METHODS FOR UTILIZING TAIL GAS AND FLUE GAS FROM A CARBON BLACK PRODUCTION PROCESS

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ABSTRACT:

Methods are described for utilizing tail gas and flue gas from a carbon black production process. The methods have the ability to reduce flue gas volumes and any NOx concentrations and further such methods are beneficial economically and environmentally. The methods involve introducing tail gas from one or more carbon black reactors into a thermal oxidizer having an inlet zone, a central zone, and an outlet zone. The tail gas is introduced into the inlet zone of the thermal oxidizer via a tail gas inlet. Fuel can be optionally introduced to the inlet zone. An oxygen-containing gas is also introduced the inlet zone. Flue gas, from one or more carbon black operations, is also introduced to the inlet zone. A combustion stream having a flame is formed in the thermal oxidizer. Additional flue gas is introduced to the central zone of the thermal oxidizer. The oxygen-containing gas and the initial flue gas are volume adjustable to control the total amount of oxygen in the inlet zone so as to collectively provide a total oxygen volume a) sufficient to maintain flame stability as measured by a flammable limit and b) maintain a fuel rich combustion stream that enters into the central zone. As a result, a gas is discharged having an oxygen content of from about 0.1 vol% to about 7 vol%.

[0001] In carbon black production processes, tail gas (TG) containing H_2, CO, N_2, CO_2, hydrocarbons, nitrogen compounds (NH_3, HCN, NOx etc.), sulfur compounds (COS, H_2S, CS_2, SOx etc.) is one of the major byproducts. Heat recovery by combusting this tail gas stream to provide heat used in carbon black processes have been utilized. For instance, feedstock heating, carbon black drying, or steam for power production are among the more popular options of this byproduct stream.

[0002] When TG is used as fuel for carbon black (CB) drying and/or feedstock heating, to meet the temperature constraints of the heating process, the combusted TG is widely cooled by excess air injecting into the burner or down-stream of the combustion chamber, and this results in a flue gas (FG) stream typically containing excess O_2, such as between 3 to 12 vol%, which is much higher than that desired for complete combustion.

[0003] During the TG combustion, nitrogen-compounds (e.g. NH_3, HCN, NOx, etc.) tend to convert to NOx (e.g., NO, NO_2, etc.) at various yields depending on the combustor design, and the sulfur compounds (COS, H_2S, CS_2, SOx, etc.) in the TG are converted to SOx (e.g., SO_2, SO_3).

[0004] NOx and SOx are regulated pollution compounds and their concentration at the FG venting stack is limited to a certain maximum concentration according to local environmental regulations. NOx reduction technologies, such as SNCR (Selective Non-Catalytic Reduction), SCR (Selective Catalytic Reduction), are common commercial practices. SOx can be removed through adsorption (gas-solid, gas-liquid) or catalytic sulfuric acid production processes. These NOx and SOx reduction technologies are all negatively impacted by an increase in FG volumetric flow, such as by contributing to diminished performance (e.g. reduced contacting time in the reduction technologies or high capital expenses due to the need to utilize larger equipment).

[0005] Reducing FG volume and its NOx concentration can financially benefit the heat recovery and environmental control processes. Cabot Corporation has made significant contributions in the past in this area, such as set forth in U.S Patent No. 9,192,891. Here, in this paper, further methods are presented to address this technology issue of reducing FG volume and achieving gas that exits a thermal oxidizer that is low in oxygen content.

[0006] In CB plants, after the usage of TG as a process heating fuel, some excess TG is incinerated in a TG burner to generate heat for steam/power production. A typical design of such an incinerator is illustrated in Figure 1 (where TG is tail gas, NG is a natural gas or fuel, LPA is air or oxygen source, DRYER FG is the dryer flue gas, TOX is the thermal oxidizer, HRSG is Heat Recovery Steam Generator, SCR is selective catalytic reduction, and FGDS is Flue Gas Desulfurization).

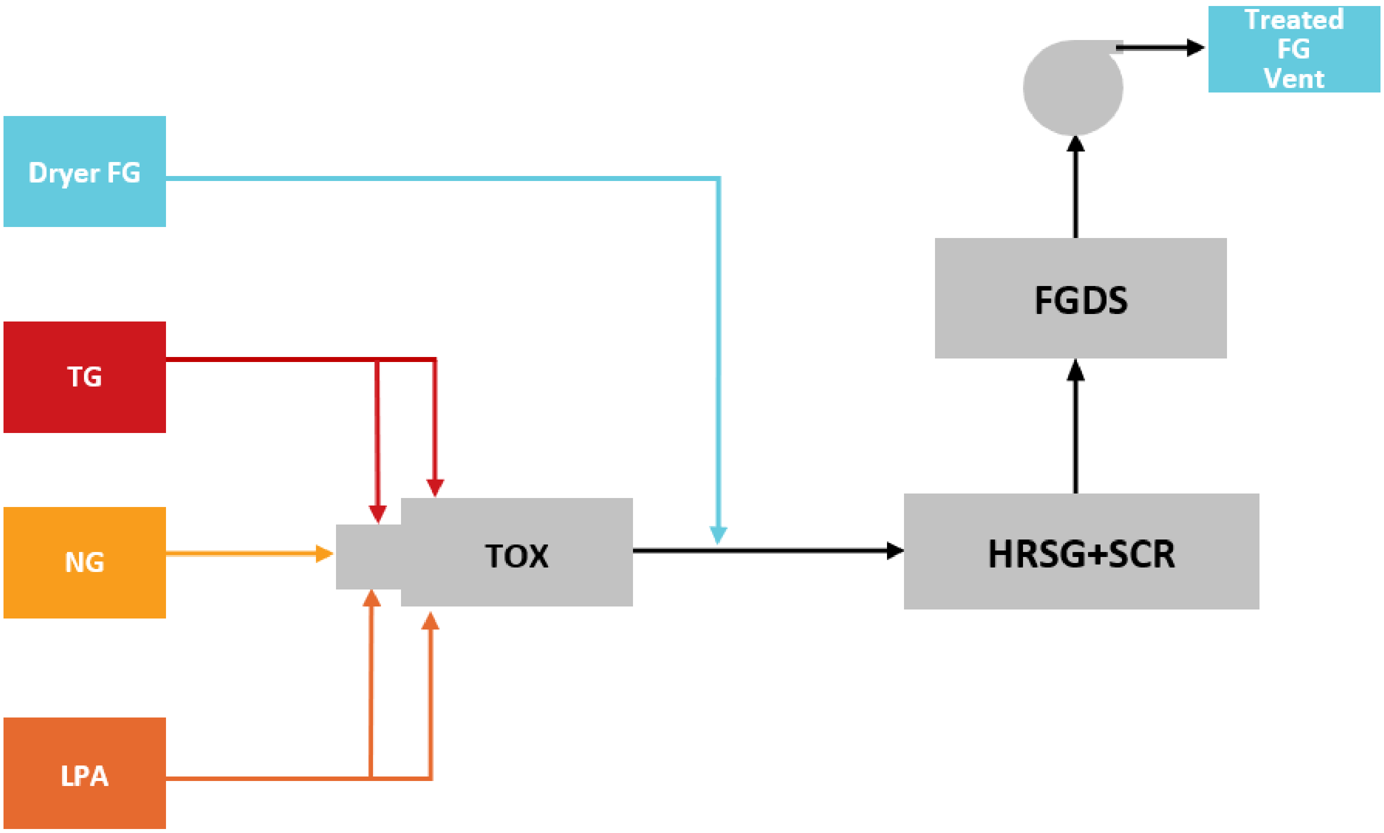

Figure 1. Conventional TG incinerator design block flow diagram

[0007] In this above process, excess TG is incinerated with excess air (typically 2-4 vol% O_2 in the combusted product) for complete combustion to generate a hot FG stream at the thermal oxidizer (the thermal oxidizer can be considered a burner, combustor, incinerator) shown as TOX in the diagram. Then the hot FG is combined with FG from other process heaters, here in this diagram represented with Dryer FG, to form a combined FG stream feeding into the Heat Recovery Steam Generator (HRSG) and NOx abatement process (shown as SCR for example). The FG exiting the HRSG, for instance at 150 to 450°C, is then conditioned and fed to a Flue Gas Desulfurization (FGDS) unit for sulfur removal.

[0008] Due to the high oxygen content and the extra N_2 volume added to the FG in the process heater FG, the combined FG feeding to HRSG can contain 4-10 vol% O_2 and carry additional inert N_2. The high oxygen content is not beneficial for the downstream process, and as indicated, this causes the need to increase downstream equipment sizing.

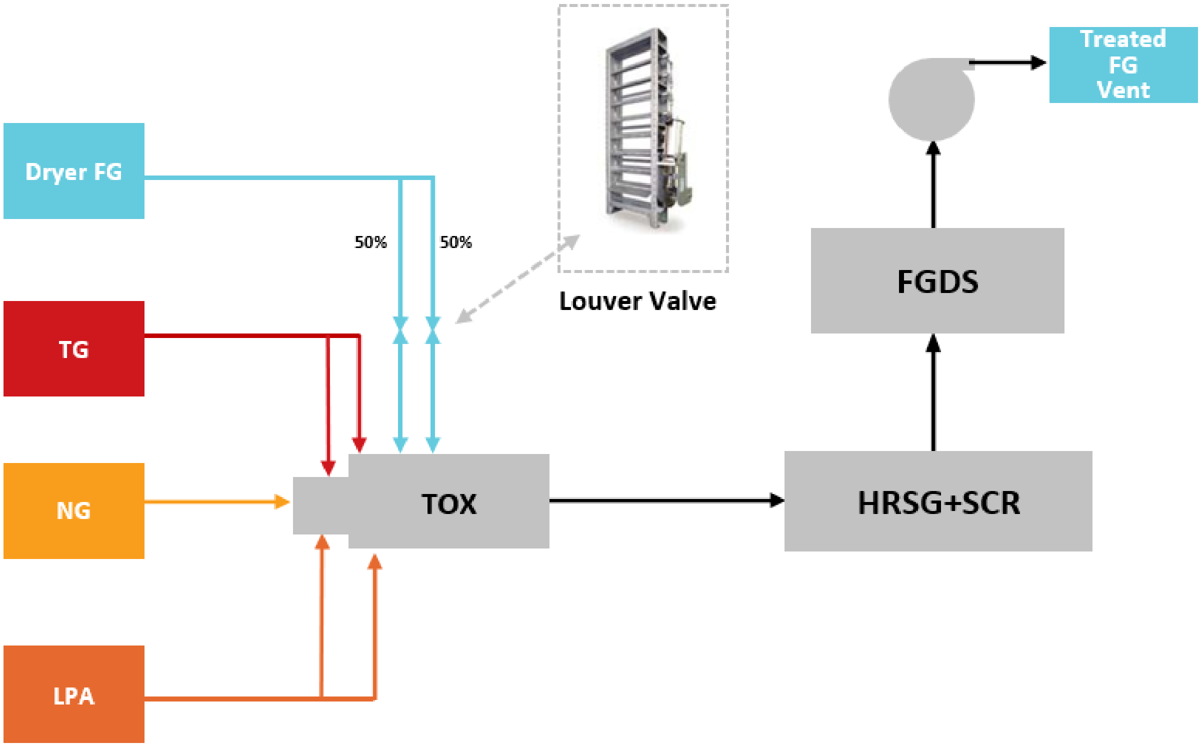

Figure 2. Block flow diagram for the new TOX design

[0009] As further shown in Figure 2 (using the same symbols as in Figure 1), with the new method presented here, the FG from process heaters (dryers, feedstock heaters etc.) is introduced into the incinerator combustion zone. The excess O_2 from the process heaters FG is used as supplemental oxidant to replace at least some of the oxidation air (shown as LPA).

[0010] In this particular example shown in Figure 2, the dryer FG is injected into the TOX through a split injection. The ratio of this split can be adjusted through a flow restrictor valve such as a louver valve shown in the diagram. Other devices can be used to achieve this split and the ratio can be any ratio. The dryer FG split ratio and LPA flow rate is controlled, thus governing the TG flow rate and its oxygen-to-burn amount (OTB, defined as the stoichiometric amount of oxygen required to burn all the flammable compounds in the TG). In practice, oxygen concentration in the FG at the TOX outlet can be continuously monitored. The LPA flow rate is controlled through an open or closed control loop using the FG O_2 concentration input. The excess oxygen at the TOX outlet is controlled, for instance around 2 vol% for complete combustion. The reduced maximum TOX temperature and reduced LPA flow result in minimizing NOx formation and low FG volume. The dryer FG split can be controlled based on the combustion chamber temperature measurement to control the flame temperature, such as to 900-1100°C, while maintaining the flame stability.

[0011] The new and improved methods for utilizing the tail gas and flue gas from carbon black production processes are presented now in more detail and examples provided.

[0012] The method includes the steps of introducing tail gas from one or more carbon black reactors into an inlet zone of a thermal oxidizer via a tail gas inlet. The thermal oxidizer can be viewed as having multiple zones. Thus, the thermal oxidizer can have the inlet zone, a central zone, and an outlet zone. For instance, see Figure 3 for an example of the zones

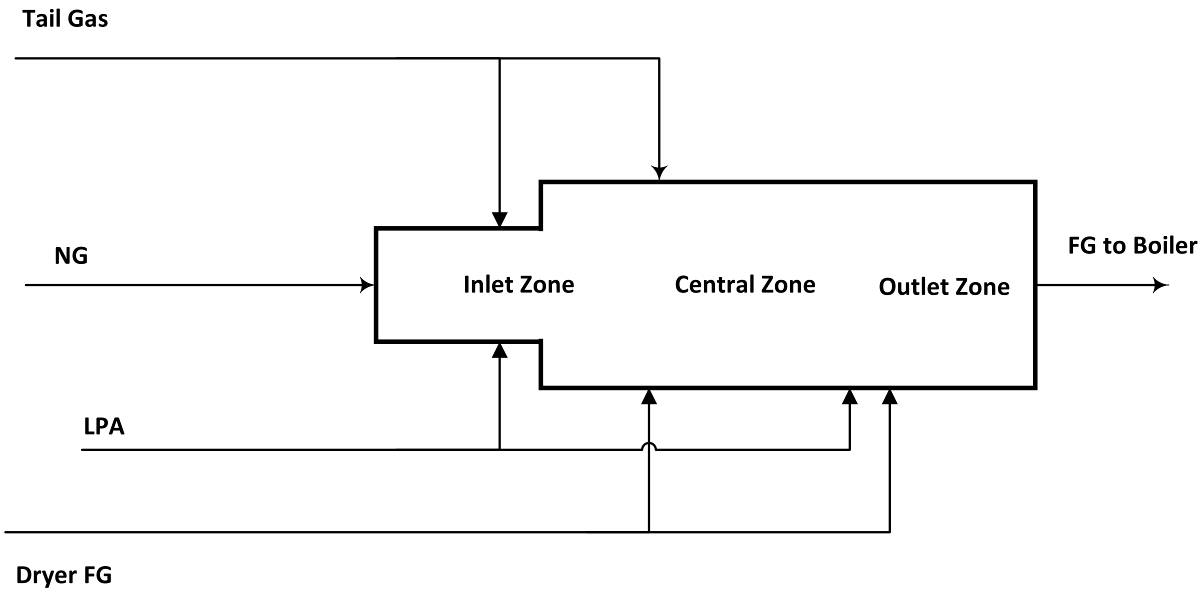

Fig.3 Illustration of new TOX concept with inlet, central and outlet zones

[0013] The inlet zone can be, for instance, the first 25% of the length of the thermal oxidizer, the central zone can be, for instance, the next 50% of the length of the thermal oxidizer (downstream of the inlet zone), and the outlet zone can be the last 25% of the length of the thermal oxidizer (downstream of the central zone).

[0014] In such a process, a fuel can optionally be introduced from a fuel source to the inlet zone of the thermal oxidizer, for instance, via a fuel inlet. The fuel here is different from the tail gas.

[0015] The process further includes the step of introducing an oxygen-containing gas to the inlet zone of the thermal oxidizer via an oxygen inlet.

[0016] The process also includes the step of introducing at least a first portion of a flue gas produced from one or more carbon black operations to the inlet zone of the thermal oxidizer via a first flue gas inlet. The flue gas is different from the oxygen-containing gas.

[0017] The process additionally includes the step of introducing a second portion of the flue gas to the central zone of the thermal oxidizer via a second flue gas inlet that is downstream of the first flue gas inlet.

[0018] In this process, the oxygen-containing gas, the tail gas, the first portion of the flue gas and optionally the fuel, combine together in the inlet region to result in a combustion stream having a flow to the outlet zone, and the combustion stream includes a flame. The oxygen-containing gas and the first portion of the flue gas are volume adjustable to control a total amount of oxygen in the inlet zone so as to collectively provide a total oxygen volume a) sufficient to maintain flame stability as measured by a flammable limit and b) maintain a fuel rich combustion stream that enters into the central zone.

[0019] The process then involves discharging, at the outlet zone, a gas that has a low oxygen content, such as from about 0.1 vol% to about 7 vol%, or from 0.5 vol% to 5 vol%, or from about 1 vol% to 2 vol%.

[0020] As a further option, after exiting the thermal oxidizer, the method can further include introducing the gas exiting the thermal oxidizer into at least one of the following: a selective catalytic reactor (SCR), a non-selective catalytic reactor, a heat recovery steam generator (HRSG), and/or a flue gas desulfurization (FGDS).

[0021] The flue gas entering the inlet zone is the primary source of oxygen for the combustion stream. For instance, the flue gas can comprise from 50% by volume to 99% by volume of the oxygen utilized in the combustion stream, or can comprise from 51% to 90% by volume or can comprise from 55% to 85% by volume, or can comprise from 60% to 80% by volume of the oxygen utilized in the combustion stream.

[0022] With respect to the flue gas and amount utilized in the first flue gas inlet and the second gas inlet, the ratio can be any amount. For instance, from about 10% to about 99% by volume of the flue gas or from about 10% to about 75% by volume, or from about 20% to about 50% by volume can be introduced into the thermal oxidizer from the first flue gas inlet. The balance of the flue gas can be introduced in the second flue gas inlet. Other ratios/amounts above or below any one of these above-mentioned amounts can be used.

[0023] Each of the gas inlets, such as the first gas inlet and/or the second gas inlet, can comprise a single inlet or be multiple inlets. If multiple inlets are used, the inlets can be located around the same circumference or can be adjacent to each other or downstream of each other. The inlet can comprise a port, a jet, or other device which permits the introduction of the gas into the thermal oxidizer.

[0024] Any device or means to distribute the flue gas between the first flue gas inlet and the second flue gas inlet can be utilized. For instance, the flue gas can be split by a flue gas splitting duct (e.g. a louver) to provide the flue gas to the first flue gas inlet and to the second flue gas inlet. Another option is to have separate flue gas sources, one for the first flue gas inlet and one for the second flue gas inlet.

[0025] With respect to the tail gas, the tail gas includes NO_x, NO_x precursors, or both (x is a positive value). The gas exiting the thermal oxidizer has reduced NO_x, NO_x precursors, or both as compared to amount in the tail gas prior to the introducing of the tail gas into the thermal oxidizer. This reduced amount can be a reduction of from 1% to 99% in volume.

[0026] The gas exiting the thermal oxidizer is at a high temperature, for instance, the temperature can be from about 850ºC to about 1150ºC, or from about 950ºC to about 1050ºC. This temperature can be a maximum measured temperature or can be an average temperature, or can be a minimum temperature.

[0027] With respect to the one or more carbon black operations, examples include, but are not limited to, one or more carbon black dryers and/or one or more carbon black feedstock heaters.

[0028] With respect to the location of the oxygen inlet and first flue gas inlet, these inlets can be relatively close to each other or adjacent to each other or facing each other in a thermal oxidizer. For instance, the oxygen inlet and the first flue gas inlet can be within a distance of each other that is 10% or less of the overall length of the thermal oxidizer, or can be a distance of each other that is equal to or less than the diameter or smallest cross-sectional width of the thermal oxidizer.

[0029] Concerning the second flue gas inlet, one purpose of this inlet is to provide a sufficient oxygen amount to combust entirely or nearly entirely any fuel remaining in the fuel rich combustion stream.

[0030] In this process, the tail gas can be incompletely combusted in the inlet zone. The residual of this tail gas enters the central zone. Thus, the flue gas from the second flue gas inlet can combine with this residual to further or continue the combustion process of the gases.

[0031] With respect to flame stability, this means that the combustion stream maintains a stable flame and this is measured by a flammable limit as described in the literature article "Calculation of Flammability and Lower Flammability Limits of Gas Mixtures for Classification Purposes", Bundesanstalt fur Materialforschung und -prufung (BAM), Division Gases, Gas Plants, Berlin, Germany.

[0032] An alternative process can involve the following steps.

[0033] Tail gas is introduced from one or more carbon black reactors to the thermal oxidizer via the tail gas inlet. The thermal oxidizer has an outlet. For purposes of this embodiment, the introducing of the tail gas occurs at a $\text{Time}_{\text{zero.}}$ The Time_{100} defines when the gas exits the thermal oxidizer from the outlet (e.g., total residence time in thermal oxidizer). Fuel can optionally be introduced from a fuel source to the thermal oxidizer via a fuel inlet at any point from $\text{Time}_{\text{zero}}$ to Time_{20}. As before, the fuel is different from the tail gas.

[0034] The step of introducing an oxygen-containing gas to the thermal oxidizer via an oxygen-containing gas inlet can occur at any point from $\text{Time}_{\text{zero}}$ to Time_{20}.

[0035] The process further includes the step of introducing at least a first portion of a flue gas produced from one or more carbon black operations to the thermal oxidizer via a first flue gas inlet at any point from $\text{Time}_{\text{zero}}$ to Time_{20}. As before, the flue gas is different from the oxygen source.

[0036] The process also includes the step of introducing a second portion of the flue gas to the thermal oxidizer via a second flue gas inlet at any point from Time_{25} to Time_{60}.

[0037] As before, the oxygen-containing gas, the tail gas, the first portion of the flue gas and optionally the fuel, combine together to result in a combustion stream having a flow to the outlet. The combustion stream includes a flame. As before, the oxygen and the first portion of the flue gas are volume adjustable to control a total amount of oxygen in the inlet zone so as to collectively provide a total oxygen volume a) sufficient to maintain flame stability as measured by a flammable limit and b) maintain a fuel rich combustion stream that enters into the central zone.

[0038] The process then includes discharging at the outlet a gas that has an oxygen content of from about 0.1 vol% to about 7 vol%.

[0039] The options and other parameters and details provided for the first process embodiment equally apply here.

[0040] For purposes herein, “tail gas” can generally refer to gaseous exhaust or effluent of any processing unit or equipment used for incinerating hydrocarbonaceous material, unless indicated otherwise. As described above, the tail gas is generally from one or more carbon black manufacturing processes, such as a furnace carbon black manufacturing process.

[0041] “Combustion” or “combusting” can refer to burning, incinerating, combusting, pyrolyzing, charring, or any combinations thereof, unless indicated otherwise.

[0042] The NOx can be or include thermal NOx and/or fuel NOx and/or prompt NOx, or any combinations thereof.

[0043] The thermal oxidizer can encompass any device or process unit that combusts a material in the presence of air or other oxygen source to produce at least one gaseous product that is NO_x and/or a precursor thereof.

[0044] For purposes herein, NO_x is an umbrella term referring to all oxides of nitrogen. The exact nature of the NO_x can vary depending on ambient conditions and oxygen level. Normally, NO_x is formed as NO but, once in the atmosphere, most of the NO_x is converted to NO_2. Because of this, most environmental authorities will use NO_2 equivalent concentrations for reporting. This convention is followed herein.

~~**[0045]**~~ Where flue gas from a carbon black dryer is used, the dryer flue gas can have a temperature, for example, greater than 100ºC to about 850ºC.

[0046] Effluent from the thermal oxidizer can be conducted to one or more NOx reduction devices or systems, such as at least one selective non-catalytic reduction unit having a temperature, for example, of from about 850ºC to about 1100ºC, or from about 900ºC to about 1050ºC, or from about 900ºC to about 1000ºC, or from about 925ºC to about 1000ºC, or from about 950ºC to about 1000ºC, or other temperature values. The SNCR volume to boiler volume can be, for example, in a ratio of from about 0.1 to about 10, or from about 0.2 to about 5, or from about 0.4 to about 3, or from about 0.5 to about 2.

[0047] The effluent can be conducted from the thermal oxidizer to the at least one selective non-catalytic reduction unit (or other NOx reduction systems) free of any intervening radiant shield reducing effluent temperature more than about 10ºC before introduction of the effluent into the at least one selective non-catalytic reduction unit.

[0048] At least one NO_x reducing agent can be introduced to at least one selective non-catalytic reduction unit located downstream of the thermal oxidizer, to the thermal oxidizer, or both, wherein the NO_x reducing agent or decomposition products thereof or both react with NO_x to produce nitrogen included with flue gas discharged from the at least one selective non-catalytic reduction unit. The NO_x reducing agent can be urea ($(NH_2)_2CO$), ammonia (NH_3), isocyanic acid (HNCO), or combinations thereof, and/or other reducing agents for NO_x. The NO_x reducing agent can comprise, for example, an aqueous urea solution, an aqueous ammonia solution, or combinations thereof. The reducing agents can comprise, for example, a dilute aqueous solution containing urea, ammonia, or both, in water in the range of from about 1% to about 25% by weight, based on active agent, or other concentrations. The introduction of reducing agent(s) may be done at a single introduction point or as staged using one or more injection nozzles positioned along the flue gas recycle flowpath (FGR). NH_3 can be generated incrementally, for example, by the decomposition or vaporization of reducing agents which are injected in the FGR or directly at the combustor, as applicable, as solids, liquid melts, emulsions, slurries, or solutions. Some ammonium salts, such as ammonium carbonate ($(NH_4)_2CO_3$), and ammonium bicarbonate ($(NH_4)HCO_3$,), can decompose essentially completely into gases, such as by releasing NH_3 and CO_2 when heated, and the carbonate also may generate water.

[0049] The tail gas compositions that can be treated by the methods and apparatus described herein to reduce NO_x levels therein are not particularly limited. The tail gas introduced to the incinerator can have a net heating value, for example, of from about 40 to about 120 BTU per standard cubic feet (scf), or from about 45 to about 110 BTU per standard cubic feet (scf), or from about 50 to about 80 BTU per standard cubic feet (scf). A fuel or source of fuel, other than the tail gas or other tail gas, can be introduced into the thermal oxidizer.

[0050] With the present designs, it is possible to reduce the oxygen amount used in a process that combust tail gas by 10% to 65%, as compared to a process as shown in Figure 1, described above. As a result, the size of the blower used to introduce the gas into the thermal oxidizer can be reduced.

[0051] With the present designs, the NOx emissions can be reduced from 10% to 60% as compared to a process as shown in Figure 1, described above.

~~[0052]~~ With the present designs, the flow through a steam generator (e.g. HRSG) can be reduced by up to 20%, which further permits a reduction in size of the steam generator by up to 20% or possibly more, as compared to a process as shown in Figure 1, described above. The present designs permit an increased in the delta temperature between the flue gas and the steam from the steam generator in part due to the increased flue gas temperature.

[0053] With the present designs, the volumetric flow through the scrubber can be reduced by up to 15% to 20%, which can result in a reduction of scrubber diameter, such as up to 10% and the slurry recirculation system (pump, pipe, and spray nozzles) by up to 15% to 20%, as compared to a process as shown in Figure 1, described above.

[0054] With the present designs, freshwater consumption can be reduced, such as by 1 to 8 MT/h, as compared to a process as shown in Figure 1, described above.

[0055] To further show the advantages of this new design set up and process, calculations were run comparing the standard process of utilizing excess tail gas with new design/process.

[0056] In one type of conventional process that is utilized in the industry, excess tail gas (TG) from each CB unit is combined and incinerated in a thermal oxidizer. The flue gas (FG) from carbon black dryers and feedstock heaters are collected and combined with the incinerated TG to form a hot FG stream to feed to a heat recovery steam generator (HRSG) to generate steam.

[0057] FG and TG volume and properties are summarized in the following Table 1 and Table 2 respectively.

Table 1: Typical Properties of the flue gas from dryers and feedstock heaters

Parameter	Unit	Value
TG flow rate	Nm3/h	199,483
TG Temperature	°C	480
Composition		
H_2O	Molar fraction	0.26623
N_2	Molar fraction	0.60940
CO_2	Molar fraction	0.04820
SO_2	Molar fraction	0.00360
NO_x	Molar fraction	0.00047
O_2	Molar fraction	0.07210

Table 2. Typical excess tail gas properties

Parameter	Unit	Value
TG flow rate	Nm3/h	128,752
TG Temperature	°C	230
Composition		
H_2O	Molar fraction	0.44411
N_2	Molar fraction	0.32450
CO_2	Molar fraction	0.01440
CO	Molar fraction	0.08620
H_2	Molar fraction	0.12340
CH_4	Molar fraction	0.00310
C_2H_2	Molar fraction	0.00140
H_2S	Molar fraction	0.00156
SO_2	Molar fraction	8.34E-05
COS	Molar fraction	0.0001658
CS_2	Molar fraction	0.0006654
HCN	Molar fraction	0.0003496
NO	Molar fraction	4.11E-05
NH_3	Molar fraction	2.06E-05

[0058] As mentioned, in some conventional designs, the approach is to burn the excess tail gas in the burner with excess air, so as to target about 2 vol% O_2 in the combusted product stream. This hot stream is then mixed with the flue gas in a duct leading to the HRSG.

[0059] The combustion product from the thermal oxidizer generally can the type of values shown in Table 3 below.

[0060] Table 3: Properties of the flue gas from the thermal oxidizer

Parameter	Unit	Value
FG flow rate	Nm3/h	209,042
FG Temperature	°C	1171
Composition		
H_2O	Molar fraction	0.35592
N_2	Molar fraction	0.55548
CO_2	Molar fraction	0.06644
SO_2	Molar fraction	0.00192
NO	Molar fraction	0.00016
O_2	Molar fraction	0.02000

[0061] Table 4 shows the combined FG properties that are feeding to the HRSG.

Table 4. Properties of FG at the HRSG inlet.

Parameter	Unit	Value
TG flow rate	Nm3/h	408,525
TG Temperature	°C	850
Composition		
H_2O	Molar fraction	0.31209
N_2	Molar fraction	0.58183
CO_2	Molar fraction	0.05753
SO_2	Molar fraction	0.00274
NO*	Molar fraction	0.00031
O_2	Molar fraction	0.04547

*This is equivalent to 664ppmv, dry base, 0%O2.

[0062] As shown in the calculations above in Table 3, the high outlet temperature of 1171°C at the thermal oxidizer increases the criteria for the duct material selection.

[0063] In the conventional design, the FG is then cooled down through a superheater/evaporator to about 450°C for feeding to a SCR reactor. The FG exiting the SCR reactor is then further cooled down to about 230°C with an evaporator/economizer to 225°C upstream of an ID fan. The ID fan increases the pressure of the FG so as to overcome any pressure drop of the wet scrubber and the SCR.

[0064] With the present design, excess TG is completely combusted with excess combustion air in a TOX to achieve about 2 vol% O2 in the FG at the TOX outlet. The TOX FG is then combined with the dryer FG to form a uniform stream feeding into the HRSG unit and APC system. FG from a dryer, containing about 7.2 vol% O2, is injected into the TOX in two stages to replace a portion of the combustion air. The TOX is preferably operated to target the outlet FG O2 concentration at about 2 vol%.

[0065] Table 5 below sets forth the simulation results comparing the conventional design to the new design.

[0066] Table 5: TOX performance comparison.

	Conventional Design	New Design
Definition	Use LPA only to burn TG in TOX to produce FG containing 2 vol% O2; Mix TOX FG with dryer FG in connection duct	Dryer FG is injected into TOX in staged manner to help TG combustion and reduce NOx production
TG Flow, NM3/h	128,752	128,752
Dryer FG, Nm3/h	199,483	199,483
LPA, Nm3/h	93736	38415
% FG to 1st stage	0%	50%
% FG to 2nd stage	NA	50%
% FG to TOX outlet	100%	NA
1st Flame T, C	1171	1065
HRSG inlet FG Temp C	850	955
NOx ppmv, Dry base, 0%O2,	664	343
Combined FG, Nm3/h	408525	352860

[0067] Table 5 compares the key operational and performance parameters for the conventional configuration vs. the new design. The major benefits of the new design configuration include:

-Reduce LPA rate by around 60%, which can reduce the size of the LPA blower.
-Reduce NOx emission by 52% theoretically.
-Reduce the flow through HRSG by 15%, adding to an increased delta T between the FG and the steam due to the increased FG temperature from 850 to 955, and the HRSG size can be reduced by 15+%.