

Simulation of a Diesel Oxidation Catalyst Used in a NO_x Storage and Reduction system for Heavy Duty Trucks

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Abstract: This work concerns the performance of an oxidation catalyst used in a NO_x storage and reduction system. The oxidation of NO is the main objective of this study. The presence of CO and hydrocarbons (modeled as propene) has been taken into account though. A combined model based on reactions described by Crocoll and Tanaka has been used. Experimental data has been determined on a monolithic oxidation catalyst mounted after a heavy duty diesel engine in a rig. The oxidation of NO to NO₂ can be simulated using fitted parameters but only in a narrow temperature range of between 220 and 260 °C. The conversion of hydrocarbons is predicted fairly well but the fit for the combustion of CO needs improvement. The temperature increase determined experimentally cannot be simulated. This leads us to believe that there must be an extra highly exothermic reaction taking place. This could be the combustion of the volatile part of diesel soot.

Keywords: Oxidation of NO, CO and HC, Diesel oxidation catalyst, Real diesel exhausts, Kinetic parameter fitting and Simulation.

1. Introduction

The large amount of diesel engines used today and the high content of NO_x, CO and Hydrocarbons (HC) in their exhausts make necessary the development of new catalyst technologies to reduce these emissions. In this work, a Diesel Oxidation Catalyst used as a part of a NO_x Storage and Reduction system is modeled and simulated. The aim was to find a model which should explain and predict its behavior making the improvement and optimization of the mentioned system easier and faster.

2. Experimental

Data for the simulation were obtained by measuring concentrations before and after the oxidation catalyst in an engine rig. The engine

was a Scania DC 1101 (11 l, Euro II calibration). An 8.4 l 400 CPSI monolithic oxidation catalyst (Pt on γ -Al₂O₃) was used to preoxidize the NO under lean conditions.

The catalyst had a diameter of 26.5 cm and a length of 15.2 cm. The details of the experimental setup and procedure are given in literature [1].

A series of experiments were performed at various combinations of load, determined by an electric brake, and rotational speed. This led to experimental conditions covering different temperatures, compositions and flows.

The aim was to find a model which would cover all the experiments performed in real diesel exhaust gases.

3. Catalyst model

The catalyst used is built up by individual channels with a geometry similar to the one shown in Figure 1.

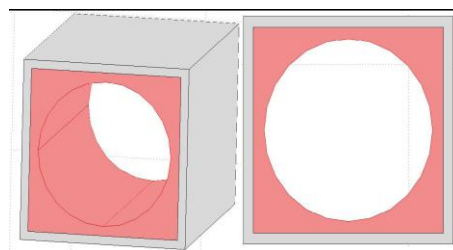


Figure 1. Catalyst geometry of an individual channel of the catalyst used in the experiments. Figure not to scale.

In this work a simplified geometrical model was used. The individual catalyst channel was supposed to be perfectly cylindrical and not of a square shape. This simplification allowed us to use a 2D model with axial symmetry for the simulation, thus saving a lot of memory and computational time compared with a 3D model. The geometry of the model used in this work is shown in Figure 2.

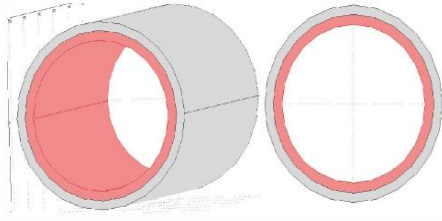


Figure 2. Geometry of the individual channel used in the simulation. Internal radius = 5.1×10^{-4} m, catalyst thickness = 6.5×10^{-5} m, wall thickness = 6×10^{-5} m, length = 0.152 m. Figure not to scale.

4. Kinetic model

Adsorption	
$O_2(g) + 2* \Rightarrow 2O^*$	$r_1 = A_1 \exp(-E_1/RT) * C_{O_2(g)} \theta^{2*}$
$NO(g) + * \Rightarrow NO^*$	$r_3 = A_3 \exp(-E_3/RT) * C_{NO(g)} \theta^*$
$NO_2(g) + * \Rightarrow NO_2^*$	$r_5 = A_5 \exp(-E_5/RT) * C_{NO_2(g)} \theta^*$
$CO(g) + * \Rightarrow CO^*$	$r_7 = A_7 \exp(-E_7/RT) * C_{CO(g)} \theta^*$
$CO_2(g) + * \Rightarrow CO_2^*$	$r_9 = A_9 \exp(-E_9/RT) * C_{CO_2(g)} \theta^*$
Desorption	
$2O^* = O_2(g) + 2*$	$r_2 = A_2 \exp(-(E_2(1 - \alpha_2 \theta_O)/RT)) * \theta_O^2$
$NO^* \Rightarrow NO(g) + *$	$r_4 = A_4 \exp(-(E_4 - \alpha_4 \theta_O)/RT) * \theta_{NO}$
$NO_2^* \Rightarrow NO_2(g) + *$	$r_6 = A_6 \exp(-(E_6(1 - \alpha_6 \theta_O)/RT)) * \theta_{NO_2}$
$CO^* \Rightarrow CO(g) + *$	$r_8 = A_8 \exp(-(E_8 - \alpha_8 \theta_{CO})/RT) * \theta_{CO}$
$CO_2^* \Rightarrow CO_2(g) + *$	$r_{10} = A_{10} \exp(-E_{10}/RT) * \theta_{CO_2}$
Surface reactions	
$NO(g) + O^* \Rightarrow NO_2^*$	$r_{13} = A_{13} \exp(-(E_{13} - \alpha_{13} \theta_O)/RT) * C_{NO(g)} * \theta_O$
$NO_2^* \Rightarrow NO(g) + O^*$	$r_{14} = A_{14} \exp(-E_{14}/RT) * \theta_{NO_2}$
$CO^* + O^* \Rightarrow CO_2^* + *$	$r_{15} = A_{15} \exp(-(E_{15} - \alpha_{15} \theta_{CO})/RT) * \theta_{CO} * \theta_O$
$CO_2^* + * \Rightarrow CO^* + O^*$	$r_{16} = A_{16} \exp(-(E_{16} + \alpha_{16} \theta_O)/RT) * \theta_{CO_2} * \theta^*$
C_3H_6 reaction	
$C_3H_6(g) + 9/2O_2(g) \Rightarrow 3CO_2(g) + 3H_2O(g)$	$r_{C_3H_6} = k_{C_3H_6} * p_{C_3H_6} * P_{O_2} / (1 + K_{C_3H_6} * p_{C_3H_6})^2$

Rate constants were assumed to follow the Arrhenius equation:

$$k_i = A_i \exp(-E_i/RT)$$

5. Use of COMSOL Multiphysics

5.1 Application model

COMSOL Multiphysics version 3.4 is the software used in this work. This program takes diffusion and flow characteristics into consideration along with kinetics of chemical reactions. The behavior of a single channel was simulated. In this work two different application modes were used, "Convection and diffusion" for mass transport and "Convection and conduction" for energy transport. The "Convection and conduction" application mode is used in all the subdomains with its respective parameters in each one. Two "Convection and diffusion" application modes are used, one for the surface species (in the catalyst layer) and one for the gaseous species (in the channel and the catalyst layer). Effective diffusivities are used in the catalyst layer. The velocity field in the open channel is given by a formula representing a laminar flow (Table 1).

5.2 Subdomain settings

The subdomain settings for each application mode and subdomain are presented below. The "Convection and conduction" mode settings are presented in Table 1 and the "Convection and diffusion" mode settings are presented in Table 2. In Table 3 the diffusivities are presented.

Table 1. Values of physical data and velocity profile used in the model.

Parameter	Channel	Catalyst layer	Cordierite wall
k (W/m,K)	0.0434	0.09	0.42
ρ (kg/m ³)	0.54	2000	1150
C_p (J/kg,K)	1050	500	1050
Q (W/m ³)	0	$\sum(H_j * r_j)$	0
r-velocity (m/s)	0	0	0
z-velocity (m/s)	$u = 2 * u_{in} * (1 - (r/r_{ext})^2)$		0

Table 2. Diffusivities, rates and initial conditions in the channel and in the catalyst layer.

Parameter	Channel	Catalyst layer
D (isotropic)	D _i _free (Table 3)	D _i _porous (Table 3)
R (mol/m ³ _{cat,s})	0	$\sum(v_{i,j} * r_j)$
Initial conc.	c _i _in	c _i _in

Table 3. Diffusivities.

Reference diffusion constants (m ² /s)		
Specie	Channel	Catalyst layer
NO	6.95e-5	2.69e-7
NO ₂	5.36e-5	2.75e-7
CO	5.38e-5	2.75e-7
CO ₂	5.41e-5	2.22e-7
O ₂	6.94e-5	2.61e-7
H ₂ O	8.15e-5	3.46e-7
C ₃ H ₆	4.38e-5	2.24e-7
N ₂	6.51e-5	2.77e-7
Ar	6.56e-5	2.34e-7

$$D = D_{reference} * \left(\frac{T(K)}{623}\right)^{1.75}$$

All chemical reactions produce heat. Heats of adsorption are exothermic. Heats of desorption have the same numeric values but are endothermic (Table 4).

Table 4. Heats of reactions (kJ/mol).

Heat of reaction	Value	Heat of reaction	Value
H_1	-136	H_2	136
H_3	-86	H_4	86
H_5	-111	H_6	111
H_7	-146	H_8	146
H_9	-27	H_10	27
H_13	-101	H_14	95
H_15	-65	H_16	97
H_C ₃ H ₆	-1926		

5.3 Solver settings

The main settings for the solver are listed below.

- Relative tolerance: 0.01
- Absolute tolerance: 0.001
- Analysis: Transient
- Solver: Time dependent

5.4 Mesh

The mesh used in the simulations is shown in Figure 3. The thickness of the catalyst layer was estimated from photographs of the catalyst. The mesh is fine enough in the gas channel and the wall, but a finer mesh in the washcoat should give a more precise profile inside the catalyst layer. Unfortunately it was impossible to use such a mesh due to memory problems.



Figure 3. Mesh used consisting of a total of 700 elements.

5.5 Boundary settings

Figure 4 and Table 5 show the numbering of the boundaries in the catalyst model and the type of boundary settings used in each boundary.

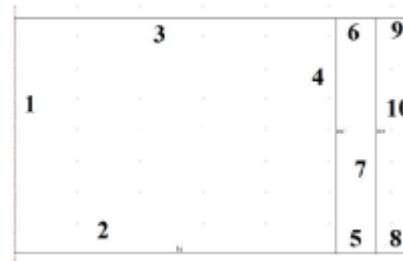


Figure 4. Numbering of the boundaries in the model.

Table 5. Boundary settings used in the simulations.

	Convection and diffusion		Convection and conduction
Boundary	Gas species	Surface species	
1	Axial symmetry		Axial symmetry
2	Convective flux		Convective flux
3	Concentration		Temperature
4	Internal boundary	Insulation/symmetry	Internal boundary
5	Convective flux	Insulation/symmetry	Convective flux
6	Insulation/symmetry	Insulation/symmetry	Temperature
7	Insulation/symmetry	Insulation/symmetry	Internal boundary
8			Thermal insulation
9			Thermal insulation
10			Thermal insulation

6. Results and discussion of fitting and simulation

Table 6. Fitted and literature values of Activation energies and pre-exponential factors in the kinetic model.

Pre-exp factors	Values		Activation energies (kJ/mol) and α values	Values	
	This work	Literature		This work	Literature
A_1	1.1e7	11	E_1	0	0
A_2	2e10	2e10	E_2	200	200
A_3	138	138	E_3	0	0
A_4	2e11	2e11	E_4	114	114
A_5	68	68	E_5	0	0
A_6	2e11	2e8	E_6	72	72
A_7	3.95e6	141	E_7	0	0
A_8	2e11	2e11	E_8	146	146
A_9	0.67	0.67	E_9	0	0
A_10	2e10	2e8	E_10	27	27
A_13	2.6e5	104	E_13	35	35
A_14	2e8	2e8	E_14	51	51
A_15	1.6e10	4e4	E_15	108	108
A_16	2e8	2e8	E_16	155	155
A_C ₃ H ₆	3.82e9	3.82e9	E_C ₃ H ₆	65	65

$$K_{C_3H_6} = 31853 \text{ atm}^{-1}$$

Table 7. Alfa values to show dependence of desorption energy on surface coverage for the kinetic model and poisoning effects of some components on reaction rates.

Alfa values	This work	Literature
α_2 (-)	0.1	0.1
α_4 (*)	10	10
α_6 (-)	0.075	0.075
α_8 (*)	33	33
α_{13} (*)	14	14
α_{15} (*)	33	33
α_{16} (*)	45	45

(*) $\alpha_4, \alpha_8, \alpha_{13}, \alpha_{15}, \alpha_{16}$ are in (kJ/mol),

The oxidation of the components NO, CO and HC (hydrocarbons, in this case C₃H₆) in the low temperature region (200 – 260 °C) could be modeled by a combination of the models of Crocoll et al. [2] and Tanaka et al. [3]. Most of the kinetic model is from Crocoll et al. [2] but the reaction of the propene has been taken from Tanaka et al. [3].

The fitting procedure was a manual one with the object of getting as good values for the NO₂ outlet molar fractions as possible. The following parameters were obtained after fitting of some of the parameters.

The results presented in Figures 5 and 6 below are from an experiment when the diesel engine is running at 1250 rpm with a load of 250 Nm. The inlet conditions to the oxidation catalyst were: 230 °C, 648 ppm NO, 56 ppm NO₂, 161 ppm HC, 101 ppm CO, 14.6 % O₂, 4.1 % CO₂, 7.4 % H₂O, 0.9 % Ar and balance N₂. The total mass flow was 532 kg/s.

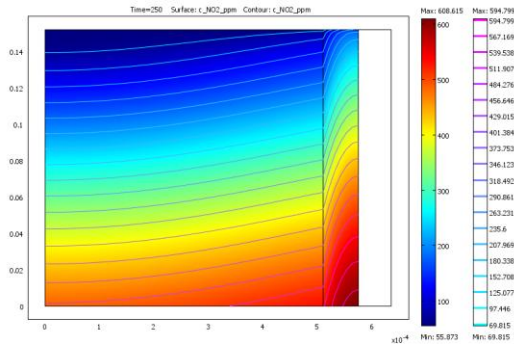


Figure 5. Simulated steady state values of the NO_2 molar fraction in the channel and the catalyst layer after 250 s.

It is clearly shown that the molar fraction of NO_2 is increasing rapidly in the catalyst layer and in the channel from inlet values at the top of the Figure to over 530 ppm at the exit in the channel. Even at this low temperature there seems to exist a considerable concentration gradient inside the catalyst layer. This fact is of course based on the thickness of the catalyst layer which could be in error.

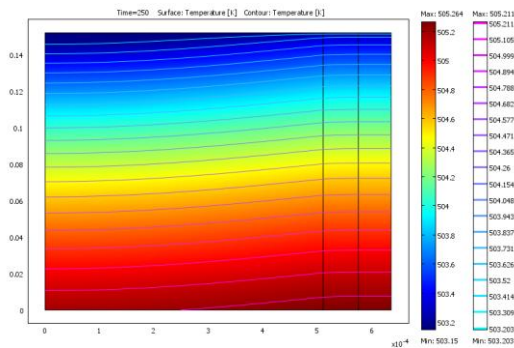


Figure 6. Simulated steady state values of the temperature in the channel and the catalyst layer after 250 s.

Figure 6 shows that the evolution of heat in the catalyst does not create any considerable temperature gradients in the catalyst or the wall. Some gradients are seen in the channel and they are caused by the variation of linear gas flow with channel radius at determined by the laminar velocity flow profile used.

The rest of the results are from a number of experiments with varying driving conditions for the engine. Concentration as well as temperature

values given below are integrated over the channel cross section to obtain a good comparison to the measured values.

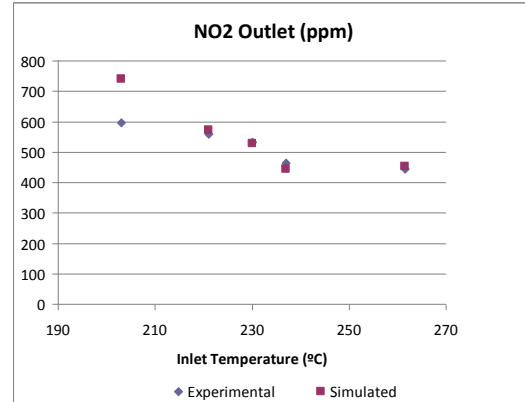


Figure 7. Simulated steady state values of the NO_2 outlet molar fractions in the channel after 250 s.

Overall it is possible to obtain a very good fit of experimental and simulated outlet molar fractions of NO_2 as shown in Figure 7. Using the fitted constants a much too high oxidation rate is predicted at temperatures higher than 260 °C.

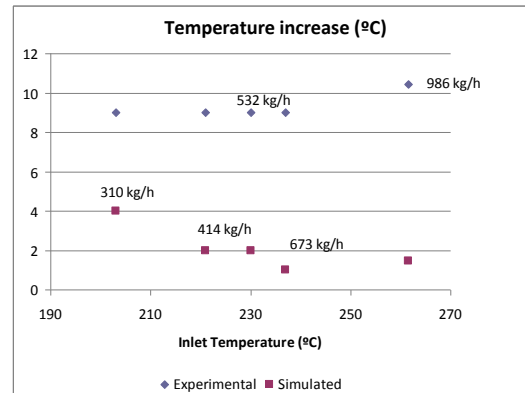


Figure 8. Simulated steady state values of the temperature increase over the catalyst in the channel after 250 s.

The temperature after the oxidation catalyst cannot be obtained with a value close to the experimental one. The temperature increase predicted is lower by a factor of 2 to 10 compared to the experimentally determined one. Thus there must be an extra reaction producing large amounts of heat. This could be the oxidation of the volatile fraction of soot. The discrepancy in

temperature is of major concern since it could change the values of kinetic parameters much.

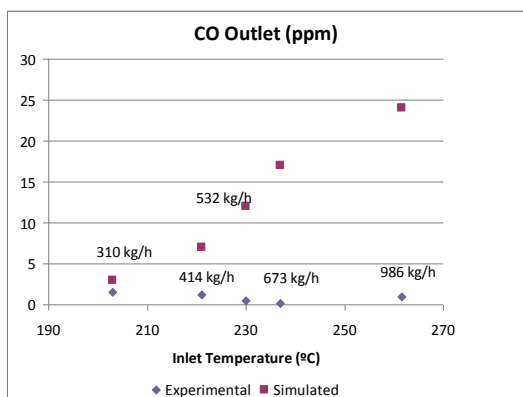


Figure 9. Simulated steady state values of the CO molar fraction in the channel after 250 s.

The prediction of the CO outlet molar fraction (Figure 9) from an inlet value of 101 ppm down to 5 to 25 ppm is somewhat underestimated. The prediction gets worse at higher loads. Thus a better fit to these values is needed.

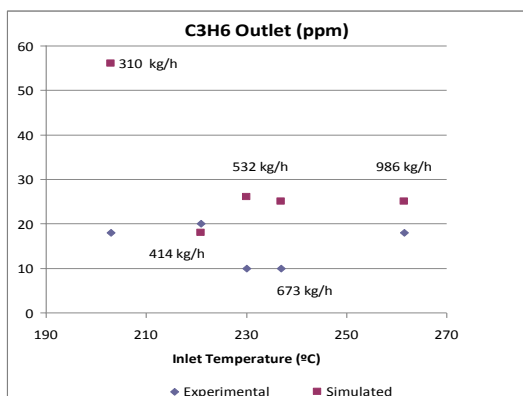


Figure 10. Simulated steady state values of the propene molar fraction in the channel after 250 s.

The prediction of the propene outlet molar fraction from an inlet value of 161 ppm down to around 20 ppm is not so much underestimated between 220 and 260 °C (Figure 10). The predicted conversion is around 84 % while the experimental one is around 91 %. No clear trend with load is observed in this case.

7. Conclusions

The behavior of the oxidation catalyst in the oxidation of NO to NO₂ could be modeled in a narrow temperature range of 220 to 260 °C. Using the constants presented a much too high oxidation rate is predicted at higher temperatures. The fitting of the parameters have been done manually and most probably a local minimum is reached when fitting the NO₂ molar fractions.

A build in function in COMSOL which would perform an automatic parameter estimation in problems like this is strongly warranted.

The temperature increase predicted is lower by a factor of 2 to 10 compared to the experimentally determined one. Thus there must be an extra reaction producing large amounts of heat. This could be the oxidation of the volatile fraction of soot.

Further studies are needed to get a better model fit to data in the whole temperature range. In this forthcoming work it is very important to get a better picture of the real size of the catalyst layer and its shape since diffusion resistance seems important.

Such work has now been started.

8. References

1. Papadakis, K., *Studies of a Heavy-Duty Diesel Aftertreatment System Based on the NO_x Storage and Reduction Technology*, Department of Chemical Engineering, Lund University, Institute of Technology, Lund (2005)
2. Crocoll, M., Kureti, S., and Weisweiler, W., Mean field modeling of NO oxidation over Pt/Al₂O₃ catalyst under oxygen-rich conditions, *Journal of Catalysis*, **229**, 480-489 (2005)
3. Tanaka, Y., Hihara, T., Nagata, M., Azuma, N., and Ueno, A., Modeling of Diesel Oxidation Catalyst, *Ind. Eng. Chem. Res.*, **44**, 8205-8212 (2005)

9. Acknowledgements

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