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(54) Title: METHOD OF REDUCING NOₓ COMPOUNDS IN FLUE GASES OF RECOVERY BOILER

(57) Abstract

A method of reducing NOₓ compounds in the odour gases of a recovery boiler. In the method, ammonia in the odour gases is separated before they are combusted, the ammonia being then introduced into a boiler at the pulp mill or into a separate catalyzer, where it reacts with nitrogen oxide forming water and molecular nitrogen.
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METHOD OF REDUCING NO\textsubscript{x} COMPOUNDS IN FLUE GASES OF RECOVERY
BOILER

The invention relates to a method of reducing nitrogen oxide emissions at a pulp mill in the combustion of odour gases that are released in different process steps at the pulp mill and contain detrimental sulphur compounds.

At a pulp mill, in a pulp cooking process, organic nitrogen originating from wood is separated in gaseous form, particularly in the form of ammonia, but also as other gaseous nitrogen compounds, during different process steps, such as cooking, evaporation, stripping etc. When methanol or turpentine is condensed from these odour gases, part of the ammonia is also condensed into liquid form with the methanol or turpentine. When odour gases are combusted in different boilers, such as a recovery boiler, a power boiler or a separate odour gas boiler, ammonia is oxidized into various nitrogen oxides, increasing nitrogen emissions at said mills. High phasing of air feed to reduce nitrogen oxide emissions easily results in an increase in ammonia and flue sulphur emissions. Similarly, combusting methanol or turpentine in different boilers induces either various nitrogen oxides or ammonia emissions. The most problematic issue is the inability to systematically avoid the formation of detrimental emissions in combustion of methanol and odour gases that contain a plurality of different compounds.

Attempts have been made to reduce emissions of nitrogen compounds, i.e. mainly nitrogen oxides, from recovery and power boilers by what is known as stepped combustion, in which air is supplied to a boiler in several successive steps to make combustion take place mainly under-stoichiometric conditions. This considerably reduces the formation of what is known as thermal NO\textsubscript{x}. Such a solution is disclosed e.g. in Swedish Published Specification No. 468 171.

Attempts have also been made to reduce NO\textsubscript{x} contents in flue gases by supplying various reagents to flue gases for preventing the formation of NO\textsubscript{x} compounds or for converting them into a form in which they can be removed as easily as possible. Such an additive may be ammonia or urea purchased outside the mill, in which case the NO present in the flue gas reacts with ammonia, forming gaseous nitrogen which can be discharged to the atmosphere. It is also possible to use various solid or liquid ammonium salts as the reagent in this so-called SNCR method known per se. The problem with
this technique is the high cost of reagents to be purchased outside the mill.

It is also known to supply hydrocarbons, such as natural gas or the like, to flue gases in a boiler, the resulting reduction in NOx compounds being due to so-called hydrocarbon radicals speeding up the reactions of nitrogen compounds. The drawbacks of such methods are the high investment and operating costs, since the additives are purchased outside the mill, and in addition, equipment is required for storing, batching, adjusting and feeding the additives.

Finnish Patent Application No. 931055 discloses a method in which oxygenous hydrocarbon, such as methanol, obtained in the pulp cooking process, is supplied to flue gases in a recovery boiler. In this method, methanol and any aqueous steam are supplied to the upper part of a recovery boiler to be mixed with flue gases, whereupon the flue gases are washed with white liquor or with an aqueous solution containing ammonia-based and/or alkali-based compounds. The method is based on the nitrogen oxide NO contained in the flue gases becoming partly oxidized and forming nitrogen dioxide NO2, which can be removed by an alkali scrubber. The drawback of this method is that it has an effect only on the reduction in oxides of already formed nitrogen, and the only reagent that can be used is methanol or a corresponding hydrocarbon derivative. In addition, the method requires a flue gas scrubber suitable for removing NO2, and the treatment of nitrogen compounds remaining in the washing liquid is still problematic.

The object of the present invention is to provide a method of reducing the number of nitrogen oxide and ammonia emissions readily caused by combustion of odour gases and methanol. The method of the invention is characterized by separating the ammonia contained in the odour gases before they are introduced into combustion.

The essential feature of the invention is that the ammonia in odour gases and methanol is separated, and, consequently, when they are combusted, this prevents the formation of ammonia-induced nitrogen oxides or pure ammonia which would be discharged to the atmosphere with the flue gases. In a preferred embodiment of the invention, the ammonia thus separated is supplied to a boiler in use at the pulp mill by what is known as the SNCR method, to remove nitrogen oxides from the flue gases of said boiler. In another preferred embodiment of the invention, ammonia is separated from odour gases and/or methanol by what is known as a molecular sieve, e.g. by
using zeolite.

The invention will be described in greater detail in the attached drawing which schematically shows the method of the invention as a block diagram.

The wood to be cooked is supplied to pulp mill cooking, in which various constituents and wood fibres are separated therefrom. Wood fibres are led forward after various washings and black liquor remaining from the cooking is led via various process steps, such as an evaporator etc., to be combusted in a recovery boiler. Pulp cooking and other steps associated with processing black liquor before it is supplied to a recovery boiler constitute a process known per se, schematically denoted in the block diagram by reference numeral 1. From this process various odour gases are separated both in cooking and in evaporators in what is known as stripping and super concentration, should the equipment comprise such a step. These odour gases are recovered and led to further processing to maintain detrimental emissions from the pulp mill as low as possible and additionally to recover both the chemicals and the combustion energy of the odour gases. In the final step of the pulp process, black liquor is sprayed to the recovery boiler 2 for combustion and recovery of the chemicals therein.

Odour gases, or at least part of them, are led to a condensing step 3, in which methanol is condensed into liquid form. At the same time, part of the ammonia is condensed with the methanol and mixed with it in a liquid form. The odour gases are then supplied to ammonia separation 4, where gaseous ammonia is separately separated from the odour gases, whereupon the odour gases are supplied to combustion in e.g. a recovery boiler 2. The gaseous ammonia obtained from ammonia separation, in turn, can be led either to a recovery boiler 2 or to a separate power boiler 5 to be used by what is known as the SNCR, or selective non-catalytic, method to react with nitrogen oxides in the flue gases and to thus form molecular nitrogen and water.

The ammonia is supplied to said boiler in a suitable temperature window, which is preferably in the temperature range from 920 to 950°C.

Methanol, in turn, is separately supplied to a second ammonia separation step 6, where ammonia is separated from methanol. Methanol can then be led to combustion either in a power boiler or to be used as support fuel in a recovery boiler, an odour gas burner 7 or a separate odour gas boiler 8. If desired, the previously mentioned odour gases can also be combusted
either in a power boiler or in a separate odour gas boiler. The ammonia separated from methanol, in turn, can be introduced in the above described manner into some boiler in use in a suitable temperature window to form molecular nitrogen and water with nitrogen oxide.

Ammonia is separated in the separation step preferably by what is known as a molecular sieve, such as zeolite, resulting in extremely pure ammonia, while other impurities are led to combustion with odour gases or methanol. The ammonia thus obtained can be used for various purposes, and, used with the SNCR method, process adjustment and, consequently, reduction in emissions can be achieved efficiently without extra non-controlled emissions.

Ammonia may also be separated from gas or methanol by a water scrubber, and in this case it naturally has to be separated from the washing solution before further processing or use.

Ammonia may also be separated from odour gases before methanol condensation, should this be easier from the technical point of view of the process. In this case only one separation step is required, and ammonia does not have to be separately removed from methanol after it has been condensed. In addition to the SNCR method, ammonia can also be used with a catalytic method, i.e. the SCR method, whereby ammonia is typically supplied to flue gases at a temperature of between 350 and 400°C to a special catalyst, simultaneously avoiding secondary reactions of sulphuric compounds. Furthermore, ammonia can be delivered from a pulp mill to other uses or be used for the preparation of ammonium sulphate for fertilizers. In view of the economic operation of a pulp mill, it is, however, preferable to use the separated ammonia to reduce nitrogen oxide emissions in a boiler in use at the pulp mill.
CLAIMS

1. A method of reducing nitrogen oxide emissions at a pulp mill in the combustion of odour gases that are released in different process steps at the pulp mill and contain detrimental sulphur compounds, characterized by separating the ammonia contained in the odour gases before they are introduced into combustion.

2. A method as claimed in claim 1, characterized by separating the ammonia from the odour gases by washing them with water, whereupon the ammonia is separated from the ammonia-water solution for further processing.

3. A method as claimed in claim 1, characterized by separating the ammonia from the odour gases by a molecular sieve, such as zeolite.

4. A method as claimed in any one of the preceding claims, characterized by separating the ammonia from the odour gases before methanol condensation.

5. A method as claimed in any one of claims 1 to 3, characterized by first separating methanol from the odour gases by condensation and separately separating the ammonia from the remaining gaseous odour gases and methanol.

6. A method as claimed in any one of the preceding claims, characterized by introducing the separated ammonia into a boiler at the pulp mill at a location in the boiler where the temperature is suitable, preferably between 920 and 950°C, to make the ammonia react with nitrogen oxide forming molecular nitrogen and water in accordance with the selective non-catalytic nitrogen oxide removal method.

7. A method as claimed in any one of claims 1 to 5, characterized by supplying the ammonia to the flue gases of a boiler at the pulp mill to a selective nitrogen oxide removal catalyst operating at a temperature of 350 to 400°C.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: D21C 11/06, D21C 11/12
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: D21C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>SE 9802979 A (AHLSTROM MACHINERY OY), 6 March 1999 (06.03.99), claim 1, &amp; DE 19840513</td>
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<td>SE 451334 B (MODO-CHEMETICS AB), 28 Sept 1987 (28.09.87), page 3, line 23 - page 4, line 4; page 5, line 15 - line 38; page 7, line 33 - page 8, line 8, page 9, line 12 - line 16</td>
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