FLAMELESS THERMAL OXIDATION APPARATUS AND METHODS

BACKGROUND OF THE INVENTION

[0001] This invention relates generally to thermal oxidizers used to oxidize organic compounds in process streams and, more particularly, to apparatus and methods of operating such thermal oxidizers using flameless thermal oxidation to decompose the organic compounds.

[0002] Thermal oxidizers are commonly used to oxidize one or more gases or vapors in a process stream by subjecting them to high temperatures before the process stream is released to the atmosphere. The gases in the process stream are commonly referred to as off-gases and typically consist of volatile organic compounds (VOCs), semi-volatile organic compounds (SVOCs), and/or hazardous air pollutants (HAPs). The process stream containing the off-gases is frequently a byproduct of an industrial, manufacturing, or power generating process.

[0003] In a conventional thermal oxidizer, the off-gases are oxidized to form carbon dioxide and water by combining the process stream with a gas stream that contains oxygen and then passing the combined stream through a flame or combustion gases produced by burning a fuel source such as natural gas. In this manner, the thermal oxidizer converts environmentally objectionable organic compounds into harmless compounds that may be safely exhausted to the atmosphere.

[0004] The use of a flame to cause thermal decomposition of compounds in thermal oxidizers, however, often results in the production of objectionable levels of air pollutants such as NOx and CO. NOx is produced as a result of localized areas of high temperature and CO is the result of incomplete combustion of the fuel gas that may occur during the combustion process in the thermal oxidizer.

[0005] In an effort to reduce the levels of NOx and CO produced during thermal decomposition of compounds, it is known to use a flameless oxidation process in a thermal oxidizer. An example of one such flameless oxidation process is disclosed in U.S. Patent No. 5,165,884. In that patent, a mixture of gases or vapors with air and/or oxygen flows into a bed matrix of solid heat-resistant material which has been preheated to a temperature above the autoignition temperature of the mixture. The mixture ignites and reacts exothermally in the bed matrix to form a self-sustaining reaction wave within the bed matrix. The process is used to minimize production of NOx, CO, and other products of incomplete combustion during destruction of a particular gas or vapor in a process stream prior to release of the process stream to the atmosphere. Emission levels of thermal-NOx of less than 0.007 lb of NOx (as NO_2) per million BTU and CO levels below 10 ppm are said to be obtainable using the described method.

[0006] The bed matrix in the above-described U.S. Patent No. 5,165,884 is advantageous in that it anchors and stabilizes the reaction wave during the combustion process. The bed matrix, however, occupies a substantial portion of the internal volume of the process reactor, thereby reducing the open volume available for the flow of the process stream. The reduction in open volume in the reactor reduces the available residence time for a given reactor size at a given throughput of the process stream, thus reducing the time available for destruction of hazardous wastes. In addition, the bed matrix creates a substantial pressure drop that adds to the operating costs of the process because the process stream must be subjected to an increased pressure before it enters the process reactor. This pressure drop tends to increase over time as particulate matter from the process stream accumulates in the bed matrix or the bed material degrades due to thermal shock. Eventually, the increase in pressure drop across the bed matrix may require replacement of the bed material.

[0007] A need has thus developed for a thermal oxidizer that generates low levels of NOx and CO without the disadvantages described above.

SUMMARY OF THE INVENTION

[0008] The present invention provides a method for thermally oxidizing components, such as those contained in a fluid stream, in an oxidation chamber having an internal lining which transfers sufficient heat for causing the thermal oxidation of the components in the fluid stream. The method comprises initially heating the oxidation chamber lining and then delivering the components to the oxidation chamber under conditions to initiate thermal oxidation of the components as a result of heat transfer from the oxidation chamber lining. The step of initially heating the oxidation chamber lining comprises heating the lining to a preselected temperature which is sufficient to radiate or otherwise transfer enough heat to initiate the thermal oxidation of the components in the fluid stream. After the refractory lining is heated to the preselected temperature, the components, which may include one or more fuels, are delivered to the oxidation chamber in a fluid stream. The conditions in the fluid stream are controlled to cause the flameless thermal oxidation of the components in the fluid stream as a result of heat transfer from the refractory lining. The present method thus relies on heat transfer from the refractory lining to initiate and sustain the flameless thermal oxidation and does not require a bed matrix, preheating of the fuel stream and/or combustion air stream, or flue gas recirculation as required by conventional flameless oxidation processes.

[0009] In one embodiment, one or more fuel components in the fluid stream are combusted in a visible flame to cause the initial heating of the refractory lining to the preselected temperature. The overall concentration of the fuel components in the fluid stream can be within

the flammability range during this startup mode. Alternatively, the overall concentration of the fuel components is outside of the flammability range, but a flammable mixture results by not completely mixing the fuel components with the combustion air which is present in the fluid stream so that a diffusion or partially premixed flame results. During the transition to the flameless thermal oxidation mode, the flame in the fluid stream is extinguished, such as by increasing the mixing of the fuel and combustion air to move the localized concentrations of the fuel components outside of the flammability range to prevent combustion of the mixture in a visible flame within the burner. Other methods for changing the localized concentrations of the fuel components outside of the flammability range can be used.

[00010] Volatile organic compounds, semi-volatile organic compounds, and/or hazardous air pollutants may be present as additional components in the fluid stream and are thermally oxidized during the flameless thermal oxidation mode. These additional components typically originate in a process stream from an industrial, manufacturing, or power generating process and must be removed prior to release of the process stream to the atmosphere. The process stream can supply some, all, or none of the combustion air required in the process.

[00011] If needed, supplemental heat can be added to the oxidation chamber to offset thermal losses through an external shell of the oxidation chamber or the cooling effect of the fluid stream. The supplemental heat can be added continuously, such as by burning one or more fuels in another fluid stream in the oxidation chamber in a visible flame. Alternatively, the supplemental heat can be added intermittently, such as by periodically operating the thermal oxidizer in the initial heating mode.

[00012] When the process of the present invention is operating in flameless oxidation mode, levels of NOx less than 5 ppm dry, less than 2 ppm dry, and even less then 1 ppm dry and levels

of CO less than 1 ppm dry have been achieved. As used herein, the levels of NOx and CO are expressed as parts per million by volume on a dry basis. Even when supplemental heat is added to the oxidation chamber, NOx levels between 1 and 12 ppm dry and CO levels below 1 ppm dry have been obtained.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[00013] In the accompanying drawings which form part of the specification and are to be read in conjunction therewith and in which like reference numerals are used to indicate like parts in the various views:

[00014] FIG. 1 is a top elevation view of a thermal oxidizer in accordance with one embodiment of the present invention with portions of the thermal oxidizer broken away to show details of construction; and

[00015] FIG. 2 is an enlarged side elevation view, taken in vertical section, of a burner portion of the thermal oxidizer with certain portions shown schematically.

DETAILED DESCRIPTION OF THE INVENTION

[00016] Turning now to the drawings in greater detail and initially to FIG. 1, one embodiment of a thermal oxidizer useful in the flameless thermal oxidation of components in a fluid stream is broadly represented by the numeral 10. The fluid stream is designated by an arrow 11 and typically is a gas or vapor stream which flows in a continuous or intermittent fashion within the thermal oxidizer 10. The oxidizable components in the fluid stream 11 can be in gas, liquid, and/or solid particulate form. Examples of these components include fuels, waste products,

organic compounds, including volatile organic compounds and semi-volatile organic compounds, and/or hazardous air pollutants.

[00017] Thermal oxidizer 10 comprises a thermal oxidation chamber 12 having an exterior shell 14 lined with one or more layers of a refractory lining 16 formed of a material, such as any of various refractory materials, having the chemical and physical properties necessary to withstand the high operating temperatures and other conditions present within the thermal oxidation chamber 12. The refractory lining 16 may be in castable, plastic, brick, blanket, fibrous, or any other suitable form and typically comprises primarily ceramic materials made from combinations of high-melting oxides such as aluminum oxide, silicon dioxide, or magnesium oxide. The refractory lining 16 may also be formed of other materials such as refractory metals. Examples of suitable refractory metals include molybdenum, tungsten, tantalum, rhenium, and niobium, as well as alloys of these metals. The innermost or "hot face" refractory lining 16 is preferably backed with a lower thermal conductivity lining 17 to further reduce thermal losses through the exterior shell 14.

[00018] The internal area within the lined shell 14 defines an open interior volume 18 within which the flameless thermal oxidation occurs, as more fully described below. The open interior volume 18 is sized so that the desired residence time is obtained for the fluid stream 11 flowing through the thermal oxidation chamber 12 at the intended volumetric flow rate for the specific process applications being performed. Normally, the residence time is selected so that complete combustion and/or the desired destruction removal efficiency is obtained for the oxidizable components in the process stream.

[00019] The shell 14 is preferably cylindrical and horizontally oriented, but it may alternatively have a cross section which is of a polygonal or other configuration and/or it may be

oriented vertically or at an intermediate angle. The shell 14 has an at least partially open upstream end 20 and an opposite, at least partially open, downstream end 22. The terms "upstream" and "downstream" are used with reference to the intended direction of flow of the fluid stream 11 through the oxidation chamber 12 during operation of the thermal oxidizer 10.

[00020] Thermal oxidizer 10 further includes a burner 24 connected to the upstream end 20 of the thermal oxidation chamber 12 by an optional transition 26. The downstream end 22 of chamber 12 is connected by a similar optional transition 28 to an exhaust stack 30 through which the flue gas reaction products resulting from the thermal oxidation process are released to the atmosphere. Alternatively, the downstream end of the chamber 12 may be in fluid flow communication with downstream equipment 31 that would benefit from a low NOx, low CO, high temperature fluid stream. Examples of such downstream equipment 31 include but are not limited to process heaters, boilers, reactor furnaces such as those of ethylene cracking units, hydrogen reformers and the like, air heaters, dryers, gas turbines, and heat exchangers. The thermal oxidizer 10 can thus be used to provide a hot flue gas stream, which is low in NOx and CO levels, in lieu of all or a portion of the traditional method for firing the downstream equipment.

[00021] Burner 24 is a forced draft burner that generates a strong vortex to insure thorough premixing of combustion air and fuel gas. Burner 24 is preferably fueled by a gas, typically natural gas or a refinery fuel gas, but other fuel gases such as hydrogen, methane, ethane, propane, butane, other hydrocarbons, carbon monoxide, and various blends thereof, can be used. Various additives and diluents, such as nitrogen, carbon dioxide, and/or water vapor can also be added to or are present in the gas. Some or all of the fuel may be in liquid or solid particulate

form. Other types of burners, such as an induced draft burner, natural draft burner, premixed burner, and partial premixed burner, can also be used.

[00022] As can best be seen in FIG. 2, in the illustrated embodiment, burner 24 comprises an exterior housing 32 which is lined with one or more layers of a refractory lining 34 of the type previously described. An insulating lining 35 may also be placed between the hot face refractory lining 34 and the inner surface of the exterior housing 32. The housing 32 is preferably cylindrical, but can have a cross section which is of polygonal or other configuration. The housing 32 has a sidewall 36 and opposed upstream and downstream ends 38 and 40, respectively. The lined housing 32 defines an open interior antechamber 42 which is in fluid-flow communication with the oxidation chamber 12 positioned downstream from the burner 24. A choke 44 formed of refractory material may be positioned at the downstream end 40 of the burner housing 32 to provide a reduced diameter passageway 45 from the antechamber 42 to the downstream oxidation chamber 12. The choke 44 may have the rectangular cross section as illustrated in the drawings or it may be formed with inwardly sloping inlet and outlet ends to form a more aerodynamic structure. The choke 44 may be omitted in certain applications.

[00023] A nozzle assembly 46 is positioned at the upstream end 38 of the burner housing 32 for delivery of a combustible fuel and air mixture into the antechamber 42. In one embodiment, nozzle assembly 46 comprises an elongated, centrally-positioned fuel gun 48 which is supplied with fuel from a fuel source 50 by a conduit 52. A suitable flow regulator 54 regulates the volumetric flow rate of fuel to the fuel gun 48. The fuel gun 48 terminates in a fuel tip 56 having orifices (not shown) through which a fuel stream designated by arrow 57 is discharged into the antechamber 42. The fuel gun 48 may be moveable in an axial direction so that the positioning of the fuel tip 56 may be varied in relation to a surrounding throat structure 58 which has a

reduced cross-sectional area, as more fully described below. Alternatively, a second fuel tip associated with the fuel gun 48 or another fuel gun (not shown) may be displaced from the first fuel tip 56 so that fuel may be injected at different positions in relation to the throat structure 58.

[00024] The fuel gun 48 is surrounded by a canister 59 in which a plurality of swirl vanes 60 are positioned in a ring-shaped opening that extends around the circumference of the canister 59. The swirl vanes 60 are mounted to spaced apart rings 63a and 63b which are secured to the canister 59 adjacent the ring-shaped opening. The ring 63a positioned closest to the fuel tip 56 has an inner diameter which is substantially the same as the inner diameter of the canister 59 so that it does not impede the flow of fluid within the canister 59 in a direction toward the fuel tip 56. The other ring 63b has an inner diameter less than the inner diameter of the canister 59 so that it operates to impede the flow of fluid within the canister 59 in a direction away from the fuel tip 56. An oxygen-containing combustion air stream or other oxidant designated by arrow 61 flows through the swirl vanes 60 into the canister 59 and subsequently into the antechamber 42. The swirl vanes 60 impart an intense rotary motion to the combustion air stream to aid mixing of the combustion air with the fuel stream discharged from the fuel tip 56. Combustion air is supplied to the canister 59 by a conduit 62 from a combustion air source 64 and the volumetric flow rate is regulated by a flow regulator 65. Other mechanisms may be used to impart the desired mixing of the fuel stream 57 with the combustion air stream 61. As but one example of such mechanisms, the combustion air stream 61 may be delivered into the canister 59 through one or more angled discharge nozzles which impart a rotary motion to the combustion air. It is to be understood that a swirling motion need not be imparted to the fuel stream 57 or combustion air stream 61 so long as sufficient turbulence is otherwise created to cause intimate mixing of the fuel stream 57 and combustion air stream 61.

[00025] The combustion air stream 61 and/or the fuel stream 57 may be supplied to the burner 24 at ambient temperatures. Alternatively, the combustion air stream 61 and/or the fuel stream 57 may be preheated by a heat exchanger 66 in which heat is supplied by the combustion process occurring within the thermal oxidizer 10 or from other suitable sources. The combustion air stream 61 and the fuel stream 57 are preferably supplied to the burner 24 at sufficient pressure to force the fluid stream 11 to flow forwardly through the oxidation chamber 12 without recirculating.

[00026] The source 64 of the combustion air stream 61 may comprise a portion, or all, of a process stream 68 containing waste products, organic compounds, including volatile organic compounds and semi-volatile organic compounds, and/or hazardous air pollutants. Examples of these compounds and pollutants include hydrocarbons, sulfur compounds, chlorinated solvents, halogenated hydrocarbon liquids, dioxins, and polychlorinated biphenyls. The process stream 68 may thus be an off-gas or byproduct of an industrial, manufacturing, or power generating process. Depending on the specific nature and oxygen content of the process stream 68, the source 64 of the combustion air stream may also comprise atmospheric air or some additional source of oxygen. In addition, one or more portions, or all, of the process stream 68 may bypass the combustion air plenum 59 and may be delivered to the antechamber 42 and/or the oxidation chamber 12 at one or more downstream locations, such as through injection ports 70, 71 and/or 72. The number and location of injection ports 70, 71, and 72 can be varied to suit particular applications. Flow regulators 73a-c are positioned to permit regulation of the flow rate of the various portions of the process stream 68. Suitable process controls 74 are used to monitor and regulate the volumetric flow rates of the various fuel, combustion air, and process streams 57, 61, and 68. The process controls 74 can regulate the flow rates by controlling one or more of the

flow regulators 54, 65, and 73a-c in an automated fashion. Alternatively, one or more of the flow regulators 54, 65, and 73a-c can be adjusted manually.

[00027] The throat structure 58 is positioned at the upstream end 38 of the antechamber 42 and, in one embodiment, comprises an annular wall 76 that converges or tapers inwardly from both ends to a throat 78 of reduced cross-sectional area. The throat structure 58 is positioned downstream from the swirl vanes 60 so that the combustion air stream 61 discharged through the swirl vanes 60 must pass through the throat structure 58 before entering the antechamber 42. An inner diameter of the throat 78 may be generally the same as the inner diameter of the ring 63b which mounts the swirl vanes 60.

[00028] During startup mode, the fuel tip 56 is positioned so that the fuel stream 57 is discharged from the fuel tip 56 at a first location downstream from a centerline of the throat 78. The combustion air stream 61 is discharged from the swirl vanes 60 at a second location which is a preselected distance upstream from the first discharge location of the fuel stream 57 so that the two streams are first mixed together at or downstream from the throat 78. At preselected combustion air-to-fuel ratios, positioning of the fuel tip 56 downstream from the throat 78 limits complete mixing of the fuel and combustion air and allows local fuel concentrations to be within the flammability range so that the fuel is combusted in a flame within the antechamber 42. Depending on flow conditions, the flame may extend from the antechamber 42 into an upstream portion of the oxidation chamber 12. As the hot combusted gases flow through the oxidation chamber 12, the refractory lining 16 of the oxidation chamber 12 is heated to a preselected temperature which is capable of sustaining flameless thermal oxidation of the specific fuel and air mixture flowing through the oxidation chamber 12. When natural gas is used as the fuel source, the present method has been demonstrated to operate successfully within the preselected

temperature range of about 1,900 °F to about 2,400 °F. With further optimization of the equipment and method, it is believed that the preselected temperature range can be extended to from about 1,700 °F to about 3,000 °F.

[00029] After the refractory lining 16 reaches the preselected temperature, the process switches from the startup mode to a flameless thermal oxidation mode in which components of the fluid stream 11 delivered to the oxidation chamber 12 are thermally oxidized. Various methods may be used to extinguish the flame in the fluid stream 11 during the transition from the startup mode to the flameless thermal oxidation mode. In the illustrated embodiment, the switch from startup to flameless thermal oxidation mode is achieved by moving the fuel tip 56 upstream from the throat 78. This movement of the fuel tip 56 causes the fuel stream 57 to be discharged from the fuel tip 56 at a second location which causes the fuel exiting the fuel tip 56 to impinge on the burner throat 78. The fuel stream 57 and swirling combustion air stream 61 are thus brought into contact with each other at a location upstream from the throat 78 to allow more complete mixing of the fuel stream 57 and combustion air stream 61 before the mixture passes through the throat 78. As a result of the more complete mixing of the fuel and combustion air streams 57 and 61, the air-to-fuel ratio throughout the mixture is below the lower flammability limit and the visible flame is extinguished in the antechamber 42. As one alternative method, fuel delivered through injection port 70 can be used for the startup mode. In this embodiment, the fuel tip 56 is fixed in a position upstream of the throat 78 and a fuel valve (not shown) switches the fuel from the injection port 70 to the fuel tip 56 after a preselected temperature is reached. In either case, the fuel and combustion air mixture nonetheless continues to thermally oxidize without a flame within the oxidation chamber 12 as a result of the heat transferred from the refractory lining 16 in the oxidation chamber 12 and without the need for flue gas

recirculation, preheating of the fuel, combustion air, and/or process streams 57, 61, or 68, and/or the use of a bed matrix within the oxidation chamber 12 as required in prior art processes. After the visible flame is extinguished, the NOx level in the flue gas drops dramatically, including to a level of less than 5, less than 2, and even less than 1 ppm dry, without an increase in CO levels. When fuel staging is not used, NOx levels less than 2 ppm dry and CO levels below 1 ppm dry have been consistently achieved at operating temperatures up to 2,380 °F. Even with staging of 14.4% of the fuel in a visible flame, NOx levels between 6 and 12 ppm dry and CO levels less than 1 ppm dry at operating temperatures of 1990 °F have been achieved. The thermal oxidation of the fuel and other components in the fluid stream 11 releases heat that, in turn, continues to heat the refractory lining 16. Depending upon the particular process conditions and compositions, the released heat extends the time that the process is capable of operating in the flameless thermal oxidation mode. Under certain conditions and compositions, the process is believed to be self-sustaining in the thermal oxidation mode for an indefinite period of time.

[00030] It is to be understood that switching from startup to flameless oxidation mode by increasing the mixing of the fuel stream 57 and the combustion air stream 61 to prevent localized concentrations within the flammability range can also be achieved in other ways. For example, as previously mentioned, rather than using a single axially-movable fuel gun 48, a second fuel tip which is axially displaced from the first fuel tip 56 may be used so that the fuel stream 57 can be injected at different axial positions in relation to the throat structure 58 and the discharge location for the combustion air stream 61. During startup mode, the fuel stream 57 is injected through the fuel tip closest to the throat structure 58 to prevent thorough mixing of the fuel stream 57 and the combustion air stream 61. The fuel stream 57 is then routed to the other fuel

tip to cause more complete mixing of the fuel stream 57 and the combustion air stream 61 during the flameless thermal oxidation mode.

[00031] In addition, or as an alternative, to increasing the mixing of the fuel stream 57 and the combustion air stream 61, the localized combustion air-to-fuel ratios can be changed during transition from the startup mode to the flameless thermal oxidation mode by simply varying the relative flow rate of the fuel stream 57 in relation to the combustion air stream 61. During the startup mode, the local combustion air-to-fuel ratios are within the flammability range. To transition to the flameless thermal oxidation mode, the combustion air-to-fuel ratio can be adjusted so that the localized ratios are sufficiently outside of the flammability range to extinguish the visible flame used during the startup mode.

[00032] Exceeding the turbulent flame speed is a general method for extinguishing the visible flame during transition to the flameless thermal oxidation mode. During startup mode, the flow rates of the fuel stream 57 and combustion air stream 61 are maintained below the upper limit of the turbulent flame speed. During the flameless oxidation mode, the flow rate of one or both of the fuel stream 57 and combustion air stream 61 are increased so that the mixture is flowing at a flow rate above the turbulent flame speed, thereby extinguishing the flame and causing thermal oxidation of the fuel and combustion air mixture in the oxidation chamber 12 as a result of heat transfer from the refractory lining 16. As another example, instead of increasing the flow rate of the fuel and combustion air mixture to a rate above the turbulent flame speed, the turbulent flame speed can be lowered to a rate below that of the fuel and combustion air mixture. This can be achieved in various ways. For example, the internal flow geometry of the burner 24 can be changed, such as by moving the location of the fuel injection during the transition from startup to flameless thermal oxidation mode in the manners previously described. As another example, a

flame holding structure (not shown) may be provided within the antechamber 42 to anchor the flame during the startup mode. The flame holding structure can then be moved or altered to lower the turbulent flame speed during the transition to flameless oxidation mode so that it no longer anchors the flame.

[00033] The process may also cycle between the startup and flameless oxidation modes at preselected intervals, such as when additional heat is required in the oxidation chamber 12 in situations where the refractory lining 16 cools below the temperature required to sustain flameless thermal oxidation of the components in the fluid stream 11. This cooling can result from thermal loses through the exterior shell 14 of the oxidation chamber 12 or from the cooling effect of the fuel, combustion air, and/or process streams 57, 61, and 68.

[00034] Depending on the conditions of the specific process and equipment being used, the flameless thermal oxidation can be self-sustaining for a period of time, such as one hour or longer, including indefinitely. In other applications, as noted above, supplemental heat may need to be added to the oxidation chamber 12 to offset thermal losses through the exterior shell 14 and the cooling effect of one or more of the fuel, combustion air, and/or process streams 57, 61, and 68 which are delivered to the burner 24 or oxidation chamber 12 at temperatures below that at which flameless oxidation is occurring. The supplemental heat could be added, for example, by continuously or intermittently preheating the fuel, combustion air, and/or process streams, introducing supplemental fuel into the oxidation chamber 12 through one or more injection ports, such as injection port(s) 71 with or without a portion of the process stream 68 and/or injection port(s) 72, by burning the supplemental fuel in a flame mode, by using electrical resistance heating elements, and/or by intermittently operating the burner 24 in the initial heating mode. Adding this supplemental heat by burning fuel with a visible flame may cause an increase in the

NOx and CO levels, but the overall levels will remain significantly below those that would result from operating the thermal oxidizer 10 by continual burning all of the fuel in a visible flame.

[00035] During operation of the thermal oxidizer 10 in flameless oxidation mode, the fluid stream 11 comprising the fuel and combustion air streams 57 and 61 and, optionally, the process stream 68, is delivered to oxidation chamber 12 as a premixed mixture with a combustion air-to-fuel ratio selected for the desired operating conditions in the specific application being conducted. The combustion air-to-fuel ratio and the respective flow rates of combustion air stream 61 and fuel stream 57 are generally regulated to supply sufficient heat as a result of thermal oxidation of the fuel and other components of the fluid stream 11 to sustain the thermal oxidation process for the desired length of time. In addition, the localized combustion air-to-fuel ratios or the localized fuel concentrations in fluid stream 11 should be below the lower flammability limit for the specific fuel or mixture of fuels being utilized or the flow rate of one or more of the fluid stream 11, combustion air stream 61, and fuel stream 57 is regulated so that the flow rate of the fluid stream 11 is above the turbulent flame speed for the fuel and other combustible components in the fluid stream 11. For example, when using natural gas comprising approximately 95% methane as the fuel, a combustion air-to-fuel ratio of approximately 20:1 or greater can be used. As long as the combustion air and fuel concentrations are outside of the flammability range at their mixture temperature within the antechamber 42 and are thoroughly premixed in the fluid stream 11 flowing through the oxidation chamber 12, the resulting thermal oxidation within the oxidation chamber 12 will be flameless. Excess air and/or diluents such as nitrogen, carbon dioxide, and/or water vapor can be injected into the antechamber 42 to lower the fuel concentration and thereby stay below the lower flammability limit to reduce the opportunity for undesirable flashback into the antechamber 42. The choke 44, if present, further

reduces the opportunity for flashback by increasing the velocity of the fluid stream 11 flowing from the antechamber 42 into the oxidation chamber 12 and shielding the antechamber 42 from radiation emanating from the oxidation chamber 12. The presence of diluents may improve fuel efficiency since the flameless process is able to operate with lower oxygen content in the combustion air stream.

[00036] The components of the fluid stream 11 which are thermally oxidized in the flameless process described above can be any compounds capable of undergoing thermal oxidation, such as fuels, waste materials, organic compounds, including volatile organic compounds and semi-volatile organic compounds, and various types of hazardous air pollutants. In situations where it is desired for the thermal oxidizer 10 to operate merely as a burner, one or more fuels would be the components in the fluid stream 11 which undergo thermal oxidation. In other words, the present invention encompasses processes where the thermal oxidizer 10 is not acting to remove pollutants from a process stream, but is instead serving as a low NOx and low CO burner which provides hot flue gases for other uses, such as in downstream equipment 31.

[00037] The burner 24 provides a convenient mechanism for preheating the oxidation chamber 12 and for subsequently premixing the fuel and combustion gas prior to delivery to the oxidation chamber 12. It is to be understood, however, that the oxidation chamber 12 can be preheated by other heat sources in place of or in addition to the burner 24. In addition, the fuel and combustion air can be premixed by other mechanisms prior to entry into, or as they enter, the oxidation chamber 12. Thus, the present invention encompasses processes where the burner 24 need not be used and the heat is supplied in other ways, or where the burner 24 is an induced draft burner, natural draft burner, premixed burner, or partial premixed burner.

[00038] The process of the present invention does not require the use of a bed matrix of the type used in U.S. Patent No. 5,165,884. Thus, all or substantially all of the open internal volume 18 of the oxidation chamber 12 is available for the flow of the fluid stream 11 undergoing flameless thermal oxidation. As a result, the previously discussed disadvantages of the bed matrix are avoided in the present process, which nonetheless is capable of achieving very low NOx and CO levels. While a bed matrix is not necessary in the flameless thermal oxidation process of the present invention, it may be desirable in certain applications to include a bluff body or other mixing device within the oxidation chamber 12 to facilitate the mixing of the fluid stream 11 and/or to anchor the flame, if used, which supplies supplemental heat. A bluff body or other mixing device may also be used as a flame holding structure in the antechamber 42. As previously mentioned, altering or moving the flame holding structure may change the turbulent flame speed of the fuel in the fluid stream 11 to facilitate the transition between the modes where the fuel is combusted in a visible flame to initially heat or reheat the oxidation chamber refractory lining 16 and the mode where the fuel is thermally oxidized without a flame by heat transfer from the refractory lining 16.

[00039] The flue gas reaction products exiting the oxidation chamber 12 may be delivered to the exhaust stack 30 for venting to the atmosphere. The flue gas may also be used as a heat exchange medium to preheat one or more components of the fluid stream 11 prior to delivery to the oxidation chamber 12. In addition, the hot flue gas may be used in the downstream equipment 31 such as process heaters, boilers, reactor furnaces such as ethylene cracking units, hydrogen reformers and the like.

[00040] The following examples are provided by way of illustration and are not to be taken as a limitation on the overall scope of the present invention.

Example 1

[00041] Combustion air in the form of air at room temperature was delivered into the antechamber 42 through swirl vanes 60 at a flow rate of 114,000 scf/hr. Fuel in the form of natural gas at room temperature was injected into the antechamber 42 through the fuel tip 56 at a flow rate of 5,550 scf/hr. The fuel and combustion air mixture was ignited and burned with a visible flame until the oxidation chamber 12 reached a temperature of 1,880 °F. Once the oxidation chamber 12 was preheated in this manner, the burner flame was extinguished by pulling the fuel tip 56 back from the centerline of the burner throat 78 approximately 3.5 inches to cause more complete mixing of the fuel and combustion air prior to passage of the mixture through the burner throat 78. The fuel and combustion air flow rates remained nearly unchanged and the premix stream of fuel and combustion air passed into the antechamber 42 through the burner throat 78 without a visible flame being present and the combustion roar that had accompanied the burning of the fuel in the flame mode disappeared. The fuel continued to oxidize in a stable flameless oxidation process as a result of heat transfer from the preheated refractory lining 16 of the oxidation chamber 12. The flameless oxidation process was substantially in equilibrium and NOx levels of less than 1 ppm dry and CO levels of less than 1 ppm dry were measured. The process ran for 8.5 hours and was shut down when the temperature in the oxidation chamber 12 just downstream from the burner 24 cooled to a temperature of 1,500 °F as a result of thermal losses through the exterior shell 14 of the oxidation chamber 12 and the cooling effect of the fuel and combustion air being delivered to the burner 24 at ambient temperatures. The outlet temperature of the oxidation chamber 12 was still at 1,880 °F when the process was shut down.

Example 2

[00042] The test of Example 1 was repeated with the following changes in parameters: (1) the combustion air flow rate was reduced to 100,200 scf/hr., and (2) the fuel flow rate through the antechamber 42 was reduced by staging the fuel. The total fuel flow was 5,500 scf/hr. and was split with 85.6% of the fuel being premixed with all of the combustion air stream prior to injection into the antechamber 42 and the remaining 14.4% of the fuel being injected through two fuel gas tips 72 positioned in the oxidation chamber 12 just downstream from the burner 24. The fuel injected through the fuel gas tips into the oxidation chamber 12 was combusted with a visible flame and provided direct heating of the refractory lining 16 to stabilize the flameless oxidation process in the oxidation chamber 12. As a result of this increased heat input, the outlet temperature of the oxidation chamber 12 was 1,990 °F. Because a portion of the fuel was combusted with a visible flame, the NOx levels increased and varied from 6 to 12 ppm dry. The CO levels remained below 1 ppm dry. The test was intentionally terminated at 44.5 hours of operation as it appeared that the process was self-sustaining.

[00043] Subsequent tests have shown that even higher operating temperatures of approximately 2,000 °F, 2,100 °F, 2,200 °F, 2,300 °F, and 2,400 °F can be achieved without exceeding the flammability limits in the antechamber 42 by staging the fuel to the gas tips downstream from the burner 24. NOx and CO levels below 1 ppm dry have been obtained even at approximately 2,000 °F at flow rates that cause intimate mixing of the fluid stream 11 with the staged fuel in the oxidation chamber 12. It is believed that still higher temperatures can be achieved.

Example 3

[00044] The test conditions presented for Example 3 demonstrate a case where, after sufficient preheating of the refractory lining 16, the turbulent flame speed was exceeded to allow for flameless operation above the lower flammability limit of the air/fuel mixture in the antechamber 42. The combustion air flow rate was 245,640 scf/hr., the natural gas flow rate was 18,357 scf/hr., and the thermal oxidizer operating temperature was 2,381 °F. The combustion air and natural gas were premixed in the antechamber 42 to yield a 5.87 vol% premixed fuel composition, which was above the ambient temperature lower flammability limit (5 vol%). The oxidation process did not flash back into the antechamber 42, indicating the turbulent flame speed through the reduced diameter passageway 45 was exceeded. The NOx emissions for this process condition were 1.3 ppm dry, with undetectable CO emissions (< 1 ppm dry).

Example 4

[00045] A blend of low O_2-combustion air was generated by combining 20,820 scf/hr. of CO_2 and 62,280 scf/hr. of fresh air, which resulted in a 14.5 vol% O_2 content. The low O_2 combustion air was delivered into the ante chamber 42 through swirl vanes 60. Fuel in the form of natural gas at room temperature was injected into the antechamber 42 through the fuel tip 56 at a flow rate of 5,475 scf/hr. The fuel and low O_2-combustion air were mixed in the antechamber 42 and exited into the thermal oxidation chamber 12 where the fuel was oxidized flamelessly. As a result of the oxidation, the O_2 concentration in the resulting flue gas was 2 vol% dry, CO concentrations were undetectable, the NOx concentration in the flue gas was 1.2 ppm dry, and the operating temperature was 1,941 °F. This test example demonstrates the ability of the thermal oxidizer 10 to operate with low-O_2 combustion air streams, flue gas recycle streams, and/or low heating value waste streams. The test also showed that the flameless process

will operate with lower O_2 content in the combustion air compared to a conventional flame-type burner. Thermal efficiency can be gained when low O_2 content combustion air sources are used since less fresh air needs to be added to the low O_2 content stream to maintain stability. Conventional burners typically require more than 18 vol% O_2 in the combustion air at ambient temperature to permit stable operation, whereas this test demonstrates stable operation with 14.5 vol% O_2 in the combustion air.

[00046] From the foregoing, it will be seen that this invention is one well adapted to attain all the ends and objectives hereinabove set forth together with other advantages which are inherent to the structure.

[00047] It will be understood that certain features and subcombinations are of utility and may be employed without reference to other features and subcombinations. This is contemplated by and within the scope of the invention.

[00048] Since many possible embodiments may be made of the invention without departing from the scope thereof, it is to be understood that all matter herein set forth or shown in the accompanying drawings is to be interpreted as illustrative and not in a limiting sense.

CLAIMS

1. A method for thermally oxidizing components in an oxidation chamber having an internal lining, said method comprising the steps of:

(a) initially heating said oxidation chamber lining; and

(b) then delivering said components to said oxidation chamber under conditions to initiate thermal oxidation of said components as a result of heat transfer from said heated oxidation chamber lining.

2. The method of claim 1, wherein said step of delivering said components to the oxidation chamber includes the step of delivering said components to said oxidation chamber in a fluid stream.

3. The method of claim 2, including the step of flowing said fluid stream through said oxidation chamber during or following said thermal oxidation of said components.

4. The method of claim 3, including the steps of providing one or more fuels among said components in said fluid stream and maintaining conditions within said oxidation chamber to thermally oxidize said one or more fuels in said fluid stream as a result of said heat transfer from said oxidation chamber lining while said fluid stream is passing through said oxidation chamber.

5. The method of claim 4, wherein the step of maintaining conditions within said oxidation chamber to thermally oxidize said one or more fuels in said fluid stream comprises providing said one or more fuels in said fluid stream at local concentrations below the lower flammability limit while said fluid stream is passing through said oxidation chamber.

6. The method of claim 5, including the step of reheating said oxidation chamber lining by changing said conditions within said oxidation chamber to cause combustion of said one or more fuels in said fluid stream.

7. The method of claim 6, wherein said step of changing said conditions within said oxidation chamber comprises changing the local concentrations of said one or more fuels to above said lower flammability limit.

8. The method of claim 4, wherein the step of maintaining conditions within said oxidation chamber to thermally oxidize said one or more fuels in said fluid stream comprises flowing said fluid stream through a reduced diameter passageway at a flow rate above a turbulent flame speed for said one or more fuels.

9. The method of claim 8, including the step of reheating said oxidation chamber lining by changing said conditions within said oxidation chamber to cause combustion of said one or more fuels in said fluid stream.

10. The method of claim 9, wherein said step of changing said conditions within said oxidation chamber comprises changing the flow rate of said fluid stream to below said turbulent flame speed for said one or more fuels.

11. The method of claim 1, wherein said step of initially heating said oxidation chamber lining comprises delivering said components to said oxidation chamber under conditions to cause combustion of said components.

12. The method of claim 11, wherein said step of initially heating said oxidation chamber lining comprises delivering said components to said oxidation chamber in a fluid stream.

13. The method of claim 12, wherein said step of initially heating said oxidation chamber lining comprises the step of providing one or more fuels among said components in said fluid stream.

14. The method of claim 1, including the steps of flowing a fluid stream containing one or more fuels through said oxidation chamber under initial conditions to cause combustion of said one or more fuels to cause said initial heating of said oxidation chamber lining, and then changing said conditions to cause said thermal oxidation of said components as a result of heat transfer from said oxidation chamber lining.

15. The method of claim 14, wherein said step of delivering said components to said oxidation chamber comprises delivering said components comprising said one or more fuels.

16. The method of claim 15, including further changing said conditions to cause combustion of said one or more fuels and reheating of said oxidation chamber lining.

17. The method of claim 16, including the steps of cycling between said step of thermal oxidation of said components and said step of reheating of said oxidation chamber lining.

18. The method of claim 14, wherein said step of changing said conditions comprises changing local concentrations of said one or more fuels from within a flammability range to outside said flammability range for said one or more fuels.

19. The method of claim 18, including the step of increasing the mixing of said one or more fuels in said fluid stream to cause said step of changing local concentrations of said one or more fuels from within a flammability range to outside said flammability range for said one or more fuels.

20. The method of claim 14, wherein said step of changing said conditions comprises changing the flow rate of said fluid stream from below a turbulent flame speed to above said turbulent flame speed for said one or more fuels.

21. The method of claim 4, including the step of including volatile organic compounds, semi-volatile organic compounds, and/or hazardous air pollutants as said components in said fluid stream.

22. The method of claim 21, including the step of adding said volatile organic compounds, semi-volatile organic compounds, and/or hazardous air pollutants to said fluid stream from a process stream.

23. The method of claim 22, including the step of adding at least a portion of said process stream to said fluid stream at a location within said oxidation chamber.

24. The method of claim 22, including the step of adding at least a portion of said process stream to said fluid stream prior to delivering said fluid stream to said oxidation chamber.

25. The method of claim 5, including the step of premixing at least a portion of said one or more fuels with combustion air in said fuel stream prior to delivering said fluid stream to said oxidation chamber.

26. The method of claim 25, including introducing another fluid stream containing one or more of said fuels to said oxidation chamber and combusting said one or more fuels in said another fluid stream in said oxidation chamber to add supplemental heat to said oxidation chamber.

27. The method of claim 1, including the step of maintaining said thermal oxidation for a period of time greater than one hour.

28. The method of claim 4, wherein said step of providing one or more fuels among said components in said fluid stream comprises providing a fuel selected from one or more of the group consisting of natural gas, refinery fuel gas, hydrogen, methane, ethane, propane, butane, other hydrocarbons, carbon monoxide, and blends thereof.

29. The method of claim 28, including the step of adding one or more diluents in said fluid stream.

30. The method of claim 4, wherein said step of providing one or more fuels among said components in said fluid stream comprises including natural gas as one of said one or more fuels.

31. The method of claim 3, including the step of preheating at least a portion of said fluid stream before said step of flowing said fluid stream through said oxidation chamber.

32. The method of claim 4, wherein said step of initially heating the oxidation chamber lining comprises heating the oxidation chamber lining to a temperature within the range of 1,800 to 3,000 °F.

33. The method of claim 32, wherein the step of providing one or more fuels comprises the step of including natural gas among said components in the fluid stream.

34. The method of claim 1, wherein the step of initially heating said oxidation chamber lining comprises the steps of creating hot flue gases by burning one or more fuels in a burner which is in fluid-flow communication with said oxidation chamber, and delivering the hot flue gases into said oxidation chamber to heat said lining to a preselected temperature.

35. The method of claim 34, including the steps of introducing said one or more fuels into an interior chamber of said burner at a first location and introducing combustion air or other

oxidant into said interior chamber at a second location a preselected distance upstream from said first location during said step of initially heating said lining in the oxidation chamber.

36. The method of claim 35, including the step of causing more complete mixing of said one or more fuels and said combustion air to cause said thermal oxidation of said components in the oxidation chamber.

37. The method of claim 2, including the step of preventing recirculation of said fluid stream.

38. A method for thermally oxidizing components of a fluid stream containing one or more fuels in an oxidation chamber having an internal refractory lining, said method comprising the steps of:

(a) providing a fluid stream comprising thermally oxidizable components, including one or more fuels, and combustion air;

(b) heating said refractory lining in the oxidation chamber to a preselected temperature; and

(c) then passing said fluid stream through said oxidation chamber under conditions to cause thermal oxidation of said components as a result of heat transfer from said refractory lining and without recirculation of said fluid stream.

39. The method of claim 38, including repeating steps (b) and (c) in sequence.

40. The method of claim 38, wherein said step of providing a fluid stream comprises providing a fluid stream comprising methane and combustion air.

41. The method of claim 38, wherein the step of heating said refractory lining in the oxidation chamber comprises the steps of creating hot flue gases by burning said one or more fuels in a burner which is in fluid-flow communication with said oxidation chamber, and

delivering the hot flue gases into said oxidation chamber to heat said lining to said preselected temperature.

42. The method of claim 41, including the steps of introducing said one or more fuels into an interior chamber of said burner at a first location and introducing combustion air into said interior chamber at a second location a preselected distance upstream from said first location during said step of heating said lining in the oxidation chamber.

43. The method of claim 42, including the step of causing more complete mixing of said one or more fuels and said combustion air to stop said burning of said one or more fuels in said burner while allowing thermal oxidation of said one or more fuels as initiated by heat transfer from said refractory lining in the oxidation chamber.

44. The method of claim 41, wherein said step of passing said fluid stream through said oxidation chamber under conditions to cause thermal oxidation of said components comprises the step of causing local concentrations of said one or more fuels in said fluid stream to be outside of a flammability range for said one or more fuels.

45. The method of claim 44, including the step of reheating said refractory lining by changing said local concentrations of said one or more fuels in said fluid stream to be within said flammability range for said one or more fuels to cause burning of said one or more fuels.

46. The method of claim 41, wherein said step of passing said fluid stream through said oxidation chamber under conditions to cause thermal oxidation of said components comprises the step of causing a flow rate of said fluid stream to be above a turbulent flame speed for said one or more fuels in said fluid stream.

47. The method of claim 46, including the step of reheating said refractory lining by reducing said flow rate of said fluid stream below said turbulent flame speed to cause burning of said one or more fuels.

48. The method of claim 38, including the step of removing said fluid stream from the oxidation chamber after said thermal oxidation of said components and delivering the fluid stream to downstream equipment.

49. The method of claim 48, wherein said downstream equipment is selected from the group consisting of process heaters, boilers, reactor furnaces, air heaters, dryers, gas turbines, and heat exchangers.

50. A thermal oxidizer comprising:

an oxidation chamber comprising a shell defining an open interior volume and having an upstream end and a downstream end and a lining; and

means for heating said lining and for causing thermal oxidation of components in a fluid stream when present in said open interior volume, said thermal oxidation occurring as a result of heat transfer from said lining.

51. The thermal oxidizer of claim 50, wherein said means comprises a burner at said upstream end of the shell for initially combusting one or more fuels in said fluid stream to cause said heating of said lining and for thermally oxidizing said one or more components.

52. The method of claim 1, including maintaining said conditions during said thermal oxidation of said components to obtain NOx levels below 12 ppm dry and CO levels below 1 ppm dry.

53. The method of claim 1, including maintaining said conditions during said thermal oxidation of said components to obtain NOx levels below 5 ppm dry and CO levels below 1 ppm dry.

54. The method of claim 1, including maintaining said conditions during said thermal oxidation of said components to obtain NOx levels below 1 ppm dry and CO levels below 1 ppm dry.