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(19) **United States**(12) **Patent Application Publication**
Xu et al.(10) **Pub. No.: US 2006/0168948 A1**(43) **Pub. Date: Aug. 3, 2006**(54) **ALUMINA-BASED LEAN NO_x TRAP
SYSTEM AND METHOD OF USE****Publication Classification**(76) Inventors: **Lifeng Xu**, Farmington Hills, MI (US);
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(57)

ABSTRACT

An alumina-based lean NO_x trap system for use in a lean burn engine such as a diesel engine is provided which includes at least one alumina-based lean NO_x trap comprising a catalyst, an alumina NO_x absorbent material, and optionally, from 0 to about 4 wt % of an alkaline earth metal oxide. The system preferably includes at least a first alumina-based lean NO_x trap, and a second lean NO_x trap which is positioned downstream from the first lean NO_x trap in an engine exhaust. The second lean NO_x trap may comprise an alumina-based trap or a conventional lean NO_x trap. The lean NO_x trap system converts at least a portion of NO_x contained in the exhaust gas to N₂ at a temperature between about 150° C. to about 500° C. The alumina-based lean NO_x trap system also undergoes efficient desulphurization and maintains its activity with extended use.

(21) Appl. No.: **11/298,805**(22) Filed: **Dec. 9, 2005****Related U.S. Application Data**

(60) Provisional application No. 60/649,331, filed on Feb. 2, 2005.

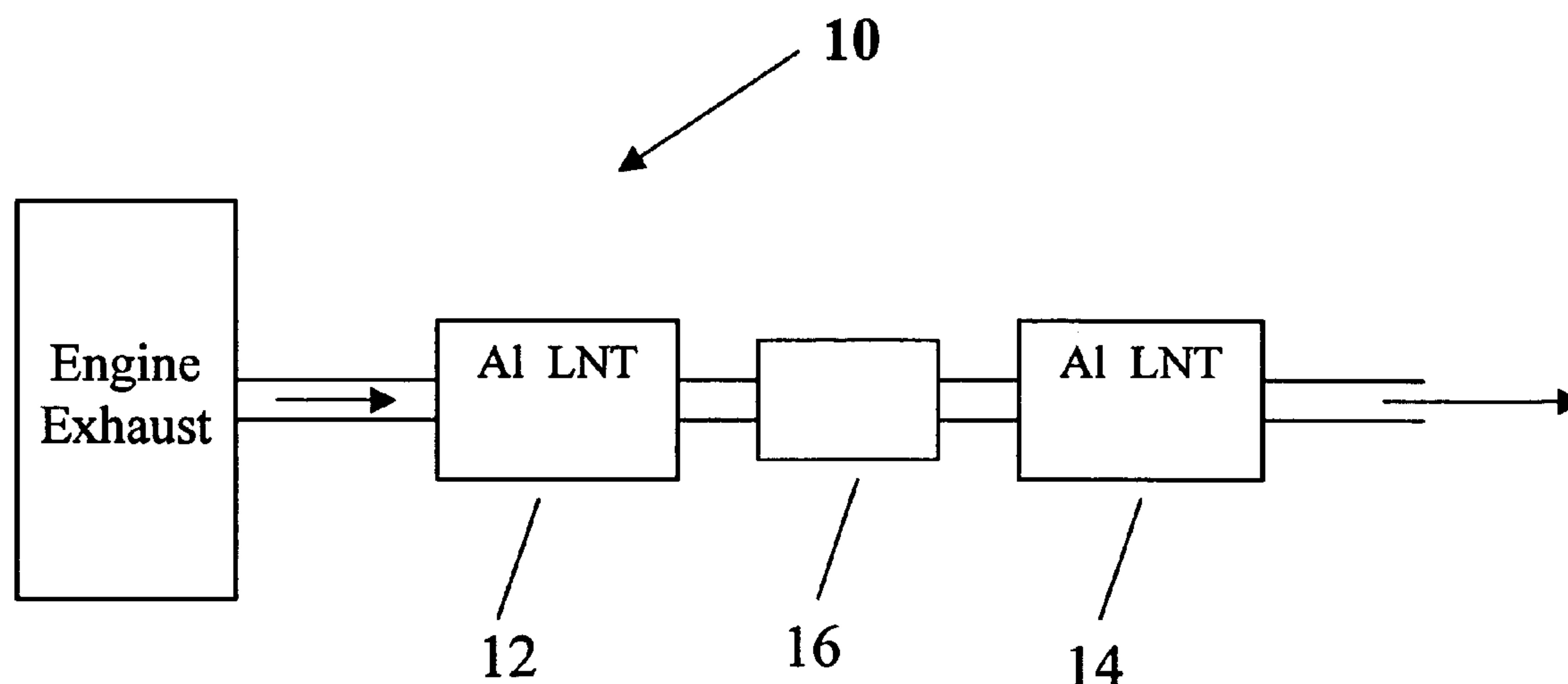


Fig. 1

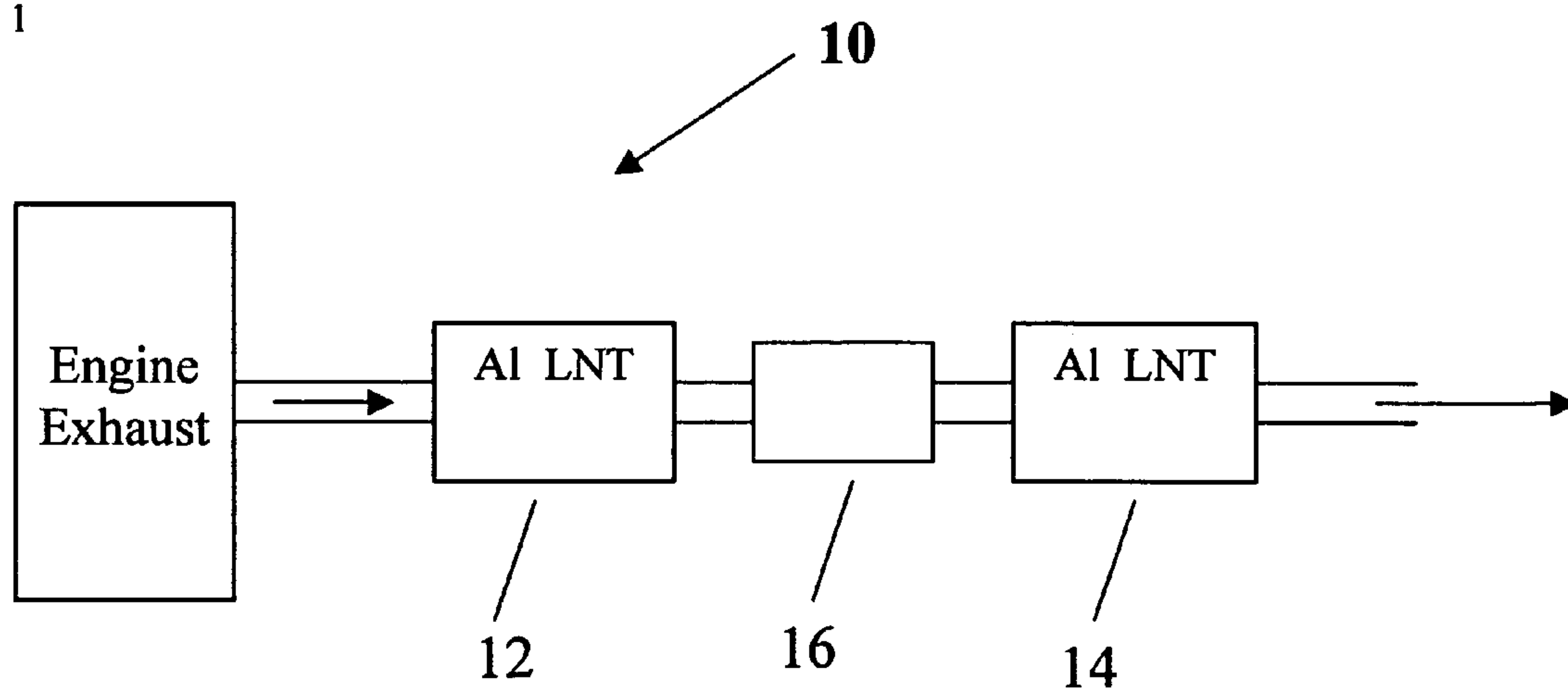


Fig. 2

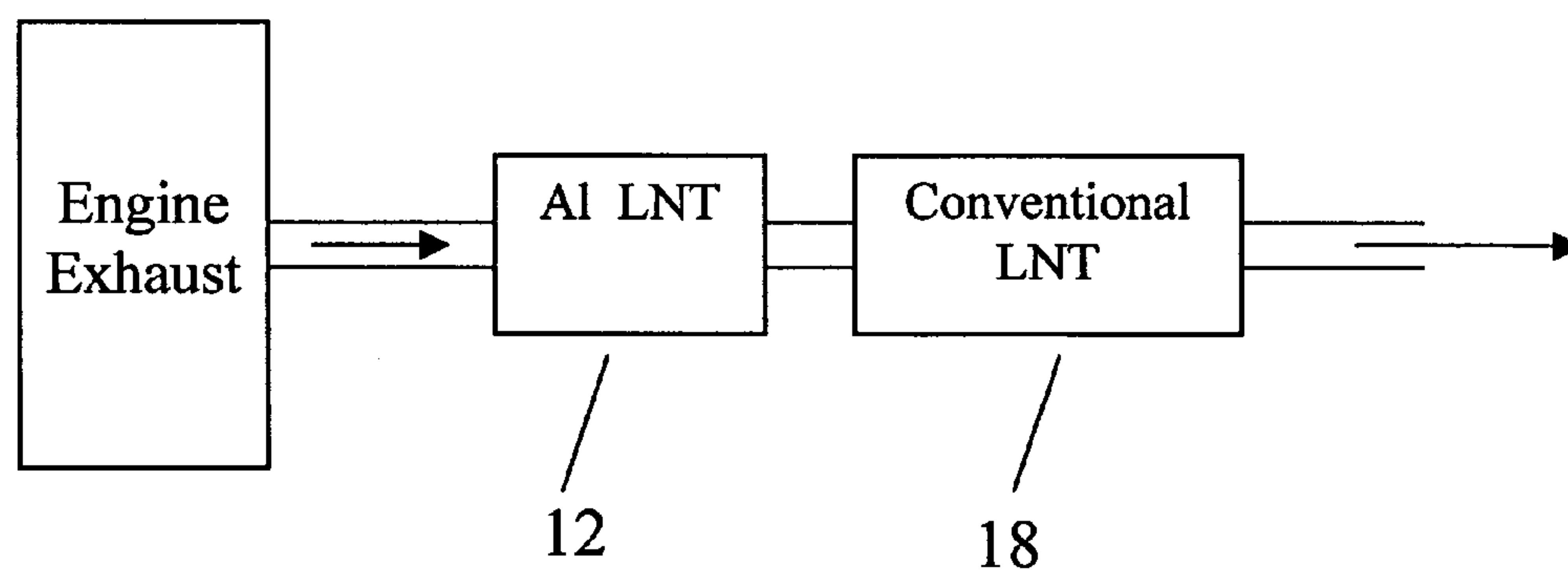


Fig. 3

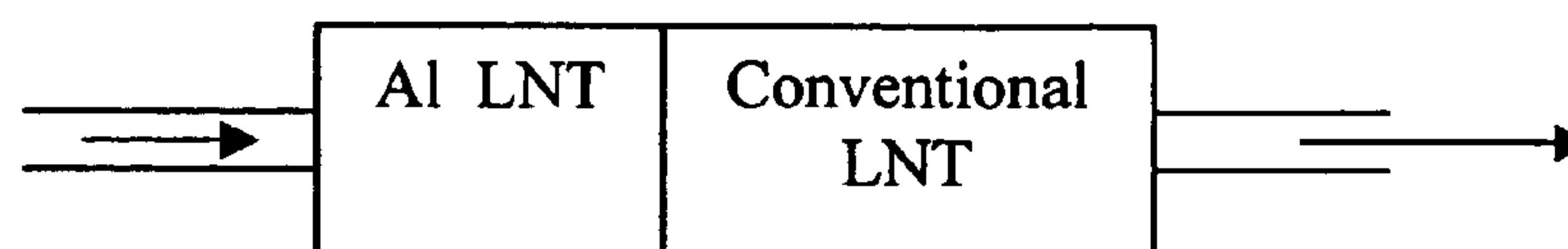


Fig. 4

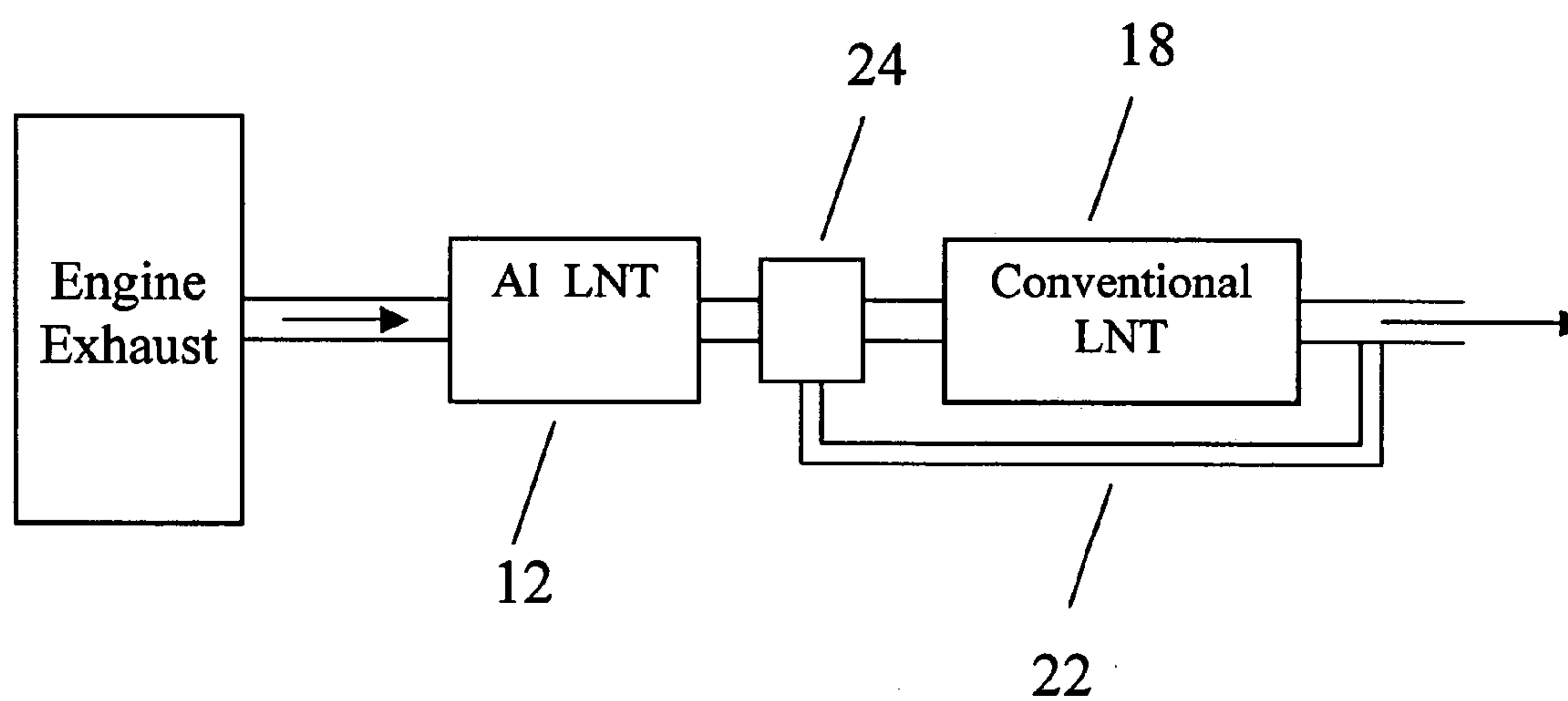


Fig. 5

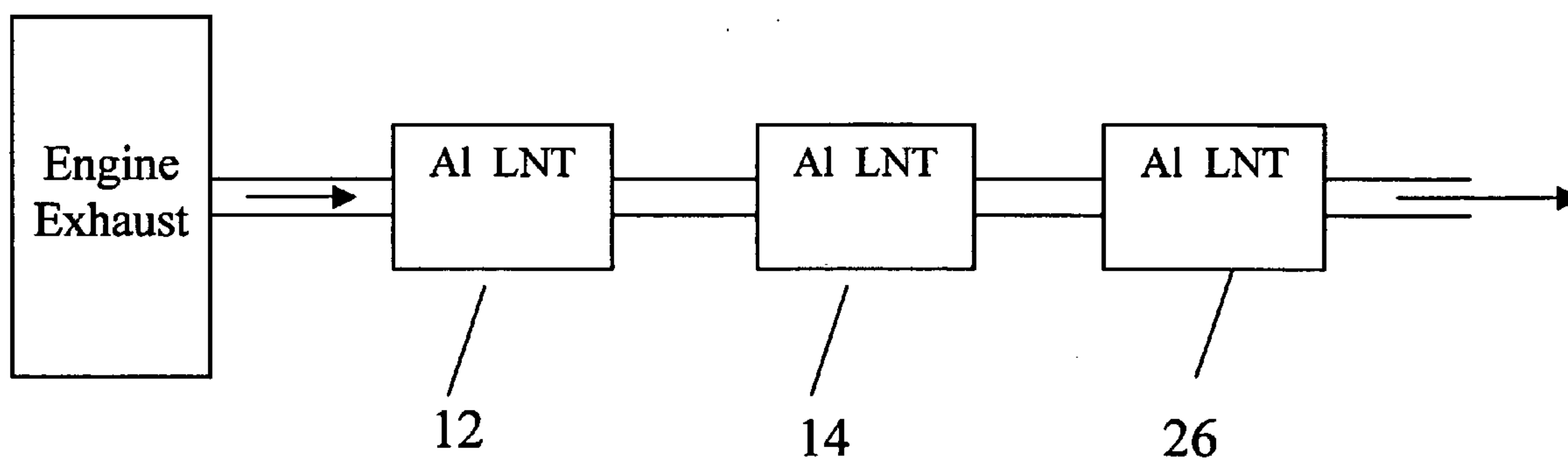


Fig. 6

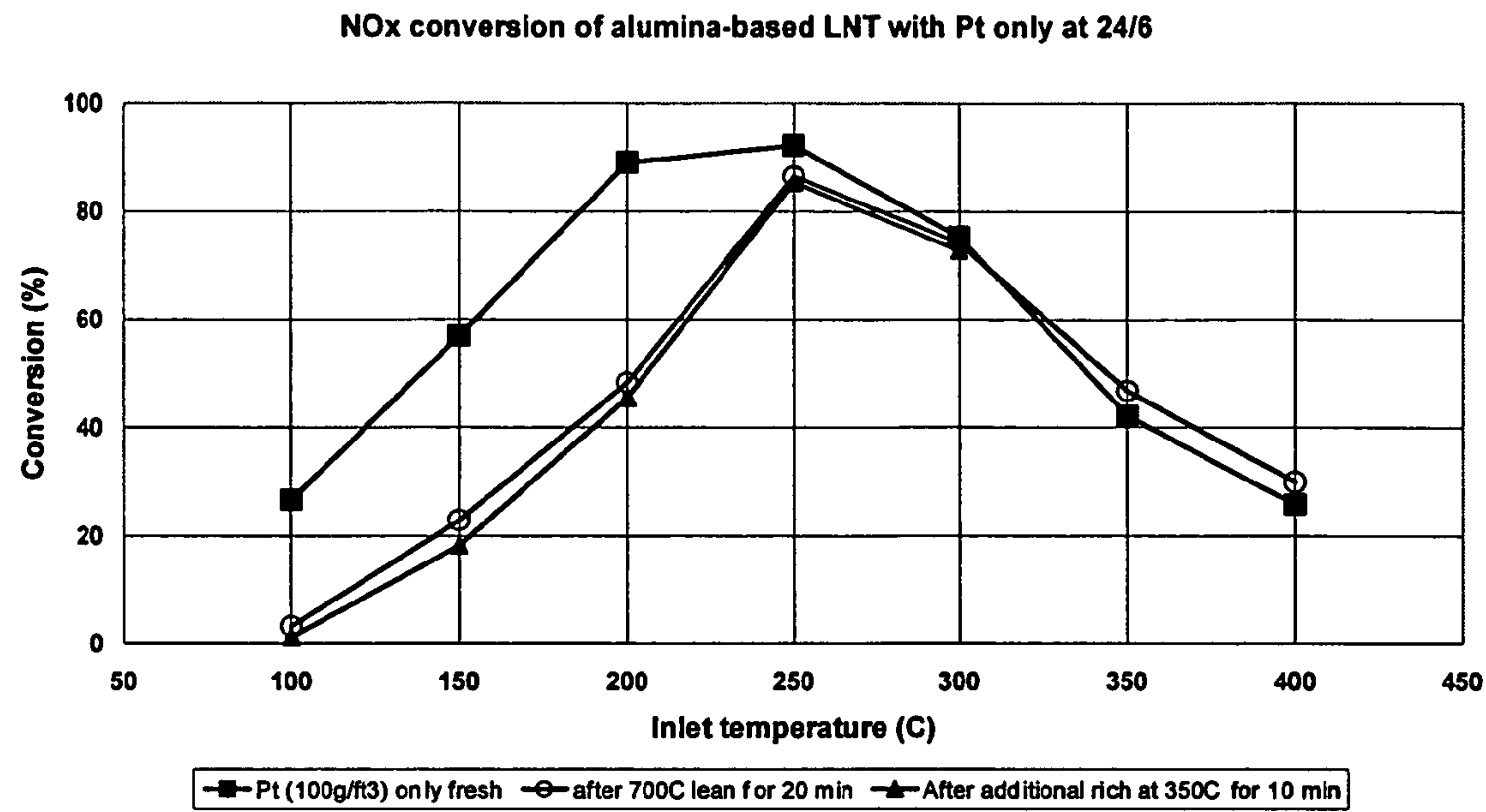


Fig.7

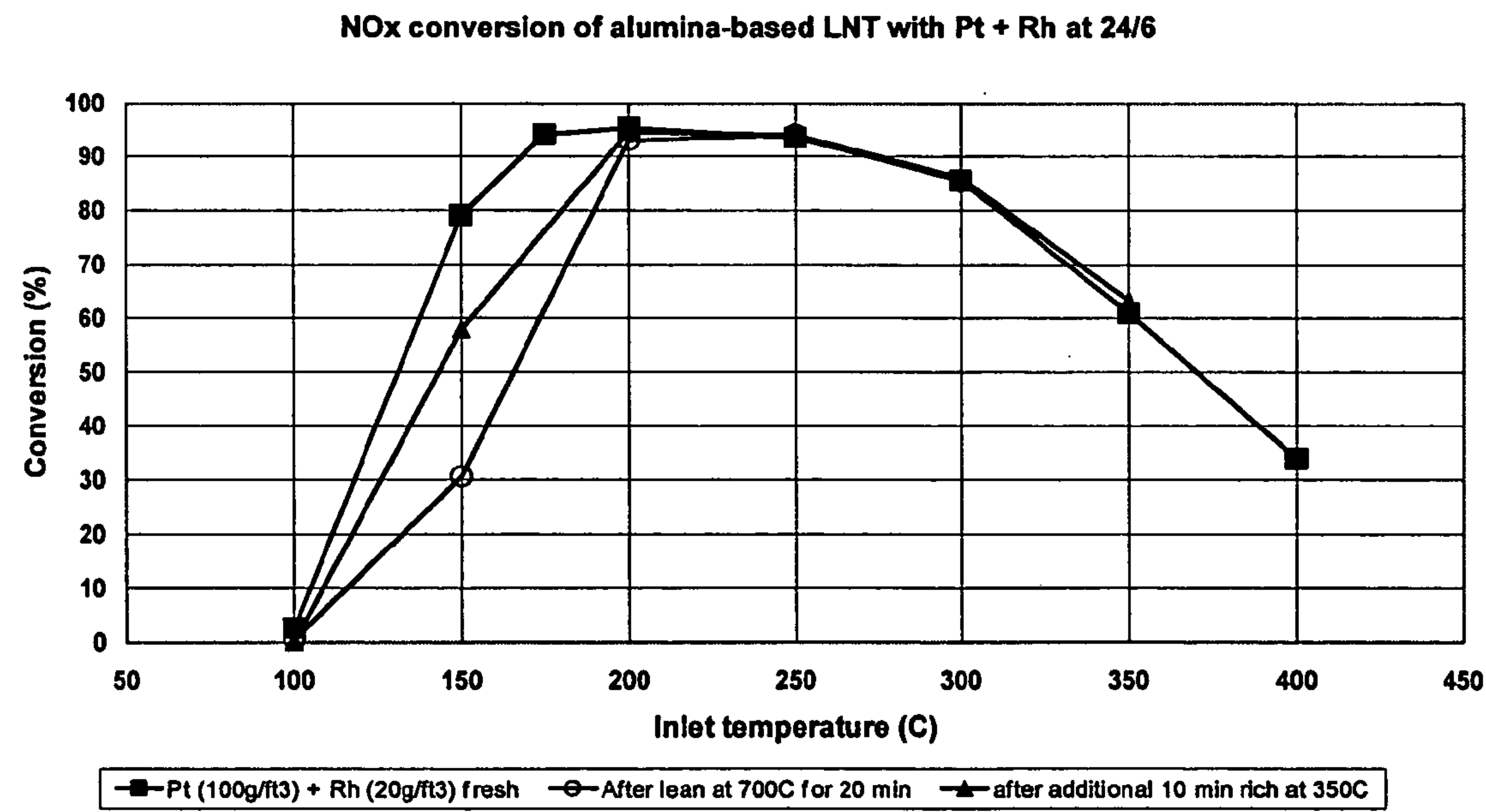


Fig. 8

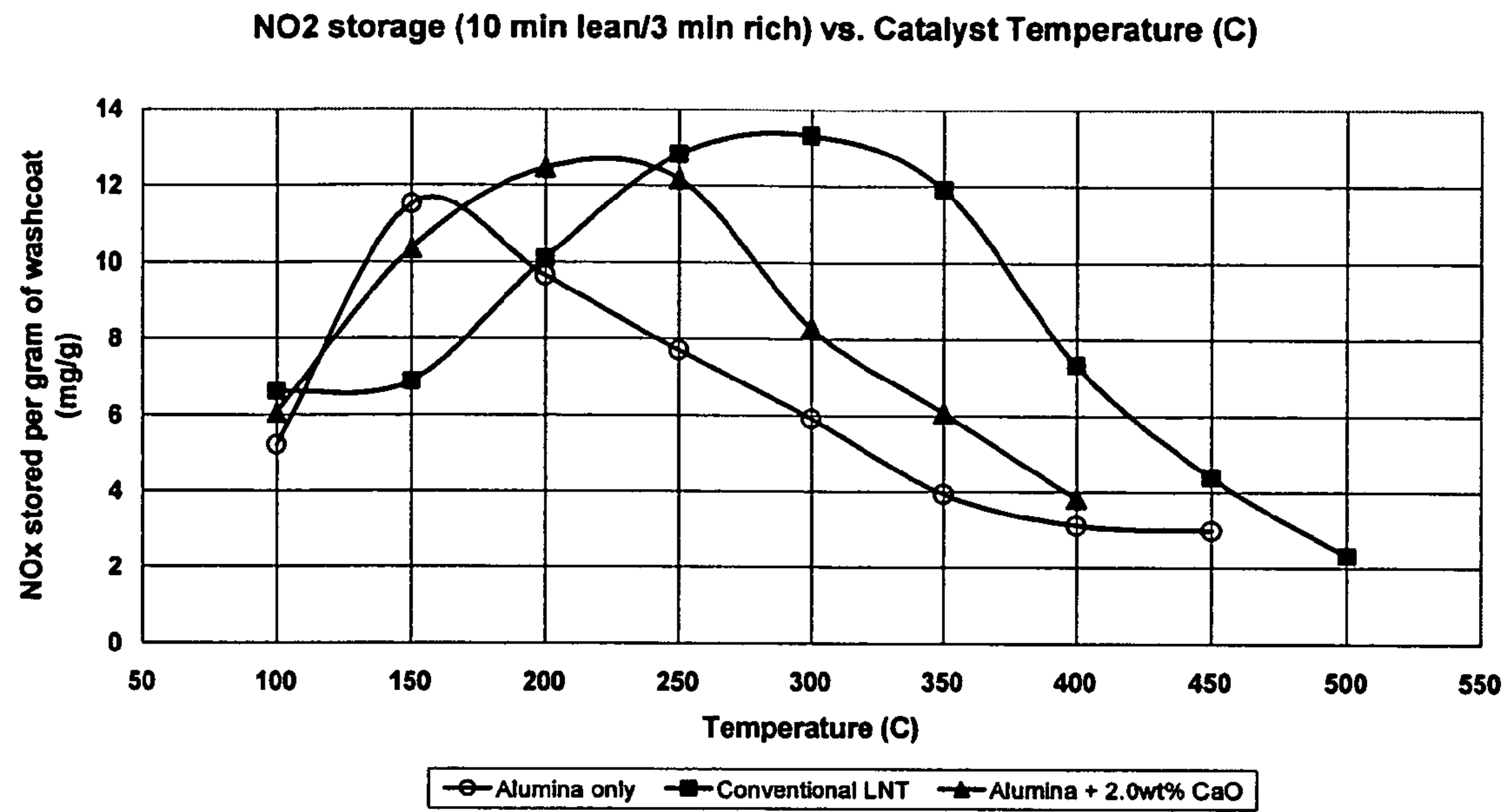


Fig. 9

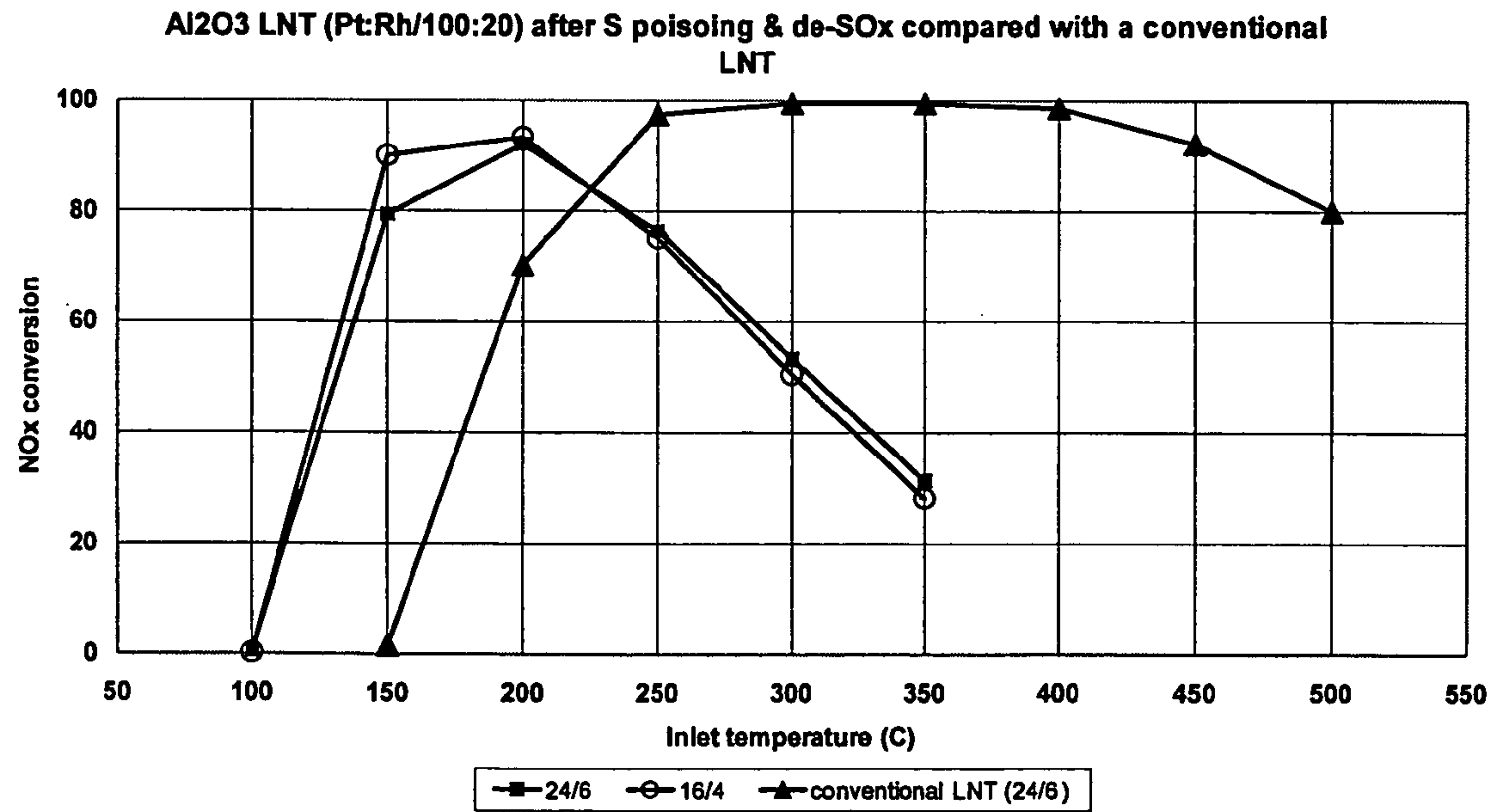


Fig. 10

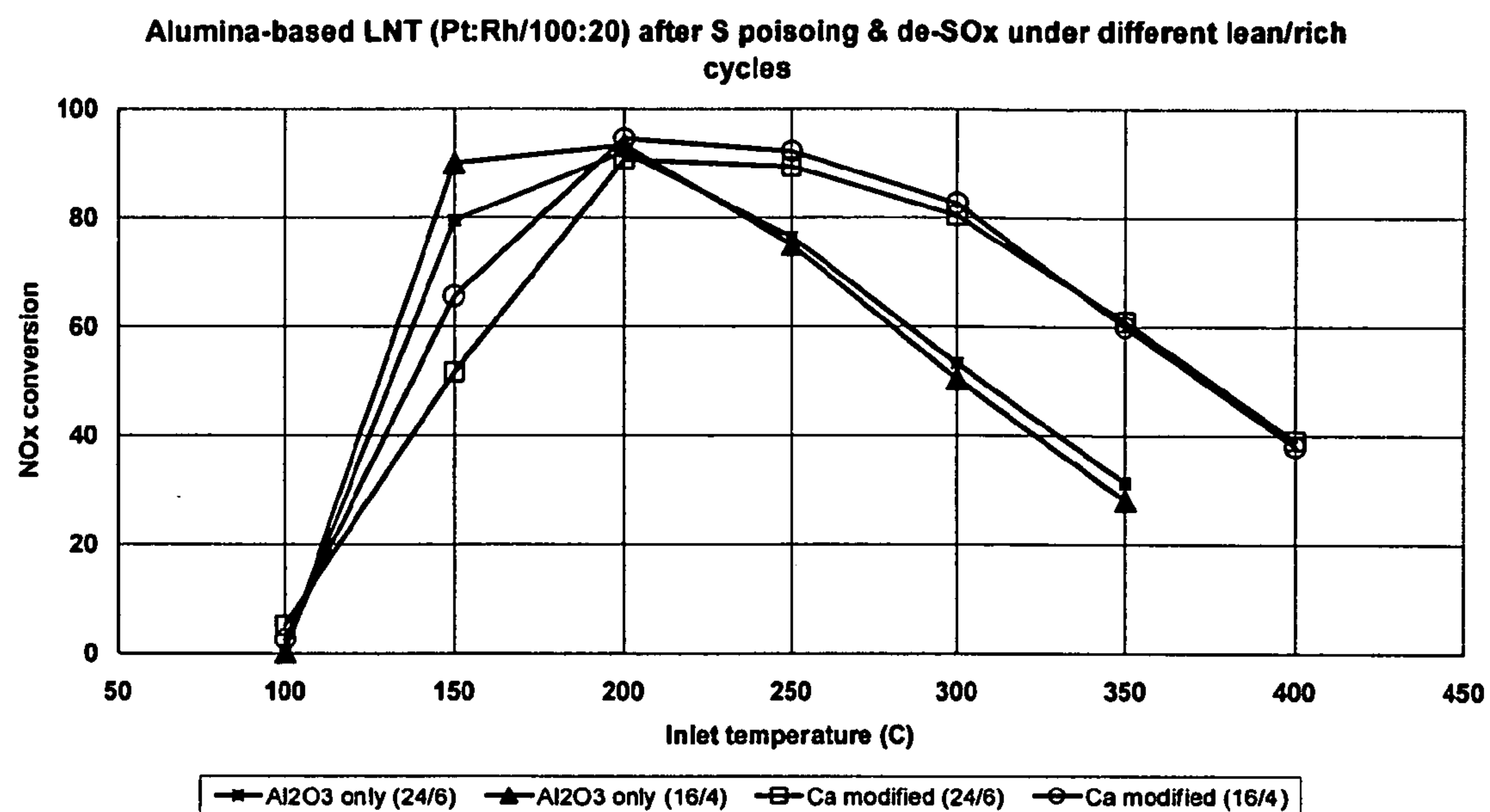


Fig. 11

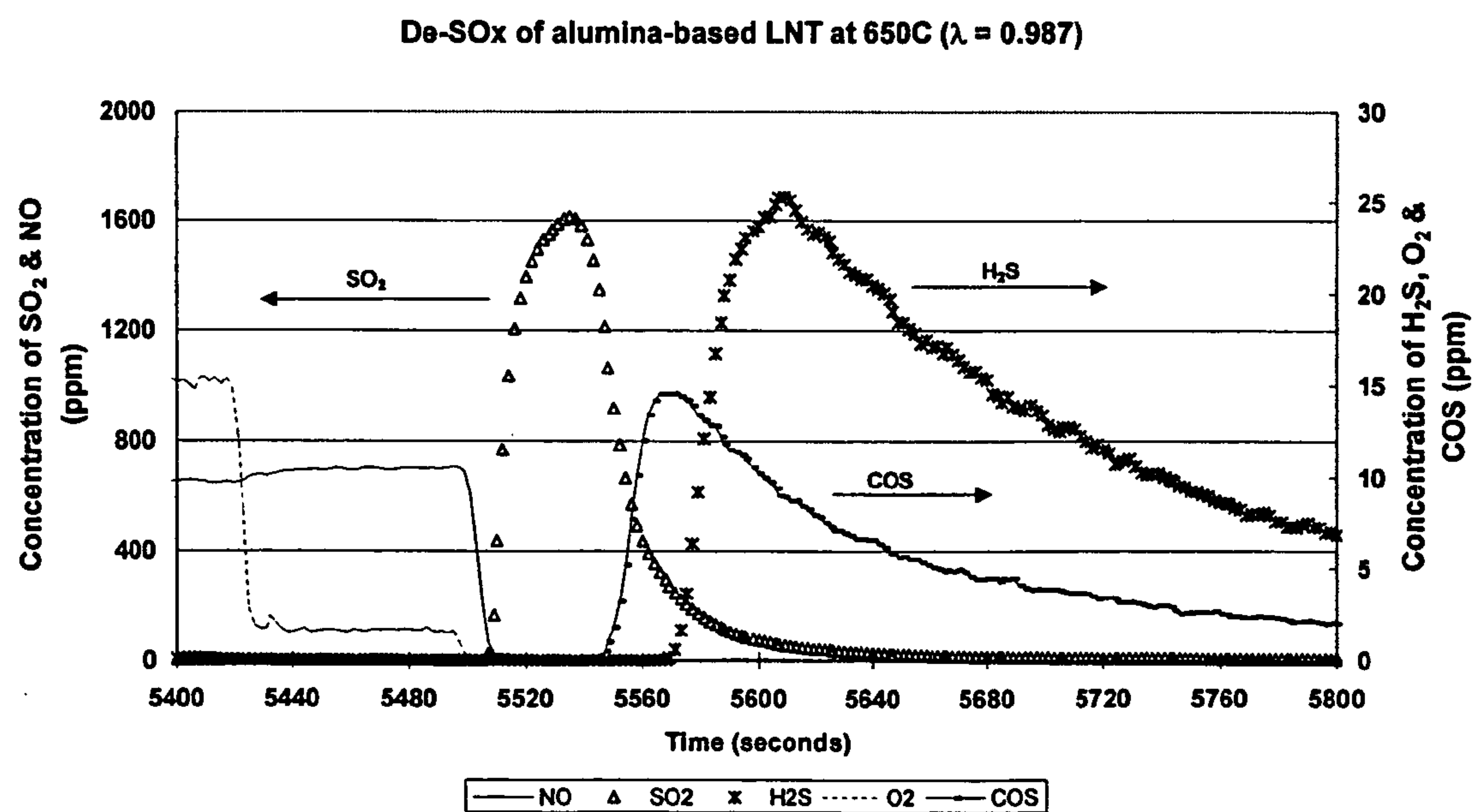


Fig. 12

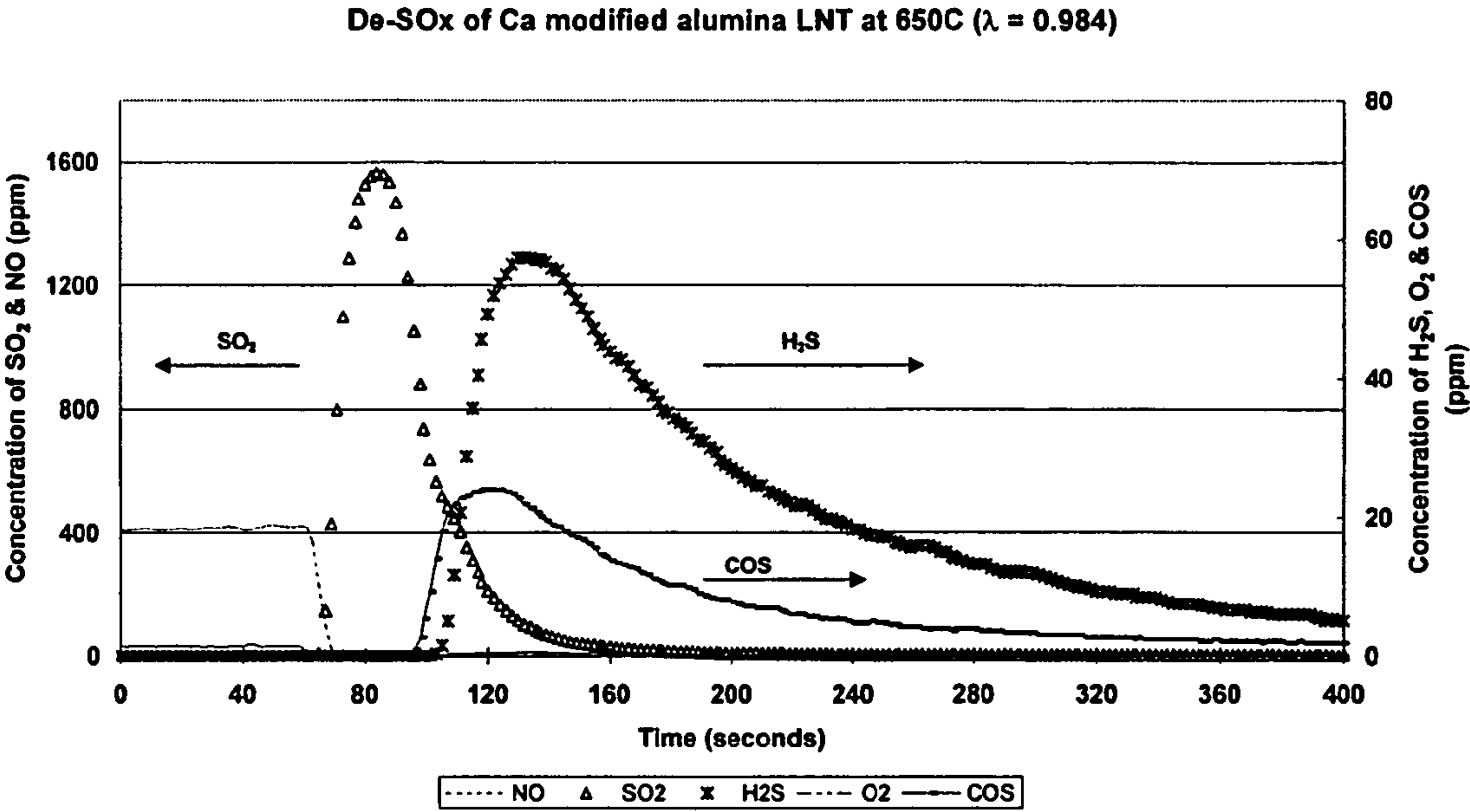


Fig. 13

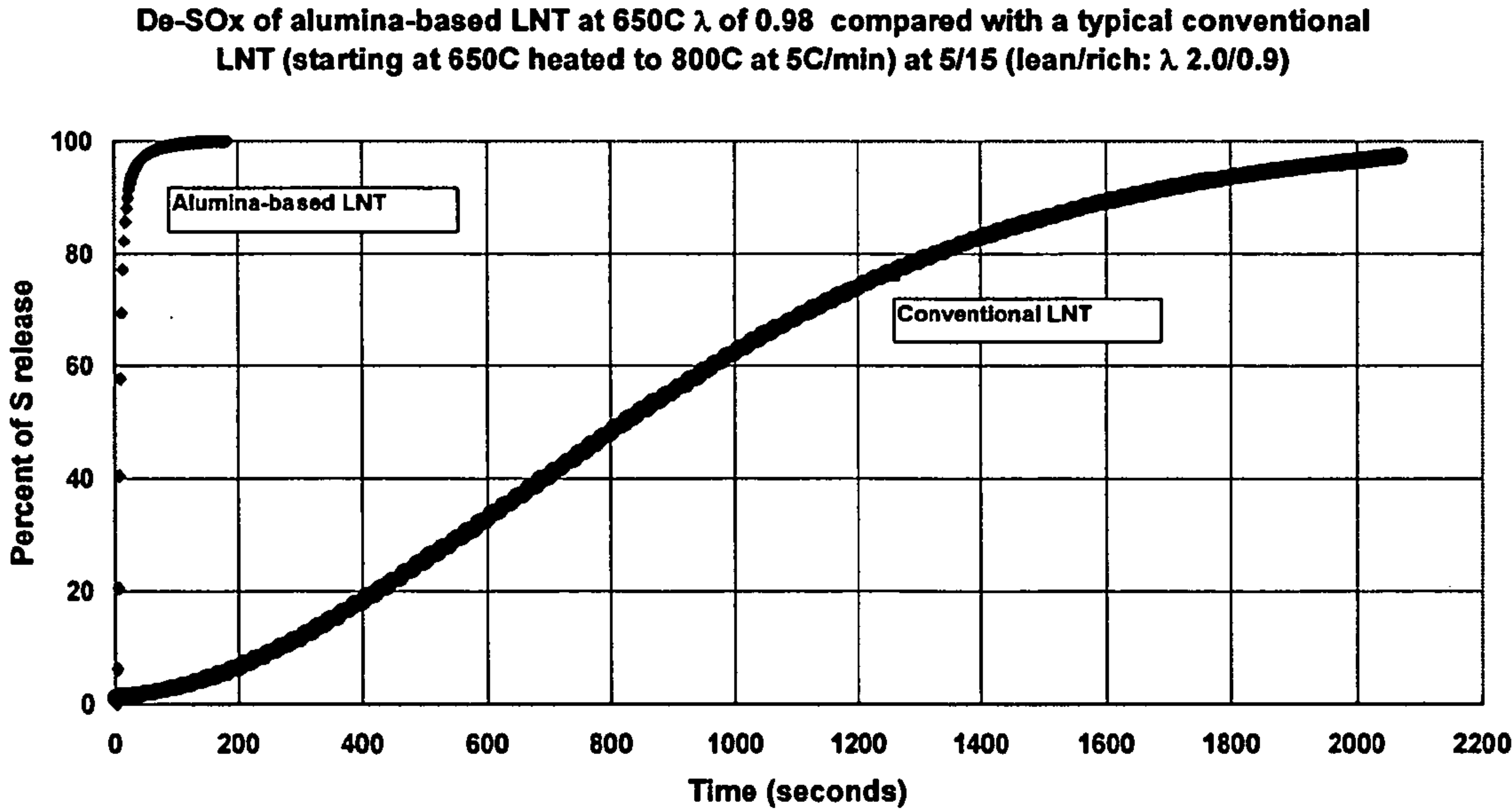


Fig. 14

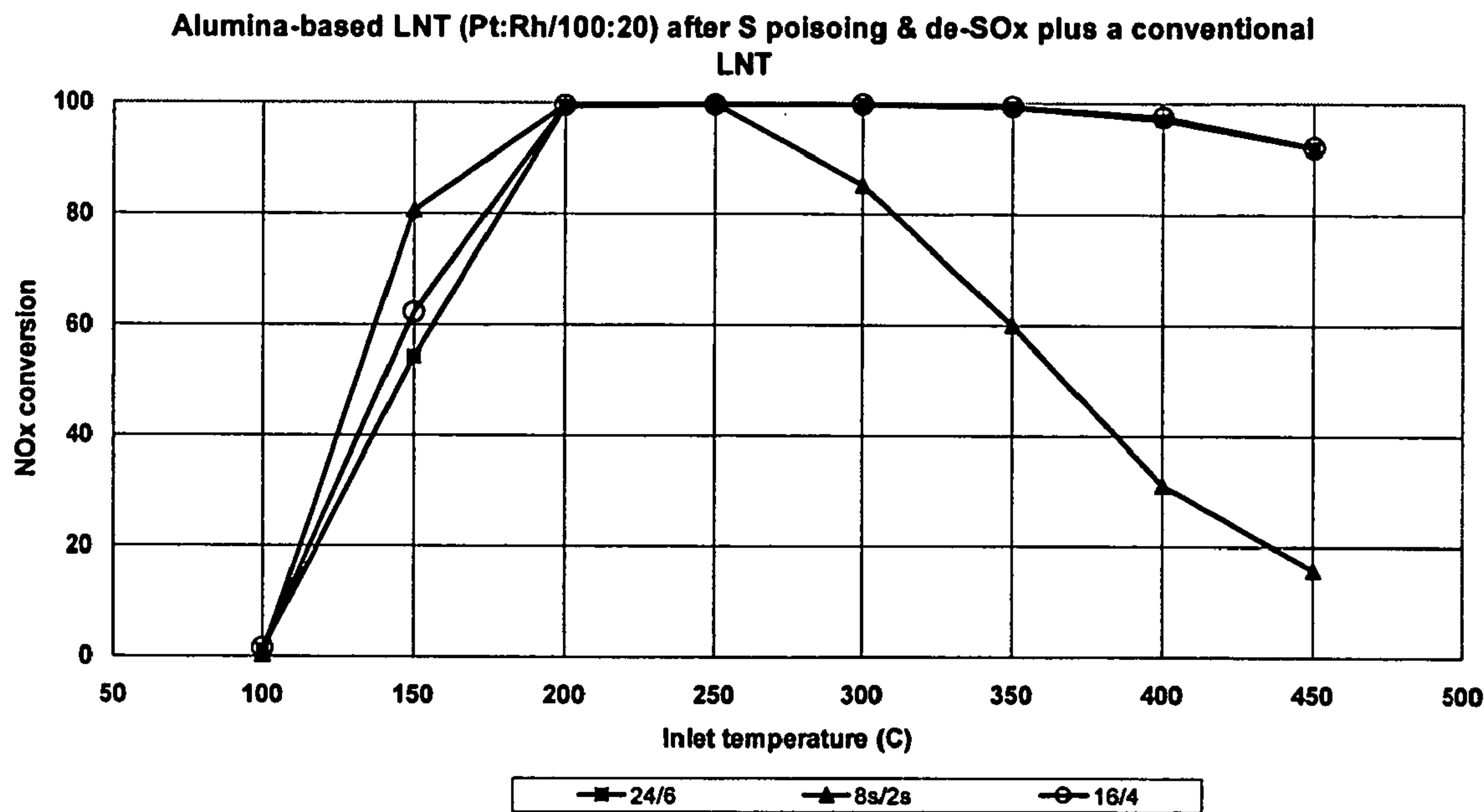


Fig. 15

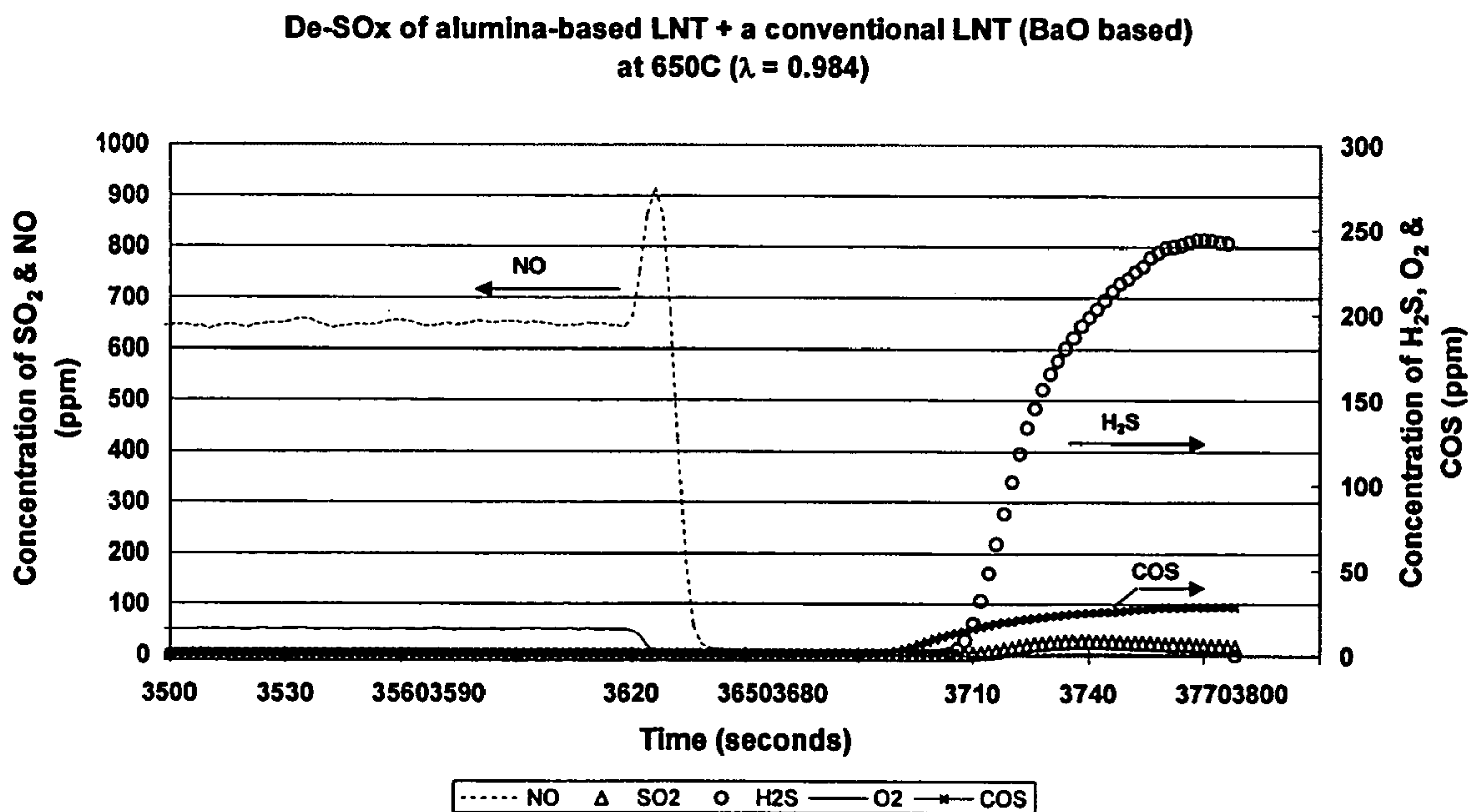


Fig. 16

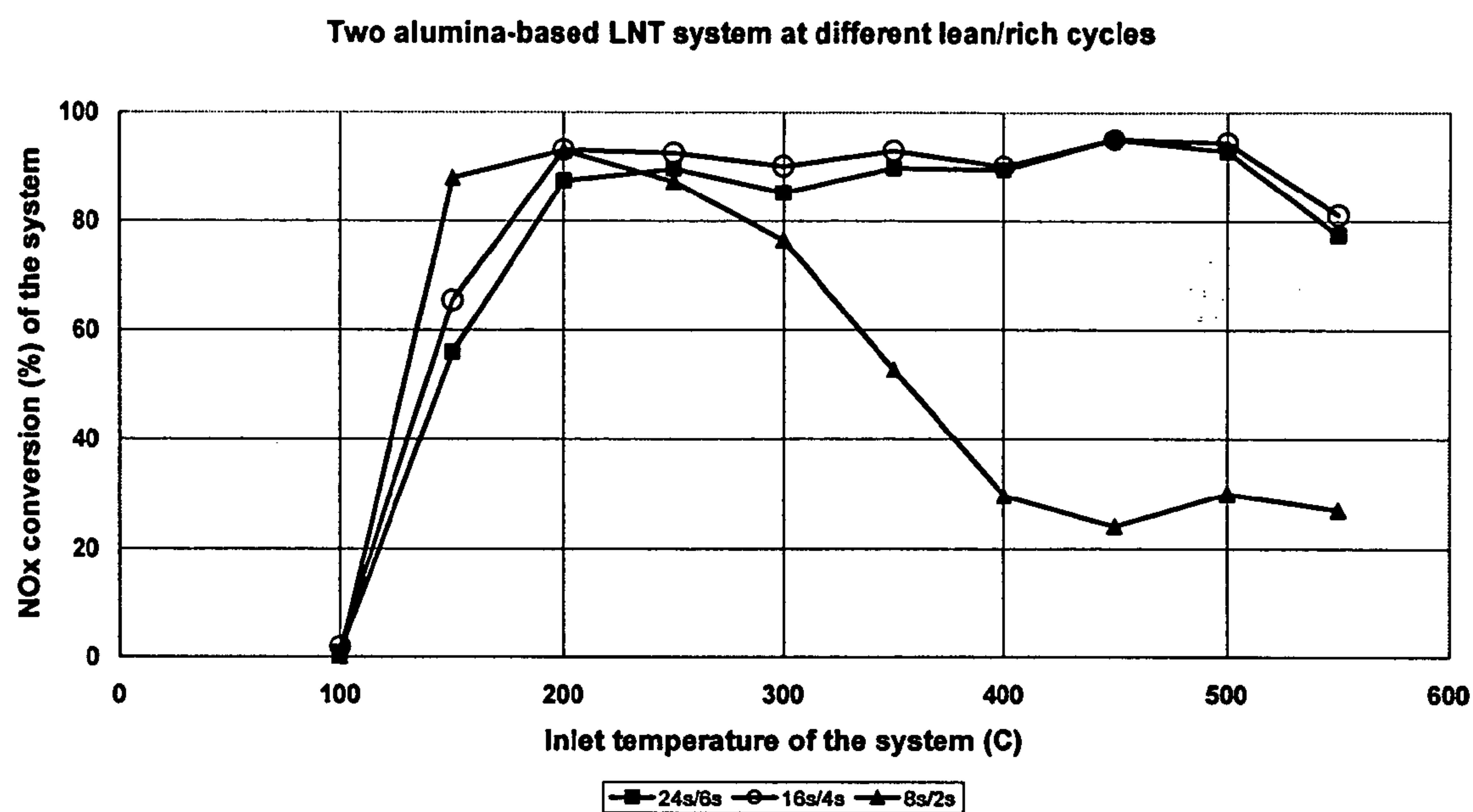


Fig. 17

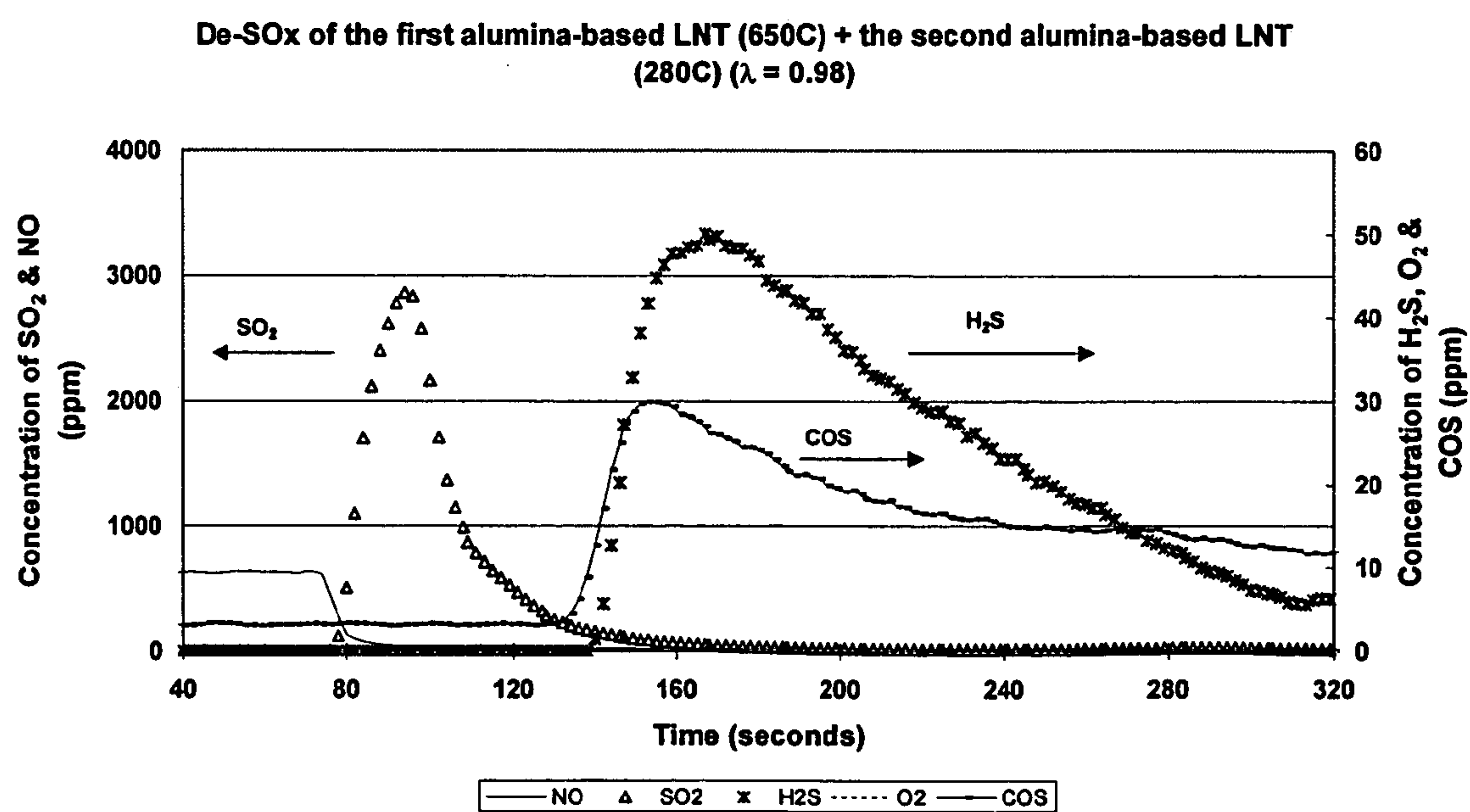
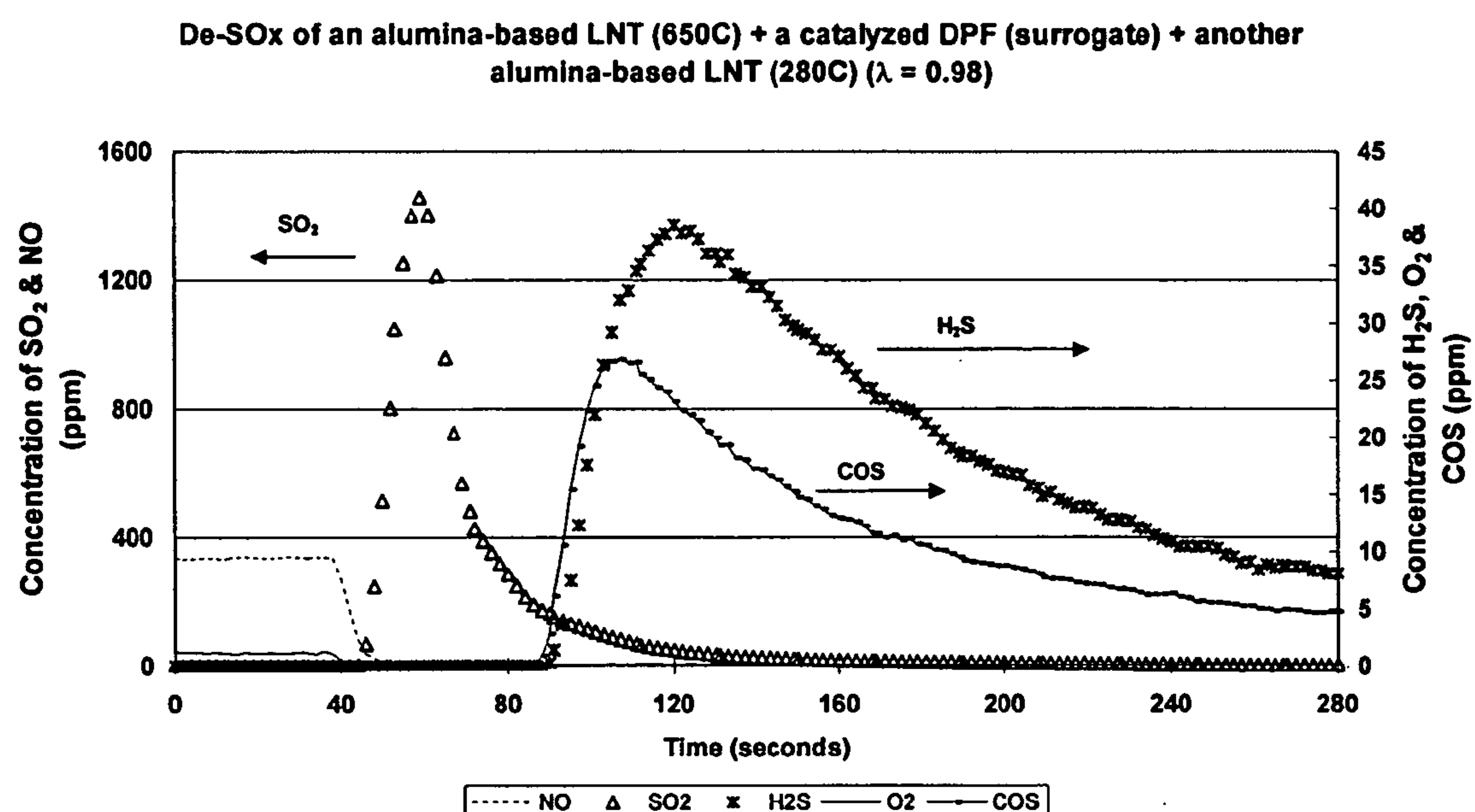


Fig. 18



ALUMINA-BASED LEAN NO_x TRAP SYSTEM AND METHOD OF USE

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 60/649,331, entitled SYSTEM FOR TREATING EMISSIONS FROM DIESEL EXHAUST GAS, filed Feb. 2, 2005. The entire contents of said application are hereby incorporated by reference.

BACKGROUND OF THE INVENTION

[0002] The present invention relates to a lean NO_x trap system for treating emissions from lean burn engines such as diesel engine exhaust gas, and more particularly, to a system including at least one lean NO_x trap which utilizes alumina as a NO_x storage material. The alumina-based lean NO_x trap achieves high NO_x conversion efficiency at low temperatures encountered in the exhaust gas of diesel engine-powered vehicles, maintains its activity with extended use, and undergoes efficient desulphurization.

[0003] Government regulations, created in response to environmental and health concerns, have necessitated the treatment of exhaust gas from vehicle engines in order to reduce the level of certain combustion by-products, including carbon monoxide (CO), hydrocarbons (HC), and nitrogen oxides (NO_x). In conventional gasoline engines (i.e., engines that operate at a stoichiometric air-to-fuel ratio), such treatment generally includes the use of a three-way catalyst (TWC). However, lean burn engines such as diesel engines, which offer 10 to 30% better fuel economy than conventional gasoline engines, require special treatment since a TWC cannot effectively reduce the level of NO_x under the oxidizing atmosphere present in the exhaust gas of such engines which are operated under fuel-lean conditions ($\lambda > 1$, where λ represents the air-to-fuel ratio divided by the stoichiometric air-to-fuel ratio).

[0004] A potential solution to this problem is the use of a lean NO_x trap (LNT), which conventionally includes a catalyst comprising one or more precious metals and an alkali metal oxide or alkaline earth metal oxide supported on a binder material such as alumina. The LNT is capable of absorbing NO_x from the exhaust gas and storing it during fuel-lean operation of the engine, then releasing and converting it to nitrogen gas when the engine operation changes to stoichiometric or rich ($\lambda < 1$).

[0005] However, the LNT has not been widely used in diesel engine-powered vehicles because the exhaust gas temperature is usually somewhat lower than the operating temperature window normally provided by the trap. For example, the exhaust gas temperature of a light-duty diesel vehicle driving under the Federal Test Procedure (FTP) is typically less than 200° C., while the temperature window of operation of a conventional LNT ranges from 200° C. to 500° C.

[0006] In addition, a conventional LNT is not very durable, suffering loss of both catalyst activity (e.g., through thermally activated coarsening of precious metal particles) and NO_x storage capacity (e.g., through aqueous-based leaching). Thermal deactivation is further aggravated because of the need to periodically purge the trap of stored

SO_x, which blocks the storage of NO_x. The SO_x accumulates on the LNT due to the combustion of fuel sulfur (and some lubricating oil). It is generally necessary to perform an occasional (every 5,000 miles of low sulfur fuel used) desulphurization (de-SO_x) treatment at relatively high temperatures (650° C. to 800° C.) for relatively long times (5 to 10 minutes). In addition, fuel rich operation is required for the de-SO_x treatment, which takes away some of the efficiency provided by diesel engine operation.

[0007] Alternative approaches to the removal of NO_x from diesel exhaust gas have included the use of an active lean NO_x catalyst, a urea (ammonia) SCR (selective catalytic reduction) catalyst, and a plasma assisted NO_x reduction catalyst. However, none of these approaches has provided a satisfactory solution to the removal of NO_x in lean exhaust gas due to low efficiency, inability to regenerate and/or undergo efficient desulphurization, and the high system cost.

[0008] Accordingly, there is still a need in the art for a lean NO_x trap which can operate at the low temperatures encountered in lean burn engines, which maintains its activity with extended use, and which undergoes efficient desulphurization.

SUMMARY OF THE INVENTION

[0009] The present invention meets those needs by providing a lean NO_x trap (LNT) system for use in lean burn engines such as diesel engines which includes at least one LNT which utilizes alumina as a NO_x storage (absorbent) material. The alumina-based LNT, when incorporated in a lean burn engine exhaust system, effectively converts NO_x at the low temperatures encountered in such engines. In addition, the alumina-based LNT maintains its activity with extended use and undergoes efficient desulphurization.

[0010] According to one aspect of the present invention, a LNT system for use in a lean burn engine exhaust operating under fuel lean/rich conditions is provided. Lean burn engines which may incorporate the LNT system of the present invention include diesel engines, H₂ ICE engines, and any other engines having an exhaust temperature ranging from between about 150 to 500° C. By "fuel lean/rich conditions," it is meant that the engine is capable of switching between operation under fuel lean conditions ($\lambda > 1$) and fuel rich conditions ($\lambda < 1$). The system comprises a first LNT comprising a catalyst, a NO_x absorbent material comprising alumina, and optionally, an alkaline earth metal oxide (also referred to herein as an alumina-based LNT); and a second LNT. Preferably, the first LNT comprises from 0 to about 4 wt % of the alkaline earth metal oxide.

[0011] In one embodiment of the invention, the second LNT in the system is an alumina-based LNT comprising a catalyst, a NO_x absorbent material comprising alumina, and optionally, from 0 to about 4 wt % of an alkaline earth metal oxide. In an alternative embodiment of the invention, the second lean NO_x trap is a conventional LNT comprising a catalyst and from about 20 to 35 wt % of a metal oxide on an alumina or silica support. The metal oxide in the conventional LNT may comprise an alkali metal oxide or an alkaline earth metal oxide.

[0012] The LNT system converts at least a portion of NO_x contained in exhaust gas from the engine exhaust to N₂ at a temperature range of between about 150° C. to about 500°

C. The system preferably has a conversion efficiency of at least 50% at a temperature between about 150° C. to about 500° C. By conversion efficiency, it is meant the difference between the levels of NO_x entering the trap and leaving the trap divided by the level entering the trap, multiplied by 100%.

[0013] The catalyst in the alumina-based LNT is preferably selected from platinum, rhodium, and combinations thereof. The alkaline earth metal in the metal oxide is preferably selected from Mg, Sr, Ba, and Ca.

[0014] The alumina-based LNT preferably further includes less than about 4 wt % of a stabilizing metal selected from La, Ce, and Ba.

[0015] In alternative embodiment of the invention, the system may further include a third (alumina-based) LNT comprising a catalyst, a NO_x absorbent material comprising alumina and optionally, from 0 to about 4 wt % of an alkaline earth metal oxide.

[0016] In a preferred embodiment of the invention, the LNT system comprises a first alumina-based LNT and a second alumina-based LNT. In this system, the second LNT is preferably positioned downstream from the first LNT. The system may further include a diesel particulate filter. The system converts at least a portion of NO_x contained in exhaust gas from said engine to N₂ at a temperature range of between about 150° C. to about 500° C.

[0017] The present invention further provides a method for treating lean burn engine exhaust gases which comprises providing a LNT system comprising at least first and second LNTs in an exhaust gas passage of a lean burn engine, where the first LNT comprises a catalyst, a NO_x absorbent material comprising alumina, and optionally, from 0 to 4 wt % of an alkaline earth metal oxide. The second LNT may comprise an alumina-based LNT, or it may comprise a conventional LNT as described above.

[0018] The LNT system is exposed to lean burn engine exhaust gas containing NO_x such that at least a portion of said NO_x contained in the exhaust gas is converted to N₂ at a temperature between about 150° C. to 500° C. Preferably, the NO_x in the (first) alumina-based LNT is converted at a temperature of between about 150° C. to about 350° C. The NO_x in the second lean NO_x trap is preferably converted at a temperature of between about 150° C. to about 350° C.

[0019] In one embodiment of the method, the second LNT is positioned downstream from the first LNT. In another embodiment, the first and second lean NO_x traps are combined.

[0020] The method preferably provides a conversion efficiency of at least 50% at a temperature between about 150° C. to about 500° C. Where the engine operates under a lean/rich cycle and the exhaust gas is subjected to a fixed lean/rich ratio ($x/y=R$, where x =lean time, y =rich time, and R =ratio), the NO_x conversion efficiency may be increased by reducing x and y at a temperature of between about 150 to 200° C. Preferably, the method includes sensing the concentration of NO_x in the exhaust gas and adjusting the lean/rich cycle of the engine accordingly to increase NO_x conversion efficiency. One or more NO_x sensors may be included downstream from the LNT system for this purpose.

[0021] The present invention also provides a method for desulphurization of a LNT system in a lean burn engine, where the system comprises a first LNT comprising a catalyst, a NO_x absorbent material comprising alumina, and optionally, an alkaline earth metal oxide (preferably from 0 to about 4 wt %), and a second LNT positioned downstream from the first LNT. In one embodiment, the second LNT is an alumina-based LNT comprising a catalyst, a NO_x absorbent material comprising alumina, and optionally, from 0 to about 4 wt % of an alkaline earth metal oxide. In an alternative embodiment of the invention, the second LNT is a conventional LNT comprising a catalyst and from about 20 to 35 wt % of a metal oxide on an alumina or silica support.

[0022] The desulphurization process is required when the first (alumina-based) LNT captures a certain amount of sulfur and/or to prevent sulfur from passing through the first LNT during normal vehicle operation. In the desulphurization method, the system is positioned in the exhaust passage of a lean burn engine such that it is exposed to exhaust gases therein; and the exhaust gases in the first LNT are heated to a temperature of between about 550° C. and about 650° C. for at least 40 seconds. Preferably, the exhaust gases are heated for about 40 to 120 seconds. Preferably, during desulphurization, λ is between about 0.98 to about 0.99.

[0023] In the embodiment where the second LNT is a conventional LNT, the system preferably further includes a bypass exhaust line for directing exhaust gas through the second LNT during normal vehicle operation but which diverts exhaust gas around the second LNT during desulphurization of the first LNT.

[0024] The desulphurization of the LNT system causes the alumina-based LNT to release a sulfur product comprising at least 90% SO₂. In addition, the alumina-based LNT maintains its activity after the desulphurization process.

[0025] Accordingly, it is a feature of the present invention to provide a LNT system including at least one alumina-based LNT which operates effectively at the low temperatures encountered in lean burn engines, which maintains its activity over time, and which undergoes efficient desulphurization. Other features and advantages will be apparent from the following description and the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026] FIG. 1 is a schematic illustration of the system of the present invention including first and second alumina-based LNTs;

[0027] FIGS. 2 is a schematic illustration of the system including a first alumina-based LNT and a second conventional LNT;

[0028] FIG. 3 is a schematic illustration of the system including an alumina-based LNT and a conventional LNT which are combined into one LNT (zone coating);

[0029] FIG. 4 is a schematic illustration of the system including an alumina-based LNT and a conventional LNT which includes a bypass exhaust line;

[0030] FIG. 5 is a schematic illustration of the system including multiple alumina-based LNTs;

[0031] FIG. 6 is a graph illustrating NO_x conversion efficiency of the alumina-based LNT of the present invention under varying conditions using only Pt as the catalyst;

[0032] FIG. 7 is a graph illustrating NO_x conversion efficiency of the alumina-based LNT of the present invention under varying conditions using both Pt and Rh as catalysts;

[0033] FIG. 8 is a graph illustrating the NO_x storage capabilities of the alumina-based LNT compared with a conventional LNT having the same Pt and Rh loadings;

[0034] FIG. 9 is a graph illustrating NO_x conversion efficiency of the alumina-based LNT of the present invention under varying lean/rich cycle times compared with a conventional LNT;

[0035] FIG. 10 is a graph illustrating NO_x conversion efficiency of the alumina-based LNT of the present invention with and without the addition of calcium oxide (less than 0.1 wt %) under varying lean/rich cycle times;

[0036] FIG. 11 is a graph illustrating the desulphurization (de-SO_x) performance of the alumina-based LNT of the present invention at 650° C. and $\lambda=0.987$;

[0037] FIG. 12 is a graph illustrating the de-SO_x performance of the alumina-based LNT with the addition of less than 2.0 wt % calcium oxide at 650° C. and $\lambda=0.984$;

[0038] FIG. 13 is a graph illustrating the de-SO_x efficiencies of the alumina-based LNT of the present invention compared with a conventional LNT;

[0039] FIG. 14 is a graph illustrating NO_x conversion efficiency of a system comprising an alumina-based LNT and a conventional LNT under varying lean/rich cycle times;

[0040] FIG. 15 is a graph illustrating the de-SO_x performance of a system comprising an alumina-based LNT and a conventional LNT system at 650° C. and $\lambda=0.980$;

[0041] FIG. 16 is a graph illustrating NO_x conversion efficiency of a system comprising two alumina-based LNTs under varying lean/rich cycle times;

[0042] FIG. 17 is a graph illustrating the de-SO_x performance of a system comprising two alumina-based LNTs with a catalyzed DPF surrogate catalyst between the two LNTs at 650° C. and $\lambda=0.984$; and

[0043] FIG. 18 is a graph illustrating the de-SO_x performance of a system comprising two alumina-based LNTs with a catalyzed DPF surrogate catalyst between the two LNTs at 650° C. and $\lambda=0.984$.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0044] We have found that the use of alumina as a NO_x storage (absorbent) material in a LNT provides more efficient release of NO_x at low temperatures than conventional LNTs which utilize alkali metal oxides or alkaline earth metal oxides as NO_x storage materials. Because alkali metals and alkaline earth metals are very basic in nature, such storage materials have a strong interaction with NO_x and slowly release NO_x at low temperatures (below 200° C.) under rich conditions. As alumina has a relatively weak interaction with NO_x it can absorb and release NO_x quickly at even lower temperatures (about 150° C.). While alumina has been widely used in conventional LNTs as a support material for catalysts, such LNTs include large amounts (e.g., about 20 to 35 wt %) of alkali metal oxides and/or alkaline earth metal oxides. Such large amounts of metal

oxides modify the alumina and dominate the NO_x absorption properties of the LNT, thus determining the activity of the LNT and its other properties, i.e., operating temperature window, desulphurization temperature, etc.

[0045] We have found that the use of an alumina-based LNT system including at least one alumina-based trap containing little or no alkaline earth metal oxides allows the alumina to dominate the NO_x absorption properties of the lean NO_x trap, resulting in high NO_x conversion efficiency at relatively low temperatures, e.g., about 150° C. The alumina-based LNT is also resistant to degradation by aqueous-based processes previously found to cause conventional traps to lose a substantial fraction of their initial NO_x storage capacity.

[0046] Desulphurization (de-SO_x) of the alumina-based LNT system is also achieved more efficiently than in a conventional LNT as desulphurization can take place at lower temperatures and slightly rich conditions for much shorter periods of time. The alumina-based LNT system of the present invention is resistant to SO₂ poisoning since the alumina-based LNT does not degrade when subjected to its unique desulphurization process. Also, production of unwanted H₂S during desulphurization is minimized.

[0047] The alumina-based LNT of the present invention is preferably prepared by coating a cordierite monolith with a catalyst washcoat (about 5 to 7 kg/ft³) comprising from about 95 to 99% by weight alumina. Optionally, a stabilizing metal comprising less than about 4% by weight of the total washcoat may be added to stabilize the alumina surface area during high temperature exposure and increase the durability of the LNT. Suitable stabilizing metals include La, Ce, and Ba.

[0048] In addition, the alumina-based LNT optionally includes from 0 to about 4.0% by weight of the total washcoat of an alkaline earth metal oxide. Preferred alkaline earth metals include Mg, Sr, Ba, and Ca. The alkaline earth metal oxide may be included in the LNT for the purpose of shifting the operating temperature window of the LNT, for example, to achieve higher operating temperatures.

[0049] We have found that the addition of such a small amount of an alkaline earth metal oxide (i.e., less than about 4.0 wt %) does not impact the basic properties of the alumina-based LNT, e.g., high NO_x conversion efficiency at low temperatures and efficient desulphurization of the LNT at relatively low temperatures for a short time. The alkaline earth metal oxide may be added to the washcoat by a conventional aqueous solution ion exchange method. For example, the alumina coated monolith is ion exchanged from one to four times with an aqueous solution of Ca cation. In the present invention, a (Ca(NO₃)₂) solution is preferred. The ion exchanges are preferably carried out at room temperature with solutions of 0.5 mol/l. After each solution ion exchange step, the coated monolith is preferably washed, dried, and calcined at about 773° K for about 4 hours prior to performing the next ion exchange step.

[0050] Precious metal catalysts are then added to the washcoated monolith. Preferred for use in the present invention are Pt and Rh, which may be added at loadings of about 100 g Pt/ft³ and 20 g Rh/ft³. The precious metals may be loaded onto the alumina coated monolith by conventional methods such as the Subtractive Deposition Method, which

includes 1) measuring the volume of the monolith and calculating the amount (Mp) of precious metal compound (e.g. H_2PtCl_6) needed for the monolith to reach a certain precious metal loading (e.g. 100 g Pt/ft³); 2) measuring the total volume ($V_{\text{H}_2\text{O}}$) of water than can be absorbed by the washcoat onto the monolith at room temperature; 3) preparing a solution of the precious metal compound with the concentration $\text{Mp}/V_{\text{H}_2\text{O}}$; 4) dipping the monolith into the prepared solution with a total volume of 2.5 times $V_{\text{H}_2\text{O}}$ at room temperature, wetting the monolith thoroughly, blowing away the residual solution and drying the monolith at 130° C. for 1 hour; and 5) where the precious metal compounds contain chlorine, removing the chlorine (Cl^-) at 500° C. in a flow reactor with a mixed gas of 1% H_2 and 10% H_2O balanced by nitrogen for 4 hours. Where more than one precious metal is loaded onto the same monolith, the procedure is repeated.

[0051] Conventional lean NO_x traps for use in the system of the present invention are well known in the art and typically include one or more precious metals and an alkali metal oxide or alkaline earth metal oxide (typically barium) supported on an alumina binder material.

[0052] Referring now to **FIG. 1**, the LNT system **10** of the present invention is illustrated, which, in a preferred embodiment, includes a first alumina-based LNT **12** and a second alumina-based LNT **14**. It should be appreciated that in embodiments where two or more alumina-based traps are included in the system, the amount of metal oxide included in each of the traps may vary so as to achieve an optimization of the temperature windows of each LNT with maximum NO_x conversion efficiency. For example, the first trap may contain 0 wt. % Ba and the second trap may contain 2.0 wt. % Ba. This optimization may also be achieved by the positions of the traps and/or by varying the inlet temperatures.

[0053] As shown, the second LNT is positioned downstream from the first LNT. The first and second traps are positioned within the engine exhaust system such that they are exposed to different vehicle exhaust temperatures. When the first LNT reaches its upper temperature limit for high NO_x conversion efficiency, the second LNT is just entering its own effective temperature window for NO_x conversion. Thus, the system's operational temperature window for NO_x conversion efficiency is extended over that of a single LNT, from about 150 to 300° C. (single LNT) to about 150 to 500° C. (two or more LNTs).

[0054] It should be appreciated that for specific diesel aftertreatment systems, a diesel particulate filter (DPF) **16** is preferably included in the system. The filter **16** may be located either between the first and second LNTs as shown, or it may be positioned in front of the first LNT.

[0055] In this arrangement, the upstream trap **12** functions as both a NO_x and SO_x trap, capturing and reducing the NO_x in its active temperature window and capturing substantially all of the SO_x produced by the engine in lean condition, while the downstream trap **14** functions only as a LNT. When the upstream trap requires desulphurization, the exhaust temperature is increased and the engine is operated in rich condition as described in further detail below.

[0056] In an alternative embodiment illustrated in **FIG. 2**, the first LNT is an alumina-based LNT **12** and the second

LNT is a conventional LNT **18**, where the second LNT is positioned downstream from the first LNT.

[0057] In yet another embodiment of the invention illustrated in **FIG. 3**, the first LNT comprises an alumina-based LNT and the second LNT comprises a conventional LNT, where the first and second LNTs are combined. This may be achieved by coating a single catalyst brick with two different LNT compositions in two separate zones. For example, the front zone may comprise the alumina-based LNT composition and the rear zone may comprise a conventional LNT composition. In the embodiment shown, the alumina-based LNT is positioned in front of the conventional LNT; however, it should be appreciated that the conventional LNT may also be positioned in front of the alumina-based LNT. It should be appreciated that while this system can undergo conventional desulphurization, it cannot undergo the unique desulphurization procedure of the present invention. However, this arrangement is still advantageous in that it can extend the temperature window of operation from 150° C. to 500° C. (compared with a conventional LNT temperature window of 200° C. to 500° C.).

[0058] In yet another embodiment of the invention illustrated in **FIG. 4**, the system comprises a first alumina-based LNT and a second conventional LNT positioned downstream from the alumina-based LNT. In this embodiment, the system preferably includes a bypass exhaust line **22** which allows exhaust gas to be directed through the conventional LNT during normal vehicle operation but which diverts exhaust around the LNT during desulphurization of the alumina-based LNT as will be explained in further detail below. The system preferably further includes a valve or other switching device **24** which controls opening and closing of the bypass line. This configuration allows the system to undergo desulphurization.

[0059] In yet another embodiment of the invention illustrated in **FIG. 5**, the system comprises multiple LNTs including a first alumina-based LNT **12**, a second alumina-based LNT **14**, and a third alumina-based LNT **26** to cover a wider operational temperature window and to allow the system to undergo desulphurization as efficiently as a single alumina-based LNT. While the system illustrated includes three alumina-based LNTs, it should be appreciated that additional LNTs may be included in the system as long as they are capable of performing in the required temperature range.

[0060] In use, the system of the present invention including at least one alumina-based LNT is placed in the exhaust of a vehicle having a lean burn engine which can operate under fuel lean/rich conditions and which contains NO_x . The system is exposed to the exhaust gas such that at least a portion of the NO_x in the gas is converted to N_2 , preferably at a temperature between about 150° C. and 500° C. The NO_x conversion may be regulated by suitable control of λ as will be described in the Examples below.

[0061] It should be noted that the NO_x conversion efficiency of the system (comprising a single alumina-based LNT, multiple alumina-based LNTs, or an alumina-based LNT and a conventional LNT) is also affected by the lean/rich times (8/2, 16/4 and 24/6), even though the ratio of the lean time versus the rich time is fixed. For example, at low temperature (<200° C.), the cycle of 8 second lean and 2 second rich leads to higher NO_x conversion efficiencies,

while the NO_x conversion efficiency is lower under this cycle at higher temperature ($>200^\circ\text{C}$). This is unique for the alumina-based LNT due to its fast release of NO_x (<2.0 seconds) during the rich cycle, which is quite different from a conventional (BaO-based) LNT. Therefore, adjusting the lean and rich times without changing the ratio of the lean/rich cycle (no change of the fuel penalty) at different temperatures can improve the NO_x reduction efficiency of the LNT system of the present invention. By obtaining feedback of the NO_x conversion efficiency of the LNT system of the present invention in a real vehicle application, the lean/rich cycle times can be automatically adjusted to the most optimal conditions for the highest NO_x reduction efficiency without extra fuel penalty. For example, a device which measures NO_x concentration, such as a NO_x sensor (not shown), may be positioned downstream from the LNT system which provides feedback (via a computer or other device) to allow adjustment of the lean/rich cycle times. Such a sensor may be placed in the exhaust manifold to measure the engine out NO_x concentration as illustrated in commonly assigned U.S. Pat. No. 6,698,191, the disclosure of which is hereby incorporated by reference.

[0062] In addition, a desulphurization (de- SO_x) process may be performed on the system illustrated in **FIGS. 1, 4** and **5**. A desulphurization process should be performed when the sulfur content on the alumina-based LNT reaches a certain threshold level. This threshold level is determined by the amount of SO_x storage materials in the first trap, the temperature, the inlet SO_x level, the duration of rich time in the lean/rich cycles, the exhaust gas flow rate, the operating history of the trap, etc. The de- SO_x timing may also be determined by a SO_x sensor (not shown) which may be positioned downstream from the first alumina-based LNT.

[0063] The alumina-based trap of the present invention has a unique desulphurization procedure which is believed to occur because of the weak interaction between the SO_x and the alumina-based storage materials of the LNT. The release of sulfur from the alumina-based trap is very efficient and provides the advantage of minimum thermal exposure and fuel penalty during desulphurization over the use of a conventional LNT alone.

[0064] Referring to **FIGS. 1 and 5**, during the desulphurization process, exhaust gases in the alumina-based LNT **12** are heated through appropriate methods of engine control to a temperature of about 650°C . for at least 40 seconds, and more preferably for about 40 to 120 seconds under slightly rich condition ($\lambda < 1.0$, and more preferably, between about 0.98 and 0.99). The resulting de- SO_x product is comprised mainly of SO_2 (more than 90 wt %), which is a more favorable sulfur product than the H_2S product typically achieved with de- SO_x of a conventional LNT. As no sulfur passes through the first LNT during lean operation and the second (and third) alumina-based NO_x trap(s) don't trap sulfur under rich conditions (de- SO_x , etc.), there is no desulphurization needed for the second (and optional third) trap(s).

[0065] Where desulphurization is performed on a system having the configuration shown in **FIG. 4**, the same process is followed with the exception that the sulfur-containing exhaust gas is directed around the conventional LNT by the bypass exhaust line **22** during desulphurization. Thus, no sulfur reaches the conventional LNT of the system during

normal lean/rich operation or during desulphurization. Therefore, no desulphurization is needed for the conventional LNT as desulphurization is performed only on the alumina-based trap.

[0066] In order that the invention may be more readily understood, reference is made to the following examples which are intended to illustrate the invention, but not limit the scope thereof.

EXAMPLE 1

[0067] An alumina-based lean NO_x trap (LNT) was prepared in accordance with the present invention using only Pt as the catalyst and was exposed to synthetic exhaust gas at temperatures ranging from about 1000 to 450°C . The composition of synthetic exhaust gas used in the LNT laboratory tests is listed in Table 1 below.

TABLE 1

Gas	Gases used in LNT Lab Test	
	Lean	Rich
CO	500 ppm	4%
H_2	167 ppm	1.33%
C_3H_6	300 ppm C_1	5000 ppm C_1
NO_x	500 ppm	500 ppm
O_2	10%	1%
CO_2	5%	5%
H_2O	5%	5%
	$\lambda = 2.0$	$\lambda = 0.90$

FIG. 6 illustrates the resulting NO_x conversion efficiency under varying conditions in a lean/rich cycle of 24 sec./6 sec. The conditions for the alumina-based LNT included operation under lean conditions at 700°C . for 20 minutes, and an additional 10 minutes under rich conditions at 350°C . As can be seen, the fresh alumina LNT exhibits good NO_x conversion efficiency at low temperatures, but the 700°C . lean treatment causes the NO_x activity to deteriorate. The rich treatment at 350°C . does not restore the activity.

EXAMPLE 2

[0068] An alumina-based LNT was prepared in accordance with the present invention using both Pt and Rh as catalysts. The trap was exposed to exhaust gas at temperatures ranging from about 100 to 450°C . **FIG. 7** illustrates the NO_x conversion efficiency under varying conditions in a lean/rich cycle of 24 s/6 s. The conditions for the alumina-based LNT included operation under lean conditions at 700°C . for 20 minutes and an additional 10 minutes under rich conditions at 350°C .

[0069] As can be seen, the fresh alumina-based LNT has good NO_x conversion efficiency at low temperatures, and the 700°C . lean treatment causes the NO_x activity to deteriorate, but the rich treatment at 350°C . largely restores the activity. It can be concluded that the combination of Pt and Rh catalysts is preferred for use in the alumina-based LNT of the present invention.

[0070] **FIG. 8** illustrates the NO_x storage capacities of the alumina-based LNTs of the present invention, with either pure alumina or alumina with added CaO comprising about 2 wt % of the total washcoat, compared with a conventional barium oxide-based LNT at different temperatures under a

lean/rich cycle of 10 minutes/3 minutes (the gas compositions are listed in Table 1 except no HC and CO in lean condition, no O₂ in rich condition, and 500 ppm NO₂ instead of NO).

[0071] The pure alumina-based LNT demonstrates high NO_x storage at relatively low temperatures (below 200° C.), the conventional, barium oxide-based LNT has high NO_x storage at higher temperatures (200 to 400° C.), and the alumina-based LNT with 2 wt % CaO shows high NO_x storage at temperatures ranging from 150 to 250° C. These results correlate to the NO_x reduction activities of these LNTs at different temperatures.

[0072] FIG. 9 illustrates the NO_x conversion efficiency of the alumina-based LNT (without any alkaline earth metal oxide) of the present invention using both Pt and Rh under varying lean/rich cycle times, such as 24/6 and 16/4 compared with a conventional LNT (24/6). Although the lean/rich ratio is not changed, the NO_x conversion efficiency of the alumina LNT of the present invention exhibits better efficiency at low temperatures (150° C.) with a shorter cycle time (16/4) than with the longer cycle time (24/6).

[0073] Also as can be seen, the alumina-based LNT of the present invention exhibits better NO_x conversion efficiency at temperatures below 200° C. than the conventional LNT.

[0074] FIG. 10 illustrates NO_x conversion efficiency of the alumina LNTs of the present invention with and without adding calcium oxide (less than 2.0 wt % through ion exchange) under varying lean/rich cycle times. The temperature window of active NO_x conversion is slightly shifted up by the addition of a very small amount of calcium oxide through ion exchange. However, the high NO_x reduction activity of the alumina-based LNT at low temperatures is not changed much since the alumina is still the dominant NO_x storage material in the LNT.

EXAMPLE 3

[0075] An alumina-based LNT was prepared in accordance with the present invention using both Pt and Rh as catalysts and was exposed to 30 ppm SO₂ at 200° C. to 450° C. and $\lambda=2.0$ for 3200 seconds. A desulphurization (de-SO_x) treatment was then performed at 650° C. under slightly rich conditions. FIG. 11 illustrates the de-SO_x process of the alumina LNT at 650° C. and $\lambda=0.987$. The sulfur loading was 1.14 g per liter and the desulphurization started at t=5500 seconds. More than 95% by weight of the sulfur was released in about 60 seconds as SO₂. Similar efficient desulphurization properties were shown when the alumina-based LNT was modified by a very small amount (less than 2.0 wt %) of calcium oxide through solution ion exchange as shown in FIG. 12.

[0076] FIG. 13 compares the de-SO_x performance of the alumina-based LNT of the present invention with a conventional LNT comprised of Ba oxide supported on alumina as the NO_x storage material with similar sulfur loading (1.14 g/liter). The conventional LNT was heated from 650 to 850° C. at 5° C./min. with a 5 s/15 s lean/rich cycle (λ of 2.0/0.9).

[0077] It is clear that the desulphurization of the alumina-based LNT of the present invention is much more efficient (95 wt % S released in about 60 seconds) than that of the conventional LNT (95 wt % S release in more than 20 minutes). The alumina-based LNT of the present invention

demonstrates a big advantage in terms of both minimum thermal exposure and fuel penalty during desulphurization over the conventional LNT. The desulphurization process of the alumina-based LNT causes almost no deactivation. Moreover, the product from the conventional LNT desulphurization process is mainly H₂S, which is toxic and has an objectionable smell.

EXAMPLE 4

[0078] A LNT system comprised of an alumina-based LNT using both Pt and Rh as catalysts positioned in front of a conventional (barium oxide-based) LNT was evaluated at different inlet temperatures. FIG. 14 illustrates the NO_x conversion of this system (configured as in FIG. 2) versus inlet gas temperature under different lean/rich cycles. The system demonstrates high NO_x conversion over a wide temperature window (150 to 450° C.).

[0079] This system was also loaded with sulfur at 1.14 g/liter and subjected to desulphurization as described in Example 3. FIG. 15 illustrates the gas compositions released from the system (after the conventional LNT) during the desulphurization. When compared with FIG. 13, it is clear that the large amount of SO₂ released from the alumina-based LNT didn't pass through the conventional LNT or was re-captured by the conventional LNT downstream. Therefore, the unique de-SO_x process for the alumina-based LNT does not work for this LNT system.

[0080] However, it should be noted that when the exhaust gas is diverted through a bypass line without passing the conventional LNT during the desulphurization, as illustrated in FIG. 4, this LNT system can take advantage of the unique efficient desulphurization of the alumina-based LNT of the present invention.

EXAMPLE 5

[0081] A LNT system was prepared comprising two alumina-based LNTs in accordance with the present invention which were spatially separated to cover a wide inlet temperature window. FIG. 16 illustrates the NO_x conversion versus the inlet temperature of the first LNT system (the inlet temperature difference of the two was about 150° C.). This LNT system largely expanded the NO_x reduction temperature window compared with that of a single alumina-based LNT. This LNT system was also loaded with sulfur (only on the first LNT) at 1.14 g/l and underwent desulphurization at 650° C. under slightly rich conditions as in Example 3. FIG. 17 demonstrates the desulphurization of this system. Although the inlet temperature of the second LNT is relatively low (280° C.), sulfur still passed through the second (downstream) alumina-based LNT. Therefore, this system can take the advantage of the unique efficient desulphurization of the alumina-based LNT as well as have a wide NO_x reduction temperature window.

[0082] It should be noted that for specific diesel aftertreatment applications, a diesel particulate filter (DPF) may be located after the first alumina-based LNT. Whether such an alumina-based LNT system can still take advantage of the unique efficient desulphurization of the alumina-based LNT depends on whether the sulfur products that are released from the first alumina-based LNT during desulphurization can pass through the DPF, especially a catalyzed DPF which is coated with a highly oxidizing catalyst system. A catalyst

with a similar formulation as the catalyzed DPF was included between the two alumina-based LNTs (configured as in **FIG. 1**). Such a system was loaded with sulfur (1.14 g/liter) and heated to 650° C. for de-SO_x at slightly rich condition as in Example 3, and the results are shown in **FIG. 18**. It is clear that the sulfur products (mainly SO₂) coming out of the first alumina-based LNT can pass through the catalyzed DPF and then the second alumina-based LNT. Accordingly, the LNT system comprising multiple alumina-based LNTs with a DPF (including a catalyzed DPF) can also remove sulfur in the same efficient way as an alumina-based LNT.

[0083] Referring to **FIGS. 9, 10, 14** and **16**, it can be seen that the NO_x conversion efficiency of the system of the present invention may be improved by adjusting the lean/rich times (8/2, 16/4 and 24/6).

[0084] While certain representative embodiments and details have been shown for purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes in the methods and apparatus disclosed herein may be made without departing from the scope of the invention, which is defined in the appended claims.

What is claimed is:

1. A lean NO_x trap system for use in a lean burn engine exhaust comprising:

a first lean NO_x trap comprising a catalyst, a NO_x absorbent material comprising alumina, and optionally, an alkaline earth metal oxide; and

a second lean NO_x trap; wherein said system converts at least a portion of NO_x contained in exhaust gas from said engine to N₂ at a temperature range of between about 150° C. to about 500° C.

2. The system of claim 1 wherein said first lean NO_x trap comprises from 0 to about 4.0 wt % of said alkaline earth metal oxide.

3. The system of claim 1 wherein said second lean NO_x trap comprises a catalyst, a NO_x absorbent material comprising alumina, and optionally, from 0 to about 4 wt % an alkaline earth metal oxide.

4. The system of claim 1 wherein said second lean NO_x trap comprises a catalyst and from about 20 to 35 wt % of a metal oxide on an alumina or silica support.

5. The system of claim 1 wherein said catalyst in said first lean NO_x trap is selected from platinum, rhodium, and combinations thereof.

6. The system of claim 1 having a conversion efficiency of at least 50% at a temperature between about 150° C. to about 500° C.

7. The system of claim 1 wherein said first lean NO_x trap further includes less than about 4 wt % of a stabilizing metal selected from La, Ce, and Ba.

8. The system of claim 1 wherein said alkaline earth metal is selected from Mg, Sr, Ba, and Ca.

9. The system of claim 1 further including a third lean NO_x trap comprising a catalyst, a NO_x absorbent material comprising alumina, and optionally, from 0 to about 4 wt % of an alkaline earth metal oxide.

10. A lean NO_x trap system for use in a lean burn engine exhaust comprising:

a first lean NO_x trap comprising a catalyst, a NO_x absorbent material comprising alumina, and from 0 to about 4.0 wt % of an alkaline earth metal oxide; and

a second lean NO_x trap comprising a catalyst, a NO_x absorbent material comprising alumina, and from 0 to about 4.0 wt % of an alkaline earth metal oxide.

11. The system of claim 10 wherein said second lean NO_x trap is positioned downstream from said first lean NO_x trap.

12. The system of claim 10 further including a diesel particulate filter.

13. The system of claim 10 further including a third lean NO_x trap comprising a catalyst, a NO_x absorbent material comprising alumina, and from 0 to about 4.0 wt % of an alkaline earth metal oxide.

14. The system of claim 13 wherein said third lean NO_x trap is positioned downstream from said second lean NO_x trap.

15. A method for treating lean burn engine exhaust gases comprising:

providing a lean NO_x trap system in an exhaust gas passage of a lean burn engine, said system comprising at least first and second lean NO_x traps; wherein said first lean NO_x trap comprises a catalyst, a NO_x absorbent material comprising alumina, and optionally, from 0 to about 4 wt % of an alkaline earth metal oxide; and

exposing said lean NO_x trap system to engine exhaust gas containing NO_x such that at least a portion of said NO_x contained in said exhaust gas is converted to N₂ at a temperature between about 150° C. to 500° C.

16. The method of claim 15 wherein said system provides a conversion efficiency of at least 50% at a temperature between about 150° C. to about 500° C.

17. The method of claim 16 wherein said engine exhaust gas is subjected to a fixed lean time/rich time ratio (x/y=R), and wherein the NO_x conversion efficiency is increased by reducing x and y at a temperature of about 150 to 200° C.

18. The method of claim 17 including sensing the concentration of NO_x in said exhaust gas and adjusting the lean/rich cycle of said engine to increase said NO_x conversion efficiency.

19. The method of claim 15 wherein said NO_x in said first lean NO_x trap is converted at a temperature of between about 150° C. to about 350° C.

20. The method of claim 15 wherein said NO_x in said second lean NO_x trap is converted at a temperature of between about 150° C. to about 350° C.

21. The method of claim 15 wherein said second lean NO_x trap is positioned downstream from said first lean NO_x trap.

22. The method of claim 15 wherein said first lean NO_x trap is positioned downstream from said second lean NO_x trap.

23. The method of claim 15 wherein said first lean NO_x trap and said second lean NO_x trap are combined.

24. The method of claim 15 wherein said second lean NO_x trap comprises a catalyst, a NO_x absorbent material comprising alumina, and optionally, from 0 to about 4 wt % of an alkaline earth metal oxide.

25. The method of claim 15 wherein said second lean NO_x trap comprises a catalyst and from about 20 to 35 wt % of a metal oxide on an alumina or silica support.

26. A method for desulphurization of a lean NO_x trap system in a lean burn engine comprising:

providing a lean NO_x trap system including a first lean NO_x trap comprising a catalyst, a NO_x absorbent material^{*} comprising alumina, and optionally, an alkaline earth metal oxide; and a second lean NO_x trap positioned downstream from said first lean NO_x trap; said system being positioned in the exhaust passage of said engine such that it is exposed to exhaust gases therein; and

heating said exhaust gases in said first lean NO_x trap to a temperature of between about 550° C. and about 650° C. for at least 40 seconds.

27. The method of claim 26 wherein said first lean NO_x trap comprises from 0 to about 4 wt % of said alkaline earth metal oxide.

28. The method of claim 26 wherein said second lean NO_x trap comprises a catalyst, a NO_x absorbent material com-

prising alumina, and optionally, from 0 to 4 wt % of an alkaline earth metal oxide.

29. The method of claim 26 wherein said second lean NO_x trap comprises a catalyst and from about 20 to 35 wt % of a metal oxide on an alumina or silica support.

30. The method of claim 26 wherein said system further includes a bypass exhaust line for directing exhaust gas through said second lean NO_x trap during normal vehicle operation but which diverts exhaust gas around said second lean NO_x trap during desulphurization of said first lean NO_x trap.

31. The method of claim 26 wherein during desulphurization, λ is between about 0.98 to about 0.99.

32. The method of claim 26 wherein said exhaust gases are heated for about 40 to 120 seconds.

33. The method of claim 26 wherein said desulphurization of said lean NO_x trap system produces a sulfur product comprising at least 90% SO₂.

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