

Notes on SCR-OBD algorithm developement

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1 Introduction

Goal:

”Developing model-based non-intrusive diagnostics for SCR-ASC that can work with commercial NO-x sensors and demonstrate the results on a real-world on-road truck data.”

Kaushal’s work:

- Diagnostic-oriented aging models for SCR-ASC.
 - Chemical Kinetics based model for SCR
 - Non-linear look-up table for ASC
- Term-by-term observer design for SCR Ammonia adsorption.
- Diagnosis algorithm
 - Sequence of filters
 - Residual generation for fault detection using the stochastic version of the models.

1.1 Available measurements

1. Engine Torque
2. Engine Speed
3. Diesel exhaust fluid (DEF) injection
4. Engine-out NO_x .
5. Diesel oxidation catalyst (DOC)-out NO_x .
6. Tail-pipe NO_x . (Test cell: NH_3 and N_2O)
7. DOC-in, DOC-out, SCR-in, SCR-out and ASC-out temperatures.
8. Exhaust flow rate.

1.2 Available data

1. Road data
 - Cold FTP (Federal Test Procedure)
 - Hot FTP
 - RMC (Ramped mode cycle)
2. Test Cell data
 - Cold FTP (Federal Test Procedure)
 - Hot FTP
 - RMC (Ramped mode cycle)

1.3 State and Parameter ranges from Test Cell data

Expt.	F (kg/min)	T ($^{\circ}C$)	$C_{NO_x,in}$ (ppm)	C_{NO_x} (ppm)	C_{NH_3} (ppm)
Aged (Cold FTP)	[0 26.64]	[28.20 262.30]	[0 558.06]	[-2.78 760.55]	[-0.60 1.40]
Aged (Hot FTP)	[0 26.50]	[134.30 269]	[0 506.48]	[-14.40 158.67]	[-0.60 11.10]
Aged (RMC)	[1.80 24.75]	[238.40 348.20]	[0 693.65]	[-2.24 109.63]	[0.80 4.40]
De-greened (Cold FTP)	[0 26.72]	[25.80 253.90]	[0 609.84]	[-116.93 518.05]	[-0.70 1.70]
De-greened (Hot FTP)	[0 26.47]	[110.10 261.80]	[0 504.92]	[-17.16 110.85]	[-0.50 3.70]
De-greened (RMC)	[1.84 24.91]	[236.20 341.30]	[0 728.04]	[-1.30 75.61]	[0.40 5.20]

Table 1: Test cell data ranges

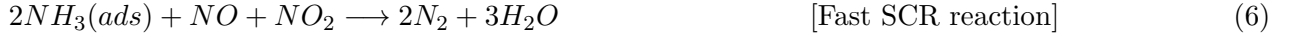
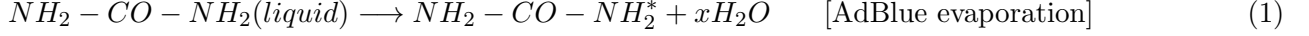
Question: Negative Concentration?

1.4 State and Parameter ranges from Road data

2 SCR-ASC Reactions and Dynamics

2.1 SCR-ASC Reactions

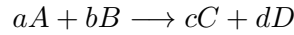
Eley Rideal reaction mechanism [1] [2], [3] is considered for the interpreting the SCR reactions. The mechanism involves the following reactions:



The PDE model for SCR reaction kinematics [3] is reduced to ODE model [4] using by assuming "continuous stirred tank reactor (CSTR)" model (Control volume approach).

2.2 General reaction kinetics

For a stoichiometric reaction of the following form:



We have the reaction rate [5]:

$$r = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$$

$$r = k[A]^m[B]^n$$

Where,

[•] – Concentration of the reactant •

k – Rate constant

m, n – Constant exponents, $(m + n)$ is the order of reaction

In the subsequent derivations, the exponents in the rate equations are limited to either zero or 1 $m, n \in \{0, 1\}$ (This is consistent with the assumption that reaction rates are proportional to gas-phase concentrations from [6]).

The rate constant can be determined using **Arrhenius equation**:

$$k = Ae^{E_a/RT}$$

Where,

A – Pre-exponential factor

E_a – Activation energy

T – Temperature

R – Universal gas constant

2.2.1 Effects of temperature change on rate constant

We have the Arrhenius equation:

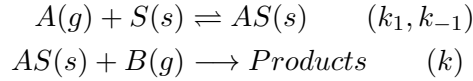
$$k = Ae^{-E_a/RT}$$

$$\implies \delta k = \delta T A \left(\frac{E_a}{RT^2} \right) e^{-E_a/RT} = \delta T k \left(\frac{E_a}{RT^2} \right)$$

In general, E_a is several orders of magnitude greater than the other parameters. Thus, small change in temperature gets amplified as the change in the rate-constant.

2.3 Eley-Rideal Mechanism

In this mechanism, proposed in 1938 by D. D. Eley and E. K. Rideal, only one of the molecules adsorbs and the other one reacts with it directly from the gas phase, without adsorbing ("non-thermal surface reaction") [7].



We have the rate of the second reaction:

$$r = kC_s\theta C_B$$

$$\theta = \frac{C_{AS}}{C_S}$$

Thus,

$$\frac{dC_{AS}}{dt} = k_1C_AC_S(1 - \theta) - k_{-1}\theta C_S - kC_S\theta C_B$$

At equilibrium :

$$\frac{dC_{AS}}{dt} = 0 \implies \theta = \frac{k_1C_AC_S}{k_1C_AC_S + k_{-1}C_S + kC_S C_B}$$

Based on the rate of individual reactions, we have the following simplifications:

1. If the limiting step is adsorption/desorption:

$$\implies kC_B \gg k_1C_A, k_{-1}$$

$$\implies \theta = 1 \implies r = kC_S C_B$$

2. If the limiting step is the reaction:

$$\implies kC_B \ll k_1C_A, k_{-1}$$

$$\implies \theta = \frac{k_1C_AC_S}{k_1C_AC_S + k_{-1}C_S} = \frac{K_{ad}C_A}{K_{ad}C_A + 1} \quad \text{where, } K_{ad} = \frac{k_1}{k_{-1}} \quad [\text{Langmuir's Isotherm}]$$

$$\implies r = kC_S C_B \frac{K_{ad}C_A}{K_{ad}C_A + 1}$$

The above expression can be further simplified based on the relative concentrations of A and B:

(a) High concentrations of A, ($C_A \gg C_B$):

$$\implies r = kC_S C_B$$

The order of the reaction is zero w.r.t A.

(b) Low concentrations of A, ($C_A \ll C_B$):

$$r = kC_S K_{ad} C_A C_B = k_r C_S C_A C_B$$

Note: Arrhenius equation can be used to model the temperature dependence of the adsorption and desorption rate constants (thermal-desorption).

2.4 Reaction Rates

Assumptions:

1. The reaction rates are only functions of gas-phase concentrations of NO , NH_3 , the adsorbed Ammonia and the available adsorption sites.
2. The concentration rates are converted into molar-rate so that the mass balance in control volume approach (CSTR) can be performed. For gaseous reactants:

$$M_g = C_g V \implies R_i = V r_i$$

The number of moles of the adsorbant is directly considered instead of their surface concentrations.

1. Standard SCR Reaction (5):

$$R_1 = k_1 V C_{NO} M_{NH_3} = k_1 V C_{NO} \Theta \theta$$

$$k_1 = A_1 e^{\frac{-E_1}{RT}}$$

2. Ammonia Oxidation (8):

$$R_3 = k_3 M_{NH_3} = k_3 \Theta \theta$$

$$k_3 = A_3 e^{\frac{-E_3}{RT}}$$

3. Ammonia Adsorption/Desorption (4):

(a) Forward:

$$R_{4F} = k_{4F} V C_{NH_3} (\Theta - M_{NH_3}) = k_{4F} V C_{NH_3} \Theta (1 - \theta)$$

$$k_{4F} = A_{4F} e^{\frac{-E_{4F}}{RT}}$$

(b) Reverse:

$$R_{4R} = k_{4R} M_{NH_3} = k_{4R} \Theta \theta$$

$$k_{4R} = A_{4R} e^{\frac{-E_{4R}}{RT}}$$

Where,

$$\theta - NH_3 \text{ storage capacity fraction in SCR} = \frac{\text{Moles of } NH_3 \text{ adsorbed}(M_{NH_3})}{\text{Total moles of } NH_3 \text{ that can be adsorbed}(\Theta)}$$

Θ – Ammonia storage capacity(*moles*)

$\Theta = S_1 e^{S_2 T}$ S_1, S_2 – Aging parameters of the catalyst (positive constants)

E_i – Activation Energy of i^{th} reaction

k_i – Pre-exponential factor

R – Universal gas constant

T – Temperature

$C_{\{\bullet\}}$ – Concentration (mol/m^3)

V – Volume of the exhaust gas in the substrate[6] (m^3)

$$V_e = \epsilon A_c L_{cat}$$

A_c – Open frontal area of the catalyst

L_{cat} – Length of the catalyst

ϵ – Void fraction

A_c – Area of the catalyst

3 Ammonia input (Urea Dosing) dynamics

The actual input to the system is urea from AdBlue (32.5% aqueous urea solution) injection that converted to ammonia (through reactions: (1), (2) and (3)). This can be modelled by the following equation [3]:

$$\dot{C}_{NH_3,in} = -\frac{1}{\tau}C_{NH_3,in} + 2\frac{1}{\tau}\frac{\eta u_{AdBlue}}{N_{urea}F}$$

where,

τ – Time constant

u_{AdBlue} – Mass injection rate of the AdBlue solution

η – Mass fraction of urea in the solution

N_{urea} – Atomic number of urea

F – Exhaust flow rate of the catalyst m^3/s

The above model is re-parametrized as follows:

$$\dot{C}_{NH_3,in} = \frac{1}{\tau}(-C_{NH_3,in} + \eta_{urea}C_{NH_3,ideal})$$

where,

η_{urea} – urea $\rightarrow NH_3$ conversion efficiency

τ – urea $\rightarrow NH_3$ time-constant

$C_{NH_3,ideal}$ – ideal $C_{NH_3,in}$ if $\eta_{urea} = 1$ (constant parameter obtained through calibration)

In the present work, $C_{NH_3,in}$ is considered as the input instead of AdBlue injection as its dynamics are completely decoupled from that of other states. Further, it is observed that AdBlue is completely converted to Ammonia at the very upstream part of the SCR catalyst [1].

4 3 state dynamic model

Assumptions :

The following are the additional assumptions along with the assumptions of 4-state model that are used to arrive at the three-state dynamic model[6]:

1. Only the standard SCR reaction is considered.
2. All NO_x in the exhaust gas is assumed to be NO .
 - The commercially available NO_x sensor (Horiba gas analyzer [3]) cannot differentiate between NO and NO_2 .
3. Slow SCR reaction is neglected.
 - The flow rate of the exhaust would ensure that the not a significant concentration of tail-pipe exhaust components are due to the slow SCR reaction [3].
4. Mass transfer is neglected. That means the chemical kinetics in the catalyst are reaction controlled.
 - The standard SCR reaction rate is faster than the flow rate of the exhaust fluids.
5. Nitrogen selectivity for ammonia oxidation is 100%.
 - This assumption is relaxed by including algebraic relationship between selectivity and the temperature (ASC model [8]).
6. Reaction rates are assumed to be a function of the gas phase concentration of NO_x and ammonia storage.

Dynamic Model Derivation:

We have the mass (moles of reactants in/out) balance from the CSTR assumption:

$$\begin{bmatrix} V\dot{C}_{NO} \\ V\dot{C}_{NH_3} \\ \dot{M}_{NH_3} \end{bmatrix} = \begin{bmatrix} -R_1 - FC_{NO} \\ -R_{4F} + R_{4R} - FC_{NH_3} \\ R_{4F} - R_{4R} - R_1 - R_3 \end{bmatrix} + F \begin{bmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} C_{NO,in} \\ C_{NH_3,in} \end{bmatrix}$$

Let, $b = \frac{F}{V}$

$$\begin{bmatrix} \dot{C}_{NO} \\ \dot{C}_{NH_3} \\ \dot{M}_{NH_3} \end{bmatrix} = \frac{1}{V} \begin{bmatrix} -R_1 - FC_{NO} \\ -R_{4F} + R_{4R} - FC_{NH_3} \\ R_{4F} - R_{4R} - R_1 - R_3 \end{bmatrix} + b \begin{bmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} C_{NO,in} \\ C_{NH_3,in} \end{bmatrix} \quad (12)$$

4.1 Dynamic Model with storage ratio (θ) as state

Let,

$$\begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} C_{NO} \\ C_{NH_3} \\ \theta \end{bmatrix} \quad \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \begin{bmatrix} C_{NO,in} \\ C_{NH_3,in} \end{bmatrix}$$

Rewriting eqn. 12:

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \end{bmatrix} = \begin{bmatrix} [k_1\Theta]x_1x_3 - bx_1 \\ -[k_{4F}\Theta]x_2(1-x_3) + [k_{4R}V^{-1}\Theta]x_3 - bx_2 \\ +[k_{4F}V]x_2(1-x_3) - [k_{4R}]x_3 - [k_1V]x_1x_3 - [k_3]x_3 \end{bmatrix} + b \begin{bmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \quad (13)$$

The following parameters are defined for convenience, based on the coefficients of product of states and individual states in each of the equations:

Coefficients of product of states:

$$\begin{array}{ccc} & x_1 & x_2 & x_3 \\ x_1 & & & f_{13} \\ x_2 & & & f_{23} \\ x_3 & f_{31} & f_{32} & \end{array}$$

Coefficients of states:

$$\begin{array}{ccc} & x_1 & x_2 & x_3 \\ x_1 & g_1 & & \\ x_2 & & g_2 & g_{23} \\ x_3 & & g_{32} & g_3 \end{array}$$

$$\begin{array}{ll} f_{13} & = k_1 \Theta \\ f_{23} & = k_{4F} \Theta \\ f_{32} & = k_{4F} V \\ f_{31} & = k_1 V \end{array} \quad \begin{array}{ll} g_1 & = b \\ g_2 & = b + k_{4F} \Theta \\ g_3 & = [k_{4R} + k_3] \\ g_{23} & = k_{4R} V^{-1} \Theta \\ g_{32} & = k_{4F} V \end{array}$$

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \end{bmatrix} = \begin{bmatrix} -f_{12}x_1x_3 - g_1x_1 \\ -g_2x_2 + f_{23}x_2x_3 + g_{23}x_3 \\ -f_{32}x_2x_3 - g_3x_3 - f_{31}x_1x_3 + g_{32}x_2 \end{bmatrix} + b \begin{bmatrix} u_1 \\ u_2 \\ 0 \end{bmatrix} \quad (14)$$

Note: Some $f_{\bullet}'s, g_{\bullet}'s$ are algebraically related.

4.1.1 Small Perturbation model

We have the small-perturbation model from eqn. 14:

$$\begin{bmatrix} \delta \dot{x}_1 \\ \delta \dot{x}_2 \\ \delta \dot{x}_3 \end{bmatrix} = \begin{bmatrix} -(g_1 + f_{12}x_{30}) & 0 & -f_{12}x_{10} \\ 0 & -(g_2 - f_{23}x_{30}) & (f_{23}x_{20} + g_{23}) \\ -f_{31}x_{30} & g_{32} - f_{32}x_{30} & -f_{32}x_{20} - g_3 - f_{31}x_{10} \end{bmatrix} \begin{bmatrix} \delta x_1 \\ \delta x_2 \\ \delta x_3 \end{bmatrix} + b \begin{bmatrix} \delta u_1 \\ \delta u_2 \\ 0 \end{bmatrix} \quad (15)$$

4.2 Dynamic Model with molar storage ratio (M_{NH_3}) as state

Let,

$$\begin{bmatrix} x_1 \\ x_2 \\ x_3 \end{bmatrix} = \begin{bmatrix} C_{NO} \\ C_{NH_3} \\ M_{NH_3} \end{bmatrix} \quad \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} = \begin{bmatrix} C_{NO,in} \\ C_{NH_3,in} \end{bmatrix}$$

Rewriting eqn. 12:

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \end{bmatrix} = \begin{bmatrix} k_1x_1x_3 - bx_1 \\ -k_{4F}x_2(\Theta - x_3) + [k_{4R}V^{-1}]x_3 - bx_2 \\ +[k_{4F}V]x_2(\Theta - x_3) - [k_{4R}]x_3 - [k_1V]x_1x_3 - k_3x_3 \end{bmatrix} + b \begin{bmatrix} 1 & 0 \\ 0 & 1 \\ 0 & 0 \end{bmatrix} \begin{bmatrix} u_1 \\ u_2 \end{bmatrix} \quad (16)$$

The following parameters are defined for convenience, based on the coefficients of product of states and individual states in each of the equations:

Coefficients of product of states:

$$\begin{array}{ccc} & x_1 & x_2 & x_3 \\ x_1 & & & f_{13} \\ x_2 & & & f_{23} \\ x_3 & f_{31} & f_{32} & \end{array}$$

Coefficients of states:

$$\begin{array}{ccc} & x_1 & x_2 & x_3 \\ x_1 & g_1 & & \\ x_2 & & g_2 & g_{23} \\ x_3 & & g_{32} & g_3 \end{array}$$

$$\begin{array}{ll}
f_{13} = k_1 & g_1 = b \\
f_{23} = k_{4F} & g_2 = b + k_{4F}\Theta \\
f_{32} = k_{4F}\Theta & g_3 = k_{4R} + k_3 \\
f_{31} = k_1V & g_{23} = k_{4R}V^{-1} \\
& g_{32} = k_{4F}V\Theta
\end{array}$$

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \end{bmatrix} = \begin{bmatrix} -f_{12}x_1x_3 - g_1x_1 \\ -g_2x_2 + f_{23}x_2x_3 + g_{23}x_3 \\ -f_{32}x_2x_3 - g_3x_3 - f_{31}x_1x_3 + g_{32}x_2 \end{bmatrix} + b \begin{bmatrix} u_1 \\ u_2 \\ 0 \end{bmatrix} \quad (17)$$

Note: Some $f'_{\bullet}s, g'_{\bullet}s$ are algebraically related.

4.2.1 Small Perturbation model

We have the small-perturbation model from eqn. 17:

$$\begin{bmatrix} \delta\dot{x}_1 \\ \delta\dot{x}_2 \\ \delta\dot{x}_3 \end{bmatrix} = \begin{bmatrix} -(g_1 + f_{12}x_{30}) & 0 & -f_{12}x_{10} \\ 0 & -(g_2 - f_{23}x_{30}) & (f_{23}x_{20} + g_{23}) \\ -f_{31}x_{30} & g_{32} - f_{32}x_{30} & -f_{32}x_{20} - g_3 - f_{31}x_{10} \end{bmatrix} \begin{bmatrix} \delta x_1 \\ \delta x_2 \\ \delta x_3 \end{bmatrix} + b \begin{bmatrix} \delta u_1 \\ \delta u_2 \\ 0 \end{bmatrix} \quad (18)$$

4.3 Parametrization w.r.t the choice of x_3

$$\begin{array}{ll}
f_{13} = k_1\Theta & g_1 = b \\
f_{23} = k_{4F}\Theta & g_2 = b + k_{4F}\Theta \\
f_{32} = k_{4F}V & g_3 = [k_{4R} + k_3] \\
f_{31} = k_1V & g_{23} = k_{4R}V^{-1}\Theta \\
& g_{32} = k_{4F}V
\end{array}$$

Parametrization if $x_3 = \theta_{NH_3}$

$$\begin{array}{ll}
f_{13} = k_1 & g_1 = b \\
f_{23} = k_{4F} & g_2 = b + k_{4F}\Theta \\
f_{32} = k_{4F}\Theta & g_3 = k_{4R} + k_3 \\
f_{31} = k_1V & g_{23} = k_{4R}V^{-1} \\
& g_{32} = k_{4F}V\Theta
\end{array}$$

Parametrization if $x_3 = M_{NH_3}$

In the second parametrization Θ is only coefficient of k_{4F} . This can reduce the variance of estimation.

5 Catalyst molar storage capacity model

The variation of storage capacity of the catalyst (Θ) with temperature is modelled using an exponential curve fit in [1] (2011) from the available experimental data from [9], [10] and [11]. The results from [12] (2012) show a similar trend.

$$\Theta = S_1 e^{-S_2 T}$$

The parameters S_1 and S_2 change with age affecting the storage capacity at a given temperature.

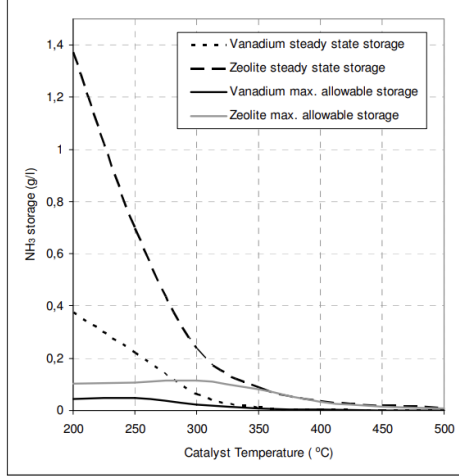
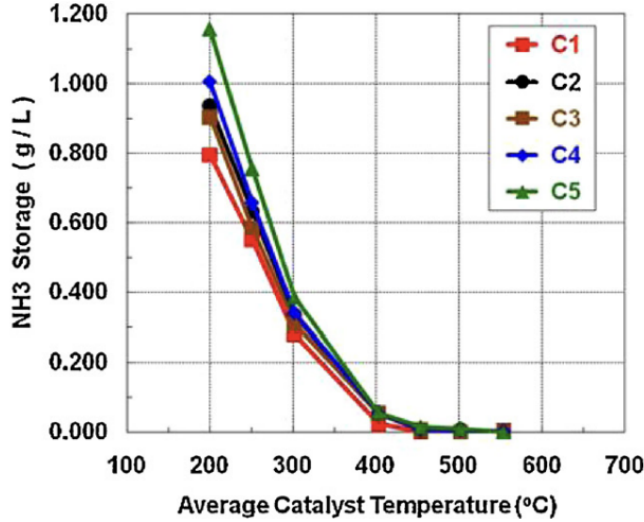


Figure 4. Steady state and maximum allowable NH_3 storage as a function of catalyst temperature, for a 34 l SCR catalyst, $\text{SV} = 25,000 \text{ h}^{-1}$, $\text{NSR} = 1.2$ and engine-out $\text{NO}_x = 250 \text{ g/h}$.

Results from [9]



Results from [12]

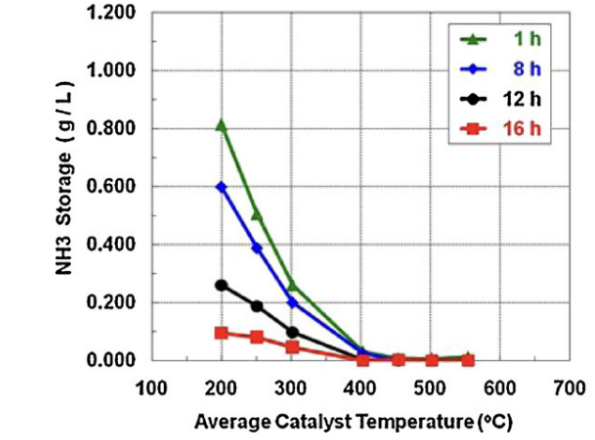
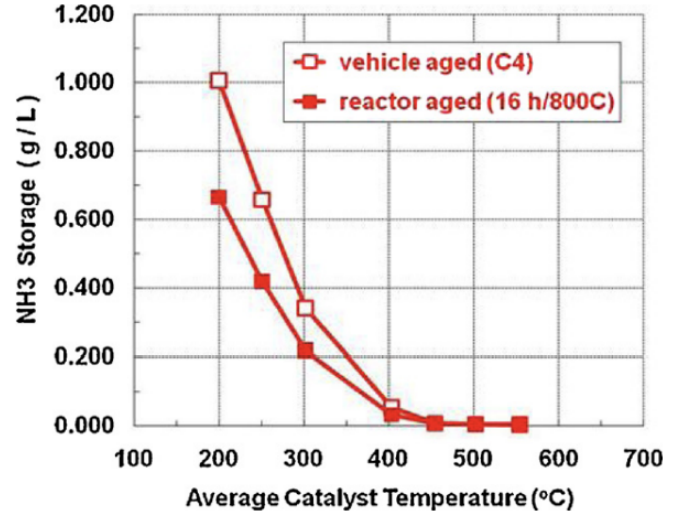


Fig. 9. NO oxidation to NO_2 , NH_3 oxidation/ NH_3 oxidation to NO_x , and NH_3 storage results after hydrothermal aging at 850°C for different times.

Results from [12]



Results from [12]

Figure 1: Temperature effects of catalyst storage capacity

5.1 Catalyst aging factor

Assumption: The aged catalyst results in small changes in S_1, S_2 .

The above assumption is valid if the catalyst's operating range is limited to a small range of storage capacity.

Using small perturbation,

$$\begin{aligned}\delta\Theta &= \left(\frac{\delta S_1}{S_1} - \delta S_2 T\right) S_1 e^{-S_2 T} \\ \Rightarrow \Theta_{aged} &= \Theta + \delta\Theta = \left(1 + \frac{\delta S_1}{S_1} - \delta S_2 T\right) S_1 e^{-S_2 T}\end{aligned}$$

Let,

$$a(T) = 1 + \frac{\delta S_1}{S_1} - \delta S_2 T = a_1 + a_2 T$$

Thus, a is the factor by which the storage capacity is reduced due to the catalyst's aging. Hence, for optimal performance:

$$a > a_{min} \quad \forall T \in [T_{min}, T_{max}]$$

Note: The above definition is consistent with that of the literature [13]. The major difference lies in its derivation and assumptions. Also, [13] considers aging factor as temperature independent fraction and has no minimum value for classifying the catalyst as aged.

Consequently, *the catalyst aging detection problem becomes estimating the aging factor and testing if it is below a_{min} in presence of uncertainties.*

5.1.1 Aging factor estimation problem formulation

Given the simplified non-linear concentration dynamics for SCR-ASC reactions with internal dynamics and sensor cross-sensitivity 19. Estimate the total molar Ammonia storage capacity of the catalyst $[\Theta(t, T)]$. Then,

$$\Rightarrow a(t, T) = \frac{\Theta(t, T)}{\Theta(0, T)}$$

No fault condition:

$$a(t, T) > a_{min} \quad \forall T \in [T_{min}, T_{max}], t > 0$$

We have the following high-level steps in fault-diagnosis:

1. Estimate cross-sensitivity factor χ .
2. Estimate the lumped model parameters f_{\bullet}, g_{\bullet} .
 - This requires an observer for ammonia storage fraction θ .
3. Using f_{\bullet}, g_{\bullet} , estimate $\Theta(t, T)$.
4. Estimate $a(t, T)$ and propagate all the uncertainties down to δ_a , the uncertainty in \hat{a} .
5. Check for no-fault condition:

$$\hat{a}(t, T) \pm \delta_a > a_{min} \quad \forall T \in [T_{min}, T_{max}]$$

6 Sensor corss-sensitivity and non-linear control from of the model

The NO_x sensor is cross-sensitive to ammonia, resulting in the following measurement model (output) of the system:

$$y = C_{NO} + \chi C_{NH_3}$$

We have the non-linear state-space model form eqn. (17):

$$\begin{bmatrix} \dot{x}_1 \\ \dot{x}_2 \\ \dot{x}_3 \end{bmatrix} = \begin{bmatrix} -f_{12}x_1x_3 - g_1x_1 \\ -g_2x_2 + f_{23}x_2x_3 + g_{23}x_3 \\ -f_{32}x_2x_3 - g_3x_3 - f_{31}x_1x_3 + g_{32}x_2 \end{bmatrix} + b \begin{bmatrix} u_1 \\ u_2 \\ 0 \end{bmatrix} \quad (19)$$

$$y = x_1 + \chi x_2 \quad (20)$$

6.1 Discrete form of the model

Let, h be the sampling interval. Using Euler discretization:

$$\begin{bmatrix} x_1[k+1] \\ x_2[k+1] \\ x_3[k+1] \end{bmatrix} = \begin{bmatrix} -hf_{12}x_1x_3 - (hg_1 - 1)x_1 \\ -(hg_2 - 1)x_2 + hf_{23}x_2x_3 + hg_{23}x_3 \\ -hf_{32}x_2x_3 - (hg_3 - 1)x_3 - hf_{31}x_1x_3 + hg_{32}x_2 \end{bmatrix} + bh \begin{bmatrix} u_1 \\ u_2 \\ 0 \end{bmatrix}$$

$$y[k] = x_1[k] + \chi(T)x_2[k]$$

7 Appencix

7.1 Logarithm Formulae

$$\begin{aligned}\log xy &= \log x + \log y \\ \frac{d}{dt} \log x &= \frac{\dot{x}}{x}\end{aligned}$$

Let, $L_x = \log x$

$$\begin{aligned}\implies \log \dot{L}_x &= \log \dot{x} - \log x \\ \implies \log \dot{x} &= \log \dot{L}_x + L_x\end{aligned}$$

7.2 4 State Dynamic Model

A four state nonlinear model for the above reactions can be developed using Arrhenius equations, CSTR assumption and further simplification based on the following assumptions:

7.3 Assumptions

1. Slow SCR reaction is neglected.
 - The flow rate of the exhaust would ensure that the not a significant concentration of tail-pipe exhaust components are due to the slow SCR reaction [3].
2. Mass transfer is neglected. That means the chemical kinetics in the catalyst are reaction controlled.
 - The standard SCR reaction rate is faster than the flow rate of the exhaust fluids.
3. Nitrogen selectivity for ammonia oxidation is 100%.
 - This assumption is relaxed by including algebraic relationship between selectivity and the temperature (ASC model [8]).
4. Reaction rates are assumed to be a function of the gas phase concentration of NO_x and ammonia storage.

7.3.1 Additional Reaction Rates

1. Fast SCR Reaction (6): $R_2 = k_2 \exp\left(-\frac{E_2}{RT}\right) C_{NO} C_{N_2O} \theta \Theta V^2$
2. NO oxidation (11): $R_5 = \underbrace{k_5 \exp\left(-\frac{E_5}{RT}\right)}_{r_5} C_{NO} C_{O_2} V^2$

7.3.2 Dynamic model

Using above assumptions and definitions, we have the dynamic model [3]:

$$\begin{bmatrix} \dot{C}_{NO} \\ \dot{C}_{NO_2} \\ \dot{C}_{NH_3} \\ \dot{\theta}_{NH_3} \end{bmatrix} = \begin{bmatrix} -r_1 C_{NO} C_{O_2} \theta_{NH_3} \Theta V - 0.5 r_2 C_{NO} C_{NO_2} \theta_{NH_3} \Theta V - r_5 C_{NO} C_{O_2} V - b C_{NO} \\ -0.5 r_2 C_{NO} C_{NO_2} \theta_{NH_3} \Theta V + r_5 C_{NO} C_{O_2} V - b C_{NO_2} \\ -C_{NH_3} [\Theta r_{rF} (1 - \theta_{NH_3}) + b] + V^{-1} r_{4R} \Theta \theta_{NH_3} \\ -\theta_{NH_3} (r_{4F} C_{NH_3} V + r_3 C_{O_2} V + r_{4R} + r_1 C_{NO} C_{O_2} V^2 + r_2 C_{NO} C_{NO_2} V^2) + r_{4F} C_{NH_3} V \end{bmatrix} + b \begin{bmatrix} C_{NO,in} \\ C_{NO_2,in} \\ C_{NH_3} \\ 0 \end{bmatrix} \quad (21)$$

Where,

$$b = \frac{F}{V}$$

7.3.3 Previously used 3-state dynamic model

The 3-state dynamic model used previously [8] is as follows:

Dynamics:

$$\begin{aligned} \dot{x}_1 &= \left(\frac{F}{V}\right)(u_1 - x_1) - K\alpha_{ads}x_1(1 - x_3) + K\alpha_{des}x_3 & \dot{u}_1 &= \frac{1}{\tau}(-u_1 + \eta_{urea}u_{1,ideal}) & [\text{actuator dynamics}] \\ \dot{x}_2 &= \left(\frac{F}{V}\right)(u_2 - x_2) - K\alpha_{SCR}x_2x_3 & K &= \frac{S_1}{V} \exp(-S_2T) \\ \dot{x}_3 &= \alpha_{ads}x_1(1 - x_3) - \alpha_{SCR}x_2x_3 - \alpha_{des}x_3 - \alpha_{oxi}x_3 & \alpha_i &= A_i \exp\left(-\frac{E_i}{RT}\right) & i = ads, des, SCR, oxi \end{aligned}$$

States:

$$\begin{aligned} x_1 &- NH_3 \text{ concentration at SCR-out } (mol/m^3) \\ x_2 &- NO_x(NO) \text{ concentration at SCR-out } (mol/m^3) \\ x_3 &- NH_3 \text{ storage capacity fraction in SCR} = \frac{\text{Moles of } NH_3 \text{ adsorbed}}{\text{Total moles of } NH_3 \text{ that can be adsorbed}} \end{aligned}$$

Inputs:

$$\begin{aligned} u_1 &- NH_3 \text{ injected concentration at SCR-in } (mol/m^3) \\ \eta_{urea} &- \text{urea} \rightarrow NH_3 \text{ conversion efficiency} \\ \tau &- \text{urea} \rightarrow NH_3 \text{ time-constant} \\ u_{1,ideal} &- \text{ideal } u_1 \text{ if } \eta_{urea} = 1 \text{ (constant parameter obtained through calibration)} \\ u_2 &- NO_x(NO) \text{ concentration at SCR-in } (mol/m^3) \end{aligned}$$

Parameters:

$$\begin{aligned} K &- \text{SCR catalyst's } NH_3 \text{ storage capacity } (mols) \\ S_1, S_2 &- \text{Aging parameters of the catalyst} \\ F &- \text{Exhaust gas volume flow rate } (m^3/s) \\ V &- \text{Volume of the catalyst } (m^3) \\ \alpha_i &- \text{Reaction rate of } i^{th} \text{ reaction} \\ E_i &- \text{Activation Energy of } i^{th} \text{ reaction} \\ A_i &- \text{Pre-exponential factor of } i^{th} \text{ reaction} \\ i : SCR &- \text{Standard SCR reaction} \\ i : ads &- NH_3 \text{ adsorption} \\ i : des &- NH_3 \text{ desorption} \\ i : oxi &- NH_3 \text{ oxidation} \end{aligned}$$

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