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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 lean burning engines, the method comprising in series the steps of contacting the exhaust gas with a catalyst being active in oxidation of volatile organic compounds and carbon monoxide, passing the treated exhaust gas through a particulate filter catalysed with a first SCR catalyst, and passing the exhaust gas leaving the particulate filter through a second SCR catalyst, wherein ammonia is injected into the exhaust upstream of the catalysed particulate filter at a temperature below or at about 220°C and wherein urea is injected into the exhaust gas between the first and the second SCR catalyst when the exhaust gas has reached a temperature of about 200°C.

**Title: 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 particular 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 cars with lean burning engines is equipped with an oxidation catalyst, a particulate filter and a catalyst for the selective reduction of NOx (SCR)in presence of a reduction agent.

Oxidation catalysts being active in the oxidation of volatile organic compounds 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 if 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 200°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 200°C.

The invention is based on using an SCR catalysed filter in combination with low temperature injection of ammonia reducing agent into exhaust gas from a lean burning engine during the cold start phase of the engine when the exhaust gas temperature is below 220°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 200°C after 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

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;

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

passing the exhaust gas leaving the filter through a second SCR catalyst for the selective reduction of nitrogen oxides, wherein ammonia reducing agent 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 or at about 220°C, and wherein injection of ammonia is discontinued and urea as precursor for the ammonia reducing agent is injected into the gas between the first and second SCR catalyst when the gas has reached a temperature of about 200°C.

As an advantage of the method according to the invention, ammonia has a very low mixing distance and injection of ammonia allows arranging the oxidation catalyst(DOC) and the SCR catalysed filter (SCR/DPF) 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 $NO_2$.

Ammonia injection can be started at an exhaust gas temperature from 160 °C. At temperatures below 200°C, ammonia re-

mains substantially unconverted when passing through the DOC.

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

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

Ammonia may be stored on board as such in a container or preferably liberated from a solid ammonia storage material, by means of e.g. thermal desorption. Solid ammonia storage materials, such as metal amine salts or ammonium compounds are known in the art e.g from WO 2206/012903.

Ammonia injection is discontinued when the exhaust temperature is about 220 °C and urea injection into exhaust gas leaving the catalysed filter is initiated at about 200°C.

This implies that only a limited amount of stored ammonia 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 to NO2 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 exclusively be used for passive soot regeneration of the filter.

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.

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 downstream the second SCR. The selective ammonia oxidation catalyst converts ammonia to nitrogen.

The invention provides additionally 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

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;

a second catalyst unit for the selective reduction of nitrogen oxides;

upstream the particulate filter, injection means for the injection of ammonia into the engine exhaust gas channel; and

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 ammonia is arranged between the engine and the of the oxidation catalyst unit.

In further an embodiment, the injection means for injection of ammonia is connected to a container holding a solid ammonia storage material.

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 he SCR catalysts, it is preferred to arrange an ammonia slip catalyst downstream the second SCR unit.

The system will have thus have one of the following configuration:

Engine→ccDOC→$NH_3$(<220°C)→ccSCR/DPF→ Urea(>200°C)→ secondSCR → ASC

alternatively

Engine→$NH_3$(<220°C)→ccDOC→ccSCR/DPF→ Urea(>200°C)→ mainSCR → ASC

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

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

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;

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

passing the exhaust gas leaving the filter through a second SCR catalyst for the selective reduction of nitrogen oxides, wherein ammonia reducing agent 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 or at about 220°C, and wherein injection of ammonia is discontinued and urea as precursor for the ammonia reducing agent is injected into the gas between the first and second SCR catalyst when the gas has reached a temperature of about 200°C.

2. The method of claim 1, wherein the ammonia reducing agent is injected into the exhaust gas prior to the contact with the oxidation catalyst.

3. The method of claim 1, wherein the ammonia reducing agent is injected into the exhaust gas between the oxidation catalyst and the SCR catalyzed particulate filter.

4. The method according to anyone of claims 1 to 3, wherein the ammonia reducing agent is released from an ammonia absorbent prior to injection into the exhaust gas.

5. The method according to anyone 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. System for use in the method according to claim 1 comprising within an engine exhaust gas channel connected to the engine, arranged in series

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;

a second catalyst unit for the selective reduction of nitrogen oxides;

upstream the particulate filter, injection means for the injection of ammonia into the engine exhaust gas channel; and

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.

7. The system of claim 6, wherein the injection means for injection of ammonia is arranged between the engine and the of the oxidation catalyst unit.

8. The system of claim 6 or 7, wherein the injection means for injection of ammonia is connecter to a container holding a solid ammonia storage material.

9. The system according to anyone of claims 6 to 8, 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.

10. The system according to anyone of the preceding claims 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.

# INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
INV. B01D53/90 B01D53/94 F01N3/035 F01N3/20 F01N3/10
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

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[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 23 November 2012 | 03/12/2012 |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| European Patent Office, P.B. 5818 Patentlaan 2<br>NL - 2280 HV Rijswijk<br>Tel. (+31-70) 340-2040,<br>Fax: (+31-70) 340-3016 | Hackenberg, Stefan |

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