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[54] **REDUCTION OF NITROGEN OXIDES FROM PRODUCTS OF HYDROCARBON COMBUSTION WITH AIR**

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Related U.S. Application Data

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[52] **U.S. Cl.** **431/10,** 431/326, 431/351

[51] **Int. Cl.** **F23l 9/00**

[58] **Field of Search** 431/10, 2, 7, 326, 328, 431/351; 23/2

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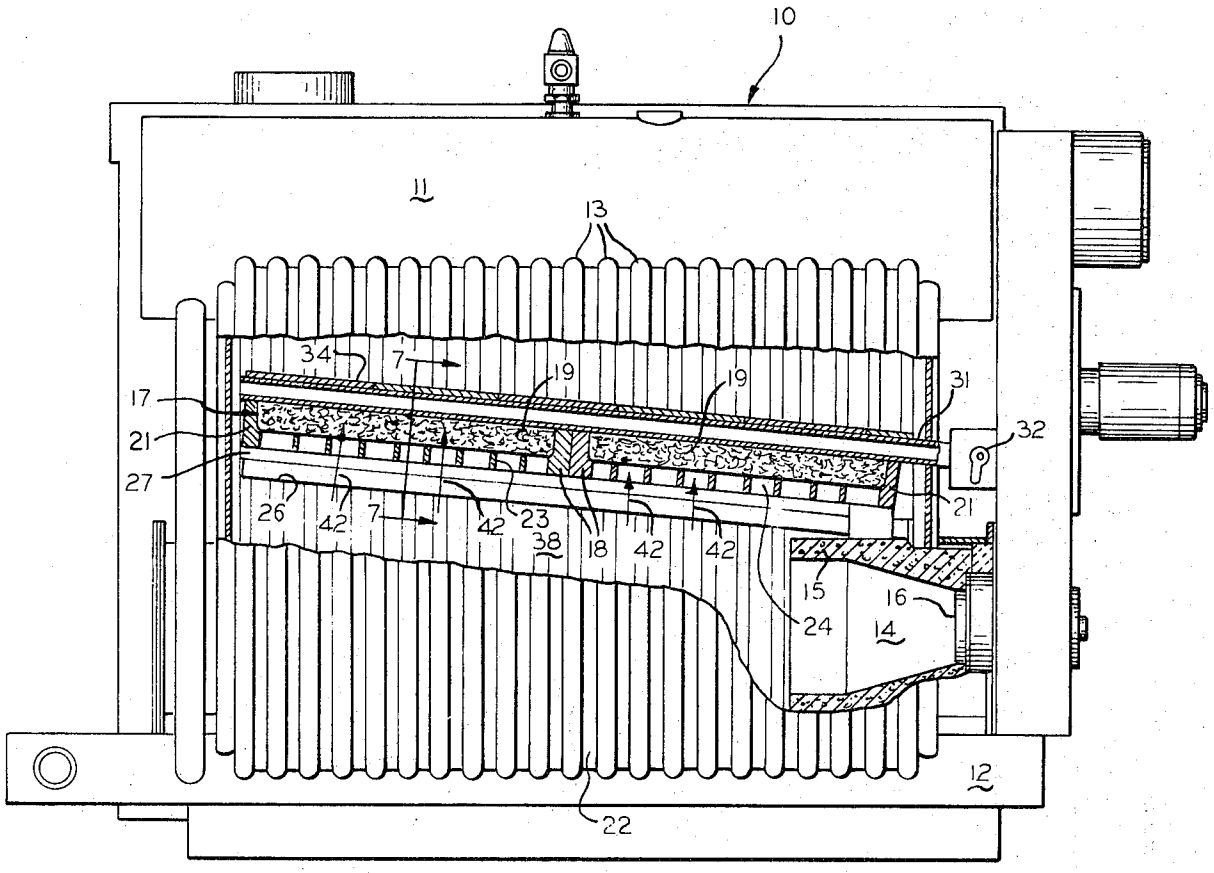
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[57] **ABSTRACT**

Fuel is burned in a primary combustion zone so that a substantial quantity of unburned hydrocarbons, such as carbon monoxide (CO) is produced along with some nitrogen oxides (NOx) and whereby essentially no oxygen remains at the completion of the combustion process. The gaseous combustion products are conducted through a gas dispersion matrix or bed in which the unburned hydrocarbons and NOx react to produce carbon dioxide (CO_2) and nitrogen (N_2). Air is then injected into the gases in a secondary combustion zone to oxidize the residual unburned hydrocarbons to CO_2 in which case the exhaust gases are substantially free of air polluting CO and NOx.

20 Claims, 4 Drawing Figures



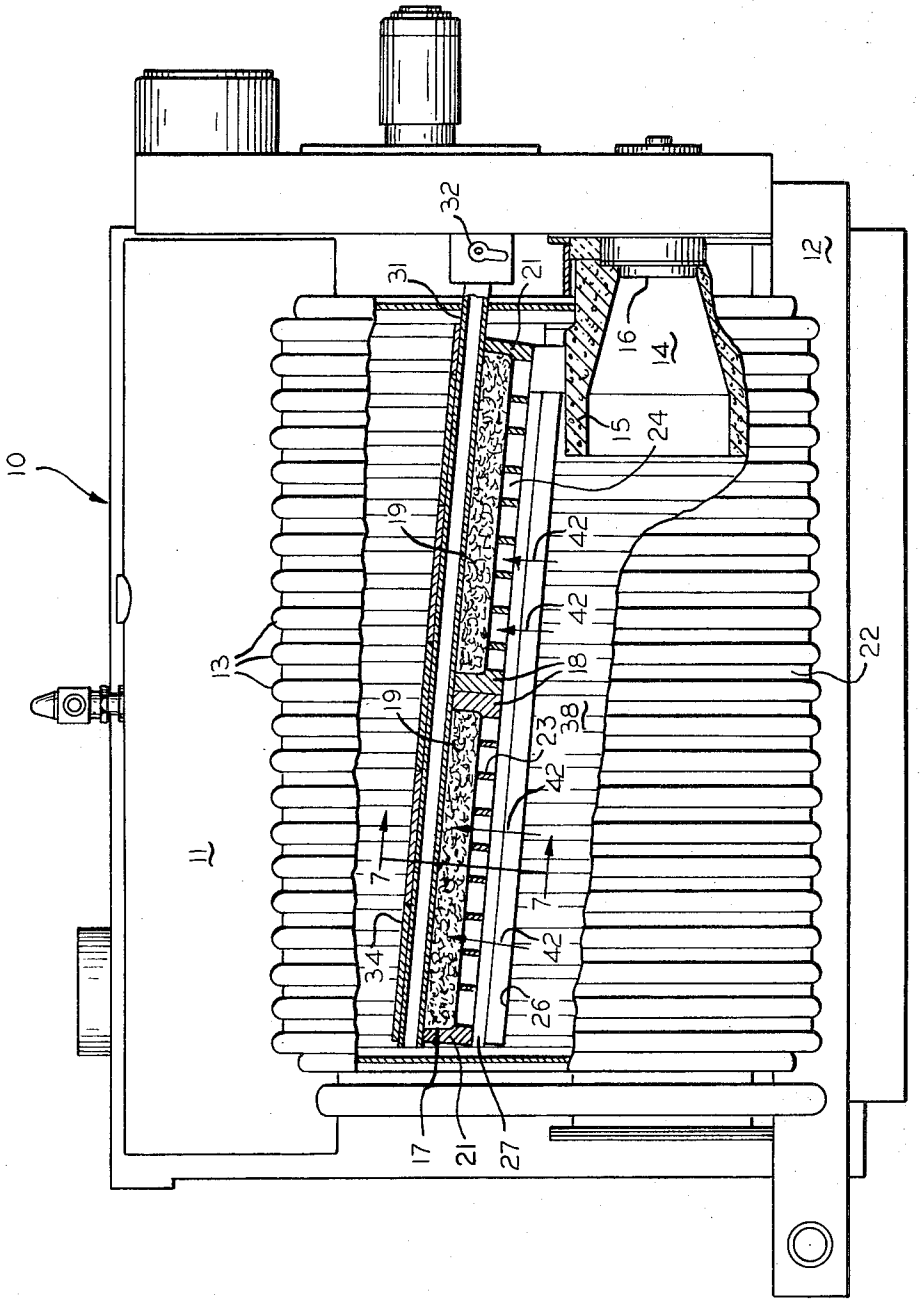


FIG. 1

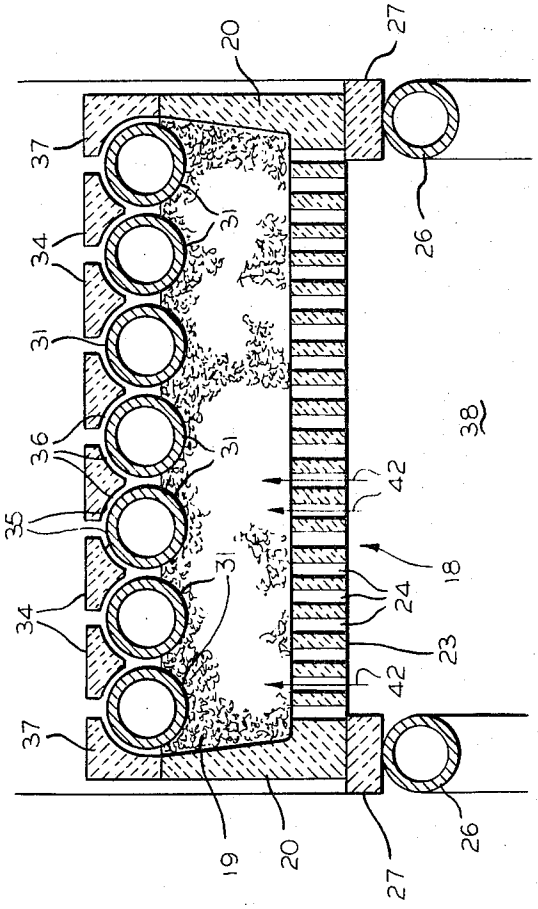

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FIG.2

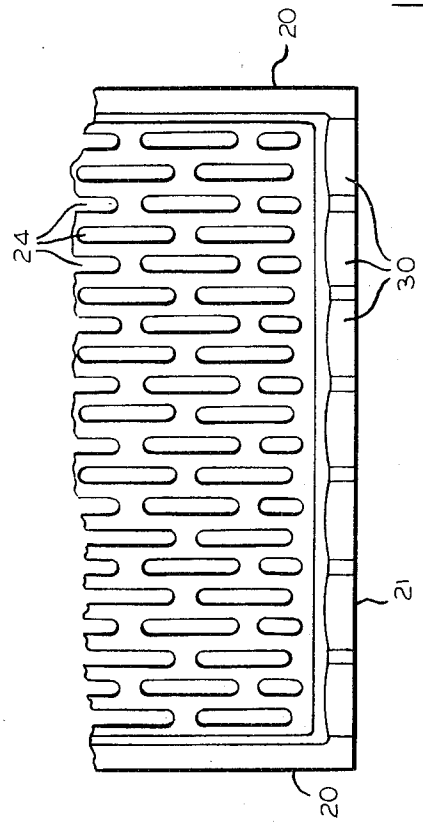

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FIG.3

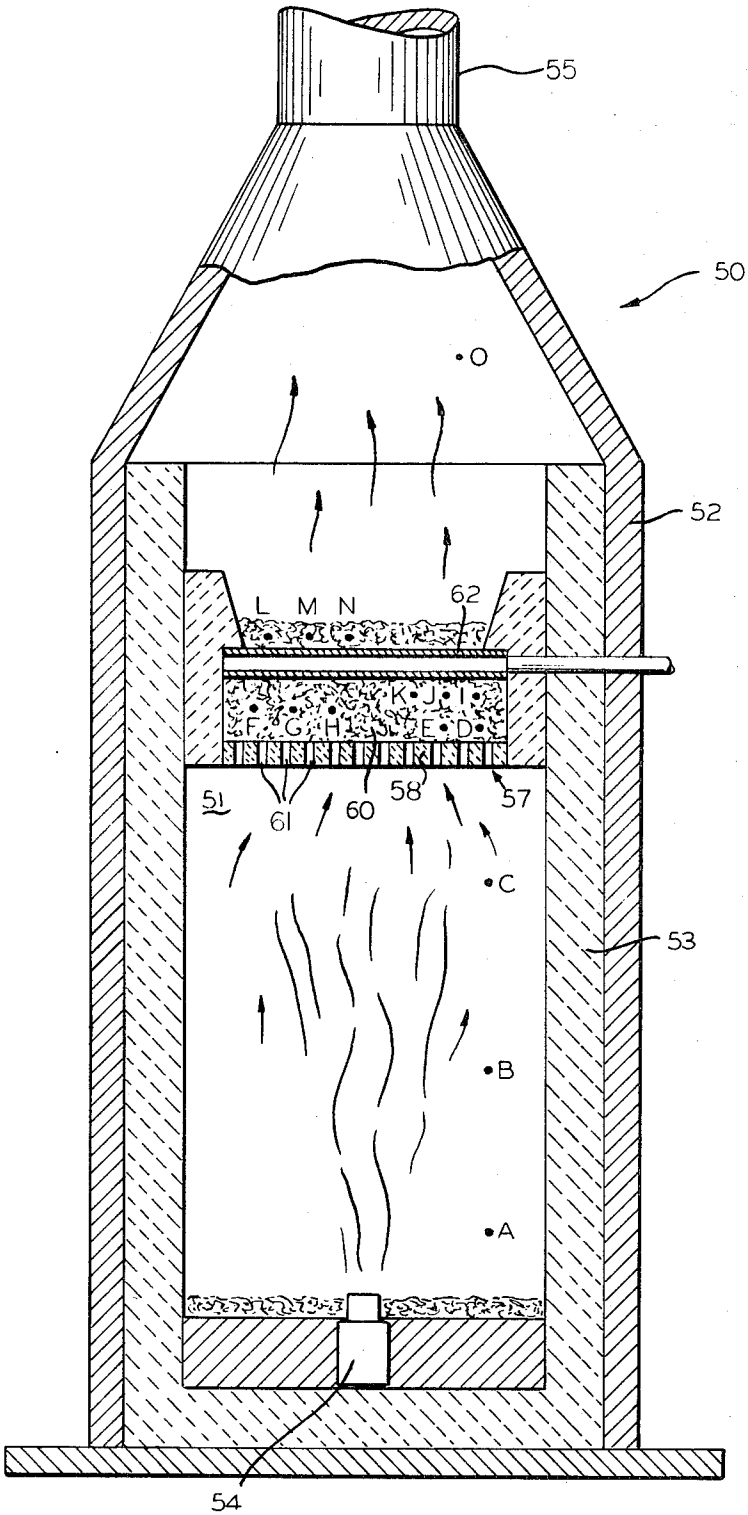


FIG.4

REDUCTION OF NITROGEN OXIDES FROM PRODUCTS OF HYDROCARBON COMBUSTION WITH AIR

CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of application Ser. No. 198,767 filed Nov. 15, 1971.

BACKGROUND OF THE INVENTION

This invention relates to reducing air polluting agents such as nitrogen oxides and unburned hydrocarbons in the exhaust gases of carbonaceous and hydrocarbon fuel burners.

SUMMARY OF THE INVENTION

It is a primary object of this invention to reduce air pollution by reducing the NO_x which is emitted to the atmosphere in the exhaust gases from carbonaceous and hydrocarbon fuel burners and to minimize the emission of carbon monoxide and other unburned hydrocarbons as well.

A further object is to provide a gas purifying device in which NO_x is reacted with unburned hydrocarbons to produce harmless N_2 and CO_2 and in which the residual hydrocarbons are completely oxidized or burned by means of second stage combustion to thereby produce harmless CO_2 which may be exhausted to the atmosphere along with the N_2.

A still further object is to provide a combustion gas purifying device which does not adversely affect the efficiency of the combustion process.

In general terms, the present invention involves dividing a combustion chamber into two stages. In the first stage hydrocarbon fuel is burned with insufficient air to completely oxidize all of the carbon in the fuel in which case a substantial amount of unburned hydrocarbon is intentionally produced in the gaseous combustion products. Some noxious nitrogen oxides are also produced but in relatively low amounts since production of these oxides is inhibited by the presence of unburned hydrocarbons, such as CO. The stream of gaseous combustion products from the first stage are conducted through a porous matrix or bed of relatively inert refractory material. The gases are dispersed in the matrix or bed and are intimately mixed whereby the NO_x and unburned hydrocarbons react to form CO_2 and N_2. Preferably, a catalyst is present in the matrix to promote this reaction. The combustion gases including CO_2, N_2, and CO are then passed through a second combustion stage where a source of oxygen, such as air, is introduced in any suitable manner such as by injection into the gas stream. This oxidizes the residual unburned hydrocarbons and carbonaceous material to CO_2 in which case the exhaust gases are comprised mainly of harmless CO_2 and N_2 which may be discharged to the atmosphere as non-pollutants. The dispersion bed or matrix and the second combustion stage are located in the combustion chamber so as to not impair the combustion process and to permit extraction of a large percentage of the heat units available from the combustion gases for useful purposes.

How the above-mentioned and other more specific objects of the invention are achieved will appear in the detailed description of an illustrative embodiment of the invention which will be set forth shortly hereinafter in reference to the drawings.

DESCRIPTION OF THE DRAWINGS

FIG. **1** is a vertical side elevation, partly in section, of a boiler incorporating a preferred embodiment of the invention;

FIG. **2** is a view taken along lines **3—3** in FIG. **1**; and

FIG. **3** is a fragmentary view of a portion of the gas purifying means illustrated in FIGS. **1** and **2**;

FIG. **4** is a schematic representation of an alternate embodiment of the invention.

DESCRIPTION OF PREFERRED EMBODIMENTS

A use of the new combustion gas purifier is exemplified in the steam generating boiler **10** which is shown in FIG. **1.** The boiler comprises an upper drum **11** which connects with a lower feed water drum **12** by means of a plurality of water filled tubes **13.** These tubes together with the drums **11** and **12** define a space in which heat is exchanged between the hot combustion gases and the tubes and drums. In the front lower region of the boiler there is a burner chamber **14** lined with refractory material **15.** A web **22** extends between each of the water tubes to define a combustion chamber.

At the front end of the burner chamber **14** is an aperture **16** in which a burner (not shown) is installed. The burner may be any of the conventional types which are used for burning vaporized fluid hydrocarbon fuel or gaseous fuel in the presence of air.

Extending transversely across the combustion chamber is a gas purifying assembly **17** consisting of a refractory holder **18** for containing gas dispersion bed **19.** The bed **19** may be comprised of any suitable refractory material which is substantially nonreactive with the combustion gases within the expected gas temperature range. The bed **19** should also be porous enough for combustion gases to be conducted therethrough without substantial pressure drop or draft loss. For example, the bed **19** may comprise such refractory materials as silicon carbide or alumina in pellet, chip, spheroidal, or other forms which will create a bed of relatively high porosity. In one nonexclusive example, the bed was formed of silicon carbide aggregate having an average size of about one quarter inch by one half inch loosely packed at random.

The refractory holder **18** may comprise a single member or in larger size units, a plurality of members as shown in FIG. **1.** Each of the holder units **18** includes side and end walls **20** and **21** respectively, and a bottom wall **23** for containing the bed material **19.** The bottom wall **23** of holder **18** is provided with suitable perforations **24** which permit the passage of flue gas therethrough but which retain the bed material **19.** While the perforations may take any convenient form, in the illustrated embodiment, they are shown to comprise a plurality of relatively short, closely spaced slots **24.** The assembly **17** may be supported within the boiler **10** in any suitable manner such as by hollow water tubes **26** which extend longitudinally at each side of the combustion chamber and which may be inclined upwardly from front to rear. A suitable insulating spacer member **27** may be disposed between each of the water tubes **26** and the holders **18.**

The end walls 21 of holders 18 are provided with a plurality of arcuate recesses 30 for supporting a plurality of elongate gas distribution tubes 31. This positions the tubes 31 in contact with the upper portion of the bed 19. The tubes 31 perform the function of distributing oxygen or an oxygen containing gas, such as air, along the upper portion of the bed 19. Toward this end, the tubes 31 may be formed of any suitable heat resistant material which may be porous or perforated. For example, a porous refractory such as silicon carbide or alumina or a perforated metallic tube, such as stainless steel, may be employed. The front end of each of tubes 31 are suitably connected to a manifold 32 which is in turn connected to a source of oxygen containing gas, such as air.

A plurality of spaced apart, refractory gas deflecting members 34 are suitably positioned in general parallelism with air tubes 31. The members 34 may be fabricated from a single member or a plurality of abutting members so that they will have substantially the same length as the air tubes 31. As seen more particularly in FIG. 3, one member 34 is positioned generally above and between each pair of adjacent air tubes 31. In addition, the members 34 are formed in vertical cross section with an arcuate surface 35 facing each of the adjacent air tubes 31 and spaced therefrom to form a gap 36 therebetween. A gas deflecting member 37 is affixed at each side of the holder 18 and each has the configuration of approximately half of the members 34 to form a similar gas directing gap 36 along each of said sides. The gas deflecting members 34 and 37 may be composed of any suitable refractory material, such as silicon carbide. As will be described more fully hereinbelow, the gaps 36 between the tubes 31 and between said tubes and the gas deflecting members 34 and 37 comprise a secondary combustion zone. The space below the tubes 31 comprises a primary combustion zone 38.

According to prior or conventional practice, an effort is made to mix sufficient air with the fuel to completely oxidize the combustible components of the fuel so as to produce, if possible, combustion gases which have a high percentage of CO_2 and a low percentage of unburned hydrocarbons such as CO. Under such combustion conditions, significant quantities of nitrogen oxide pollutants are also produced as a result of nitrogen and oxygen from the combustion air combining at the high temperatures normally present. It has been found that a substantially greater quantity of nitrogen oxides or NO_x is produced in the absence of unburned hydrocarbons such as CO at temperatures in excess of approximately 2500° F. Under conventional combustion conditions an excess of air is usually introduced in an effort to assure that at least the stoichiometric amount of oxygen will be available from the air to completely oxidize the carbon, hydrogen and other combustible elements in the fuel at every point in the combustion zone. The excess oxygen present, particularly atomic oxygen, contributes to increased production of NO_x at elevated temperatures.

In accordance with the invention, combustion is controlled in the primary combustion zone 38 to insure the presence of unburned hydrocarbons and/or the lack of atomic oxygen. Because the reaction between carbon and oxygen is preferential to that between oxygen and nitrogen, the presence of unburned hydrocarbons inhibits the formation of NO_x. Toward this end the combustion in the primary combustion zone 38 is controlled in any manner well known in the art, such as by adjustment of the fuel-air ratio.

As seen in FIGS. 1 and 2, the stream of gaseous combustion products identified by reference numeral 42 passes upwardly through the slots 24 and into the gas dispersion bed 19. There gases include a substantial amount of unburned hydrocarbons, such as CO and some nitrogen oxides. In the dispersion bed the gases are intimately mixed where the CO and NO_x react to form N_2 and CO_2. In accordance with the invention, the gas exiting from the primary combustion zone 38 should include unburned hydrocarbons and carbonaceous material as reflected by an excess of 400 ppm CO in order to fully react with the NO_x present. In one example, which has been successfully employed, 2000 ppm CO were found to be satisfactory.

The refractory bed 19 may also include a catalyst to promote the reaction between CO and NO_x. Although the optimum concentration of the catalyst in the bed 19 will vary in accordance with concentrations of the various gases in the combustion gas stream, in an illustrative case the catalyst was in the form of metal strips of approximately 1/64 inch by 1/8 inch by several inches in length. The catalyst was dispersed in a 3½ inches thick bed of silicon carbide (SiC). Of course, the bed thickness and the amount of catalyst depends on combustion gas flow conditions and will differ from case to case. Suitable catalysts include iron, nickel, chromium, copper and platinum as compounds or as alloys and mixtures thereof. This list of catalysts is not necessarily exhaustive of catalysts which will promote the reaction between CO and NO_x. In the example given above, the catalytic metal strips were type 18-8 stainless steel alloy which is effective as a catalyst because it contains iron, nickel and chromium at least. The catalysts may also be fused or dissolved in the silicon carbide or other refractory material of which the bed 19 is comprised. Some grades of SiC may contain impurities which may serve as catalysts. The catalyst may also be sprayed, metallized or otherwise deposited on the surface of the refractory material grains of the bed. The object in any case is to thoroughly disperse the combustion gases in the bed and to effectuate intimate contact between the gases and the catalytic agent if one is used.

The combustion gases evolving from the dispersion bed 19 include significant quantities of N_2, CO_2, and unburned hydrocarbons, such as CO. This residual unburned CO, which has not reacted with the NO_x in the bed 19, passes upwardly and into the secondary combustion zone 36 between the air tubes 31 and the members 34. In addition, secondary combustion air, which evolves into the secondary combustion zone 36 from the air tubes 31 causes the complete oxidation of the unburned hydrocarbons to CO_2, which is an exothermic reaction. The engagement between the air tubes 31 and the bed 19 insures adequate mixing of the combustion air and the gases passing through the bed 19. Because nitrogen in air can be converted to NO_x at temperatures of approximately 2700° F or above, the temperature in the secondary combustion zone 36 is maintained below about 2500° F. The temperature of zone 36 is dependent upon the radiation of heat away therefrom and the temperature and quantity of air discharged from pipes 31. These factors are controlled to maintain the temperature in zone 36 below that wherein significant quantities of NO_x are formed. The

radiation of heat away from the bed **19** is enhanced by its being exposed to the heat absorbing surfaces represented by the water tubes **13.**

The means for reacting unburned hydrocarbons and carbonaceous material with NO_x and for introducing secondary combustion air for oxidizing any of the former that may remain to CO_2, may be devised in a way that permits eliminating the bed of refractory material if desired. For instance, instead of the bed **19** of refractory aggregate materials an open celled metallic sponge, a mat of gas transmissive metallic or refractory filamentary material, or monolithic porous refractory member can be used to disperse the combustion gases and effect the reaction of unburned hydrocarbons and/or carbonaceous material and NO_x. A catalyst, if desired, can be incorporated in or deposited on the material of which the mat, sponge porous refractory is comprised. This could be in a refractory chamber in which the secondary air for oxidizing the unburned hydrocarbons to CO_2 and water is introduced remotely from the mat or sponge so as to not overheat these elements.

As implied, the location, configuration and operating temperature of the new combustion gas purifying device in a particular combustion apparatus will depend on a number of variables including the primary and secondary combustion rates, the quantity of hot gases to be handled, the temperature of the primary combustion gases and the tolerable radiation from the device itself. In any case, it will be desirable to have the gas reside in the bed **19** and secondary combustion chamber **36** for a long enough period to obtain sufficient reactions between the unburned hydrocarbons and the NO_x in the bed and between CO and O_2 and the secondary combustion zone. The residence time of the gases in bed **19** depends on the thickness, porosity and location of the bed **19,** and reaction rate and temperature.

Generally, the amount of air injected in the secondary combustion stage needed will depend on the unburned hydrocarbons discharged from the primary combustion zone **38** and available for reaction in the secondary combustion zone **36.** In one embodiment, the secondary combustion air needed amounted to about 10 percent of the stoichiometrically required air for complete combustion of the fuel. In other words, 90 percent of the total air for complete combustion was used in the primary stage and the remaining 10 percent was injected in the secondary combustion stage to convert the residual CO to CO_2. In reality, of course, more than the stoichiometrically required amount of air is used since not all of the oxygen in the air mixes thoroughly enough with the secondary combustion gases to become involved in the oxidation reactions.

The effectiveness of the invention in removing NO_x from discharge gases is illustrated with respect to the test apparatus shown in FIG. **4.** Here the combustion device **50** includes a chamber **51** defined by a metallic shell **52** having a refractory lining **53.** A suitable burner **54** is provided at the lower end of shell **51** and a discharge stack **55** adjacent its upper end. A gas dispersion bed **57** is disposed intermediate the ends of chamber **51** and includes a refractory holder **58** for containing a silicon carbide refractory aggregate **60.** The lower end of holder **58** includes a plurality of suitable apertures **61** to permit the flow of gases therethrough.

Secondary combustion air may be introduced through a porous refractory pipe **60** which is below the upper surface of the refractory bed **62.**

In the experimental apparatus, number **2** fuel oil was burned in less than sufficient air to effect stoichiometric combustion. Measurements of carbon dioxide, carbon monoxide and oxygen were measured above and below the dispersion bed **57** and measurements of NO_x were taken at points A–K and O and temperature at points A–L as indicated in FIG. **2.** Also, Bacharach numbers, which is a measurement of soot concentration, were also taken above and below the dispersion bed **57.** The following results were obtained:

	BELOW	ABOVE
CO_2	15.0% of total	10.2% of total
O_2	0.2% of total	6.0% of total
CO	2000 ppm	None Detected
Bacharach No.	9	2

POINT	NOx ppm	TEMP – °F
A	96	2520
B	98	2600
C	89	2560
D	106	2560
E	105	2570
F	107	2540
G	85	2570
H	86	2570
I	90	2500
J	88	2510
K	84	2550
L	—	2300
M	—	2330
N	—	2290
O	70	2040

It can be seen that the NO_x concentration in the discharge area was about 70 ppm. This compares favorably with typical pollution control standards which permit 100–150 ppm NO_x. In addition the soot concentration was held within acceptable limits while no carbon monoxide was detected.

Although the new combustion gas purifying device has been described in particular reference to a steam or hot water generating boiler, it will be understood by those skilled in the art that the device and a comparable operating mode may be adapted for use in various devices which fall within the generic class of fuel burning or reacting devices such as residential and commercial furnaces and space heaters, hot water heaters, incinerators, heating and power generating boilers, other combustion apparatus which burn liquid or gaseous hydrocarbon or carbonaceous fuels. Thus, the foregoing description should be considered illustrative of the manner in which the invention is used and the scope of the invention should be governed by interpretation of the claims which follow.

We claim:

1. A combustion device adapted for reducing nitrogen oxides in its exhaust gas, comprising:

a. an enclosure having fuel burning means and an outlet,

b. means within said enclosure for defining a first combustion zone, means for introducing fuel and oxygen into said first combustion zone and for limiting the amount of oxygen to less than the amount required for complete combustion to produce combustible products including unburned hydrocarbons,

c. means within said enclosure for defining a second combustion zone coupled to said first combustion zone for receiving combustion products therefrom and including gas pervious tube means disposed within said second combustion zone for introducing oxygen at plural points into said gaseous combustion products whereby to oxidize residual combustible products including unburned hydrocarbons therein before discharge.

2. The invention set forth in claim **1** and including means for maintaining the temperature in said secondary combustion zone below about 2700°F.

3. The invention set forth in claim **2** wherein

said enclosure also includes a gas dispersion means between said first combustion zone and said second combustion zone, said gas dispersion means being arranged so that the combustion products emitted from said first combustion zone pass therethrough before being received in said second combustion zone.

4. The invention set forth in claim **3** wherein:

a. said gas dispersion means comprises a porous, refractory matrix.

5. The invention set forth in claim **4** wherein:

a. said matrix includes a catalyst for promoting the reaction of nitrogen oxides with unburned hydrocarbon and carbonaceous materials.

6. The invention set forth in claim **4** wherein:

a. said refractory material matrix comprises silicon carbide fragments forming a porous bed.

7. The invention set forth in claim **3** wherein:

a. said gas pervious tube means comprise porous tubes of refractory material.

8. The invention set forth in claim **3** wherein:

a. said gas dispersion means comprises a porous layer of catalytic material.

9. The invention set forth in claim **3** wherein:

a. said dispersion means comprises a metallic element selected from the group consisting of iron, nickel, chromium, copper and platinum and alloys thereof.

10. The invention set forth in claim **1** wherein said gas pervious tube means includes at least one hollow tube disposed in said second zone and having plural, spaced apart gas permeable means formed in said hollow tube for permitting the flow of gas therethrough.

11. The invention set forth in claim **10** wherein said gas pervious tube means has a plurality of apertures formed therein.

12. The device set forth in claim **1** and including heat absorbing means located in said enclosure downstream from said second combustion zone for absorbing heat from said second combustion zone and for maintaining the temperature in said second combustion zone below a predetermined level.

13. The method of reducing nitrogen oxides in exhaust gases comprising:

providing a primary combustion zone,

incompletely oxidizing a fuel in said primary combustion zone to provide gaseous combustion products including unburned hydrocarbons,

passing said gases through a second combustion zone,

introducing a source of oxygen into said secondary combustion zone whereby to oxidize the residual unburned hydrocarbons in said stream before discharge thereof,

maintaining the temperature in said secondary combustion zone at less than 2700°F,

said unburned hydrocarbon comprises carbon monoxide having concentration in excess of 400 parts per million.

14. A combustion device adapted for reducing nitrogen oxides in its exhaust gas, comprising:

a. an enclosure having fuel burning means and an outlet,

b. a first combustion zone in said enclosure wherein fuel is burned with incomplete oxidation to produce combustible products including unburned hydrocarbons and including gas dispersion means through which said gaseous combustion products are conducted,

c. a second combustion zone including porous silicon carbide tube means for introducing oxygen into said gaseous combustion products whereby to oxidize residual combustion products including unburned hydrocarbons therein before discharge, and

d. means for maintaining the temperature in said secondary combustion zone below about 2700°F.

15. A combustion device adapted for reducing nitrogen oxides in its exhaust gas, comprising:

means defining a first combustion zone, first means for introducing fuel and less than the amount of oxygen and nitrogen containing gas required for complete combustion wherein fuel is burned with incomplete oxidation to produce combustible products including unburned carbonaceous materials,

means defining a second combustion zone,

means for conducting said combustible products to said second combustion zone,

said second combustion zone including plural tube means extending into said zone, said tube means being constructed and arranged to supply air to plural zones within said second combustion zone whereby to oxidize residual combustible products including unburned carbonaceous materials therein before discharge.

16. The combustion device set forth in claim **15** wherein said tube means extends generally transversely to the direction of gas flow in said secondary zone whereby said gases from said primary zone are forced to flow around said tube means to promote mixing with said air.

17. The invention set forth in claim **16** and including a common manifold connected to at least one end of each of said tube means for delivering air thereto.

18. The invention set forth in claim **17** and said tube means are formed of silicon carbide material.

19. The invention set forth in claim **18** wherein said tube means are porous.

20. The invention set forth in claim **19** wherein each of said tube means has a plurality of apertures formed therein.

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