1-D mathematical modeling of a diesel oxidation catalyst for transient hot start drive cycle

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Abstract. The need to obey with increasingly stringent emission regulations has amplified the importance of after treatment devices, and therefore, reliable tools need to be developed for the evolution of better aftertreatment devices. Even though the upcoming regulations paved the way for improved combustion engines, their high carbon monoxide and hydrocarbon emissions increased the load on catalytic converters. Numerical modeling is one such tool which is extremely useful in providing the basic information which helps in designing the reactor, understanding its operation, and predicting the performance. In this context, the utmost aim of the numerical modeling is to simulate the driving cycle where inlet conditions to the catalytic converter vary with respect to time. Such a simulation must include the calculations of transient temperature-field of the monolith substrate and converter-out mass emissions. In this paper, a one-dimensional mathematical modeling of an oxidation catalyst has been implemented to simulate a hot start New European Drive Cycle (NEDC). The transient engine data was taken from the literature, and the measured instantaneous traces at the outlet of the catalyst were compared with the model predictions. This model has been developed to investigate the CO conversion performance of the catalyst. The comparison between model predictions and experiments has shown a satisfactory agreement in terms of both substrate temperature and CO emission at the catalyst outlet, confirming the effectiveness of the methodology applied. The reliability of the 1-D model was also proved with the probability density function of the conversion efficiency.

1. Introduction

The ever-growing population has led to a drastic increase in the use of automobiles around the world for satisfying the needs of our daily life. However, this has caused a growth in environmental pollution as a number of toxic pollutants are emitted to the atmosphere. Pollutants from vehicles contribute to various types of air pollution, can cause greenhouse effect, and are believed to cause respiratory problems in human beings. Emission norms are required to control these pollutants, and over the past decade, these norms are becoming increasingly stringent due to growing environmental pollution. For example, in India, the government has forced to change to BS-VI norms by 2020. Upcoming regulations on CO₂ forced to improve the combustion efficiency in engines paving the way for modern techniques like dual-fuel and low-temperature combustion (LTC) engines. These engines are capable to reduce nitrogen oxides and particulate matter pollutants at the same time, but at low and medium engine operating loads, their CO and HC emissions, however, are very high [1]. Another major worry is the cold start emissions from diesel engines, as this itself donates a major portion of total CO and HC emissions emitted [2]. Therefore, an exhaust aftertreatment system is necessary to satisfy future emission regulations. The exhaust aftertreatment system of a diesel engine typically consists of diesel oxidation catalyst (DOC), diesel particulate filter and lean NOₓ trap or selective catalytic reduction. The traditional approach to reduce
carbon monoxide and hydrocarbon emissions is by using the DOC. But the improvements in the combustion efficiency has led to lower exhaust gas temperatures from engines [1] and cold start period along with this makes it even more difficult as DOC functionality primarily depends on temperature. The emergence of reliable numerical models has played a crucial role in the development of effective aftertreatment systems. Relying only on the basis of experimental iterations for desired catalyst performance is very expensive and time-consuming, hence numerical modeling is critical.

Numerical modeling studies of catalytic converter have been developed in the past, and those include 1-D mathematical modeling and 2-D or 3-D computational fluid dynamics codes. Also modeling full-scale catalytic converter using conventional CFD techniques is computationally very expensive [3]. Instead, a 1-D modeling with global kinetics is a feasible option to describe the events inside the catalytic converter, and thus, consuming low computational time, and providing useful information which helps in designing the converter. One of the earliest kinetic models was derived by Voltz et al. [4] which can replicate the results even with a real engine exhaust. Kinetic data for CO and \( \text{C}_3\text{H}_6 \) was established, and it was found that oxidation rate increases when \( \text{O}_2 \) concentration increases, and oxidation rate decreases with the increase of CO and \( \text{C}_3\text{H}_6 \) concentrations. Many such studies of catalytic converter have been based on the kinetic model of [4], and in most of them, a 1-D modeling with global reaction rates is considered. The transient study of a monolithic converter was conducted by [5] where the response of conversion to step change in feedstream temperature was tested utilizing the kinetic model of [4] with slight modifications. Mohapatra and Mittal [6] when they developed a 1-D mathematical model to study the CO conversion performance of an oxidation catalyst used a simplified kinetics model and was validated for two different case setups. However, the ultimate goal considered in modeling is the simulation of drive cycles i.e. varying inlet conditions with respect to time. Oh et al. [7] conducted an initial work where the authors developed a 1-D model for cold start portion of the transient FTP cycle and validated the predictions of the model with emissions data available at the outlet of the converter. A 3-D simulation of a catalytic converter was also done by Braun et al. [8], where they used the CFD code DETCHEM to study the transient behavior and the chemical reactions were modeled by a detailed reaction mechanism.

The present work is aimed to develop an oxidation catalyst model which focusses on emissions from new-generation diesel engines like dual-fuel and LTC engines whose emissions are excess at low operating loads. Even though each component of this large exhaust system has an impact on another, our effort was solely to understand the performance of DOC. We emphasized on first developing a reliable and accurate 1-D model of the oxidation catalyst with respect to transient engine data and later to use this model to inspect the outcome of electrical heating on the conversion performance under transient conditions. A simplified kinetic model was presented and was tested for a hot start NEDC drive cycle. The NEDC was selected for our work, as the urban part of this cycle is identified by low engine load along with low gas temperature, and it is difficult to meet emission standards at these conditions. The transient engine data was taken from Robinson et al. [9], and the experimentally determined values of exhaust mass flow rate, inlet temperature, and species concentrations were provided as inputs to the model. The 1-D model predictions were compared with instantaneous traces measured at the catalyst outlet.

### 2. 1-D mathematical modeling of the DOC

The 1-D mathematical model was built on assumptions like incompressible and laminar flow in channels, adiabatic modeling of the converter, and neglect of radial heat conduction. Simplified models are able to manage long transient simulations rather than detailed models and are effective once tuned properly [10]. The whole converter modeling is classified into bulk gas and surface modeling by using species and energy equations and as the pressure is almost constant throughout, the momentum equation was neglected. Species conservation equation is solved to get concentrations of species, while the energy equation solves for the temperature both at the surface and in the bulk gas. Unlike in detailed reaction rate model, global reaction rate model neglects the effects of surface adsorption-desorption and pore diffusion through the washcoat, as these effects are fused into the rate expressions in the kinetic model [11].
The energy and material equations for the gas phase are:

\[ GC_{p_g} \frac{\partial T_g}{\partial x} + a_s h (T_g - T_s) = 0 \]  \( (1) \)

\[ \varepsilon \frac{\partial \bar{c}_{g,j}}{\partial t} = -v \varepsilon \frac{\partial \bar{c}_{g,j}}{\partial x} - k_{m,j} a_s (\bar{c}_{g,j} - \bar{c}_{s,j}) \]  \( (2) \)

The energy and material equations for the solid phase are:

\[ (1 - \varepsilon) \rho_s C_s \frac{\partial T_s}{\partial t} = (1 - \varepsilon) k_s \frac{\partial T_s}{\partial x} + a_s h (T_g - T_s) + a(x) H_f R_j \]  \( (3) \)

\[ \frac{d \bar{c}_{s,j}}{dt} = \frac{k_{m,j} a_s}{1 - \varepsilon} (\bar{c}_{g,j} - \bar{c}_{s,j}) - \frac{a(x) R(j)}{1 - \varepsilon} \]  \( (4) \)

The heat and mass transfer coefficients \( h \) and \( k_{m,j} \), respectively, in the above equations are defined as,

\[ h = \frac{Nu_{so} k_g}{2 R_h} \]  \( (5) \)

\[ k_{m,j} = \frac{Sh_{so} D_{j,N2}}{2 R_h} \]  \( (6) \)

Slattery-Bird formula is used to estimate \( D_{j,N2} \), which is the diffusivity of species \( j \) [12],

\[ D_{j,N2} = \left( \frac{p_{e,N2}}{p_{c,j} p_{e,N2}} \right)^{\frac{1}{3}} \left( T_{c,j} T_{e,N2} \right)^{\frac{5}{12}} \left( \frac{1}{M_j} + \frac{1}{M_{N2,j}} \right)^{\frac{1}{3}} \times 2.745 \times 10^{-4} \times x \left( \frac{T_s}{T_{c,j} T_{e,N2}} \right)^{1.823} \]  \( (7) \)

Finite difference method (FDM) is used to solve the above equations. The energy equation of the solid phase, equation (3), is discretized based on the forward-time central-space (FTCS) method. In order to make sure the consistency and accuracy of the solution, along with fast computational speed, a first-order difference method has been used to discretize the energy and species equations of the bulk gas (equations (1) and (2), respectively). The discretization of species equation of the solid phase, equation (4), is done implicitly such that the stiffness due to the kinetic expression of the reaction term is avoided.

In order to solve the 1-D catalyst model, several boundary and initial conditions are needed and are as follows,

\[ T_S(x,0) = T_{S0}(x) \]  \( (8) \)

\[ T_g(0,t) = T_{g0} \]  \( (9) \)

\[ \bar{c}_{g,j}(0,t) = \bar{c}_{g,j0} \]  \( (10) \)

\[ \bar{c}_{s,j}(0,t) = \bar{c}_{s,j0} \]  \( (11) \)

\[ \left. \frac{\partial T_s}{\partial x} \right|_{(0,t)} = \left. \frac{\partial T_s}{\partial x} \right|_{(L,t)} = 0 \]  \( (12) \)

The global kinetic model accounted for CO and HC oxidation reactions. Initially, a simplified kinetic model for CO oxidation was developed [6]. This kinetic model was modified in the present work to
include HC oxidation and tested by fitting the model with the experimental data. Even though THCs are constituted by both light short and heavy long chain HCs, we have assumed C$_3$H$_6$ to be the representative of the hydrocarbons oxidized in this DOC model.

\[
CO + \frac{1}{2} O_2 \rightarrow CO_2 \tag{13}
\]

\[
C_5H_{10} + \frac{9}{2} O_2 \rightarrow 3CO_2 + 3H_2O \tag{14}
\]

\[
R_{CO} = -\frac{k_{CO}C_{CO}C_{O2}}{I} \tag{15}
\]

\[
R_{C_3H_6} = -\frac{k_{C_3H_6}C_{C_3H_6}C_{O2}}{I} \tag{16}
\]

\[
I = T_s \left(1 + K_1C_{CO} + K_2C_{C_3H_6}\right)^2 \left(1 + K_3C_{CO}^2C_{C_3H_6}^2\right) \tag{17}
\]

\[
K_1 = 65.5 \exp \left(\frac{961}{T_s}\right) \tag{18}
\]

\[
K_2 = 2080 \exp \left(\frac{361}{T_s}\right) \tag{19}
\]

\[
K_3 = 3.98 \exp \left(\frac{11611}{T_s}\right) \tag{20}
\]

\[
k_i = A_i \exp \left(-\frac{E_{a,i}}{R_u T_s}\right), \text{where } i = CO \& C_3H_6 \tag{21}
\]

\[
R_{O_2} = 0.5R_{CO} + 4.5R_{C_3H_6} \tag{22}
\]

\[
R_{CO_2} = -R_{CO} - 3R_{C_3H_6} \tag{23}
\]

\[
R_{H_2O} = -3R_{C_3H_6} \tag{24}
\]

3. Results and discussions

The transient analysis of the oxidation catalyst conducted using Matlab is discussed in this section and its performance has been analysed with the experimental results from [9]. The experiments were carried out on a four-cylinder 2.0-l CI engine and were coupled to a transient dynamometer. The data was recorded upstream and downstream of Pt on alumina DOC. Specifications and properties of the DOC from [9] are listed in table 1. In the first part of this section, the 1-D model developed by [6] was modified to include C$_3$H$_6$ oxidation along with high CO concentration case and was validated with the experimental data, so that the basic DOC model is complete. The effect of C$_3$H$_6$ inhibition on CO oxidation was also studied. Later, this DOC model was used to study the transient case and substrate temperature, and instantaneous emission and cumulative mass of CO at the DOC outlet provided in [9] was used for validation.
3.1. Completion of the 1-D model of DOC

The mathematical model used in [6] to predict the performance of catalyst was modified by adding \( \text{C}_3\text{H}_6 \) oxidation, and for this, the case from Missy et al. [13] was used for the validation. Missy et al. [13] used a ceramic catalytic converter having 400 CPSI, length of 0.1524 m, wall thickness of 6.5 mil, and substrate diameter of 0.1016 m. The mass flow rate of exhaust is 95.2 kg/h, and the exhaust temperature at the inlet was increased at a ramp of 14.5 K/min from 380 K to 560 K. Figures 1 and 2 compare the conversion performance of CO and \( \text{C}_3\text{H}_6 \). The CO conversion in the presence of \( \text{C}_3\text{H}_6 \) (figure 1) proves that there was a significant inhibition of \( \text{C}_3\text{H}_6 \) on CO conversion at high temperatures when compared with the result from [6]. The authors [6] also stated that this effect might be due to the presence of \( \text{C}_3\text{H}_6 \) which was neglected in their model. \( \text{C}_3\text{H}_6 \) conversion in figure 2 also compares well with the data. Hence, upon addition of \( \text{C}_3\text{H}_6 \), a basic DOC model was completed.

| Table 1. Specifications of the DOC. |
|-----------------------------------|
| Substrate material | Cordierite |
| Cell density | 400 (CPSI) |
| Substrate diameter | 105.7 (mm) |
| Density | 1430 (kgm\(^{-3}\)) |
| Length | 114.3 (mm) |
| Cell width | 1.1 (mm) |

![Figure 1. Comparison of CO conversion.](image1)

![Figure 2. Comparison of \( \text{C}_3\text{H}_6 \) conversion.](image2)

3.2. Hot start NEDC

The DOC model developed has been used for the analysis of transient drive cycles. Note that the values of lambda unlike species concentrations of CO, THC and NO in the exhaust for the NEDC transient...
cycles used in [9] were not available. Lambda is a critical parameter which provides the concentration of oxygen (O$_2$) in the exhaust, and this was necessary from the modeling perspective. Therefore, to predict the lambda values an artificial neural network (ANN) model was developed. The model made use of steady state measurements performed across a range of conditions in the NEDC provided in [9]. These steady state values of O$_2$ helped in determining the lambda values by using 90% of this data randomly to train the ANN model using Levenberg-Marquardt algorithm whose objective is to minimize the mean square error. The remaining 10% of the data was used for validation. The combination of number of neurons in the hidden layer and transfer function of the hidden and output layers were optimized to maximize the performance of the model. The ANN model using hyperbolic tangent sigmoid function in the hidden layer with 8 neurons and hyperbolic tangent sigmoid function in the output layer showed the best performance. The model was able to predict the lambda values accurately (mean square error = 1.34 x 10$^{-04}$, R=0.9983).

The modeling results obtained at the converter outlet location over a hot start NEDC test are compared with the experimental data [9]. Figure 3 reveals the solid phase temperature of the monolith at a location of 105 mm from the inlet. From figure 3 it was understood that the modeling result of wall temperature is in good accordance with the experimental results for the entire duration of 1200s. The 1-D model results show that the substrate temperature, which was warm at the beginning, decreases slightly as the wall temperature has a similar trend to the inlet gas temperature. In the UDC part, even though some points of the cycle have a difference in temperature of about 10K, the overall agreement seems to be really good. For the remaining period of the EUDC, the 1-D model results differ less than 1% from the experimental data. Figures 4 and 5 focus the attention on CO emission, and it shows that the agreement between simulated and experimental results of instantaneous CO emission to be very close and this is supported by the cumulative emission comparison over the entire cycle duration. In the UDC part of the cycle, as the catalyst temperature is already above the light-off, the 1-D model predicted very high conversion, and as the inlet temperature was decreased there was a drop-in conversion. Even though the model was able to capture the substrate temperature to a fair extent, assuming C$_3$H$_6$ as a representative of THCs might have caused those deviations from accurate conversion prediction at some points as observed in figure 4. But as the EUDC part of the cycle comes, complete conversion of CO could be achieved. Also, in order to test the reliability of the 1-D mathematical model developed for transient cycles, probability distribution functions (PDFs) of CO conversion efficiency for hot NEDC was calculated, and shown in figure 6. The range of conversion efficiency chosen is between 85% - 100%, as this region is of more interest from the point of view of conversion. From figure 6, it is understood that the conversion efficiency with highest probability was around the mean value obtained from experiments, thus proving the reliability and accuracy of the model.
Figure 3. Comparison of wall temperature profile in a hot NEDC.

Figure 4. Comparison of simulated and measured instantaneous CO emission in a hot NEDC.
Figure 5. Comparison of simulated and measured cumulative CO emission in a hot NEDC.

Figure 6. Calculated PDF for CO conversion efficiency of 1-D model for hot NEDC (mean value from experiment is represented by vertical line).
4. Conclusion
In this paper, we presented the development of a 1-D mathematical model of a DOC for new-generation diesel engines which uses technology like dual-fuel and LTC. The simulation of the monolith converter has helped in understanding both physical and chemical phenomena in a converter through CFD and kinetic modeling. The process started from setting up and completing a basic DOC model, and later evolving this model for the transient simulation of hot start NEDC. The kinetics developed for modeling the DOC in earlier studies have been transferred to model the transient cases. The 1-D model developed is then used for validation with respect to the transient emissions data measured in NEDC. A satisfactory agreement between 1-D model predictions and emissions data for both substrate temperature and CO conversion at the outlet of DOC, affirmed the efficacy of the methodology applied. Also, the reliability and accuracy of the model developed has been proved through probability study conducted. The future work includes testing the model under cold start NEDC and to analyse the effect of electrical heater on converter under cold start. This would be effective in cases when the exhaust temperature of engines is reducing due to improvements in combustion to meet upcoming regulations. Considering this as a general modeling approach, this tool could also now be extended to develop other aftertreatment systems for diesel engines in the future.

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Nomenclature

- \( a_s \): geometric surface area per unit reactor volume, \( m^2/m^3 \)
- \( a(x) \): catalytic surface area per unit reactor volume, \( m^2/m^3 \)
- \( \bar{c}_{i,1} \): concentration of species \( j \) in bulk phase, \( mol/m^3 \)
- \( C_{pq} \): specific heat capacity of gas at constant pressure, \( J/kg \cdot K \)
- \( D_{ij,2} \): diffusion coefficient of species \( j \) diffusing in the mixture, \( cm^2/s \)
- \( G \): rate of mass flow of gas, \( kg/m^2 \cdot s \)
- \( h \): heat transfer coefficient, \( J/m^2 \cdot s \cdot K \)
- \( H_j \): heat of reaction of species \( j \), \( J/mol \)
- \( I \): resistance term for the inhibition effect
- \( k_{m,i} \): mass transfer coefficient, \( m/s \)
- \( k_i \): rate constant for species reaction, \( mol/m^2 \cdot s \)
- \( K_i \): adsorption constant
- \( P_{c,i} \): critical pressure of species \( j \), atm
- \( R(j) \): specific reaction rate of species \( j \), \( mol/m^2 \cdot s \)

Greek Letters

- \( \varepsilon \): void fraction of the monolith
- \( \rho_s \): solid density, \( kg/m^3 \)

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