Exhaust after-treatment modelling: Fundamental applications and future challenges

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Abstract

Validated exhaust after-treatment simulation tools already support the development of highly efficient, compact and low-cost exhaust after-treatment systems by substituting expensive experimental work. These models need to take into account multiple coupled transfer and reaction phenomena, numerous species interactions and synergies together with possible temperature and 3-D flow effects. The target of the present work is to provide an overview of state-of-the-art and discuss current and future challenges.

Introduction

The concern regarding environment is constantly growing due to the increased use of diesel and gasoline vehicles around the world. In order to conserve and improve the ambient air quality in these adverse conditions continuously more stringent emission standards are legislated. Additionally strong pressure is imposed for the reduction of the CO2 emissions which is expected to lead to a decrease of the average exhaust temperature making it even more difficult to meet the challenge. In this context, the pressure on the automotive industry to develop highly efficient and low-cost after-treatment systems that can achieve the imposed emission standards is constantly increasing.

In this direction, modern vehicles are equipped with complex exhaust after treatment systems which usually comprise more than one devices in series, e.g. a Diesel Oxidation Catalyst (DOC) and a Diesel Particulate Filter (DPF). In more complex cases, in order to gain space in the limited chassis dimensions and to create low-cost systems, it is desirable to integrate multiple functionalities and exploit any possible synergies in a single substrate, as it is done for example in the SCR-coated Diesel Particulate Filters (SCRF). Obviously, the possibilities are numerous and relying only on experimental investigations for choosing and optimizing the exhaust system is not practical both in terms of time and cost. Good validated exhaust after-treatment simulation tools provide invaluable support in this case.

These models are complex because they have to describe multiple physical phenomena such as mass and heat transfer together with chemical reactions which take place simultaneously in the devices, e.g.(Koltsakis et al.,1997; Sampara et al.,2007). There are generally well established equations describing the transfer phenomena in the literature which successfully account for the mass transfer limitation effects imposed on the reactions. Extra care is necessary, however, in the case of modern systems (especially multilayer ones) where species diffusion within the active material must be taken into account (Koltsakis et al., 2010). Nevertheless, the main “bottleneck” for achieving accurate modeling results is still considered to be the determination of the governing reactions scheme and the respective reaction rate coefficients. The difficulty comes initially from the fact that the exhaust gas contains numerous species which can interact in any possible way or which can be stored on the device. The problem is becoming more difficult taking into consideration the variety of the available technologies, the synergies that may appear when combining different technologies and the fact that each catalytic formulation exhibits its own activity or that the performance of the systems is affected during their life time by a number of parameters (e.g. ageing). Finally, possible 3-D effects originating from strange geometries, segmentations or temperature/flow maldistribution need also to be considered.

In the present work we discuss the abovementioned challenges and demonstrate how they can be met through efficient modelling. Following a brief presentation of some state-of-the-art modeling approaches, the discussion will be structured on selected application cases.

Model overview

The modeling results included in the present paper were generated with Exothermia software *axisuite*®, a dedicated tool for the simulation of exhaust after-treatment devices. The software modules have been originally developed at the Laboratory of Applied Thermodynamics of Aristotle University of Thessaloniki.. As it can be seen in Figure 1, it consists of 4 separate modules which cover all commercially available exhaust after-treatment devices.

axisuite						
module	principle	TWC	DOC	LNT	SCR	DPF
axicat	flow-through	✓	✓	✓	✓	–
axitrap	wall-flow	✓	✓	✓	✓	✓
axifoam	deep-bed	✓	✓	✓	✓	✓
axiheat	exhaust pipe	single-wall / double-wall / insulating material / reacting flow				

Figure 1: Overview of axisuite® modules

The flow-through catalysts model can be used to simulate three way catalysts (TWC) (Koltsakis et al.,1997), diesel oxidation catalysts (DOC) (Pontikakis et al.,2001), deNOx catalysts (Kandylas et al.,1999), lean NOx traps (LNT) (Koltsakis et al.,2006) and selective catalytic reduction (SCR) catalysts (Tsinoglou and Koltsakis,2007). The main differential and algebraic equations for the heat and mass transfer in the converter including modelling of the wall are given in Figure 2a. More details on the model can be found in the above referenced publications.

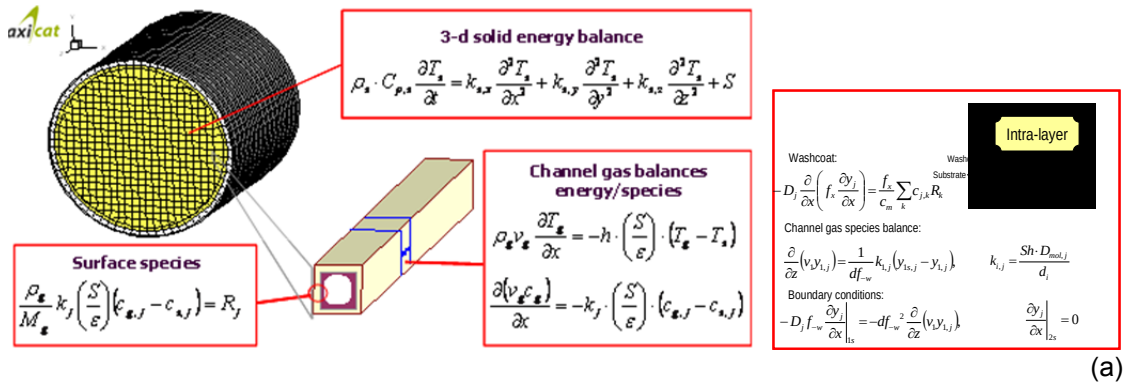


Figure 2: Basic model equations for (a) axicat, (b) axitrap and (c) axiheat

The wall flow model can be used to simulate bare and catalyzed Diesel Particulate Filters in terms of flow distribution, pressure drop, heat/mass transfer and soot oxidation. The basic

differential model equations are summarized in Figure 2b, whereas more details can be found in previous publications (Koltsakis,1996; Koltsakis and Stamatelos,1997; Kandylas and Koltsakis,2002; Haralampous et al.,2004; Haralampous et al.,2004; Haralampous and Koltsakis,2004).

The deep-bed filter model can be used to simulate devices which operate by accumulating the particulates within their body. The reaction scheme and rate expressions are identical to those used in the flow-through and wall-flow models and thus cover all possible catalytic applications, incl. DOC, LNT, SCR etc.

When simulating the complete after-treatment system, also connecting pipes have to be considered. The respective pipe model describes the heat transfer phenomena in exhaust pipes and the main differential equations used are summarized in Figure 2c**.** Details on the model, and application examples can be found in earlier publications (Kandylas and Stamatelos,1998).

Reactions schemes and model calibration

There are numerous species of interest in the exhaust gas which depending on the after-treatment technology may participate in several reactions of different characteristics, i.e. surface reactions (reversible and not reversible), adsorption/desorption or storage reactions. In addition, each catalytic formulation exhibits its own activity and therefore, the proper reaction scheme has to be chosen and the rate parameters have to be calibrated for every new formulation.

Although it is possible to implement elementary reaction mechanisms, “global” reaction rate expressions were proven to give a good compromise between complexity, ease of calibration, calculation accuracy and computational cost. As it will be shown, these rate expressions are able to successfully consider the effect of temperature, species surface concentration and species inhibition effects on the reaction rate.

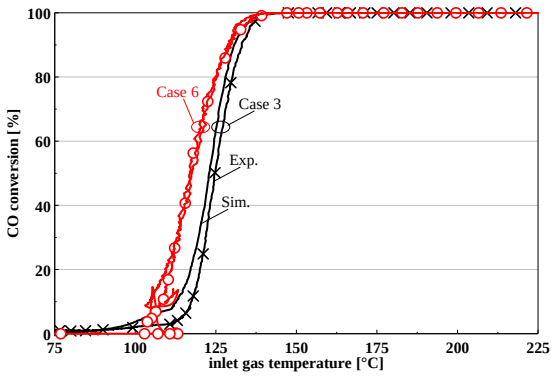


Figure 3: Example of experiments used for the calibration of the CO oxidation parameters (Feed gas composition: Case 6:CO/O2/CO2/NO, Case 3:CO/O2/CO2/HC/NO) (Lafossas et al.,2011)

Reaction examples together with indicative calibration guidelines are given next. Detailed calibration procedures can be found in Lafossas et al.,2011 for a DOC, in Koltsakis et al.,2010 for an LNT and an SCR, in Hajireza et al.,2010 for a cDPF and in Koltsakis et al.,1997 for a TWC.

<u>Surface (PGM) reactions</u>

This group of reactions includes the oxidation/reduction reactions that normally take place on the Platinum Group Metals (PGM). Typical examples are the non-reversible CO and HC and the reversible NO reaction with O2. Other more specialized reactions of this type are the reaction of CO and HC with NO2 or the reversible reaction of CO with H2O (water gas shift reaction).

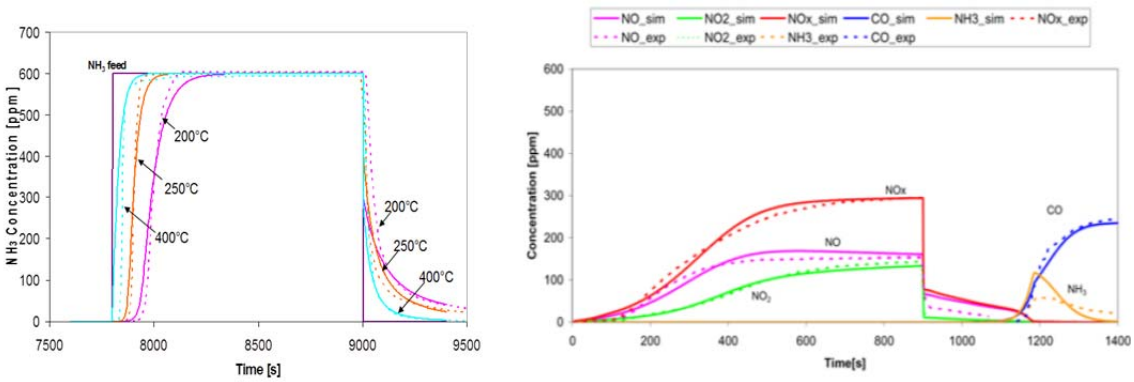
$$Rco = \frac{k[CO][O2]}{T(1+k1[CO]+k2[HC])^2(1+k3[CO]^2[HC]^2)(1+k4[NO]^{0.7})}, \text{ where } ki = Aie^{-Ei/RT} \quad \text{Eq.1}$$

The CO oxidation reaction is discussed as a characteristic surface reaction. As it can be seen in Eq.1, the respective reaction rate depends on the concentration of CO and O2 and it is inhibited (reduced) by the presence of CO (self-inhibition effect), HC and NO. In this “global” expression,

the inhibition effects are taken into account by including the respective concentration terms in the denominator of the rate. In order to correctly predict CO consumption it is necessary to determine (calibrate) all *ki* values included in Eq.1. This can be done with simple light-off/cool-down (LO) tests conducted on the synthetic gas bench (SGB), as those shown for example in Figure 3. The only difference between these two LO experiments is the presence of HC in the feed gas composition of the Case 3 experiment. As it can be seen the presence of HC reduces the CO conversion efficiency of the sample for a given temperature due to the HC inhibition effect which is expressed by the *k2* term in Eq. 1. It is therefore possible to determine the *k2* value from these two experiments. As it will be discussed later in the text, the parameters that are calibrated from SGB experiments need to be validated with real engine exhaust experiments.

Adsorption/desorption and storage reactions

A periodic storage/release of various exhaust species may also take place on the catalyst. This may be related to chemical storage. A typical example is NOx storage on Barium under lean engine operation. It takes place through the formation of Ba nitrites or nitrates, which are decomposed when the engine operation is switched to rich. The correct calculation of the stored species is very important since it affects the amount of Ba sites that are still available for NOx storage and thus also the prediction of total NOx reduction in the LNT. Alternatively species may be directly adsorbed on the catalyst, e.g. HC adsorption at low temperature on zeolite containing DOCs or NH3 adsorption in SCRs. These species are released from the catalyst when its temperature rises. These phenomena are very important in real world applications especially during the warm-up phase since they determine not only the available species quantities but also the temperature response of the device.



(a) (b)

Figure 4: Storage/release reaction modelling examples: (a) NH3 storage/release reactions on an SCR catalyst and (b) of NOx storage/release in Lean NOx trap (Koltsakis et al.,2010)

The respective models must calculate the instantaneous saturation level of each storage component and the relative storage/release kinetic rates. The adsorption model frequently applied in zeolite containing catalysts is described in Pontikakis et al., 2001 while the chemical storage model is described in Tsinoglou et al., 2002. Obviously, it is necessary to calibrate these models. Simple storage/release experiments can be used for the calibration of the adsorption/desorption reactions, e.g. (Koltsakis et al.,2012) while experiments were the feed gas composition is switched from lean/rich can be used for the calibration of the chemical storage reactions e.g. (Koltsakis et al.,2006). Figure 4a presents an example of successful prediction of NH3 adsorption in an SCR catalyst while Figure 4b presents similarly good simulation results for the prediction of NOx storage on an LNT catalyst.

HC speciation

There is a large number of hydrocarbon species in real diesel exhaust (Jensen et al.,1992; Bohac et al.,2006), which present different chemical activity (Dubien et al.,1998). Since it is not possible to individually take them all into account, a common practice is to group the HC according to their oxidation and adsorption properties, e.g. in (a) slowly oxidized, not adsorbable, (b) fast oxidized, not adsorbable (c) fast oxidized, moderate adsorbable and (d) fast

oxidized, strongly adsorbable. The breakdown of the total measured HC concentration to each one of the groups (HC speciation) is then to be decided based on targeted experiments with real exhaust. Choosing the correct HC speciation is crucial for the correct simulation of real-world behaviour since it does not only affect the correct prediction of the HC conversion but also the way that HCs inhibit other reactions.

In order to demonstrate these effects, two experimental CO oxidation cool-down curves are compared in Figure 5a. The only difference between the SGB and the small scale with real exhaust tests lied in the HC speciation (the total HC concentration and the space velocity was the same in both cases). C3H6 was used in the first case and real exhaust directly from the engine was used in the second case. As it can be seen, different CO oxidation profiles were determined in both cases. The difference is attributed to the different characteristics of the HC mixture, which presents a stronger inhibition on the CO oxidation in the case of real exhaust. As a next step the kinetics determined from the calibration of these experiments were used for the simulation of a full-scale experiment with the same catalyst. The corresponding results are presented in Figure 5b. As it can be seen the kinetics determined by using the SGB curve for calibration cannot be directly transferred to the real-exhaust kinetics. On the other hand the kinetics determined from the small scale experiment with real exhaust can lead to accurate simulation results in the full scale.

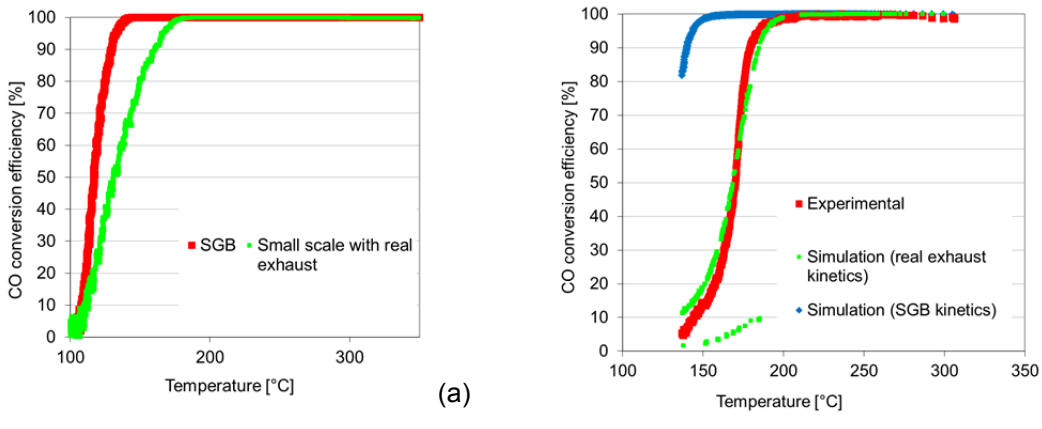


Figure 5: HC speciation effects: (a) CO oxidation curves determined from an SGB and a small scale experiment with real exhaust and (b) Simulation of a full scale experiment using kinetic parameters determined from the experiments shown in (a)

Intra-layer modelling

In simple flow – through devices and under the usual operating conditions, the diffusion phenomena in the wall can be usually neglected since it can be assumed that diffusion is fast relatively to the oxidation rates. When investigating wall-flow or dual-layer systems, however, the coupling of reaction/diffusion phenomena can be very important and the negligence of these phenomena can lead to inaccurate results.

One characteristic example is the dual-layer SCR-LNT system investigated by Koltsakis et al.,2010. The concept of the dual layer LNT-SCR system relies on the fact that NH3, which is produced in the bottom LNT layer under rich conditions, is being stored in the top SCR layer before diffusing back to the gas phase. The stored NH3 is subsequently used to reduce NOx during lean mode. The calculated concentration profiles presented in Figure 6a reveal the spatial transitivity of the concentration which has to be taken into account in order to accurately determine the total NOx reduction of the device.

An even more complicated dual-layer system is one that integrates PM and NOx control into a single device, namely an SCR-coated Diesel Particulate Filter (SCRF). Colombo et al.,2011 performed a simulation study on such a system which investigated among others also the competition between passive soot oxidation with NO2 and the DeNOx processes involving NO_2. Figure 6b presents characteristic calculated NO2 radial profiles at 500°C in the soot cake (radial dimensions <0) and in the wall (radial dimensions >0) for two different soot loadings. As it can

be seen, the passive regeneration of soot can lead to the alteration of the local NO_2/NOx ratio depending on the soot loading. This ratio affects strongly the SCR performance and depending on the other operating conditions, it can result either in a promoting or in a detrimental effect of the deNOx performance. In a direct correlation, the SCR reactions competitively consume NO2 affecting the DPF regeneration performance. It is therefore of the utmost importance to accurately know the local NO2/NOx ratio which can only be done with intra-layer modelling.

Intra-layer modelling is also important for simple DPF systems. It can improve the accuracy of the filtration efficiency simulation, which is related to the correct estimation of soot density and soot mass accumulated inside the wall (Koltsakis et al.,2006). Additionally, it can improve the prediction of the correlation of the pressure drop vs soot loading which depends on the partial regeneration history. This is the so-called pressure drop hysteresis effect. According to that effect the cake soot does not allow the incoming soot to penetrate the wall after an incomplete regeneration. Therefore, the pressure drop correlation with soot loading changes dramatically and can only be simulated accurately by intra-layer modelling (e.g. Koltsakis et al.,2009). Finally, intra-layer modelling is necessary in the case of advanced filtration material, such as wall of multiple layers inside or on top of the wall structure with variable geometrical/filtration properties (Bollerhoff et al.,2011).

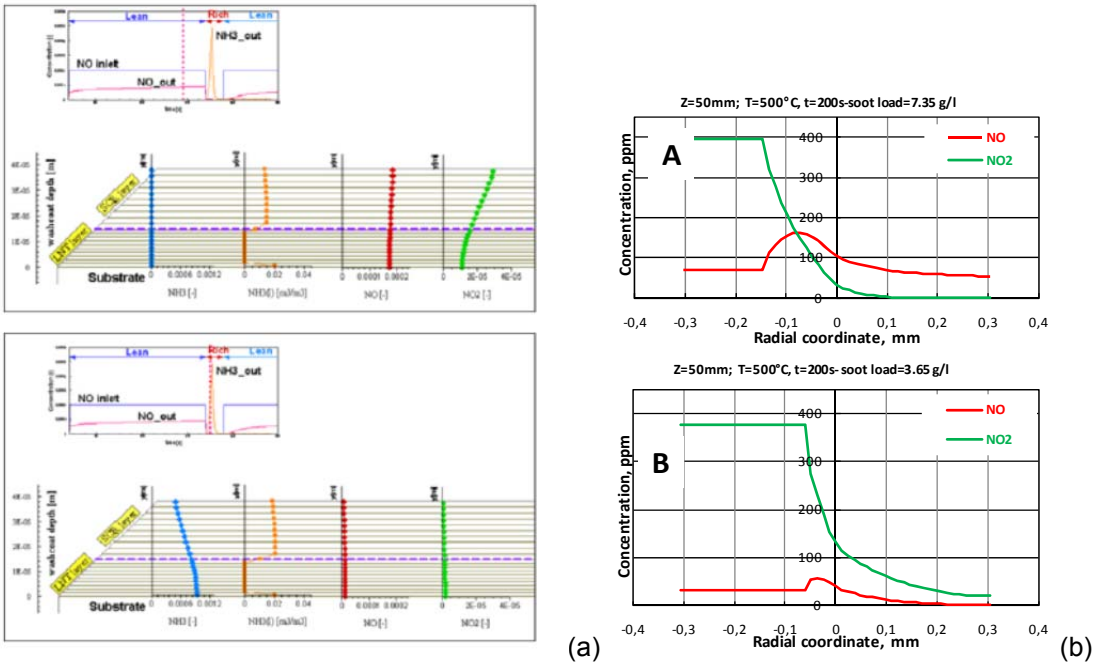


Figure 6: Calculated intralayer concentration profiles in (a) a dual LNT-SCR system (Koltsakis et al.,2010) and (b) an SDPF system (Colombo et al.,2011)

3-D thermal effects

Although 1D or 2D simulations are generally used in exhaust aftertreatment, in some cases it is necessary to take into account the 3D thermal effects.

The most important application in this case maybe the modeling of exhaust after-treatment devices used in hybrid architectures, which are expected to be more and more extensively used in the future in order to optimize fuel efficiency and reduce CO2 emissions. Hybrid operation is typically achieved with frequent engine start-and-stops. The cooling of the exhaust system during engine stop may pose problems if the substrate temperature drops below the light-off temperature. Therefore, the correct prediction of the temperature profile inside the catalyst during these periods is necessary. In order to achieve this it is necessary to carefully consider the 3-dimensional heat transfer problem which must take into account heat transfer in zero flow conditions and the free convection and radiation from the front and rear substrate faces. Figure 7 (Koltsakis et al.,2011) demonstrates the importance of the later phenomena. As it can be seen the temperature of the catalyst and consecutively its conversion efficiency is overestimated when the adiabatic model is used.

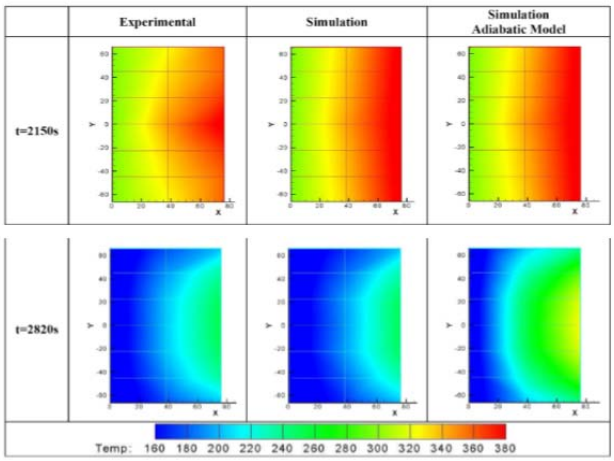


Figure 7: Experimental vs 3D thermal model vs adiabatic model Koltsakis et al.,2011

The determination of the full 3D temperature field can also be used to evaluate the DPF soot mass limit if it is coupled with thermomechanical strees analysis (Koltsakis and Atmakidis,2012). The failure during 'worst-case' regeneration events may either be a result of overheating or exceeding the critical mechanical stress limit. In the latter case the failure is substantially linked with thermal gradients resulting from local non-uniformities of the temperature, flow and soot distributions in the DPF which can be systematically investigated by 3D simulation tools.

Summary

The main challenges of exhaust after-treatment modelling can be summarized as follows: (a) there are numerous possible interactions between the species that must be taken into account by as simple as possible yet accurate reaction equations, (b) although it is possible to determine the reaction rates through simple SGB experiments, the determined parameters must always be validated with real exhaust experiments, (c) the implementation of intra-layer modelling is absolutely necessary for the accurate simulation of DPFs and complex dual-layer systems and finally (d) although 1d modeling can be sufficient for basic concept analysis studies, 3d modeling is necessary for detailed component optimization. Considering the significant progress in developing efficient model calibration techniques, the role of simulation is expected to further increase and facilitate the exhaust system optimization process.

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