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(54) Benævnelse: **Fremgangsmåde og system til fjernelse af giftige forbindelser fra røggas under anvendelse af en SCR katalysator**

(56) Fremdragne publikationer:
US-A1- 2011 041 481
US-A1- 2011 200 505
US-A1- 2013 149 225
US-A1- 2015 336 051

DESCRIPTION

[0001] The present invention relates to a method and system for reducing emission of nitrogen oxides (NOx) from off-gasses. In particular, the method and system of the invention provides an improved reduction of NOx during cold start of the engine.

[0002] Flue gases from different combustion facilities, e.g. boilers in solid or liquid fired power plants gas, oil-fired generators or cement kilns, biofuel fuelled combustion plants and waste incineration plants contain a number of environmentally problematic or even poisonous compounds. These comprise NOx.

[0003] Catalytic cleaning of flue gas reduces the amount of NOx and is therefore beneficial for the environment in general. In most areas, legislation requires reduction of NOx in the flue gas.

[0004] In Selective Catalytic Reduction (SCR) of NOx, nitrous oxide compounds are selectively reduced to harmless nitrogen and water by reaction with a reduction agent, e.g. ammonia, over a catalyst.

[0005] US 2015/336051 A1, US 2011/200505 A1, US 2013/149225 A1 and US 2011/041481 A1 all disclose exhaust gas cleaning methods for the reduction of nitrogen oxides by selective catalytic reduction (SCR).

[0006] In power plants typically a heat recovery unit steam generator unit (HRSG) is installed that recovers heat from a hot flue gas stream.

[0007] The HRSG unit comprises a superheater, an evaporator and an economizer.

[0008] In the superheater and evaporator, the heat in the flue gas is used to superheat steam and to preheat feed water before it is pumped to the boiler, which increases the boiler efficiency of the power plant. The flue gas temperature is thereby typically cooled to approximately 150°C.

[0009] The low temperature of the flue gas downstream the evaporator encounters a problem in the NOx removal by means of SCR.

[0010] The problem with the known SCR catalysts is the relatively low efficiency at flue gas temperatures below 250°C.

[0011] This usually means that the evaporator section of the HRSG will have to be split and the SCR placed in between the two sections.

[0012] The SCR catalyst is typically installed downstream the superheater and upstream the economizer.

[0013] It is known that the SCR reaction can be considerably accelerated, and the low temperature activity can be significantly raised at equimolar amounts of NO and NO_2 in the flue gas by the so-called "fast" SCR reaction:

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O.$$

[0014] This invention is based on forming NO_2 externally to the flue gas duct and injecting the prepared NO_2 into the flue gas in an amount that promotes the fast SCR reaction. NO_2 can be formed from NH_3 by oxidation of the NH_3 to NO over a precious metal containing catalyst in a first step and subsequently oxidation of NO to NO_2 in a second step.

[0015] Thus, the invention provides in a first aspect a method for the removal of nitrogen oxides from flue gas from combustion facilities, comprising the steps of
passing the flue gas through a catalyst for selective reduction of nitrogen oxides in presence of ammonia added to the flue gas either as such or in form of a precursor thereof;
at a flue gas temperature of below 250°C further injecting an effluent gas containing nitrogen dioxide into the flue gas upstream the catalyst for selective reduction of nitrogen oxides;
providing the effluent gas containing nitrogen dioxide by steps of
catalytically oxidizing ammonia or a precursor thereof with an oxygen containing atmosphere to an effluent gas comprising nitrogen monoxide and oxygen in presence of an oxidation catalyst;
cooling the effluent gas to ambient temperature and oxidizing the nitrogen monoxide in the cooled effluent gas to nitrogen dioxide.

[0016] The problem with the known methods and systems is the relatively low efficiency of the SCR catalyst at flue gas temperatures below 250°C, as mentioned hereinbefore. This problem is solved by the invention with injection of NO_2 into the flue gas at the low temperatures to promote the "fast" SCR reaction. This reaction is responsible for the promotion of low temperature SCR.

[0017] At flue gas temperatures above 250°C, SCR catalysts have sufficient efficiency and injection of NO_2 into the flue gas can be disrupted when the gas temperature reaches 250°C.

[0018] A particular advantage of the invention is that tail end SCR installations (i.e. downstream the ecomonizer) are possible without the need of re-heat the gas to higher temperatures needed for reducing the catalyst volume.

[0019] Thus, a flue gas reheater unit, which is typically arranged upstream the SCR catalyst in the known flue gas cleaning systems can be omitted or much reduced in duty.

[0020] Ammonia oxidation to NO externally to the flue gas duct, is usually performed in a reactor with a noble metal catalyst, typically platinum or an alloy of platinum with other precious metals as minor components at reaction temperatures of between 250 and 800°C in presence of oxygen containing atmosphere.

[0021] To provide the required reaction temperature, the oxidation reactor can be heated by e.g. electrical heating or induction heating.

[0022] In an embodiment, the oxygen containing atmosphere includes hot recirculated gas which provides then additionally part of the oxidation reactor heating duty.

[0023] NO formed from NH_3 by oxidation of the NH_3 in contact with a precious metal containing catalyst in a first step, is subsequently oxidized to NO_2 in the NO containing effluent gas from the first step by cooling the gas to ambient temperature to push the equilibrium reaction $2NO+O_2 \rightleftarrows 2NO_2$ towards formation of NO_2 in the above reaction scheme.

[0024] The term "ambient temperature" as used herein, shall mean any temperature prevailing in the surroundings of a combustion facility employing the method and system of the invention. Typically, the ambient temperature will be between -20°C and 40°C.

[0025] Cooling and oxidation of the NO containing effluent gas can be performed in an aging reactor sized so that the residence time of the gas is about 1 minute or longer.

[0026] In an embodiment the oxidation reaction is performed in presence of a catalyst promoting the oxidation of NO to NO_2. Those catalysts are known in the art and include Pt on TiO_2, Pt on SiO_2 and activated carbon or Pt and/or Pd on alumina.

[0027] As mentioned hereinbefore the desired fast SCR reaction requires equal amounts of NO and NO_2. Consequently, the amount of NO_2 injected into the flue gas at cold start conditions with a temperature below 250°C is controlled to result in 45 to 55% by volume of the nitrogen oxides content in the flue gas is NO_2 at inlet to the SCR catalyst unit.

[0028] In a further aspect, the invention provides a system for use in the method according to the invention.

[0029] The system comprises within a flue gas duct a catalyst for selective reduction of nitrogen oxides;
upstream the catalyst for selective reduction of nitrogen oxides, injection means for injection of ammonia or a urea solution into the flue gas duct;
upstream the catalyst for selective reduction of nitrogen oxides, injection means for injection of nitrogen dioxide containing effluent gas; and
outside the flue gas duct,
an ammonia oxidation catalyst; and
means for cooling and oxidizing nitrogen monoxide from the ammonia oxidation catalyst to

nitrogen dioxide containing effluent gas connected at its outlet end to the injection means for injection of nitrogen dioxide containing effluent gas.

[0030] As mentioned above, the oxidation reaction of NO to NO_2 needs a residence time of the NO containing gas of at least 1 minute. Typically, 1-2 minutes.

[0031] This can be achieved in a heat exchanger either gas cooled or water cooled or alternatively when shaping the cooling and oxidizing means as a spirally wound tube with a length resulting in the desired residence time of the gas passing through the tube.

[0032] In another embodiment, the means for cooling and oxidizing nitrogen monoxide containing effluent gas is provided with an oxidation catalyst is provided with an oxidation catalyst promoting the oxidation of NO to NO_2.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- US2015336051A1 [0005]
- US2011200505A1 [0005]
- US2013149225A1 [0005]
- US2011041481A1 [0005]

Title: Fremgangsmåde og system til fjernelse af giftige forbindelser fra røggas under anvendelse af en SCR katalysator

1. Fremgangsmåde til at fjerne nitrogenoxider fra røggas fra forbrændingsanlæg, omfattende trinnene
   - at føre røggassen igennem en katalysator for selektiv reduktion af nitrogenoxider i tilstedeværelse af ammoniak tilsat røggassen enten som sådan eller i form af en forløber deraf;
   - ved en røggastemperatur under 250°C at indsprøjte en spildgas indeholdende nitrogendioxid i røggassen opstrøms katalysatoren for selektiv reduktion af nitrogenoxider;
   - at tilføre spildgassen indeholdende nitrogendioxid via trinnene
     - katalytisk oxidering af ammoniak eller en forløber deraf med en oxygenholdig atmosfære til en spildgas indeholdende nitrogenmonoxid og oxygen ved tilstedeværelse af en oxidationskatalysator;
     - køling af spildgassen til omgivelsestemperatur på mellem -20 og 40°C og oxidere nitrogenmonoxiden i den afkølede spildgas til den nitrogendioxidindeholdende spildgas.

2. Fremgangsmåde ifølge krav 1, hvori den oxygenholdige atmosfære indeholder røggas.

3. Fremgangsmåde ifølge krav 1, hvori den oxygenholdige atmosfære er omgivelsesluft.

4. Fremgangsmåde ifølge ethvert af kravene 1 til 3, hvori den nitrogendioxidholdige spildgas indsprøjtes i røggassen i en mængde, der resulterer i at 45 til 55 vol% af nitrogenoxiderne er nitrogendioxid ved indgangen til katalysatoren for selektiv reduktion af nitrogenoxiderne.

5. Fremgangsmåde ifølge ethvert af kravene 1 til 4, hvori oxideringen af nitrogenmonoxid i den afkølede spildgas til den nitrogendioxidindeholdende spildgas udføres i tilstedeværelse af en oxidationskatalysator.

6. System til anvendelse i fremgangsmåde ifølge ethvert af kravene 1 til 5, omfattende en katalysator til selektiv reduktion af nitrogenoxider i en røggaskanal;
opstrøms katalysatoren til selektiv reduktion af nitrogenoxider indsprøjtningsmidler til indsprøjtning af ammoniak eller en ureaopløsning i røggaskanalen;
opstrøms katalysatoren til selektiv reduktion af nitrogenoxider indsprøjtningsmidler til indsprøjtning af nitrogendioxidholdig spildgas; og
udenfor røggaskanalen en ammoniakoxidationskatalysator; og
midler til at afkøle og oxidere nitrogenmonoxidholdig spildgas fra ammoniakoxidationskatalysatoren til den nitrogendioxidholdig spildgas, der ved dens udløbsende er forbundet til indsprøjtningsmidlerne til indsprøjtning af den nitrogendioxidindeholdende spildgas.

7. System ifølge krav 6, hvori midlerne til afkøling og oxidering af den nitrogenmonoxidindeholdende spildgas er i form af en varmeveksler.

8. System ifølge krav 6, hvori midlerne til afkøling og oxidering af den nitrogenmonoxidholdige spildgas er i form af et spiralviklet rør.

9. System ifølge ethvert af kravene 6 til 8, hvori midlerne til afkøling og oxidering af den nitrogenmonoxidholdige spildgas indeholder en oxidationskatalysator.