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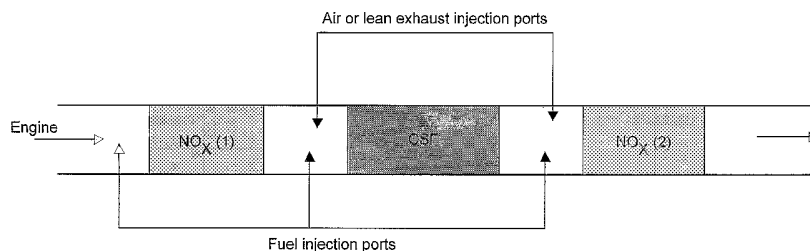
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(54) Title: EXHAUST SYSTEM FOR LEAN BURN IC ENGINE INCLUDING PARTICULATE FILTER AND NO<sub>x</sub> ABSORBENT



(57) Abstract: An exhaust system for a lean burn internal combustion engine comprises a particulate filter (CSF), a first NO<sub>x</sub> absorbent (NO<sub>x</sub>(1)) disposed upstream of the filter and a second NO<sub>x</sub> absorbent (NO<sub>x</sub>(2)) disposed downstream of the filter.

WO 2004/079170 A1

**EXHAUST SYSTEM FOR LEAN BURN IC ENGINE INCLUDING  
PARTICULATE FILTER AND NO<sub>x</sub> ABSORBENT**

The present invention relates to an exhaust system for a lean burn internal  
5 combustion engine, and in particular it relates to an exhaust system comprising a  
particulate filter and a NO<sub>x</sub> absorbent.

Generally, the level of acceptable emissions from vehicular internal combustion  
engines is regulated by legislation. Such levels are being tightened in the years to come,  
10 and so the challenge for vehicle manufacturers (original equipment manufacturers or  
OEMs) is how to meet them. Amongst the legislated exhaust gas components are  
particulate matter (PM), nitrogen oxides (NO<sub>x</sub>), carbon monoxide (CO) and hydrocarbons  
(HC). A widely adopted measure to meet legislated levels on PM is the particulate or soot  
filter. Broadly, such filters increase the residence time of PM in an exhaust system to  
15 enable it to be destroyed and can include ceramic wall-flow filters or wire mesh filters.

Typically, a wall-flow filter is in the form of a honeycomb. The honeycomb has an  
inlet end and an outlet end, and a plurality of cells extending from the inlet end to the  
outlet end, the cells having porous walls wherein part of the total number of cells at the  
20 inlet end are plugged, e.g. to a depth of about 5 to 20 mm, along a portion of their lengths,  
and the remaining part of the cells that are open at the inlet end are plugged at the outlet  
end along a portion of their lengths, so that a flowing exhaust gas stream passing through  
the cells of the honeycomb from the inlet end flows into the open cells, through the cell  
walls, and out of the filter through the open cells at the outlet end. A composition for  
25 plugging the cells is described in US patent no. 4,329,162 (incorporated herein by  
reference). A typical arrangement is to have every other cell on a given face plugged, as in  
a chequered pattern.

A problem associated with the use of particulate filters is how to destroy the PM  
30 collected from an exhaust gas throughout a lean burn engine cycle. Generally, diesel PM  
combusts in oxygen (O<sub>2</sub>) at above about 550°C. However, diesel exhaust gas temperatures,  
particularly in light-duty diesel engines, can be as low as 150°C during certain phases of a  
drive cycle due, for example, to the increasingly heavy use of exhaust gas recirculation  
(EGR) to lower NO<sub>x</sub> emissions. If PM is allowed to build up, the back-pressure can

increase thereby increasing the load on the engine. Increased engine load can lead to increased fuel consumption and, in a worst case, engine wear or destruction of the filter caused by uncontrolled combustion of large amounts of PM. Whilst increasing the engine load, e.g. through increased back-pressure due to PM build-up, can also increase the exhaust gas temperature sufficiently to combust the PM, such temperature increase can be insufficient reliably to keep the filter clear.

Light-duty diesel engines are defined in European legislation by European Directive 70/220/EEC, as amended by 93/59/EC and 98/69/EC. In the USA passenger vehicles, light light-duty trucks (LLDT), below 6000 lbs gross vehicle weight rating (GVWR) and heavy light-duty trucks (HLDT), above 6000 lbs are included in the light-duty diesel category. The exhaust gas temperatures emitted from light-duty diesel engines are generally lower than those of heavy-duty diesel engines (as defined by the relevant legislation).

It is known to catalyse particulate filters in order to lower the soot combustion temperature to facilitate regeneration of the filter passively by oxidation of PM under exhaust temperatures experienced during regular operation of the engine/vehicle, typically in the 300-400°C range. In the absence of the catalyst, PM can be oxidized at appreciable rates at temperatures in excess of 500°C, which are rarely seen in diesel engines during real-life operation. Such catalysed filters are often called catalysed soot filters (or CSFs).

A common problem with passive filter regeneration is that driving conditions can prevent exhaust gas temperatures achieving even the lower temperatures facilitated by catalysing the filter frequently enough to reliably prevent PM from building up on the filter. Such driving conditions include extended periods of engine idling or slow urban driving and the problem is particularly acute for exhaust gas from light-duty diesel engines. One solution to this problem which has been adopted by OEMs is to use active techniques to regenerate the filter either at regular intervals or when a predetermined filter backpressure is detected in addition to passive regeneration. A typical arrangement in a light-duty diesel vehicle is to position a diesel oxidation catalyst (DOC) on a separate monolith upstream of the CSF and to regulate in-cylinder fuel combustion by various engine management techniques in order to introduce increased amounts of unburned fuel

into the exhaust gas. The additional fuel is combusted on the DOC, increasing the temperature in the downstream CSF sufficiently to promote combustion of PM thereon.

A significant advance in treating PM was made with our discovery that diesel PM  
5 can be combusted in nitrogen dioxide (NO<sub>2</sub>) at up to 400°C (see our EP-B-0341832  
(incorporated herein by reference)). NO<sub>2</sub> can be obtained by oxidising nitrogen monoxide  
(NO) in the exhaust gas over a suitable oxidation catalyst and reacted with PM on a  
downstream filter. This advance enables the PM to be destroyed within a normal exhaust  
gas temperature window for many diesel engines. We market devices incorporating this  
10 process as CRT<sup>®</sup>. However, whilst the process has been adopted successfully in heavy-  
duty diesel applications, there still remain difficulties with its use in certain lean burn  
internal combustion engines, particularly light-duty diesel engines. The recurring problem  
is low exhaust gas temperature, e.g. thermodynamic limitation on PM combustion in NO<sub>2</sub>  
and the NO to NO<sub>2</sub> equilibrium.

15

The process of absorbing NO<sub>x</sub> from a lean exhaust gas on a NO<sub>x</sub> absorbent such as  
barium to “store” it as the nitrate and release the stored NO<sub>x</sub> and reduce it to dinitrogen  
(N<sub>2</sub>) in exhaust gas containing less oxygen is known, e.g. from EP 0560991 (incorporated  
herein by reference). Typically, when this technology is used in practice, techniques are  
20 employed to assess the remaining capacity of the NO<sub>x</sub> absorbent and for controlling the  
engine to switch transiently and intermittently to running conditions producing exhaust gas  
having a lower O<sub>2</sub> concentration relative to normal lean running conditions (i.e. enriched  
exhaust gas) in order to remove the stored NO<sub>x</sub> as dinitrogen (N<sub>2</sub>), thereby to regenerate  
the NO<sub>x</sub> absorbent.

25

The term “absorbent” used herein embraces both “adsorbent”, i.e. a solid that takes  
up onto its surface another solid, a vapour or a gaseous species in contact therewith, and  
“absorbent”, i.e. a material that can take up and incorporate a solid, a vapour or a gaseous  
species in contact therewith.

30

The term “enriched” used herein means a lower O<sub>2</sub> concentration relative to normal  
lean running conditions and embraces both  $\lambda > 1$  and  $1 > \lambda$  values.

Devices comprising a NO<sub>x</sub> absorbent including catalysts, such as platinum, to promote oxidation of NO to NO<sub>2</sub> in lean exhaust gas conditions and e.g. rhodium to catalyse the reduction of NO<sub>x</sub> released from the NO<sub>x</sub> absorbent to N<sub>2</sub> during periodic rich conditions are known as lean NO<sub>x</sub> traps or simply NO<sub>x</sub> traps.

5

We have now discovered a way of using a NO<sub>x</sub> absorbent to improve the emissions of PM and NO<sub>x</sub> over a drive cycle of a lean burn internal combustion engine, such as a light-duty diesel engine.

10

According to one aspect, the invention provides an exhaust system for a lean burn internal combustion engine, which system comprising a particulate filter, a first NO<sub>x</sub> absorbent disposed upstream of the filter and a second NO<sub>x</sub> absorbent disposed downstream of the filter.

15

By the term "particulate filter", we mean any device that increases the residence time of PM in the device relative to a flow through monolith constructed of like material, wall thickness, open frontal area and cell density comprising an array of straight, parallel channels disposed parallel to the direction of flow of an exhaust gas. Examples of such devices are wall flow filters constructed of cordierite or silicon carbide, metal filters e.g. of wire mesh and devices including channels which present a twisting path to exhaust gases

20

flowing therethrough, e.g. EP 1057519 (incorporated herein by reference).

25

The use of NO<sub>x</sub> absorbents in association with the process of combusting PM in NO<sub>2</sub> is described in EP 0758713 (incorporated herein by reference). However, in that arrangement the single NO<sub>x</sub> absorbent is disposed downstream of the filter.

30

In one embodiment, the first NO<sub>x</sub> absorbent is adapted to release stored NO<sub>x</sub> during lambda > 1 conditions at about 300°C and above. In this embodiment, the first NO<sub>x</sub> absorbent can comprise a material capable of absorbing NO<sub>x</sub> at up to about 300°C in lean exhaust gas conditions. Such materials can include at least one of cerium, lanthanum, alumina (Al<sub>2</sub>O<sub>3</sub>), iron, zinc, calcium, sodium and magnesium and mixtures of any two or more thereof. It is believed that, in lean conditions, the aforesaid elements will be in the form of their oxide compounds, although they may also be present as carbonates and/or hydroxides. These compounds are understood to form nitrates when in contact with the

NO<sub>x</sub>. However, these nitrates are believed to be thermodynamically unstable above about 300°C, even in lean exhaust gas, and may decompose to release NO<sub>x</sub> as NO or NO<sub>2</sub>. At lower oxygen concentrations in the presence of a reducing catalyst such as rhodium, the released NO and NO<sub>2</sub> can be reduced to N<sub>2</sub>.

5

An aspect of the invention is that NO<sub>x</sub> in an exhaust gas can be absorbed by the first NO<sub>x</sub> absorbent when the exhaust gas temperature is low, for example following cold-start or during periods of a drive cycle where the exhaust gas temperature drops, and can be released as NO<sub>2</sub> during lean running conditions for combustion of PM held on the filter downstream when temperatures are more thermodynamically favourable for combustion of the PM, according to the process described in EP 0341832, mentioned above.

10

Generally, NO<sub>x</sub> stored on the first NO<sub>x</sub> absorbent may be desorbed at lower temperatures in a rich exhaust gas composition. In this instance, the NO<sub>x</sub> can be reduced to N<sub>2</sub> if the first NO<sub>x</sub> absorbent comprises a NO<sub>x</sub> reduction catalyst such as rhodium. Rhodium is unlikely, however, to result in the net reduction of NO<sub>x</sub> released during lean running conditions.

15

According to a further embodiment, the second NO<sub>x</sub> absorbent disposed downstream of the filter is capable of storing NO<sub>x</sub> at from about 300°C to about 550°C during lambda > 1 conditions. Suitable materials for the second NO<sub>x</sub> absorbent comprise at least one alkali metal, such as potassium or caesium, at least one alkaline earth metal e.g. strontium or barium, or at least one rare earth metal or a mixture of any two or more thereof.

25

The at least one rare earth metal can be yttrium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium or a mixture of any two or more thereof.

30

An advantage of using the above-mentioned materials in the first NO<sub>x</sub> absorbent is that NO<sub>x</sub> can be treated in the system during periods of low exhaust gas temperature e.g. following cold-start or extended periods of idling or slow driving. NO<sub>x</sub> released from this first NO<sub>x</sub> absorbent can be treated using the second NO<sub>x</sub> absorbent, positioned e.g. underfloor, when it has reached a desired operational temperature.

According to a further embodiment, at least one of the first and second NO<sub>x</sub> absorbent includes at least one platinum group metal (PGM). Such at least one PGM can be platinum, palladium or rhodium, for example. Whilst both the first and second NO<sub>x</sub> absorbents can include platinum and rhodium, or palladium, in one embodiment, the first NO<sub>x</sub> absorbent includes platinum as the sole PGM. This is for at least two reasons. Firstly, in the embodiment where the first NO<sub>x</sub> absorbent is designed to release stored NO<sub>x</sub> at temperatures of about 300°C and above in lean exhaust gas, the presence of rhodium for the purpose of reducing released NO<sub>x</sub> to N<sub>2</sub> in enriched exhaust gas is unnecessary.

10

Secondly, if enriched engine-derived exhaust gas is intended to regenerate the second NO<sub>x</sub> absorbent, the presence of rhodium on the first NO<sub>x</sub> absorbent could undesirably remove some HC upstream of the second NO<sub>x</sub> absorbent.

15

In a further embodiment, the filter in the exhaust system is catalysed. The catalyst can comprise at least one PGM, which PGM can be supported directly by the material forming the filter or supported on a high surface area particulate refractory oxide and coated on the filter substrate. Methods of making the directly supported substrate are known and include soaking the filter material, e.g. cordierite, in an aqueous solution of the PGM, then drying and firing the resulting piece.

20

If the PGM is supported on a particulate refractory oxide, it can be fixed to the refractory oxide by calcination before coating on the substrate or a washcoat of the refractory oxide can be coated on the substrate and subsequently impregnated with an aqueous PGM solution using known techniques. However, it is important that the size of the particulate support is chosen so that the refractory oxide does not block the pores of the filter substrate so that the back-pressure of the filter is significantly increased, relative to an uncoated filter, or the filtration efficiency may be impaired. We have found that, in general, pores of up to 25 µm, e.g. 15-25 µm, are useful for filtering diesel PM, and so we prefer that the particulate refractory oxide should be smaller than this size. This means that washcoat particles can sit within the pores without totally blocking them.

25

30

Alternatively, or in addition, the catalyst can comprise a soot combustion catalyst comprising a molten salt selected from the group consisting of an alkali metal salt of

vanadium, tungsten or molybdenum, an alkaline earth metal salt of vanadium, tungsten or molybdenum or a lanthanum salt of vanadium, tungsten or molybdenum, vanadium pentoxide, silver vanadate and copper vanadate. Suitable alkali metals include one or both of potassium or caesium. Alkaline-earth metals can be selected from magnesium, calcium, strontium, barium and any two or more thereof.

A further aspect of the invention is to use the components of the exhaust system of the present invention to manage heat in the system more efficiently, and thereby to improve conversion of target exhaust gas components. As mentioned above, a problem for treating exhaust gases from lean burn internal combustion engines, particularly light-duty diesel engines, is that the exhaust gas temperature can be undesirably low during certain phases of a drive cycle. This can make it difficult catalytically to treat exhaust gases in order to meet legislated limits. By more effectively managing the retention, or generation of heat within the system, such problems can be reduced or avoided.

15

Whereas the invention is capable of increasing the extent of PM combustion by  $\text{NO}_2$  at moderate temperatures, it is envisaged that the PM may contain fractions readily combustible with  $\text{O}_2$ . Operation of the invention may include combustion of PM on the filter in  $\text{O}_2$  at higher temperatures (relative to combustion in  $\text{NO}_2$ ) in lean conditions, whereas the  $\text{NO}_x$  trap regeneration typically requires higher temperatures and/or enriched conditions to remove  $\text{NO}_x$  and even higher temperatures and preferably rich conditions to remove sulfur oxides ( $\text{SO}_x$ ).

20

In order to promote lean combustion of PM at higher temperatures on the filter, a catalyst in the first  $\text{NO}_x$  absorbent can be used to combust HC in the exhaust gas, either post-injected HC or engine-derived HC from modulation of the engine air-to-fuel ratio, thereby to increase the temperature of the filter.  $\text{O}_2$  to combust HC and/or CO to generate the exotherm can be provided by injection of secondary air or lean exhaust gas (e.g. from a parallel exhaust line) between the first  $\text{NO}_x$  absorbent and the filter. Alternatively, or in addition, an oxygen storage component (OSC), e.g. ceria or a ceria-zirconia mixed oxide, can be disposed downstream of the first  $\text{NO}_x$ -absorbent, optionally downstream of any HC injector, or between the first  $\text{NO}_x$  absorbent and the particulate filter. The first  $\text{NO}_x$  absorbent may also be regenerated in part or in full by action of the HC for generating the exotherm. An additional exotherm can be generated on the filter catalyst, where present.

25  
30



The generation of an exotherm, and increased temperatures, in the filter can result in an increase in the temperature of the second NO<sub>x</sub> absorbent, yet typically the exhaust gas contacting the second NO<sub>x</sub> absorbent will be lean. Accordingly, means can be provided for  
5 introducing HC between the filter and the second NO<sub>x</sub> absorbent for changing the exhaust gas composition to enrich the exhaust gas to release NO<sub>x</sub> and/or SO<sub>x</sub>, as desired. Of course, in certain embodiments, e.g. where the filter is uncatalysed, the system can be arranged so that sufficient HC is allowed to slip the filter to regenerate the second NO<sub>x</sub> absorbent so that the provision of an injector for HC between the filter and the second NO<sub>x</sub>  
10 absorbent can be avoided, or the amount of HC required to be injected can be reduced. Additional O<sub>2</sub> to combust HC to generate an exotherm over the second NO<sub>x</sub> absorbent can also be provided (whilst maintaining a rich exhaust gas composition) if desired by injection of secondary air or lean exhaust gas between the filter and the second NO<sub>x</sub> absorbent or by providing an OSC downstream of the point of HC injection.

15

Control of the enrichment of the exhaust gas with a reductant, e.g. a hydrocarbon, such as the fuel that powers the engine, and introduction of secondary air or a lean exhaust gas can be controlled, in use, by an engine control unit (ECU) including, for example, a suitably programmed processor or computer 'chip'.

20

In a further embodiment, the system includes an oxidation catalyst for oxidising NO in an exhaust gas to NO<sub>2</sub>, which catalyst can be disposed between the first NO<sub>x</sub> absorbent and the filter. This embodiment adopts an arrangement described in EP 341832, mentioned above. An advantage of this arrangement, and/or the embodiment where the  
25 filter is catalysed, is that HC slip is minimised during NO<sub>x</sub> absorbent regeneration of the first NO<sub>x</sub> absorbent. According to another embodiment, the oxidation catalyst can be disposed between the exhaust manifold and the first NO<sub>x</sub> absorbent, preferably upstream of any HC injector.

30

In a particular embodiment, the oxidation catalyst and the OSC are combined. In one such arrangement, the catalyst comprises ceria, e.g. a ceria-zirconia mixed oxide, optionally comprising at least one PGM supported thereon.

The or each NO<sub>x</sub> absorbent and any filter catalyst or NO oxidation catalyst for use in the invention can comprise a support comprising alumina, silica, silica-alumina, zirconia, titania, ceria, ceria-zirconia or a mixture of any two or more thereof or a mixed oxide or composite oxide of any two or more thereof.

5

By "composite oxide" herein, we mean a largely amorphous oxide material comprising oxides of at least two elements which are not true mixed oxides consisting of at least two metals.

10

The support can be stabilised with at least one rare earth metal, as is known in the art. The at least one rare earth metal can be lanthanum, yttrium, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium or mixtures of any two or more thereof.

15

According to a further aspect, the invention provides a lean burn internal combustion engine including an exhaust system according to the invention. In one embodiment, the engine is a diesel engine, preferably a light-duty diesel engine.

20

According to a further aspect, the invention provides a method of controlling NO<sub>x</sub> in the exhaust system of a lean burn internal combustion engine, which method comprising collecting PM from an exhaust gas downstream of a first NO<sub>x</sub> absorbent, absorbing NO<sub>x</sub> in the first NO<sub>x</sub> absorbent when the first NO<sub>x</sub> absorbent is at up to 300°C in temperature, desorbing absorbed NO<sub>x</sub> when the first NO<sub>x</sub> absorbent is at above 300°C to add to pre-existing NO<sub>x</sub> in the exhaust gas, combusting the collected soot in NO<sub>2</sub> in the exhaust gas and absorbing NO<sub>x</sub> derived from the combustion of soot in the NO<sub>2</sub>.

25

In order that the invention may be more fully understood, an illustrative embodiment and an Example are provided by way of illustration only and with reference to the accompanying drawings, in which:

30

Figure 1 is a schematic diagram of the exhaust system according to the invention;

Figure 2 is a schematic diagram explaining the operation of the exhaust system when cold, e.g. following cold start or during periods of a drive cycle generating cooler exhaust gases;

5 Figure 3 is a schematic diagram explaining the operation of the exhaust system at temperatures of 300°C and above;

Figure 4 is a schematic diagram explaining the operation of the exhaust system in regenerating the first NO<sub>x</sub> absorbent;

10

Figure 5 is a schematic diagram explaining the operation of the exhaust system in regenerating the catalysed soot filter and the second NO<sub>x</sub> absorbent;

15 Figure 6 is a trace of gas concentration against time showing speciation of NO<sub>x</sub> downstream of NO<sub>x</sub> trap (1);

Figure 7 is a trace of exhaust gas temperature against time showing reductant combustion with residual oxygen during a rich pulse causes an exotherm over NO<sub>x</sub> trap (1);

20

Figure 8 is a trace of exhaust gas lambda value taken upstream and downstream of NO<sub>x</sub> trap (1) with air-injection downstream of NO<sub>x</sub> trap (1);

25 Figure 9 is a trace of exhaust gas temperature taken upstream and downstream of a catalysed soot filter following air-injection between NO<sub>x</sub> trap (1) and the filter;

Figure 10 is a trace of exhaust gas temperature against time showing lean exotherm generation over NO<sub>x</sub> trap (1); and

30

Figure 11 is a trace of NO<sub>x</sub> concentration against time showing how NO<sub>x</sub> trap (2) stores NO<sub>x</sub> that slips from NO<sub>x</sub> trap (1) in both normal lean mode and during a rich pulse where air is injected in between the CSF and NO<sub>x</sub> trap (1).

We believe that the annotations to Figures 1-5 inclusive are self-explanatory. "NO<sub>x</sub> (1)" in the Figures is the first NO<sub>x</sub> absorbent; "NO<sub>x</sub> (2)" is the second NO<sub>x</sub> absorbent; and "CSF" is an acronym for catalysed soot filter.

5

#### EXAMPLE

A light-duty Diesel engine with a rich in-cylinder calibration was fitted with an exhaust system comprising the arrangement shown in Figure 1, except in that engine management was used to provide engine-derived hydrocarbon enrichment of the exhaust gas, i.e. no fuel was injected downstream of the exhaust manifold, and an air injector was disposed between the NO<sub>x</sub> trap (1) and a catalysed soot filter. The catalysed soot filter was a cordierite wall-flow filter catalysed with a washcoat comprising platinum supported on both an alumina-based particulate refractory oxide and by the filter material itself. The filter was prepared by coating the uncoated filter with a washcoat comprising the refractory oxide, drying and calcining the resulting piece and then impregnating the washcoated filter using an aqueous solution of a platinum salt to a loading of 100 gft<sup>-3</sup>.

NO<sub>x</sub> trap (1) was a low temperature trap comprising a ceramic flow-through monolith substrate coated with a washcoat comprising an alumina-based particulate refractory oxide and an OSC supporting platinum, barium, cerium and rhodium. The high temperature NO<sub>x</sub> trap (2) had a similar construction except in that the formulation included caesium.

Running at an exhaust temperature of 350°C, Figure 6 shows speciation of NO<sub>x</sub> slip after NO<sub>x</sub> trap (1). NO<sub>2</sub> concentration upstream of the NO<sub>x</sub> trap is 14 ppm (6% of total NO<sub>x</sub>). It can be seen that a high proportion of the NO<sub>x</sub> is NO<sub>2</sub> (up to 30% of total NO<sub>x</sub> slip), which is available therefore to react with soot in the downstream CSF according to the process disclosed in EP 0341832.

30

The system was configured to cycle between lean and rich running conditions at an engine-out exhaust temperature of 450°C. Lean periods were adjusted to 300s long, each rich period was 8s long. It can be seen from Figure 7 that introducing a rich pulse over NO<sub>x</sub> trap (1) by reducing the oxygen concentration in the exhaust gas upstream of NO<sub>x</sub> trap (1) results in a temperature increase of the exhaust gas as reductant is combusted in the

remaining oxygen. This extra heat can be used to regenerate NO<sub>x</sub> trap (1) for NO<sub>x</sub> or SO<sub>x</sub> under the rich condition.

Introducing air after NO<sub>x</sub> trap (1) during a rich pulse results in constant lean  
5 conditions in the downstream CSF as can be seen in Figure 8. The results of Figures 7 and  
8 show that the exhaust lambda is rich before NO<sub>x</sub> trap (1), allowing NO<sub>x</sub> trap regeneration  
(see Figure 7) and air injection post NO<sub>x</sub> trap (1) can provide constant lean conditions in  
the CSF downstream of NO<sub>x</sub> trap (1). The elevated temperatures from reductant  
10 combustion over NO<sub>x</sub> trap (1) (Figure 7) can be high enough to allow soot regeneration of  
the CSF to occur in the lean conditions. Alternatively, excess reductant can slip through  
NO<sub>x</sub> trap (1) and be combusted over the CSF under the lean conditions resulting from  
air/lean exhaust injection, again resulting in high CSF temperatures which can allow soot  
regeneration to occur, see Figure 9 which shows an increase in CSF temperature due to  
15 rich pulse reductant combustion in lean conditions caused by air injection after NO<sub>x</sub> trap  
(1) but before CSF.

Extra fuel was introduced into the exhaust gas upstream of NO<sub>x</sub> trap (1), but only  
enough to maintain a lean composition overall. This creates an exotherm that can be used  
to regenerate the soot in the CSF (see Figure 10). NO<sub>x</sub> can also be thermally released from  
20 NO<sub>x</sub> trap (1) in the same way, resulting in an increased in NO<sub>2</sub> concentration upstream of  
the CSF, which is available for reaction with soot on the CSF according to the process  
described in EP 0341832.

NO<sub>x</sub> trap (2) can store NO<sub>x</sub> that slips from NO<sub>x</sub> trap (1) and the CSF (see Figure  
25 11) in both the lean and (when air injection is present in between NO<sub>x</sub> trap (1) and the  
CSF) during the rich pulse. Regeneration of NO<sub>x</sub> trap (2) could be readily accomplished  
with fuel injection in between the CSF and NO<sub>x</sub> trap (2) as per normal NO<sub>x</sub> trap operation  
(see EP 0758713).

**CLAIMS:**

1. An exhaust system for a lean burn internal combustion engine, which system comprising a particulate filter, a first NO<sub>x</sub> absorbent disposed upstream of the filter and a second NO<sub>x</sub> absorbent disposed downstream of the filter.  
5
2. A system according to claim 1, wherein the first NO<sub>x</sub> absorbent is adapted to release stored NO<sub>x</sub> during lambda > 1 conditions at about 300°C and above.
- 10 3. A system according to claim 2, wherein the first NO<sub>x</sub> absorbent comprises at least one of cerium, lanthanum, alumina (Al<sub>2</sub>O<sub>3</sub>), iron, zinc, calcium, sodium, magnesium and mixtures of any two or more thereof.
4. A system according to claim 1, 2 or 3, wherein the second NO<sub>x</sub> absorbent is capable of storing NO<sub>x</sub> at from about 300°C to about 550°C during lambda > 1 conditions.  
15
5. A system according to claim 4, wherein the second NO<sub>x</sub> absorbent comprises at least one alkali metal, at least one alkaline earth metal or at least one rare earth metal or a mixture of any two or more thereof.  
20
6. A system according to claim 5, wherein the at least one alkali metal is potassium or caesium or a mixture thereof.
7. A system according to claim 5 or 6, wherein the at least one alkaline earth metal is strontium or barium or a mixture thereof.  
25
8. A system according to claim 5, 6 or 7, wherein the at least one rare earth metal is yttrium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium or a mixture of any two or more thereof.  
30
9. A system according to any preceding claim, wherein the first and/or the second NO<sub>x</sub> absorbent comprises at least one platinum group metal (PGM).

10. A system according to claim 9, wherein the at least one PGM of the first NO<sub>x</sub> absorbent consists of platinum.
- 5 11. A system according to claim 9, wherein the at least one PGM comprises platinum and rhodium.
12. A system according to any preceding claim, wherein the filter is catalysed.
- 10 13. A system according to claim 12, wherein the filter catalyst comprises at least one PGM.
14. A system according to claim 13, wherein the at least one PGM is supported by the material forming the filter.
- 15 15. An engine according to claim 12, 13 or 14, wherein the at least one additional catalyst comprises a soot combustion catalyst comprising a molten salt selected from the group consisting of an alkali metal salt of vanadium, tungsten or molybdenum, an alkaline earth metal salt of vanadium, tungsten or molybdenum or a lanthanum salt of vanadium, tungsten or molybdenum, vanadium pentoxide, silver vanadate and  
20 copper vanadate.
16. A system according to any preceding claim, comprising an oxidation catalyst for oxidising NO in an exhaust gas to NO<sub>2</sub>, which catalyst is disposed between the first NO<sub>x</sub> absorbent and the filter and/or between the exhaust manifold and the first NO<sub>x</sub>  
25 absorbent.
17. A system according to claim 16, wherein the NO oxidation catalyst comprises at least one PGM.
- 30 18. A system according to any preceding claim, comprising an oxygen storage component (OSC) disposed between the first NO<sub>x</sub> absorbent and the filter and/or between the filter and the second NO<sub>x</sub> absorbent.

19. A system according to claim 18, wherein the OSC comprises ceria, optionally a ceria-zirconia mixed oxide.
- 5 20. A system according to any preceding claim, wherein each NO<sub>x</sub> absorbent and, where present, the filter catalyst and/or the NO oxidation catalyst comprises a support of alumina, silica, silica-alumina, zirconia, titania, ceria, ceria-zirconia or a mixture of any two or more thereof or a mixed oxide or composite oxide of any two or more thereof.
- 10 21. A system according to claim 20, wherein the oxidation catalyst comprises platinum supported on alumina.
22. A system according to claim 20 or 21, wherein the support is stabilised with at least one rare earth metal.
- 15 23. A system according to claim 22, wherein the at least one rare earth metal is lanthanum, yttrium, cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium or a mixture of any two or more thereof.
- 20 24. A system according to any preceding claim, comprising first means for enriching an exhaust gas with a reductant upstream of the first NO<sub>x</sub> absorbent.
- 25 25. A system according to claim 24, wherein the first enriching means comprises a first port for injecting the reductant which first port is disposed between the exhaust manifold and the first NO<sub>x</sub> absorbent.
- 30 26. A system according to claim 24 or 25, comprising second means for enriching an exhaust gas with a reductant between the first NO<sub>x</sub> absorbent and the filter, which second enriching means comprising a second port for injecting the reductant which second port is disposed between the first NO<sub>x</sub> absorbent and the filter.



27. A system according to claim 24, 25 or 26, comprising first means for introducing secondary air or a lean exhaust gas into exhaust gas between the first NO<sub>x</sub> absorbent and the filter.
- 5 28. A system according to any of claims 24 to 27, comprising third means for enriching an exhaust gas with a reductant between the filter and the second NO<sub>x</sub> absorbent, which third enriching means comprising a third port for injecting the reductant which third port is disposed between the filter and the second NO<sub>x</sub> absorbent.
- 10 29. A system according to any of claims 24 to 28, comprising second means for introducing secondary air or a lean exhaust gas into exhaust gas between the filter and the second NO<sub>x</sub> absorbent.
- 15 30. A system according to any of claims 24 to 29, comprising means, in use, for controlling the enrichment of an exhaust gas with a reductant between the exhaust manifold and the first NO<sub>x</sub> absorbent.
- 20 31. A system according to any of claims 26 to 30, comprising means, in use, for controlling the enrichment of an exhaust gas with a reductant between the first NO<sub>x</sub> absorbent and the filter.
- 25 32. A system according to any of claims 28 to 31, comprising means, in use, for controlling the enrichment of an exhaust gas with a reductant between the filter and the second NO<sub>x</sub> absorbent.
- 30 33. A system according to claim 27 and any of claims 28 to 32 when appendant to claim 26, comprising means, in use, for controlling the introduction of secondary air or a lean exhaust gas into an exhaust gas between the first NO<sub>x</sub> absorbent and the filter.
34. A system according to claim 29 and any of claims 30 to 33 when appendant to claim 29, comprising means, in use, for controlling the introduction of secondary air or a lean exhaust gas into an exhaust gas between the first NO<sub>x</sub> absorbent and the filter.

35. A system according to any of claims 30 to 34, wherein the control means comprises an engine control unit (ECU).
36. A system according to any of claims 24 to 35, wherein the reductant is a hydrocarbon, optionally the hydrocarbon that fuels the engine.
37. A lean burn internal combustion engine including an exhaust system according to any preceding claim.
38. An engine according to claim 37, wherein it is a diesel engine, preferably a light-duty diesel engine.
39. A method of controlling nitrogen oxides ( $\text{NO}_x$ ) and particulate matter (PM) in the exhaust system of a lean burn internal combustion engine, which method comprising collecting PM from an exhaust gas downstream of a first  $\text{NO}_x$  absorbent, absorbing  $\text{NO}_x$  in the first  $\text{NO}_x$  absorbent when the first  $\text{NO}_x$  absorbent is at up to  $300^\circ\text{C}$  in temperature, desorbing absorbed  $\text{NO}_x$  when the first  $\text{NO}_x$  absorbent is at above  $300^\circ\text{C}$  to add to pre-existing  $\text{NO}_x$  in the exhaust gas, combusting the collected soot in  $\text{NO}_2$  in the exhaust gas and absorbing  $\text{NO}_x$  derived from the combustion of soot in the  $\text{NO}_2$ .

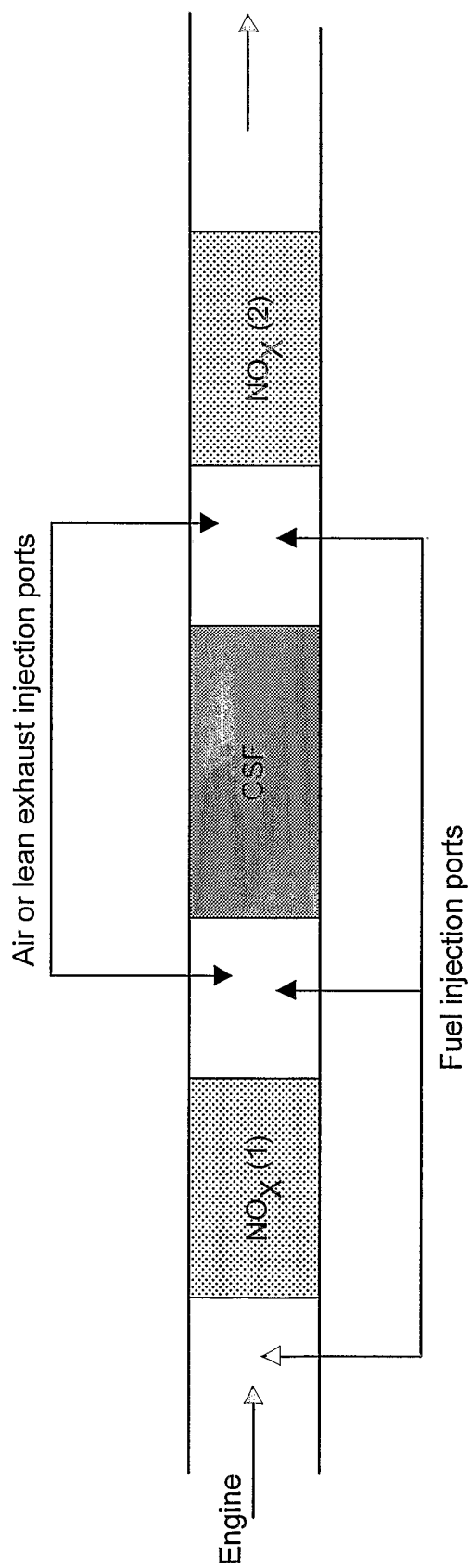
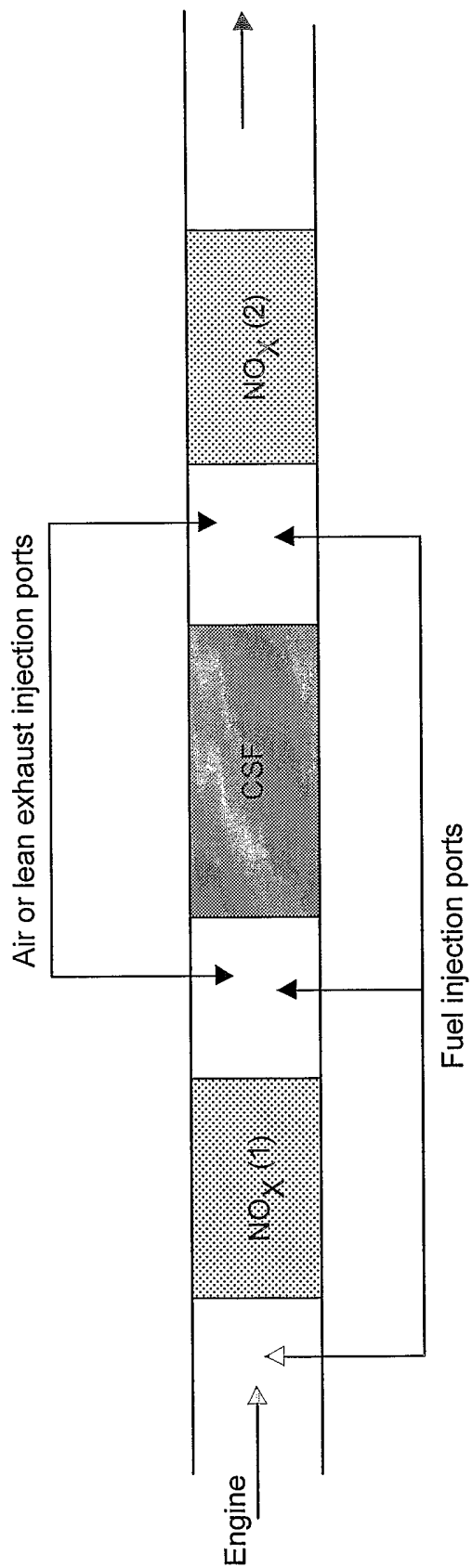
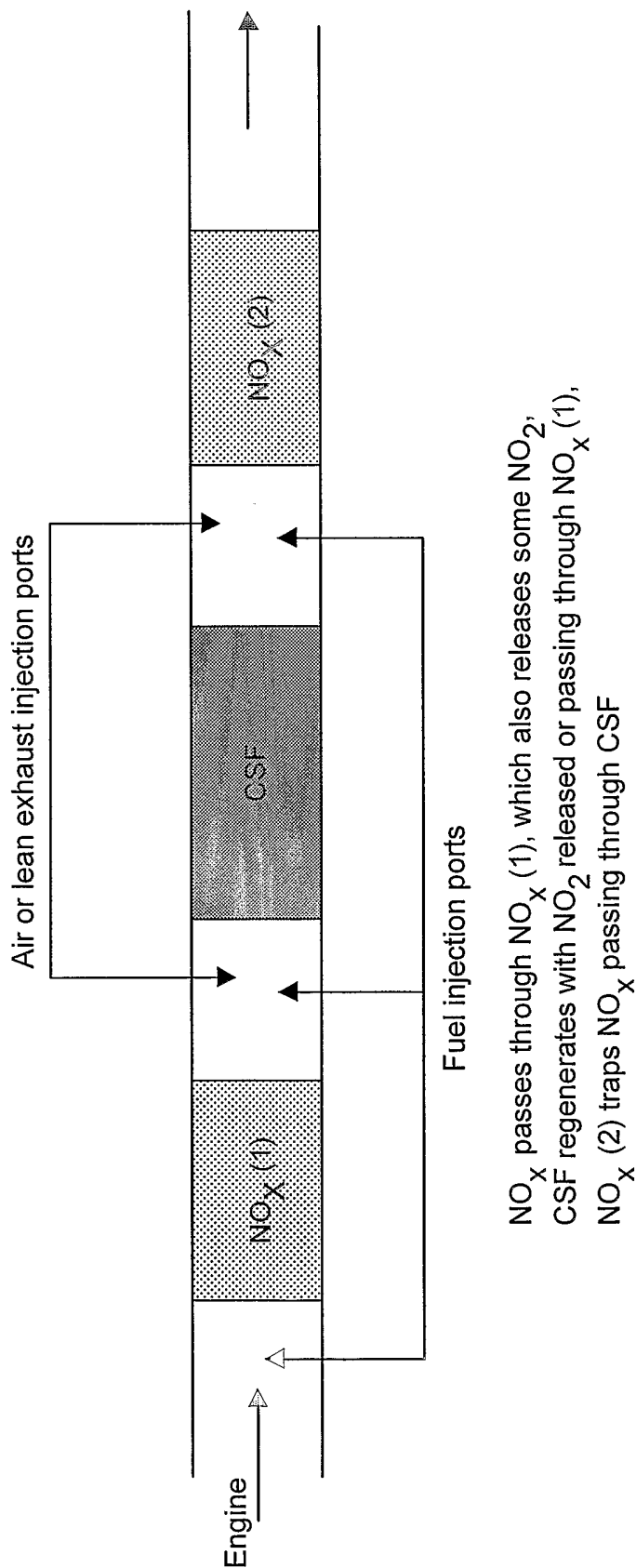


FIG. 1



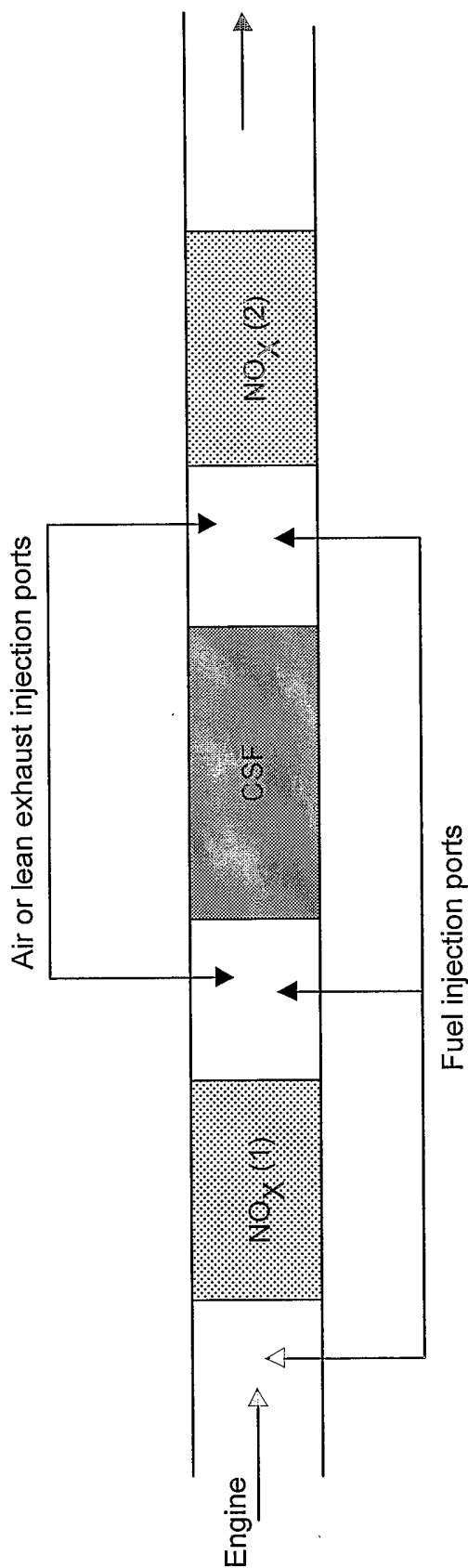
$NO_x$  is stored over  $NO_x(1)$ , particulates trapped over CSF

FIG. 2



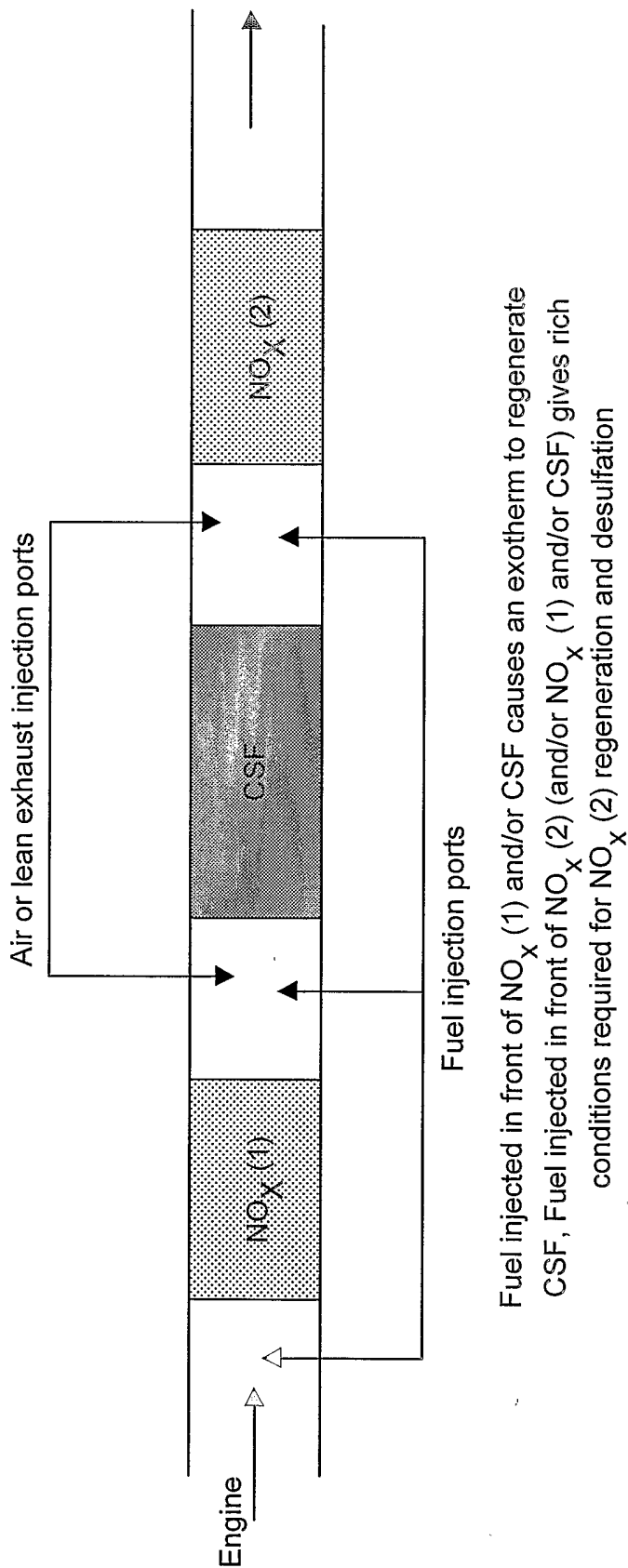
NO<sub>x</sub> passes through NO<sub>x</sub> (1), which also releases some NO<sub>2</sub>,  
CSF regenerates with NO<sub>2</sub> released or passing through NO<sub>x</sub> (1),  
NO<sub>x</sub> (2) traps NO<sub>x</sub> passing through CSF

FIG. 3



Fuel injected in front of  $\text{NO}_x$  (1) causes an exotherm and rich conditions to regenerate or desulphate  $\text{NO}_x$  (1). Air or lean exhaust injected in front of CSF gives lean conditions and creates a greater exotherm as unburned CO, HC are oxidised.

FIG. 4



Fuel injected in front of NO<sub>x</sub> (1) and/or CSF causes an exotherm to regenerate CSF, Fuel injected in front of NO<sub>x</sub> (2) (and/or NO<sub>x</sub> (1) and/or CSF) gives rich conditions required for NO<sub>x</sub> (2) regeneration and desulfation

FIG. 5

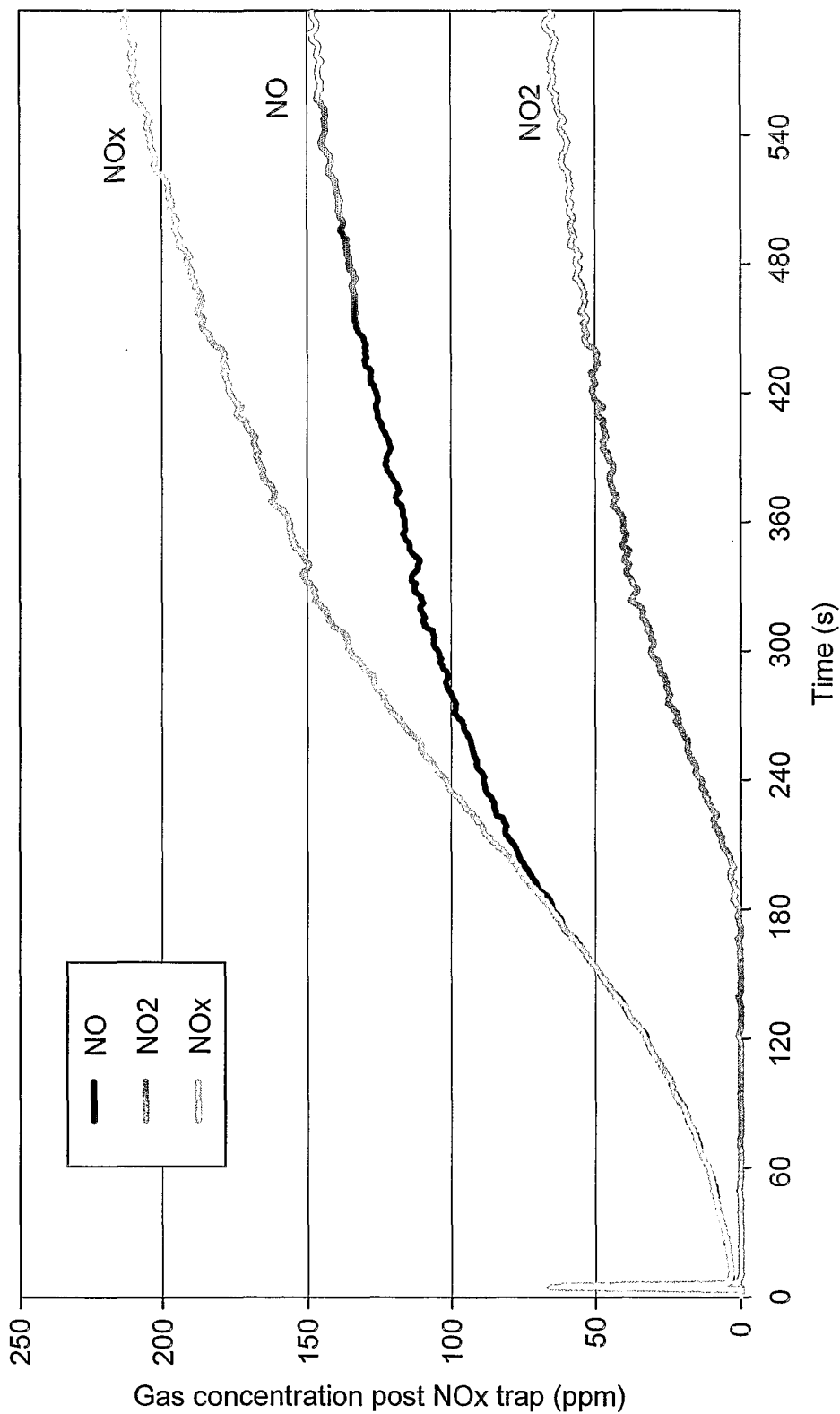


FIG. 6



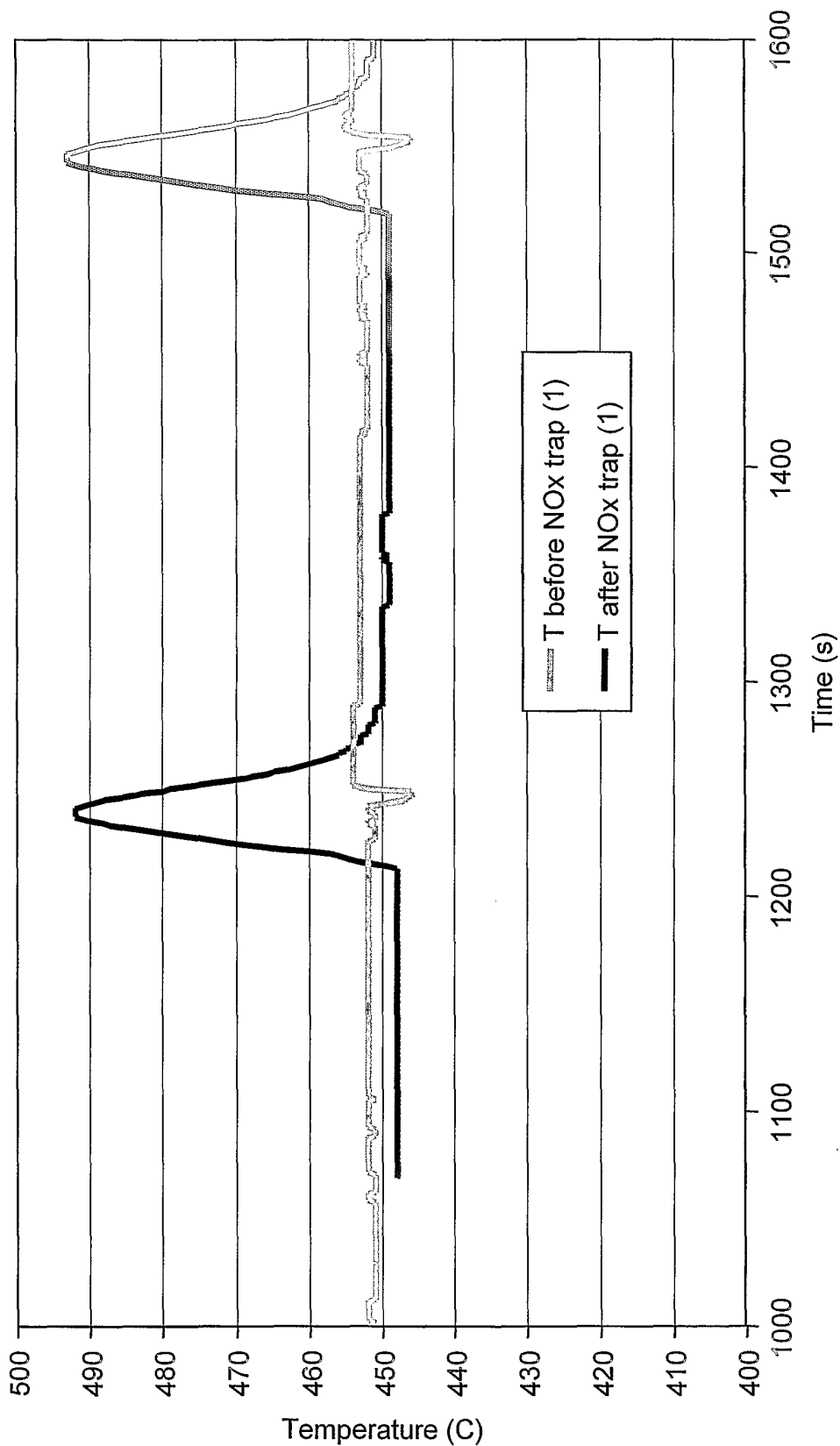


FIG. 7

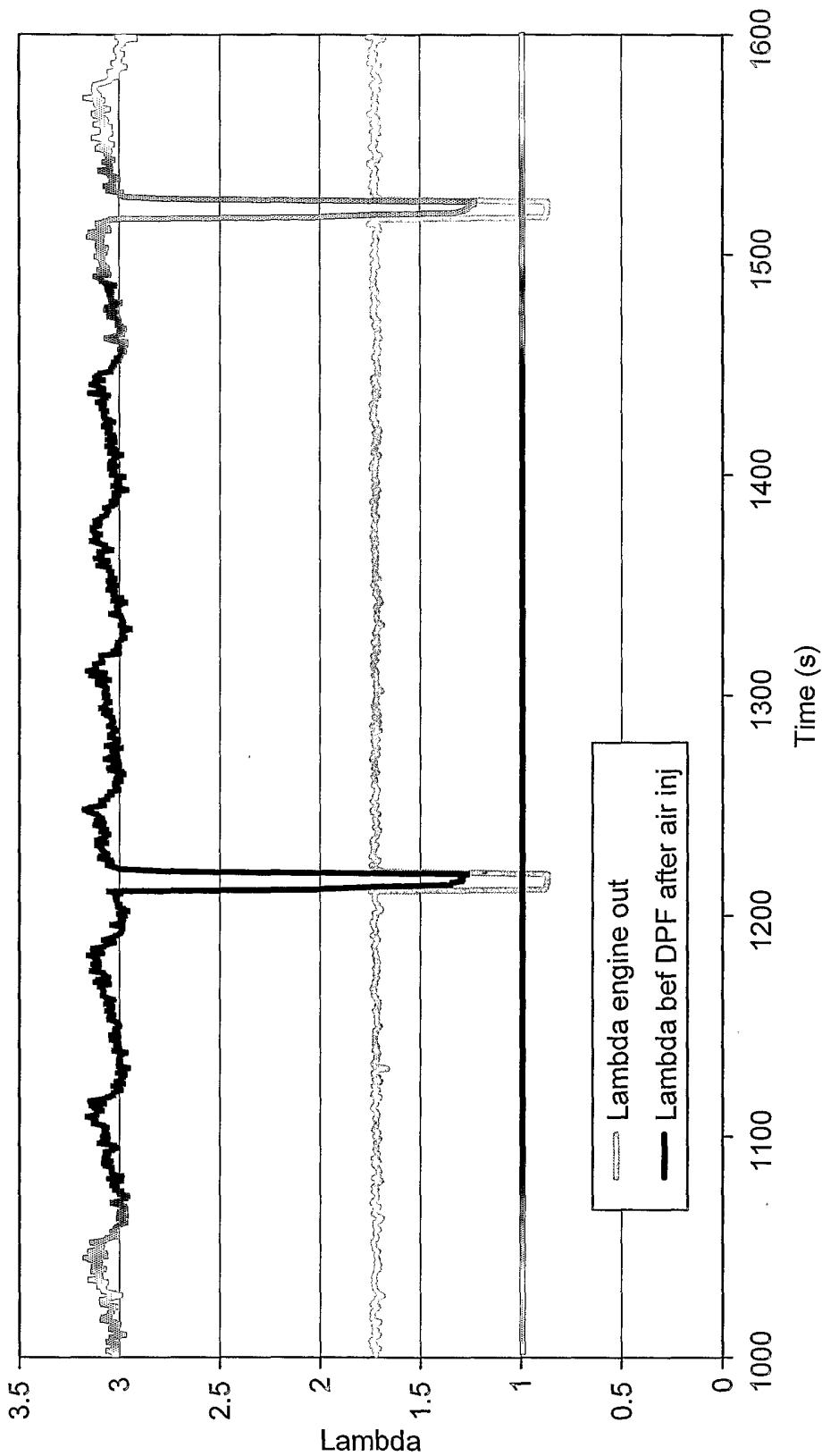


FIG. 8

9 / 11

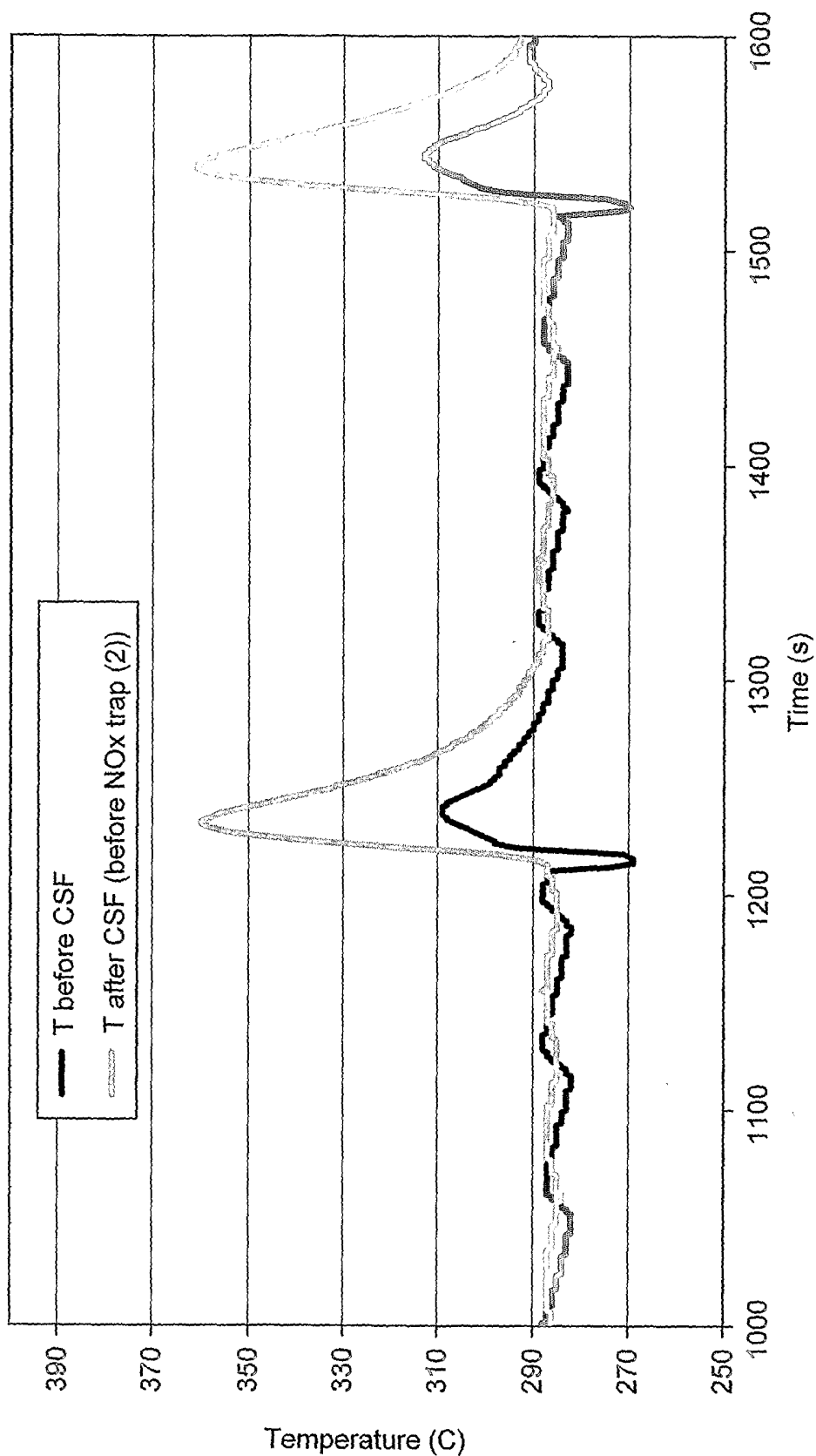


FIG. 9

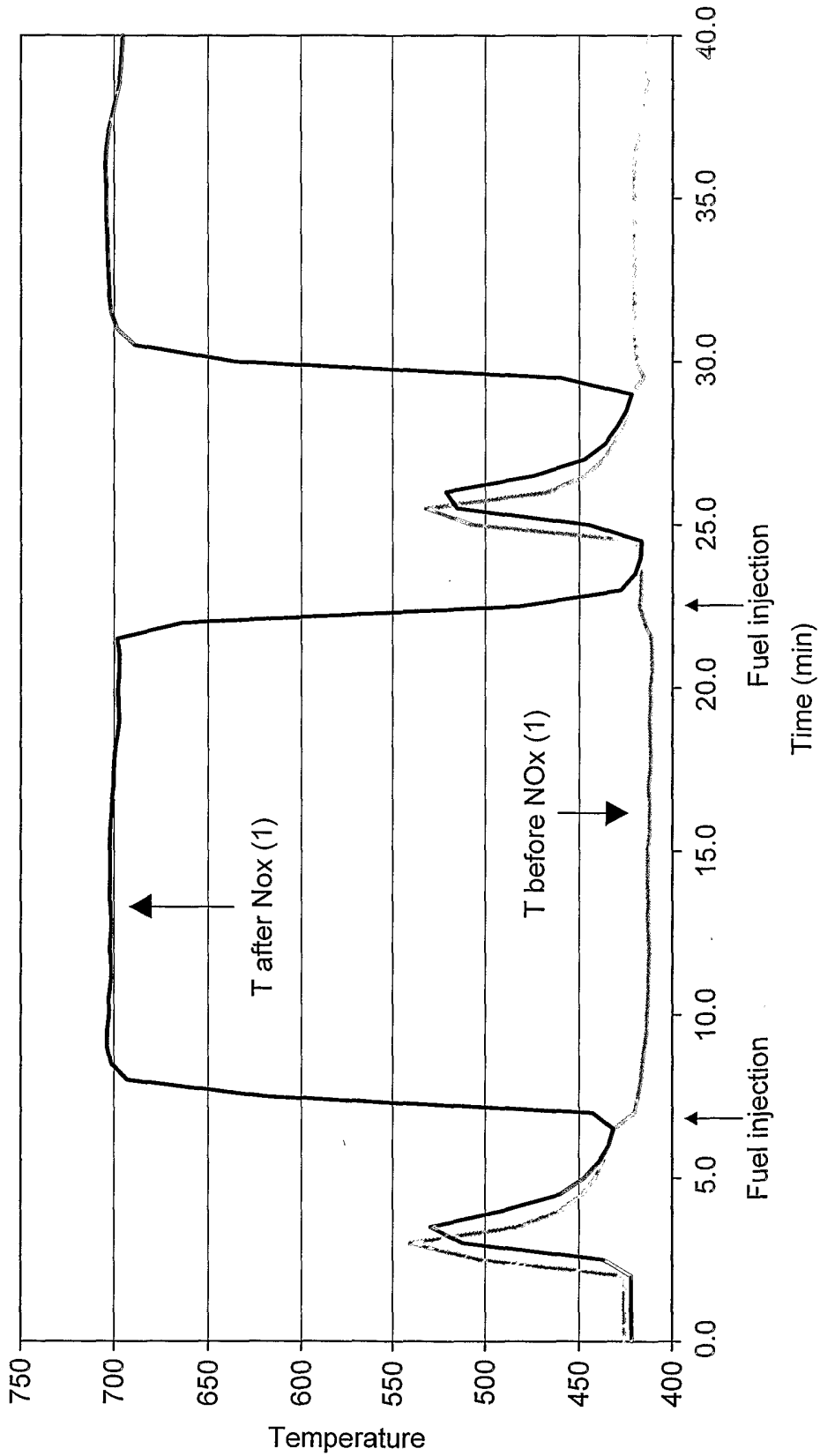


FIG. 10

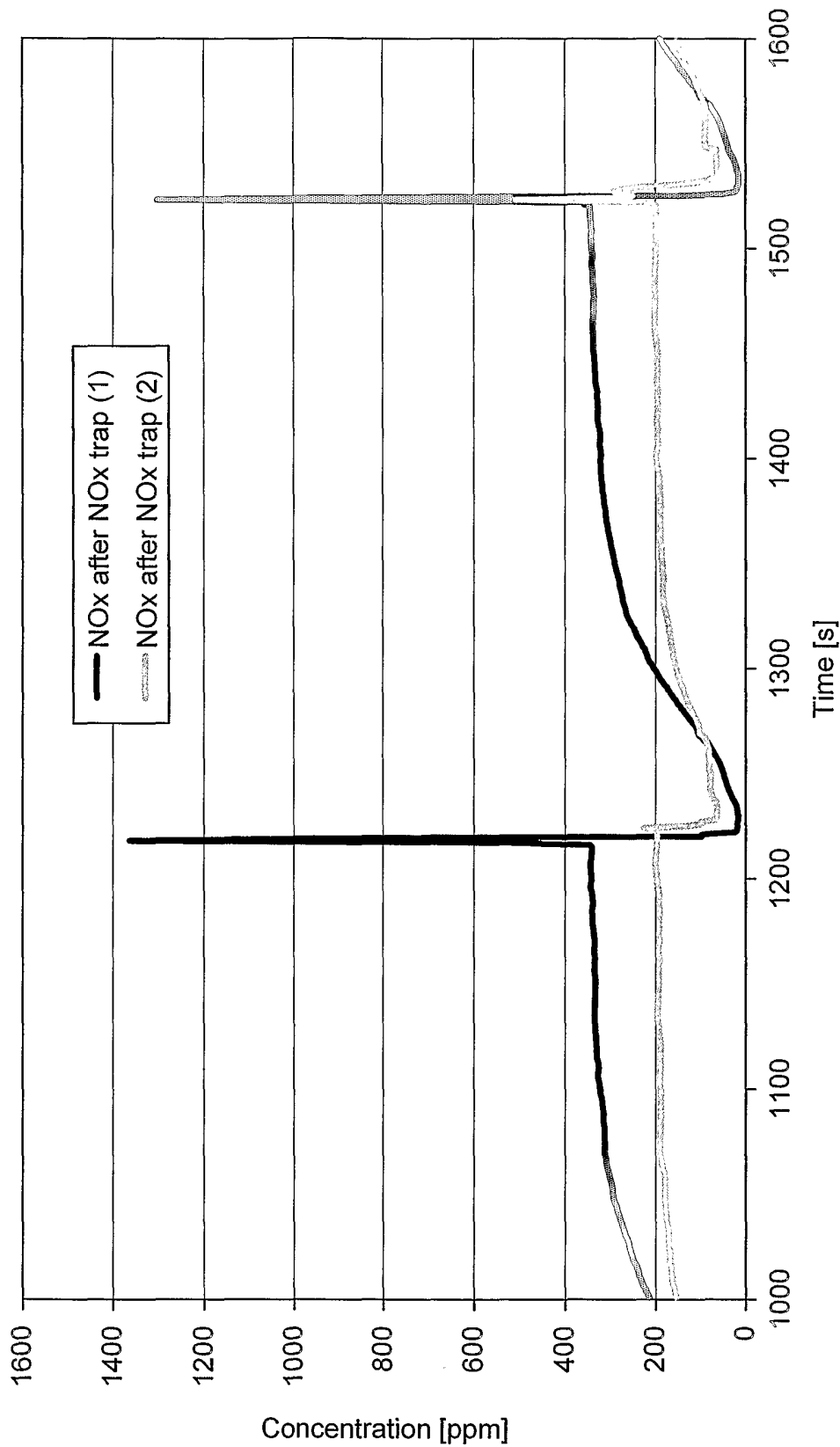


FIG. 11

# INTERNATIONAL SEARCH REPORT

International Application No.  
PCT/GB2004/000994

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 F01N3/08 F01N3/023 F01N3/20 F01N3/025 F01N3/035

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)  
 IPC 7 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 practical, search terms used)  
 EPO-Internal

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	column 2, line 66 - column 3, line 7; figure 3	9, 18, 24, 25, 30, 32, 36
Y	EP 1 217 196 A (ISUZU MOTORS LTD) 26 June 2002 (2002-06-26)	9
Y	column 5, line 51 - line 58; figure 3	
Y	US 2002/081238 A1 (SCHOMMERS JOACHIM ET AL) 27 June 2002 (2002-06-27)	18
Y	page 2, paragraph. 22; figure 4	
Y	WO 00/21647 A (JOHNSON MATTHEY PLC ; TWIGG MARTYN VINCENT (GB)) 20 April 2000 (2000-04-20)	24, 25, 30, 32, 36
	page 7, line 29 - page 8, line 17; figure	
	-/--	

Further documents are listed in the continuation of box C.       Patent family members are listed in annex.

° Special categories of cited documents :

<p>*A* document defining the general state of the art which is not considered to be of particular relevance</p> <p>*E* earlier document but published on or after the international filing date</p> <p>*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)</p> <p>*O* document referring to an oral disclosure, use, exhibition or other means</p> <p>*P* document published prior to the international filing date but later than the priority date claimed</p>	<p>*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</p> <p>*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</p> <p>*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.</p> <p>*&amp;* document member of the same patent family</p>
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Date of the actual completion of the international search	Date of mailing of the international search report
7 May 2004	02/06/2004

Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer  Torle, E
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INTERNATIONAL SEARCH REPORT

In          onal Application No  
PCT/GB2004/000994

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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P,X	EP 1 304 455 A (OPEL ADAM AG) 23 April 2003 (2003-04-23) column 6, line 24 - line 54; figure 1  -----	1,12-14, 20,37,38

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