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(54) Title: CALIBRATION METHOD AND APPARATUS FOR SCR CATALYST SYSTEMS



Fig. 1

(57) Abstract: The invention is directed to a procedure for fitting relevant parameters in SCR catalyst models and to an apparatus for carrying out such procedures. Following the procedure of the present invention, it is possible to make a first estimate of the SCR model parameters by fitting the parameters individually. This is possible because of special measurements that simplify and isolate reactions in the SCR model. The set of parameters determined via this method are used as a starting point for a global optimization of the model parameters.
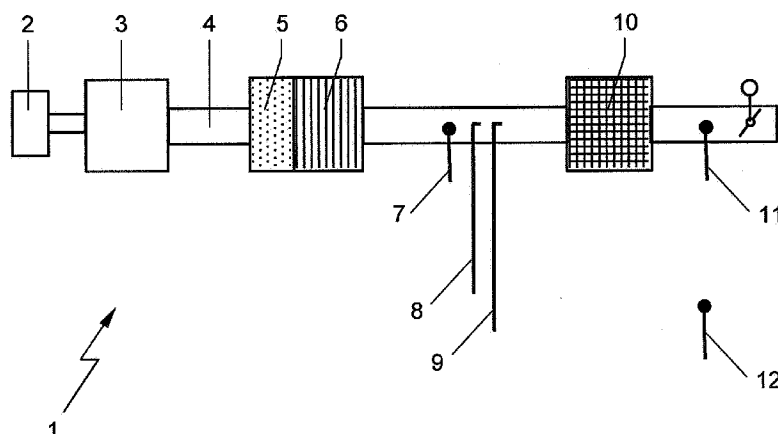
Title:      Calibration method and apparatus for SCR catalyst systems

The invention is directed to a procedure for fitting relevant parameters in SCR catalyst models and to an apparatus for carrying out such procedures.

The calculation of the right values for parameters in chemical
5    models to fit them to the process variables ("model fitting") involves the comparison of experimental data with a model, such that the relevant parameters in the model can be assigned values, which minimize the difference between theoretical (model) predictions and measured real-life response, for a given set of input variables. Finding the right values of the
10   model's parameters determines to a large extent the model's reliability. Model fitting can be a tedious task and may result in errors because of the large amount of factors involved. By result, the outcome of the fitting process is often unpredictable and results may give a false sense of security.

At the same time, having a reliable model is of great importance for
15   a number of reasons. For instance, a good model for SCR catalyst systems can be used for simulation purposes, thus reducing the requirement for expensive real-life tests. Also a reliable model can be used in the design process of catalyst systems. Furthermore a reliable model is required in process control when the catalyst system is installed.

20        For SCR catalyst systems there is a long felt need for reliable models, because the use of SCR catalyst is already widespread and still increasing. Most models that are applied today may still give incorrect results, which make such models unreliable.

In one aspect, the present invention is directed to an improved
25   procedure for fitting the parameters in an SCR model to experimental data, which experimental data is obtained in a modified engine testbench, which produces engine off-gases that are obtained under real-life (*i.e.* automotive) conditions or nearly real-life conditions.

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US-A-6 105 365 describes an apparatus for concentrating adsorbable pollutants (such as NOx and SOx) using a Pt/Rh on Al₂O₃ adsorption material. This is a so-called NOx trap (NOx storage) system. Selective catalytic reduction of NOx is not disclosed. In addition, the engine of US-A-6 105 365

5    does not seem to comprise an adjustable engine break and no indication of the required torque is given, only an indication of engine speed and requested air-to-fuel ratio being provided. Thus, real-life automotive conditions or nearly real-life conditions are not disclosed, nor suggested.

By way of example, a typical SCR model comprises the following

10   equations.

**Reaction equations:**

$$r_{pyr}: \quad H_4N_2CO \rightarrow NH_3 + HNCO \tag{1}$$

$$r_{hyd}: \quad HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{2}$$

$$r_{st}: \quad 4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{3}$$

$$r_{sn}: \quad 2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \tag{4}$$

$$r_{la}: \quad 8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O \tag{5}$$

$$r_{oxn2}: \quad 4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \tag{6}$$

$$r_{oxno}: \quad 4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \tag{7}$$

$$r_{\leftrightarrow}: \quad 2NO + O_2 \leftrightarrow 2NO_2 \tag{8}$$
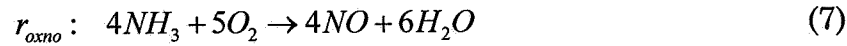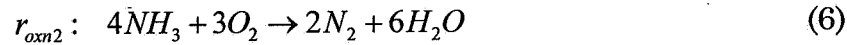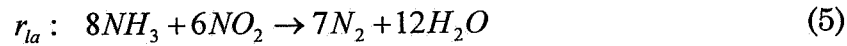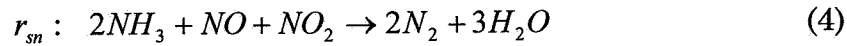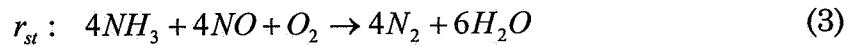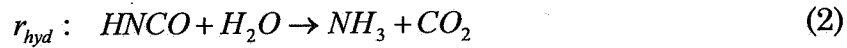
Non-catalytic urea decomposition:

$$\rho_{rg} = \frac{M_{rg} \cdot P}{R \cdot T_{rg}} \tag{9}$$

$$v_{pijp} = \frac{\Phi_{rg}}{\rho_{rg} \cdot \frac{\pi}{4} \cdot D_{pijp}^2} \tag{10}$$

$$C_{H_4N_2CO}^1 = C_{H_4N_2CO}^0 \cdot \exp\left(\frac{-k_{H_4N_2CO} \cdot L_{pijp}}{v_{pijp}}\right) \tag{11}$$

$$k_{H_4N_2CO} = k^0_{H_4N_2CO} \cdot \exp\left(\frac{-E_{H_4N_2CO}}{R} \cdot \left(\frac{1}{T_g} - \frac{1}{T_{ref}}\right)\right) \tag{12}$$

$$C^1_{HNCO} = C^0_{H_4N_2CO} - C^1_{H_4N_2CO} \tag{13}$$

$$C^1_{NH_3} = C^1_{HNCO} \tag{14}$$

Reactions in SCR-catalyst:

Mass balance SCR catalyst surface:

$$\frac{\partial \theta_{NH_3}}{\partial t} = r_a - r_d - r_{st} - 2r_{sn} - \tfrac{4}{3}r_{la} - r_{oxn2} - r_{oxno} \tag{15}$$

Mass balance gasfase:

$$v_{kat} = \frac{\Phi_{rg}}{\rho_{rg} \cdot \frac{\pi}{4} \cdot D^2_{kat} \cdot \varepsilon_{kat}} \tag{16}$$

$$\frac{\partial C_{H_4N_2CO}}{\partial t} = -v_{kat}\frac{\partial C_{H_4N_2CO}}{\partial x} - r_{H_4N_2CO} \tag{17}$$

$$\frac{\partial C_{HNCO}}{\partial t} = -v_{kat}\frac{\partial C_{HNCO}}{\partial x} + r_{H_4N_2CO} - r_{HNCO} \tag{18}$$

$$\frac{\partial C_{NH_3}}{\partial t} = -v_{kat}\frac{\partial C_{NH_3}}{\partial x} + r_{H_4N_2CO} + r_{HNCO} - \Omega \cdot (r_a - r_d) \tag{19}$$

$$\frac{\partial C_{NO}}{\partial t} = -v_{kat}\frac{\partial C_{NO}}{\partial x} - \Omega \cdot (r_{st} + r_{sn} - r_{oxno} + r_\rightarrow - r_\leftarrow) \tag{20}$$

$$\frac{\partial C_{NO2}}{\partial t} = -v_{kat}\frac{\partial C_{NO2}}{\partial x} - \Omega \cdot (r_{sn} + r_{la} - r_\rightarrow + r_\leftarrow) \tag{21}$$

Reaction rates equations:

$$r_{H_4N_2CO} = k^{kat}_{H_4N_2CO} \cdot \exp\left(\frac{-E^{kat}_{H_4N_2CO}}{R} \cdot \left(\frac{1}{T_s} - \frac{1}{T_{ref}}\right)\right) \cdot C_{H_4N_2CO} \tag{22}$$

$$r_{HNCO} = k^0_{HNCO} \cdot \exp\left(\frac{-E^0_{HNCO}}{R} \cdot \left(\frac{1}{T_s} - \frac{1}{T_{ref}}\right)\right) \cdot C_{HNCO} \tag{23}$$

$$r_a = k^0_a \cdot C_{NH_3} \cdot (1 - \theta_{NH_3}) \tag{24}$$

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$$r_d = k_d^0 \cdot \exp\left(\frac{-E_d^0 \cdot (1 - \alpha \cdot \theta_{NH_3})}{R} \cdot \left(\frac{1}{T_s} - \frac{1}{T_{ref}}\right)\right) \cdot \theta_{NH_3} \qquad (25)$$

$$r_{st} = k_{st}^0 \cdot \exp\left(\frac{-E_{st}}{R} \cdot \left(\frac{1}{T_s} - \frac{1}{T_{ref}}\right)\right) \cdot C_{NO} \cdot \theta_{NH_3}^* \cdot \left(1 - \exp\left(\frac{-\theta_{NH_3}}{\theta_{NH_3}^*}\right)\right) \qquad (26)$$

$$r_{sn} = k_{sn}^0 \cdot \exp\left(\frac{-E_{sn}}{R} \cdot \left(\frac{1}{T_s} - \frac{1}{T_{ref}}\right)\right) \cdot C_{NO} \cdot C_{NO_2} \cdot \theta_{NH_3}^* \cdot \left(1 - \exp\left(\frac{-\theta_{NH_3}}{\theta_{NH_3}^*}\right)\right) \qquad (27)$$

$$r_{la} = k_{la}^0 \cdot \exp\left(\frac{-E_{la}}{R} \cdot \left(\frac{1}{T_s} - \frac{1}{T_{ref}}\right)\right) \cdot C_{NO_2} \cdot \theta_{NH_3}^* \cdot \left(1 - \exp\left(\frac{-\theta_{NH_3}}{\theta_{NH_3}^*}\right)\right) \qquad (28)$$

$$r_{oxn2} = k_{oxn2}^0 \cdot \exp\left(\frac{-E_{oxn2}}{R} \cdot \left(\frac{1}{T_s} - \frac{1}{T_{ref}}\right)\right) \cdot \theta_{NH_3} \qquad (29)$$

$$r_{oxno} = k_{oxno}^0 \cdot \exp\left(\frac{-E_{oxno}}{R} \cdot \left(\frac{1}{T_s} - \frac{1}{T_{ref}}\right)\right) \cdot \theta_{NH_3} \qquad (30)$$

$$r_\rightarrow = k_\rightarrow^0 \cdot \exp\left(\frac{-E_\rightarrow}{R} \cdot \left(\frac{1}{T_s} - \frac{1}{T_{ref}}\right)\right) \cdot C_{NO} \cdot \sqrt{C_{O_2}} \qquad (31)$$

$$r_\leftarrow = \frac{k_\rightarrow^0}{K_\leftrightarrow} \exp\left(\frac{-E_\rightarrow}{R} \cdot \left(\frac{1}{T_s} - \frac{1}{T_{ref}}\right)\right) \cdot C_{NO_2} \qquad (32)$$

Equilibrium constants:

$$K_\leftrightarrow = \sqrt{\frac{R \cdot T_S}{P}} \cdot \exp\left(\frac{-\Delta G_\leftrightarrow}{R \cdot T_S}\right) \qquad (33)$$

$$\Delta G_\leftrightarrow = G_{NO_2}^\circ - G_{NO}^\circ - \tfrac{1}{2} G_{O_2}^\circ \qquad (34)$$

$$G_i^\circ = H_i^\circ - T_s \cdot S_i^\circ \qquad (35)$$

$$H_i^\circ = 10^3 \cdot \left(A_i \cdot \left(\frac{T_s}{10^3}\right) + \frac{B_i}{2} \cdot \left(\frac{T_s}{10^3}\right)^2 + \frac{C_i}{3} \cdot \left(\frac{T_s}{10^3}\right)^3 + \frac{D_i}{4} \cdot \left(\frac{T_s}{10^3}\right)^4 - E_i \cdot \left(\frac{10^3}{T_s}\right) + F_i\right)$$

(36)

$$S_i^\circ = A_i \cdot \ln\left(\frac{T_s}{10^3}\right) + B_i \cdot \left(\frac{T_s}{10^3}\right) + \frac{C_i}{2} \cdot \left(\frac{T_s}{10^3}\right)^2 + \frac{D_i}{3} \cdot \left(\frac{T_s}{10^3}\right)^3 - \frac{E_i}{2} \cdot \left(\frac{10^3}{T_s}\right)^2 + G_i \qquad (37)$$

5

The notation used in these equations is explained in Tables 1a-1c.

## Table 1a

| Parameter | Description | Unit |
|---|---|---|
| $k^0_a$ | Pre exponential factor adsorption | $m^3 \cdot mol^{-1} \cdot s^{-1}$ |
| $E^0_a$ | Activation energy adsorption | $J \cdot mol^{-1}$ |
| $k^0_d$ | Pre exponential factor desorption | $s^{-1}$ |
| $E^0_d$ | Activation energy desorption | $J \cdot mol^{-1}$ |
| $\alpha$ | Alfa | - |
| $\Omega$ | Storage capacity | $mol \cdot m^{-3}$ |
| $\theta^*_{NH3}$ | Critical surface coverage | - |
| $k^{cat}_{H4N2CO}$ | Pre exponential factor pyrolysis | $s^{-1}$ |
| $E^{cat}_{H4N2CO}$ | Activation energy pyrolysis | $J \cdot mol^{-1}$ |
| $k^0_{HNCO}$ | Pre exponential factor hydrolysis | $s^{-1}$ |
| $E_{HNCO}$ | Activation energy hydrolysis | $J \cdot mol^{-1}$ |
| $k^0_{st}$ | Pre exponential factor NO reaction | $m^3 \cdot mol^{-1} \cdot s^{-1}$ |
| $E_{st}$ | Activation energy NO reaction | $J \cdot mol^{-1}$ |
| $k^0_{sn}$ | Pre exponential factor NO+NO$_2$ reaction | $m^6 \cdot mol^{-2} \cdot s^{-1}$ |
| $E_{sn}$ | Activation energy NO+NO$_2$ reaction | $J \cdot mol^{-1}$ |
| $k^0_{la}$ | Pre exponential factor NO$_2$ reaction | $m^3 \cdot mol^{-1} \cdot s^{-1}$ |
| $E_{la}$ | Activation energy NO$_2$ reaction | $J \cdot mol^{-1}$ |
| $k^0_{oxno}$ | Pre exponential factor oxidation reaction | $s^{-1}$ |
| $E_{oxno}$ | Activation energy oxidation reaction | $J \cdot mol^{-1}$ |
| $L_{pijp}$ | length between urea injection point and SCR catalyst | m |
| $D_{pijp}$ | diameter pipe between urea injection point and SCR catalyst | m |
| $T_{ref}$ | reference temperature | K |
| R | gas constant | J/mol*K |

## Table 1b

| Rates | Description | Unit |
|---|---|---|
| $r_{pyr}$ | reaction rate pyrolysis | |
| $r_{hyd}$ | reaction rate hydrolysis | |
| $r_{st}$ | *reaction rate NO* | |
| $r_{sn}$ | *reaction rate NO+NO$_2$* | |
| $r_{la}$ | *reaction rate NO$_2$* | |
| $r_{oxn2}$ | *reaction rate oxidation NH$_3$ to N$_2$* | |
| $r_{oxno}$ | *reaction rate oxidation NH$_3$ to NO* | |
| $r_{<->}$ | reaction rate NO <-> NO$_2$ | |

### Table 1c

| Signal | Description | |
|---|---|---|
| C | concentration | $mol/m^3$ |
| $\theta_{NH3}$ | NH3 storage | - |
| $T_g$ | temperature gas | K |
| This | temperature SCR brick | K |
| $v_{kat}$ | Gas speed in SCR brick | m/s |
| P | gas pressure | $N/m^2$ |
| $A_i, B_i, C_i, D_i, E_i, F_i$ | polynomial constants | |
| $H^o_i$ | Species enthalpy | J |
| G | Species Gibbs energy | J |
| $S_i$ | Species entropy | J/K |

The procedure of the present invention is developed based on
measurements that can be carried out on a specifically designed engine test-
bench and will be illustrated by means of the above-mentioned SCR model.

The test-bench of the present invention is schematically depicted in
Figure 1. The test set-up (1) comprises an engine (3), connected to an engine
brake (2). The engine may be any commercially available or newly developed
model, which provides for realistic process conditions. By combining the engine
(3) with adjustable brake (2), specific working points (WP) can be chosen, *i.e.* a
combination of a specific torque (Nm) at a certain engine speed (RPM). The
engine off-gases are fed trough outlet (4) into a bed of oxidation catalyst (5),
which is optional. Subsequently the gases are fed trough soot filter (6), which
is also optional. At a measurement point labeled "pre-SCR" (7) various process
conditions can be measured, such as concentrations of the relevant gases (NO,
NO2, NH3, *etc.*), temperature, total pressure and the like. One of the specific
features of the apparatus of the present invention is that it uses a combination
of NH3 injection (8) and urea injection (9). This allows for measurements from
which data can be derived that can be used to gain knowledge of the urea
decomposition mechanism. Urea is used in real life deNOx facilities as a source
of NH3. NH3 itself is generally too dangerous to handle in realistic deNOx
applications, whereas urea is much more easy to handle. Because NH3 plays
an important role in the reaction mechanisms that are at the basis of the

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model, the option to switch between urea and NH₃ in accordance with the present invention results in very reliable results.

After the gases are contacted with urea and/or NH₃, they are fed to SCR catalyst (10), where the actual deNOx reaction takes place.

5        After the gases leave the catalyst they are analyzed again at a measurement point labeled "post-SCR" (11). Also ambient conditions are monitored (temperature, pressure) at measurement point labeled "ambient measurement" (12).

The set-up of the present invention provides much more realistic

10      results than fitting the equation on a flow bench with idealized circumstances (*e.g.* synthetic, simulated off-gases).

Following the procedure of the present invention, it is possible to make a first estimate of the SCR model parameters by fitting the parameters individually. This is possible because of special measurements that simplify

15      and isolate reactions in the SCR model. The set of parameters determined via this method are used as a starting point for a global optimization of the model parameters. It was found that this is a far better approach than directly fitting all parameters with a global optimization. When starting with a random model parameter-set, the risk is big that the global optimization gives an unrealistic

20      parameter-set.

Hereinbelow, first the test set-up that is required to perform the tests and the signals that should be measured during the tests are described. Then the tests to characterize the catalyst are described. Next the procedure to find the SCR catalyst parameters is detailed.

25

**Test setup and measured signals**

A catalyst model can be fitted and validated by performing specific measurements on the SCR catalyst. In the prior art, these measurements are often performed with a flow reactor. According to the present invention the

30      test method is carried out on an engine testbench (and possibly even on a

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chassis dynometer). The engine is a real life engine or similar thereto in its operation variables (in particular temperature development and off-gas composition).

The engine is connected to an engine brake. This can be a steady

5    state or a transient brake. In accordance with the present invention, the exhaust line minimally contains a SCR catalyst and can contain a pre-oxidation catalyst and soot filter. Catalysts behind the SCR catalysts can be installed to set a back pressure.

SCR catalyst usually contain two catalyst modules, usually in the

10   form of a well-known monolith ("honeycomb structure") with parallel channels (herein referred to as "bricks"). In accordance with the present invention, one brick should be used for characterization. This gives more information on the conversion potential of the SCR catalyst.

Before the SCR catalyst a $NH_3$ and urea solution (usually AdBlue™)

15   injection point should be installed. It is important that the $NH_3$ and urea (e.g. AdBlue) is homogeneously distributed in radial direction before it enters the SCR catalyst, which can be secured using common distributor means. For the urea injection it is important that the urea has enough residence time for the thermolysis process.

20   In one embodiment of the present invention the following signals are measured during the characterization of the SCR catalyst (see Table 2). An "X" means the corresponding signal is measured at the indicated point.

9

## Table 2: Measured signals on test set-up

| Measured | Measurement point pre SCR | Measurement point post SCR | Measurement point ambient |
|---|---|---|---|
| Pressure gas | X | X | X |
| Temperature gas | X | X | X |
| Exhaust mass-flow | X | | |
| CO | X | X | |
| Hydrocarbon | X | X | |
| $CO_2$ | X | X | |
| $O_2$ | X | X | |
| NOx | X | X | |
| NO | X | X | |
| $N_2O$ | X | X | |
| $NH_3$ | | X | |

## Test program SCR catalyst characterization

5        To characterize the SCR catalyst system certain tests should be performed with the test set-up. Tests can be performed with $NH_3$ injection and with urea (*e.g.* AdBlue) injection. Also if an oxidation catalyst is used pre SCR, the system can be tested with and without SCR catalyst. The measurements that can be performed are summarized in Table 3.

10

## Table 3: Test program

| Injection | SCR | Oxidation catalyst | Test |
|---|---|---|---|
| $NH_3$ | - | X | validation of test set-up |
| urea (*e.g.* AdBlue) | - | X | validation of test set-up, thermolysis |
| $NH_3$ | X | X | initial characterisation, characterisation sequence |
| $NH_3$ | X | | initial characterisation, characterisation sequence |
| Urea (*e.g.* AdBlue) | X | X | characterisation sequence, driving cycle |

10

### Validation of test set-up and thermolysis measurements

The first step is to do measurements with the test set-up without the SCR catalyst. This means that the exhaustline is used as shown in Figure 1, but without the SCR catalyst. With this set-up the equipment can be validated

5   by performing specific tests. Also the thermolysis before the SCR catalyst can be characterized by performing measurements without SCR catalyst.

This part of the test-procedure typically comprises the following steps:

- Test communication

10      - Determine low temperature engine working point (for example 200 °C) with a maximum Space Velocity

- Determine reference engine working point (for example 300 °C) with a maximum Space Velocity

- Determine regeneration working point

15      With the following measurements the test set-up can be validated:

- Compare analyzers before and after the SCR catalyst

- Inject $NH_3$ and check if it corresponds with value on $NH_3$ analyzer

- Low temperature point

- Reference point

20      - Regeneration point

- Check cross sensitivity analyzers for $NH_3$ by switching $NH_3$ injection on/off in reference point

- Check if $NH_3$ analyzer is working properly when making a transient from low temperature working point to the regeneration point

25      - Determine time delay between analyzers while making a transient from the reference point to the regeneration point

After that the thermolysis measurements are also performed without the SCR catalyst:

- Measure thermolysis in exhaustline at low temperature, reference

30   and regeneration point with stochiometric urea injection.

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After these measurements the SCR catalyst can be installed.

With the SCR catalyst installed the following initial measurements are used to validate the system:

5      Steady state

- Inject NH₃ (NSR=1; NSR is the normal stoichiometric ratio. This term is used to describe the NH₃/NOx molar ratio of the reagent injected to uncontrolled NOx concentrations. If one mole of anhydrous ammonia is injected for each mole of NOx in the flue gas, the NSR is one, as one mole of

10     ammonia will react with one mole of NOx. If one mole of urea is injected into the flue gas for each mole of NOx, the NSR is two. This is because one mole of urea will react with two moles of NOx. For both reagents, the higher the NSR, the greater the level of NOx reduction. Increasing NSR beyond a certain point, however, will have a diminishing effect on NOx reduction, with reagent

15     utilization decreasing beyond this point) in reference point and check mass balance

        - Inject urea (*e.g.* AdBlue) (NSR=1) in reference point and check mass balance

20     Transient

        - Switch NH₃ injection on (NSR=1) and off in reference point

        - Switch urea (*e.g.* AdBlue) injection on (NSR=1) and off in reference point

        **Initial characterization SCR catalyst**

25     With this part of the procedure an initial estimate of the model parameters can be determined. This is realized with a specific measurement program, that simplifies the model and isolates specific reactions.

        For the initial parameter estimate procedure the assumption was made that the NOx conversion will remain constant when the NSR is

30     increased above a certain value. This must be verified by running a test in

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which the NSR is increased in steps while the SCR catalyst temperature and Space Velocity remain constant (see Figure 2).

The test should be realized in the low temperature point and reference point.

5      The test procedure for determining the relation between NH₃ storage and NOx conversion is shown schematically in Figure 2. The test begins with a high temperature working point to regenerate a soot filter if present, but also to remove absorbed emissions as hydrocarbons in the SCR catalyst. After this a constant working point is run. During this steady state

10     operation of the engine the NH₃ injection is switched on and off. For determining the intervals it is important that the intervals are long enough for reaching steady state conditions. The NH₃ injection starts with high values and is reduced with small steps to finally reach no injection. This test is performed in the low temperature point and the reference point.

15     If the NOx conversion saturates at the high NSR values, the fit can be performed using the measurements from Figure 2.

$$r_{NO} = k_{NO} \exp\left(-\frac{E_{NO}}{RT}\right) \cdot \left(1 - \exp\left(\frac{-\theta_{NH_3}}{\theta^*_{NH_3}}\right)\right) \quad \text{(Equation 1)}$$

An example of the fit with $\theta^*_{NH_3}$ is given in Figure 3, which shows a

20     fit of $\theta^*$NH3 based on NH₃ storage measurements.

If the NOx conversion is not saturating, the NSR values where the NOx conversion starts to decrease should not be used for the fit. The NSR values used in the experiments described in this document should be limited accordingly.

25     To characterize the catalyst, the catalyst performance should be measured at different temperatures and space velocities (SV). These different temperatures and SVs are realized by running the engine on the testbench in different working points. In accordance with the present invention a minimum number of working points is required, from which a maximum amount of

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information can be obtained. Preferably at least thirteen working points are used. Minimizing the number of working points results in considerably less experimentation time and consequently may save costs. When choosing the working points the following considerations are important:

5          The working points should be chosen such that a desired SCR catalyst temperature and SV are obtained. At the light-off temperature of the SCR catalyst extra working points should be chosen in temperature and SV direction. Figure 4 schematically depicts engine working points based on SV and $T_{catalyst}$. The working points should be tuned for a specific SCR catalyst.

10   This should be done based on the $NO_x$ conversion potential in a working point. The $NO_x$ conversion potential is measured by injecting a $NH_3$ quantity resulting in ±30 ppm $NH_3$ slip. In accordance with the present invention the working points should have about the following $NO_x$ conversion (see Table 4).

15          Table 4: Indication $NO_x$ conversion for each working point

| WP | indication $NO_x$ conversion (in %) |
|----|--------------------------------------|
| 1  | 30   |
| 2  | 0    |
| 3  | 80   |
| 4  | 30   |
| 5  | 80   |
| 6  | 30   |
| 7  | 80   |
| 8  | 30   |
| 9  | <90  |
| 10 | 50   |
| 11 | 70   |
| 12 | <90  |
| 13 | <90  |

Preferably certain working points should have the same SCR temperature and a variation in the Space Velocity: WP1 and 2, WP3 and 4, WP 5 and 6, WP7 and 8, WP9 and 10. By changing the Space Velocity, the $NO_2/NO$

20   ratio oxidation catalyst out changes (when an oxidation catalyst is used and

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placed before the SCR catalyst). Preferably the high Space Velocity working points (WP2, 4, 6, 10) should have a $NO_2/NO$ ratio below 1 and the low Space Velocity working points (WP1, 3, 5, 7) should have a $NO_2/NO$ ratio higher than 1.

5        If NOx conversion is not equal to desired value in a certain working point, the engine speed and/or torque should be changed to get the right NOx conversion.

         The working points determined above are used for the tests in the remainder of the present application. An initial estimate of the $NH_3$

10     adsorption/desorption parameters is made using the test shown schematically in Figure 5, which shows a test sequence that can be used to get first estimate of storage and adsorption/desorption parameters. The test starts with a regeneration. After that the engine switches between two working points. A high and a low temperature working point. During the working point $NH_3$

15     injection is switched on and off. The dosing of the $NH_3$ injection is set too a high value, in order to simplify model parameterization.

         The interval of the working points and $NH_3$ injection should be chosen long enough to realize steady state conditions. The first part of the test is to fit the relative difference between adsorption/desorption parameters. With

20     the second test and the result from the first test, the individual adsorption/desorption parameters can be fitted.

         The following sequences can be run:

         In the first sequence the following working points are used:

         WP13 (NSR=2); WP2 (NSR=6); WP9 (NSR=3.5); WP2 (NSR=2); WP9

25     (NSR=2); WP2 (NSR=1.5); WP9); WP2 (NSR=1.2); and WP9

         In the second sequence the following working points are used:

         WP13 (NSR=2); WP4 (NSR=6); WP7 (NSR=3.5); WP4 (NSR=2); WP7 (NSR=2); WP4 (NSR=1.5); WP7); WP4 (NSR=1.2); and WP7.

         When using the high NSR values as used in the tests, the

30     assumption can be made that $r_a=r_d$ and therefore that the $NH_3$ that is used to

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convert NOx is negligible. The equation that should be solved is therefore (see Equation 2).

$$r_a = r_d \quad \Rightarrow \quad \theta_{NH_3} = f\left(\frac{k_a^0}{k_d^0}, E_a - E_d\right) \quad \text{(Equation 2)}$$

5 An example of the fit of the parameters $\left(\dfrac{k_a^0}{k_d^0}, E_a - E_d\right)$ is shown in Figure 6. The measured points (the crosses in Figure 6) are a result from the first part of the test shown in Figure 5.
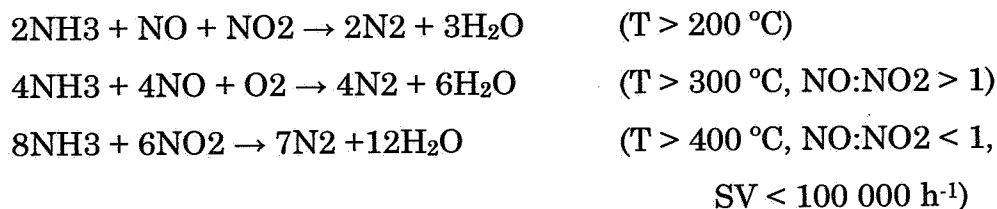
With the second part of the measurements in Figure 5 and the parameters $k_a/k_d$, $E_a$-$E_d$, the individual parameters can be determined. An

10 example of this fit is shown in Figure 7.

The NOx conversion parameters are fitted with a different test sequence. The test sequence comprises a series of working points. The characterization test sequence for SCR catalyst with high NSR is shown schematically in Figure 8. The sequence of the working points is: WP13

15 (NSR=1.5); WP1 (NSR=2); WP5 (NSR=1.5); WP11 (NSR=1.5); WP3 (NSR=1.5); WP12 (NSR=2); WP7 (NSR=2); WP4 (NSR=1.5); WP8 (NSR=1.5); WP6); and WP10 (NSR=1.5).

During the operation in a working point, $NH_3$ is injected with a high NSR value. The high dosing should guarantee a homogeneous NOx conversion

20 distribution through the length of the SCR catalyst. This simplifies the fitting of the NOx conversion parameters The duration of each working point should be chosen long enough to reach steady state conditions. Especially at low temperatures this can take significant time.

With the test a first estimate of the NOx conversion parameters can

25 be made ($k_{NO2}$, $E_{NO2}$, $k_{NO}$, $E_{NO}$, $k_{la}$, $E_{la}$).

In order to fit the six parameters in the three NOx reaction equations (see below) enough variation in the $NO/NO_2$ ratio at the inlet of the SCR catalyst is required.

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$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \qquad (T > 200\ °C)$$
$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \qquad (T > 300\ °C,\ NO{:}NO_2 > 1)$$
$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O \qquad (T > 400\ °C,\ NO{:}NO_2 < 1,$$
$$SV < 100\ 000\ h^{-1})$$

5

**Optimization fit SCR catalyst**

With the previous measurements an initial fit of the model parameters can be made. This is realized by isolating and fitting individual parameters. The fit of the model can be improved by optimizing the

10    parameterset for more realistic $NH_3$ injection quantities. For this the following test sequence is used (see Figure 9, showing the test sequence for SCR catalyst with realistic NSR). This test sequence was also used for finding the initial NOx conversion parameters. During this test however more realistic NSR values are used. The NSR values used should result in a $NH_3$ slip of about 30

15    ppm in each working point. Finally, the decomposition reaction parameters in the SCR catalyst can be fitted. This can be realized by repeating the test sequence as in Figure 9, but now with AdBlue injection. The decomposition reaction parameters can be fitted indirectly by comparing the NOx conversion and $NH_3$ slip over the test between $NH_3$ and AdBlue injection.

20         The parameter fitting process of the present invention provides for the possibility of limiting the amount of time and costs involved for SCR catalyst model developing. The method of the invention can be conveniently automated and presented in the form of a software tool.

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## Claims

1.      Apparatus for carrying out an SCR catalyst system calibration method comprising an engine (3), operable connected to an adjustable engine brake (2), which engine is connected to outlet (4) for off-gas, which outlet (4) is optionally connected to an oxidation catalyst (5), which is optionally connected to a soot filter (6), further comprising a pre-SCR measurement point (7), a $NH_3$ injection point (8) and a urea injection point (9), an SCR catalyst (10), a measurement point labeled "post-SCR" (11) and a measurement point labeled "ambient measurement" (12).

2.      Process for fitting parameters in a SCR catalyst model, comprising the steps of operating the apparatus of claim 1, comprising operating said engine (3), whereby an NOx-comprising offgas is produced, and carrying out at least two different measurements on said offgas, the first measurement being determining the NOx-conversion by said SCR catalyst (10) using $NH_3$ from said $NH_3$ injection point (8) and the second measurement being determining the NOx-conversion by said SCR catalyst (10) using urea from said urea injection point (9) and using said measurement in said fitting of parameters.

3.      Process according to claim 2, comprising the steps of:

- determining at least two working points;

- determining the relation between $NH_3$ storage and NOx conversion carrying out saturation measurements;

- running tests using high $NH_3$ injection;

- running tests with normal $NH_3$ injection; and
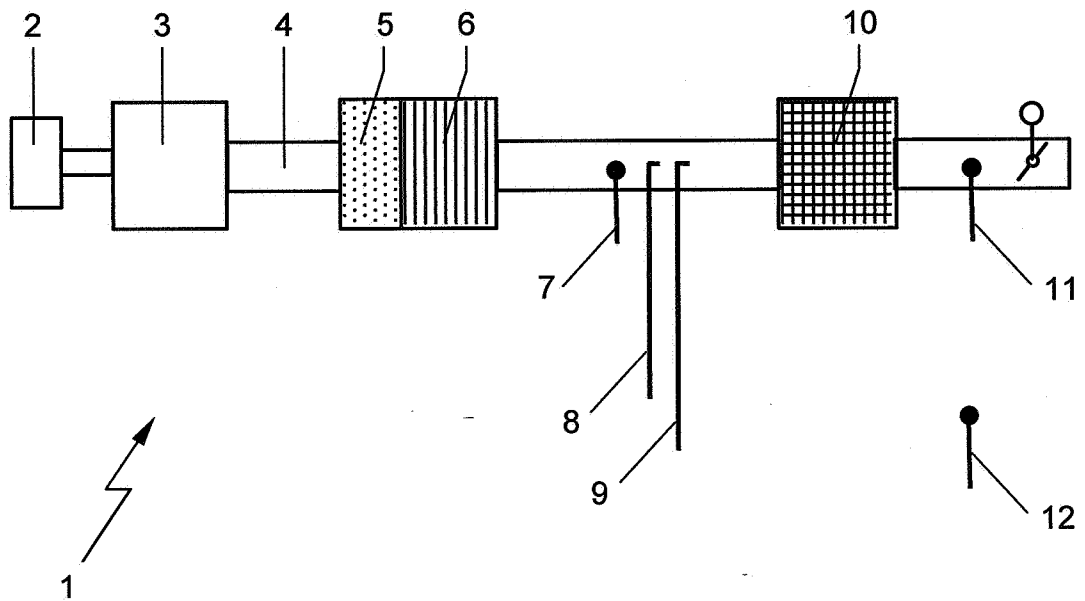
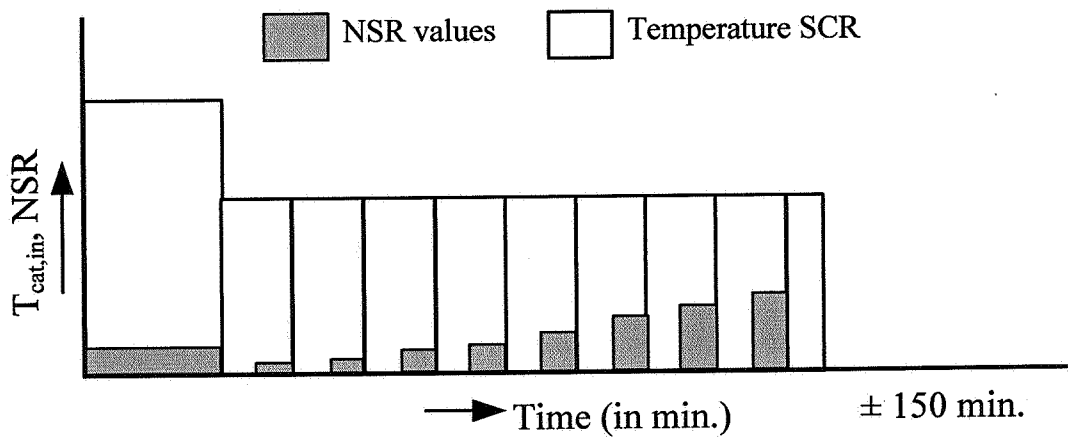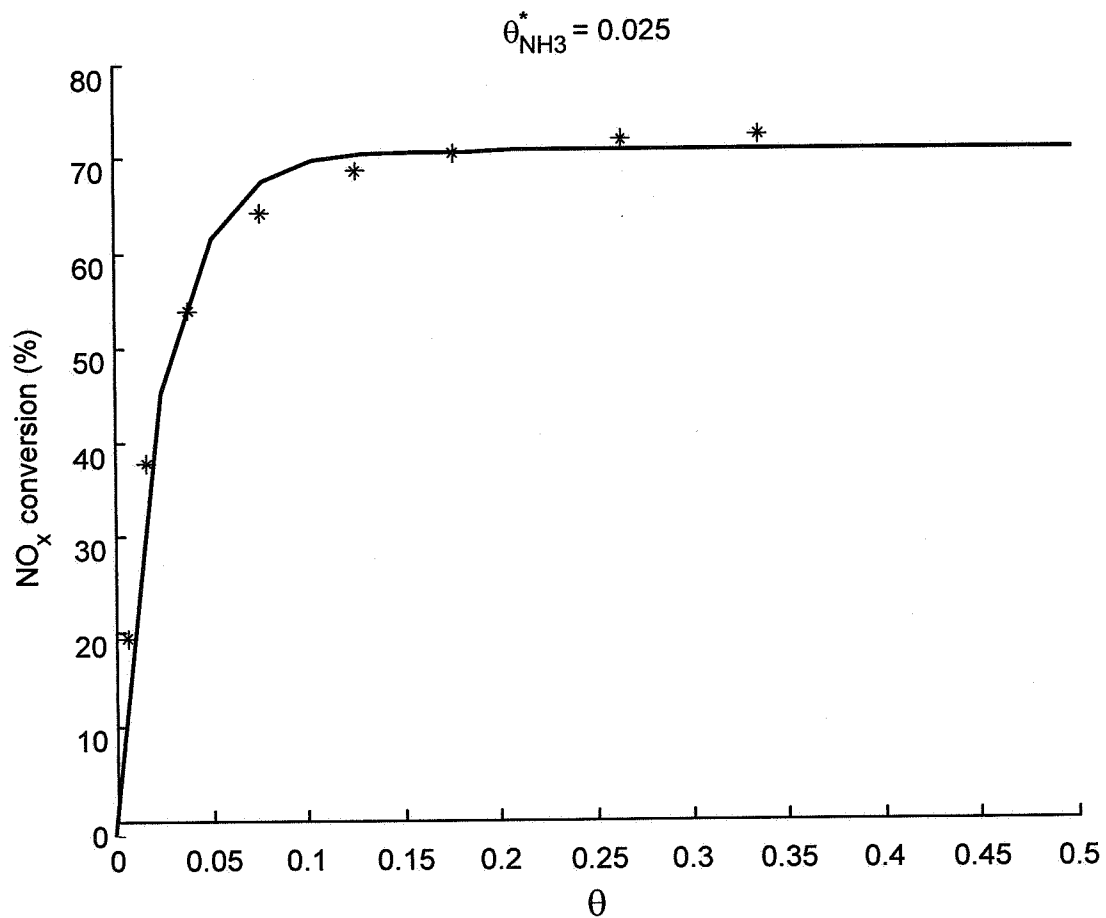- running tests with normal urea injection.

Fig. 1

Fig. 2



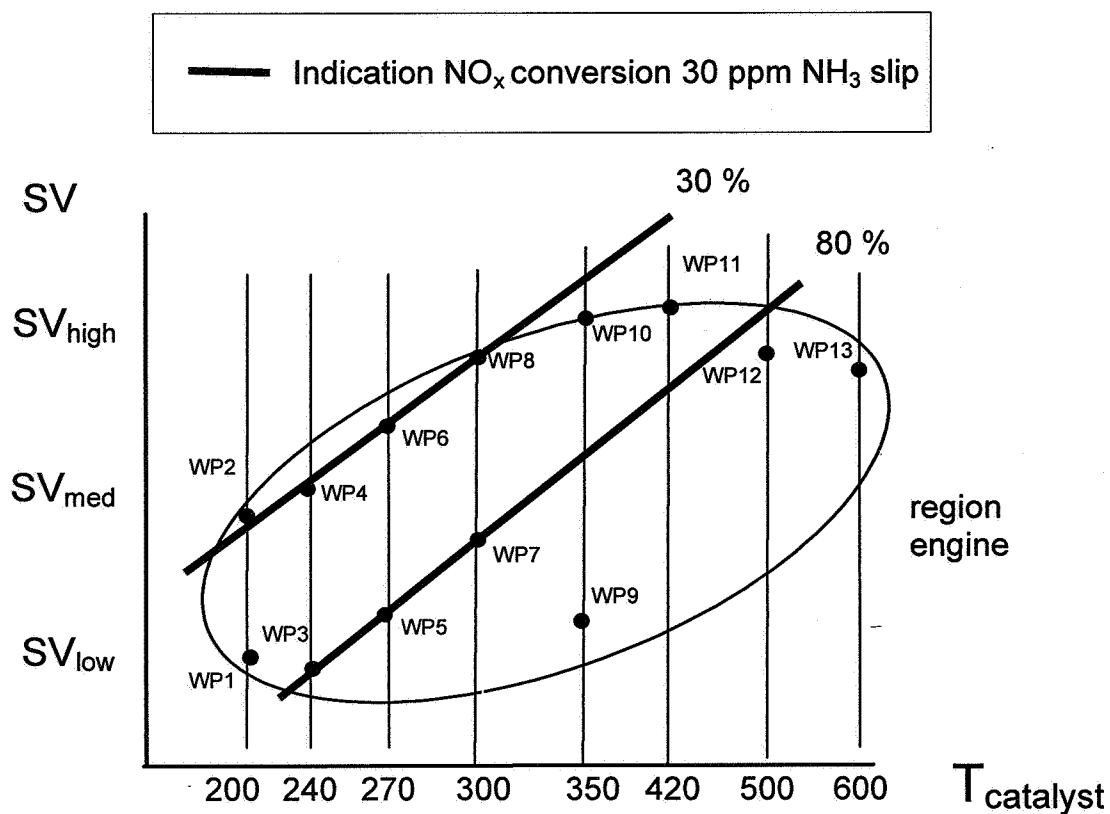$\theta^*_{NH3} = 0.025$

Fig. 3

Fig. 4



Fig. 5

$$k_a / k_d = 22.87 \;,\; E_a - E_d = -52456 \;,\; \alpha = 0.80$$
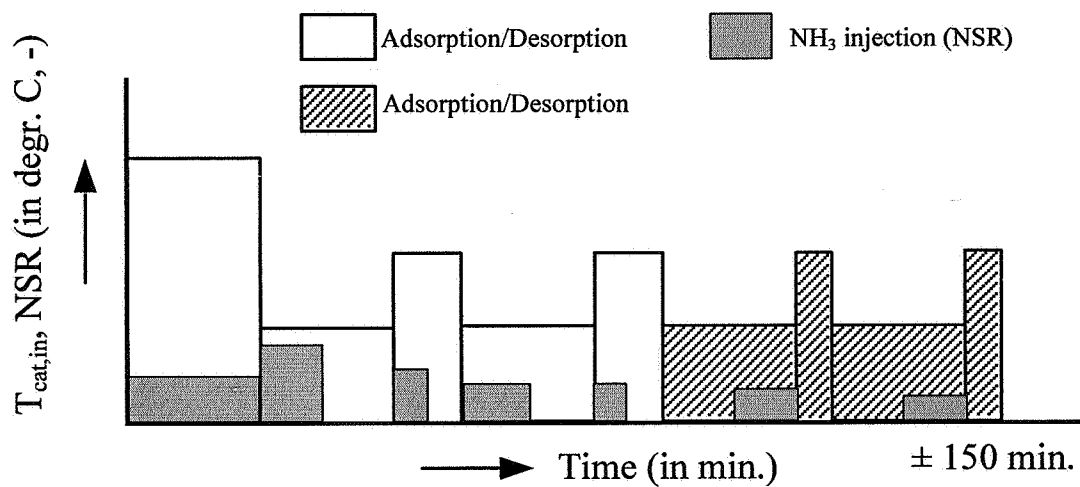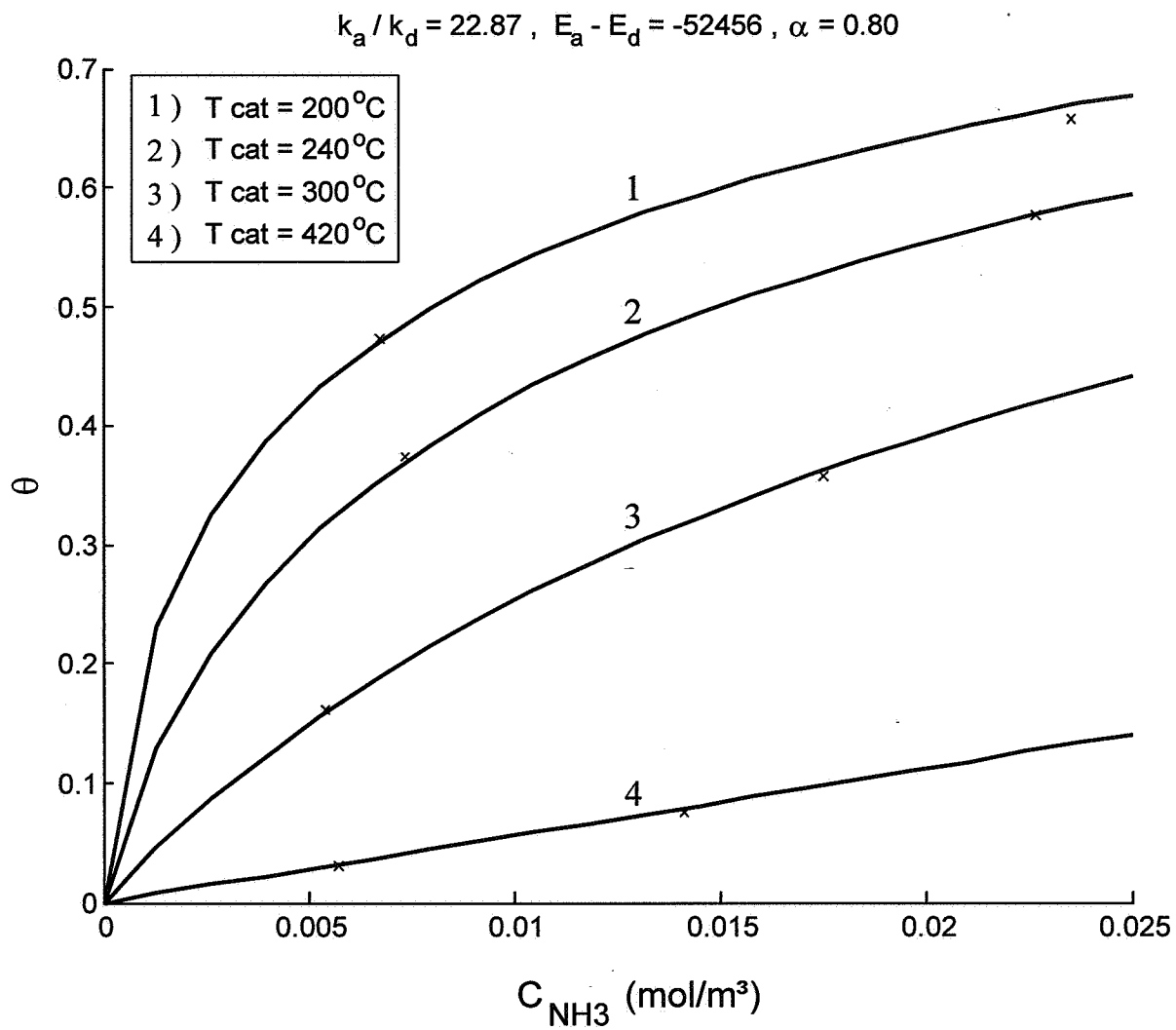


Fig. 6
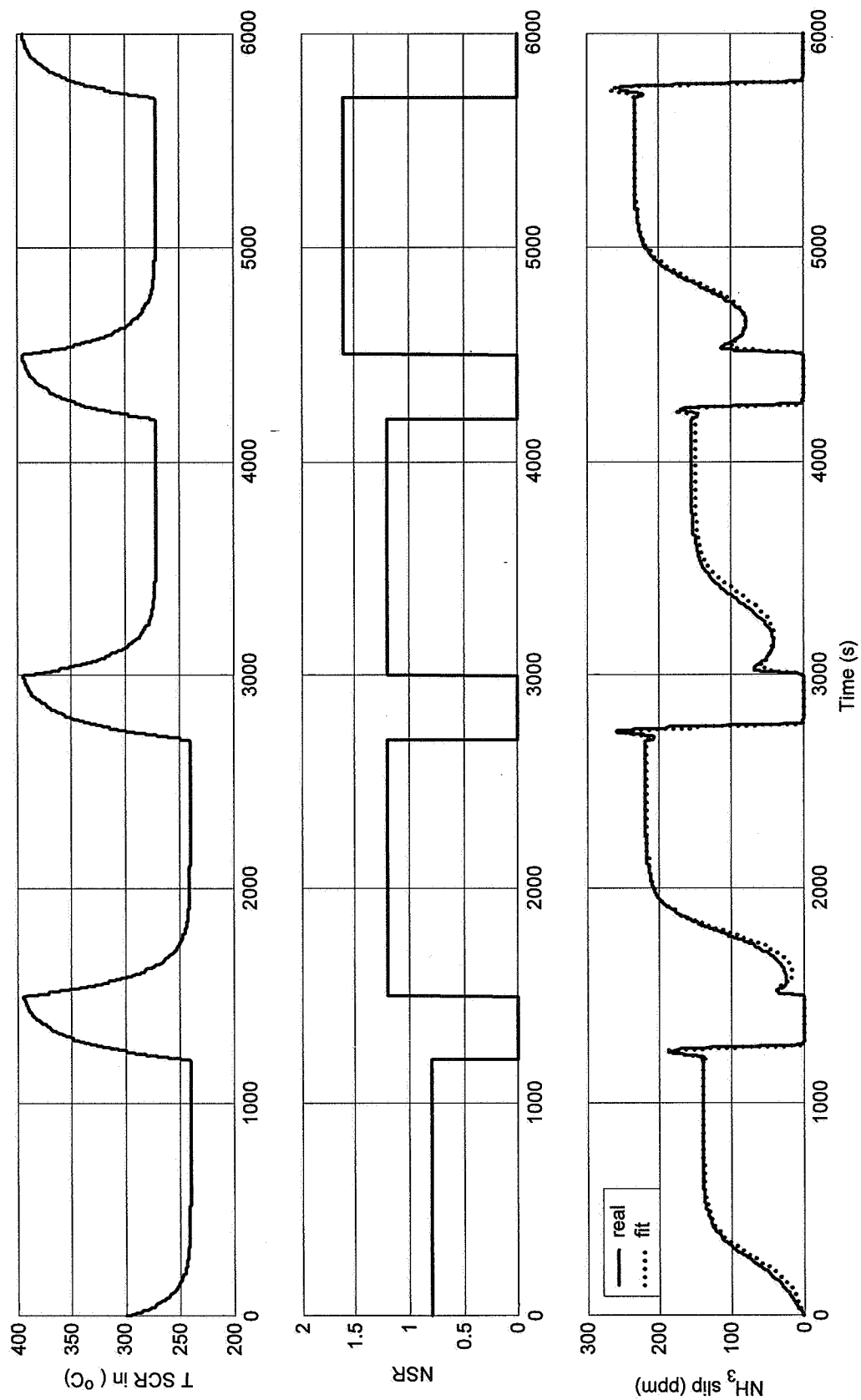
Fig. 7
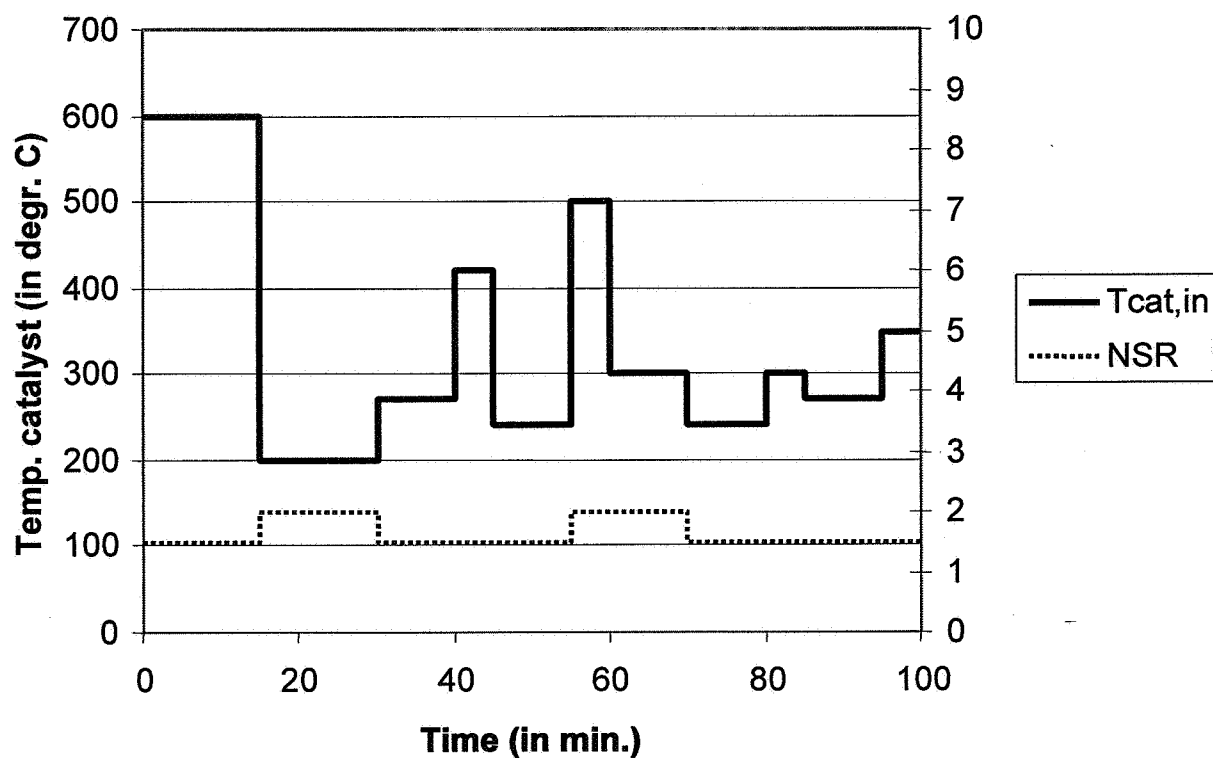
Fig. 8



Fig. 9

# INTERNATIONAL SEARCH REPORT

**A. CLASSIFICATION OF SUBJECT MATTER**
INV.   B01D53/94      F01N3/20

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)
B01D   F01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| A | US 6 742 330 B2 (GENDEREN) 1 June 2004 (2004-06-01) column 6, line 40 - column 6, line 44 column 15, line 29 - column 18, line 22 | 1-3 |
| A | EP 1 367 248 A (CATERPILLAR INC.) 3 December 2003 (2003-12-03) column 3, paragraph 9 - column 6, paragraph 31 | 1-3 |
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☐ Further documents are listed in the continuation of Box C.    ☒ See patent family annex.

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| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 24 July 2008 | 31/07/2008 |

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

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