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(54) Title: METHOD AND SYSTEM FOR THE REMOVAL OF NOXIOUS COMPOUNDS FROM ENGINE EXHAUST GAS

(57) Abstract: Method and system for the removal of noxious compounds from exhaust gas of a lean burning internal compression ignition engine, the method comprising passing the exhaust gas through a particulate filter being catalysed with a first SCR catalyst for selective reduction of nitrogen oxides; wherein aqueous ammonium nitrate is injected into the exhaust gas upstream the catalysed particulate filter during a cold start phase of the engine when the gas has a temperature of below 250°C, and wherein - when the exhaust gas has reached a temperature of about 220-250°C - injection of ammonium nitrate is discontinued and urea is injected into the gas, either upstream the first SCR catalyst or downstream the first SCR catalyst and upstream a second SCR catalyst for the selective reduction of nitrogen oxides.

Method and system for the removal of noxious compounds from engine exhaust gas

The present invention relates to a method and system for reducing emission of nitrogen oxides (NOx) and particulate matter being present in the exhaust from a lean burning internal compression ignition engine. In particular, the method and system of the invention provides an improved reduction of NOx during cold start of the engine.

The exhaust system of modern vehicles with lean burning engines is equipped with an oxidation catalyst, a particulate filter and a catalyst for the selective reduction of NOx (SCR) in the presence of a reducing agent.

Oxidation catalysts being active in the oxidation of volatile organic compounds, nitrogen monoxide and carbon monoxide and SCR catalysts are known in the art and disclosed in numerous publications.

Typically used particulate filters are the so called wall flow filters with a plurality of inlet and outlet channels. The inlet channels are closed at their outlet and the outlet channels are closed at their inlet, so that the gas flowing into the filter is forced through porous walls defining the channels, whereby particulate matter is filtered off the gas.

In the SCR treatment, ammonia is commonly employed as the reducing agent. Ammonia is a noxious compound and it is preferred to generate ammonia in situ by thermal decomposi-

tion of a urea solution being injected as ammonia precursor into the hot exhaust gas upstream the SCR catalyst.

Even if urea is innocuous and relatively easy to store on board of a car, use of a liquid solution of urea as a precursor of ammonia reducing agent is problematic in particular in the cold start phase of the engine, i.e. when the exhaust gas temperature is below 180°C.

When injected as liquid solution in the exhaust gas, urea decomposes to ammonia in sufficient amounts for the SCR only at a temperature from about 180°C.

The invention is based on using an SCR catalysed filter in combination with low temperature injection of ammonium nitrate into exhaust gas from a lean burning engine during the cold start phase of the engine when the exhaust gas temperature is below 250°C and a second SCR catalyst, wherein the necessary reducing agent is formed by decomposition of urea introduced into the exhaust gas at temperatures above 180°C in the cold start phase. Thereby it is possible to obtain a NOx reduction rate of more than 99% in the engine exhaust gas in a complete driving cycle.

Thus, the invention provides a method for the removal of noxious compounds from exhaust gas of a lean burning internal compression ignition engine comprising in series the steps of

passing the exhaust gas through a particulate filter being catalysed with a first SCR catalyst for selective reduction of nitrogen oxides; and

wherein aqueous ammonium nitrate is injected into the exhaust gas upstream the catalysed particulate filter during a cold start phase of the engine when the gas has a temperature of below 250°C, and wherein – when the exhaust gas has reached a temperature of about 220-250°C – injection of ammonium nitrate is discontinued and urea is injected into the gas, either upstream the first SCR catalyst or downstream the first SCR catalyst and upstream a second SCR catalyst for the selective reduction of nitrogen oxides.

Of particular interest is the method which additionally comprises the step of contacting the exhaust gas with a catalyst being active in oxidation of volatile organic compounds and carbon monoxide to carbon dioxide and water and nitrogen oxide to nitrogen dioxide, upstream of said particulate filter, wherein the ammonium nitrate may be injected into the exhaust gas stream prior to, or after, contact with the oxidation catalyst. Injection of ammonium nitrate prior to contact with the oxidation catalyst near the engine manifold with short mixing distance has the potential to the earliest injection during the cold start and thus improving the NOx removal.

The invention allows the oxidation catalyst (DOC) and the SCR catalysed filter (SCR/DPF) to be arranged in close coupled position. The close coupled position together with a small volume of DOC and SCR/DPF will facilitate a fast heat up of these units and thus a sufficient catalyst activity in an early phase after cold start. The DOC will early in

the cold start phase form NO_2 from NO in exhaust and the close coupled filter SCR/DPF will have temperature conditions for passive soot regeneration with NO_2.

Ammonium nitrate is injected in the form of an aqueous solution. Injection can be started at an exhaust gas temperature from 160 °C, preferably from 170 °C.

Thus, in an embodiment of the invention ammonium nitrate is injected into the exhaust gas prior to the contact with the DOC.

Alternatively, ammonium nitrate can be injected between the DOC and the SCR/DPF.

In one aspect, a close-coupled SCR catalyst is present upstream the SCR catalyzed particulate filter, and both said urea and said aqueous ammonium nitrate are injected upstream the close-coupled SCR catalyst.

Ammonium nitrate may be stored on board as such in a container, e.g. as an aqueous solution. Ammonium nitrate will convert NO to NO_2 at the lower temperatures according to the reaction:

$$NO + NH_4NO_3 \rightarrow NO_2 + N_2 + 2H_2O$$

Ammonium nitrate injection is discontinued when the exhaust temperature is about 220-250 °C and urea injection into exhaust gas leaving the catalysed filter is initiated at about 180°C.

This implies that only a limited amount of stored ammonium nitrate is required for the total NOX reduction during the cold start phase. In the main driving cycle when the exhaust gas is above 220°C, ammonia is formed by decomposition of a urea solution being injected into the hot exhaust gas between the SCR/DPF and the second SCR.

Above 200°C the NO in the exhaust gas is oxidised to NO_2 by contact with the DOC. The formed NO_2 is used in the passive regeneration of the DPF. Thus, above temperatures of 220°C all the amount of formed NO_2 can be used for passive soot regeneration of the filter and fast SCR from low temperatures.

With modern low soot emission engines it is possible to rely on passive soot regeneration and the maximum inlet temperature to the second SCR catalyst can be kept below 550°C. This implies that the second SCR catalyst can be selected from cheaper vanadium or zeolite catalyst compounds.

As further an advantage of the method according to the invention the passive regeneration is more effective because ammonia is not present in the exhaust gas during the main driving cycle and the SCR function of the SCR/DPF is interrupted.

In addition, expensive oxidation catalyst (DOC) may even be fully omitted, and cold start facilitated in the following configurations:

Engine → NH_4NO_3 + urea → SCR/DPF → ASC → out

or

Engine → NH_4NO_3 + urea → SCR/DPF → urea → SCR → ASC → out

or

Engine → NH_4NO_3 + urea → SCR/DPF → SCR → ASC → out

or

Engine → NH_4NO_3 → SCR/DPF → urea → SCR → ASC → out

or

Engine → NH_4NO_3 + urea → ccSCR → SCR/DPF → ASC → out

(ASC = ammonium slip catalyst)

When a DOC is fully omitted, injection of ammonium nitrate before SCR/DPF will also assist soot combustion at low temperature above about 200 °C as NO_2 is directly formed. Above this temperature is also an option to use blends of urea and ammonia solutions. Urea – ammonium nitrate (UAN) solutions, used as fertilizers, are commercially available

Small amounts of ammonia may be present in the exhaust gas from the second SCR. It is thus preferred to pass the exhaust gas from the second SCR through a selective ammonia oxidation catalyst (ASC) downstream the second SCR. The selective ammonia oxidation catalyst converts ammonia to nitrogen.

Additionally, the invention provides a system for use in the method according to the invention.

The system comprises within an engine exhaust gas channel connected to the engine, arranged in series

optionally, an oxidation catalyst unit for the oxidation of volatile organic compounds and carbon

monoxide to carbon dioxide and water and nitrogen oxide to nitrogen dioxide;
a particulate filter comprising a first catalyst for selective reduction of nitrogen oxides;
optionally, a second catalyst unit for the selective reduction of nitrogen oxides;
upstream the particulate filter, injection means for the injection of aqueous ammonium nitrate in aqueous solution into the engine exhaust gas channel; and
upstream the particulate filter, or between the particulate filter and the second catalyst for the selective reduction of nitrogen oxides, injection means for the injection of urea into the engine exhaust gas channel.

In an embodiment of the invention, the injection means for injection of ammonium nitrate is arranged between the engine and the inlet of the oxidation catalyst unit.

In further an embodiment, the injection means for injection of ammonium nitrate is connected to a container.

When the DOC and SCR/DPF are arranged in close-coupled position, temperature loss is limited, which facilitates higher temperatures and increased NO_2 formation over the DOC and higher temperatures in the filter resulting in an improved passive soot regeneration.

To remove small amounts of ammonia having not been converted in the SCR catalysts, it is preferred to arrange an ammonia slip catalyst (ASC) downstream the second SCR unit.

As already mentioned hereinbefore, suitable catalysts for use in the invention are known in the art and are not the subject of the present invention.

Preferably, the first SCR catalyst integrated in the filter for use in the inventive method and system is based on thermostable copper and/or iron promoted zeolites or silica alumina phosphate compounds.

The second SCR catalyst for use in the inventive method and system is preferably selected from vanadium on titania, copper and/or iron promoted zeolites, copper and/or iron promoted silica alumina phosphates, optionally combined with cerium oxides with zirconium and aluminium oxides.

Suitably, a close-coupled SCR catalyst is present upstream the SCR catalyzed particulate filter, and injection means for both urea and aqueous ammonium nitrate are present upstream the close-coupled SCR catalyst.

Claims

1. A method for the removal of noxious compounds from exhaust gas of a lean burning internal compression ignition engine comprising in series the steps of passing the exhaust gas through a particulate filter being catalysed with a first SCR catalyst for selective reduction of nitrogen oxides; and wherein aqueous ammonium nitrate is injected into the exhaust gas upstream the catalysed particulate filter during a cold start phase of the engine when the gas has a temperature of below 250°C, and wherein - when the exhaust gas has reached a temperature of about 220-250°C - injection of ammonium nitrate is discontinued and urea is injected into the gas, either upstream the first SCR catalyst or downstream the first SCR catalyst and upstream a second SCR catalyst for the selective reduction of nitrogen oxides.

2. The method according to claim 1, additionally comprising the step of contacting the exhaust gas with a catalyst being active in oxidation of volatile organic compounds and carbon monoxide to carbon dioxide and water and nitrogen oxide to nitrogen dioxide, upstream of said particulate filter, wherein the ammonium nitrate may be injected into the exhaust gas stream prior to, or after, contact with the oxidation catalyst.

3. The method according to any one of the preceding claims, wherein the ammonium nitrate is injected

into the exhaust gas prior to the contact with the oxidation catalyst.

4. The method according to any one of claims 1-2, wherein the ammonium nitrate is injected into the exhaust gas between the oxidation catalyst and the SCR catalyzed particulate filter.

5. The method according to any one of claims 1 to 4, wherein the exhaust gas is further passed through an ammonia oxidation catalyst for selective oxidation of ammonia downstream the second SCR catalyst.

6. The method according to any one of the preceding claims, wherein the ammonium nitrate is comprised in an aqueous solution of urea and ammonium nitrate.

7. The method according to any one of the preceding claims, wherein a close-coupled SCR catalyst is present upstream the SCR catalyzed particulate filter, and both said urea and said aqueous ammonium nitrate are injected upstream the close-coupled SCR catalyst.

8. System for use in the method according to any one of claims 1-7 comprising within an engine exhaust gas channel connected to the engine, arranged in series
optionally, an oxidation catalyst unit for the oxidation of volatile organic compounds and carbon

monoxide to carbon dioxide and water and nitrogen oxide to nitrogen dioxide;
a particulate filter comprising a first catalyst for selective reduction of nitrogen oxides;
optionally, a second catalyst unit for the selective reduction of nitrogen oxides;
upstream the particulate filter, injection means for the injection of aqueous ammonium nitrate in aqueous solution into the engine exhaust gas channel; and
upstream the particulate filter, or between the particulate filter and the second catalyst for the selective reduction of nitrogen oxides, injection means for the injection of urea into the engine exhaust gas channel.

9. The system according to claim 8, wherein the injection means for injection of ammonium nitrate as an aqueous solution is arranged between the engine and the inlet of the oxidation catalyst unit.

10. The system according to any one of claims 8-9, wherein the oxidation catalyst unit and the particulate filter comprising a first catalyst for selective reduction of nitrogen oxides are arranged in close-coupled position.

11. The system according to anyone of claims 8-10 being further provided with a catalyst unit for the selective oxidation of ammonia to nitrogen downstream the second catalyst unit for the selective reduction of nitrogen oxides.

12. The system according to any one of claims 8-11, wherein a close-coupled SCR catalyst is present upstream the SCR catalyzed particulate filter, and injection means for both urea and aqueous ammonium nitrate are present upstream the close-coupled SCR catalyst.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/068621

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/90 B01D53/94 F01N3/035 F01N3/20
ADD.

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)
B01D F01N

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/145548 A1 (VOLVO LASTVAGNAR AB [SE]; HINZ ANDREAS [SE]; JANSSON JONAS [SE]; BERNL) 21 December 2007 (2007-12-21) page 1, lines 6-11 page 3, line 31 - page 4, line 11 page 5, lines 8-29 page 8, line 4 - line 9 figure 1 -----	8-12
X	WO 2008/126118 A1 (MILANO POLITECNICO [IT]; FORZATTI PIO [IT]; TRONCONI ENRICO [IT]; NOVA) 23 October 2008 (2008-10-23) page 5, lines 14-19 page 6, line 8 - page 7, line 16 page 10, line 4 - line 14 examples 1-8 figures 1-3 -----	1-7
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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 November 2012	06/12/2012

Name and mailing address of the ISA/	Authorized officer
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Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/068621

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2004/076037 A1 (UMICORE AG & CO KG [DE]; PFEIFER MARKUS [DE]; VAN SETTEN BARRY [DE]; S) 10 September 2004 (2004-09-10) page 3, line 33 - page 4, line 21 page 5, lines 3-10 page 5, line 34 - page 6, line 21 page 7, lines 7-9 figure 1 -----	1-12
A	JP 2007 138887 A (BABCOCK HITACHI KK) 7 June 2007 (2007-06-07) paragraphs [0002], [0005], [0011] - [0018] figures 2,3 claims 1-3 -----	1-12

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/EP2012/068621

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☒ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-4, 6, 7(all partially)

   method for removal of noxious compounds from lean burn engine comprising the steps of passing the exhaust gas through a particulate filter catalysed with a first SCR catalyst, wherein ammonium nitrate is injected upstream of the particulate filter during cold start when the exhaust gas has a temperature below 250°C and wherein the injection of ammonium nitrate is discontinued and urea is injected upstream of the particulate filter when the exhaust gas temperature has reached a temperature of about 220°C-250°C

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2. claims: 5(completely); 1-4, 6, 7(partially)

   method for removal of noxious compounds from lean burn engine comprising the steps of passing the exhaust gas through a particulate filter catalysed with a first SCR catalyst and passing the exhaust gas through a second SCR catalyst downstream of the particulate filter, wherein ammonium nitrate is injected upstream of the particulate filter during cold start when the exhaust gas has a temperature below 250°C and wherein the injection of ammonium nitrate is discontinued and urea is injected downstream of the particulate filter and upstream of the second SCR catalyst when the exhaust gas temperature has reached a temperature of about 220°C-250°C

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3. claims: 8-10, 12(all partially)

   system for removal of noxious compounds from lean burn engine comprising a particulate filter catalysed with a first SCR catalyst, an injection means for ammonium nitrate upstream of the particulate filter and an injection means for urea upstream of the particulate filter

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4. claims: 11(completely); 8-10, 12(partially)

   system for removal of noxious compounds from lean burn engine comprising a particulate filter catalysed with a first SCR catalyst, an injection means for ammonium nitrate upstream of the particulate filter, an second SCR catalyst downstream of the particulate filter and an injection means for urea downstream of the particulate filter and upstream of the second SCR catalyst

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/068621

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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