(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
24 November 2016 (24.11.2016)

WIPO | PCT

(10) International Publication Number
WO 2016/184774 A1

(51) International Patent Classification:
F01N 3/035 (2006.01) *F01N 3/10* (2006.01)
F01N 3/20 (2006.01) *F01N 13/00* (2010.01)

(21) International Application Number:
PCT/EP2016/060682

(22) International Filing Date:
12 May 2016 (12.05.2016)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
PA 2015 70290 19 May 2015 (19.05.2015) DK

(71) Applicant: **HALDOR TOPSØE A/S** [DK/DK]; Haldor Topsøes Allé 1, 2800 Kgs. Lyngby (DK).

(72) Inventor: **GABRIELSSON, Pär L. T.**; Karl X Gustavsgatan 7, 25438 Helsingborg (SE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to the identity of the inventor (Rule 4.17(i))*

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii))*

[Continued on next page]

(54) **Title**: METHOD, MULTIFUNCTIONAL FILTER AND SYSTEM FOR THE REMOVAL OF PARTICULATE MATTER AND NOXIOUS COMPOUNDS FROM ENGINE EXHAUST GAS

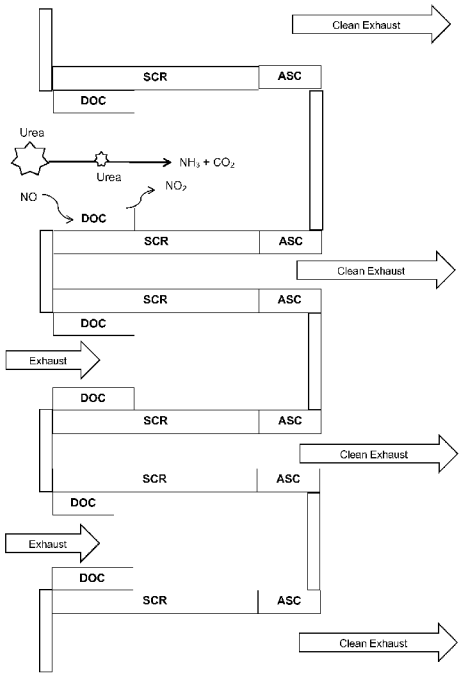


Fig. 1

(57) **Abstract**: A multifunctional wall flow filter and a system having same performing removal of noxious compounds comprising nitrogen oxides, volatile organic compounds and carbon monoxide and particulate matter from exhaust gas of a compression ignition engine by performing in series the steps of (a) adding an amount of SCR reductant in form of droplets of an aqueous urea solution to the exhaust gas; (b) introducing the exhaust gas admixed with the droplets of the aqueous urea solution into inlet channels of a wall flow filter and oxidizing the volatile organic compounds and carbon monoxide to carbon dioxide and water and nitrogen monoxide to nitrogen dioxide in presence of an oxidation catalyst arranged on permeable porous partition walls at inlet side of the wall flow filter, the oxidation catalyst active in; (c) subsequently evaporating and decomposing the droplets of the aqueous urea solution in the exhaust gas from step (b) to ammonia; (d) passing the exhaust gas containing the ammonia through the permeable porous partition walls of the wall flow filter to outlet channels of the filter and capturing the particulate matter on surface of the permeable porous partition walls facing the inlet channels of the filter; (e) removing continuously the captured particulate matter by reaction with the nitrogen dioxide contained in the exhaust gas; and (f) subsequently removing remaining amounts of nitrogen dioxide from the exhaust gas by reaction with the ammonia in presence of an SCR active catalyst arranged within the gas permeable porous partition walls and/or on wall side facing the outlet channels of the wall flow particle filter.

WO 2016/184774 A1

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

Method, multifunctional filter and system for the removal of particulate matter and noxious compounds from engine exhaust gas

The present invention relates to a method, multifunctional filter and system for reducing emission of nitrogen oxides (NOx) and particulate matter present in the exhaust from a lean burning internal compression ignition engine.

The exhaust system of modern cars with lean burning engines is typically 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 employed particulate filters (DPF) in diesel exhaust gas cleaning systems, are wall flow filters with a plurality if inlet and outlet channels. The inlet channels are closed at their outlet side and the outlet channels are closed at their inlet side, so that the gas flowing into the filter is forced through porous walls defining the channels, whereby particulate matter is filtered off from the gas.

To meet future emission regulations for diesel passenger cars and trucks requires usage of both diesel particulate filter technology and NOx reduction catalyst. Due to its

potential for fuel optimization and high efficiency in NOx removal, SCR is often the preferred technology for NOx reduction. DOC (diesel oxidation catalyst), DPF (diesel particulate filter) and SCR (selective catalytic reduction) catalysts are combined sequentially in the exhaust system but such sequential system configurations have several drawbacks: 1) large volume; 2) insufficient temperature for the SCR catalyst during cold start when DPF is placed in front of SCR; and 3) unfavourable conditions for passive filter regeneration (lower NO2 and temperature) if SCR is placed upstream of the DPF.

Particulate matter accumulated on the filter walls at inlet side of the filter must be removed either by active regeneration, wherein particulate matter is catalytically burned off in contact with an oxidation catalyst supported on the filter walls in combination with oxygen in exhaust gas at increased exhaust gas temperatures or by non-catalytic passive regeneration.

Passive filter regeneration is facilitated by oxidation of carbon at 250°C-450°C with NO2 formed on an upstream DOC by the following reactions

$$C + NO_2 \rightarrow CO + NO \quad (1)$$

$$C + 2NO_2 \rightarrow CO_2 + 2NO \quad (2)$$

And as the particulate matter typically contains a hydrocarbon as SOF (Soluble Organic Fraction), here typified as the hydrocarbon "CH"

$$\text{"CH"} + 2.5NO_2 \rightarrow CO_2 + 2.5NO + 0.5H_2O \quad (3)$$

The fast SCR reaction

$$4NH_3 + 2NO + 2NO_2 \rightarrow 4\ N_2 + 6H_2O \quad (4)$$

competes with the above carbon reactions for the availability of NO_2.

The problems can potentially be solved by integrating the DOC and SCR catalysts into the particulate filter as one multifunctional unit.

One of the challenges of integrating the oxidation function into one unit is that it might consume or oxidize ammonia reductant before it reaches the SCR catalyst. The DOX is important for the production of NO_2 from NO which is used to oxidize the soot in the soot filter. The oxidation of the soot by NO_2 keeps the filter clean and assures a low pressure drop in the system. The solution according to the invention is that only the inlet of the filter is zone coated with the DOC functionality. NO, which is a gas, will diffuse down into the catalytic material and react to NO_2, while the urea, which is used as a precursor for NH_3 and is a liquid will pass through the zone with the DOC and hydrolyse to NH_3 after the DOC, as shown in Fig.1. The upper layer of the DOC might be passivated by adding a thin coat of a more inert material, which does not react with the urea.

Thus, a first aspect of the invention resides in a method for the removal of noxious compounds and particulate matter from exhaust gas of a compression ignition engine comprising in series the steps of

(a) adding an amount of SCR reductant in form of droplets of an aqueous urea solution to the exhaust gas;

(b) introducing the exhaust gas admixed with the droplets of the aqueous urea solution into inlet channels of a wall flow filter and oxidizing the volatile organic compounds and carbon monoxide to carbon dioxide and water and nitrogen monoxide to nitrogen dioxide in presence of an oxidation catalyst arranged on permeable porous partition walls at inlet side of the wall flow filter;

(c) subsequently evaporating and decomposing the droplets of the aqueous urea solution in the exhaust gas from step (b) to ammonia;

(d) passing the exhaust gas containing the ammonia through the permeable porous partition walls of the wall flow filter to outlet channels of the filter and capturing the particulate matter on surface of the permeable porous partition walls facing the inlet channels of the filter;

(e) removing continuously the captured particulate matter by reaction with the nitrogen dioxide contained in the exhaust gas ; and

(f) subsequently removing remaining amounts of nitrogen dioxide from the exhaust gas by reaction with the ammonia in presence of an SCR active catalyst arranged within the gas permeable porous partition walls and/or on wall side facing the outlet channels of the wall flow particle filter.

A second aspect of the invention is multifunctional wall flow filter for cleaning exhaust gas from a compression ignition engine comprising a plurality of exhaust gas inlet flow channels and a plurality of exhaust gas outlet channels separated by gas permeable porous partition walls;

a diesel oxidation catalyst applied in the exhaust gas inlet flow channels on the partition walls at exhaust gas inlet side;
and an SCR catalyst for selective reduction of nitrogen oxides applied within the partition walls and/or on surface of the partition walls facing the outlet channels in a region between the exhaust gas inlet side and outlet side, wherein upper layer of the diesel oxidation catalyst is passivated with a coat of an inert material.

A third aspect of the invention is a system for cleaning exhaust gas from a diesel engine comprising an injector and a downstream multifunctional wall flow filter with a plurality of exhaust gas inlet flow channels and a plurality of exhaust gas outlet channels separated by gas permeable porous partition walls;
a diesel oxidation catalyst applied in the exhaust gas inlet flow channels on the partition walls at exhaust gas inlet side;
and an SCR catalyst for selective reduction of nitrogen oxides applied within the partition walls and/or on surface of the partition walls facing the outlet channels in a region between the exhaust gas inlet side and outlet side, wherein the injector is adapted to inject droplets of a urea-water-solution into exhaust gas upstream of the multifunctional wall flow filter so that the urea-water-solution comes in contact with the diesel oxidation catalyst in liquid form or the injector is arranged at a distance to the inlet of multifunctional wall flow filter resulting in a droplet size of the urea-water-solution so that the urea-water-solution comes in contact with the diesel oxidation catalyst in liquid form.

At the typical distance of 0.5 m from the injector to the multifunctional wall flow filter as in the case of diesel vehicles, it is necessary to provide the size of the droplets to at least 7 micrometers in order to prevent gasification of the droplets in the gas phase upstream of the filter and within the DOC .

With a droplet size of the urea-water-solution larger less than 7 micrometers the distance of the injector must be reduced to below 0.5 meters in order to prevent evaporation of the solution within the DOC.

The further advantages of the method, the multifunctional filter and the system according to the above aspects of the invention are besides physical separation, a thermal decoupling of the particulate matter and NOx reactions, as NO2 is primarily needed for the fast SCR reaction in the temperature range of 180°C-280°C while NO2 for passive particulate matter combustion is needed in the range of 280°C-450°C. During a vehicle cold start, the NO2 will therefore be fully available for the needed NOx conversion, and the combustion of accumulated particulate matter can wait for the system to be heated up.

Further preferred embodiments of the invention are disclosed in the dependent claims.

Suitable oxidation and SCR catalysts for use in the invention are well known in the art.

To name a few, vanadium-based catalyst formulations of the family V2O5/WO3/TiO2 have shown high deNOx performance and durability. Copper and iron zeolites with the beta framework have been commercialized for some years and are currently used as SCR catalyst for diesel exhaust clean-up. Cu-zeolite types with the chabazite structure have a promising combination of high-temperature stability and high low-temperature activity. Of those, Cu-SAPO-34 and Cu-SSZ-13 SCR catalysts are preferred.

Oxidation catalysts forming nitrogen dioxide for use in the invention are platinum or mixtures of platinum and palladium. These metals are deposited on alumina and/or titania and or silica. Stabilisation with rare earth metal oxides can be beneficial.

Claims

1. A method for the removal of noxious compounds comprising nitrogen oxides, volatile organic compounds and carbon monoxide and particulate matter from exhaust gas of a compression ignition engine comprising in series the steps of

(a) adding an amount of SCR reductant in form of droplets of an aqueous urea solution to the exhaust gas;

(b) introducing the exhaust gas admixed with the droplets of the aqueous urea solution into inlet channels of a wall flow filter and oxidizing the volatile organic compounds and carbon monoxide to carbon dioxide and water and nitrogen monoxide to nitrogen dioxide in presence of an oxidation catalyst arranged on permeable porous partition walls at inlet side of the wall flow filter, the oxidation catalyst active in;

(c) subsequently evaporating and decomposing the droplets of the aqueous urea solution in the exhaust gas from step (b) to ammonia;

(d) passing the exhaust gas containing the ammonia through the permeable porous partition walls of the wall flow filter to outlet channels of the filter and capturing the particulate matter on surface of the permeable porous partition walls facing the inlet channels of the filter;

(e) removing continuously the captured particulate matter by reaction with the nitrogen dioxide contained in the exhaust gas ; and

(f) subsequently removing remaining amounts of nitrogen dioxide from the exhaust gas by reaction with the ammonia in presence of an SCR active catalyst arranged within the gas permeable porous partition walls and/or on wall side facing the outlet channels of the wall flow particle filter.

2. The method of claim 1, further comprising a step of removing excess of ammonia contained in the exhaust gas by contact with an ammonia slip catalyst arranged at outlet of the outlet channels of the wall flow filter.

3. The method of claim 1 or 2, wherein droplet size of the aqueous urea solution is at least 7 micrometer.

4. The method according to any one of claims 1 to 3, wherein the SCR catalyst comprises oxides of vanadium and/or tungsten and titania.

5. The method according to any one of claims 1 to 3, wherein the SCR active catalyst comprises one or more copper or iron promoted beta-zeolites.

6. The method according to any one of claims 1 to 3, wherein the SCR active catalyst comprises copper promoted SAPO-34 and/or copper promoted SSZ-13.

7. The method according to any one of claims 1 to 6, wherein the oxidation catalyst comprises platinum and/or palladium.

8. The method according to claim 2, wherein the ammonia slip catalyst comprises platinum and CuSAPO-34 and/or SSZ-13.

9. Multifunctional wall flow filter for cleaning exhaust gas from a compression ignition engine comprising a plurality of exhaust gas inlet flow channels and a plurality of

exhaust gas outlet channels separated by gas permeable porous partition walls;
a diesel oxidation catalyst applied in the exhaust gas inlet flow channels on the partition walls at exhaust gas inlet side;
and an SCR catalyst for selective reduction of nitrogen oxides applied within the partition walls and/or on surface of the partition walls facing the outlet channels in a region between the exhaust gas inlet side and outlet side,
wherein upper layer of the diesel oxidation catalyst is passivated with a coat of an inert material.

10. Multifunctional wall flow filter according to claim 9, wherein the outlet side of the outlet channels is additionally provided with an ammonia slip catalyst.

11. Multifunctional wall flow filter according to claim 9 or 10, wherein the SCR catalyst comprises, oxides of vanadium and/or tungsten and titania.

12. Multifunctional wall flow filter according to claim 9 or 10, wherein the SCR active catalyst comprises one or more copper or iron promoted beta-zeolites.

13. Multifunctional wall flow filter according to claim 9 or 10, wherein the SCR catalyst comprises copper promoted SAPO-34 and/or copper promoted SSZ-13.

14. Multifunctional wall flow filter according to any one of claims 9 to 13, wherein the oxidation catalyst comprises platinum and/or palladium.

15. Multifunctional wall flow filter according to claim 10, wherein the ammonia slip catalyst comprises platinum and CuSAPO-34 and/or SSZ-13.

16. Multifunctional wall flow filter according to any one of claims 9 to 15, wherein the coat of an inert layer comprises a material, which does not hydrolyse urea to ammonia.

17. A system for cleaning exhaust gas from a diesel engine comprising an injector and a downstream multifunctional wall flow filter with a plurality of exhaust gas inlet flow channels and a plurality of exhaust gas outlet channels separated by gas permeable porous partition walls;
a diesel oxidation catalyst applied in the exhaust gas inlet flow channels on the partition walls at exhaust gas inlet side;
and an SCR catalyst for selective reduction of nitrogen oxides applied within the partition walls and/or on surface of the partition walls facing the outlet channels in a region between the exhaust gas inlet side and outlet side,
wherein the injector is adapted to inject droplets of a urea-water-solution into exhaust gas upstream of the multifunctional wall flow filter so that the urea-water-solution comes in contact with the diesel oxidation catalyst in liquid form or the injector is arranged at a distance to the inlet of multifunctional wall flow filter resulting in a droplet size of the urea-water-solution so that the urea-water-solution comes in contact with the diesel oxidation catalyst in liquid form.

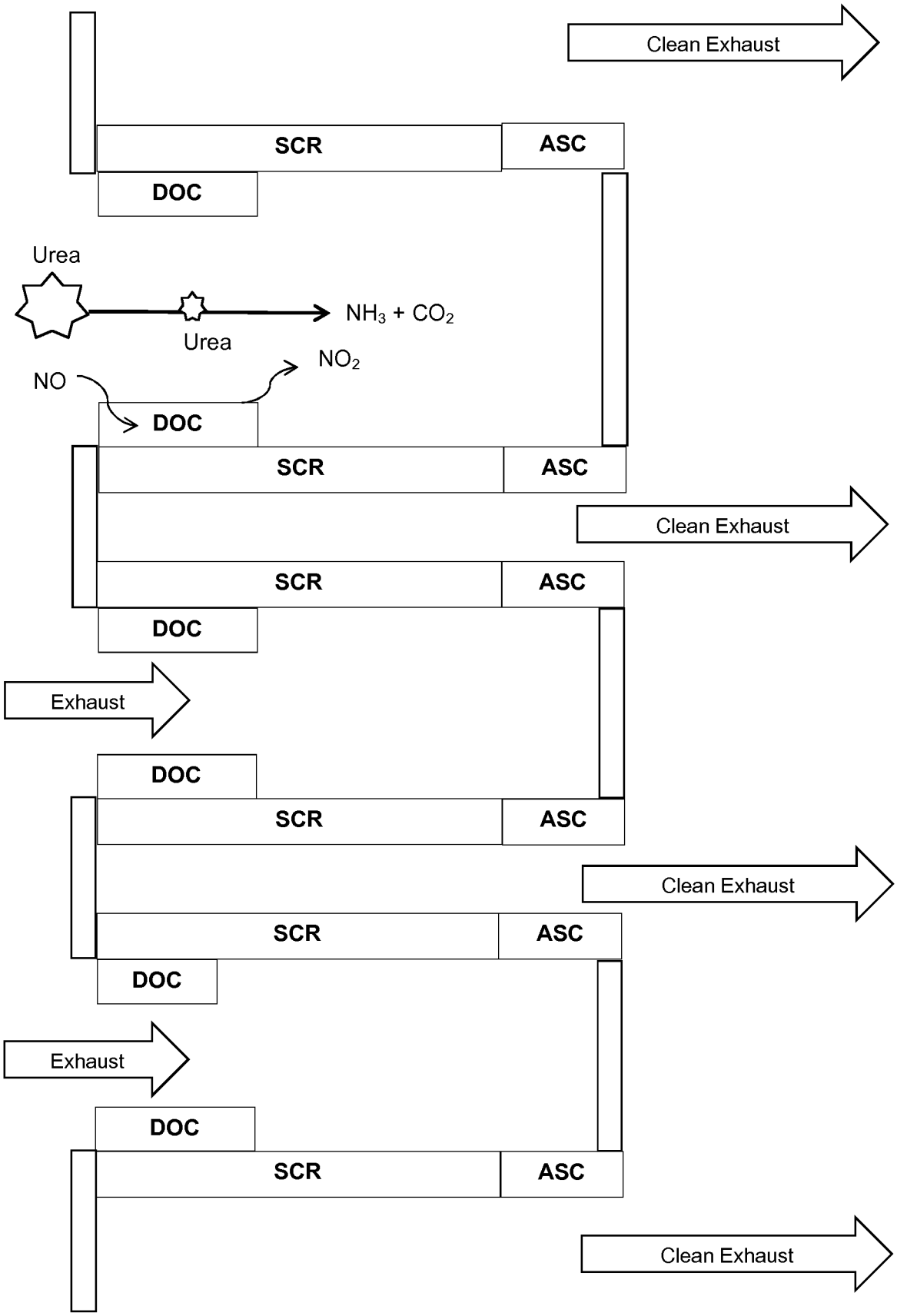

Clean Exhaust
SCR
ASC
DOC
Urea
$NH_3 + CO_2$
Urea
NO_2
NO
DOC
SCR
ASC
Clean Exhaust
SCR
ASC
DOC
Exhaust
DOC
SCR
ASC
Clean Exhaust
SCR
ASC
DOC
Exhaust
DOC
SCR
ASC
Clean Exhaust

Fig. 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/060682

A. CLASSIFICATION OF SUBJECT MATTER
INV. F01N3/035 F01N3/20 F01N3/10 F01N13/00
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)
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	DE 10 2008 038736 A1 (MAN NUTZFAHRZEUGE AG [DE]) 18 February 2010 (2010-02-18) abstract; figures 1, 3 paragraphs [0025], [0042], [0045] paragraphs [0009] - [0029]	1-17
X	US 2008/256936 A1 (ZUBERI BILAL [US]) 23 October 2008 (2008-10-23)	1-4,7, 9-11,14, 16,17
A	abstract; claims 13-20; figures 1,6,19,18 paragraphs [0079], [0089] paragraphs [0024] - [0027]	5,6,8, 12,13,15

-/--

[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
8 July 2016	18/07/2016

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

3

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/060682

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2010/175372 A1 (LAMBERT CHRISTINE KAY [US] ET AL) 15 July 2010 (2010-07-15)	1-3,5, 7-10,12, 14-17
A	abstract; figure 2 paragraphs [0019] - [0023], [0048], [0050]	4,6,11, 13

X	US 2013/276432 A1 (CREHAN GABRIEL [FR]) 24 October 2013 (2013-10-24)	1,3,7,9, 14,16,17
A	abstract; figure 1 paragraphs [0060], [0064] paragraphs [0016] - [0048]	2,4-6,8, 10-13,15

3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2016/060682

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
DE 102008038736 A1	18-02-2010	CN 101676527 A	24-03-2010
		DE 102008038736 A1	18-02-2010
		EP 2154343 A1	17-02-2010
		RU 2009130676 A	20-02-2011
		US 2010037600 A1	18-02-2010
US 2008256936 A1	23-10-2008	US 2008256936 A1	23-10-2008
		US 2010247396 A1	30-09-2010
US 2010175372 A1	15-07-2010	NONE	
US 2013276432 A1	24-10-2013	CN 103314192 A	18-09-2013
		EP 2663748 A1	20-11-2013
		FR 2970294 A1	13-07-2012
		US 2013276432 A1	24-10-2013
		WO 2012095573 A1	19-07-2012