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(54) Fluid catalytic cracking regenerator with reduced NOx emissions

(57) A method for inhibiting the formation of nitrogen oxides in a carbon monoxide boiler 22 using fuel gas to burn the carbon monoxide downstream of an FCC re-

generator 2 by introducing an oxygen-enriched gas into the boiler 22. Preferably, a nitrogen-enriched gas is simultaneously added to the boiler which further reduces the formation of nitrogen oxides.

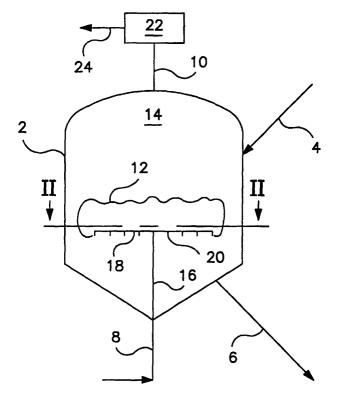


FIG. I

Description

FIELD OF THE INVENTION

[0001] The present invention provides for a fluid catalytic cracker (FCC) regeneration process having low NO_{x} emissions. The present invention more specifically provides for reducing the NO_{x} emissions from the carbon monoxide boiler downstream of the FCC regeneration unit.

BACKGROUND OF THE INVENTION

[0002] In catalytic cracking processes hydrocarbon feedstock is injected into the riser section of a hydrocarbon cracking reactor, where it cracks into lighter, valuable products on contacting hot catalyst circulated to the riser-reactor from a catalyst regenerator vessel. As the endothermic cracking reactions take place, the catalyst gets covered with coke deposits. The catalyst and hydrocarbon vapors are carried up the riser to the disengagement section of the reactor, where they are separated. Subsequently, the catalyst flows into the stripping section, where the hydrocarbon vapors entrained with the catalyst are stripped by steam injection, and the stripped catalyst flows through a spent catalyst standpipe and into the catalyst regenerator vessel.

[0003] Typically, the catalyst is regenerated by introducing air into the regenerator vessel to burn coke off the catalyst, thereby rejuvenating it. The coke combustion reactions are highly exothermic and heat the catalyst. The hot, reactivated catalyst flows through the regenerated catalyst standpipe back to the riser to complete the catalyst cycle. The coke combustion exhaust gas stream rises to the top of the regenerator and leaves the regenerator through the regenerator flue. The exhaust gas contains nitrogen and carbon dioxide (CO_2) , and generally also contains carbon monoxide (CO), oxygen, sulfur oxides (SO_x) , nitrogen oxides (NO_x) and reduced nitrogen species, such as ammonia.

[0004] The catalyst regenerator may be operated in complete combustion mode, which has now become the standard combustion mode, or in partial CO combustion mode. In complete combustion operation, the coke on the catalyst is completely burned to CO_2 . This is typically accomplished by conducting the regeneration in the presence of excess oxygen, provided in the form of excess air. The exhaust gas from complete combustion operations comprises primarily CO_2 , nitrogen and excess oxygen, but also contains NO_x and SO_x .

[0005] In partial carbon monoxide combustion mode operation, the catalyst regenerator is operated with insufficient air to burn all of the coke in the catalyst to CO_2 , consequently the coke is combusted to a mixture of CO and CO_2 . The CO is oxidized to CO_2 in a downstream CO boiler. The effluent from the CO boiler comprises primarily CO_2 and nitrogen, but also contains NO_x and SO_x .

[0006] Recently, there has been considerable concern about the amount of NO_x and SO_x being released to the environment in refinery flue gases. It is now the accepted view that most of the NO_x present in catalyst regenerator exhaust comes from coke nitrogen, i.e. nitrogen contained in the coke in the form of heterocompounds such as condensed cyclic compounds, and that little or none of the NO_x contained in the exhaust gas is derived from the nitrogen contained in the air feed to the regenerator. The mechanism by which the coke nitrogen ends up as NO_x differs, depending on whether the regenerator is operated in complete combustion mode or in partial combustion mode. In complete combustion mode regenerator operation, coke nitrogen is converted to a mixture of NO_x and elemental nitrogen. In this operational mode, the amount of NO_x in catalyst regenerator flue gas tends to increase as the excess oxygen concentration from the regenerator increases.

[0007] When the regenerator is operated in partial CO combustion mode, very little NO_x is produced in the regenerator, and coke nitrogen leaves the regenerator as reduced nitrogen species, such as ammonia. The reduced nitrogen species are unstable in the CO boiler, and they are easily converted to NO_x and elemental nitrogen.

[0008] Several approaches have been used in industry to reduce NO_x in cracking catalyst regenerator exhaust gases. These include capital-intensive and expensive options, such as pretreatment of reactor feed with hydrogen and flue gas post-treatment options; intermediate cost options, such as split-feed injection to the hydrocarbon reactor, and less expensive options, such as the use of catalysts and catalyst additives.

SUMMARY OF THE INVENTION

[0009] According to the present invention there is provided a method for inhibiting the formation of nitrogen oxides in a carbon monoxide boiler using fuel gas to burn the carbon monoxide downstream of a fluid catalytic cracking regenerator comprising introducing an oxygen-enriched gas stream into said boiler.

[0010] The FCC regenerator operating in partial combustion mode typically is at a temperature of 1240°F to 1400°F and a pressure of 15 psig to 50 psig. Oxygenenriched air is preferably used as the combustion gas with oxygen levels preferably higher than 24% and more preferably higher than 27% by volume is employed. The flue gas typically has a CO content between 15% and 1% by volume.

[0011] The downstream boiler or carbon monoxide boiler is used for combusting unconverted carbon monoxide and typically also waste heat recovery. The present invention replaces the air that is used for combustion with oxygen-enriched gas containing at least 24% but preferably more than 25% oxygen. Fuel gas is added to stabilize the burning of the carbon monoxide due to the low adiabatic flame temperature of CO com-

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bustion and low concentration of CO in the FCC flue gas stream. The use of the oxygen-enriched gas being added to the carbon monoxide burner results in less fuel gas used to ensure a stable flame.

[0012] This will result in fuel gas savings but will also reduce the peak temperature in the areas of the flame that are rich in fuel gas and thereby reduce the formation of NO_x via the prompt and thermal NO_x mechanisms.

[0013] The present invention also further relates to a method for inhibiting the formation of NO_x in a carbon monoxide boiler downstream of an FCC regenerator comprising introducing a nitrogen-enriched gas stream into said boiler in conjunction with the oxygen-enriched gas stream.

[0014] The nitrogen-enriched gas stream preferably contains at least 80% nitrogen. The nitrogen-enriched gas may be obtained from any convenient source and can be fed through a separate feed at the same time as the oxygen-enriched gas is fed to the carbon monoxide boiler.

[0015] In a preferred embodiment of the present invention, a nitrogen-enriched air stream is co-fired around the fuel gas ports in the boiler. This stream which can be the byproduct stream of an oxygen generator will further reduce the maximum flame temperature as well as quenching of NO_x precursors by the atomic nitrogen radicals generated around the fuel gas flame.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016] The method according to the present invention will now be described by way of example with reference to the accompanying drawings, in which:

- Fig. 1 is a cross sectional view of a catalyst regeneration vessel of an FCC plant.
- Fig. 2 is a cross sectional view of a carbon monoxide boiler.

DETAILED DESCRIPTION OF THE INVENTION

[0017] Various flow lines, hydrocarbon cracking reactor and related processing equipment have not been illustrated as they are not necessary for an understanding of the invention.

[0018] Turning to the embodiment illustrated in Fig. 1, hydrocarbon cracking catalyst regenerator 2 is provided externally with spent catalyst transport line 4, regenerated catalyst transport line 6, oxygen-containing gas supply line 8, and exhaust gas line 10. A combustion zone, designated generally as 12, and a reducing zone, designated generally as 14, are located in the lower and upper regions, respectively, of the regenerator 2. Feed line 16 connects supply line 8 to the center of gas distributor 18. Distributor 18 is fitted with nozzles 20.

[0019] Combustion zone 12 is the area within the regenerator 2 where combustion of the coke takes place. Since combustion of the coke is effected by contact of

the oxygen with the hot coke, combustion zone 12 is defined by the oxygen entering the regenerator 2. The nozzles 20 may be directed downwards thusly enlarge the combustion zone 12.

[0020] Exhaust gas line 10 connects the upper region of the regenerator 2 with the carbon monoxide boiler 22, which in turn is fitted with a vent line 24. The carbon monoxide boiler is described in more detail regarding the description of Fig. 2.

[0021] In the process practiced in the system illustrated in Fig. 1, spent hydrocarbon cracking catalyst is transferred from a hydrocarbon cracking reactor (not shown) to regenerator 4 via spent catalyst line 4. The spent catalyst swirls around the interior of regenerator 2 in a tangential motion. A dilute fluidized bed forms in the upper part of regenerator 2 and a dense fluidized bed forms in the lower region of the regenerator. As the catalyst comes into contact with the oxygen in the incoming feed gas, the coke on the surfaces of the catalyst ignites and burns, thus producing combustion gases containing carbon dioxide, carbon monoxide, water vapor, nitrogen oxides and sulfur oxides.

[0022] The total oxygen content of the gas entering regenerator 2 is insufficient to convert all of the coke to carbon dioxide. Accordingly, the regenerator 2 is said to be operating in partial combustion mode. However, the incoming feed gas is rich enough in oxygen to cause substantial quantities of the reduced nitrogen in the coke compounds to convert to nitrogen oxides. If the incoming feed gas were less concentrated in oxygen, some of the coke nitrogen would be converted to reduced nitrogen compounds, such as ammonia.

[0023] The combustion gases rapidly rise to the top of the regenerator 2 and enter reducing zone 14, wherein the concentration of carbon monoxide is sufficiently high to create a reducing environment. Much of the nitrogen oxides in the exhaust gas are converted to elemental nitrogen as the gas passes through reducing zone 14.

[0024] Turning to Fig. 2 this exhaust gas containing carbon monoxide, carbon dioxide, nitrogen, oxygen is directed through exhaust gas line 10 into the carbon monoxide boiler 22. Fuel gas is added to the boiler 22 via fuel gas line 26. The fuel gas will stabilize the burning of the carbon monoxide due to its low adiabatic flame temperature, and the low, roughly 8 to 10%, concentration of carbon monoxide in the FCC flue gas exhaust stream. Typically the fuel gas burns at a temperature of about 800° to 1500°C.

[0025] In one embodiment of the present invention, a gas stream containing at least 24% by volume of oxygen is added to the carbon monoxide boiler via line 28. The amount of fuel gas consequently being inputted through line 26 can be lowered as a stable flame depicted as 32 is produced. The peak temperature of the areas of the flame rich in fuel gas is reduced. This reduces the production of NO_x compounds via the prompt and thermal NO_x mechanisms.

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[0026] In a preferred embodiment of the present invention, nitrogen-enriched gas containing at least 80% nitrogen is simultaneously along with the oxygen-enriched gas added to the carbon monoxide boiler 22 via line 30. This stream which may come from the byproduct stream of the oxygen generator (not shown) will co-fire around the fuel gas port of line 26. This co-firing is enabled in part by the use of the oxygen-enriched gas for carbon monoxide production and will enable the minimization of the maximum flame temperature. NO_x precursors are also quenched as a result of the nitrogen radicals, N•, generated around the fuel gas flame.

[0027] The NO_x reduced gas is primarily composed of carbon dioxide and is removed from the boiler via vent line 24.

nitrogen-enriched gas is introduced into said boiler separately from said oxygen-enriched gas.

Claims

- A method for inhibiting the formation of nitrogen oxides in a carbon monoxide boiler using fuel gas to burn the carbon monoxide downstream of a fluid catalytic cracking regenerator comprising introducing an oxygen-enriched gas stream into said boiler.
- 2. A method as claimed in claim 1, wherein said oxygen-enriched gas stream comprises at least 24% by volume of oxygen.
- 3. A method as claimed in claim 2, wherein said oxygen-enriched gas stream comprises more than 25% by volume of oxygen.
- **4.** A method as claimed in any one of the preceding claims, wherein the flue gas entering the boiler contains 1 to 15% carbon monoxide.
- **5.** A method as claimed in claim 4, wherein the flue gas entering the boiler contains 8 to 10% carbon dioxide.
- **6.** A method as claimed in any one of the preceding claims, wherein the temperature of the burning carbon monoxide is from 800 to 1500°C.
- A method as claimed in any one of the preceding claims, wherein said fluid catalytic cracking regenerator is operating under partial combustion.
- **8.** A method according to any one of the preceding claims, additionally comprising introducing a nitrogen-enriched gas stream into the boiler.
- **9.** A method as claimed in claim 8, wherein said nitrogen-enriched gas comprises at least 80% by volume of nitrogen.
- 10. A method as claimed in claim 8 or 9, wherein said

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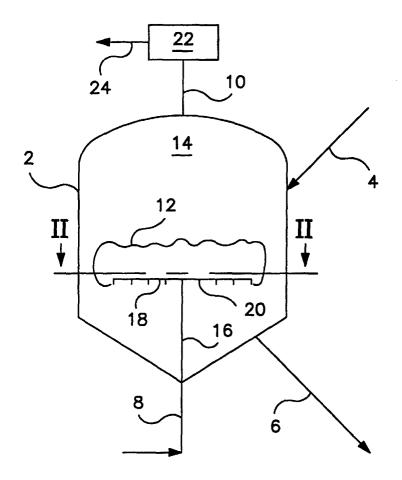


FIG. I

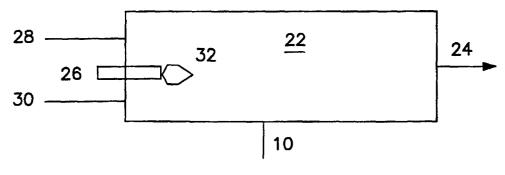


FIG. 2