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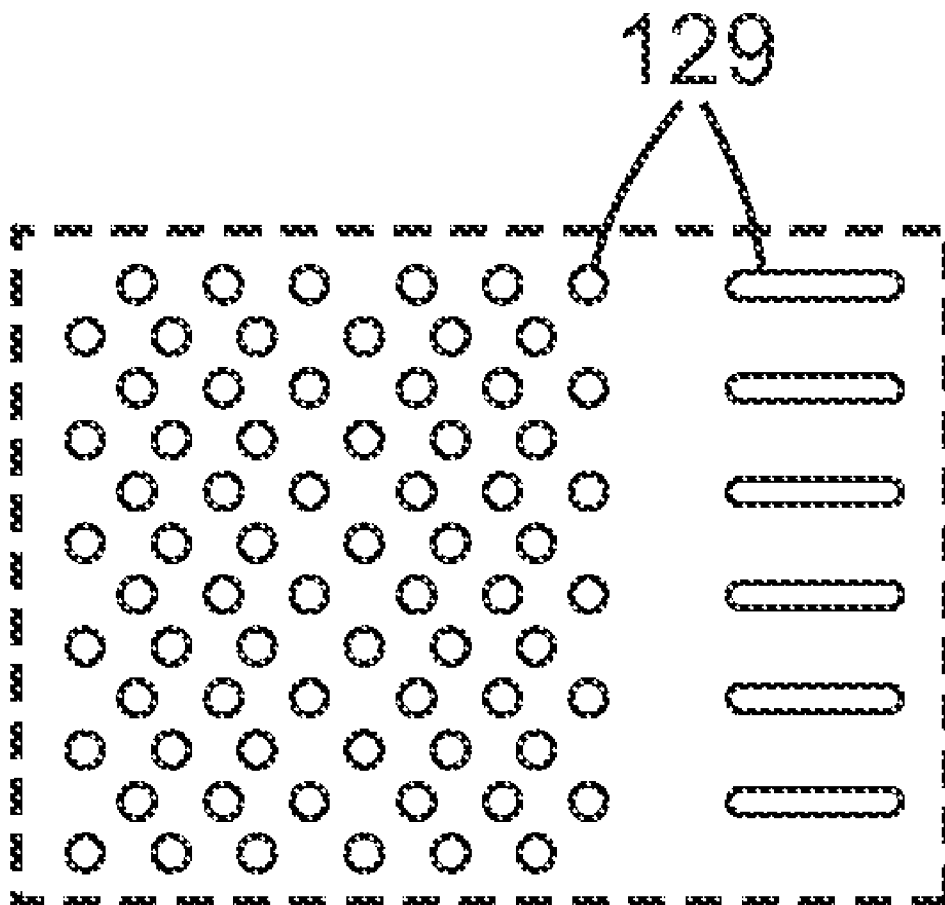
(19) **United States**(12) **Patent Application Publication**
Beaber et al.(10) **Pub. No.: US 2015/0330623 A1**(43) **Pub. Date: Nov. 19, 2015**(54) **CATALYTIC BURNER****Publication Classification**(71) Applicant: **3M INNOVATIVE PROPERTIES COMPANY**, Saint Paul, MN (US)(51) **Int. Cl.**
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F23C 13/00 (2006.01)(72) Inventors: **Aaron R. Beaber**, Minneapolis, MN (US); **Thomas E. Wood**, Stillwater, MN (US); **Adam C. Schendel**, Big Lake, MN (US); **Badri Veeraraghavan**, Woodbury, MN (US); **Evan Koon Lun Yuuji Hajime**, Woodbury, MN (US)(52) **U.S. Cl.**
CPC **F23D 14/18** (2013.01); **F23C 13/00** (2013.01)(73) Assignee: **3M INNOVATIVE PROPERTIES COMPANY**, ST. Paul, MN (US)(57) **ABSTRACT**(21) Appl. No.: **14/651,543**(22) PCT Filed: **Nov. 21, 2013**(86) PCT No.: **PCT/US2013/071258**

§ 371 (c)(1),

(2) Date: **Jun. 11, 2015****Related U.S. Application Data**

(60) Provisional application No. 61/736,173, filed on Dec. 12, 2012.

A catalytic burner includes a porous diffuser member and a porous distributor member. At least one seal extends between the porous diffuser member and the porous distributor member thereby defining an oxidation chamber. Catalyst media particles for catalyzing an oxidation reaction of a fuel stream to produce heat and an exhaust stream is disposed within the oxidation chamber. The catalyst media particles comprise carrier particles. The carrier particles comprise refractory material, and at least some of the carrier particles have thereon an outer coating comprising an oxidation catalyst. The catalyst media particles have a void fraction of at least 0.6.



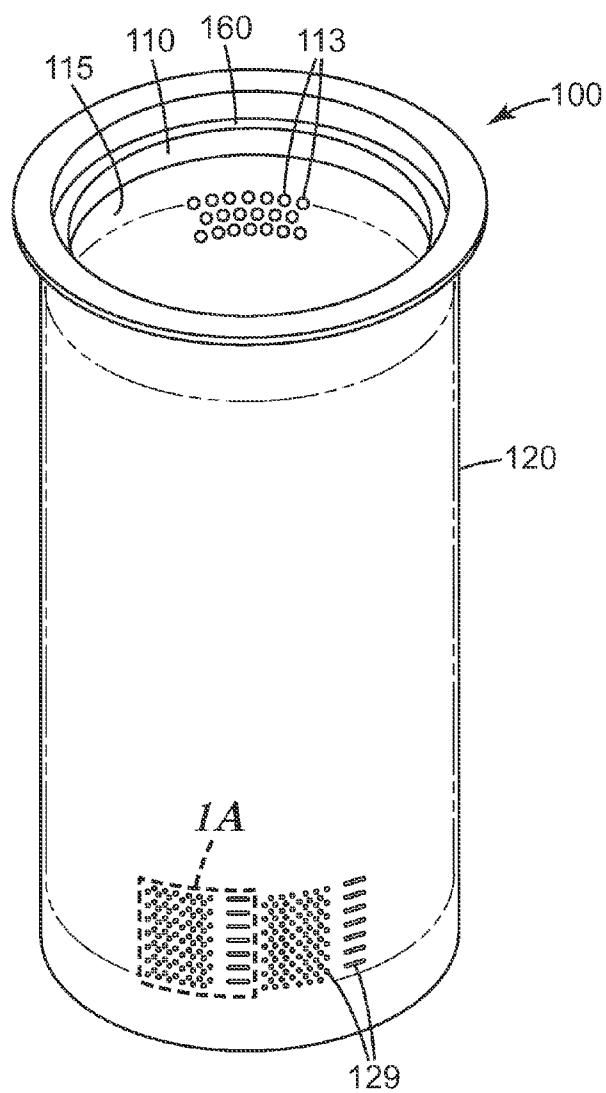


FIG. 1

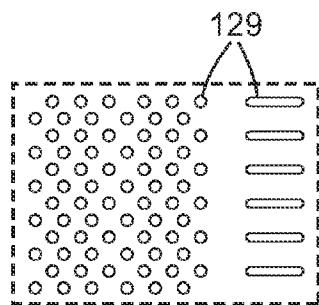


FIG. 1A

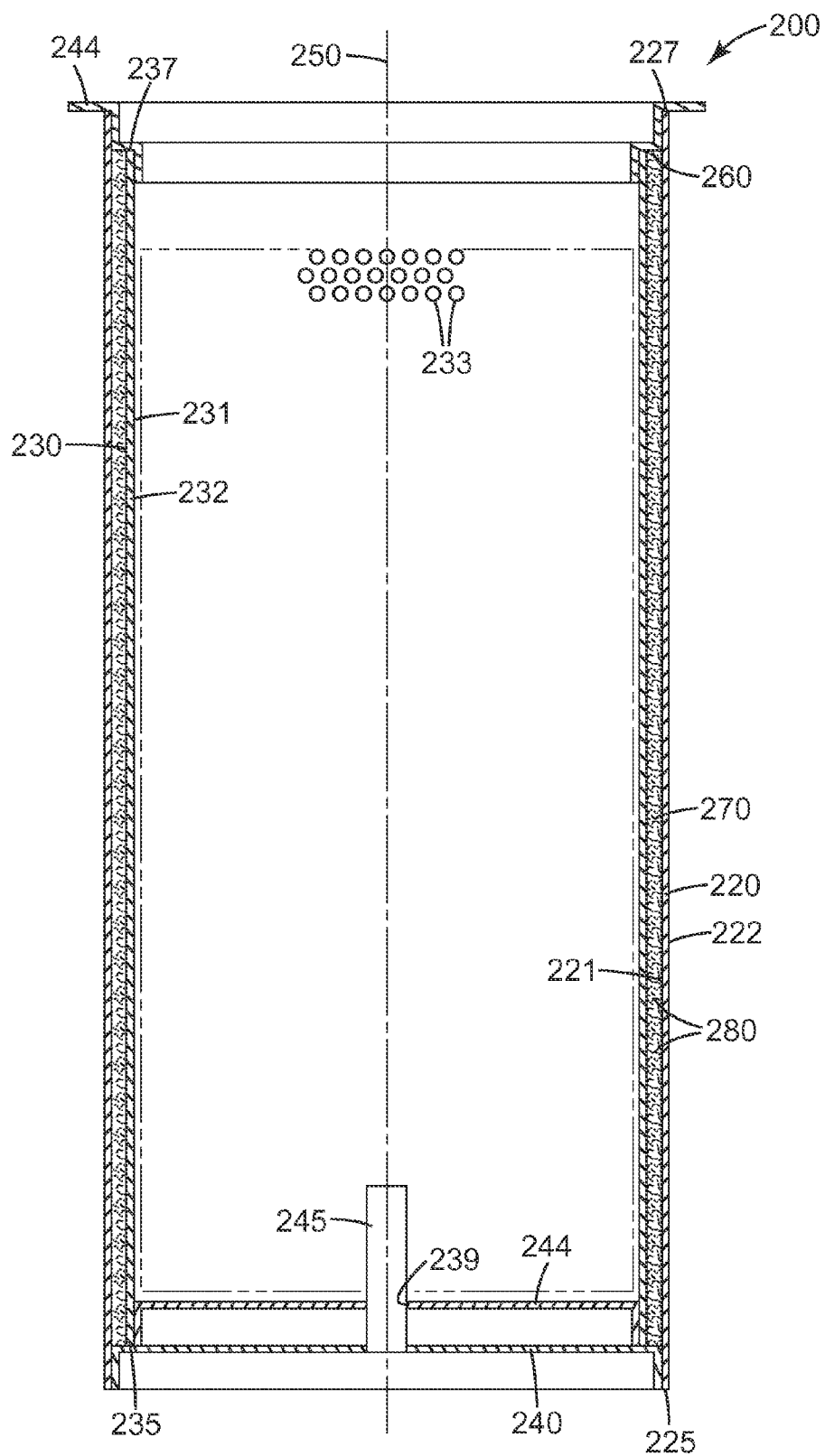


FIG. 2

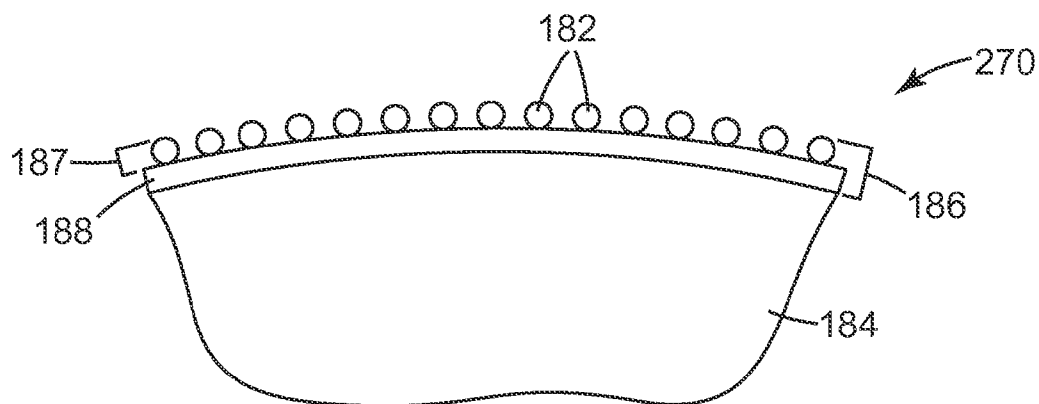
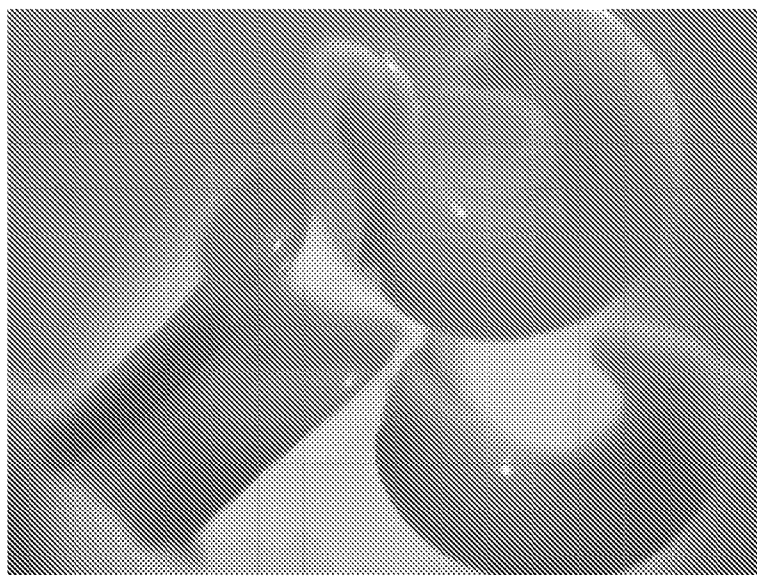


FIG. 3



1.0 mm

FIG. 5

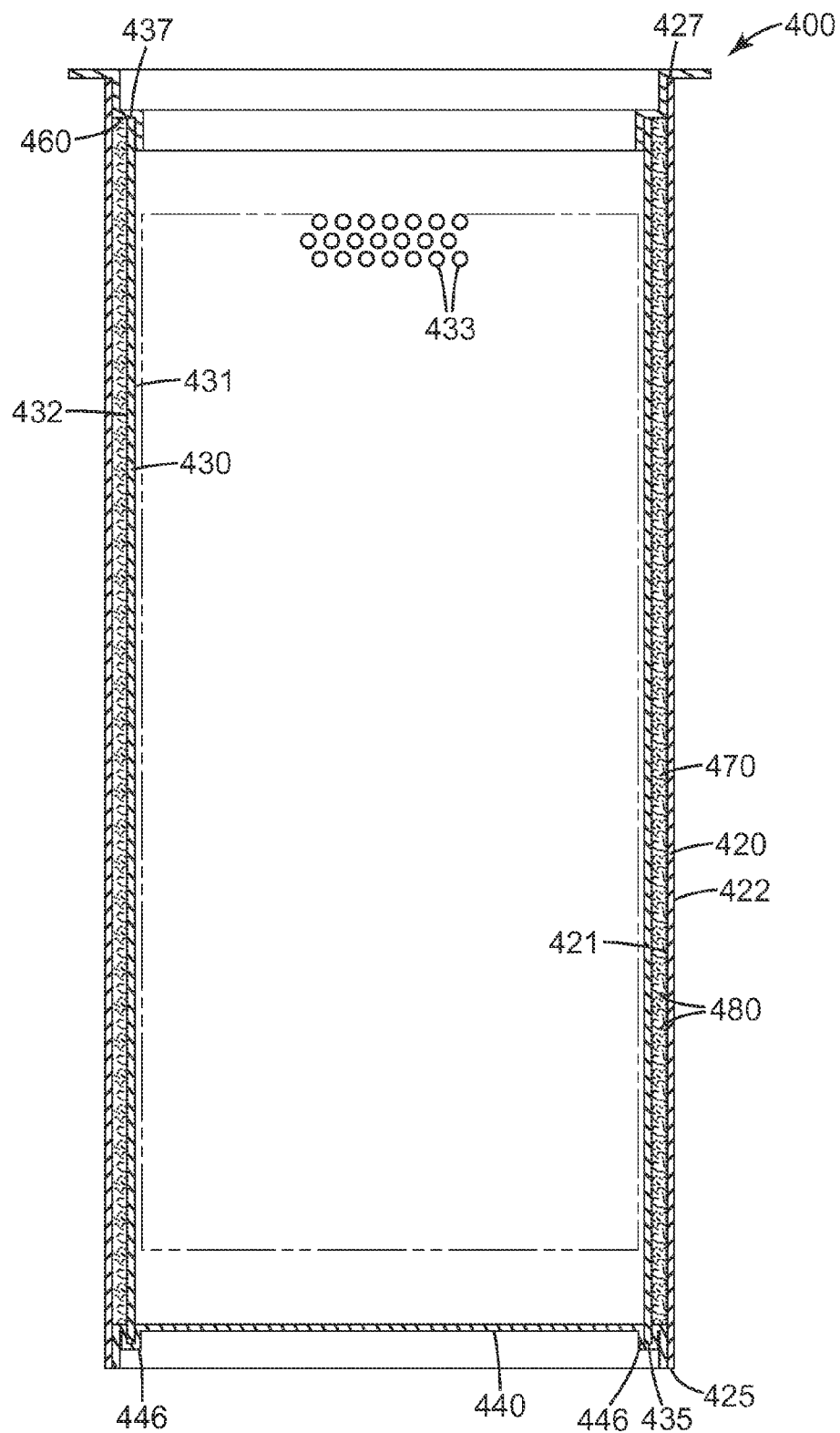


FIG. 4

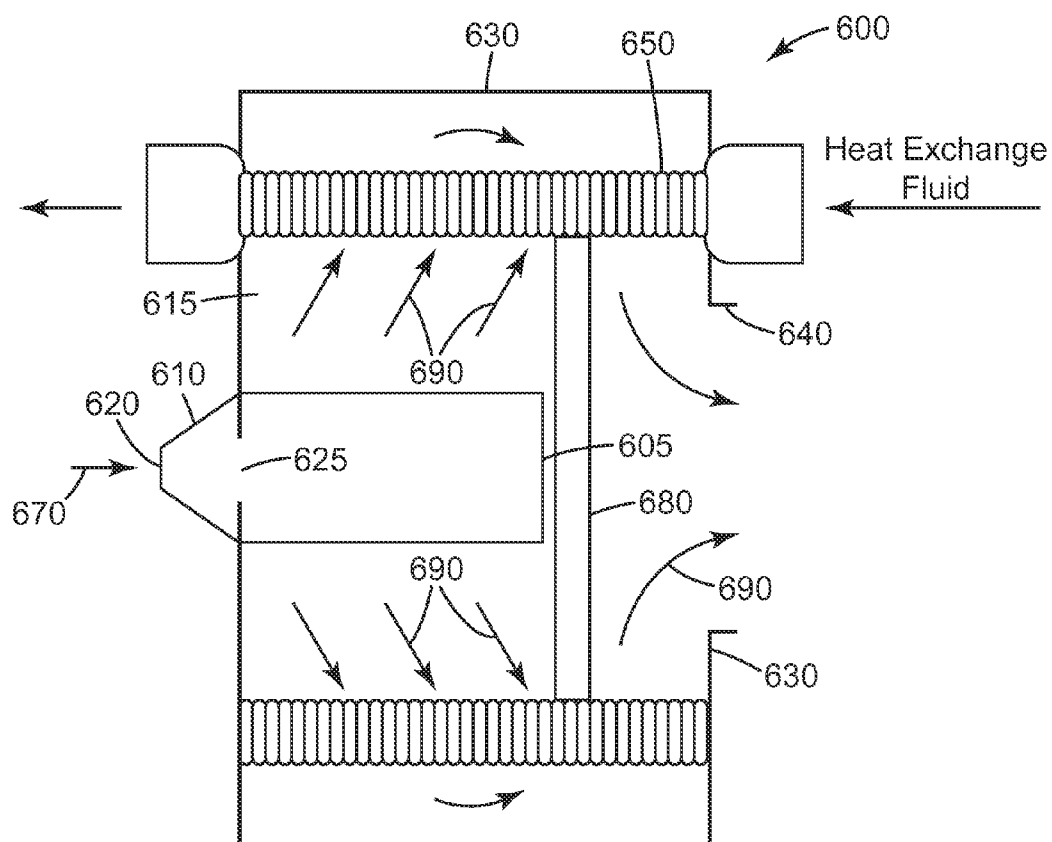


FIG. 6

CATALYTIC BURNER

STATEMENT OF FEDERALLY-SPONSORED
RESEARCH

[0001] This invention was made with Government support under Contract No. DE-EE0003491, awarded by the Department of Energy. The Government has certain rights in this invention.

TECHNICAL FIELD

[0002] The present disclosure relates to catalytic burners and catalytic media used in them.

BACKGROUND

[0003] In commercial boilers, gaseous hydrocarbon fuel sources are converted to thermal energy inside a heat exchanger contained within the boiler. Typically, the space inside the heat exchanger is kept small to minimize the size of the boiler. To minimize operating and environmental cost, it is desirable that the fuel is efficiently converted to thermal energy and the amount of deleterious byproducts (e.g., NO_x, CO) is minimized.

[0004] Previous attempts to address this problem were directed to controlling the fluid dynamics of the gas-air mixture through perforated distributor and diffuser plates (this term of art is commonly used even though the “plates” may not be flat), which are commonly oriented as concentric, coaxial cylinders and constructed of a heat-resistant metal such as stainless steel. While these designs are compact and reduced the NO_x emissions, the reductions are becoming insufficient to meet increasingly stringent emissions standards.

SUMMARY

[0005] The present disclosure overcomes the foregoing problems by creating a high void fraction packed catalyst media particle bed disposed between the distributor and diffuser plates. The catalyst media particles lower the effective combustion temperature, and thus reduces the amount of thermal NO_x generated. A packed catalyst media particle bed is desirable to achieve adequate residence time of the fuel in the presence of the catalyst. However, the thickness (or depth) and void fraction (ε) of the catalyst media particle bed greatly affect the rate of heat transfer of the combusted fuel in the catalyst media particle bed. For a catalyst media particle bed that is too thick and/or has too low of a void fraction, the heat from the combustion reaction is ineffectively removed from the catalyst media particle bed, causing the temperature of the bed to increase rapidly and potentially exceed the stability limit temperature of the catalyst, thus making it inactive.

[0006] Depending on the thickness of the catalyst media particle bed, at low void fractions such as in the case of spherical catalyst media particles (e.g., monodisperse spherical particles having a void fraction of about 0.36) or crushed particles the bed temperature may exceed 800° C.

[0007] As used herein, the term “void fraction” refers to the ratio of the volume of void space between particles to the total container volume ($V_{\text{container}}$, expressed in cubic centimeters (cm³)) in a container packed full with the particles and is defined by the following expression:

$$\frac{V_{\text{container}} - V_{\text{exterior}}}{V_{\text{container}}} \quad (1)$$

where V_{exterior} is the exterior volume in cubic centimeters (cm³), including all solid material, open pores, and impervious portions. The exterior volume is defined as

$$V_{\text{exterior}} = W - S \quad (2)$$

where W is the saturated weight in grams, S is the suspended weight in grams, and the test liquid is water having a density of 1 gram per cubic centimeter (g/cm³). These terms can be calculated, for example, according to the procedure described for burned refractory brick in ASTM Designation C20-00 (Reapproved 2010), “Standard Test Methods for Apparent Porosity, Water Absorption, Apparent Specific Gravity, and Bulk Density of Burned Refractory Brick and Shapes by Boiling Water” from ASTM International, West Conshohocken, Pa.

[0008] High bed temperatures can cause the catalyst to become deactivated and/or volatilize off the surface and be carried away from the system with the exhaust stream. While the catalyst media particles can achieve low NO_x emissions, the high catalyst bed temperatures progressively reduce the effectiveness of the catalyst.

[0009] At greater void fractions the bed temperature falls with increasing void fraction, accompanied by increasing catalyst media particles life, until at void fractions greater than 0.6, the bed temperature typically does not exceed 800° C., and the palladium catalyst exhibits long life while still achieving low NO_x emissions.

[0010] In some embodiments, the catalyst media particles are substantially free of, or even free of, internal void space.

[0011] Accordingly, in one aspect, the present disclosure provides a catalytic burner comprising:

[0012] a porous diffuser member;

[0013] a porous distributor member;

[0014] at least one seal extending between the porous diffuser member and the porous distributor member, thereby defining an oxidation chamber; and

[0015] catalyst media particles for catalyzing an oxidation reaction of a fuel stream to produce heat and an exhaust stream, wherein the catalyst media particles is disposed within the oxidation chamber, wherein the catalyst media particles comprise carrier particles, each carrier particle comprising refractory material, wherein at least some of the carrier particles have thereon an outer coating comprising an oxidation catalyst, and wherein the catalyst media particles have a void fraction of at least 0.6.

[0016] In some embodiments, the porous diffuser member and the porous distributor member comprise substantially parallel porous plates. In some embodiments, the porous diffuser member comprises a first open end, the porous distributor member is disposed at least partially inside the porous diffuser member, and the porous distributor member comprises a second open end.

[0017] Features and advantages of the present disclosure will be further understood upon consideration of the detailed description as well as the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0018] FIG. 1 is a schematic perspective view of an exemplary catalytic burner 100 according to the present disclosure.

[0019] FIG. 1A is an enlarged detail of region 1A in FIG. 1.

[0020] FIG. 2 is a schematic cross-sectional view of exemplary catalytic burner 200.

[0021] FIG. 3 is an enlarged schematic cross-sectional view of an exemplary catalyst media particle 270.

[0022] FIG. 4 is a schematic cross-sectional view of exemplary catalytic burner 400.

[0023] FIG. 5 is a photomicrograph of an exemplary saddle-shaped carrier particle prepared in the PREPARATION OF CATALYST MEDIA PARTICLES E.

[0024] FIG. 6 is a schematic cross-sectional view of an exemplary boiler including a catalytic burner according to the present disclosure.

[0025] Repeated use of reference characters in the specification and drawings is intended to represent the same or analogous features or elements of the disclosure. It should be understood that numerous other modifications and embodiments can be devised by those skilled in the art, which fall within the scope and spirit of the principles of the disclosure. The figures may not be drawn to scale.

DETAILED DESCRIPTION

[0026] Referring to FIG. 1, exemplary catalytic burner 100 has inlet opening 110, adjacent seal 160, for a fuel stream (not shown) that passes through holes 113 (see FIG. 1A) in porous distributor member 115, is oxidized internally within the burner, and then released as an exhaust stream (not shown) through holes 129 in porous diffuser member 120.

[0027] Components of the catalytic burner, other than the catalyst media particles, may comprise any material capable of withstanding the heat (e.g., up to at least 800° C.) and corrosion due to the oxidation of the fuel stream. Stainless steels (e.g., in grade 304 or 316) are exemplary such materials.

[0028] The catalytic burner may have any suitable design, for example, as known in the art, including ones not exemplified herein. Examples of various designs include cylindrical (e.g., as shown in FIGS. 1-3), frustoconical (e.g., as described in PCT Publ. Appl. No. WO 2011/076220A1 (Möller)), parallel plate, and spheroidal configurations (e.g., as described in U.S. Pat. No. 5,474,443 (Viessmann et al.)).

[0029] The porous distributor member typically comprises a wall with a plurality of holes extending therethrough may be shaped, for example, as a cylindrical tube, conical tube, hollow spheroid, or a combination thereof, although this is not a requirement. The holes may be of any shape (e.g., slits and/or round holes) and pattern, but are preferably sufficiently sized that the catalyst media particles do not pass through them. In some embodiments, the plurality of holes in the wall of the porous distributor member comprises from 1 to 30 area percent, preferably from 5 to 25 area percent, and more preferably 5 to 15 area percent, based on the total surface area of the wall, although this is not a requirement. Preferably, the holes should be sufficiently small that flash back ignition is prevented. The selection of hole shape and size may depend on the composition of the fuel stream and its pressure, and will be known to those of ordinary skill in the art. In some embodiments, the porous distributor member comprises a sintered porous metal frit.

[0030] Likewise, the porous diffuser member typically comprises a wall with a plurality of holes extending there-

through may be shaped, for example, as a cylindrical tube, conical tube, hollow spheroid, or a combination thereof, although this is not a requirement. As before, the holes may be of any shape and pattern, but are preferably sufficiently sized that the catalyst media particles do not pass through them. In some embodiments, the plurality of holes in the wall of the porous distributor member comprises from 10 to 90 area percent, preferably from 15 to 45 area percent, based on the total surface area of the wall, although this is not a requirement. In some embodiments, the porous diffuser member comprises a wire mesh.

[0031] Typically, the porous diffuser member is adapted to at least partially enclose the porous distributor member while creating an oxidation chamber (e.g., at least partially filled with catalyst media particles) that has a substantially constant gap between the porous diffuser member and the porous distributor member. For use in residential boilers the gap is typically from 0.5 millimeter to 3 millimeters, while higher gaps are typical with larger burners intended for use with commercial and industrial boilers.

[0032] In some embodiments, the porous distributor member and/or the porous diffuser member is/are hollow.

[0033] In one embodiment, shown in FIG. 2, catalytic burner 200, having the same exterior general appearance of catalytic burner 100 (shown in FIG. 1), comprises porous diffuser member 220, which comprises a cylindrical conduit 221 having a wall 222 with a plurality of holes (not shown) therethrough, and which comprises first and second open ends 225, 227. Porous distributor member 230, which comprises a cylindrical conduit 231 having a wall 232 with a plurality of holes 233 therethrough, is disposed inside porous diffuser member 220 and comprises third and fourth open ends 235, 237. First open end 225 is covered by first end cap 240 and comprises an alignment pin 245 inwardly extending along longitudinal axis 250 of porous diffuser member 220. Second end cap 244 covers fourth open end 237, except for central opening 239 adapted to receive alignment pin 245. Annular seal 260 extends between porous diffuser member 220 and porous distributor member 230, thereby defining (in combination with first end cap 240) oxidation chamber 270.

[0034] Catalyst media particles 280 are disposed within oxidation chamber 270, and catalyze an oxidation reaction in the fuel stream to produce heat and an exhaust stream. Catalyst media particles 280 comprise carrier particles 284 that comprise refractory material. The catalyst media particles pack with a void fraction of at least 0.6.

[0035] Optionally a tubular screen may be disposed inside the porous distributor member to prevent any fragments of catalyst media particles that may form from passing inwardly through holes in porous diffuser member.

[0036] Referring now to FIG. 3, carrier particle 184 has an outer coating 186 comprising an oxidation catalyst 182. Outer coating 186 comprises inner layer 188 comprising cerium oxide in contact with carrier particle 184 and supports outer layer 189 comprising the oxidation catalyst.

[0037] In another embodiment, shown in FIG. 4, cylindrically-shaped catalytic burner 400, having the same exterior general appearance of catalytic burner 100 (shown in FIG. 1), comprises porous diffuser member 420, which comprises a cylindrical conduit 421 having a wall 422 with a plurality of holes (not shown) therethrough, and which comprises first and second open ends 425, 427. Cylindrically-shaped porous distributor member 430, which comprises a cylindrical conduit 431 having a wall 432 with a plurality of holes 433

therethrough, is disposed inside porous diffuser member 420 and comprises third and fourth open ends 435, 437. First open end 425 is covered by end cap 440. Third open end 435 engages groove 446 in end cap 440 thereby forming a seal. Annular seal 460 extends between porous diffuser member 420 and porous distributor member 430, thereby defining (in combination with end cap 440) oxidation chamber 470. Catalyst media particles 480 are disposed within oxidation chamber 470.

[0038] In use, the catalyst media particles catalyze an oxidation reaction of fuel stream to produce heat and an exhaust stream. The catalyst media particles comprise a plurality of carrier particles, at least some of which have an outer coating on at least a portion of their respective outer surface. The carrier particles are typically intentionally shaped (i.e., not randomly shaped as, for example, with crushed particles or powders) due to the process used to make them (e.g., by extruding or molding), although this is not a requirement. The selection of dimensions of the catalyst media particles is typically controlled, at least in part, by the size of the burner and the spacing between the porous distributor member and the porous diffuser member. In some embodiments, the catalyst media particles have an average particle diameter (i.e., the largest dimension of the particle) or largest of 0.5 to 20 millimeters, 0.5 to 6 millimeters, 0.5 to 3 millimeters, although other particle diameters can also be used. Since the outer coating is typically relatively thin, the shape and size of the catalyst media particles is typically substantially the same as that of the carrier particles.

[0039] The average spacing between the diffuser member and the distributor member is generally larger than the average particle diameter of the catalyst media particles. In some embodiments, the average spacing between the diffuser member and the distributor member is from 0.5 to 20 millimeters, from 0.5 to 10 millimeters, or from 1 to 6 millimeters, although this is not a requirement.

[0040] In some embodiments, the shape of the carrier particles is predetermined, for example, such as would result from a molding process. The carrier particles comprise, and may be composed of refractory material (i.e., one or more refractory materials). Examples of suitable refractory materials include aluminas (e.g., alpha alumina, beta alumina, gamma alumina, eta alumina, and/or theta alumina), mullite, aluminum titanate, zirconia, zircon, silica, fireclay (an impure kaolinite), cordierite, silicon carbide, and mixtures thereof. Additional examples of suitable refractory materials include oxides of metals selected from the group consisting of magnesium, aluminum, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, cerium, copper, zinc, gallium, germanium, strontium, yttrium, zirconium, niobium, molybdenum, ruthenium, rhodium, silver, samarium, indium, iron, tin, antimony, barium, lanthanum, hafnium, tungsten, rhenium, iridium, platinum, and combinations thereof. Preferred refractory materials comprise inorganic metal oxides (e.g., aluminas and mullite). Preferably, the refractory material has relatively low thermal coefficient of expansion and/or are capable of enduring many thermal cycles without fracture and fragmentation.

[0041] Useful carrier particles may be obtained from commercial sources or prepared, for example, according to known methods. For example, alumina carrier particles can be made by extruding and optionally shaping (e.g., curling) a slurry or sol-gel comprising an alumina precursor (e.g., colloidal boehmite), cutting the extrudate to the desired length, drying the

extrudate particles, optionally calcining them, and then sintering them generally as described in U.S. Pat. No. 4,314,827 (Leitheiser et al.); U.S. Pat. No. 4,518,397 (Leitheiser et al.); U.S. Pat. No. 4,881,951 (Monroe et al.). Suitable saddle-shaped carrier particles can be prepared by extruding a boehmite sol-gel through a hollow needle with a bent tip as described in the PREPARATION OF CATALYST MEDIA PARTICLES E in the examples section hereinbelow, and shown in FIG. 5.

[0042] In some embodiments, the carrier particles have a substantially constant cross-sectional profile along their length. This is especially the case for carrier particles that are formed by an extrusion process.

[0043] The catalyst media particles pack with substantial space between them (e.g., they pack with a void fraction of at least 0.6). In some embodiments, the void fraction is at least 0.63, at least 0.65, at least 0.68, at least 0.70, at least 0.72, at least 0.75, at least 0.78, or even at least 0.80. Preferably, the catalyst media particles do not pack in an ordered array.

[0044] Any shape or combination of shapes that packs with the desired void fraction can be used. Examples of shaped particles that may pack with the desired void fraction include bent rods, bent tubes, and saddle-shaped particles (e.g., as in the examples hereinbelow).

[0045] The catalyst media particles may have any suitable theoretical density. For example, they may have an theoretical density of at least 1.5 g/cm³, at least 1.7 g/cm³, at least 1.9 g/cm³, at least 2.1 g/cm³, at least 2.3 g/cm³, at least 2.5 g/cm³, at least 2.7 g/cm³, at least 2.9 g/cm³, at least 3.0 g/cm³, at least 3.1 g/cm³, at least 3.3 g/cm³, at least 3.5 g/cm³, at least 3.6 g/cm³, at least 3.7 g/cm³, at least 3.8 g/cm³, or even at least 3.9 g/cm³.

[0046] At least some of the carrier particles, preferably at least a majority or even all of the carrier particles, have an outer coating on at least a portion of their outer surface. The degree of coverage by the outer coating will typically depend on the process used to deposit it on the carrier particles. For example, a solvent coating process may be effective to coat the entire surface, while physical vapor deposition may result in partial coverage of the surface of individual carrier particles. The outer coating may comprise one or more layers (e.g., one, two, or three layers). The outer layer may have any thickness, but is typically relatively thin. For example, it may have a thickness of from 1 nanometer (nm) to 10 microns, preferably from 1 nanometer to 1 micron.

[0047] The outer coating comprises an oxidation catalyst for oxidizing the oxidizable gas in the fuel stream. Such materials are well known in the art and include, for example, materials comprising platinum, iridium, osmium, palladium, ruthenium, rhodium, alloys thereof, oxides thereof, and combinations thereof. Of these palladium and its oxides are preferred.

[0048] Palladium-based catalysts are known to possess high catalytic activity for methane oxidation. The most active phases in these catalysts are believed to be in the oxide form which is typically stable between 300 to 600° C. At elevated temperatures above about 800° C., in addition to a decrease in active surface area through, e.g., sintering, palladium oxide (PdO) decomposes to Pd metal which is believed to be less active than the oxide form. Importantly, the metallic form also has a higher volatility than the oxide, and therefore poses a greater risk for catalyst material loss through vaporization processes during burner operation. These considerations indicate that an optimal temperature range between 300 to 600°

C. results in efficient and long-term use of palladium catalysts in catalytic burners according to the present disclosure.

[0049] In some embodiments, the outer coating comprises an inner layer and an outer layer, which layers may comprise different materials. In one embodiment, the inner layer (i.e., the layer in contact with the carrier particle) comprises cerium oxide. The inner layer supports the outer layer comprising the oxidation catalyst. An exemplary two-layer construction and its preparation are described in the PREPARATION OF CATALYST MEDIA PARTICLES G in the examples hereinafter.

[0050] In some exemplary embodiments, catalytically-active palladium is deposited onto the carrier particles using physical vapor deposition. Physical vapor deposition refers to the physical transfer of palladium from a palladium-containing source or target to the carrier particles. Physical vapor deposition may be viewed as involving atom-by-atom deposition, although in actual practice, the palladium may be transferred as extremely fine bodies constituting more than one atom per body. Once at the surface of the carrier particles, the palladium may interact with the surface physically, chemically, ionically, and/or otherwise.

[0051] There are different approaches for carrying out physical vapor deposition (PVD). Representative approaches include sputter deposition, evaporation, and cathodic arc deposition. Any of these or other PVD approaches may be used, although the nature of the PVD technique used can impact catalytic activity. For instance, the energy of the physical vapor deposition technique used can impact the mobility, and hence tendency of the deposited palladium atoms and clusters to agglomerate into larger bodies on the surface of the support. Higher energy tends to correspond to an increased tendency of the palladium to agglomerate. Increased agglomeration, in turn, tends to reduce catalytic activity. Generally, the energy of the depositing species is lowest for evaporation, higher for sputter deposition (which may include some ion content in which a small fraction of the impinging metal species are ionized), and highest for cathodic arc (which may be several tens of percents of ion content). Accordingly, if a particular PVD technique yields deposited palladium that is more mobile than might be desired, it may be useful to use a PVD technique of lesser energy instead.

[0052] Physical vapor deposition generally is a line of sight/surface coating technique between the palladium source and the carrier particles. This means that only the exposed, outer surfaces of the carrier particles, but not inner pores (if any) that are well within the substrate, are directly coated. While the inner surfaces not in a direct line of sight with the source will also tend not to be directly coated with palladium, on some substrates, the atoms and small clusters of the deposited palladium can penetrate by diffusion a small distance into porous carrier particles.

[0053] In some preferred embodiments, the active palladium species is collected essentially completely on the outermost portion of the carrier particles. This can be desirable since this is the surface of the catalyst system that interacts most readily with an oxidizable gas, for instance in a burner system.

[0054] The palladium metal may be in the form of metal, an oxide, or some other oxidized form, and may have an oxidation state of, for instance, 0, +2, or +4. In general, it is preferable that at least a portion of the palladium be present in an oxidized form during the periods where the catalytic burner is promoting combustion.

[0055] The palladium metal that is physically vapor deposited on the carrier particles may, in some embodiments, have a thickness of from 0.1 nm to 500 nm, from 1 nm to 400 nm, or even from 5 nm to 250 nm.

[0056] For use in a boiler, the catalytic burner is typically coupled to an inlet member having an inlet port in fluid communication with the inlet opening for supplying a fuel stream from a source, and mounted within the boiler.

[0057] Referring now to FIG. 6, exemplary boiler 600 comprises catalytic burner 605 coupled to inlet member 610 and disposed within cavity 615 in housing 630. Inlet member 610 comprises inlet port 620 in fluid communication with the inlet opening 625 of catalytic burner 605 for supplying fuel stream 670 from a source. Housing 630 has exhaust port 640 and heat exchanger coils 650 for circulating a heat exchange fluid (e.g., water). Once oxidized, the fuel stream is converted to exhaust stream 690 that is emitted from catalytic burner 600, passes around insulated baffle 680, through heat exchange coils 650, then is exhausted through exhaust port 640.

[0058] The boiler may further include one or more additional components such as, for example, a drain for condensate.

[0059] Typical fuel streams are gaseous and typically comprise an oxidizable component and an oxidizing component (i.e. an oxidizer). Examples of suitable oxidizable components include acetylene, methane, ethane, propane, butane, pentane, and combinations thereof although other oxidizable gaseous materials may also be used. Examples of suitable oxidizing components include air, oxygen (pure or in combination with other gas(es) such as nitrogen, carbon dioxide, and/or noble gases, for example, as in air), or another oxidizing gas (e.g., nitrous oxide).

[0060] Catalytic burners according to the present disclosure are useful, for example, in residential, commercial, and/or industrial boilers.

[0061] As used herein, forms of the words “comprise”, “have”, and “include” are legally equivalent and open-ended. Therefore, additional non-recited elements, functions, steps or limitations may be present in addition to the recited elements, functions, steps, or limitations.

SELECT EMBODIMENTS OF THE PRESENT DISCLOSURE

[0062] In a first embodiment, the present disclosure provides a catalytic burner comprising:

[0063] a porous diffuser member;

[0064] a porous distributor member;

[0065] at least one seal extending between the porous diffuser member and the porous distributor member, thereby defining an oxidation chamber; and

[0066] catalyst media particles for catalyzing an oxidation reaction of a fuel stream to produce heat and an exhaust stream, wherein the catalyst media particles is disposed within the oxidation chamber, wherein the catalyst media particles comprise carrier particles, each carrier particle comprising refractory material, wherein at least some of the carrier particles have thereon an outer coating comprising an oxidation catalyst, and wherein the catalyst media particles have a void fraction of at least 0.6.

[0067] In a second embodiment, the present disclosure provides a catalytic burner according to the first embodiment, wherein the porous diffuser member comprises a first open end, wherein the porous distributor member is disposed at

least partially inside the porous diffuser member, wherein the porous distributor member comprises a second open end.

[0068] In a third embodiment, the present disclosure provides a catalytic burner according to the first or second embodiment, further comprising a first end cap, wherein the porous diffuser member further comprises a third open end, and wherein the first end cap covers the first open end.

[0069] In a fourth embodiment, the present disclosure provides a catalytic burner according to the third embodiment, further comprising a second end cap, wherein:

[0070] the first end cap comprises an alignment pin inwardly extending therefrom along a longitudinal axis of the porous distributor member;

[0071] the porous distributor member further comprises a fourth open end; and

[0072] the second end cap covers the fourth open end, except for a central opening in the second end cap adapted to receive the alignment pin.

[0073] In a fifth embodiment, the present disclosure provides a catalytic burner according to the third or fourth embodiment, wherein the porous diffuser member comprises at least one of a cylindrical conduit or a frustoconical conduit.

[0074] In a sixth embodiment, the present disclosure provides a catalytic burner according to any one of the first to fifth embodiments, wherein the porous diffuser member comprises a spheroidal portion.

[0075] In a seventh embodiment, the present disclosure provides a catalytic burner according to any one of the first to sixth embodiments, wherein the outer coating is discontinuous.

[0076] In an eighth embodiment, the present disclosure provides a catalytic burner according to any one of the first to seventh embodiments, wherein the void fraction is at least 0.65.

[0077] In a ninth embodiment, the present disclosure provides a catalytic burner according to any one of the first to eighth embodiments, wherein the porous distributor member and the porous diffuser member are separated from each other by an average distance of from 1 to 6 millimeters.

[0078] In a tenth embodiment, the present disclosure provides a catalytic burner according to any one of the first to ninth embodiments, wherein the catalyst media particles have an average particle diameter of from 0.5 millimeter to 3 millimeters.

[0079] In an eleventh embodiment, the present disclosure provides a catalytic burner according to any one of the first to tenth embodiments, wherein the carrier particles are saddle-shaped.

[0080] In a twelfth embodiment, the present disclosure provides a catalytic burner according to any one of the first to eleventh embodiments, wherein the carrier particles have a substantially constant cross-sectional profile along their length.

[0081] In a thirteenth embodiment, the present disclosure provides a catalytic burner according to the twelfth embodiment, wherein the oxidation catalyst comprises palladium.

[0082] In a fourteenth embodiment, the present disclosure provides a catalytic burner according to the thirteenth embodiment, wherein the palladium is deposited by physical vapor deposition.

[0083] In a fifteenth embodiment, the present disclosure provides a catalytic burner according to any one of the first to fourteenth embodiments, wherein the outer coating com-

prises an inner layer comprising cerium oxide in contact with the carrier particle and supporting an outer layer comprising the oxidation catalyst.

[0084] In a sixteenth embodiment, the present disclosure provides a catalytic burner according to any one of the second embodiment, further comprising a gas inlet member covering the first open end of the porous distributor member, wherein the gas inlet member comprises a gas inlet port.

[0085] In an eighteenth embodiment, the present disclosure further comprises a screen disposed at least partially inside the porous distributor member.

[0086] In a nineteenth embodiment, the present disclosure provides a boiler comprising:

[0087] a catalytic burner according to the present disclosure disposed within a cavity in a housing, wherein the catalytic burner is coupled to an inlet member comprising an inlet port for supplying a fuel stream;

[0088] a heat exchanger for circulating a heat exchange fluid disposed within the housing, and in fluid communication with the catalytic burner, wherein the housing further comprises an exhaust port in fluid communication with the inlet port through the catalytic burner.

[0089] Objects and advantages of this disclosure are further illustrated by the following non-limiting examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this disclosure.

EXAMPLES

[0090] Unless otherwise noted, all parts, percentages, ratios, etc. in the Examples and the rest of the specification are by weight.

Palladium Content Determination Method

[0091] Palladium content for catalyst media particles was determined using inductively coupled plasma-optical emission spectroscopy (ICP-OES) equipment (obtained under the trade designation OPTIMA 4300DV from Perkin Elmer, Waltham, Mass.). The catalyst media particles was analyzed against external calibration curves generated using acid-matched solution standards containing 0, 0.5, 1, and 2 parts per million (ppm) of palladium. A 0.5 ppm quality-control standard was used to monitor the accuracy of the calibration curves during the analysis. A 0.5 ppm solution of scandium was run in-line with the catalyst media particles and standards to serve as an internal standard.

[0092] Catalyst media particles were measured as duplicate samples. About 100 mg of each duplicate sample were weighed into respective acid-washed quartz beakers. About 2 mL of concentrated sulfuric acid were added to the sample beakers and to two empty control beakers. The beakers were covered with acid-washed quartz watch glasses and heated at reflux (approximately 337° C.) for two hours. Next, the beakers were partially uncovered to allow the excess acid to evaporate until a solution volume of approximately 0.5 mL was obtained. About 1 mL of 30% hydrogen peroxide followed by 4 mL of aqua regia (3:1 HCl:HNO₃) were added to each beaker, and the solutions were heated to approximately 90-100° C. for 15 minutes. About 10 mL of deionized water were then added, and the solutions were heated gently until the remaining solid had partially dissolved. The duplicate samples and controls were cooled, quantitatively transferred into polypropylene centrifuge tubes, diluted to 25 mL with

deionized water, and placed into the ICP-OES equipment. Palladium content is reported as weight percent of palladium based on the total weight of the catalyst media particles.

Preparation of Catalyst Media Particles

Preparation of Catalyst Media Particles A

[0093] 1.8 mm gamma-alumina spheres (Sasol LLC, Houston, Tex.) were initially heat treated at 1200° C. for 8 hrs (hereinafter CARRIER PARTICLES A). The void fraction of CARRIER PARTICLES A is 0.38 as calculated using Equations 1 and 2, and ASTM C20-00 (each described hereinabove). A nanoporous support material composed of oxides of cerium and aluminum (5.25 wt %), based on a modified synthesis found in Haneda et al., *Bull. Chem. Soc. Jpn.* (1993), vol. 66, pp. 1279-1288, was then deposited through controlled solvent evaporation of metal oxide sols and metal salt solutions onto the surface of the CARRIER PARTICLES A. Briefly, CARRIER PARTICLES A were wet (to near incipient wetness) with an acidic aqueous sol containing boehmite and cerium nitrate, and the solvent removed to produce partially dried, coated spheres, which were then calcined at 600° C. for 4 hours to form a metal oxide (hereinafter referred to as a "Ce/Al oxide") coating. Based on weight gain, the typical weight percentage of the Ce/Al oxide was about 5 weight percent of the resultant coated carrier particles.

[0094] Palladium was then deposited by physical vapor deposition (PVD) onto the Ce/Al oxide coated carrier particles to various loading levels using magnetron sputtering and a particle agitator system. Each sample of the Ce/Al oxide coated carrier particles was placed in the PVD apparatus described in FIGS. 1 and 2, and especially in paragraphs [0074]-[0076] of U.S. Patent Appl. Publ. No. 2009/054230 A1 (Veeraraghavan et al.), except that blades 42 did not contain holes 44. The particle agitator 16 had a blade gap of 6.3 mm. The vacuum chamber 14 was then evacuated to a background pressure of about 5×10^{-5} Torr (6.6 mPa) or less, and argon sputtering gas was admitted to the chamber at a pressure of about 10 mTorr (133.3 mPa). A mass flow controller with read out (obtained from MKS Instruments, Inc., Wilmington, Mass.) was used to control the flow rate of argon in the chamber, and the argon flow rate was kept at 47 standard cubic centimeters per minute (sccm). The palladium deposition process was then carried out by applying power to the palladium sputter target 32 for a pre-set period of time of 2 hours, with the particle agitator shaft 40 and blades 42 being rotated at 6 rpm. The duration of the palladium deposition process was 2 hours. The applied palladium sputter target power was 110 watts.

[0095] After the palladium deposition process was completed, the vacuum chamber was vented with air to ambient conditions, and the resultant coated particles (CATALYST MEDIA PARTICLES A) were removed from the PVD apparatus. The palladium content was determined according to the PALLADIUM CONTENT DETERMINATION METHOD (hereinafter) to be 0.19 weight percent Pd.

Preparation of Catalyst Media Particles B

[0096] CATALYST MEDIA PARTICLES B was a mixture of 50% (by volume) CARRIER PARTICLES A with 50% CATALYST MEDIA PARTICLES A.

Preparation of Catalyst Media Particles C

[0097] Palladium was deposited on CARRIER PARTICLES A as in the preparation of CATALYST MEDIA PARTICLES A, resulting in CATALYST MEDIA PARTICLES C. CATALYST MEDIA PARTICLES C does not contain a Ce/Al oxide coating. The palladium content was determined according to the PALLADIUM CONTENT DETERMINATION METHOD (hereinafter) to be 0.18 weight percent Pd.

Preparation of Catalyst Media Particles D

[0098] Preparation of CATALYST MEDIA PARTICLES D was a mixture of 50% (by volume) CARRIER PARTICLES A with 50% CATALYST MEDIA PARTICLES C.

Preparation of Catalyst Media Particles E

[0099] Saddle-shaped carrier particles were created using a needle extrusion process with a 40 weight percent solids boehmite gel as follows. Boehmite alumina powder (4824 parts, available as "DISPERAL" from Sasol North America Inc. Houston Tex.) was dispersed by high shear mixing a solution containing water (7087 parts) and 70% aqueous nitric acid (212 parts) for 13 minutes. The resulting sol-gel was aged for at least 1 hour before use.

[0100] The aged sol-gel was extruded through a 10-gauge needle crimped along the long axis with the end cut to about 45° to induce curling of the extruded parts. Once extruded, saddle-shaped sol-gel particles were sheared off, dried, and fired. The firing profile was a 20° C./min ramp to 750° C., 18 min soak, 20° C./min ramp to 1200° C., 48 min soak, and a 20° C./min cooling to 25° C.

[0101] FIG. 5 is a representative optical microscopy image of a fired saddle-shaped alpha-alumina carrier particle. The fired saddle-shaped alpha-alumina carrier particles had an average longest dimension of about 2 millimeters. The void fraction of these particles is 0.61 as calculated using Equations 1 and 2, and ASTM C20-00 (each described hereinabove). This media is henceforth referred to as CARRIER PARTICLES B. Palladium was deposited on CARRIER PARTICLES B as in the preparation of CATALYST MEDIA PARTICLES A, resulting in a Pd content of 0.21 weight percent, resulting in CATALYST MEDIA PARTICLES E. CATALYST MEDIA PARTICLES E does not contain the Ce/Al oxide coating.

Preparation of Catalyst Media Particles F

[0102] CATALYST MEDIA PARTICLES F was a mixture of 50% (by volume) CARRIER PARTICLES B with 50% CATALYST MEDIA PARTICLES E.

Preparation of Catalyst Media Particles G

[0103] FeCrAl metal fiber mesh, available under the trade designation BEKAERT BEKINIT 100 from Bekaert, Kortrijk, Belgium, having a thickness of approximately 1.5 mm and an areal density of 1,500 g/m² was heat treated to 900° C. for 4 hours resulting in CARRIER MESH A. Ce/Al oxide was applied using a method analogous to those described in CATALYST MEDIA PARTICLES A resulting in a Ce/Al oxide content of 3.56 weight percent. Physical vapor deposition was used to then vapor coat CARRIER MESH A with Pd at 250 watts for 5 min to give a Pd content of 0.06 weight percent (relative to the total substrate mass). The PVD appa-

ratus described in FIGS. 1 and 2, and especially in paragraphs [0074]-[0076], of U.S. Patent Appl. Publ. No. 2009/054230 A1 (Veeraraghavan et al.), except that the substrate was mounted on a planar support (in place of 16) that was parallel to the Pd target.

Performance Testing

Pressure-Drop Testing

[0104] Pressure-drop across a bed of CARRIER PARTICLES A and B was measured in a vertically packed tube with an inner diameter of 17 mm and a bed thickness of 3 to 20 mm. The bed of particles or mesh was held in place by mesh screens (150-160 micron opening stainless steel mesh on either side, with metered air entering at the bottom of the bed, traveling through the particle bed, and then exhausting to the atmosphere at the top. The differential pressure was calculated by measuring the pressure just upstream of the media and atmospheric pressure downstream. The same apparatus was used to measure the pressure drop across the CARRIER MESH A, where the fiber mesh replaces the packed bed and has a diameter equal to the inner diameter of the test apparatus. Tables 1 and 2 (below) report the results for CARRIER PARTICLES A and B, and CARRIER MESH A.

TABLE 1

FLOW RATE (slm)	PRESSURE DROP (kPa) CARRIER MESH A	PRESSURE DROP (kPa), bed thickness = 3 mm thick	
		CARRIER PARTICLES A	CARRIER PARTICLES B
20	0.13	0.14	0.08
40	0.38	0.43	0.24
60	0.76	0.88	0.47
80	1.24	1.44	0.74

TABLE 2

FLOW RATE (slm)	PRESSURE DROP (kPa) bed thickness = 20 mm	
	CARRIER PARTICLES A	CARRIER PARTICLES B
20	0.69	0.25
40	2.16	0.78
60	4.5	1.62
80	7.48	2.7

Example 1

[0105] Boiler testing was conducted in a residential sized boiler (NTI Trinity Ti150, commercially available from NY Thermal—St. John, New Brunswick, Calif.). The burner is commercially available with a FeCrAl metal fiber mesh. This mesh was removed and replaced with various media for testing. Experiments were run at 30% excess air (EA) and firing rates of 15.8-158 MJ/hr (15-150 kBTu/hr) (equivalent to input power densities of 544-5440 MJ/hr/m² (48-480 kBTu/hr/ft²). Boiler inlet water temperature was held constant at 60° C., with a temperature rise through the boiler (outlet minus inlet temperature) of 11° C. Gas emissions were sampled off the exhaust flue of the boiler and passed through a chiller to remove any water vapor before being sent to a series of gas analyzers. Carbon dioxide, carbon monoxide, and methane

concentrations in the sampled gas were determined by infrared absorption methods using a Horiba VIA-510 gas analyzer, Irvine, Calif. Nitrogen oxide (NO_x) concentrations were measured by chemiluminescence using a Teledyne T200m NO_x analyzer from Teladyne Advanced Pollution Instrumentation, San Diego, Calif. Emission data was dilution-corrected to 0% oxygen in the sampled gas. Table 3 reports NO_x emissions results from these tests.

[0106] The first two sets of data compare CARRIER MESH A to CATALYST MEDIA PARTICLES G. Throughout the firing range, CATALYST MEDIA PARTICLES G show no significant deviation from the CARRIER MESH A. This is due to the line of sight limitation of physical vapor deposition, resulting in a surface coating with limited penetration through the mesh thickness. This surface concentrated coverage provides inadequate contact between the fuel and the catalyst and limits its effectiveness. The second two sets of data are for CATALYST MEDIA PARTICLES B and CATALYST MEDIA PARTICLES A. The packed media shows significant decreases in the NO_x emissions at both the low and high firing rates relative to the CARRIER MESH A and CATALYST MEDIA PARTICLES G.

TABLE 3

NO _x EMISSIONS (ppm by volume)					
FIRING RATE	CARRIER	CATALYST MEDIA PARTICLES	CATALYST MEDIA PARTICLES	CATALYST MEDIA PARTICLES	
		MESH A	G	B	A
kBTu/hr	kW				
15	4.4	5.8	4.7	3.1	1.5
30	8.8	9.3	9.3	8.0	11.6
50	14.7	12.8	11.7	13.7	12.8
100	29.3	24.5	24.5	15.7	14.2
150	44.0	23.4	22.2	14.8	14.0

Example 2

[0107] Burner testing was conducted in a custom open air burner. Methane and dry air were metered using mass flow controllers (available as AALBORG GFCS-010066 from Aalborg, Orangeburg, N.Y.) and sent through a mixing chamber containing a series of perforated discs. The premixed gas was then combusted in a half cylindrical burner head that mimics the geometry of the boiler burner in Example 1 and is mounted on a flat face. The temperature of the packed bed was monitored using K-type thermocouples (Omega Engineering, Stamford, Conn.) while the emissions were measured using methods described in Example 1. Due to the entrainment of ambient gases in the gas sampling, the measured carbon dioxide and unburned methane concentrations were used to scale the NO_x results to the appropriate combustion products for the known inputs. Table 4, 5 summarizes the NO_x emissions and packed bed temperature data for CARRIER B, CARRIER A, CATALYST MEDIA PARTICLES D, and CATALYST MEDIA PARTICLES F. Comparing first the effect of the catalyst on NO_x emissions, there is a significant drop in emissions for both CARRIER B and CARRIER A when the media is catalyzed. The NO_x emissions for the CATALYST MEDIA PARTICLES F, though, show minimal improvements over CATALYST MEDIA PARTICLES D, despite the pressure drop differences shown in Table 1, 2. There is however a significant difference in the media tem-

perature data. For CATALYST MEDIA PARTICLES F, not only does the packed bed temperature stay below 600° C. at all of the firing conditions, it also maintains a stable 322-575° C. over the entire firing range rather than dropping to less than 200° C. (as seen with CATALYST MEDIA PARTICLES D). Additionally, CATALYST MEDIA PARTICLES F do not undergo the 1200° C. temperature spike at the low fire conditions as is seen with the catalyzed spheres during initial cycling. This leads to a wider operating range where the catalyst is active yet thermally stable. This has significant implications for the catalyst lifetime.

TABLE 4

NO _x EMISSIONS (ppm by volume)					
POWER DENSITY, BTU/hr/ft ²	POWER DENSITY (kW/m ²)	CARRIER PARTICLES B	CARRIER PARTICLES A	CATALYST MEDIA PARTICLES D	CATALYST MEDIA PARTICLES F
29000	92	20.3	11.1	not measured	not measured
58000	183	12.7	17.5	7.7	3.9
116000	366	28.7	27.9	4.3	15.0
174000	549	41.9	43.4	22.7	15.6
232000	732	48.0	63.2	21.7	20.1
290000	915	68.3	72.9	29.7	22.4
348000	1098	89.5	97.0	34.0	28.3
406000	1281	79.8	74.3	26.1	22.8
464000	1464	90.3	87.2	32.3	30.0

TABLE 5

PACKED BED TEMPERATURE, ° C.					
POWER DENSITY (BTU/hr/ft ²)	POWER DENSITY (kW/m ²)	CARRIER PARTICLES B	CARRIER PARTICLES A	CATALYST MEDIA PARTICLES D	CATALYST MEDIA PARTICLES F
29000	92	306	286	not measured	not measured
58000	183	256	238	641	566
116000	366	192	173	1177	503
174000	549	125	101	147	457
232000	732	84	69	113	428
290000	915	64	56	90	402
348000	1098	53	50	78	378
406000	1281	50	43	67	358
464000	1464	46	42	61	342

[0108] Other modifications and variations to the present disclosure may be practiced by those of ordinary skill in the art, without departing from the spirit and scope of the present disclosure, which is more particularly set forth in the appended claims. It is understood that aspects of the various embodiments may be interchanged in whole or part or combined with other aspects of the various embodiments. All cited references, patents, or patent applications in the above application for letters patent are herein incorporated by reference in their entirety in a consistent manner. In the event of inconsistencies or contradictions between portions of the incorporated references and this application, the information in the preceding description shall control. The preceding description, given in order to enable one of ordinary skill in the art to practice the claimed disclosure, is not to be construed as limiting the scope of the disclosure, which is defined by the claims and all equivalents thereto.

1. A catalytic burner comprising:
 - a porous diffuser member;
 - a porous distributor member;

at least one seal extending between the porous diffuser member and the porous distributor member, thereby defining an oxidation chamber; and

catalyst media particles for catalyzing an oxidation reaction of a fuel stream to produce heat and an exhaust stream, wherein the catalyst media particles is disposed within the oxidation chamber, wherein the catalyst media particles comprise carrier particles, each carrier particle comprising refractory material, wherein at least some of the carrier particles have thereon an outer coat-

ing comprising an oxidation catalyst, and wherein the catalyst media particles have a void fraction of at least 0.6.

2. The catalytic burner of claim 1, wherein the porous diffuser member comprises a first open end, wherein the porous distributor member is disposed at least partially inside the porous diffuser member, wherein the porous distributor member comprises a second open end.

3. The catalytic burner of claim 1, further comprising a first end cap, wherein the porous diffuser member further comprises a third open end, and wherein the first end cap covers the first open end.

4. The catalytic burner of claim 3, further comprising a second end cap, wherein:

the first end cap comprises an alignment pin inwardly extending therefrom along a longitudinal axis of the porous distributor member;

the porous distributor member further comprises a fourth open end; and

the second end cap covers the fourth open end, except for a central opening in the second end cap adapted to receive the alignment pin.

5. The catalytic burner of claim 3, wherein the porous diffuser member comprises at least one of a cylindrical conduit or a frustoconical conduit.

6. The catalytic burner of claim 1, wherein the outer coating is discontinuous.

7. The catalytic burner of claim 1, wherein the void fraction is at least 0.65.

8. The catalytic burner of claim 1, wherein the porous distributor member and the porous diffuser member are separated from each other by an average distance of from 1 to 6 millimeters.

9. The catalytic burner of claim 1, wherein the catalyst media particles have an average particle diameter of from 0.5 millimeter to 3 millimeters.

10. The catalytic burner of claim 1, wherein the carrier particles are saddle-shaped.

11. The catalytic burner of claim 1, wherein the carrier particles have a substantially constant cross-sectional profile along their length.

12. The catalytic burner of claim 1, wherein the oxidation catalyst comprises palladium.

13. The catalytic burner of claim 12, wherein the palladium is deposited by physical vapor deposition.

14. The catalytic burner of claim 1, wherein the outer coating comprises an inner layer comprising cerium oxide in contact with the carrier particle and supporting an outer layer comprising the oxidation catalyst.

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