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(72) Inventor(s):

Hai-Ying Chen
Joseph Michael Fedeyko
Neil Greenham
Mikael Larsson
Jing Lu
Per Marsh
David Micallef
Andrew David Newman

(73) Proprietor(s):

Johnson Matthey Public Limited Company
(Incorporated in the United Kingdom)
5th Floor, 25 Farringdon Street, LONDON, EC4A 4AB,
United Kingdom

(74) Agent and/or Address for Service:

Johnson Matthey PLC
Group Intellectual Property Department, Gate 20,
Orchard Road, Royston, SG8 5HE, United Kingdom

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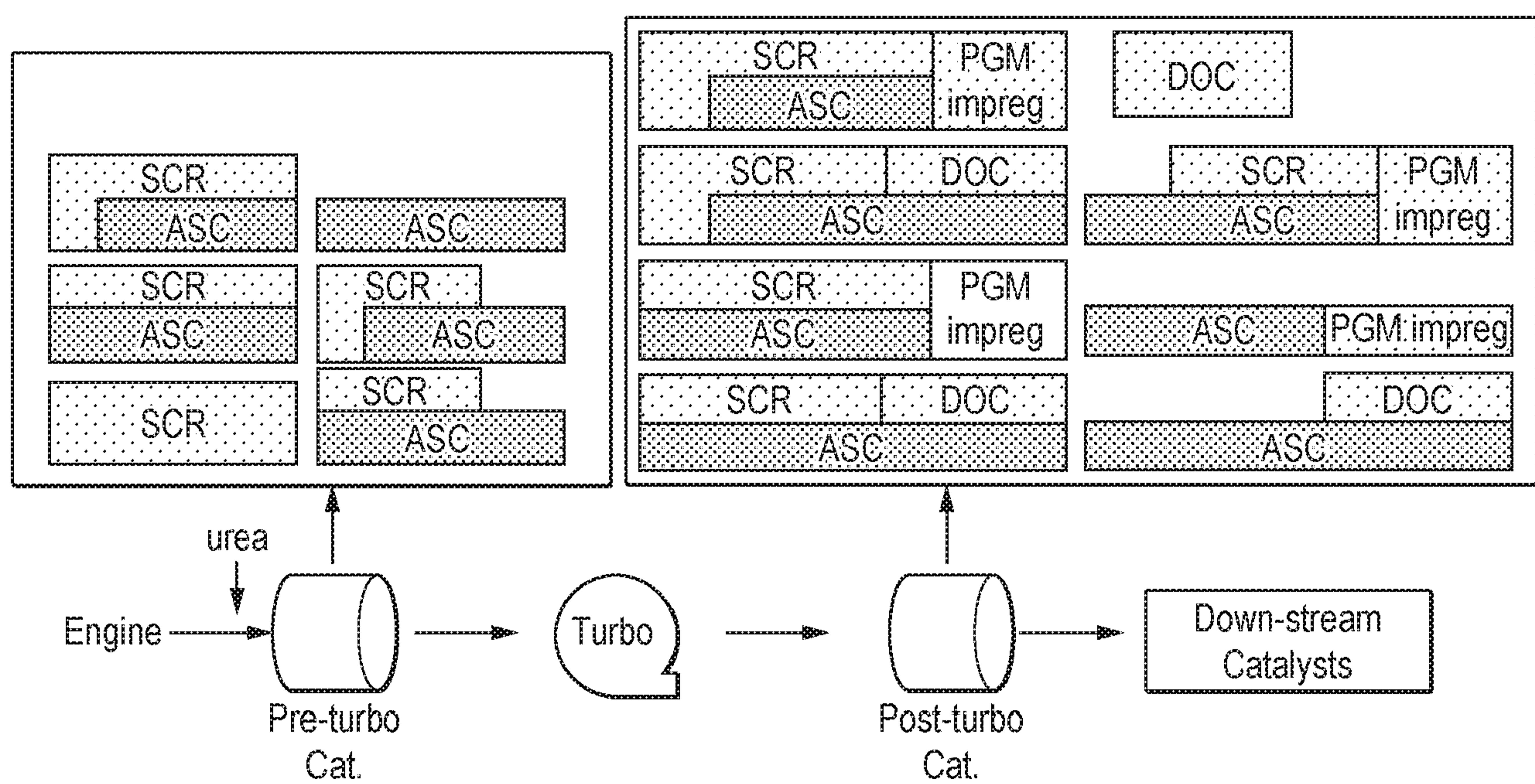


FIG. 1

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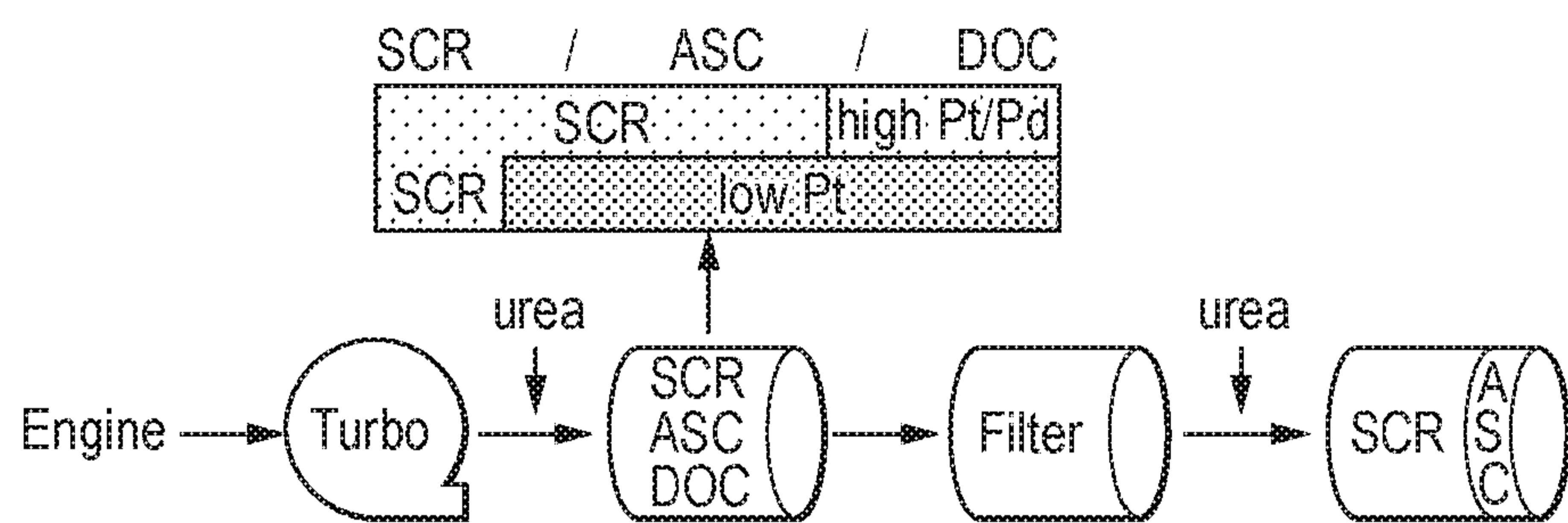


FIG. 2

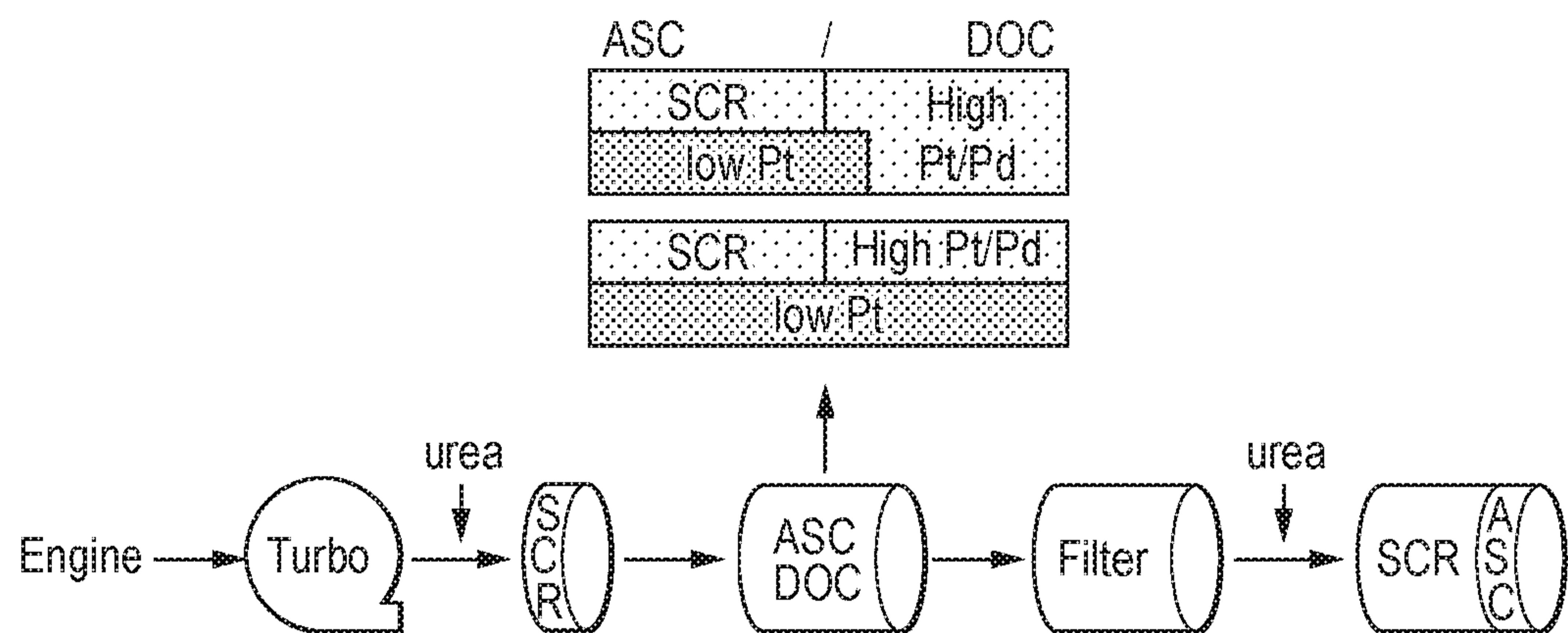


FIG. 3

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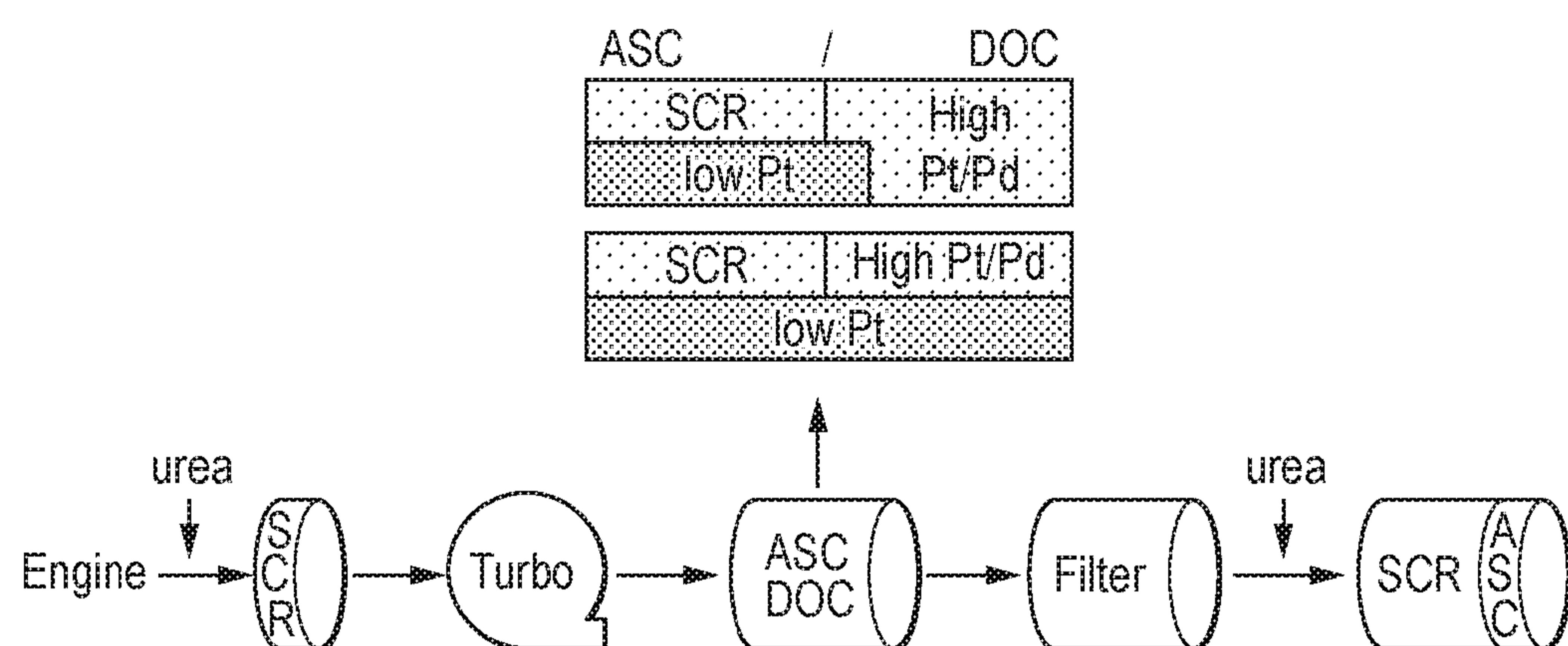


FIG. 4

18 05 18

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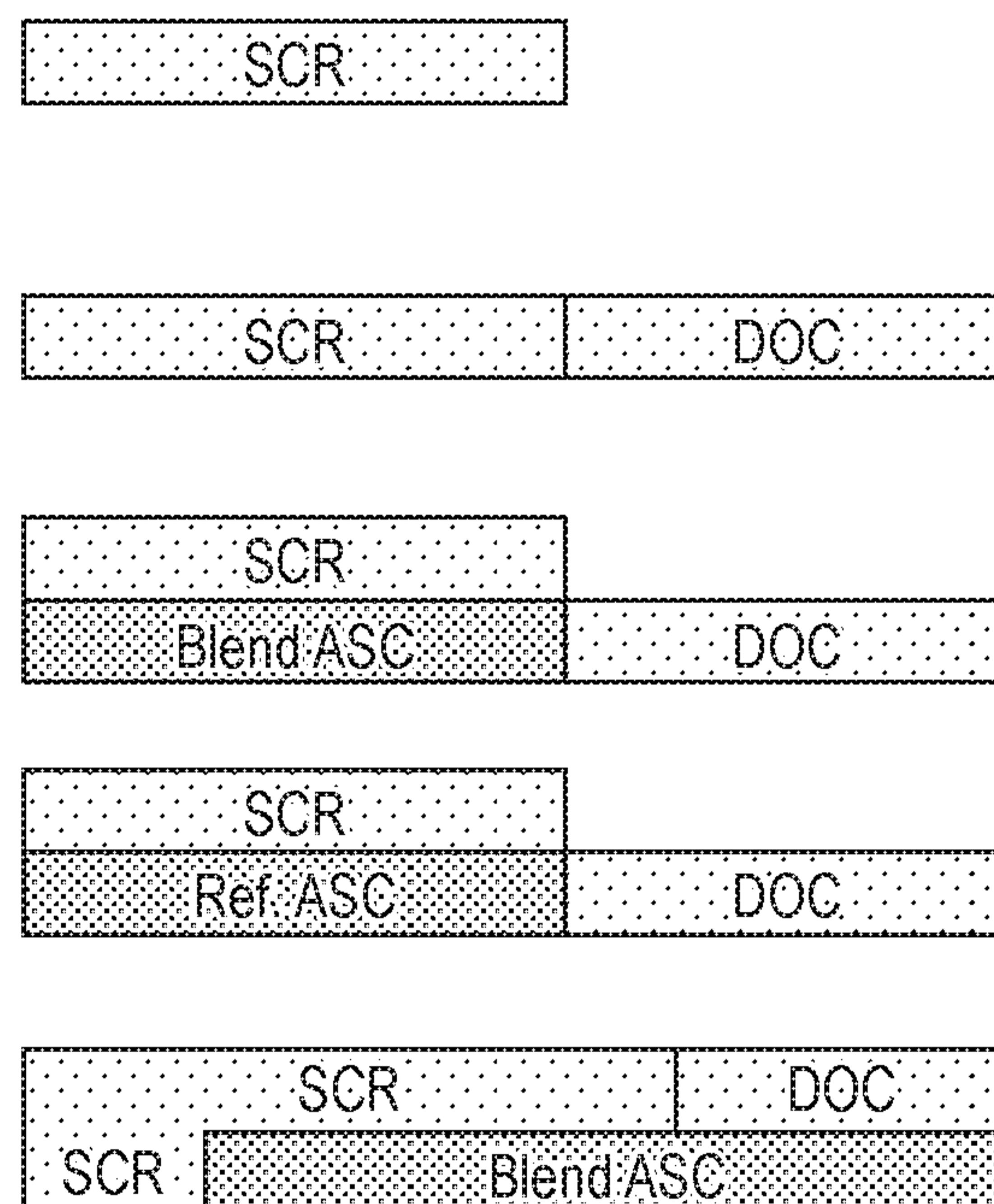


FIG. 5

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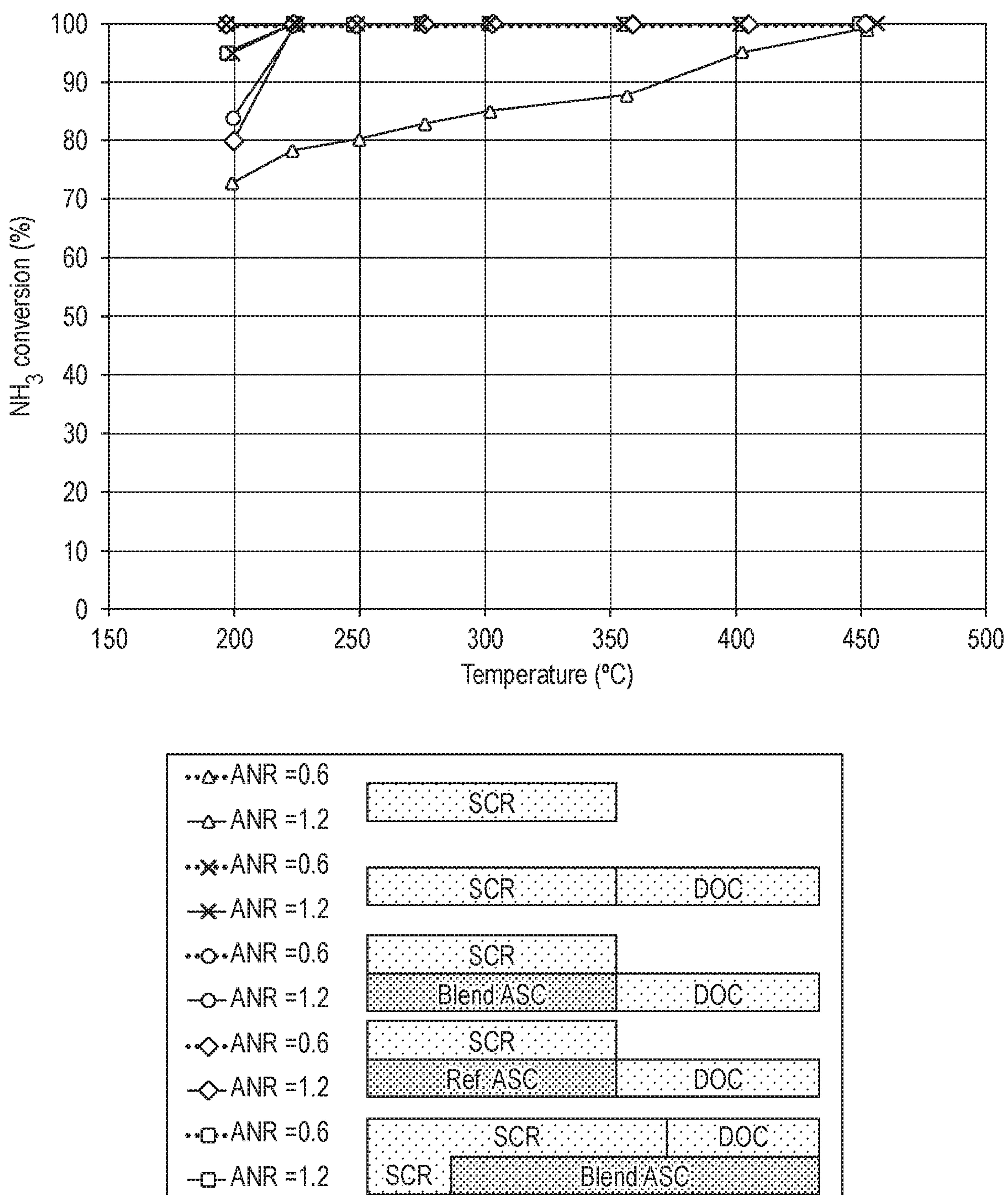


FIG. 6

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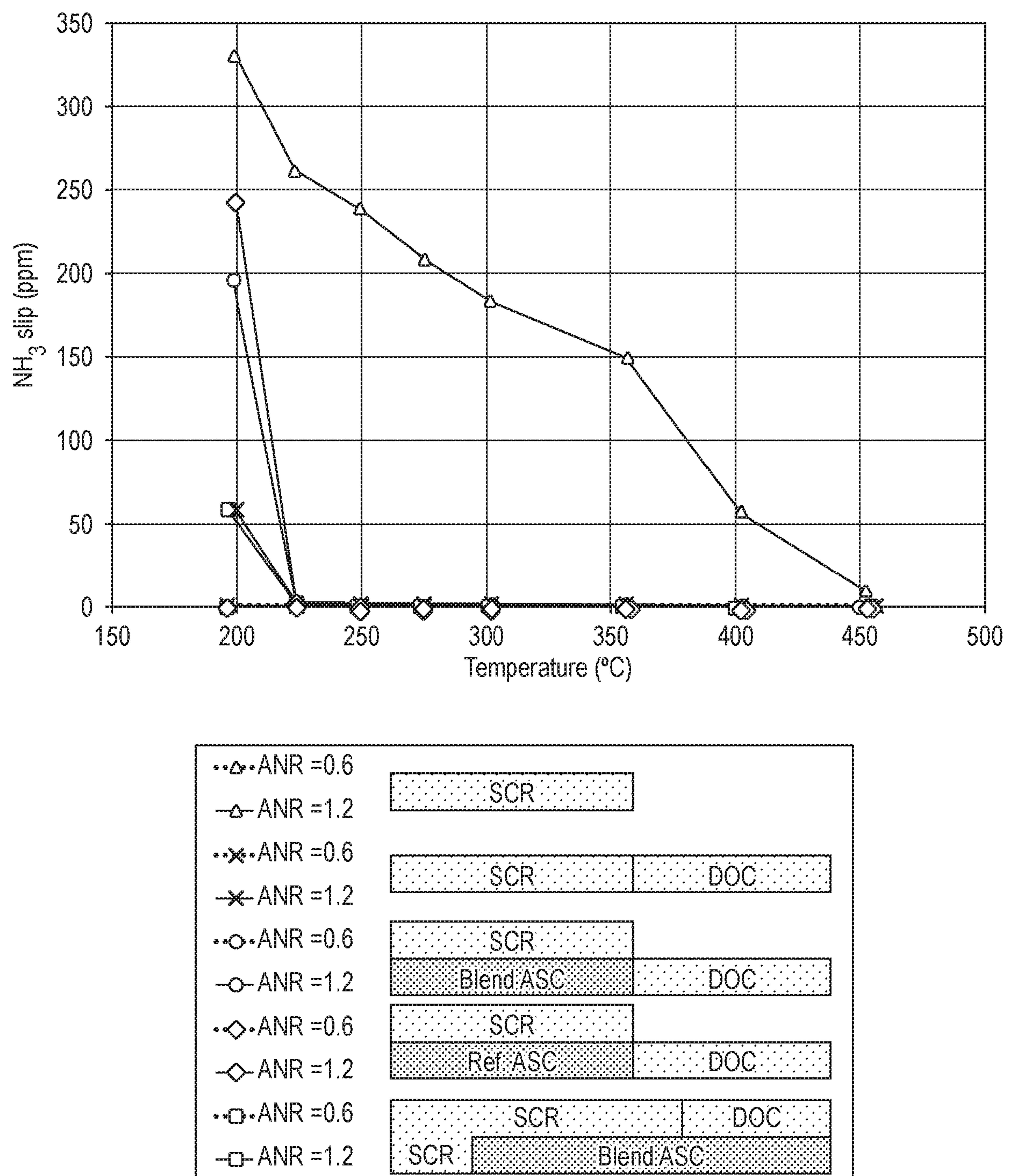


FIG. 7

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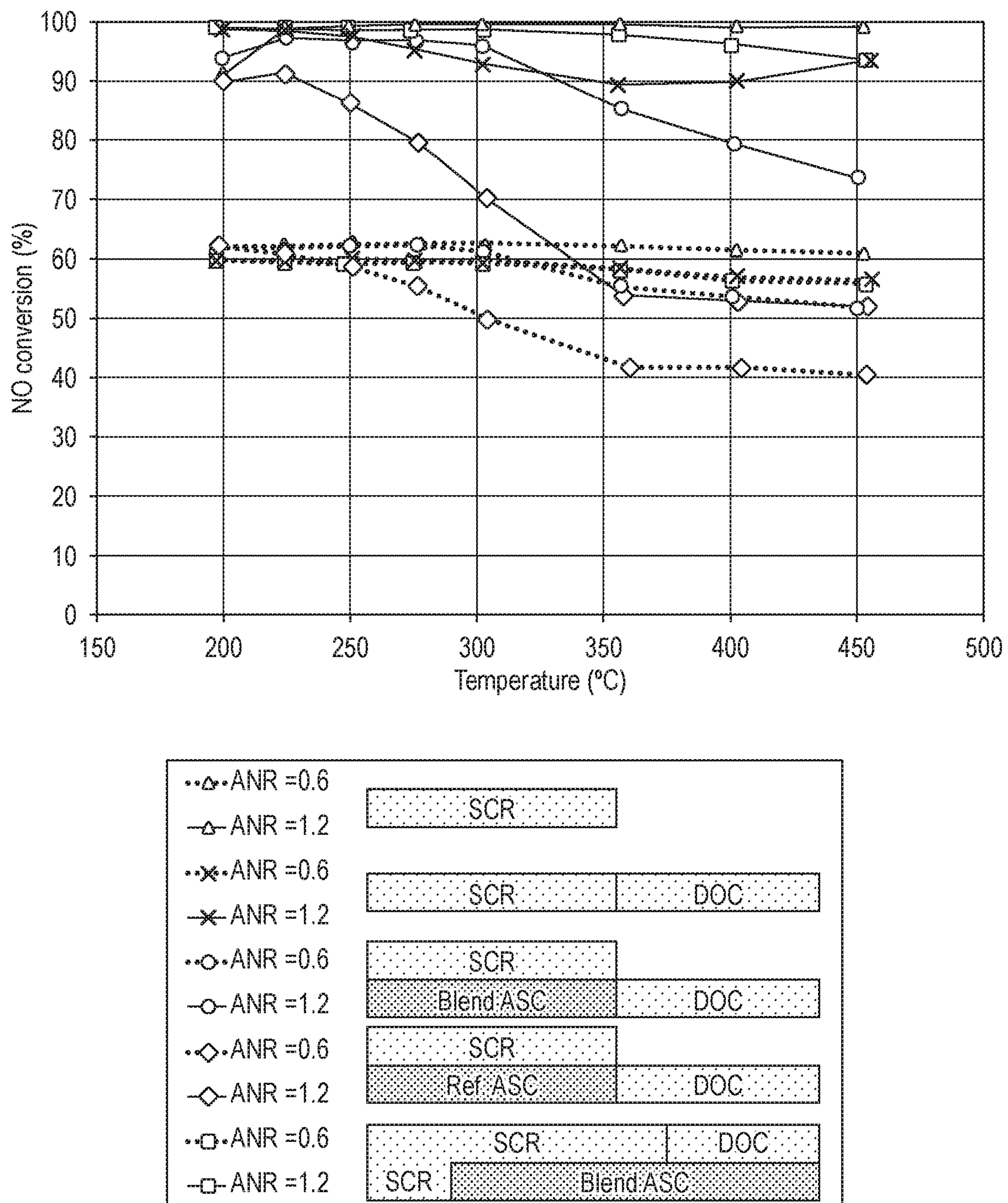


FIG. 8

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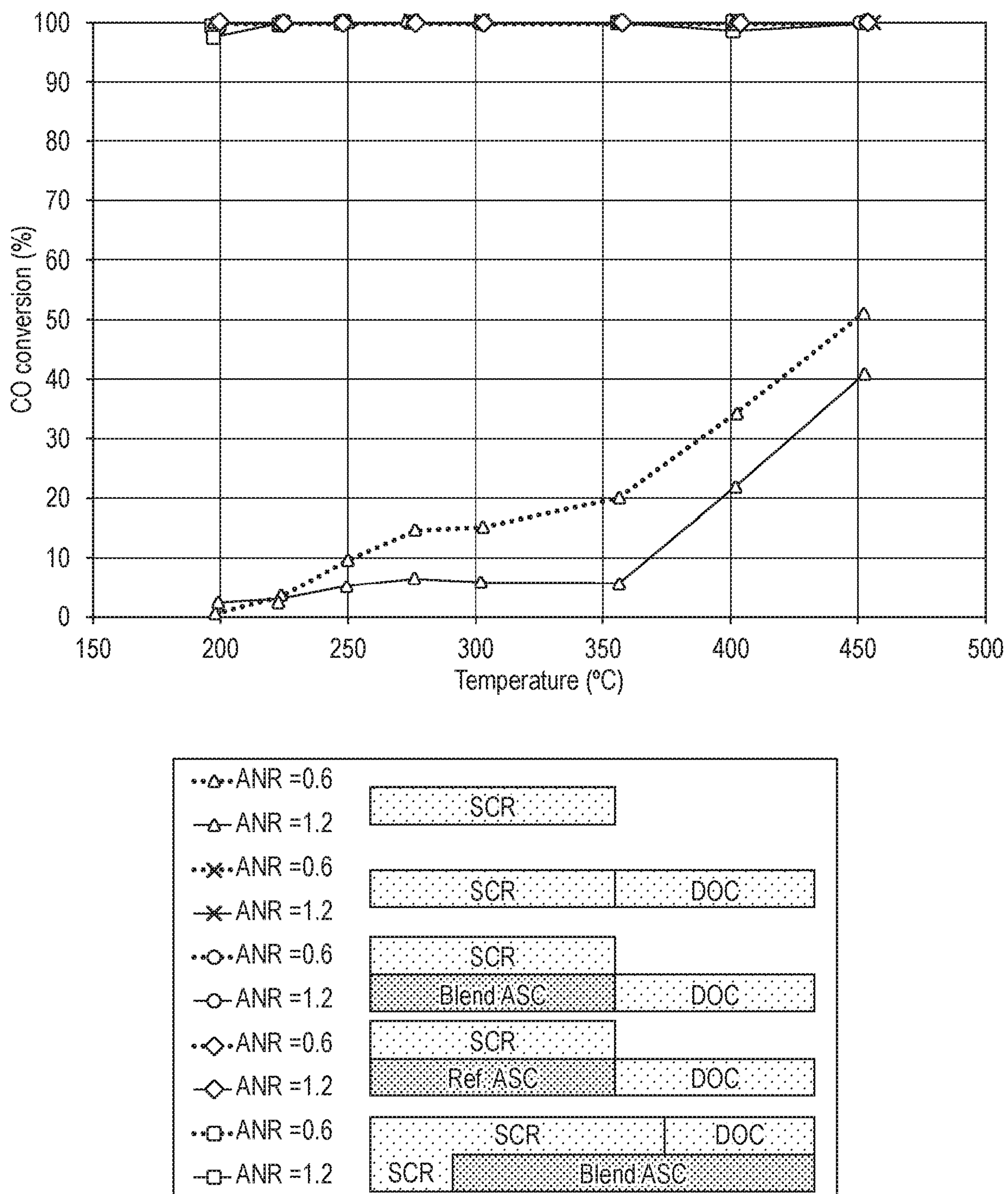


FIG. 9

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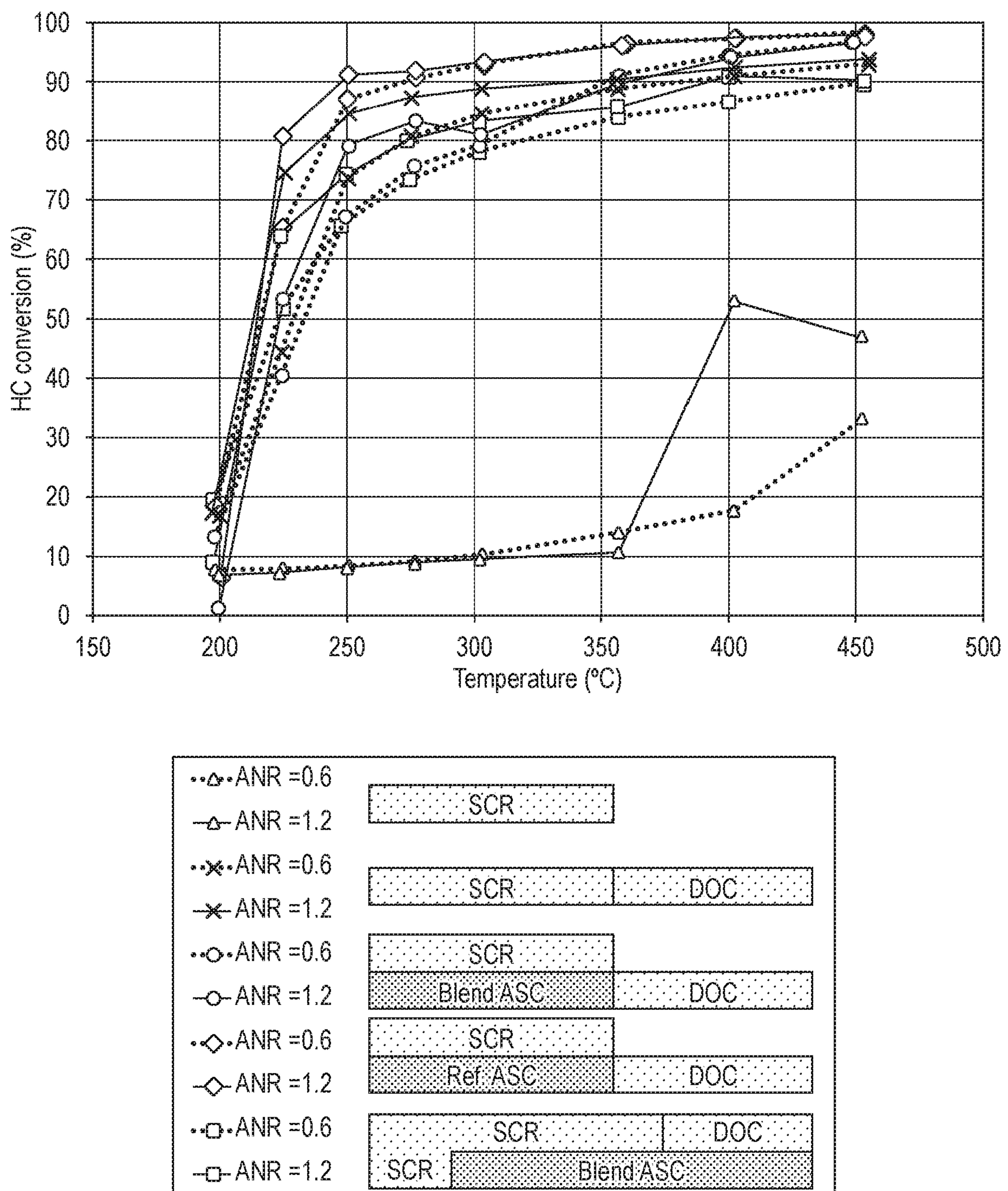


FIG. 10

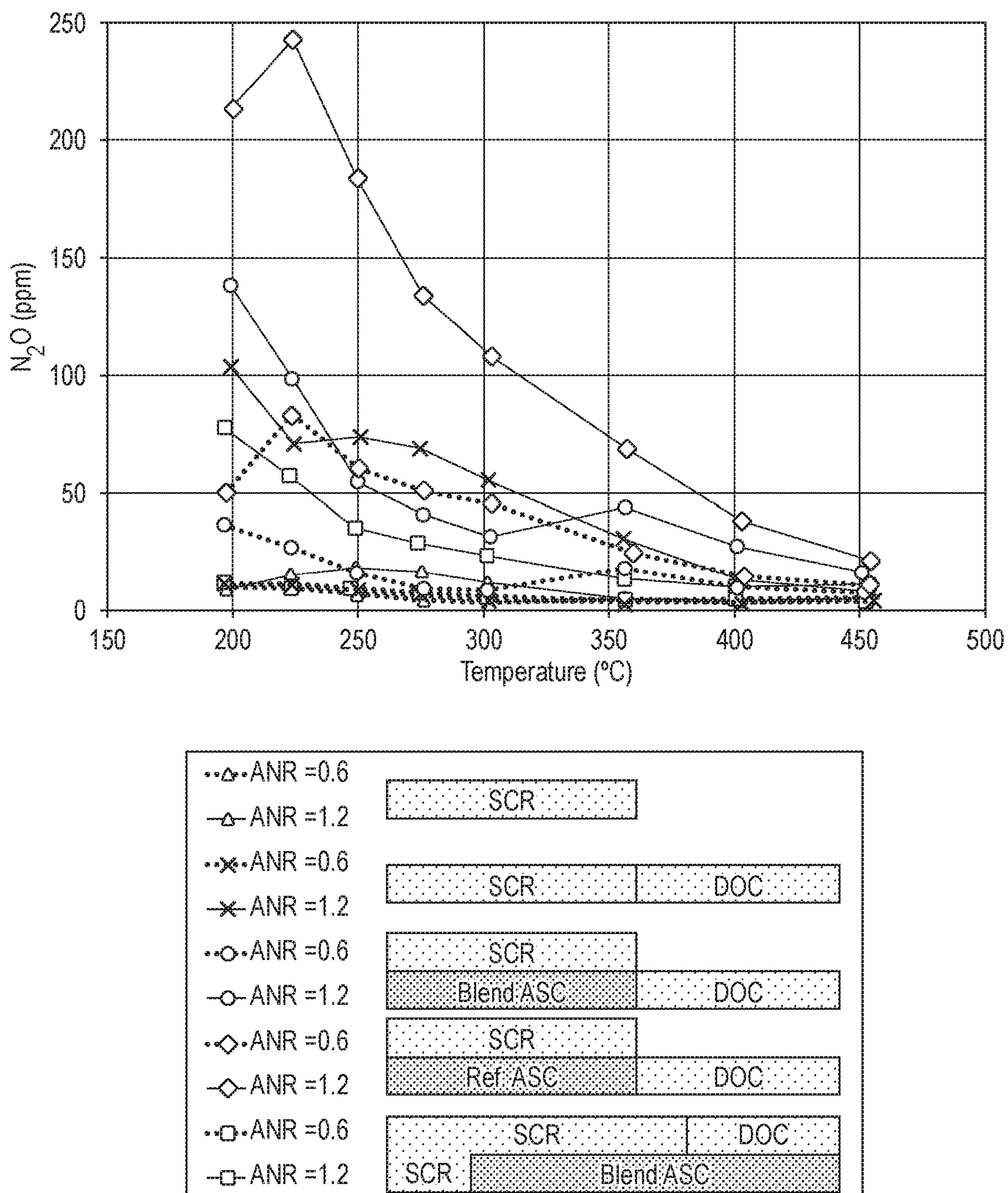


FIG. 11

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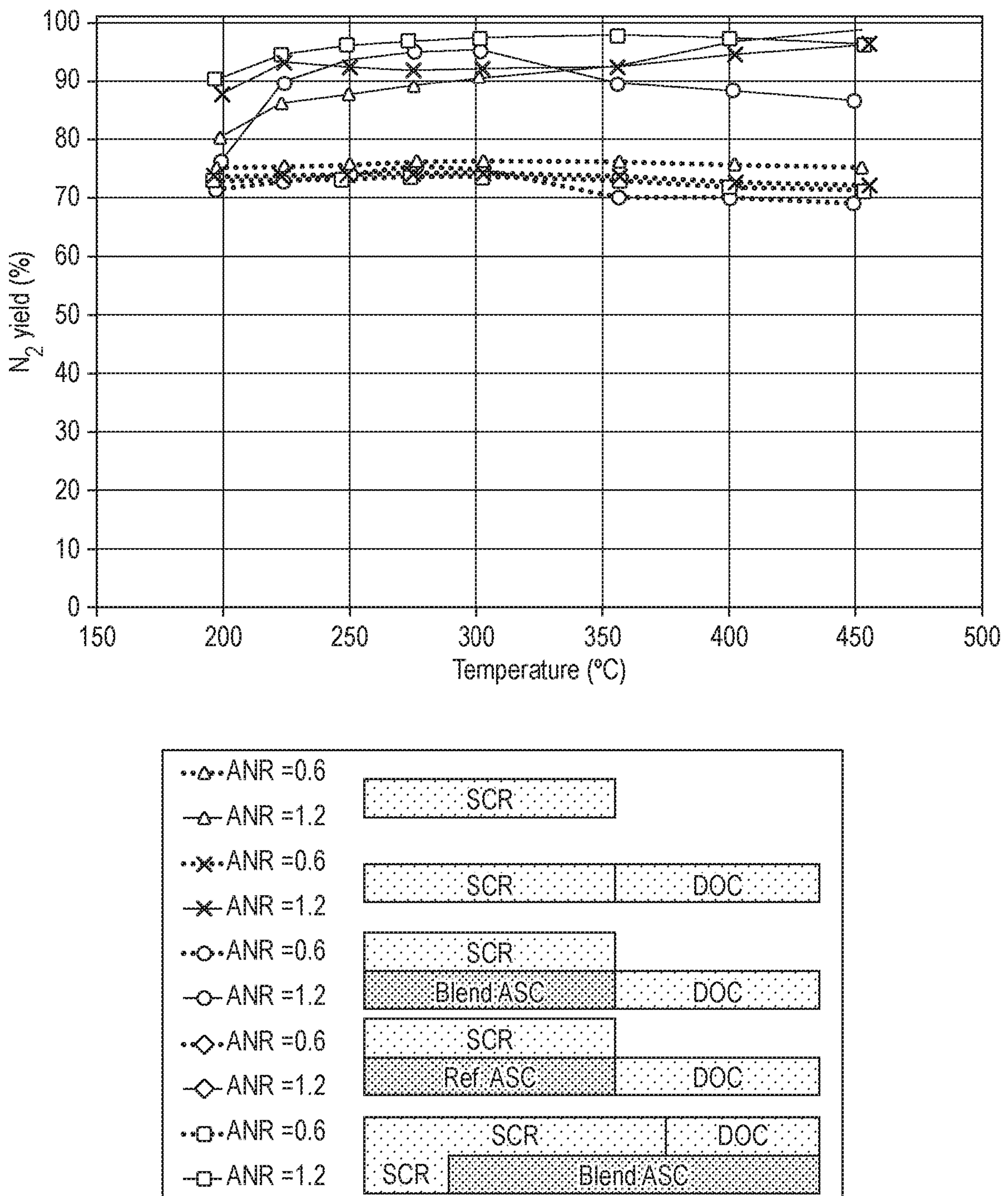


FIG. 12

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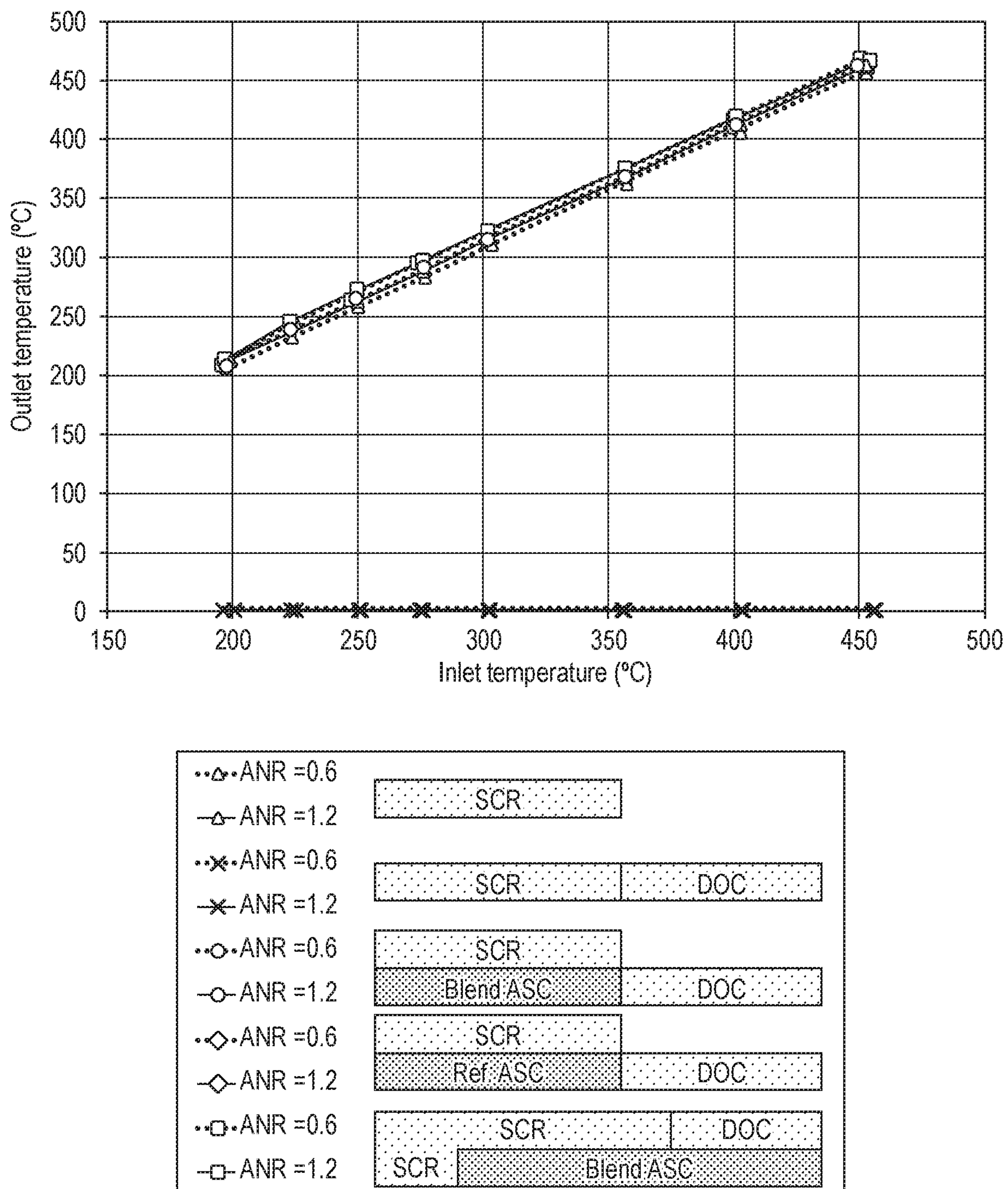


FIG. 13

TITLE

SCR WITH TURBO AND ASC/DOC CLOSE-COUPLED SYSTEM

BACKGROUND OF THE INVENTION

Hydrocarbon combustion in diesel engines, stationary gas turbines, and other systems generates exhaust gas that must be treated to remove nitrogen oxides (NOx), which comprises NO (nitric oxide) and NO₂ (nitrogen dioxide), with NO being the majority of the NOx formed. NOx is known to cause a number of health issues in people as well as causing a number of detrimental environmental effects including the formation of smog and acid rain. To mitigate both the human and environmental impact from NO_x in exhaust gas, it is desirable to eliminate these undesirable components, preferably by a process that does not generate other noxious or toxic substances.

Exhaust gas generated in lean-burn and diesel engines is generally oxidative. NOx needs to be reduced selectively with a catalyst and a reductant in a process known as selective catalytic reduction (SCR) that converts NOx into elemental nitrogen (N₂) and water. In an SCR process, a gaseous reductant, typically anhydrous ammonia, aqueous ammonia, or urea, is added to an exhaust gas stream prior to the exhaust gas contacting the catalyst. The reductant is absorbed onto the catalyst and the NO_x is reduced as the gases pass through or over the catalyzed substrate. In order to maximize the conversion of NOx, it is often necessary to add more than a stoichiometric amount of ammonia to the gas stream. However, release of the excess ammonia into the atmosphere would be detrimental to the health of people and to the environment. In addition, ammonia is caustic, especially in its aqueous form. Condensation of ammonia and water in regions of the exhaust line downstream of the exhaust catalysts can result in a corrosive mixture that can damage the exhaust system. Therefore the release of ammonia in exhaust gas should be eliminated. In many conventional exhaust systems, an ammonia oxidation catalyst (also known as an ammonia slip catalyst or "ASC") is installed downstream of the SCR catalyst to remove ammonia from the exhaust gas by converting it to nitrogen. The use of ammonia slip catalysts can allow for NO_x conversions of greater than 90% over a typical diesel driving cycle.

It would be desirable to have a catalyst and systems including a catalyst that provides for both NOx removal by SCR and for selective ammonia conversion to nitrogen, where ammonia conversion occurs over a wide range of temperatures in a vehicle's driving cycle, and minimal nitrogen oxide and nitrous oxide byproducts are formed.

SUMMARY OF THE INVENTION

According to some embodiments of the present invention, a catalyst article includes a substrate with an inlet end and an outlet end, a first zone and a second zone, where the first zone comprises: a) an ammonia slip catalyst (ASC) bottom layer comprising a platinum group metal on a support; and b) an SCR layer comprising a second SCR catalyst, the SCR layer located over the ASC bottom layer; where the second zone comprises a catalyst (“second zone catalyst”) selected from the group consisting of a diesel oxidation catalyst (DOC) and a diesel exotherm catalyst (DEC); wherein the ASC bottom layer extends into the second zone; and where the first zone is located upstream of the second zone. The ASC bottom layer may include a blend of: (1) the platinum group metal on a support and (2) a first SCR catalyst. In some embodiments, the first SCR and/or the second SCR catalyst includes Fe, Mn, Cu, or combinations thereof.

In certain embodiments, the ASC bottom layer extends from the outlet end to less than a total length of the substrate; the SCR layer extends from the inlet end to less than a total length of the substrate, and which at least partially overlaps the ASC bottom layer; and the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, where the second layer is located on top of the ASC bottom layer and is shorter in length than the ASC bottom layer.

In some embodiments, the ASC bottom layer extends from the inlet end to less than a total length of the substrate; the SCR layer extends from the inlet end to less than a total length of the substrate, where the SCR layer is located on top of the ASC bottom layer and does not extend further toward the outlet end than the ASC bottom layer; and the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, where the second layer at least partially overlaps the ASC bottom layer.

In some embodiments, the ASC bottom layer extends from the inlet end to less than a total length of the substrate; the SCR layer extends from the inlet end to less than a total length of the substrate, where the SCR layer is located on top of the ASC bottom layer and extends further toward the outlet end than the ASC bottom layer; and the second zone catalyst is included in a layer which extends from the outlet end to less than a total length of the substrate.

In some embodiments, the ASC bottom layer covers a total length of the substrate; the SCR layer extends from the inlet end to less than a total length of the substrate, wherein the SCR layer is located on

top of the ASC bottom layer; and the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, wherein the second layer is located on top of the ASC bottom layer.

In some embodiments, the second zone catalyst is located within the substrate. The support may include a siliceous material such as, for example, a material selected from the group consisting of: (1) silica; (2) a zeolite with a silica-to-alumina ratio higher than 200; and (3) amorphous silica-doped alumina with SiO_2 content $\geq 40\%$. In some embodiments, the platinum group metal is present on the support in an amount of about 0.1 wt% to about 10 wt%; about 0.5 wt% to about 10 wt%, about 1 wt% to about 6 wt%, or about 1.5 wt% to about 4 wt% of the total weight of the platinum group metal and the support. In some embodiments, the platinum group metal comprises platinum, palladium or a combination of platinum and palladium. In some embodiments, the platinum group metal comprises platinum.

Within the blend, a weight ratio of the first SCR catalyst to the platinum group metal on a support may be about 3:1 to about 300:1; about 5:1 to about 100:1; or about 10:1 to about 50:1. In some embodiments, the first SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof. In some embodiments, the first SCR catalyst includes copper. In some embodiments, the second SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof.

In some aspects of the invention, the first zone and the second zone are located on a single substrate and the first zone is located on the inlet side of the substrate and the second zone is located on the outlet side of the substrate. In some embodiments, the substrate comprises a first substrate and a second substrate, where the first zone is located on the first substrate and the second zone is located on the second substrate and the first substrate is located upstream of the second substrate.

According to some embodiments of the present invention, a method of reducing emissions from an exhaust stream includes contacting the exhaust stream with a catalytic article comprising a substrate with an inlet end and an outlet end, a first zone and a second zone, where the first zone comprises: (a) an ammonia slip catalyst (ASC) bottom layer comprising a platinum group metal on a support; and (b) an SCR layer comprising a second SCR catalyst, the SCR layer located over the ASC bottom layer; where the second zone comprises a catalyst (“second zone catalyst”) selected from the group consisting of a diesel oxidation catalyst (DOC) and a diesel exotherm catalyst (DEC); wherein the ASC bottom layer extends into the second zone; and where the first zone is located upstream of the second zone. In some embodiments, the ASC bottom layer comprises a blend of: (1) the platinum group metal on a support and

(2) a first SCR catalyst. The first SCR catalyst and/or second SCR catalyst may include Fe, Mn, Cu, or combinations thereof.

According to some embodiments of the present invention, an exhaust purification system for reduction of emissions from an exhaust stream includes: (a) a turbocharger; (b) a third SCR catalyst; and (c) a catalyst article including a substrate with an inlet end and an outlet end, a first zone and a second zone, where the first zone comprises: (i) an ammonia slip catalyst (ASC) bottom layer comprising a platinum group metal on a support; and (ii) an SCR layer comprising a second SCR catalyst, the SCR layer located over the ASC bottom layer; where the second zone comprises a catalyst (“second zone catalyst”) selected from the group consisting of a diesel oxidation catalyst (DOC) and a diesel exotherm catalyst (DEC); wherein the ASC bottom layer extends into the second zone; and where the first zone is located upstream of the second zone. In some embodiments, the third SCR catalyst is located upstream of the turbocharger. In some embodiments, the third SCR catalyst is located downstream of the turbocharger. In some embodiments, the ASC bottom layer comprises a blend of: (1) the platinum group metal on a support and (2) a first SCR catalyst. The first SCR catalyst and/or the second SCR catalyst may comprise, for example, Fe, Mn, Cu, or combinations thereof.

In some embodiments, the third SCR catalyst and the catalyst article are located on a single substrate, with the third SCR catalyst located upstream of the first zone and the second zone. In some embodiments, the third SCR catalyst is located on a substrate upstream of the catalyst article substrate. In some embodiments, the third SCR catalyst is close-coupled with the catalyst article.

In some embodiments, the system may further include a filter, a downstream SCR catalyst located downstream from the catalyst article, a pre-turbo SCR catalyst located upstream of the turbocharger, a reductant injector located upstream of the third SCR catalyst, a reductant injector located upstream of the downstream SCR catalyst, and/or a reductant injector located upstream of the pre-turbo SCR catalyst.

In some aspects, the ASC bottom layer extends from the outlet end to less than a total length of the substrate; the SCR layer extends from the inlet end to less than a total length of the substrate, and which at least partially overlaps the ASC bottom layer; and the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, where the second layer is located on top of the ASC bottom layer and is shorter in length than the ASC bottom layer.

In some embodiments, the ASC bottom layer extends from the inlet end to less than a total length of the substrate; the SCR layer extends from the inlet end to less than a total length of the substrate, where the SCR layer is located on top of the ASC bottom layer and does not extend further toward the outlet end than the ASC bottom layer; and the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, where the second layer at least partially overlaps the ASC bottom layer.

In some embodiments, the ASC bottom layer extends from the inlet end to less than a total length of the substrate; the SCR layer extends from the inlet end to less than a total length of the substrate, where the SCR layer is located on top of the ASC bottom layer and extends further toward the outlet end than the ASC bottom layer; and the second zone catalyst is included in a layer which extends from the outlet end to less than a total length of the substrate.

In some embodiments, the ASC bottom layer covers a total length of the substrate; the SCR layer extends from the inlet end to less than a total length of the substrate, wherein the SCR layer is located on top of the ASC bottom layer; and the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, wherein the second layer is located on top of the ASC bottom layer.

In some embodiments, the second zone catalyst is located within the substrate. In some embodiments, the support comprises a siliceous material such as, for example, a material selected from the group consisting of: (1) silica; (2) a zeolite with a silica-to-alumina ratio higher than 200; and (3) amorphous silica-doped alumina with SiO_2 content $\geq 40\%$.

In some embodiments, the platinum group metal is present on the support in an amount of about 0.1 wt% to about 10 wt%; about 0.5 wt% to about 10 wt%, about 1 wt% to about 6 wt%, or about 1.5 wt% to about 4 wt% of the total weight of the platinum group metal and the support. In some embodiments, the platinum group metal comprises platinum, palladium or a combination of platinum and palladium. In some embodiments, the platinum group metal comprises platinum.

Within the blend, a weight ratio of the first SCR catalyst to the platinum group metal on a support may be about 3:1 to about 300:1; about 5:1 to about 100:1; or about 10:1 to about 50:1. In some embodiments, the first SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof. In some embodiments, the first SCR catalyst includes

copper. In some embodiments, the second SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof.

In some aspects of the invention, the first zone and the second zone are located on a single substrate and the first zone is located on the inlet side of the substrate and the second zone is located on the outlet side of the substrate. In some embodiments, the substrate comprises a first substrate and a second substrate, where the first zone is located on the first substrate and the second zone is located on the second substrate and the first substrate is located upstream of the second substrate.

According to some embodiments of the present invention, an exhaust purification system for reduction of emissions from an exhaust stream includes: (a) a turbocharger; (b) a third SCR catalyst; and (c) a catalyst article comprising a substrate comprising an inlet end and an outlet end, a first zone and a second zone, where the first zone comprises an ammonia slip catalyst (ASC) comprising a platinum group metal on a support and a first SCR catalyst; where the second zone comprises a catalyst selected from the group consisting of a diesel oxidation catalyst (DOC) and a diesel exotherm catalyst (DEC); and where the first zone is located upstream of the second zone. In some embodiments, the third SCR catalyst is located upstream of the turbocharger. In some embodiments, the third SCR catalyst is located downstream of the turbocharger. The third SCR catalyst may include, for example, V, Fe, Mn, Cu, or combinations thereof. In some embodiments, the third SCR catalyst and the catalyst article are located on a single substrate, with the third SCR catalyst located upstream of the first zone and the second zone. In some embodiments, the third SCR catalyst is located on a substrate upstream of the catalyst article substrate. In some embodiments, the third SCR catalyst is close-coupled with the catalyst article.

In some embodiments, the system may further include a filter, a downstream SCR catalyst located downstream from the catalyst article, a pre-turbo SCR catalyst located upstream of the turbocharger, a reductant injector located upstream of the third SCR catalyst, a reductant injector located upstream of the downstream SCR catalyst, and/or a reductant injector located upstream of the pre-turbo SCR catalyst.

In some embodiments, the first zone comprises: (a) a bottom layer comprising a blend of: (1) the platinum group metal on a support and (2) the first SCR catalyst; and (b) a top layer comprising a second SCR catalyst, the top layer located over the bottom layer.

In some embodiments, the support comprises a siliceous material such as, for example, a material selected from the group consisting of: (1) silica; (2) a zeolite with a silica-to-alumina ratio higher than 200; and (3) amorphous silica-doped alumina with SiO₂ content $\geq 40\%$.

In some embodiments, the platinum group metal is present on the support in an amount of about 0.1 wt% to about 10 wt%; about 0.5 wt% to about 10 wt%, about 1 wt% to about 6 wt%, or about 1.5 wt% to about 4 wt% of the total weight of the platinum group metal and the support. In some embodiments, the platinum group metal comprises platinum, palladium or a combination of platinum and palladium. In some embodiments, the platinum group metal comprises platinum.

Within the blend, a weight ratio of the first SCR catalyst to the platinum group metal on a support may be about 3:1 to about 300:1; about 5:1 to about 100:1; or about 10:1 to about 50:1. In some embodiments, the first SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof. In some embodiments, the first SCR catalyst includes copper. In some embodiments, the second SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof.

In some aspects of the invention, the first zone and the second zone are located on a single substrate and the first zone is located on the inlet side of the substrate and the second zone is located on the outlet side of the substrate. In some embodiments, the substrate comprises a first substrate and a second substrate, where the first zone is located on the first substrate and the second zone is located on the second substrate and the first substrate is located upstream of the second substrate.

According to some embodiments of the present invention, an exhaust purification system for reduction of emissions from an exhaust stream includes: (a) a turbocharger; (b) a third SCR catalyst; and (c) a catalyst article comprising a substrate comprising an inlet end and an outlet end, a first zone, a second zone, and a third zone, where the first zone comprises a second SCR catalyst; where the second zone comprises an ammonia slip catalyst (ASC) comprising a blend of: (1) a platinum group metal on a support and (2) a first SCR catalyst; where the third zone comprises a catalyst (“third zone catalyst”) selected from the group consisting of a diesel oxidation catalyst (DOC) and a diesel exotherm catalyst (DEC); and where the first zone is located upstream of the second zone, and the second zone is located upstream of the third zone. In some embodiments, the third SCR catalyst is located upstream of the turbocharger. In some embodiments, the third SCR catalyst is located downstream of the turbocharger.

The third SCR catalyst may include, for example, V, Fe, Mn, Cu, or combinations thereof. In some embodiments, the third SCR catalyst and the catalyst article are located on a single substrate, with the third SCR catalyst located upstream of the first zone and the second zone. In some embodiments, the third SCR catalyst is located on a substrate upstream of the catalyst article substrate. In some embodiments, the third SCR catalyst is close-coupled with the catalyst article.

In some embodiments, the system may further include a filter, a downstream SCR catalyst located downstream from the catalyst article, a pre-turbo SCR catalyst located upstream of the turbocharger, a reductant injector located upstream of the third SCR catalyst, a reductant injector located upstream of the downstream SCR catalyst, and/or a reductant injector located upstream of the pre-turbo SCR catalyst.

In some embodiments, the ASC is included in a first layer; the third zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, where the second layer is located on top of the first layer and is shorter in length than the first layer; and the second SCR catalyst is included in a layer which extends from the inlet end to less than a total length of the substrate, and which at least partially overlaps the first layer. In some embodiments, the first layer extends from the outlet end to less than a total length of the substrate. In some embodiments, the first layer extends from the inlet end to less than a total length of the substrate.

In some embodiments, the support comprises a siliceous material such as, for example, a material selected from the group consisting of: (1) silica; (2) a zeolite with a silica-to-alumina ratio higher than 200; and (3) amorphous silica-doped alumina with SiO_2 content $\geq 40\%$.

In some embodiments, the platinum group metal is present on the support in an amount of about 0.1 wt% to about 10 wt%, about 0.5 wt% to about 10 wt%, about 1 wt% to about 6 wt%, or about 1.5 wt% to about 4 wt% of the total weight of the platinum group metal and the support. In some embodiments, the platinum group metal comprises platinum, palladium or a combination of platinum and palladium. In some embodiments, the platinum group metal comprises platinum.

Within the blend, a weight ratio of the first SCR catalyst to the platinum group metal on a support may be about 3:1 to about 300:1; about 5:1 to about 100:1; or about 10:1 to about 50:1. In some embodiments, the first SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof. In some embodiments, the first SCR catalyst includes copper. In some embodiments, the second SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof.

In some embodiments, the first zone, the second zone, and the third zone are located on a single substrate and the first zone is located on the inlet side of the substrate and the third zone is located on the outlet side of the substrate. In some embodiments, the substrate comprises a first substrate and a second substrate, where the first zone and second zone are located on the first substrate and the third zone is located on the second substrate and the first substrate is located upstream of the second substrate. In some embodiments, the substrate comprises a first substrate, a second substrate, and a third substrate, where the first zone is located on the first substrate, the second zone is located on the second substrate, and the third zone is located on the third substrate, and the first substrate is located upstream of the second substrate and the second substrate is located upstream of the third substrate.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 depicts system configurations of embodiments of the present invention, including a pre-turbo and post-turbo close coupled catalyst.

Figure 2 depicts a system configuration of embodiments of the present invention, including a post-turbo close coupled SCR/ASC/DOC catalyst.

Figure 3 depicts a system configuration of embodiments of the present invention, including a post-turbo close coupled SCR catalyst followed by an ASC/DOC catalyst.

Figure 4 depicts a system configuration of embodiments of the present invention, including a pre-turbo close coupled SCR catalyst followed by a post-turbo ASC/DOC catalyst.

Figure 5 depicts the catalyst configurations tested under simulated engine out conditions with systematically varied functionalities: (1) SCR-only, (2) SCR/DOC, (3) ASC/DOC and (4) SCR/ASC/DOC.

Figure 6 shows NH₃ conversion of inventive and reference catalysts.

Figure 7 shows NH₃ slip of inventive and reference catalysts.

Figure 8 shows NO conversion of inventive and reference catalysts.

Figure 9 shows CO conversion of inventive and reference catalysts.

Figure 10 shows HC conversion of inventive and reference catalysts.

Figure 11 shows N₂O formation of inventive and reference catalysts.

Figure 12 shows N₂ yield of inventive and reference catalysts.

Figure 13 shows outlet temperature of inventive and reference catalysts.

DETAILED DESCRIPTION OF THE INVENTION

Catalysts of the present invention relate to catalyst articles including various configurations of SCR catalyst(s), ASC, and DOC or DEC. The catalysts and specific configurations are described in further detail below. Systems of the present invention relate to such SCR/ASC/DOC or DEC catalysts in various system configurations with a turbocharger. Systems and specific configurations are described in further detail below.

Two Zone Configurations

Embodiments of the present invention relate to a catalyst article comprising a substrate with an inlet end and an outlet end, a first zone and a second zone, where the first zone is located upstream of the second zone. The first zone can include an ammonia slip catalyst (ASC) bottom layer with a platinum group metal on a support; and an SCR layer having an SCR catalyst, where the SCR layer is located over the ASC bottom layer. The second zone may include a diesel oxidation catalyst (DOC) or a diesel exotherm catalyst (DEC). In such catalyst articles, the ASC bottom layer may extend into the second zone. In some embodiments, the ASC bottom layer includes a blend of (1) the platinum group metal on a support and (2) a first SCR catalyst.

In some embodiments, the ASC bottom layer extends from the outlet end to less than a total length of the substrate; the SCR layer extends from the inlet end to less than a total length of the substrate, and which at least partially overlaps the ASC bottom layer; and the second zone catalyst (the DOC or DEC) is included in a second layer which extends from the outlet end to less than a total length of the substrate, where the second layer is located on top of the ASC bottom layer and is shorter in length than the ASC bottom layer.

In some embodiments, the ASC bottom layer extends from the inlet end to less than a total length of the substrate, and the SCR layer extends from the inlet end to less than a total length of the substrate.

In some embodiments, the SCR layer may be located on top of the ASC bottom layer and does not extend further toward the outlet end than the ASC bottom layer. The second zone catalyst (the DOC or DEC) may be included in a second layer which extends from the outlet end to less than a total length of the substrate, where the second layer at least partially overlaps the ASC bottom layer.

In some embodiments, the ASC bottom layer extends from the inlet end to less than a total length of the substrate, and the SCR layer extends from the inlet end to less than a total length of the substrate. In some embodiments, the SCR layer may be located on top of the ASC bottom layer and extends further toward the outlet end than the ASC bottom layer. The second zone catalyst (the DOC or DEC) may be included in a layer which extends from the outlet end to less than a total length of the substrate.

In some embodiments, the ASC bottom layer covers a total length of the substrate, and the SCR layer extends from the inlet end to less than a total length of the substrate. The SCR layer may be located on top of the ASC bottom layer, and the second zone catalyst (the DOC or DEC) may be included in a second layer which extends from the outlet end to less than a total length of the substrate, wherein the second layer is located on top of the ASC bottom layer.

In some embodiments, the second zone catalyst is located within the substrate.

In some embodiments, the first and second zone are located on a single substrate, with the first zone located on the inlet side of the substrate and the second zone located on the outlet side of the substrate. In another embodiment, the first zone is located on a first substrate and the second zone is located on a second substrate, wherein the first substrate is located upstream of the second substrate. The first and second substrate may be close coupled. When the first and second substrate are close coupled, the second substrate may be placed close to and/or directly downstream from the first substrate.

Embodiments of the present invention relate to catalyst articles having a first zone and a second zone, the first zone including an ammonia slip catalyst (ASC) comprising a platinum group metal on a

support and a first SCR catalyst; and the second zone including a diesel oxidation catalyst (DOC) or diesel exotherm catalyst (DEC). The first zone may be configured to include a bottom layer including a blend of (1) the platinum group metal on a support, and (2) the first SCR catalyst; and a top layer including a second SCR catalyst, wherein the top layer is located over the bottom layer. In some embodiments, the first and second zone are located on a single substrate, with the first zone located on the inlet side of the substrate and the second zone located on the outlet side of the substrate. In another embodiment, the first zone is located on a first substrate and the second zone is located on a second substrate, wherein the first substrate is located upstream of the second substrate. The first and second substrate may be close coupled. When the first and second substrate are close coupled, the second substrate may be placed close to and/or directly downstream from the first substrate.

A method of reducing emissions from an exhaust stream may include contacting the exhaust stream with a catalyst article as described herein.

Three Zone Configuration

Embodiments of the present invention relate to catalyst articles having a first zone, a second zone, and a third zone. The first zone may include an SCR catalyst. The second zone may include an ASC having a blend of a platinum group metal on a support with a first SCR catalyst. The third zone may include a catalyst (“third zone catalyst”) such as a DOC or DEC. The first zone is located upstream of the second zone, and the second zone is located upstream of the third zone.

In some embodiments, the ASC is included in a first layer. The third zone catalyst may be located in a second layer which extends from the outlet end to less than a total length of the substrate, and the second layer is located on top of the first layer and is shorter in length than the first layer. The second SCR catalyst may be included in a layer which extends from the inlet end to less than a total length of the substrate, and which at least partially overlaps the first layer. In some embodiments, the first layer extends from the outlet end to less than a total length of the substrate. In some embodiments, the first layer extends from the inlet end to less than a total length of the substrate.

In some embodiments, the first zone, the second zone, and the third zone are located on a single substrate and the first zone is located on the inlet side of the substrate and the third zone is located on the outlet side of the substrate. In some embodiments, the first zone and second zone are located on a first substrate and the third zone is located on a second substrate, and the first substrate is located upstream of the second substrate. The first and second substrate may be close coupled. When the first and second

substrate are close coupled, the second substrate may be placed close to and/or directly downstream from the first substrate.

In some embodiments, the first zone is located on a first substrate, the second zone is located on a second substrate, and the third zone is located on a third substrate, where the first substrate is located upstream of the second substrate and the second substrate is located upstream of the third substrate. The first, second, and/or third substrate may be close coupled. When the first, second, and/or third substrate are close coupled, the second substrate may be placed close to and/or directly downstream from the first substrate, and the third substrate may be placed close to and/or directly downstream from the second substrate.

A method of reducing emissions from an exhaust stream may include contacting the exhaust stream with a catalyst article as described herein.

System Configurations

System configurations of the present invention may include a turbocharger, an upstream SCR catalyst, and a catalytic article having a two- or three-zone configuration as described in the preceding sections. The upstream SCR catalyst may be located upstream of the catalytic article having a two- or three-zone configuration as described in the preceding sections; in some embodiments, the upstream SCR catalyst and the catalytic article may be close-coupled. In some embodiments, the upstream SCR catalyst and the catalytic article are located on a single substrate, with the upstream SCR catalyst located upstream of the first and second (and third, if present) zones of the catalytic article. In some embodiments, the upstream SCR catalyst is located upstream of the turbocharger. When the upstream SCR catalyst is located upstream of the turbocharger, the upstream SCR catalyst is combined with an ASC. In some embodiments, the upstream SCR catalyst is located downstream of the turbocharger.

The catalytic article having a two- or three-zoned configuration as described above may be located downstream of the turbocharger. In some embodiments, the system includes an SCR catalyst located downstream of the catalytic article having a two- or three-zoned configuration as described above. In some embodiments, a system may also include a filter.

The system may include one or more reductant injectors, for example, upstream of any SCR catalyst in the system. In some embodiments, the system includes a reductant injector upstream of the SCR catalyst and/or the catalytic article having a two- or three-zone configuration as described above. In

a system having a downstream SCR catalyst, a reductant injector may be included upstream of the downstream SCR catalyst.

Referring to Figure 1, systems of the present invention may include a number of combinations of catalyst components. In general, the system may include a pre-turbo and post-turbo close coupled catalyst which may include any combination of the catalysts depicted in Figure 1. As shown in Figure 1, a system may include a pre-turbo catalyst which may include an SCR catalyst, an ASC, or an SCR/ASC of various configurations. The SCR/ASC pre-turbo catalyst configurations may include a bottom layer including an ASC and a top layer including an SCR catalyst. The ASC bottom layer may extend across the entire length of the substrate, or may extend from the outlet end towards the inlet end and cover less than the entire length of the substrate. The top layer SCR catalyst may extend from the inlet end of the substrate toward the outlet end and may at least partially overlap the ASC bottom layer. The top layer SCR catalyst may extend the entire length of the substrate, or may extend from the inlet end and cover less than the entire length of the substrate.

As shown in Figure 1, the system may include a urea injector upstream of the pre-turbo catalyst. The post-turbo catalyst may include an SCR catalyst, an ASC, and/or a DOC as described herein and as depicted in Figure 1. The post-turbo catalyst may be configured to include: 1) just a DOC, 2) an ASC and DOC, or 3) an SCR, ASC and DOC combination. The post-turbo catalyst may include a bottom layer including an ASC and a top layer including an SCR catalyst. The ASC bottom layer may extend across the entire length of the substrate, or may extend from the outlet end towards the inlet end and cover less than the entire length of the substrate. The top layer SCR catalyst may extend from the inlet end of the substrate toward the outlet end and may at least partially overlap the ASC bottom layer. The top layer SCR catalyst may extend the entire length of the substrate, or may extend from the inlet end and cover less than the entire length of the substrate. The DOC may be included in a top layer extending from the outlet end of the substrate toward an inlet end, covering less than an entire length of the substrate, and may be located on top of the ASC bottom layer. The DOC may be impregnated with a solution of platinum nitrate or palladium nitrate or a mixture of platinum and palladium nitrate.

The ASC sections shown in Figure 1 may comprise a blend as described herein. The downstream catalyst may include a filter and/or an SCR/ASC with another urea/NH₃ injection before SCR/ASC.

Referring to Figure 2, a system of the present invention may include a turbocharger, and urea injector, a close-coupled SCR/ASC/DOC catalyst, a filter, another urea injector, and an SCR/ASC

catalyst. As shown in Figure 2, the SCR/ASC/DOC catalyst may include an ASC bottom layer extending from the outlet end of the substrate toward the inlet end and covering less than the entire length of the substrate, a DOC layer extending from the outlet end of the substrate toward the inlet end and covering less than the entire length of the substrate and located on top of the ASC bottom layer, and an SCR catalyst layer extending from the inlet end toward the outlet end of the substrate and at least partially overlapping the ASC bottom layer. The ASC sections shown in Figure 2 may comprise a blend as described herein.

Referring to Figure 3, a system configuration of embodiments of the present invention can include a post-turbo close coupled SCR catalyst followed by an ASC/DOC catalyst. A system may include a turbocharger, a urea injector, an SCR catalyst and ASC/DOC catalyst, a filter, another urea injector, and an SCR/ASC catalyst. The ASC/DOC catalyst may include an ASC bottom layer which extends from the inlet end toward the outlet end of the substrate. In one configuration, the ASC bottom layer extends across the entire length of the substrate, with an SCR top layer extending from the inlet end toward the outlet end and covering less than the entire length of the substrate, and a DOC top layer extending from the outlet end toward the inlet end and covering less than the entire length of the substrate, where the SCR top layer and the DOC top layer are located on top of the ASC bottom layer. In another configuration, the ASC bottom layer extends from the inlet end toward the outlet end and covers less than the entire length of the substrate, with an SCR top layer located on top of the ASC bottom layer and extending from the inlet end toward the outlet end and covering less than the entire length of the substrate, and a DOC layer extending from the outlet end toward the inlet end and covering less than an entire length of the substrate. The DOC layer may partially overlap the ASC bottom layer. The ASC sections shown in Figure 3 may comprise a blend as described herein.

Figure 4 depicts a system configuration of embodiments of the present invention, including a pre-turbo close coupled SCR catalyst followed by a post-turbo ASC/DOC catalyst. A system may include a urea injector upstream of the SCR catalyst, followed by the turbocharger, an ASC/DOC catalyst, a filter, another urea injector, and an SCR/ASC catalyst. The ASC/DOC catalyst may include an ASC bottom layer which extends from the inlet end toward the outlet end of the substrate. In one configuration, the ASC bottom layer extends across the entire length of the substrate, with an SCR top layer extending from the inlet end toward the outlet end and covering less than the entire length of the substrate, and a DOC top layer extending from the outlet end toward the inlet end and covering less than the entire length of the substrate, where the SCR top layer and the DOC top layer are located on top of the ASC bottom layer. In another configuration, the ASC bottom layer extends from the inlet end toward the outlet end and covers less than the entire length of the substrate, with an SCR top layer located on top of the ASC bottom layer

and extending from the inlet end toward the outlet end and covering less than the entire length of the substrate, and a DOC layer extending from the outlet end toward the inlet end and covering less than an entire length of the substrate. The DOC layer may partially overlap the ASC bottom layer. The ASC sections shown in Figure 4 may comprise a blend as described herein.

Ammonia Oxidation Catalyst

Catalyst articles of the present invention may include one or more ammonia oxidation catalysts, also called an ammonia slip catalyst (“ASC”). One or more ASC may be included with or downstream from an SCR catalyst, to oxidize excess ammonia and prevent it from being released to the atmosphere. In some embodiments the ASC may be included on the same substrate as an SCR catalyst, or blended with an SCR catalyst. In certain embodiments, the ammonia oxidation catalyst material may be selected to favor the oxidation of ammonia instead of the formation of NO_x or N_2O . Preferred catalyst materials include platinum, palladium, or a combination thereof. The ammonia oxidation catalyst may comprise platinum and/or palladium supported on a metal oxide. In some embodiments, the catalyst is disposed on a high surface area support, including but not limited to alumina.

In some embodiments, the ammonia oxidation catalyst comprises a platinum group metal on a siliceous support. A siliceous material may include a material such as: (1) silica; (2) a zeolite with a silica-to-alumina ratio of at least 200; and (3) amorphous silica-doped alumina with SiO_2 content $\geq 40\%$. In some embodiments, a siliceous material may include a material such as a zeolite with a silica-to-alumina ratio of at least 200; at least 250; at least 300; at least 400; at least 500; at least 600; at least 750; at least 800; or at least 1000. In some embodiments, a platinum group metal is present on the support in an amount of about 0.1 wt% to about 10 wt% of the total weight of the platinum group metal and the support; about 0.5 wt% to about 10 wt% of the total weight of the platinum group metal and the support; about 1 wt% to about 6 wt% of the total weight of the platinum group metal and the support; about 1.5 wt% to about 4 wt% of the total weight of the platinum group metal and the support; about 10 wt% of the total weight of the platinum group metal and the support; about 0.1 wt% of the total weight of the platinum group metal and the support; about 0.5 wt% of the total weight of the platinum group metal and the support; about 1 wt% of the total weight of the platinum group metal and the support; about 2 wt% of the total weight of the platinum group metal and the support; about 3 wt% of the total weight of the platinum group metal and the support; about 4 wt% of the total weight of the platinum group metal and the support; about 5 wt% of the total weight of the platinum group metal and the support; about 6 wt% of the total weight of the platinum group metal and the support; about 7 wt% of the total weight of the platinum group metal and the support; about 8 wt% of the total weight of the platinum group metal and

the support; about 9 wt% of the total weight of the platinum group metal and the support; or about 10 wt% of the total weight of the platinum group metal and the support.

In some embodiments, the siliceous support can comprise a molecular sieve having a BEA, CDO, CON, FAU, MEL, MFI or MWY Framework Type.

SCR Catalyst

Systems of the present invention may include one or more SCR catalyst. In some embodiments, a catalyst article may include a first SCR catalyst and a second SCR catalyst. In some embodiments, the first SCR catalyst and the second SCR catalyst may comprise the same formulation as each other. In some embodiments, the first SCR catalyst and the second SCR catalyst may comprise different formulations than each other.

The exhaust system of the invention may include an SCR catalyst which is positioned downstream of an injector for introducing ammonia or a compound decomposable to ammonia into the exhaust gas. The SCR catalyst may be positioned directly downstream of the injector for injecting ammonia or a compound decomposable to ammonia (e.g. there is no intervening catalyst between the injector and the SCR catalyst).

The SCR catalyst includes a substrate and a catalyst composition. The substrate may be a flow-through substrate or a filtering substrate. When the SCR catalyst has a flow-through substrate, then the substrate may comprise the SCR catalyst composition (i.e. the SCR catalyst is obtained by extrusion) or the SCR catalyst composition may be disposed or supported on the substrate (i.e. the SCR catalyst composition is applied onto the substrate by a washcoating method).

When the SCR catalyst has a filtering substrate, then it is a selective catalytic reduction filter catalyst, which is referred to herein by the abbreviation “SCRF”. The SCRF comprises a filtering substrate and the selective catalytic reduction (SCR) composition. References to use of SCR catalysts throughout this application are understood to include use of SCRF catalysts as well, where applicable.

The selective catalytic reduction composition may comprise, or consist essentially of, a metal oxide based SCR catalyst formulation, a molecular sieve based SCR catalyst formulation, or mixture thereof. Such SCR catalyst formulations are known in the art.

The selective catalytic reduction composition may comprise, or consist essentially of, a metal oxide based SCR catalyst formulation. The metal oxide based SCR catalyst formulation comprises vanadium or tungsten or a mixture thereof supported on a refractory oxide. The refractory oxide may be selected from the group consisting of alumina, silica, titania, zirconia, ceria and combinations thereof.

The metal oxide based SCR catalyst formulation may comprise, or consist essentially of, an oxide of vanadium (e.g. V_2O_5) and/or an oxide of tungsten (e.g. WO_3) supported on a refractory oxide selected from the group consisting of titania (e.g. TiO_2), ceria (e.g. CeO_2), and a mixed or composite oxide of cerium and zirconium (e.g. $Ce_xZr_{(1-x)}O_2$, wherein $x = 0.1$ to 0.9 , preferably $x = 0.2$ to 0.5).

When the refractory oxide is titania (e.g. TiO_2), then preferably the concentration of the oxide of vanadium is from 0.5 to 6 wt% (e.g. of the metal oxide based SCR formulation) and/or the concentration of the oxide of tungsten (e.g. WO_3) is from 5 to 20 wt%. More preferably, the oxide of vanadium (e.g. V_2O_5) and the oxide of tungsten (e.g. WO_3) are supported on titania (e.g. TiO_2).

When the refractory oxide is ceria (e.g. CeO_2), then preferably the concentration of the oxide of vanadium is from 0.1 to 9 wt% (e.g. of the metal oxide based SCR formulation) and/or the concentration of the oxide of tungsten (e.g. WO_3) is from 0.1 to 9 wt%.

The metal oxide based SCR catalyst formulation may comprise, or consist essentially of, an oxide of vanadium (e.g. V_2O_5) and optionally an oxide of tungsten (e.g. WO_3), supported on titania (e.g. TiO_2).

The selective catalytic reduction composition may comprise, or consist essentially of, a molecular sieve based SCR catalyst formulation. The molecular sieve based SCR catalyst formulation comprises a molecular sieve, which is optionally a transition metal exchanged molecular sieve. It is preferable that the SCR catalyst formulation comprises a transition metal exchanged molecular sieve.

In general, the molecular sieve based SCR catalyst formulation may comprise a molecular sieve having an aluminosilicate framework (e.g. zeolite), an aluminophosphate framework (e.g. AlPO), a silicoaluminophosphate framework (e.g. SAPO), a heteroatom-containing aluminosilicate framework, a heteroatom-containing aluminophosphate framework (e.g. MeAlPO, where Me is a metal), or a heteroatom-containing silicoaluminophosphate framework (e.g. MeAPSO, where Me is a metal). The heteroatom (i.e. in a heteroatom-containing framework) may be selected from the group consisting of boron (B), gallium (Ga), titanium (Ti), zirconium (Zr), zinc (Zn), iron (Fe), vanadium (V) and combinations of any two or more thereof. It is preferred that the heteroatom is a metal (e.g. each of the above heteroatom-containing frameworks may be a metal-containing framework).

It is preferable that the molecular sieve based SCR catalyst formulation comprises, or consist essentially of, a molecular sieve having an aluminosilicate framework (e.g. zeolite) or a silicoaluminophosphate framework (e.g. SAPO).

When the molecular sieve has an aluminosilicate framework (e.g. the molecular sieve is a zeolite), then typically the molecular sieve has a silica to alumina molar ratio (SAR) of from 5 to 200 (e.g. 10 to 200), 10 to 100 (e.g. 10 to 30 or 20 to 80), such as 12 to 40, or 15 to 30. In some embodiments, a suitable molecular sieve has a SAR of > 200; > 600; or > 1200. In some embodiments, the molecular sieve has a SAR of from about 1500 to about 2100.

Typically, the molecular sieve is microporous. A microporous molecular sieve has pores with a diameter of less than 2 nm (e.g. in accordance with the IUPAC definition of “microporous” [see *Pure & Appl. Chem.*, 66(8), (1994), 1739-1758)]).

The molecular sieve based SCR catalyst formulation may comprise a small pore molecular sieve (e.g. a molecular sieve having a maximum ring size of eight tetrahedral atoms), a medium pore molecular sieve (e.g. a molecular sieve having a maximum ring size of ten tetrahedral atoms) or a large pore molecular sieve (e.g. a molecular sieve having a maximum ring size of twelve tetrahedral atoms) or a combination of two or more thereof.

When the molecular sieve is a small pore molecular sieve, then the small pore molecular sieve may have a framework structure represented by a Framework Type Code (FTC) selected from the group consisting of ACO, AEI, AEN, AFN, AFT, AFX, ANA, APC, APD, ATT, CDO, CHA, DDR, DFT, EAB, EDI, EPI, ERI, GIS, GOO, IHW, ITE, ITW, LEV, LTA, KFI, MER, MON, NSI, OWE, PAU, PHI, RHO, RTH, SAT, SAV, SFW, SIV, THO, TSC, UEI, UFI, VNI, YUG and ZON, or a mixture and/or an intergrowth of two or more thereof. Preferably, the small pore molecular sieve has a framework structure represented by a FTC selected from the group consisting of CHA, LEV, AEI, AFX, ERI, LTA, SFW, KFI, DDR and ITE. More preferably, the small pore molecular sieve has a framework structure represented by a FTC selected from the group consisting of CHA and AEI. The small pore molecular sieve may have a framework structure represented by the FTC CHA. The small pore molecular sieve may have a framework structure represented by the FTC AEI. When the small pore molecular sieve is a zeolite and has a framework represented by the FTC CHA, then the zeolite may be chabazite.

When the molecular sieve is a medium pore molecular sieve, then the medium pore molecular sieve may have a framework structure represented by a Framework Type Code (FTC) selected from the

group consisting of AEL, AFO, AHT, BOF, BOZ, CGF, CGS, CHI, DAC, EUO, FER, HEU, IMF, ITH, ITR, JRY, JSR, JST, LAU, LOV, MEL, MFI, MFS, MRE, MTT, MVY, MWW, NAB, NAT, NES, OBW, -PAR, PCR, PON, PUN, RRO, RSN, SFF, SFG, STF, STI, STT, STW, -SVR, SZR, TER, TON, TUN, UOS, VSV, WEI and WEN, or a mixture and/or an intergrowth of two or more thereof. Preferably, the medium pore molecular sieve has a framework structure represented by a FTC selected from the group consisting of FER, MEL, MFI, and STT. More preferably, the medium pore molecular sieve has a framework structure represented by a FTC selected from the group consisting of FER and MFI, particularly MFI. When the medium pore molecular sieve is a zeolite and has a framework represented by the FTC FER or MFI, then the zeolite may be ferrierite, silicalite or ZSM-5.

When the molecular sieve is a large pore molecular sieve, then the large pore molecular sieve may have a framework structure represented by a Framework Type Code (FTC) selected from the group consisting of AFI, AFR, AFS, AFY, ASV, ATO, ATS, BEA, BEC, BOG, BPH, BSV, CAN, CON, CZP, DFO, EMT, EON, EZT, FAU, GME, GON, IFR, ISV, ITG, IWR, IWS, IWV, IWW, JSR, LTF, LTL, MAZ, MEI, MOR, MOZ, MSE, MTW, NPO, OFF, OKO, OSI, -RON, RWY, SAF, SAO, SBE, SBS, SBT, SEW, SFE, SFO, SFS, SFV, SOF, SOS, STO, SSF, SSY, USI, UWY, and VET, or a mixture and/or an intergrowth of two or more thereof. Preferably, the large pore molecular sieve has a framework structure represented by a FTC selected from the group consisting of AFI, BEA, MAZ, MOR, and OFF. More preferably, the large pore molecular sieve has a framework structure represented by a FTC selected from the group consisting of BEA, MOR and MFI. When the large pore molecular sieve is a zeolite and has a framework represented by the FTC BEA, FAU or MOR, then the zeolite may be a beta zeolite, faujasite, zeolite Y, zeolite X or mordenite.

In general, it is preferred that the molecular sieve is a small pore molecular sieve.

The molecular sieve based SCR catalyst formulation preferably comprises a transition metal exchanged molecular sieve. The transition metal may be selected from the group consisting of cobalt, copper, iron, manganese, nickel, palladium, platinum, ruthenium and rhenium.

The transition metal may be copper. An advantage of SCR catalyst formulations containing a copper exchanged molecular sieve is that such formulations have excellent low temperature NO_x reduction activity (e.g. it may be superior to the low temperature NO_x reduction activity of an iron exchanged molecular sieve). Systems and method of the present invention may include any type of SCR catalyst, however, SCR catalysts including copper (“Cu-SCR catalysts”) may experience more notable benefits from systems of the present invention, as they are particularly vulnerable to the effects of

sulfation. Cu-SCR catalyst formulations may include, for example, Cu exchanged SAPO-34, Cu exchanged CHA zeolite, Cu exchanged AEI zeolites, or combinations thereof.

The transition metal may be present on an extra-framework site on the external surface of the molecular sieve or within a channel, cavity or cage of the molecular sieve.

Typically, the transition metal exchanged molecular sieve comprises an amount of 0.10 to 10 % by weight of the transition metal exchanged molecular, preferably an amount of 0.2 to 5 % by weight.

In general, the selective catalytic reduction catalyst comprises the selective catalytic reduction composition in a total concentration of 0.5 to 4.0 g in⁻³, preferably 1.0 to 3.0 4.0 g in⁻³.

The SCR catalyst composition may comprise a mixture of a metal oxide based SCR catalyst formulation and a molecular sieve based SCR catalyst formulation. The (a) metal oxide based SCR catalyst formulation may comprise, or consist essentially of, an oxide of vanadium (e.g. V₂O₅) and optionally an oxide of tungsten (e.g. WO₃), supported on titania (e.g. TiO₂) and (b) the molecular sieve based SCR catalyst formulation may comprise a transition metal exchanged molecular sieve.

When the SCR catalyst is an SCRF, then the filtering substrate may preferably be a wall flow filter substrate monolith. The wall flow filter substrate monolith (e.g. of the SCR-DPF) typically has a cell density of 60 to 400 cells per square inch (cpsi). It is preferred that the wall flow filter substrate monolith has a cell density of 100 to 350 cpsi, more preferably 200 to 300 cpsi.

The wall flow filter substrate monolith may have a wall thickness (e.g. average internal wall thickness) of 0.20 to 0.50 mm, preferably 0.25 to 0.35 mm (e.g. about 0.30 mm).

Generally, the uncoated wall flow filter substrate monolith has a porosity of from 50 to 80 %, preferably 55 to 75 %, and more preferably 60 to 70 %.

The uncoated wall flow filter substrate monolith typically has a mean pore size of at least 5 μ m. It is preferred that the mean pore size is from 10 to 40 μ m, such as 15 to 35 μ m, more preferably 20 to 30 μ m.

The wall flow filter substrate may have a symmetric cell design or an asymmetric cell design.

In general for an SCRF, the selective catalytic reduction composition is disposed within the wall of the wall-flow filter substrate monolith. Additionally, the selective catalytic reduction composition may be disposed on the walls of the inlet channels and/or on the walls of the outlet channels.

Blend

Embodiments of the present invention may include a blend of (1) a platinum group metal on a support, and (2) an SCR catalyst. In some embodiments, within the blend, a weight ratio of the SCR catalyst to the platinum group metal on a support is about 3:1 to about 300:1; about 3:1 to about 250:1; about 3:1 to about 200:1; about 4:1 to about 150:1; about 5:1 to about 100:1; about 6:1 to about 90:1; about 7:1 to about 80:1; about 8:1 to about 70:1; about 9:1 to about 60:1; about 10:1 to about 50:1; about 3:1; about 4:1; about 5:1; about 6:1; about 7:1; about 8:1; about 9:1; about 10:1; about 15:1; about 20:1; about 25:1; about 30:1; about 40:1; about 50:1; about 75:1; about 100:1; about 125:1; about 150:1; about 175:1; about 200:1; about 225:1; about 250:1; about 275:1; or about 300:1.

DOC

Catalyst articles and systems of the present invention may include one or more diesel oxidation catalysts. Oxidation catalysts, and in particular diesel oxidation catalysts (DOCs), are well-known in the art. Oxidation catalysts are designed to oxidize CO to CO₂ and gas phase hydrocarbons (HC) and an organic fraction of diesel particulates (soluble organic fraction) to CO₂ and H₂O. Typical oxidation catalysts include platinum and optionally also palladium on a high surface area inorganic oxide support, such as alumina, silica-alumina and a zeolite.

Substrate

Catalysts of the present invention may each further comprise a flow-through substrate or filter substrate. In one embodiment, the catalyst may be coated onto the flow-through or filter substrate, and preferably deposited on the flow-through or filter substrate using a washcoat procedure.

The combination of an SCR catalyst and a filter is known as a selective catalytic reduction filter (SCRF catalyst). An SCRF catalyst is a single-substrate device that combines the functionality of an SCR and particulate filter, and is suitable for embodiments of the present invention as desired. Description of and references to the SCR catalyst throughout this application are understood to include the SCRF catalyst as well, where applicable.

The flow-through or filter substrate is a substrate that is capable of containing catalyst/adsorber components. The substrate is preferably a ceramic substrate or a metallic substrate. The ceramic substrate may be made of any suitable refractory material, e.g., alumina, silica, titania, ceria, zirconia, magnesia, zeolites, silicon nitride, silicon carbide, zirconium silicates, magnesium silicates, aluminosilicates, metallo aluminosilicates (such as cordierite and spudomene), or a mixture or mixed oxide of any two or more thereof. Cordierite, a magnesium aluminosilicate, and silicon carbide are particularly preferred.

The metallic substrates may be made of any suitable metal, and in particular heat-resistant metals and metal alloys such as titanium and stainless steel as well as ferritic alloys containing iron, nickel, chromium, and/or aluminum in addition to other trace metals.

The flow-through substrate is preferably a flow-through monolith having a honeycomb structure with many small, parallel thin-walled channels running axially through the substrate and extending throughout from an inlet or an outlet of the substrate. The channel cross-section of the substrate may be any shape, but is preferably square, sinusoidal, triangular, rectangular, hexagonal, trapezoidal, circular, or oval. The flow-through substrate may also be high porosity which allows the catalyst to penetrate into the substrate walls.

The filter substrate is preferably a wall-flow monolith filter. The channels of a wall-flow filter are alternately blocked, which allow the exhaust gas stream to enter a channel from the inlet, then flow through the channel walls, and exit the filter from a different channel leading to the outlet. Particulates in the exhaust gas stream are thus trapped in the filter.

The catalyst/adsorber may be added to the flow-through or filter substrate by any known means, such as a washcoat procedure.

Reductant/Urea Injector

The system may include a means for introducing a nitrogenous reductant into the exhaust system upstream of the SCR and/or SCRF catalyst. It may be preferred that the means for introducing a nitrogenous reductant into the exhaust system is directly upstream of the SCR or SCRF catalyst (e.g. there is no intervening catalyst between the means for introducing a nitrogenous reductant and the SCR or SCRF catalyst).

The reductant is added to the flowing exhaust gas by any suitable means for introducing the reductant into the exhaust gas. Suitable means include an injector, sprayer, or feeder. Such means are well known in the art.

The nitrogenous reductant for use in the system can be ammonia per se, hydrazine, or an ammonia precursor selected from the group consisting of urea, ammonium carbonate, ammonium carbamate, ammonium hydrogen carbonate, and ammonium formate. Urea is particularly preferred.

The exhaust system may also comprise a means for controlling the introduction of reductant into the exhaust gas in order to reduce NO_x therein. Preferred control means may include an electronic control unit, optionally an engine control unit, and may additionally comprise a NO_x sensor located downstream of the NO reduction catalyst.

Benefits

Catalyst articles of the present invention may provide higher catalytic activity and selectivity. Additionally, in some embodiments, HC oxidation and exotherm generation may be concentrated in the rear zone, thereby protecting the front ASC zone from hydrothermal degradation.

In some embodiments, catalyst articles of the present invention may have equivalent or enhanced NO_x conversion compared to a catalyst article which is equivalent except does not include the SCR in the bottom layer. In some embodiments, catalyst articles of the present invention may have enhanced NO_x conversion compared to a catalyst article which is equivalent except does not include the first SCR catalyst, the inventive catalyst article showing an improvement in NO_x conversion of about 40% to about 50%.

In some embodiments, catalyst articles of the present invention may have reduced activity for N₂O formation at temperatures below about 350°C compared to a catalyst article which is equivalent except does not include the SCR in the ASC bottom layer. In some embodiments, catalyst articles of the present invention may have reduced activity for N₂O formation at temperatures below about 350°C compared to a catalyst article which is equivalent except does not include the first SCR catalyst, the inventive catalyst article showing a reduction in N₂O formation of greater than about 60%.

As used in this specification and the appended claims, the singular forms "a", "an" and "the" include plural referents unless the context clearly indicates otherwise. Thus, for example, reference to "a catalyst" includes a mixture of two or more catalysts, and the like.

The term “ammonia slip”, means the amount of unreacted ammonia that passes through the SCR catalyst.

The term “support” means the material to which a catalyst is fixed.

The term “calcine”, or “calcination”, means heating the material in air or oxygen. This definition is consistent with the IUPAC definition of calcination. (IUPAC. Compendium of Chemical Terminology, 2nd ed. (the "Gold Book"). Compiled by A. D. McNaught and A. Wilkinson. Blackwell Scientific Publications, Oxford (1997). XML on-line corrected version: <http://goldbook.iupac.org> (2006-) created by M. Nic, J. Jirat, B. Kosata; updates compiled by A. Jenkins. ISBN 0-9678550-9-8. doi:10.1351/goldbook.) Calcination is performed to decompose a metal salt and promote the exchange of metal ions within the catalyst and also to adhere the catalyst to a substrate. The temperatures used in calcination depend upon the components in the material to be calcined and generally are between about 400 °C to about 900 °C for approximately 1 to 8 hours. In some cases, calcination can be performed up to a temperature of about 1200 °C. In applications involving the processes described herein, calcinations are generally performed at temperatures from about 400 °C to about 700 °C for approximately 1 to 8 hours, preferably at temperatures from about 400 °C to about 650 °C for approximately 1 to 4 hours.

When a range, or ranges, for various numerical elements are provided, the range, or ranges, can include the values, unless otherwise specified.

The term “N₂ selectivity” means the percent conversion of ammonia into nitrogen.

The terms “diesel oxidation catalyst” (DOC), “diesel exotherm catalyst” (DEC), “NO_x absorber”, “SCR/PNA” (selective catalytic reduction/pассивный NO_x адсорбент), “cold-start catalyst” (CSC) and “three-way catalyst” (TWC) are well known terms in the art used to describe various types of catalysts used to treat exhaust gases from combustion processes.

The term “platinum group metal” or “PGM” refers to platinum, palladium, ruthenium, rhodium, osmium and iridium. The platinum group metals are preferably platinum, palladium, ruthenium or rhodium.

The terms “downstream” and “upstream” describe the orientation of a catalyst or substrate where the flow of exhaust gas is from the inlet end to the outlet end of the substrate or article.

The following examples merely illustrate the invention; the skilled person will recognize many variations that are within the spirit of the invention and scope of the claims.

Example

In this example, three close-coupled catalyst configurations were tested under simulated engine out conditions with systematically varied functionalities: (1) SCR-only, (2) SCR/DOC, (3) ASC/DOC and (4) SCR/ASC/DOC. In addition, tests were performed with both $\text{ANR} < 1$ and $\text{ANR} > 1$ to understand the impact of NH_3 slip and ASC functionality in overall system performance.

The tested configurations depicted in Figure 5. Test conditions: 600/1200 ppm NH_3 , 1000 ppm NO, 500ppm (C1-based) $\text{C}_{10}\text{H}_{22}$, 200ppm CO, 10% O_2 , 4.5% CO_2 , 4.5% H_2O , total SV = 30,000 h-1, 40,000 h-1 and 50,000 h-1 for SCR/DOC, SCR/ASC/DOC and SCR catalyst, respectively. Results are shown in Figures 6-13.

In configuration (1) with only an SCR catalyst, the system has the highest NOx conversion and lowest N_2O formation, but has very poor HC/CO conversion and lacks NH_3 slip control, especially when $\text{ANR} > 1$. As shown in configuration (2), the NH_3 slipped from the SCR catalyst is oxidized on the rear DOC zone with very high N_2O selectivity at low temperatures ($T \leq 350$ °C); furthermore, at higher temperatures ($T \geq 350$ °C), NH_3 oxidation on DOC has high selectivity towards NOx formation, which reduces total NOx conversion of the system.

To minimize NH_3 slip to downstream DOC, configuration (3) with ASC/DOC was evaluated with either the blend ASC or a traditional Pt/alumina-type ASC both at 3 g/ft³ Pt loading. As shown in Figure 11, configuration (3) with traditional ASC in the front zone, the system produces an even higher amount of N_2O than that in configuration (2) due to insufficient SCR functionality and unselective NO + NH_3 reaction on Pt from the ASC. In contrast, when configuration (3) is tested with the blend ASC, N_2O formation is reduced by > 60% at temperatures below 350 °C. In fact, at most relevant temperatures between 250 °C and 350 °C, N_2O from this system is even 30-50% lower than that in configuration (2). Similarly, configuration (3) with blend ASC also showed high selectivity at higher temperatures comparing to that with a traditional ASC, resulting in 40-50% increase in total NOx conversion. (See Figure 8). Those results suggest the inventive ASC preferentially promotes selective NO + NH_3 reaction catalyzed by Cu-SCR catalyst while minimizing unselective NO + NH_3 reaction and NH_3 oxidation catalyzed by Pt, making it highly suitable for the close-coupled application.

To further improve the system performance, a three zoned configuration (configuration (4)) with an additional front SCR zone was evaluated. As shown in Figures 8 and 12, the three zoned configuration with blend ASC in the middle zone showed further improved NO conversion and N₂ selectivity compare to the two zoned configuration with the blend ASC in front. The overall performance of configuration (4) has similar NOx conversion and N₂O formation as configuration (1) (i.e. SCR-only), and similar NH₃, HC and CO conversions as configuration (2) and (3) (i.e. SCR/DOC and ASC/DOC). (See Figures 8, 11, 6, 10, and 9).

In the aforementioned configurations, each zone/functionality can be coated on a single substrate or separate substrates; and in an engine system equipped with a turbo charger, those functionalities can be divided into pre- and post-turbo catalysts.

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Claims

1. A catalyst article comprising a substrate comprising an inlet end and an outlet end, a first zone and a second zone,
 - where the first zone comprises:
 - a. an ammonia slip catalyst (ASC) bottom layer comprising a blend of: (1) a platinum group metal on a support and (2) a first SCR catalyst; and
 - b. an SCR layer comprising a second SCR catalyst, the SCR layer located over the ASC bottom layer;
 - where the second zone comprises a catalyst (“second zone catalyst”) selected from the group consisting of a diesel oxidation catalyst (DOC) and a diesel exotherm catalyst (DEC);
 - wherein the ASC bottom layer extends into the second zone; and
 - where the first zone is located upstream of the second zone.
2. The catalyst article of claim 1, wherein the second SCR catalyst comprises Fe, Mn, Cu, or combinations thereof.
3. The catalyst article of claim 1, wherein the first SCR catalyst comprises Fe, Mn, Cu, or combinations thereof.
4. The catalyst article of claim 1, wherein
 - the ASC bottom layer extends from the outlet end to less than a total length of the substrate;
 - the SCR layer extends from the inlet end to less than a total length of the substrate, and which at least partially overlaps the ASC bottom layer; and
 - the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, where the second layer is located on top of the ASC bottom layer and is shorter in length than the ASC bottom layer.
5. The catalyst article of claim 1, wherein
 - the ASC bottom layer extends from the inlet end to less than a total length of the substrate;

the SCR layer extends from the inlet end to less than a total length of the substrate, where the SCR layer is located on top of the ASC bottom layer and does not extend further toward the outlet end than the ASC bottom layer; and

the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, where the second layer at least partially overlaps the ASC bottom layer.

6. The catalyst article of claim 1, wherein

the ASC bottom layer extends from the inlet end to less than a total length of the substrate;

the SCR layer extends from the inlet end to less than a total length of the substrate, where the SCR layer is located on top of the ASC bottom layer and extends further toward the outlet end than the ASC bottom layer; and

the second zone catalyst is included in a layer which extends from the outlet end to less than a total length of the substrate.

7. The catalyst article of claim 1, wherein

the ASC bottom layer covers a total length of the substrate;

the SCR layer extends from the inlet end to less than a total length of the substrate, wherein the SCR layer is located on top of the ASC bottom layer; and

the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, wherein the second layer is located on top of the ASC bottom layer.

8. The catalyst article of claim 1, wherein the second zone catalyst is located within the substrate.

9. The catalyst article of claim 1, wherein the support comprises a siliceous material.

10. The catalyst article of claim 9, wherein the siliceous material comprises a material selected from the group consisting of: (1) silica; (2) a zeolite with a silica-to-alumina ratio higher than 200; and (3) amorphous silica-doped alumina with SiO_2 content $\geq 40\%$.

11. The catalyst article of claim 1, wherein the platinum group metal is present on the support in an amount of 0.1 wt% to 10 wt% of the total weight of the platinum group metal and the support.

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12. The catalyst article of claim 1, wherein the platinum group metal is present on the support in an amount of 1 wt% to 6 wt% of the total weight of the platinum group metal and the support.
13. The catalyst article of claim 1, wherein the platinum group metal is present on the support in an amount of 1.5 wt% to 4 wt% of the total weight of the platinum group metal and the support.
14. The catalytic article of claim 1, where the platinum group metal comprises platinum, palladium or a combination of platinum and palladium.
15. The catalyst article of claim 1, wherein the platinum group metal comprises platinum.
16. The catalyst article of claim 1, wherein, within the blend, a weight ratio of the first SCR catalyst to the platinum group metal on a support is 3:1 to 300:1.
17. The catalyst article of claim 1, wherein, within the blend, a weight ratio of the first SCR catalyst to the platinum group metal on a support is 5:1 to 100:1.
18. The catalyst article of claim 1, wherein, within the blend, a weight ratio of the first SCR catalyst to the platinum group metal on a support is 10:1 to 50:1.
19. The catalyst article of claim 1, where the first SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof.
20. The catalyst article of claim 1, wherein the first SCR catalyst comprises copper.
21. The catalyst article of claim 1, where the first zone and the second zone are located on a single substrate and the first zone is located on the inlet side of the substrate and the second zone is located on the outlet side of the substrate.
22. The catalyst article of claim 1, where the substrate comprises a first substrate and a second substrate, where the first zone is located on the first substrate and the second zone is located on the second substrate and the first substrate is located upstream of the second substrate.
23. The catalyst article of claim 1, where the second SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof.

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24. A method of reducing emissions from an exhaust stream, comprising contacting the exhaust stream with a catalytic article comprising a substrate comprising an inlet end and an outlet end, a first zone and a second zone,
 - where the first zone comprises:
 - a. an ammonia slip catalyst (ASC) bottom layer comprising a blend of: (1) a platinum group metal on a support and (2) a first SCR catalyst; and
 - b. an SCR layer comprising a second SCR catalyst, the SCR layer located over the ASC bottom layer;
 - where the second zone comprises a catalyst (“second zone catalyst”) selected from the group consisting of a diesel oxidation catalyst (DOC) and a diesel exotherm catalyst (DEC);
 - wherein the ASC bottom layer extends into the second zone; and
 - where the first zone is located upstream of the second zone.
25. The method of claim 24, wherein the second SCR catalyst comprises Fe, Mn, Cu, or combinations thereof.
26. The method of claim 24, wherein the first SCR catalyst comprises Fe, Mn, Cu, or combinations thereof.
27. The method of claim 24, wherein
 - the ASC bottom layer extends from the outlet end to less than a total length of the substrate;
 - the SCR layer extends from the inlet end to less than a total length of the substrate, and which at least partially overlaps the ASC bottom layer; and
 - the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, where the second layer is located on top of the ASC bottom layer and is shorter in length than the ASC bottom layer.
28. The method of claim 24, wherein
 - the ASC bottom layer extends from the inlet end to less than a total length of the substrate;
 - the SCR layer extends from the inlet end to less than a total length of the substrate, where the SCR layer is located on top of the ASC bottom layer and does not extend further toward the outlet end than the ASC bottom layer; and

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the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, where the second layer at least partially overlaps the ASC bottom layer.

29. The method of claim 24, wherein

the ASC bottom layer extends from the inlet end to less than a total length of the substrate;

the SCR layer extends from the inlet end to less than a total length of the substrate, where the SCR layer is located on top of the ASC bottom layer and extends further toward the outlet end than the ASC bottom layer; and

the second zone catalyst is included in a layer which extends from the outlet end to less than a total length of the substrate.

30. The method of claim 24, wherein

the ASC bottom layer covers a total length of the substrate;

the SCR layer extends from the inlet end to less than a total length of the substrate, wherein the SCR layer is located on top of the ASC bottom layer; and

the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, wherein the second layer is located on top of the ASC bottom layer.

31. The method of claim 24, wherein the second zone catalyst is located within the substrate.

32. The method of claim 24, wherein the support comprises a siliceous material.

33. The method of claim 32, wherein the siliceous material comprises a material selected from the group consisting of: (1) silica; (2) a zeolite with a silica-to-alumina ratio higher than 200; and (3) amorphous silica-doped alumina with SiO_2 content $\geq 40\%$.

34. The method of claim 24, wherein the platinum group metal is present on the support in an amount of 0.1 wt% to 10 wt% of the total weight of the platinum group metal and the support.

35. The method of claim 24, wherein the platinum group metal is present on the support in an amount of 1 wt% to 6 wt% of the total weight of the platinum group metal and the support.

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36. The method of claim 24, wherein the platinum group metal is present on the support in an amount of 1.5 wt% to 4 wt% of the total weight of the platinum group metal and the support.
37. The method of claim 24, where the platinum group metal comprises platinum, palladium or a combination of platinum and palladium.
38. The method of claim 24, wherein the platinum group metal comprises platinum.
39. The method of claim 24, wherein, within the blend, a weight ratio of the first SCR catalyst to the platinum group metal on a support is 3:1 to 300:1.
40. The method of claim 24, wherein, within the blend, a weight ratio of the first SCR catalyst to the platinum group metal on a support is 5:1 to 100:1.
41. The method of claim 24, wherein, within the blend, a weight ratio of the first SCR catalyst to the platinum group metal on a support is 10:1 to 50:1.
42. The method of claim 24, where the first SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof.
43. The method of claim 24, wherein the first SCR catalyst comprises copper.
44. The method of claim 24, where the first zone and the second zone are located on a single substrate and the first zone is located on the inlet side of the substrate and the second zone is located on the outlet side of the substrate.
45. The method of claim 24, where the substrate comprises a first substrate and a second substrate, where the first zone is located on the first substrate and the second zone is located on the second substrate and the first substrate is located upstream of the second substrate.
46. The method of claim 24, where the second SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof.
47. An exhaust purification system for reduction of emissions from an exhaust stream, comprising:
 - a. a turbocharger;
 - b. a third SCR catalyst;
 - c. a catalyst article comprising a substrate comprising an inlet end and an outlet end, a first zone and a second zone,

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where the first zone comprises:

- i. an ammonia slip catalyst (ASC) bottom layer comprising a blend of: (1) a platinum group metal on a support and (2) a first SCR catalyst; and
- ii. an SCR layer comprising a second SCR catalyst, the SCR layer located over the ASC bottom layer;

where the second zone comprises a catalyst (“second zone catalyst”) selected from the group consisting of a diesel oxidation catalyst (DOC) and a diesel exotherm catalyst (DEC);

wherein the ASC bottom layer extends into the second zone; and

where the first zone is located upstream of the second zone.

48. The system of claim 47, wherein the third SCR catalyst is located upstream of the turbocharger.
49. The system of claim 47, wherein the third SCR catalyst is located downstream of the turbocharger.
50. The system of claim 47, wherein the second SCR catalyst comprises Fe, Mn, Cu, or combinations thereof.
51. The system of claim 47, wherein the first SCR catalyst comprises Fe, Mn, Cu, or combinations thereof.
52. The system of claim 47, wherein the third SCR catalyst comprises V, Fe, Mn, Cu, or combinations thereof.
53. The system of claim 47, wherein the third SCR catalyst and the catalyst article are located on a single substrate, with the third SCR catalyst located upstream of the first zone and the second zone.
54. The system of claim 47, wherein the third SCR catalyst is located on a substrate upstream of the catalyst article substrate.
55. The system of claim 47, wherein the third SCR catalyst is close-coupled with the catalyst article.
56. The system of claim 47, further comprising a filter.
57. The system of claim 47, further comprising a downstream SCR catalyst, located downstream from the catalyst article.

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58. The system of claim 47, further comprising a pre-turbo SCR catalyst, located upstream of the turbocharger.
59. The system of claim 47, further comprising a reductant injector located upstream of the third SCR catalyst.
60. The system of claim 57, further comprising a reductant injector located upstream of the downstream SCR catalyst.
61. The system of claim 58, further comprising a reductant injector located upstream of the pre-turbo SCR catalyst.
62. The system of claim 47, wherein
 - the ASC bottom layer extends from the outlet end to less than a total length of the substrate;
 - the SCR layer extends from the inlet end to less than a total length of the substrate, and which at least partially overlaps the ASC bottom layer; and
 - the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, where the second layer is located on top of the ASC bottom layer and is shorter in length than the ASC bottom layer.
63. The system of claim 47, wherein
 - the ASC bottom layer extends from the inlet end to less than a total length of the substrate;
 - the SCR layer extends from the inlet end to less than a total length of the substrate, where the SCR layer is located on top of the ASC bottom layer and does not extend further toward the outlet end than the ASC bottom layer; and
 - the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, where the second layer at least partially overlaps the ASC bottom layer.
64. The system of claim 47, wherein
 - the ASC bottom layer extends from the inlet end to less than a total length of the substrate;

the SCR layer extends from the inlet end to less than a total length of the substrate, where the SCR layer is located on top of the ASC bottom layer and extends further toward the outlet end than the ASC bottom layer; and

the second zone catalyst is included in a layer which extends from the outlet end to less than a total length of the substrate.

65. The system of claim 47, wherein

the ASC bottom layer covers a total length of the substrate;

the SCR layer extends from the inlet end to less than a total length of the substrate, wherein the SCR layer is located on top of the ASC bottom layer; and

the second zone catalyst is included in a second layer which extends from the outlet end to less than a total length of the substrate, wherein the second layer is located on top of the ASC bottom layer.

66. The system of claim 47, wherein the second zone catalyst is located within the substrate.

67. The system of claim 47, wherein the support comprises a siliceous material.

68. The system of claim 67, wherein the siliceous material comprises a material selected from the group consisting of: (1) silica; (2) a zeolite with a silica-to-alumina ratio higher than 200; and (3) amorphous silica-doped alumina with SiO_2 content $\geq 40\%$.

69. The system of claim 47, wherein the platinum group metal is present on the support in an amount of 0.1 wt% to 10 wt% of the total weight of the platinum group metal and the support.

70. The system of claim 47, wherein the platinum group metal is present on the support in an amount of 1 wt% to 6 wt% of the total weight of the platinum group metal and the support.

71. The system of claim 47, wherein the platinum group metal is present on the support in an amount of 1.5 wt% to 4 wt% of the total weight of the platinum group metal and the support.

72. The system of claim 47, where the platinum group metal comprises platinum, palladium or a combination of platinum and palladium.

73. The system of claim 47, wherein the platinum group metal comprises platinum.

74. The system of claim 47, wherein, within the blend, a weight ratio of the first SCR catalyst to the platinum group metal on a support is 3:1 to 300:1.
75. The system of claim 47, wherein, within the blend, a weight ratio of the first SCR catalyst to the platinum group metal on a support is 5:1 to 100:1.
76. The system of claim 47, wherein, within the blend, a weight ratio of the first SCR catalyst to the platinum group metal on a support is 10:1 to 50:1.
77. The system of claim 47, where the first SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof.
78. The system of claim 47, wherein the first SCR catalyst comprises copper.
79. The system of claim 47, where the first zone and the second zone are located on a single substrate and the first zone is located on the inlet side of the substrate and the second zone is located on the outlet side of the substrate.
80. The system of claim 47, where the substrate comprises a first substrate and a second substrate, where the first zone is located on the first substrate and the second zone is located on the second substrate and the first substrate is located upstream of the second substrate.
81. The system of claim 47, where the second SCR catalyst is a base metal, an oxide of a base metal, a molecular sieve, a metal exchanged molecular sieve or a mixture thereof.