between them. A gasket **30** may be added between the nut **26** and the top plate, so that a gas-tight joint results. Within the well **20** is the temperature responsive means **32** in the form of a thermo-couple which has leads **34** leading to any suitable indicating apparatus, or controlling apparatus for controlling the heating of the generator by independent heating means, to be later described, for producing heat to be absorbed in endothermal reaction of the gases.

As shown in Fig. 1, the pipes **22** and **24** are concentrically arranged with the pipe **24** being the gas inlet pipe and the pipe **22** the gas outlet pipe in this instance. The gas inlet pipe is, of course, of the larger diameter and is welded to the top plate **14** in a gas-tight manner with a lower portion extending below the top plate **14** and an upper portion extending thereabove. The lower portion of the pipe preferably terminates at the top of the chamber **10**, while the upper portion is provided with a feed inlet **36** through which any desired ratio of hydrocarbon fuel and air may be fed to the generator.

As shown, the outlet pipe **22** is considerably longer than the inlet pipe **24**, and has a bottom opening **38** near the lower part of the chamber **10**. The pipe **22** has an upper portion extending through the pipe **24** to a pipe T **40** having one opening closed by a plug **42**, and another opening adapted for connection to any further pipe system that may be necessary for leading the outflowing gases wherever it be desired.

From the structure thus far described, it is quite apparent that any mixture of gases usually under pressure and fed to the inlet pipe **24** will flow downwardly into the chamber **10** where the gases will react, and the resulting products of combustion and reaction will be forced to the bottom chamber to the inlet end **38** of the outlet pipe **22**, from whence the gases flow upwardly through the pipe **22** and out through outlet openings **44** of the pipe T **40**.

The top of the inlet pipe must, of course, be plugged by any suitable means, which I have shown as comprising a metallic ring **46** resting on an edge of the pipe **24** and in a cut-out groove **48** in a coupling **50** threaded on the end of the pipe **24**. A suitable externally-threaded, annular nut **52** surrounding the pipe **22** fits the upper end of the coupling **50** which is internally threaded to receive the nut and which can be tightened to compress an asbestos packing **54** upon the ring **46** to assure a gas-tight plugging.

The gases which are fed to the generator to be reacted usually comprise any readily-available hydrocarbon fuel mixed with air in the desired ratio before being admitted through the inlet **36**. In order to promote and complete the reactions between the fuel gas and air, the chamber 10 of the generator is filled with a divided catalyst 56 whose temperature is maintained by means of a spirally-formed, electrical heating unit 58 embedded therein having upper and lower terminals 60 and 62 for connection to a power source at a side of the gas generator, these terminals extending through a side wall 4 and out of the shell 2. Any suitable construction, indicated in entirety by the reference numerals 64, may be employed to electrically insulate the terminals from the shell and, at the same time, assure a gas-tight enclosure. The heating unit 58 is in the form of the conventional resistor used for high-temperature electrical heating. This resistor is in the form of a ribbon which is solid in cross section, as shown, and because of its numerous return bends inside the reaction chamber, the effective heating length of the heating unit is considerably in excess of any linear dimension of the reaction chamber, and produces a thorough heating of the catalyst so that the desired gas reaction is carried out to a high completion within the small space of the small generator provided.

In the operation of the generator, a rich mixture of the hydrocarbon fuel and air in controlled proportions is admitted through the inlet 36, and passes downward through the annular space between the concentric pipes 22 and 24, and into the reaction chamber 10. As the mixture progresses downward through the catalyst 56 which is maintained heated by energy supplied to the spiral resistor 58, the hydrocarbons are burned, decomposed, or reacted with the air to form product gases consisting chiefly of nitrogen, hydrogen, carbon monoxide and containing very small amounts, if any, of carbon dioxide, water vapor and methane, the conditions being deliberately controlled to give the desired composition. The ultimate protective atmosphere formed in the generator will flow through the pipe opening 38 at the bottom of the chamber 10, up through the outlet pipe 22, and to the outlet 44, from whence it may be piped wherever desired, either for further processing or directly to a furnace.

For the catalyst, I may employ activated alumina impregnated with nickel formate. However, any other effective catalyst may be employed as, for example, nickel or iron turnings with or without an admixture of crushed refractory material. However, if metallic catalyst is used it must be insulated from the heater winding.

The spiral, electric heating resistor 58 may be of any suitable heat-resistant alloy, and I have found that an alloy of 35% nickel, 20% chromium and the balance iron is suitable for the particular service of this generator. In operation, I prefer to supply the heating element 58 with sufficient heat to maintain the catalyst at an operative temperature of about 1000° C. or slightly above, and that at this temperature a catalyst volume of three cubic inches per cubic foot of product gas per hour is sufficient to give satisfactory gas reaction. The supply of electrical energy to the heating resistor 58 may be controlled by any suitable apparatus under the supervision of the thermo-couple 32.

As has been mentioned previously, the composition of the product gas depends primarily on the composition and proportions of the fuel in the feed and secondarily on the temperature of the catalyst. A typical product derived from Pittsburgh natural gas and air in a feed ratio of approximately one part gas to 2.5 parts air contained substantially 40% nitrogen, 39% hydrogen, 20% carbon monoxide, 1% methane, and carbon dioxide and water vapor in amounts less than 0.1% each. Such a gas is richer than is required for the prevention of decarburization of most steels but it must be understood that by controlling the ratio of the feed gases and the catalytic temperature, I may change the proportions of the different product gases to best suit the heat-treatment of any particular metal. Thus with a 3 : 1 air to gas ratio fed to the generator held at 1050° C., the resultant products contained substantially 1% carbon dioxide, 19% carbon monoxide, 34.8% hydrogen, .1% methane, and the balance practically all nitrogen.

It may be observed that as the supply mixture passes downward through the annular space between the inlet and outlet pipes, it is preheated by the counterflow of the hot outgoing product gases and, therefore, receives heat therefrom, while at the same time cooling the outflowing gases. In my particular embodiment, I make the inlet pipe 24 and, therefore, also the outlet pipe 22, of a length to provide sufficient heat exchange surfaces to cool the outflowing gases from the temperature maintained within the reaction chamber 10 to a temperature sufficiently low to render the rich product gases relatively inert when in contact with iron, nickel or other metallic catalytic surfaces which might be contained in the pipe material. Throughout this extent of the pipes, and as a matter of precaution somewhat beyond this extent, I line the pipe 22 with a refractory 66 extending from the hot zone outward.

This refractory is preferably non-catalytic and its purpose is to prevent the carbon monoxide in the outflowing rich gas product from decomposing with the resultant formation of carbon dioxide and soot, when in contact with iron, stainless steel, nickel or certain other metallic catalytic surfaces, particularly so at temperatures ranging from 400° C. upward to 500° C., and even higher. I have found that a tube made of fused silica or porcelain extending through the critical temperature range admirably serves my purpose. It may be observed here that it may also be desirable to line the outside of the pipe 22 as well as the inside of the pipe 24 if it is found that the incoming gases are of a composition that would cause the undesirable deposition of soot in the temperature ranges existing in the feeding path of the pipes.

While I have shown my invention in a preferred form thereof, it is obvious that many changes may be made within the scope and spirit of my invention by those skilled in the art.

I claim as my invention:

1. A structure of the class described in which hydrocarbon gases are to be reacted with an oxygen-containing gas in the presence of a catalyst, having a container with an elongated reaction chamber, comprising heat-resistant and insulating walls with a gas-impervious shell on their outside, a divided catalyst substantially filling said chamber, gas inlet and outlet means comprising a pipe passing through a wall of said container at one end thereof, and terminating at one end of said chamber, a second pipe passing through the first said end of said container, and terminating in said chamber at one end thereof opposite its first said end, one of said pipes being a gas inlet pipe and the other a gas outlet pipe, said outlet pipe having an extension

beyond said container, and cooling means for said extension for cooling the outflowing gases passing through the last said pipe, the surfaces of said extension in contact with said gases being non-catalytic with respect to carbon-containing gases, such as carbon monoxide, during an extent of the said pipe sufficient to cool said gases to a state where they would be inactive even in the presence of a catalyst, such as iron.

2. A structure of the class described in which hydrocarbon gases are to be reacted with an oxygen-containing gas in the presence of a catalyst, having a container having an elongated reaction chamber, comprising heat-resistant and insulating walls with a gas-impervious shell on their outside, a divided catalyst substantially filling said chamber, gas inlet and outlet means comprising a pipe passing through a wall of said container at one end thereof and terminating at one end of said chamber, a second pipe passing through the first said end of said container and through a substantial part of said catalyst, and terminating in said chamber at an end thereof opposite its first said end, one of said pipes being an inlet pipe and the other an outlet pipe, said outlet pipe having an extension beyond said container, and cooling means for said extension for cooling the outflowing gases passing through the last said pipe, the surfaces of said extension in contact with said gases being non-catalytic with respect to carbon-containing gases, such as carbon monoxide, during an extent of the said pipe sufficient to cool said gases to a state when they would be inactive, even in the presence of a catalyst, such as iron, and heating means for heating said chamber.

3. A structure of the class described in which carbon-containing and oxygen-containing gases are to be reacted in the presence of a catalyst comprising a container having heat-resistant and insulating walls with a gas-impervious shell on their outside, said container having a reaction chamber therein, a divided catalyst substantially filling said chamber, gas inlet means passing through a wall of said container for admitting a mixture of gases to be reacted in said chamber, gas outlet means passing through a wall of said container for directing the gas products out of said container after admitted gases have passed through said catalyst, said outlet means including a lining pipe extending from said container having surfaces which the hot gases contact formed of a non-metallic, refractory substance non-catalytic with respect to gases containing oxides of carbon.

4. A structure of the class described in which gases are to be reacted in the presence of a catalyst comprising a container having heat-resistant and insulating walls including a top wall defining part of a reaction chamber, a metallic shell encasing said walls, said shell having a top plate for said top wall, said top plate being secured to the remaining portions of said shell, a gas inlet pipe extending through said top wall and plate which are provided with apertures for the purpose, said pipe terminating at said chamber, a ferrous, gas outlet pipe substantially concentric with said inlet pipe and of smaller size, and extending into said chamber and terminating near the bottom thereof, both said pipes having extensions beyond said container providing a heat-exchange zone whereby incoming gases will be preheated by the outflowing gases, and the outflowing gases will be cooled, said outlet pipe being provided with a non-metallic refractory lining along said zone.

5. A structure in which hydrocarbon gases and air are to be reacted to yield a gas rich in carbon monoxide, comprising a container having a reaction chamber, heating means for heating said reaction chamber, gas inlet pipes to said chamber, gas-product outlet pipes from said chamber, said pipes having portions in heat exchange relation forming a heat exchange zone, the portions of said outlet pipes having a non-metallic refractory lining in said heat exchange zone which the gas-product contacts, said lining being inert with respect to gases containing oxides of carbon, such as carbon monoxide, in the range where the temperatures are in the neighborhood of between 400° C. and 500° C.

6. A structure of the class described in which gases are to be endothermally reacted in the presence of a catalyst with the continuous application of heat, comprising a container having heat-resistant and insulating walls with a gas-impervious shell on their outside, said container having a gas reaction chamber therein, a divided catalyst which converts a mixture of oxygen-containing gases and hydrocarbons into product gases containing inappreciable amounts of carbon dioxide and water vapor, substantially filling said reaction chamber, gas inlet means passing through a wall of said container for admitting to said reaction chamber a mixture of gases to be reacted in said reaction chamber, gas outlet means passing through a wall of said container for directing product gases out of said container after the admitted gases have passed through said catalyst, and an electric heating means comprising a relatively elongated return-bend solid-in-section heating resistor embedded in, and distributed through, said catalyst, being in direct contact with said catalyst, and means for connecting said electric heating means to an electrical power source.

7. A structure of the class described in which gases are to be endothermally reacted in the presence of a catalyst with the continuous application of heat, comprising a container having heat-resistant and insulating walls with a gas-impervious shell on the outside, said container having an elongated substantially cylindrical gas-reaction chamber therein, a divided catalyst which converts a mixture of oxygen-containing and hydrocarbon gases into product gases containing inappreciable amounts of carbon dioxide and water vapor, substantially filling said chamber, gas inlet means for admitting to said chamber a mixture of gases to be reacted in said chamber, gas outlet means for directing product gases out of said container after the admitted gases have passed through said catalyst, electric heating means comprising a helical electrical resistor embedded in, in direct contact with, said catalyst, said resistor having its axis substantially parallel to that of said chamber, and leads passing through walls of said container for connecting said electric heating means to an electric power source.

8. A structure of the class described in which gases are to be endothermally reacted in the presence of a catalyst with the continuous application of additional heat, comprising a container having a reaction chamber, said container comprising heat-resistant and insulating walls with a gas-impervious shell in their outside, a divided catalyst of the type which converts a mixture of air and hydrocarbon gases into prod-

uct gases containing inappreciable amounts of carbon dioxide and water vapor, substantially filling said reaction chamber, gas inlet means for admitting to said reaction chamber a mixture of said gases to be reacted in said reaction chamber, gas outlet means for directing product gases out of said container after the admitted gases have passed through said catalyst, electric heating means for thoroughly heating the catalyst in said reaction chamber, said heating means having considerable heating surface in direct contact with said catalyst, and leads for connecting said electric heating means to an electric power source.

9. A structure of the class described in which gases are to be endothermally reacted in the presence of a catalyst with the continuous application of additional heat, comprising a container having an elongated reaction chamber, said container comprising heat-resistant and insulating walls with a gas-impervious shell in their outside, a divided catalyst comprising a non-metallic refractory impregnated with a metal salt for converting a mixture of air and hydrocarbon gases into product gases containing inappreciable amounts of carbon dioxide and water vapor, substantially filling said reaction chamber, gas inlet and outlet means comprising a pipe passing through a wall of said container at one end thereof and terminating at one end of said chamber, a second pipe passing through the said one end of said container and extending through a substantial part of said catalyst, terminating in said chamber at an end thereof opposite its first said end, electric heating means comprising an elongated return-bend electrical resistor for heating said catalyst, said resistor being about, and spaced from said second pipe and embedded in said catalyst.

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