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NO_x sensor ammonia cross sensitivity analysis using a simplified physics based model

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1. Abstract

A simplified physic-based NO_x sensor model is developed to remove ammonia cross sensitivity from production NO_x sensors. A linear model is used to consider the effect of ammonia contamination on NO_x sensor output signal using a cross sensitivity factor. The effect of temperature on NO_x sensor cross sensitivity to ammonia is investigated by considering NH₃ oxidation inside the sensor. The model considers the effect of temperature on cross sensitivity based on three global reactions. N₂O, NO and NO₂ are considered as the main products of NH₃ oxidation inside the sensor. Finally, a relation is derived for cross sensitivity factor in terms of concentration of N₂O, NO and NO₂. This model provides a simplified physic-based model for detailed NO_x sensor cross sensitivity analysis.

2. Introduction

The high efficiency and fuel economy advantages of Direct Injection (DI) Diesel engines make them interesting for power generation systems [1]. However, new engine control strategies and after treatment systems are needed to meet stringent NO_x and particulate emission regulations [2, 3]. In general, thermal and long-term stability, reproducibility, sensitivity and cross sensitivity are the most important challenging issues of gas sensors operating at high temperatures up to 1000 C [4].

Urea-based Selective Catalytic Reduction (SCR) is an effective technique to reduce NO_x emissions and to satisfy future emission standard regulations [5, 6]. Measuring the NO_x concentration in the exhaust gas is essential for closed-loop control of SCR systems [7, 8]. However, the NO_x sensors are cross-sensitive to ammonia (NH₃). Due to this cross sensitivity, the NO_x sensor reading can defer from the actual value [9, 10]. Determining actual NO_x is an important challenge for urea injection control of SCR systems. Cross sensitivity of NO_x sensors to ammonia, makes it difficult to achieve maximum NO_x conversion in SCR closed-loop control. The time delay in the urea injection and SCR catalyst dynamics are the other important factors that limit the performance of closed loop SCR control [11, 12, 13]. Cross sensitivity of NO_x sensors to ammonia is mainly due to ammonia oxidation inside the sensor oxygen pump [14]. N₂O, NO and NO₂ are the main products of NH₃ oxidation [15, 16] and their concentrations are affected by the gas temperature and the cross sensitivity of NO_x sensors is a strong function of temperature.

The cross-sensitivity of NO_x sensors to ammonia are being actively investigated. In [17, 18], the cross-sensitivity factor is taken as a constant. A time variant cross sensitivity factor is detailed in [9]. In [19], the cross sensitivity factor is defined as a function of normalized stoichiometric ratio, ammonia, NO, and NO₂ concentrations. An empirical model for NO_x sensor cross sensitivity is developed and validated in [20] in which the cross sensitivity is defined as a function of temperature, time and dimension-less ammonia slip rate. The goal of NO_x sensors ammonia cross sensitivity analysis for robust and fast closed-loop SCR control still remains to be achieved.

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In this work, a simplified physics based NO_x sensor model is developed to investigate the ammonia cross sensitivity of a production NO_x sensor. The NO_x sensor output signal is modeled as a linear function of NO_x and NH_3 concentrations considering cross sensitivity factor. The effect of temperature on NO_x sensor cross sensitivity to ammonia is then investigated considering ammonia oxidation global reaction mechanism [15] where N_2O , NO and NO_2 are the main oxidation products. The cross sensitivity factor is finally derived as a function of ammonia oxidation products concentrations.

3. NO_x sensor model

A linear form of a NO_x sensor model from [21] is:

$$C_{\text{NO}_x} = \overline{C_{\text{NO}_x}} - c_{\text{CS}} C_{\text{NH}_3} \quad (1)$$

where $\overline{C_{\text{NO}_x}}$, c_{CS} , C_{NO_x} and C_{NH_3} are the sensor output signal, the cross sensitivity factor and the actual NO_x and NH_3 concentrations respectively.

The experimental data in [14] is used to evaluate different cross sensitivity models. The experimental conditions of the points used for this study are summarized in Table 1. A schematic of experimental setup used in [14] is shown in Fig. 1. The measured values from Horiba MEXA 7500 gas analyzer after the first SCR and NO_x concentration estimates for several constant cross sensitivity factors are shown in Fig. 2 and 3, where C_{NO_x} , C_{NH_3} are measured from downstream of the SCR and the temperature is for exhaust gas upstream of the SCR. Both tests have transient AdBlue injection [14].

Test number	Test 1	Test 2
Engine speed range [rpm]	1700	1000
Engine torque range [N.m]	265-285	235-250
Gas Temperature before SCR [K]	543-606	518-523
AdBlue Inj. Rate [$\frac{\text{mg}}{\text{Sec}}$]	145	107

Table 1: Operating Conditions [14]

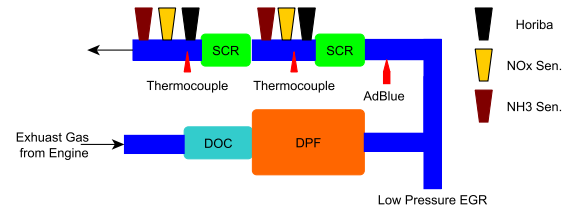


Figure 1: Experimental Setup

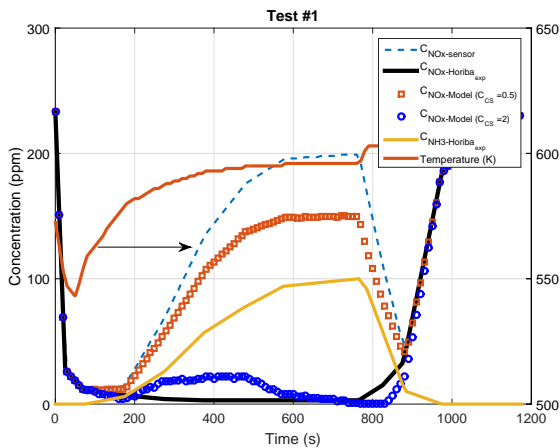


Figure 2: Modeled NO_x concentration for constant cross sensitivity factors vs. actual concentration - test 1

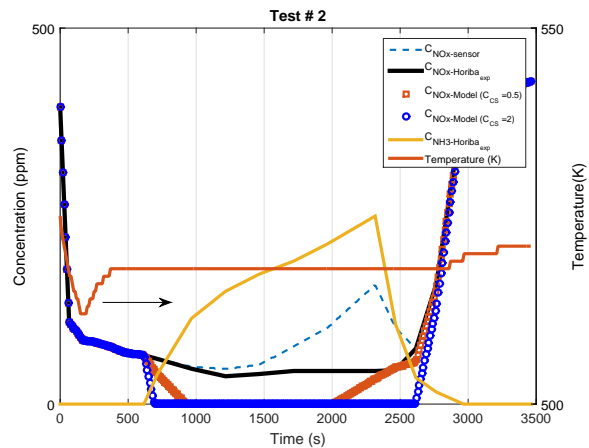


Figure 3: Modeled NO_x concentration for constant cross sensitivity factors vs. actual concentration - test 2

There is a significant deviation between the production NO_x sensor output signal (the dot-dashed blue line) and the actual one measured by Horiba gas analyzer (the solid black line) as shown in Fig. 2 and 3. Several cross-

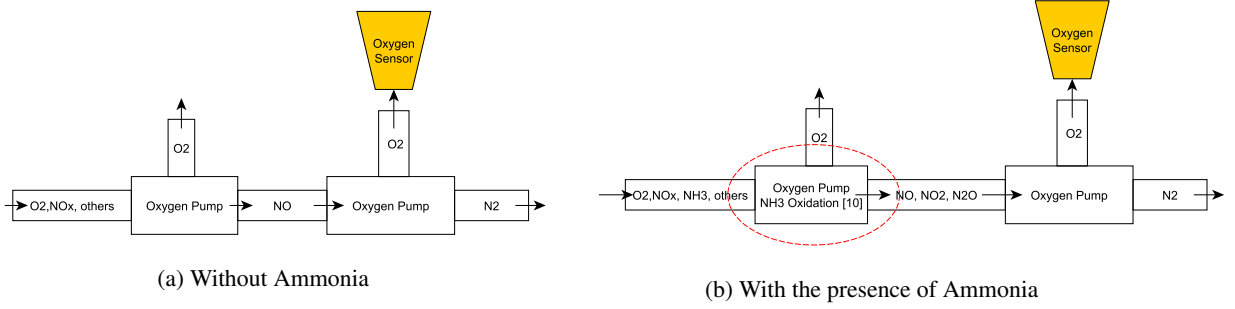


Figure 4: Principle of NO_X sensor operation

sensitivity factors are checked using the ammonia slip, the NO_X sensor reading and the actual NH₃ concentration. The results shown in Fig. 2 and 3 indicate that the cross sensitivity factor plays important role in the accuracy of NO_X sensor reading. In order to estimate accurate cross sensitivity factor, a simplified physics based model is developed considering ammonia oxidation reactions inside the sensor oxygen pump.

4. Physics based model

A schematic diagram of a NO_X sensor is shown in Fig 4a. First, the zirconia based oxygen pump removes the oxygen molecules and reduces NO₂ to NO. Then, NO breaks down into N₂ and O₂ in the second oxygen pump. The NO_X concentration is calculated based on the oxygen concentration measurement in the second oxygen pump. NO, NO₂ and N₂O are produced with the presence and oxidation of ammonia in exhaust gas as shown in Fig. 4b. The ammonia oxidation products affect oxygen concentration measurement and NO_X sensor output signal.

The effect of ammonia on NO_X sensor cross sensitivity is considered by investigating the ammonia oxidation in the left oxygen pump (see Fig. 4b). The system is open to the transfer of mass and energy (see Fig. 5). The oxygen pump is modeled as a constant volume reactor. Quasi-steady, adiabatic, one dimensional flow equations are used to predict mass flow enters and leaves the system. The upstream gas temperature, pressure and mixture composition are defined based on exhaust manifold condition while the downstream pump is modeled as a constant volume whose pressure and temperature are determined by solving mass and energy equations. The exhaust manifold gas composition is determined using Olikara and Borman equilibrium model [22].

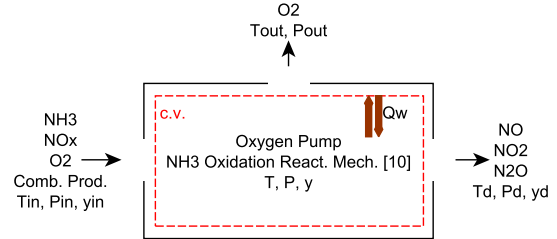


Figure 5: Schematic presentation of conservation of mass and energy in the left oxygen pump (see Fig. 4b)

Energy conservation is used to obtain a differential equation for the change in system temperature. For the oxygen pump (see Fig. 5), conservation of energy is

$$\frac{dU}{dt} = \sum_j \dot{m}_j h_j + \dot{Q}_W + \dot{Q}_{HR} \quad (2)$$

where U is the internal energy, \dot{Q}_W is the heat transfer rate into or from the system, \dot{Q}_{HR} is the rate of heat release from ammonia oxidation, and h_j is the j^{th} species entering or leaving the system. It is assumed that the system is adiabatic ($\dot{Q}_W=0$). For the purpose of ammonia heat release calculation, the products are assumed to contain only NO, NO₂, N₂O and H₂O. The heat of combustion at time t is calculated as

$$Q_{Tot,t} = H_{prod} - H_{react} \quad (3)$$

where H_{prod} and H_{react} are the enthalpy of products and reactants respectively. Then, the ammonia oxidation heat release rate is calculated as

$$\dot{Q}_{HR} = Q_{Tot,t+\Delta t} - Q_{Tot,t} \quad (4)$$

The conservation of gas species in the oxygen pump is

$$\dot{y}_i = \sum_j \frac{\dot{m}_j}{m} (y_j - y_i) + \frac{\dot{\omega}_i M_i}{\rho} \quad (5)$$

where $\dot{\omega}$ is the net chemical production rate, M is the molar mass and m is the total mass within the oxygen pump. The indexes i and j denote species and flux respectively. The net chemical production rate is calculated using ammonia oxidation equilibrium model. A global reaction mechanism for ammonia oxidation considering 3 reactions and 6 species are used [14, 15] as



where the equilibrium constants are function of temperature and are defined based on the values reported in [15] and JANAF thermodynamic tables [23].

5. Results & Discussion

The simulation results for the case that engine fueled with n-heptane are shown in Fig. 6 and 7. The exhaust gas temperature is varied between 515 K and 605 K. At low temperatures (below 523 K), NH_3 is mainly converted to N_2O and each N_2O molecule produces 0.5 O_2 molecule in the sensing chamber as shown in Fig. 6. It means that the sensor cross sensitivity is around 0.25 at low temperatures as two NH_3 molecules are converted to one N_2O molecule. At high temperatures (above 575 K) reaction 8 is the dominant reaction in which NO_2 is produced. Each NO_2 molecule produces two O_2 molecules in the sensing chamber that changes the sensor cross sensitivity to approximately 2 at high temperatures. Therefore, the NO_x sensor model in Eqn. (1) can be modified as

$$\overline{C_{NO_x}} = C_{NO_x} + (C_{NO} + c_1 \times C_{N_2O} + c_2 \times C_{NO_2}) \quad (9)$$

where C_{NO} , C_{N_2O} and C_{NO_2} are the NO, N_2O and NO_2 concentrations due to ammonia oxidation in the left oxygen pump shown in Fig. 4b. c_1 and c_2 are constants ($c_1=0.5$, $c_2=2$). The sensor cross-sensitivity factor is then derived as

$$c_{CS} = c_3 \times (C_{NO} + c_1 \times C_{N_2O} + c_2 \times C_{NO_2}) \quad (10)$$

where $c_3 = \frac{1}{C_{NH_3}}$.

As illustrated in Fig. 7, cross sensitivity of NO_x sensor to ammonia is a strong function of gas temperature which is consistent with [14, 20]. The cross sensitivity factor varies from approximately 0.25 to 2 over the temperature range of 515 K to 610 K.

As the temperature increases, the concentration of N_2O decreases while NO concentration increases in a limited temperature range. NO_2 concentration also increases as temperature increases. Finally for temperatures higher than 580 K, the dominant production of NH_3 oxidation is NO_2 which causes a higher oxygen concentration in the

sensing cell of Fig. 4b.

As the oxygen concentration in the sensing chamber increases, the sensor output signal increases despite constant NO_x concentration. This is shown in the cross sensitivity factor of the sensor as illustrated in Fig.7. To examine the relative importance of temperature on NO_x sensor error, a normalized sensitivity function ($S_{CCS} = \left| \frac{\Delta c_{CS}}{\Delta T} \right| \times \frac{T_b}{c_{CSb}}$) is used, where index b denotes for the base point. It is shown in Fig.7 that S_{CCS} increases up to the maximum value of 41.46 at 545 K which causes 5.97 ppm/K [$41.46 \times \frac{c_{CSb}}{T_b} \times 100$ (Ammonia Concentration)] and 29.85 ppm/K [$41.46 \times \frac{c_{CSb}}{T_b} \times 500$ (Ammonia Concentration)] error in NO_x sensor signal reading for ammonia concentrations of 100 ppm and 500 ppm respectively.

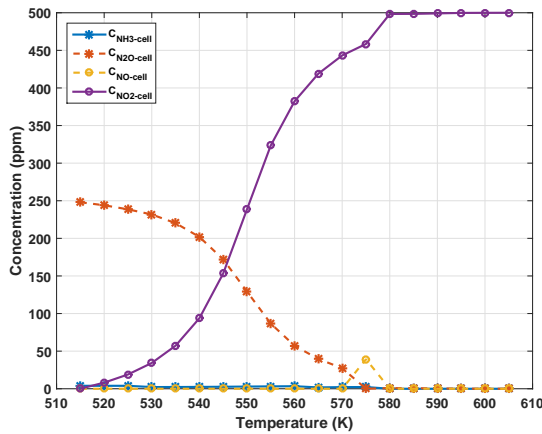


Figure 6: Ammonia oxidation products in zirconia based oxygen pump

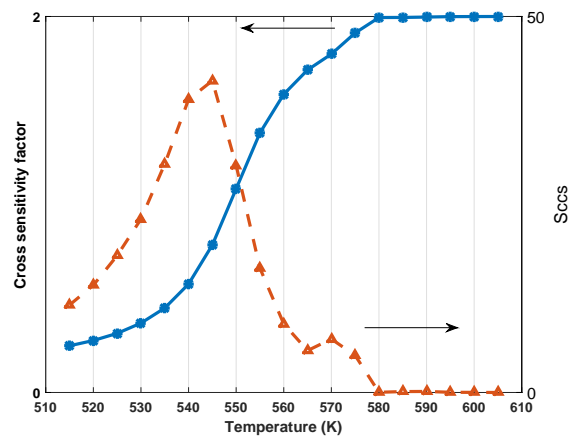


Figure 7: NO_x sensor ammonia cross sensitivity factor (Eqn. 10) and Normalized sensitivity function

6. Conclusions

The NO_x sensor ammonia cross-sensitivity is detailed using a simplified physics based model. N_2O , NO and NO_2 are assumed as the main ammonia oxidation products inside the NO_x sensor oxygen pump. The cross-sensitivity factor is derived based on the concentration of the ammonia oxidation products. The temperature effect is investigated on ammonia oxidation reactions and the sensor cross-sensitivity. This model provides a good platform for NO_x sensor ammonia cross sensitivity analysis.

Although cross sensitivity of a NO_x sensor to ammonia is directly affected by the temperature inside the sensor cells, the variation of this cross sensitivity can be decreased by externally controlling the cell temperature. Inaccurate control of sensor temperature can cause 5.97 and 29.85 ppm/K error in NO_x sensor reading for ammonia concentrations of 100 ppm and 500 ppm respectively. A sensor heating system that is able to control the actual cell temperature, can eliminate the effect of temperature on cross sensitivity variation of NO_x sensor.

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