

Kinetic Modelling and Model based Control of SCR Deposit

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Abstract. Selective catalytic reduction (SCR) is widely used for on-highway as well as off-road applications to fulfil stringent nitrogen oxide (NO_x) emission standards. However, in the practical operations, urea deposits occur under unfavourable conditions, which bring about urea dosing strategy failures, affect SCR system de-NO_x performance and decrease fuel economy by increase engine back pressure. This paper presents a 1D kinetic model of SCR system, which can predict SCR reaction and deposit formation process. Furthermore, a model-based control strategy has been designed for real engine applications. The ETC test shows the deposits quantity can be reduced by 41.8% with this model.

1 Introduction

Nowadays, the selective catalytic reduction is a promising solution to fulfill stringent nitrogen oxide (NO_x) emission standards enforced by worldwide regulation bodies for lean burning engines. However, in the practical operations, the rapid change of engine working conditions leads to a rapid change of exhaust temperature, space velocity (SV) and urea dosage rate, which makes it difficult to obtain a complete evaporation and decomposition of urea before the catalyst. Consequently, urea deposits occur under unfavorable conditions, which bring about a failure of dosing strategy. Moreover, the formed deposits may increase the back pressure of the engine and affect engine system performance.

Theoretically, it would be no deposits formation in the SCR system if there is no contact between urea droplets and pipe/mixer wall, which is impossible due to the restricted packaging space of the practical applications. Therefore, the SCR system performance which include the uniformity of the reducing agent, the pressure drop, the de-NO_x efficiency and the risk of deposits of the system, should be evaluated in the product development stage. Owing to the variety of different exhaust gas configurations, the evaluation requires appropriate support from numerical simulation in order to obtain the required objectives. Nowadays, the evaluation of the spray preparation and de-NO_x efficiency has become state of the art [1-4]. In contrast, the studies of the reliable prediction methods for deposit risk through numerical simulation are relatively scarce.

This paper presents a kinetic model for SCR system, which can predict SCR reaction and deposit formation process. Furthermore, could be used for urea dosing control strategy optimization.

2 Experimental Setup

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The experimental setup consists of an 11.12 L diesel engine as Table 1, a 21.75 L V₂O₅-WO₃/TiO₂ catalyst. The aftertreatment system is equipped with urea dosing pump, NO_x sensors, inlet and outlet catalyst temperature sensors, an AVL AMA i60 emission analyzer and a Siemens ammonia analyser.

Table 1. Engine Information.

Engine model	Parameters
Features	Inline 6-cylinder, CRDI, TCI
Displacement	11.12 L
Cylinder bore × travel	123mm×156mm
Compression ratio	16.4
Rated power	303 kW at 1900 rev/min
Maximum torque	1870 Nm at 1300 rev/min

3 1D Kinetic Model Description

3.1 Structure

The injection, wallfilm and deposits formation process are shown in Figure 1. The liquid that injected into the exhaust pipe impact on the solid surface and a part of the liquid become wallfilm. The deposits would appear due to urea precipitation and the by-products generated in the urea thermolysis.

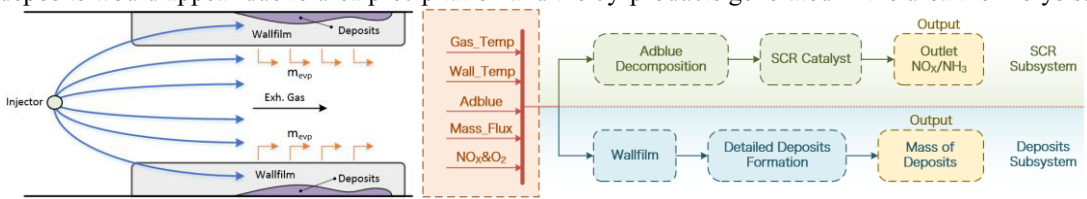


Figure 1. Injection Process.

Figure 2. The structure of the 1D kinetic model.

Many researches have shown that the by-products formed in the urea thermolysis can be ignored in the simulation of system-out NO_x and NH₃. Therefore, the 1D Model presented in this paper calculates the NO_x/NH₃ concentration and deposits respectively Figure 2, which would obtain a good balance between the computation precision and speed.

3.2 SCR Subsystem

The SCR subsystem includes tow pars, one is the urea decomposition block which is used to simulate the water evaporation, urea thermolysis and HNCO hydrolysis, the other is the SCR catalyst block which is used to simulate the reactions occurring inside the porous catalyst. In the urea decomposition block, instantaneous water evaporation in the gas phase is assumed and heat of evaporation is taken from the gas phase. The urea thermolysis and HNCO hydrolysis was simulated in CSTR method and the reaction rates are calculated by equation (1) and (2), respectively.

$$\dot{m}_{urea} = -m_{urea} \cdot K_{urea} \cdot \exp\left(-\frac{E_{urea}}{R \cdot T_g}\right) \tag{1}$$

$$\dot{m}_{HNCO} = -m_{HNCO} \cdot K_{HNCO} \cdot \exp\left(-\frac{E_{HNCO}}{R \cdot T_g}\right) \tag{2}$$

Where T_g is the exhaust gas temperature.

SCR Catalyst block is based on the geometry of a honeycomb monolith that consists of numerous parallel open channels. As the geometrical properties of all channels, their catalyst distribution, and

the inlet conditions are assumed identical, the flow through the monolith is modeled by solving the corresponding mass and energy balances for a one-dimensional single channel. Seven reactions are considered as Table 2, including urea thermolysis, HNCO hydrolysis, NH₃ ad/desorption, standard SCR, fast SCR, slow SCR, NH₃ oxidation, NO/NO₂ equilibrium, N₂O formation.

Table 2. Reaction Mechanism for SCR Catalyst Block.

Reaction	Rate equation
$(NH_2)_2CO \rightarrow NH_3 + HCNO$	$r_1 = K_1 \cdot \exp\left(-\frac{E_1}{RT_s}\right) \cdot c_{urea}$
$HCNO + H_2O \rightarrow NH_3 + CO_2$	$r_2 = K_2 \cdot \exp\left(-\frac{E_2}{RT_s}\right) \cdot c_{HCNO} \cdot c_{H_2O}$
$NH_3 + * \rightarrow NH_3^*$	$r_3 = K_3 \cdot \exp\left(-\frac{E_3}{RT_s}\right) \cdot c_{NH_3} \cdot (1 - \theta_{NH_3})$
$NH_3^* \rightarrow NH_3 + *$	$r_4 = K_4 \cdot \exp\left(-\frac{E_4 \cdot (1 - \varepsilon \cdot \theta_{NH_3})}{RT_s}\right) \cdot \theta_{NH_3}$
$4NH_3^* + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$	$r_5 = K_5 \cdot \exp\left(-\frac{E_5}{RT_s}\right) \cdot c_{NO} \cdot \theta_{NH_3}^* \cdot \left(1 - \exp\left(-\frac{\theta_{NH_3}}{\theta_{NH_3}^*}\right)\right)$
$4NH_3^* + 2NO + 2NO_2 \rightarrow 4N_2 + 6H_2O$	$r_6 = K_6 \cdot \exp\left(-\frac{E_6}{RT_s}\right) \cdot c_{NO} \cdot c_{NO_2} \cdot \theta_{NH_3}^* \cdot \left(1 - \exp\left(-\frac{\theta_{NH_3}}{\theta_{NH_3}^*}\right)\right)$
$8NH_3^* + 6NO_2 \rightarrow 7N_2 + 12H_2O$	$r_7 = K_7 \cdot \exp\left(-\frac{E_7}{RT_s}\right) \cdot c_{NO_2} \cdot \theta_{NH_3}^* \cdot \left(1 - \exp\left(-\frac{\theta_{NH_3}}{\theta_{NH_3}^*}\right)\right)$
$4NH_3^* + 3O_2 \rightarrow 2N_2 + 6H_2O$	$r_8 = K_8 \cdot \exp\left(-\frac{E_8}{RT_s}\right) \cdot \theta_{NH_3}^*$
$NO + 0.5O_2 \leftrightarrow NO_2$	$r_9 = K_9 \cdot T_s^t \cdot \exp\left(-\frac{E_9}{RT_s}\right) \cdot \left(c_{NO}^2 \cdot c_{O_2} - \frac{c_{NO_2}^2}{K_{eq}}\right) \cdot (1 - \theta_{NH_3})$
$2NH_3^* + 2NO_2 \rightarrow N_2 + N_2O + 3H_2O$	$r_{10} = K_{10} \cdot \exp\left(-\frac{E_{10}}{RT_s}\right) \cdot c_{NO_2} \cdot \theta_{NH_3}$

3.3 Deposits Subsystem

In the wallfilm block, the fraction xstored which is stored in the wallfilm during the injection process at different temperature, mass flux and dosage. It worth noting that, in this case, the fraction is significantly increased with the increasing of deposits mass due to the enclosed area created by the deposits Figure 3, which is modeled by a piecewise function.

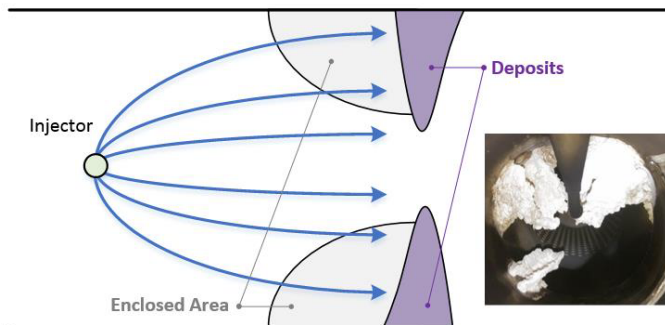


Figure 3. The enclosed area created by the deposits.

The mass and temperature of wallfilm can be calculated by equation (3) and (4), respectively.

$$\frac{\partial m_i}{\partial t} = x_{stored} \cdot \dot{m}_{inj,i} + \dot{m}_{evap,i} + \dot{m}_{de,i} \tag{3}$$

$$\rho_f \cdot V_f \cdot \frac{\partial (c_{p,f} \cdot T_f)}{\partial t} = \dot{m}_m \cdot c_{p,f} \cdot (T_{inj} - T_f) + A_f \cdot k_{fb} \cdot (T_s - T_f) + A_f \cdot k_{fg} \cdot (T_g - T_f) \tag{4}$$

Where m_{inj} is mass of the injected urea, m_{evap} is mass of evaporated water, m_{de} is urea mass which involved in the themolysis reaction, ρ_f is wallfilm density, $c_{p,f}$ is wallfilm specific heat, V_f is wallfilm volume, T is temperature, A_f is wallfilm area, k is heat transfer coefficient. The wallfilm exchanges heat with the gas phase and with the solid wall are calculated by equation (5) and (6), respectively.

$$k_{fg} = 0.0234 \cdot Pr \cdot Re \cdot \frac{\lambda_g}{d_{hyd}} \cdot A_f \tag{5}$$

$$k_{fs} = \frac{2}{\frac{d_f}{\lambda_{film}} + \frac{d_s}{\lambda_{solid}}} \cdot A_f \tag{6}$$

Where λ is thermal conductivity, d_{hyd} is pipe diameter, d_f and d_s are thickness of the wallfilm and pipe wall respectively.

Kontin showed that the impact of oversaturation in the urea water solutions leading to urea precipitation can be significant at low temperatures [5]. As a consequence, urea can be present in different forms (solid, dissolved, molten) depending on the operating conditions. Urea stat to decompose before melting, so that the existence of the molten phase is restricted to a quite narrow temperature range [6-7]. Therefore, the reactions are supposed to take place in solid phase and the mechanism presented by Ebrahimian [8] is used in this paper.

4 Model-based Optimization for Urea Dosing Strategy

4.1 Urea Dosing Strategy

The 1D Kinetic model can be applied to optimize the urea dosing strategy. This paper takes the strategy shown in the Figure 4 as an example to illustrates the optimization process under the objective of minimizing system-out NO_x , NH_3 slip and deposits.

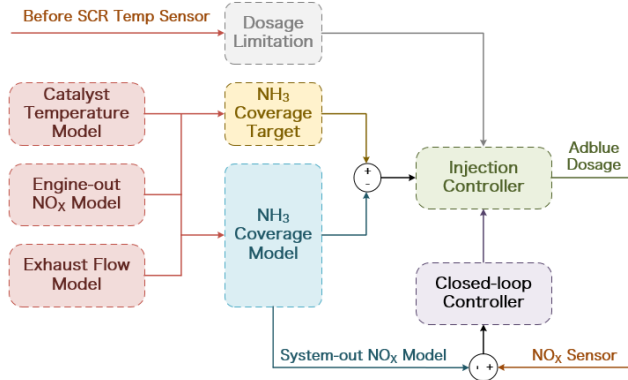


Figure 4. Urea Dosing Strategy.

As shown in Figure 4, the core of the open-loop part is an embedded chemical model which accounting for the main parameters that influence NO_x conversion and resulting NH_3 coverage. The amount of ammonia added to the SCR catalyst at every time instance is dictated by an optimized look-up table (Coverage Table), which relates average catalyst temperatures to optimal target average ammonia surface coverage. Moreover, the urea dosage at different temperature is limited by an optimized look-up table (limitation Table), which relates inlet gas temperature to optimal dosage limitation. The urea dosage rate is calculated by the equation (7)

$$V_{Adblue,open} = \begin{cases} (\theta_{desired} - \theta_{actual}) \cdot \sigma \cdot A_{trans} \cdot V_{cat} \cdot 0.5 \cdot 60 / 0.325 / 1.085 / 0.2 \cdot 3600 & < limit \\ limitation & > limit \end{cases} \tag{7}$$

Where V_{Adblue} is urea dosing rate (ml/h), σ is site density, A_{trans} is geometrical reaction surface.

In the closed-loop part, a two-stage integral prediction method (TIP method) is used to provide robustness of the system in the real world. Research shows that the NH₃ slip mainly occurs under the transient conditions with an immediate increase of exhaust temperature or a sudden reduction of engine load [9]. Therefore, a pre-integrator in the closed-loop controller is used in the transient conditions and a main integrator is used in the steady conditions. Then, if there is a significantly increase of temperature, or the torque keeps reducing in 1 sec or the engine gets into motored condition, the data in the pre-integrator would be removed and the closed-loop correction factor is calculated only with the data in the main integrator. However, the data in pre-integrator and in main integrator would both be used. What's more, in order to minimize the over-shooting risk, a moving average numeric filter is used in the calculation. The correction factor and the final urea dosage rate is calculated by equation (8) and (9).

$$CF_{closed} = \frac{1}{N} \cdot \sum_{i=0}^{N-1} \left(\frac{InNO_x - ObNO_x}{InNO_x - RfNO_x} \right) \tag{8}$$

$$V_{Adblue,final} = V_{Adblue,open} \cdot CF_{closed} \tag{9}$$

Where InNO_x, ObNO_x and RfNO_x is the integral of the engine-out NO_x mass flux, observed NO_x mass flux (NO_x sensor) and referenced NO_x mass flux (System-out NO_x model). N is filter order (N=3). In order to prevent the failure of closed-loop control, the correction factor CF_{closed} would be reset to 1 if the CF_{closed} and the observed NO_x mass flux are continuously increased at the same time.

4.2 Model-based Optimization

In this work, the optimization of urea dosing strategy was based on ETC test. The baseline engine-out NO_x of ETC test is 11 g/kWh and system-out NO_x target is 2 g/kWh due to NO_x reduction capability of catalyst. Therefore, beside meet NO_x emission target, also need to follow below constraints:

$$\max[NH_{3,slip}] \leq 25 \text{ ppm} \tag{10}$$

$$Mass_{Deposits} \leq 1\text{g} \tag{11}$$

Where NH₃ slip is the mole fraction of system-out NH₃, Mass_{Deposits} is the mass of deposits.

The optimization of the coverage table and limitation table is completed using a trust-region algorithm for a constrained, non-linear optimization problem. The values for the two tables before and after the optimization are shown in the Figure 5.

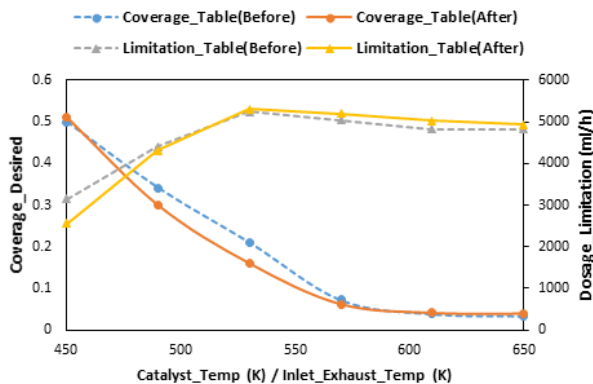


Figure 5. Coverage Table and Limitation Table.

As shown in Figure 6 and Figure 7, the system out NO_x, NH₃ slip and deposits mass of the ETC test are all satisfy the target after the optimization. Deposits mass reduced from 1.196g to 0.696g and the reduction ratio is 41.8%.

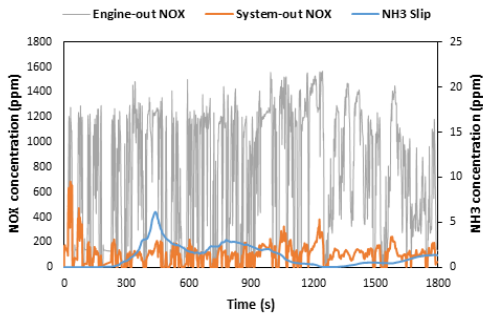


Figure 6. System-out NO_x and NH₃ slip of ETC

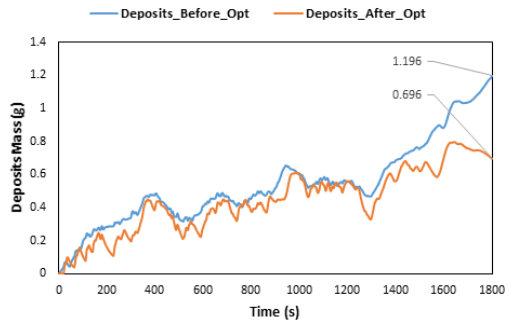


Figure 7. Deposits mass before and after the optimization.

5 Conclusion

This paper gives a comprehensive analysis of the 1D Kinetic model for SCR deposits. From the results, the following conclusions can be drawn:

1. The model can predict the SCR reaction and deposit formation process at the same time, the output contains the NO_x specific emission, NH₃ slip and deposits mass.
2. The model can predict deposit component including urea, biuret, CYA, ammelide and has good agreement with the experiment data.
3. A 1D Kinetic model is presented which can be applied to optimize the urea dosing strategy. The deposits mass of ETC test reduced by 41.8% after the optimization.

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