

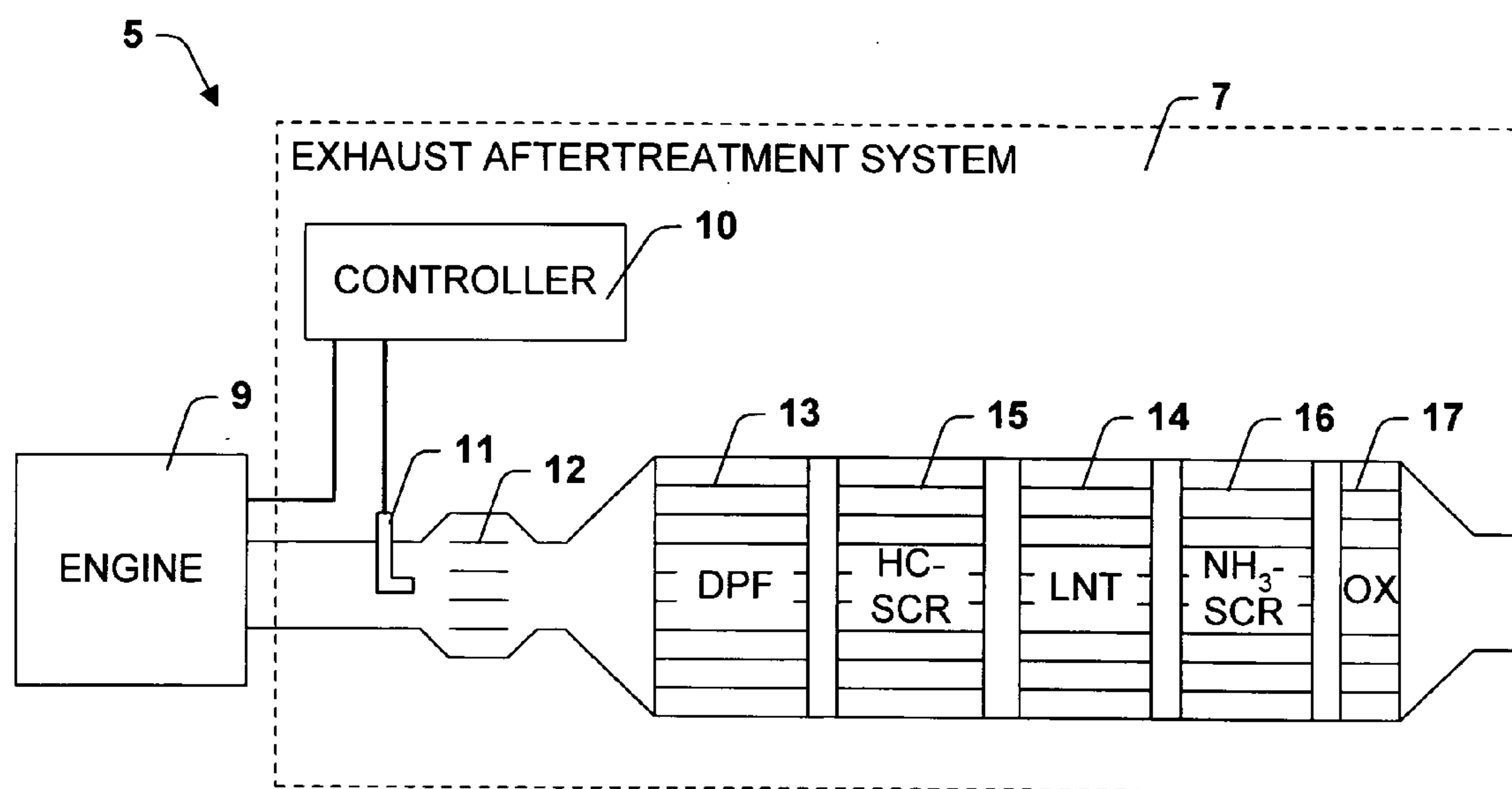
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(19) **United States**(12) **Patent Application Publication**
Hu(10) **Pub. No.: US 2007/0012032 A1**(43) **Pub. Date: Jan. 18, 2007**(54) **HYBRID SYSTEM COMPRISING HC-SCR,
NOX-TRAPPING, AND NH₃-SCR FOR
EXHAUST EMISSION REDUCTION**(52) **U.S. Cl. 60/286; 60/295; 60/301**(75) **Inventor: Haoran Hu, Novi, MI (US)**

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F01N 3/10 (2006.01)(57) **ABSTRACT**

An exhaust aftertreatment system is provided with a first SCR catalyst, a NO_x adsorber-catalyst, and an ammonia-SCR catalyst. The first catalyst is generally a hydrocarbon-SCR catalyst, but can be a carbon monoxide-SCR catalyst or a hydrogen-SCR catalyst. The first catalyst is functional to reduce NO_x in lean exhaust using the corresponding reductant. The NO_x adsorbant-catalyst is functional to adsorb NO_x and to produce ammonia during regeneration. The ammonia SCR catalyst is configured to adsorb ammonia so produced and is functional to subsequently use that ammonia to reduce NO_x in lean exhaust. The first SCR catalyst is useful to reduce the frequency with which the NO_x adsorber-catalyst needs to be regenerated, and can thereby extend the life of that catalyst. In one embodiment, reductant for the first SCR catalyst is stored during regeneration of the NO_x adsorber-catalyst and is used to convert additional NO_x in a subsequent lean phase.



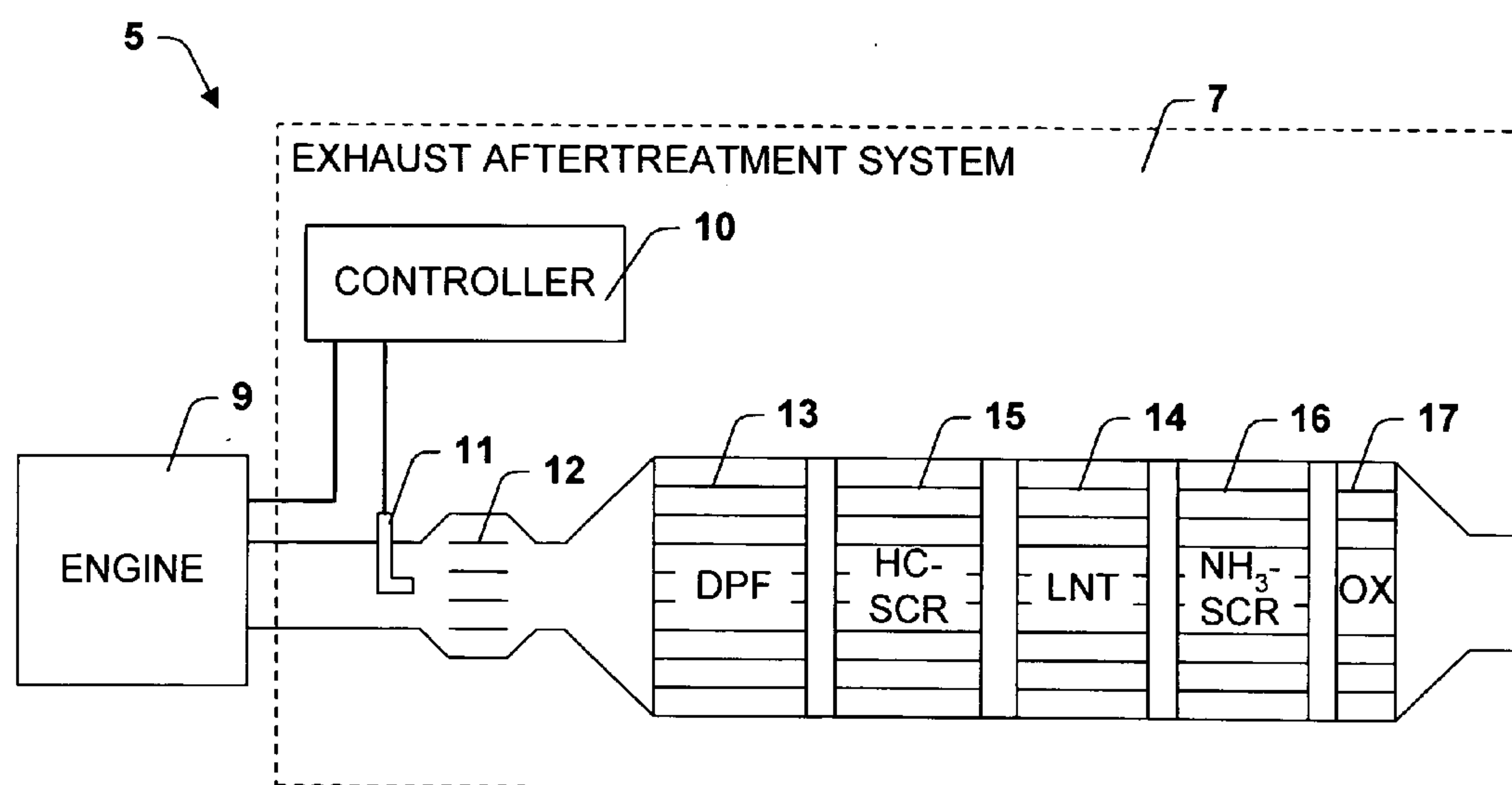


Fig. 1

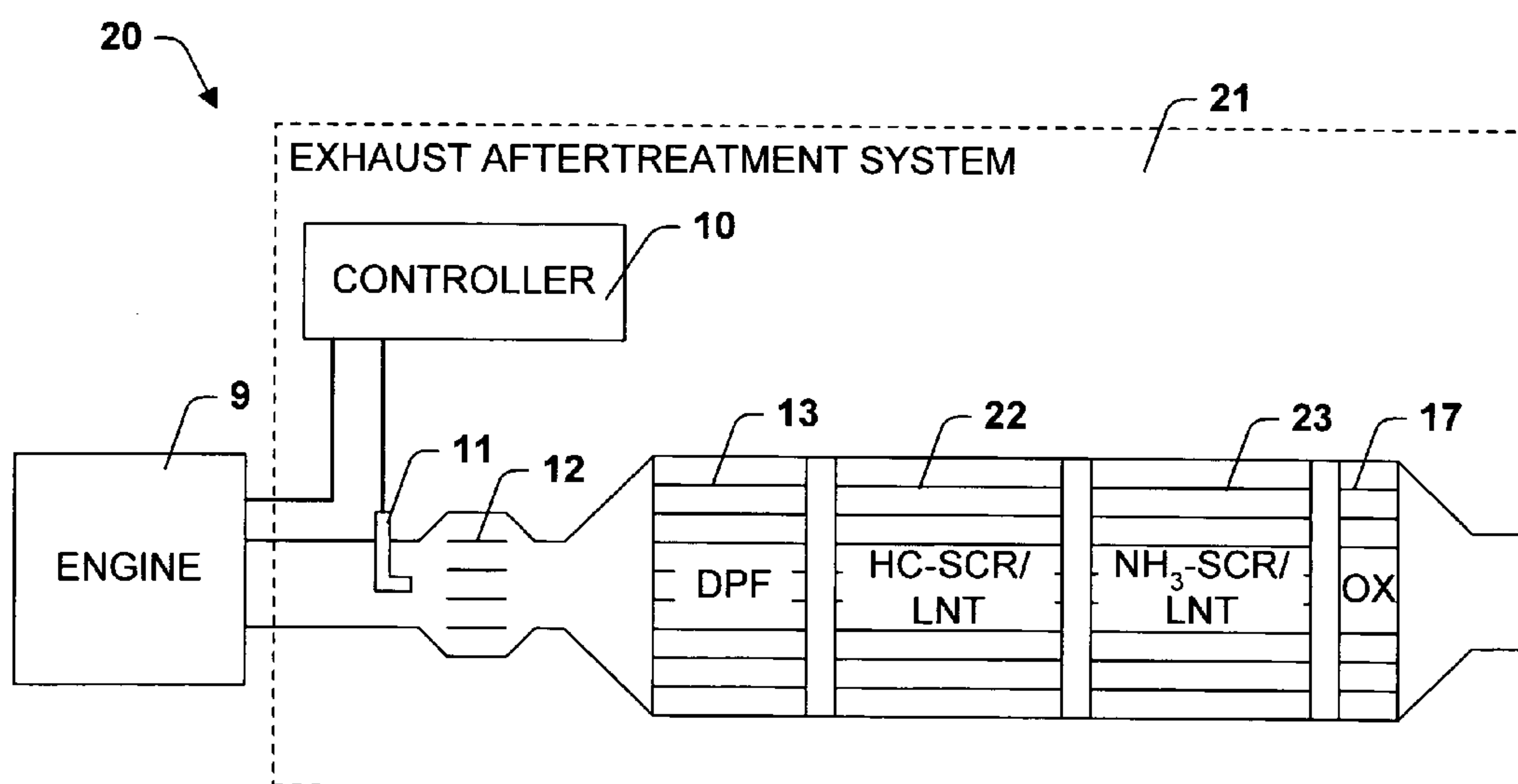


Fig. 2

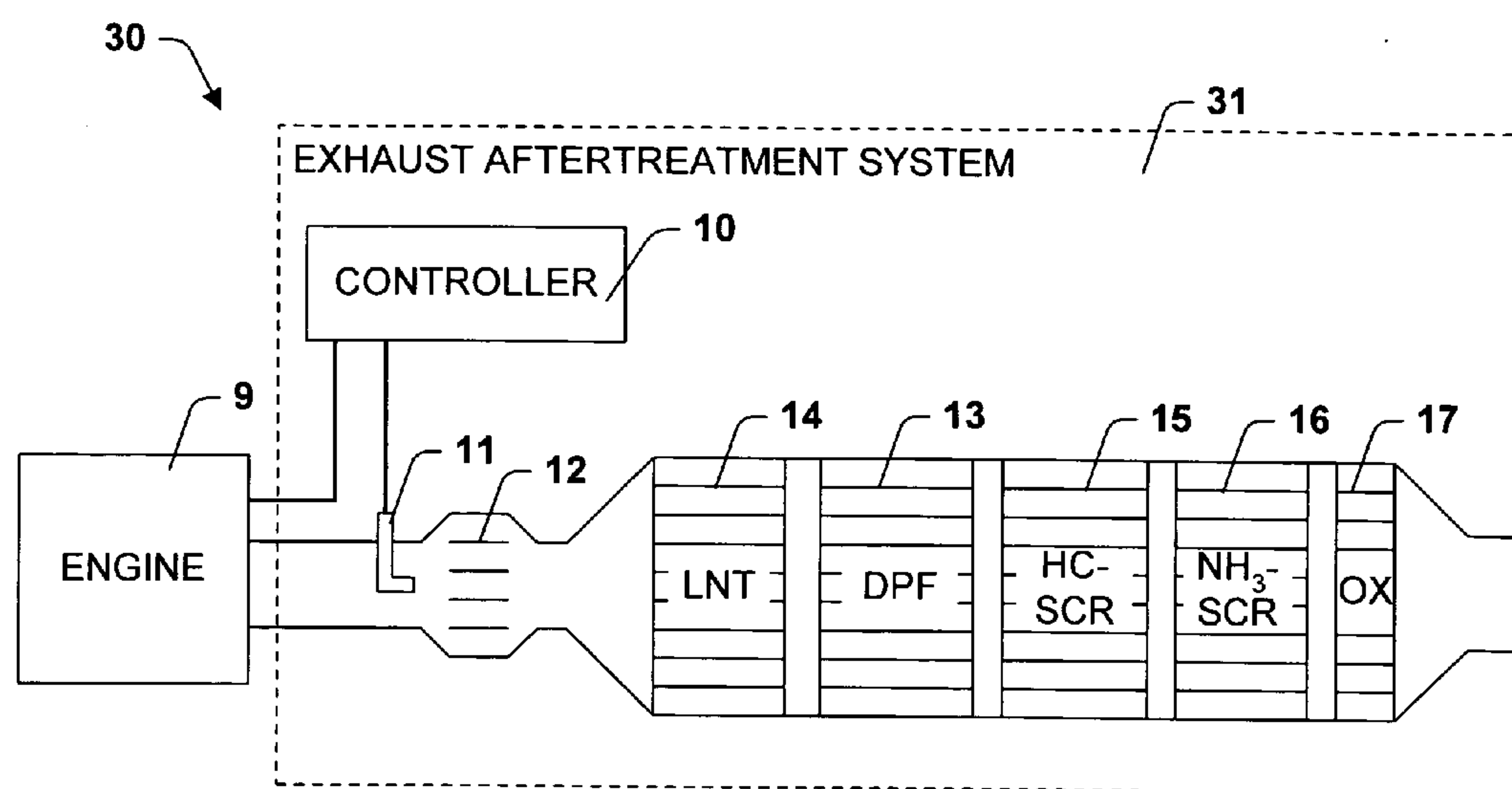


Fig. 3

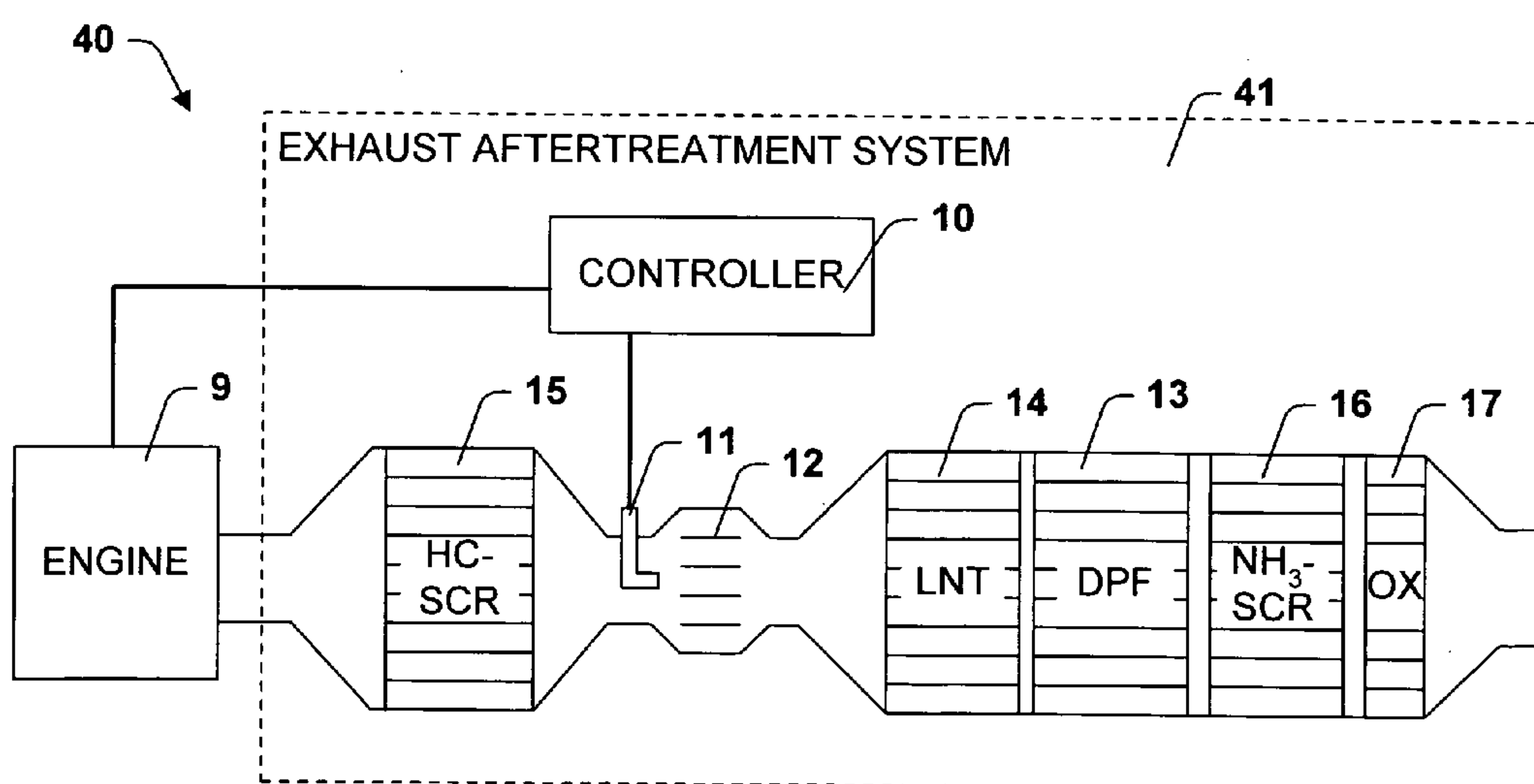


Fig. 4

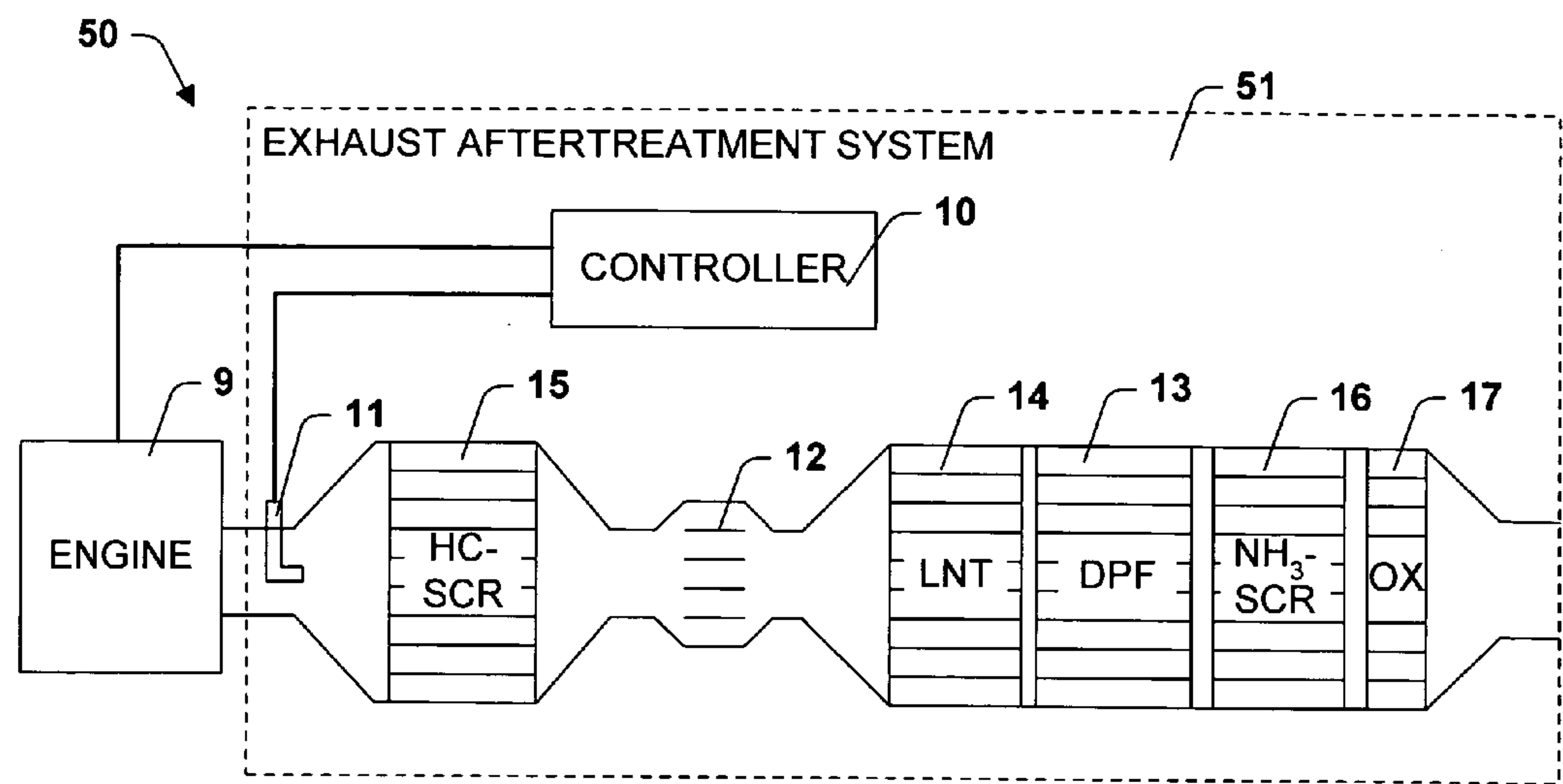


Fig. 5

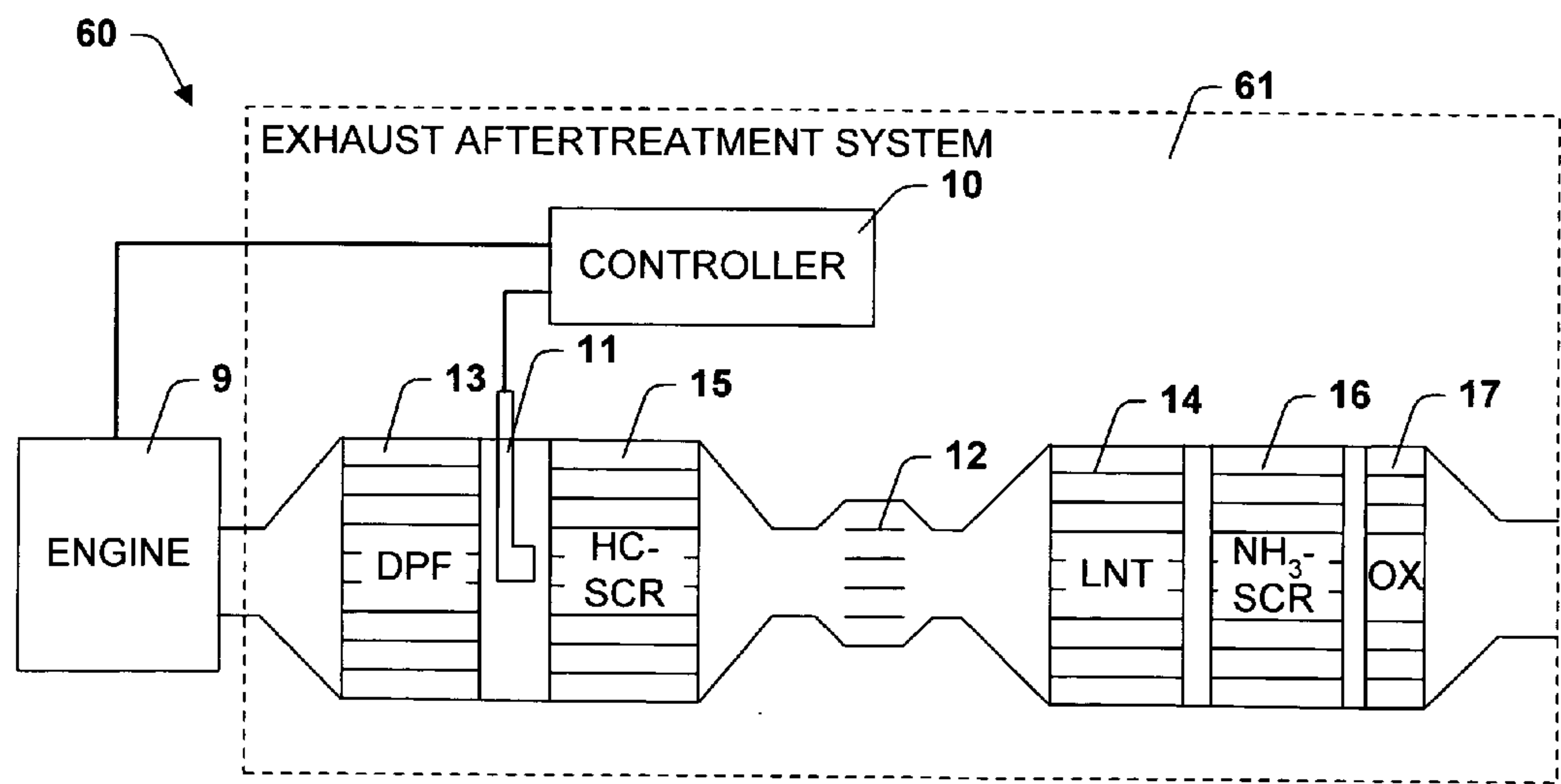


Fig. 6

HYBRID SYSTEM COMPRISING HC-SCR, NOX-TRAPPING, AND NH3-SCR FOR EXHAUST EMISSION REDUCTION

FIELD OF THE INVENTION

[0001] The present invention relates to pollution control systems and methods for diesel engines.

BACKGROUND

[0002] NO_x emissions from diesel engines are an environmental problem. Several countries, including the United States, have long had regulations pending that will limit NO_x emissions from trucks and other diesel-powered vehicles. Manufacturers and researchers have already put considerable effort toward meeting those regulations.

[0003] In gasoline powered vehicles that use stoichiometric fuel-air mixtures, three-way catalysts have been shown to control NO_x emissions. In diesel-powered vehicles, which use compression ignition, the exhaust is generally too oxygen-rich for three-way catalysts to be effective.

[0004] Several solutions have been proposed for controlling NO_x emissions from diesel-powered vehicles. One set of approaches focuses on the engine. Techniques such as exhaust gas recirculation and partially homogenizing fuel-air mixtures are helpful, but these techniques alone will not eliminate NO_x emissions. Another set of approaches remove NO_x from the vehicle exhaust. These include the use of lean-burn NO_x catalysts, selective catalytic reduction (SCR), and lean NO_x traps (LNTs).

[0005] Lean-burn NO_x catalysts promote the reduction of NO_x under oxygen-rich conditions. Reduction of NO_x in an oxidizing atmosphere is difficult. It has proved challenging to find a lean-burn NO_x catalyst that has the required activity, durability, and operating temperature range. Currently, peak NO_x conversion efficiencies for lean-burn catalysts are unacceptably low. The introduction of a reductant, such as diesel fuel, into the exhaust is generally required and introduces a fuel economy penalty of 3% or more.

[0006] Ammonia-SCR refers to selective catalytic reduction of NO_x by ammonia. Often, this is referred to simply as SCR. The reaction takes place even in an oxidizing environment. The NO_x can be temporarily stored in an adsorbant or ammonia can be fed continuously into the exhaust. SCR can achieve high levels of NO_x reduction, but there is a disadvantage in the lack of infrastructure for distributing ammonia or a suitable precursor. Another concern relates to the possible release of ammonia into the environment.

[0007] LNTs are NO_x adsorbers combined with catalysts for NO_x reduction. The adsorbant is typically an alkaline earth oxide adsorbant, such as BaCO₃ and the catalyst is typically a precious metal, such as Pt or Ru. In lean exhaust, the catalyst speeds oxidizing reactions that lead to NO_x adsorption. Accumulated NO_x is removed by creating a rich environment within the LNT through the introduction of a reductant. In a rich environment, the catalyst activates reactions by which adsorbed NO_x is reduced and desorbed, preferably as N₂.

[0008] A LNT must periodically be regenerated to remove accumulated NO_x. This type of regeneration may be referred to as denitration in order to distinguish desulfation,

described below. The conditions for denitration can be created in several ways. One approach uses the engine to create a rich fuel-air mixture. For example, the engine can inject extra diesel fuel into the exhaust of one or more cylinders prior to expelling the exhaust. Reductant may also be injected into the exhaust downstream of the engine. In either case, a portion of the reductant is generally expended to consume excess oxygen in the exhaust.

[0009] Reductant can consume excess oxygen by either combustion or reforming reactions. Typically, the reactions take place upstream of the LNT over an oxidation catalyst or in a reformer. The reductant can also be oxidized directly in the LNT, but this tends to result in faster thermal aging.

[0010] U.S. Pat. Pub. No. 2003/0101713 describes an exhaust system with a fuel reformer placed inline with the exhaust and upstream of an LNT. The reformer includes both oxidation and reforming catalysts. The reformer both removes excess oxygen and converts the diesel fuel reductant into more reactive reformate.

[0011] In addition to accumulating NO_x, LNTs accumulate SO_x. SO_x is the combustion product of sulfur present in ordinarily diesel fuel. Even with reduced sulfur fuels, the amount of SO_x produced by diesel combustion is significant. SO_x adsorbs more strongly than NO_x and necessitates a more stringent, though less frequent, regeneration. Desulfation requires elevated temperatures as well as a reducing atmosphere. The elevated temperatures required for desulfation can be produced by oxidizing reductant.

[0012] A NO_x adsorber-catalyst can produce ammonia during denitration. The ammonia can be captured by a downstream SCR catalyst for subsequent use in reducing NO_x, thereby improving conversion efficiency over a stand-alone NO_x adsorber-catalyst with no increase in fuel penalty or precious metal usage. U.S. Pat. No. 6,732,507 describes a system with an ammonia SCR catalyst configured downstream of a LNT for this purpose. U.S. Pat. Pub. No. 2004/0076565 describes such systems wherein both components are encased by a single shell and/or co-disbursed. WO 2004/090296 describes such a system wherein there is an inline reformer upstream of the NO_x adsorber-catalyst and the SCR catalyst.

[0013] U.S. Pat. No. 5,727,385 describes a system in which a hydrocarbon-SCR (HC—SCR) catalyst is configured upstream of an LNT. The two components together are said to provide higher NO_x conversion than either of the components individually.

[0014] U.S. Pat. No. 6,677,264 describes a combined LNT/HC—SCR catalyst. The catalyst comprises two layers on a support. The first layer is a NO_x adsorber-catalyst and the second layer is an HC—SCR catalyst having a HC-storing function provided by a zeolite. The HC-storage function is intended to concentrate hydrocarbon reductants in the vicinity of the catalyst and thereby increase activity.

[0015] U.S. Pat. No. 6,202,407 describes an HC—SCR catalyst that has a hydrocarbon-storing function. In one embodiment, a diesel fuel reductant supply is pulsed and the catalyst continues to show activity for extended periods between the pulses.

[0016] In spite of advances, there continues to be a long felt need for an affordable and reliable exhaust treatment

system that is durable, has a manageable operating cost (including fuel penalty), and can practically be used to reduce NOx emissions across the spectrum of diesel engines to a satisfactory extent in the sense of meeting U.S. Environmental Protection Agency (EPA) regulations effective in 2010 and other such regulations.

SUMMARY

[0017] One concept relates to an exhaust aftertreatment system. The system comprises a first SCR catalyst, a NOx adsorber-catalyst, and an ammonia-SCR catalyst. The first catalyst is generally a hydrocarbon-SCR catalyst, but can be a carbon monoxide-SCR catalyst or a hydrogen-SCR catalyst. The first catalyst is functional to reduce NOx in lean exhaust using the corresponding reductant. The NOx adsorbent-catalyst is functional to adsorb NOx from lean exhaust and to produce ammonia during regeneration. The ammonia SCR catalyst is configured to adsorb ammonia so produced and is functional to subsequently use that ammonia to reduce NOx in lean exhaust. The first SCR-catalyst is useful to reduce the frequency with which the NOx adsorber-catalyst needs to be regenerated and can thereby extend the life of that catalyst. In one embodiment, reductant for the first SCR-catalyst is stored during regeneration of the NOx adsorber-catalyst and is used by the first SCR-catalyst to convert additional NOx during a subsequent lean phase.

[0018] Another concept relates to a method of treating NOx-containing lean exhaust. The method includes a first phase in which: the exhaust is contacted with a first SCR catalyst to reduce a portion of the NOx by reactions with a first reductant; the exhaust is contacted with a NOx adsorber-catalyst to remove another portion of the NOx from the exhaust by adsorption; and the exhaust is contacted with an ammonia-SCR catalyst to reduce a further portion of the NOx by reactions with stored ammonia. In a second phase, the environment of the NOx-adsorber catalyst is made rich, whereby stored NOx is reduced. In the process, ammonia is generated and becomes stored in the SCR catalyst. The first reductant can be provided and stored in the second phase, or can be limited to that normally present in the exhaust.

[0019] A further concept relates to a method of treating NOx-containing lean exhaust. The method includes a first phase comprising: contacting the exhaust with a first SCR catalyst to reduce a portion of the NOx by reactions with a stored reductant selected from the group consisting of hydrocarbons, carbon monoxide, and hydrogen; contacting the exhaust with a NOx adsorber-catalyst to remove another portion of the NOx from the exhaust by adsorption; and contacting the exhaust with an ammonia-SCR catalyst to reduce a further portion of the NOx by reactions with stored ammonia. The method also includes a second phase comprising: making the exhaust rich; storing the first reductant in the first SCR catalyst; and reducing NOx stored in the NOx adsorber-catalyst and in the process producing ammonia that becomes stored by the SCR-catalyst.

[0020] The primary purpose of this summary has been to present certain of the inventor's concepts in a simplified form to facilitate understanding of the more detailed description that follows. This summary is not a comprehensive description of every one of the inventor's concepts or every combination of the inventor's concepts that can be consid-

ered "invention". Other concepts of the inventor will become apparent to one of ordinary skill in the art from the following detailed description and annexed drawings. The concepts disclosed herein may be generalized, narrowed, and combined in various ways with the ultimate statement of what the inventor claims as his invention being reserved for the claims that follow.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] FIG. 1 is a schematic illustration of an exemplary power generation system.

[0022] FIG. 2 is a schematic illustration of another exemplary power generation system.

[0023] FIG. 3 is a schematic illustration of a further exemplary power generation system.

[0024] FIG. 4 is a schematic illustration of a further exemplary power generation system.

[0025] FIG. 5 is a schematic illustration of a further exemplary power generation system.

[0026] FIG. 6 is a schematic illustration of a further exemplary power generation system.

DETAILED DESCRIPTION

[0027] FIG. 1 is a schematic illustration of an exemplary power generation system 5. The system 5 comprises an engine 9 and an exhaust aftertreatment system 7. The exhaust aftertreatment system 7 includes a controller 10, a fuel injector 11, a reformer 12, a diesel particulate filter (DPF) 13, a first selective catalytic reduction (SCR) catalyst 15 (illustrated as a hydrocarbon-SCR catalyst), a lean NOx-trap (LNT) 14, an ammonia SCR catalyst 16, and a clean-up oxidation catalyst 17. The controller 10 may be an engine control unit (ECU) that also controls the exhaust aftertreatment system 7 or may include two or more control units that collectively perform these functions. The first SCR catalyst is a catalyst selected from the group consisting of HC-SCR catalysts, CO-SCR catalyst, and hydrogen-SCR catalysts.

[0028] The engine 9 is operational to produce lean exhaust that contains NOx and particulate matter. During normal operation, the fuel injector 11 and the fuel reformer 12 are inactive and exhaust from the engine 9 passes these devices substantially unchanged. The DPF 13 removes most of the particulates from the exhaust. The first SCR catalyst 15 reduces a portion of the NOx by reaction with a first reductant species, if that species is available. The first reductant species is generally one present in the engine exhaust, although in one embodiment the first SCR catalyst 15 has a storage capacity for the first reductant. In the later case and the first reductant may be available from storage. The LNT 14 adsorbs another portion of the NOx. The ammonia-SCR catalyst 16 reduces a further portion of the NOx by reaction with ammonia, if ammonia is available. Where ammonia is available, it is generally ammonia stored in the ammonia-SCR catalyst from a previous regeneration of the LNT 14. The oxidation catalyst 17 may serve to oxidize CO and unburned hydrocarbons remaining in the exhaust.

[0029] From time-to-time, the LNT 14 must be regenerated to remove accumulated NOx. The need or desirability

of regenerating the LNT 14 can be determined in any suitable fashion. In one example, regeneration is begun based on the NOx removal rate falling below acceptable limits. An acceptable limit may involve one or more of a peak NOx concentration, an instantaneous brake-specific NOx emission rate, an average brake-specific NOx emission rate over a period, or a NOx conversion efficiency. In another example, the NOx production rate of the engine 9 is determined by measurement, model, or a combination of the two. The amount of NOx accumulated in the LNT 14 is estimated from this data and compared against an estimated storage capacity for the LNT 14. Regeneration is initiated when the LNT 14 has reached a certain percentage of its estimated storage capacity. In further examples, without limitation, regeneration is based on miles driven or fuel consumed. In general, the time at which to regenerate is determined by the controller 10 and the regeneration process is managed by the controller 10.

[0030] The foregoing control processes generally utilize one or more sensors. A sensor may be used to determine the NOx rate supplied to the LNT 14. Such a sensor is preferably placed just downstream of the HC—SCR catalyst. If the adsorption of the LNT is modeled, a temperature sensor for the LNT 14 is generally used. If the regeneration is based on a NOx conversion efficiency or emission rate, a NOx sensor with generally be placed downstream of the LNT 14, optionally also downstream of the SCR catalyst 16. Additional sensors may be employed to facilitate control over regeneration.

[0031] Regeneration involves starting the reformer 12, consuming excess oxygen in the exhaust, and supplying reformat to the LNT 14. Starting the reformer 12 generally involves heating the reformer 12 to a minimum operational temperature, typically in the range from about 600 to about 700° C. The reformer 12 can be heated by supplying it with diesel fuel at a rate that leaves excess oxygen in the exhaust to fully combust the fuel. Diesel fuel can be injected into the exhaust stream by the fuel injector 11 or the engine 9. Once the reformer 12 is started, diesel fuel is injected at a rate that provides a rich exhaust composition and the diesel fuel that is not combusted by the reformer 12 is generally converted to reformat. The reformer 12 consumes excess oxygen by reforming and/or combusting diesel fuel. The exhaust carries the reformat to the LNT 14.

[0032] In this example, the LNT 14 is regenerated with reformed diesel fuel (reformat). Another suitable reductant can be used instead. Examples of suitable reductants include gasoline, diesel fuel, ammonia, and ammonia precursors.

[0033] In one embodiment, the first reductant is present in the exhaust during regeneration of the LNT 14 and is stored by the first SCR catalyst 15. The first reductant can be the same or different from the reductant used to regenerate the LNT 14. For example, the reductant used by the first SCR catalyst 15 may be hydrocarbon while the LNT 14 is regenerated primarily with hydrogen and CO.

[0034] Where the reductant for the first SCR catalyst 15 is hydrocarbon and the first SCR catalyst 15 has a hydrocarbon storage capacity, it may be desirable to operate the reformer 12 in a way that ensures a large quantity of hydrocarbon is made available to the SCR catalyst 15 for storage. Specifically, it may be desirable to inject diesel fuel into the exhaust at a rate that provides diesel fuel to the reformer 12 at a rate

in excess of the stoichiometric rate based on oxygen sources in the exhaust. Oxygen sources in the exhaust are O₂, H₂O and CO₂. A stoichiometric feed ideally results in all the oxygen source being consumed by reactions that produce syn gas, such as:



wherein CH_{1.85} represents diesel fuel with a 1.85 ratio between carbon and hydrogen. Similar equations can be written for consuming water and carbon dioxide. If diesel fuel is injected at greater than the stoichiometric rate, some hydrocarbons must necessarily break through the reformer 12 to where they can be adsorbed by the first SCR catalyst 15. Ideally, most of the diesel fuel breaking through the reformer 12 is broken down into smaller hydrocarbon molecules that are more easily stored and used.

[0035] The system 7 can achieve high NOx conversions without the first SCR-catalyst 16. The value of this catalyst is in reducing the burden on the LNT 14. By removing some of the NOx, the SCR-catalyst 16 reduces the frequency with which the LNT 14 needs to be denitrated and/or desulfated in order to meet emission requirements. The inventor believes this will extend the life of the LNT 14.

[0036] Without a reductant storage capacity, the first SCR catalyst 15 is expected to remove at least about 10% of the NOx in the exhaust, more preferably at least about 15%, still more preferably at least about 20%. With reductant storage capacity, the first SCR catalyst 15 more easily meets these goals and can potentially meet loftier goals, such as removing at least about 30% or at least about 50% of the NOx produced by the engine 9 during a normal driving cycle.

[0037] From time-to-time, the LNT 14 must be desulfated to remove accumulated SOx. The need or desirability of desulfation can be determined in any suitable fashion. In one example, a NOx sensor downstream of the LNT 14 is used to determine whether the NOx removal rate measured following denitration has fallen below an acceptable limit. In other examples, without limitation, the SOx accumulation is estimated based on miles driven, fuel consumed, or number of denitrations. When SOx has accumulated to an appropriate degree, a full or partial desulfation is initiated. In general, the time at which to desulfate is determined by the controller 10 and the desulfation process is managed by the controller 10.

[0038] Desulfation of the LNT 14 involves starting the reformer 12, heating the LNT 14 to a desulfating temperature, and providing the heated LNT 14 with a reducing atmosphere. A typical desulfation temperature is in the range from about 650 to about 750° C. Below the minimum temperature, desulfation is very slow. Above the maximum temperature, the LNT 14 may be damaged. Preferably, the desulfation temperature is at least about 670° C., more preferably at least about 710° C.

[0039] Normal desulfation temperatures may gradually inactivate the LNT 14. For this reason, measures that reduce the frequency with which desulfation is required or that reduce the required duration for desulfation processes are desirable. One approach is to over-design the system 7, whereby extended intervals between desulfation are permissible. Long periods between desulfation result in high sulfur concentrations. Desulfating with a higher sulfur concentration may allow desulfation to proceed more quickly in the

sense of a rate based on grams sulfur removed per minute. Desulfation may be terminated when desulfation efficiency has dropped rather than when all possible sulfur has been removed. Less time at desulfation temperatures and fewer temperature cycles are expected to extend the life of the LNT 14.

[0040] U.S. EPA 2007 standards will limit engine NOx production to 1.2 g/bhp-hr over emissions test cycles. U.S. EPA 2010 standards will limit tailpipe NOx emissions to 0.2 g/bhp-hr over the test cycles. An exhaust aftertreatment system with an average NOx conversion of 83% could adapt a vehicle with an engine meeting the U.S. EPA 2007 standard to satisfy the U.S. EPA 2010 standard for NOx tailpipe emissions. Allowing a 15% margin, a typical NOx conversion target is 87%.

[0041] In one embodiment, the system 7 is overdesigned to meet a conversion target when the LNT 14 is sulfur-poisoned to 50% of its original efficiency, e.g., twice the NOx break-through rate at full efficiency. In another embodiment, the system 7 is overdesigned to meet the conversion target when the LNT 14 is sulfur-poisoned to 40% of its original efficiency. In a further embodiment, the LNT 14 meets the target when sulfur-poisoned to 30% of its original efficiency.

[0042] Desulfation temperatures are generally obtained by operation of the reformer 12. It may not be possible to operate the reformer 12 continuously through the duration of a regeneration cycle without overheating the reformer 12 or the LNT 14. In such a case, the fuel supply to the reformer 12 can be pulsed. Pulsing allows devices to cool between fuel pulses.

[0043] The first SCR catalyst 15 and/or the ammonia-SCR catalyst 16 may be damaged by desulfation temperatures. FIG. 3 is a schematic illustration of a system 30 showing one method one of avoiding such damage. A device providing a large thermal mass has been placed between the LNT 14 and the and the SCR catalysts. In this example, the device is the DPF 13, although another device or an inert thermal mass could be used instead. The DPF 13 damps temperature pulse transmitted by the exhaust from the LNT 14 to downstream devices.

[0044] In order for such damping to be effective, high temperatures must not be maintained in the LNT 14 for an overly long time. If necessary, the temperature of the LNT 14 can be pulsed during desulfation. In between pulses, the LNT 14 cools to below desulfation temperatures. Provided the pulses are short enough and the thermal mass between the devices is large enough, the SCR catalysts will experience peak temperatures closer to the average cycle temperature than the peak temperatures experienced by the LNT 14.

[0045] FIG. 4 is a schematic of a system 40 illustrating another approach to protecting the first SCR catalyst 15 from desulfation temperatures. In this example, the first SCR catalyst 15 is placed upstream of the reformer 12. An addition possible potential advantage of this configuration is that oxygen remains available to the first SCR catalyst 15 during regeneration of the LNT 14. Oxygen is required for some SCR catalysts to be effective. The presence of oxygen upstream of the reformer 12 assures the first SCR catalyst 15 will continue to be active through regeneration.

[0046] FIG. 5 is a schematic of a system 50 illustrating a further possible improvement. In this example, the fuel

injector 11 has been placed upstream of the first SCR catalyst 15, whereby injected fuel passes through the first SCR catalyst 15 before entering the reformer 12. For this configuration, the first SCR catalyst 15 is generally a HC—SCR catalyst. During periods of fuel injection, a very high concentration of reductant is available for reducing NOx. The high concentration of reductant may also facilitate hydrocarbon storage for use in reduction even after fuel injection stops. The configuration of FIG. 5 is particularly suited to an HC—SCR catalyst that is adapted to store long chain hydrocarbons. An HC—SCR catalyst with a hydrocarbon storage function may be better adapted to store or use either long or short chain hydrocarbons.

[0047] The first SCR catalyst 15 can be either an HC—SCR catalyst, a CO—SCR catalyst, or a H₂-SCR catalyst. Examples of HC—SCR catalysts include transitional metals loaded on refractory oxides or exchanged into zeolites. Examples of transition metals include copper, chromium, iron, cobalt, nickel, cadmium, silver, gold, iridium, platinum and manganese, and mixtures thereof. Exemplary of refractory oxides are alumina, zirconia, silica-alumina, and titania. Useful zeolites include ZSM-5, Ba/Y, and Na/Y. Preferred zeolites have Si:Al ratios greater than about 20. Specific examples of zeolite-based HC—SCR catalysts include Cu-ZSM-5, Fe-ZSM-5, and Co-ZSM-5. A CeO₂ coating may reduce water and SO₂ deactivation of these catalysts. Cu/ZSM-5 is effective in the temperature range from about 300 to about 450° C. Specific examples of refractory oxide-based catalysts include alumina-supported silver. Two or more catalysts can be combined to extend the effective temperature window.

[0048] Where a hydrocarbon-storing function is desired, zeolites can be effective. U.S. Pat. No. 6,202,407 describes HC—SCR catalysts that have a hydrocarbon storing function. The catalysts are amphoteric metal oxides. The metal oxides are amphoteric in the sense of showing reactivity with both acids and bases. Specific examples include gamma-alumina, Ga₂O₃, and ZrO₂. Precious metals are optional. Where precious metals are used, the less expensive precious metals such as Cu, Ni, or Sn can be used instead of Pt, Pd, or Rh.

[0049] In the present disclosure, the term hydrocarbon is inclusive of all species consisting essentially of hydrogen and carbon atoms, however, a HC—SCR catalyst does not need to show activity with respect to every hydrocarbon molecule. For example, some HC—SCR catalysts will be better adapted to utilizing short-chain hydrocarbons and HC—SCR catalysts in general are not expected to show substantial activity with respect to CH₄.

[0050] Examples of CO—SCR catalysts include precious metals on refractory oxide supports. Specific examples include Rh on a CeO₂-ZrO₂ support and Cu and/or Fe ZrO₂ support.

[0051] Examples of H₂-SCR catalysts also include precious metals on refractory oxide supports. Specific examples include Pt supported on mixed LaMnO₃, CeO₂, and MnO₂, Pt supported on mixed ZrO₂ and TiO₂, Ru supported on MgO, and Ru supported on Al₂O₃.

[0052] The engine 9 is preferably a compression ignition diesel engine, however, the various concepts of the invention are applicable to power generation systems with lean-burn

gasoline engines or any other type of engines that produces an oxygen rich, NOx-containing exhaust. For purposes of the present disclosure, NOx consists of NO and NO₂.

[0053] The fuel injector **11** can be of any suitable type. It can inject the fuel co-current, cross-current, or counter-current to the exhaust flow. Preferably, it provides the fuel in an atomized or vaporized spray. The fuel may be injected at the pressure provided by a fuel pump for the engine **9**. Preferably, however, the fuel passes through a pressure intensifier operating on hydraulic principles to at least double the fuel pressure from that provided by the fuel pump to provide the fuel at a pressure of at least about 4 bar.

[0054] A fuel reformer is a device that converts heavier fuels into lighter compounds without fully combusting the fuel. A fuel reformer can be a catalytic reformer, a steam reformer, an autothermal reformer, or a plasma reformer. Preferably, the reformer **12** is a partial oxidation catalytic reformer. A partial oxidation catalytic reformer comprises a reformer catalyst. Examples of reformer catalysts include precious metals, such as Pt, Pd, or Ru, and oxides of Al, Mg, and Ni, the later group being typically combined with one or more of CaO, K₂O, and a rare earth metal such as Ce to increase activity. A reformer is preferably small in size as compared to an oxidation catalyst or a three-way catalyst designed to perform its primary functions at temperatures below 500° C. A partial oxidation catalytic reformer is generally operative at temperatures from about 650 to about 850° C.

[0055] The NOx adsorber-catalyst **14** can comprise any suitable NOx-adsorbing material. Examples of NOx adsorbing materials include oxides, carbonates, and hydroxides of alkaline earth metals such as Mg, Ca, Sr, and Be or alkali metals such as K or Ce. Further examples of NOx-adsorbing materials include molecular sieves, such as zeolites, alumina, silica, and activated carbon. Still further examples include metal phosphates, such as phosphates of titanium and zirconium. Generally, the NOx-adsorbing material is an alkaline earth oxide. The adsorbant is typically combined with a binder and either formed into a self-supporting structure or applied as a coating over an inert substrate.

[0056] The LNT **14** also comprises a catalyst for the reduction of NOx in a reducing environment. The catalyst can be, for example, one or more precious metals, such as Au, Ag, and Cu, group VIII metals, such as Pt, Pd, Ru, Ni, and Co, Cr, Mo, or K. A typical catalyst includes Pt and Rh, although it may be desirable to reduce or eliminate the Rh to favor the production of NH₃ over N₂. Precious metal catalysts also facilitate the adsorbant function of alkaline earth oxide adsorbers. Typical effective operating temperatures for a LNT are in the range from about 300 to about 450° C.

[0057] The LNT **12** may be combined with one or both of the SCR catalysts. FIG. 2 provides an example in which the LNT **14**, the HC—SCR catalyst **15**, and, the ammonia-SCR catalyst **16** are replaced by a combined HC—SCR/NOx-adsorber catalyst **22** and a combined ammonia-SCR/NOx-adsorber catalyst **23**. Combining adsorbants and catalysts in this manner can increase efficiencies. Combining may involve layering or codispersing.

[0058] Adsorbant and catalysts according to the present invention are generally adapted for use in vehicle exhaust

systems. Vehicle exhaust systems create restriction on weight, dimensions, and durability. For example, a NOx adsorbant bed for a vehicle exhaust systems must be reasonably resistant to degradation under the vibrations encountered during vehicle operation.

[0059] An adsorbant bed or catalyst brick can have any suitable structure. Examples of suitable structures may include monoliths, packed beds, and layered screening. A packed bed is preferably formed into a cohesive mass by sintering the particles or adhering them with a binder. When the bed has an adsorbant function, preferably any thick walls, large particles, or thick coatings have a macro-porous structure facilitating access to micro-pores where adsorption occurs. A macro-porous structure can be developed by forming the walls, particles, or coatings from small particles of adsorbant sintered together or held together with a binder.

[0060] The ammonia-SCR catalyst **16** is a catalyst effective to catalyze reactions between NOx and NH₃ to reduce NOx to N₂ in lean exhaust. Examples of ammonia-SCR catalysts include oxides of metals such as Cu, Zn, V, Cr, Al, Ti, Mn, Co, Fe, Ni, Pd, Pt, Rh, Rd, Mo, W, and Ce, zeolites, such as ZSM-5 or ZSM-11, substituted with metal ions such as cations of Cu, Co, Ag, Zn, or Pt, and activated carbon.

[0061] The particulate filter **13** can have any suitable structure. Examples of suitable structures include monolithic wall flow filters, which are typically made from ceramics, especially cordierite or SiC, blocks of ceramic foams, monolith-like structures of porous sintered metals or metal-foams, and wound, knit, or braided structures of temperature resistant fibers, such as ceramic or metallic fibers. Typical pore sizes for the filter elements are about 10 μm or less. Optionally, one or more of the the LNT **14**, the first SCR catalyst **15**, or the ammonia SCR catalyst **16** is integrated as a coating on the DPF **13**.

[0062] From time-to-time, the DPF **13** is regenerated to remove accumulated soot. The DPF **13** can be of the type that is regenerated continuously or intermittently. For intermittent regeneration, the DPF **13** is heated, using the reformer **12** for example. The DPF **13** is heated to a temperature at which accumulated soot combusts with O₂. This temperature can be lowered by providing the DPF **13** with a suitable catalyst. After the DPF is heated, soot is combusted in an oxygen rich environment. Regeneration of the DPF **13** can be combined with desulfation of the LNT **14** by heating and then switching between lean and rich conditions.

[0063] For continuous regeneration, the DPF **13** may be provided with a catalyst that promotes combustion of soot with NO₂. Examples of catalysts that promote the oxidation of soot by NO₂ include oxides of Ce, Zr, La, Y, and Nd. To completely eliminate the need for intermittent regeneration, it may be necessary to provide an additional oxidation catalyst to promote the oxidation of NO to NO₂ and thereby provide sufficient NO₂ to combust soot as quickly as it accumulates. Where regeneration is continuous, the DPF **13** is suitably placed upstream of the reformer **13** as illustrated in FIG. 6. An advantage of this configuration is an additional portion of NOx is removed by the DPF **13**, further reducing demands on the downstream aftertreatment devices.

[0064] Where the DPF **13** is not continuously regenerating, the DPF **13** is preferably positioned downstream of the

reformer 12. Placing the DPF 13 immediately downstream of the reformer 12 facilitates protecting downstream devices, such as the LNT 12, from temperature excursions during denitration. Placing the DPF 13 between the LNT 12 and downstream SCR catalysts can be useful in protecting those downstream devices during desulfation, as described previously.

[0065] The clean-up oxidation catalyst 17 is preferably functional to oxidize unburned hydrocarbons from the engine 9, unused reductants, and any H₂S released from the NOx adsorber-catalyst 13 and not oxidized by the SCR catalyst 15. Any suitable oxidation catalyst can be used. A typical oxidation catalyst is a precious metal, such as platinum. To allow the clean-up catalyst 17 to function under rich conditions, the catalyst may include an oxygen-storing component, such as ceria. Removal of H₂S, where required, may be facilitated by one or more additional components such as NiO, Fe₂O₃, MnO₂, CoO, and CrO₂.

[0066] The invention as delineated by the following claims has been shown and/or described in terms of certain concepts, components, and features. While a particular component or feature may have been disclosed herein with respect to only one of several concepts or examples or in both broad and narrow terms, the components or features in their broad or narrow conceptions may be combined with one or more other components or features in their broad or narrow conceptions wherein such a combination would be recognized as logical by one of ordinary skill in the art. Also, this one specification may describe more than one invention and the following claims do not necessarily encompass every concept, aspect, embodiment, or example described herein.

The claims are:

1. A power generation system comprising an exhaust aftertreatment system, comprising:

an effective amount of a first SCR catalyst selected from the group consisting of hydrocarbon-SCR catalysts, carbon monoxide-SCR catalysts, and hydrogen-SCR catalysts;

an effective amount of a NOx adsorbant-catalyst; and

an effective amount of an ammonia-SCR catalyst;

wherein the first SCR catalyst is functional to reduce NOx in lean exhaust using a reductant selected from the group consisting of hydrocarbons, carbon monoxide, and hydrogen;

the NOx adsorbant-catalyst is functional to adsorb NOx from lean exhaust and to produce ammonia during regeneration; and

the SCR catalyst is configured to adsorb ammonia so produced and is function to use that ammonia to reduce NOx in exhaust.

2. The system of claim 1, wherein the first SCR catalyst is configured upstream of the ammonia-SCR catalyst

3. The system of claim 1, wherein the first SCR catalyst is a hydrocarbon-SCR catalyst

4. The system of claim 1, further comprising an in-line reformer configured upstream of the first SCR catalyst, the NOx-adsorber catalyst, and the ammonia-SCR catalyst.

5. The system of claim 1, further comprising a in-line reformer configured downstream of the first SCR catalyst, but upstream of the NOx-adsorber catalyst, and the ammonia-SCR catalyst.

6. The system of claim 5, wherein the power generation system is configured to inject diesel fuel into the exhaust before the first SCR catalyst, which is a hydrocarbon-SCR catalyst.

7. The system of claim 6, wherein the hydrocarbon-SCR catalyst is adapted to store hydrocarbon and effectively use it to reduce NOx after diesel fuel injection into the exhaust ceases.

8. The system of claim 1, wherein the first SCR catalyst is functional to adsorb the reductant during regeneration of the NOx adsorber-catalyst and is functional to subsequently use that reductant to reduce NOx in lean exhaust.

9. The system of claim 8, wherein the reductant is produced by the reformer.

10. The system of claim 1, wherein the first SCR catalyst is combined with the NOx-adsorber catalyst.

11. The system of claim 1, wherein the ammonia-SCR catalyst is combined with the NOx-adsorber catalyst.

12. A method of treating NOx-containing lean exhaust, comprising:

in a first phase:

contacting the exhaust with a first SCR catalyst selected from the group consisting of hydrocarbon-SCR catalysts, and carbon monoxide-SCR catalysts to reduce a portion of the NOx by reactions with hydrocarbons or CO contained in the exhaust;

contacting the exhaust with a NOx adsorber-catalyst to remove another portion of the NOx from the exhaust by adsorption; and

contacting the exhaust with an ammonia-SCR catalyst to reduce a further portion of the NOx by reactions with stored ammonia;

and in a second phase:

enriching the exhaust to reduce NOx stored in the NOx adsorber-catalyst and in the process produce ammonia that becomes stored in the SCR catalyst.

13. The method of claim 12, wherein the ammonia-SCR catalyst is downstream of the first SCR catalyst.

14. The method of claim 12, wherein:

the exhaust is enriched in the second phase by injecting diesel fuel; and

the enriched exhaust is processed through a reformer upstream of the first SCR catalyst.

15. The method of claim 14, wherein the diesel fuel is injected at a rate in excess of a stoichiometric rate for producing reformat, whereby insufficient oxygen is available in the reformer to completely reform all the injected diesel fuel.

16. The method of claim 12, wherein:

the exhaust is enriched in the second phase by injecting diesel fuel upstream of the first SCR catalyst; and

the enriched exhaust is processed through a reformer downstream of the first SCR catalyst.

17. The method of claim 12, wherein at least about 15% of the NOx is reduced by the first SCR catalyst.

18. The method of claim 12, wherein at least about 30% of the NOx is reduced by the first SCR catalyst.

19. A method of treating NOx-containing lean exhaust, comprising:

in a first phase:

contacting the exhaust with a first SCR catalyst selected from the group consisting of hydrocarbon-SCR catalysts, carbon monoxide-SCR catalysts, and hydrogen-SCR catalysts to reduce a portion of the NOx by reactions with a stored first reductant selected from the group consisting of hydrocarbons, carbon monoxide, and hydrogen;

contacting the exhaust with a NOx adsorber-catalyst to remove another portion of the NOx from the exhaust by adsorption; and

contacting the exhaust with an ammonia-SCR catalyst to reduce a further portion of the NOx by reactions with stored ammonia;

and in a second phase:

making the exhaust rich;

storing the first reductant in the first SCR catalyst; and

reducing NOx stored in the NOx adsorber-catalyst and in the process producing ammonia that becomes stored by the SCR-catalyst.

20. The method of claim 19, wherein making the exhaust rich comprises injecting diesel fuel into the exhaust and processing the diesel fuel through a reformer to produce reformat while removing excess oxygen from the exhaust.

21. The method of claim 20, wherein the first SCR catalyst is a hydrocarbon-SCR catalyst and the first reductant is hydrocarbon.

22. The method of claim 21, wherein the hydrocarbon-SCR catalyst is configured upstream of the reformer.

23. The method of claim 20, wherein the first reductant is produced by the reformer.

24. The method of claim 23, wherein the diesel fuel is injected at a rate in excess of a stoichiometric rate for producing reformat, whereby insufficient oxygen is available in the reformer to completely reform all the injected diesel fuel.

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