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Modeling Catalytic Regeneration of Diesel Particulate Filters, Taking into Account Adsorbed Hydrocarbon Oxidation

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Initiation of the regeneration of porous ceramic diesel particulate filters at low exhaust gas temperatures and the subsequent control of the soot oxidation rate is necessary in order to allow a wide applicability of filter systems in diesel-powered vehicles. The use of catalysts in this respect, in particular catalytic fuel additives, has been proven to be successful, leading to a minimization of the system's cost and additional fuel consumption. Better understanding and modeling of the catalytic activity at low temperatures necessitates that one takes into account the oxidation not only of dry particulate but also of the volatile hydrocarbons adsorbed on the particulate. In this paper, the oxidation of the hydrocarbons adsorbed on the particulate is modeled, to allow a better understanding of the filter regeneration behavior at very low temperatures (150–300 °C). A simplified reaction scheme and tunable kinetics are employed in the description of adsorbed hydrocarbon oxidation. The mechanism is incorporated in an existing mathematical model, and specific computational case studies are invoked to explain and to model regeneration at low temperatures. The results compare well with experimental evidence and indicate certain directions for further research to better understand this complex process which is essential to the successful application of diesel particulate filters.

Introduction

Engine and combustion improvements have substantially reduced NO_x and particulate emissions from modern diesel engines, so far without the application of any exhaust aftertreatment. Only oxidation catalysts have become widespread on diesel passenger cars in Europe, but they do not solve the problems of high NO_x emissions and the health effects of particulate emissions. Whatever future improvements emerge for reducing engine-out emissions, an aftertreatment technology that can reduce 50–90% of the remainder may be necessary.[1] Thus, the interest in diesel engine exhaust after-treatment systems is ever-growing in view of the stricter US and European emission legislation amendments planned for the near future (2004). As regards particulate emissions, the wall-flow particulate filter is today the most efficient aftertreatment device, attaining filtration efficiencies on the order of 90% (for dry particulate) under nominal operation conditions.[2] Typical diesel particulate consist mainly of a carbonaceous core (soot formed during combustion), adsorbed compounds such as unburnt and partially oxygenated hydrocarbons, sulfates (due to the oxidation of the sulfur contained in the fuel), and metal oxides.[3]

A trap oxidizer system is based on a durable temperature resistant filter—the trap—which mechanically filters particulate matter from the exhaust gas. The accumulated particulate raises trap backpressure—the pressure difference across the trap that is necessary to force the exhaust through it. High backpressure is undesirable, since it increases fuel consumption and reduces engine brake torque. Thus, it is necessary to clean the trap periodically by burning off (oxidizing) the collected particulate. This process is known as regeneration. Under the space velocity and oxygen availability conditions usually met in the particulate filters placed
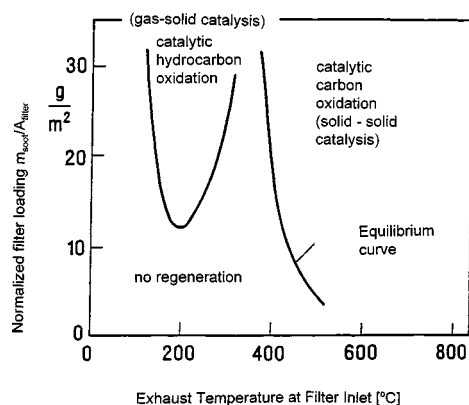
in diesel exhaust, the required reaction rates for complete filter regeneration, without catalysts, are attained at temperatures above 550 °C. Exhaust temperatures of that order are observed only at high load operation of the diesel engine, which is scarcely attained in city driving. Thus, the only feasible solution so far is the application of catalytic regeneration aids. In the currently available technology, the catalyst is used as a fuel additive, which is burnt in the combustion chamber and subsequently emitted and accumulated in the filter in very close contact with the particulate, which ensures high catalytic activity. The use of catalytic fuel additives is critical to the design of a successful trap system, because it leads to a more or less continuous regeneration during city driving, at a range of exhaust temperatures between 150 and 300 °C.[4–7] A significant number of prototype and pilot installations of this type of trap systems have been tested over the last 15 years, with varying degrees of success. On the basis of this vast experience, the general conclusion can be drawn that the design of successful filter systems must be supported by a good understanding and modeling of catalytic filter regeneration at low temperatures.[2]

Catalytic regeneration by use of fuel additives is a quite complex process which is not yet well understood and modeled. In ref 8, an approach based on modeling the transient oxygen storage characteristics of metal oxides was presented in order to explain and model catalytic regeneration by use of fuel additives. The authors presented a zero-dimensional model, which was proven capable of predicting certain aspects of fuel additive activity in diesel filters. For example, Figure 1 presents the computed dependence of equilibrium temperature (that is, the filter inlet temperature that leads to a regeneration reaction rate equal to the loading rate) on the filter loading and the fuel additive dosimetry. To better understand and model the filter behavior under low space velocity conditions that are important in certain aspects of filter operation, in [9] an improved 1-D model of catalytic regeneration is presented, which

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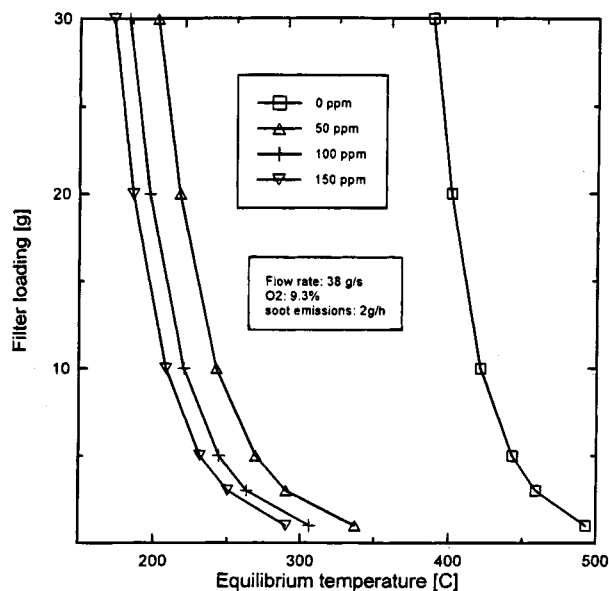
Figure 1. Predicted equilibrium regeneration ranges with the previous models. Comparison with the measured results of Figure 2 makes apparent the failure to predict erratic regeneration behavior.[8]

Figure 2. Measured equilibrium filter loading as function of exhaust temperature at filter inlet. Steady-state experiments were performed with the reference engine at 2000 rpm and constant exhaust gas temperature by compensating engine load. Catalyst-doped fuel was used.[7]

additive, this behavior is observed in the range of temperatures between 150 and 300 °C. Above 300 °C, regeneration is not observed, until about 370 °C, where the so-called deterministic regeneration starts.

The reaction schemes employed in the previously mentioned models do not take into account the oxidation of the adsorbed hydrocarbons, and this is the reason they fail to predict the erratic regeneration behavior. Comparison of the computational results of Figure 1 with the measured behavior of Figure 2 makes apparent the deficiency of the previous category models. Moreover, as shown in Figure 1, in order for these models to give a good overall prediction of the behavior of diesel filters in full scale tests (e.g., transient modes of operation or full driving cycles[11]), the tuning of the kinetics for the thermal and catalytic oxidation of the soot (assumed as dry soot), was wrongly done to produce higher reaction rates and thus account also indirectly for the adsorbed hydrocarbon activity. Naturally, this technique does not give a good representation of real world filter operation. The lack of regeneration in the range between 300 and 370 °C is not predicted, and also, the kinetics at higher temperatures are significantly more enhanced.

In the present paper, a modeling approach for hydrocarbon oxidation is developed and presented which is capable of better modeling and explaining the measured catalytic regeneration behavior of diesel filters.

Experimental Evidence of Hydrocarbon Activity

Due to the previously mentioned effect of erratic regeneration behavior, in certain automotive applications, continuous regeneration conditions may be set on the filter during low speed city driving.[12] However, when the vehicle is driven at higher average velocity, with exhaust temperatures on the order of 250–350 °C, erratic regeneration is rare or completely absent, and a high soot mass could be accumulated in the filter. Whenever higher exhaust temperatures are produced by increasing vehicle velocity (and engine load), or just by the increased backpressure levels that throttle engine exhaust, the onset of deterministic regeneration is observed, which is characterized by significantly higher reaction rates and may lead to filter overheating and cracking.

The characteristic behavior of catalytic regeneration at low temperatures, which has presented difficult-to-solve problems to the researchers, was systematically studied for the first time in a dedicated, exhaustive series of experiments, and presented in two related papers.[7,13] In the present computational work, we employ a small number of results from the work of these researchers, to tune and validate our improved model.

We refer to a series of engine bench experiments conducted by Lepperhoff et al.,[13] aiming at evaluating different additives and concentrations regarding their behavior for promoting filter regeneration. This part of the work was conducted by the above-mentioned researchers on a passenger car diesel engine (main data in Table 1) equipped with a commercial trap (Table 2). The results are presented by means of measured filter backpressure traces over time, at steady-state engine operation with a constant exhaust temperature at filter inlet (variation of engine load to balance the effect of backpressure increase to exhaust temperature). (Figure 3). In the same figure, recordings of CO emissions

is capable of predicting the spatial propagation of the regeneration front and its dependence on reactor design, process conditions, and catalytic dosimetry. This improved model was tested and validated against a series of specially designed engine bench experiments.[10]

Both the 0-D and 1-D models were characterized by a minimal number of tunable parameters, to represent the complex chemistry of fuel additive assisted soot oxidation. Their main drawback is that they consider only dry soot oxidation, without separately addressing adsorbed hydrocarbons (the so-called volatile organic fraction—VOF), which are able to be oxidized at significantly lower temperatures, on the order of 150–250 °C, and desorb from the particulate at higher temperatures.

The real world situation has been extensively measured by Lepperhoff et al. and presented in ref 7, by means of specially designed steady-state experiments (Figure 2). According to this figure, the hydrocarbons adsorbed in the particulates are observed to be oxidized at very low temperatures, with moderate filter loading levels, producing the so-called erratic regeneration behavior. In the example of Figure 2 with Cerium fuel

Table 1. Main Data for the Engine Employed in the Experiments Reported[13]

manufacturer	Volkswagen AG
engine type	IDI (swirl chamber), NA
cylinders	4, in-line
displacement	1896 cm^3
rated power/rpm	50 kW/4400 rpm
rated torque/rpm	120 Nm/2000 rpm
fuel consumption (NEDC)	12 l/100 km

Table 2. Thermophysical Properties of the Particulate Filter and Fuel Borne Catalyst Employed in the Experiments Reported[13]

filter material	cordierite	(EX47)
cell density	100	cells/in^2
wall thickness	0.43	mm
porosity	50	%
diameter	143.8	mm
length	152.4	mm
specific surface	568	m^2/m^3
substrate specific heat capacity	1120	J/kgK
insulation thickness	2.3	mm
substrate conductivity	0.85	W/mK
substrate density	1700	kg/m^3
fuel borne catalyst	cerium oxide	
catalyst dosimetry in diesel fuel	100	ppm
average engine soot emissions at 2000 rpm	3.0	g/h
percentage of VOF in dry soot collected	100	%
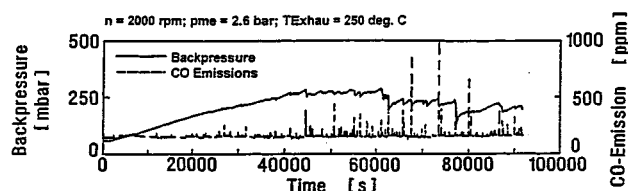
Figure 3. Erratic regeneration behavior of a particulate trap installed on a 1.9-liter IDI diesel engine by use of cerium fuel additive.[13]

downstream of the filter are also shown to better present the erratic regeneration behavior. Exhaust temperatures at different points inside the filter were also measured in this experiment by the above-mentioned researchers.[13] These temperatures recordings present peaks corresponding to the erratic regeneration occurrences shown in the sudden drops in the backpressure trace of Figure 3. Peak temperatures range from 260 to 350 °C. Each regeneration is associated with a more pronounced temperature peak in one thermocouple at a time, in a random manner. The recorded behavior is dependent on the specific additive employed. In these experiments erratic regeneration, which is clearly observed during variable speed and load engine operation during on-road vehicle driving, was demonstrated for the first time under controlled conditions on an engine bench.[13]

The causes of erratic regeneration behavior have been also investigated by the same researchers.[7] According to their reasoning, erratic regeneration behavior has its roots in the presence of the volatile hydrocarbons in the accumulated soot. The volatile hydrocarbons originate in unburnt fuel and lubricating oil and are found adsorbed or condensed on the carbon particulate at temperatures below 300 °C. These hydrocarbons present a much better contact with the catalyst oxides, and thus they may be oxidized at temperatures as low as 200 °C. In such cases, a slow oxidation starts at low temperatures, whenever the local soot loading, composition, and temperatures are favorable. The associated heat release may, under certain circumstances, heat up neighboring carbon particulate, which is then further oxidized by the

additive oxides at temperatures higher than 350 °C. The resulting additional exothermic reactions may further locally increase the temperature to above 500 °C, thus allowing fast oxidation of carbon by exhaust gas oxygen. This leads to a more or less complete regeneration of the filter.

The hydrocarbons present as the soluble organic fraction of the particulate are completely gasified and desorbed at higher temperatures, and eventually, soot is composed exclusively of dry carbon particulate, at temperatures beyond 400 °C.

Volatile Hydrocarbons in Diesel Soot

Once the decision is taken to enhance the reaction mechanism of diesel particulate oxidation, to include oxidation of volatile hydrocarbons at low temperatures, the following issues arise.

•The percentage of volatile organic fraction (VOF) in the particulate emitted by a diesel engine varies considerably with engine type (DI, IDI, turbocharged), injection pressure, exhaust gas recirculation (EGR) rate, and engine operation point (speed and load; exhaust temperature).

•The percentage of VOF that will eventually remain adsorbed in the dry soot accumulated in the filter depends on the filter temperature; that is, if the filter temperature exceeds 370−400 °C, most VOF is vaporized and only dry soot remains accumulated on the filter wall.

•Prolonged operation of a filter highly loaded with relatively dry soot, under low exhaust temperature (low engine speed and load) conditions, may lead to the readsorption of heavy hydrocarbons emitted in the particulate layer, thus increasing again its VOF content. (For this reason, the filter efficiency with respect to the VOF is variable, depending on the soot loading and VOF content.)

Thus, any attempt to model the catalytic activity associated with oxidation of hydrocarbons adsorbed in the particulates should rely on at least an elementary knowledge of the composition of engine particulate emissions over the engine map, as well as the adsorption and desorption rates of VOF as function of temperature.

First, it should be noted that the process of adsorption of hydrocarbons on a soot-loaded ceramic filter is not yet experimentally investigated and understood. The only related process that is well studied in the literature is the adsorption of hydrocarbons in diluted exhaust on Teflon-coated glass fiber filters.[14,15]

As a first step in attacking this complex problem, one might consider an extremely simplified situation where the volatile organic fraction of the particulate evaporates and desorbs from the particulate according to a distillation curve, that could resemble that of the diesel fuel from which it originates. As an example, Figure 4 compares distillation curves for typical diesel fuels. These curves are derived from heating a sample of liquid collected in a volume calibrated buret. It is apparent that most diesel fuels evaporate in the range between 200 and 380 °C (when vapor is in its own presence and not in a mixture with exhaust gas products, as in real diesel exhaust). The observation that low temperature catalytic activity in the diesel filters diminishes as we approach 380 °C, along with the fact that hydrocarbons emitted by the engine are mainly composed of either unburnt or incompletely burnt diesel

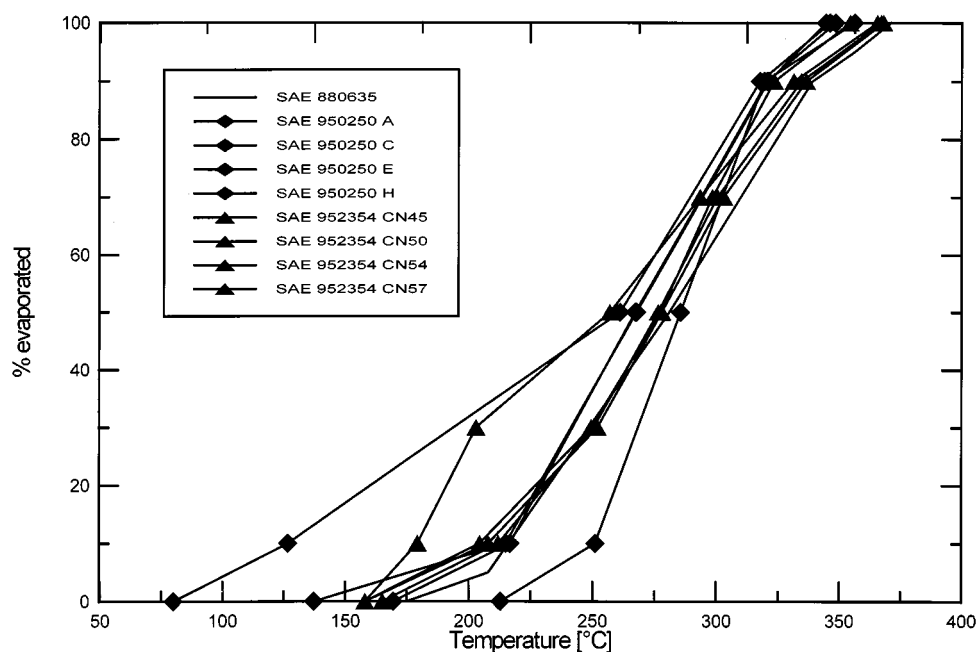## Distillation curves of different diesel fuels

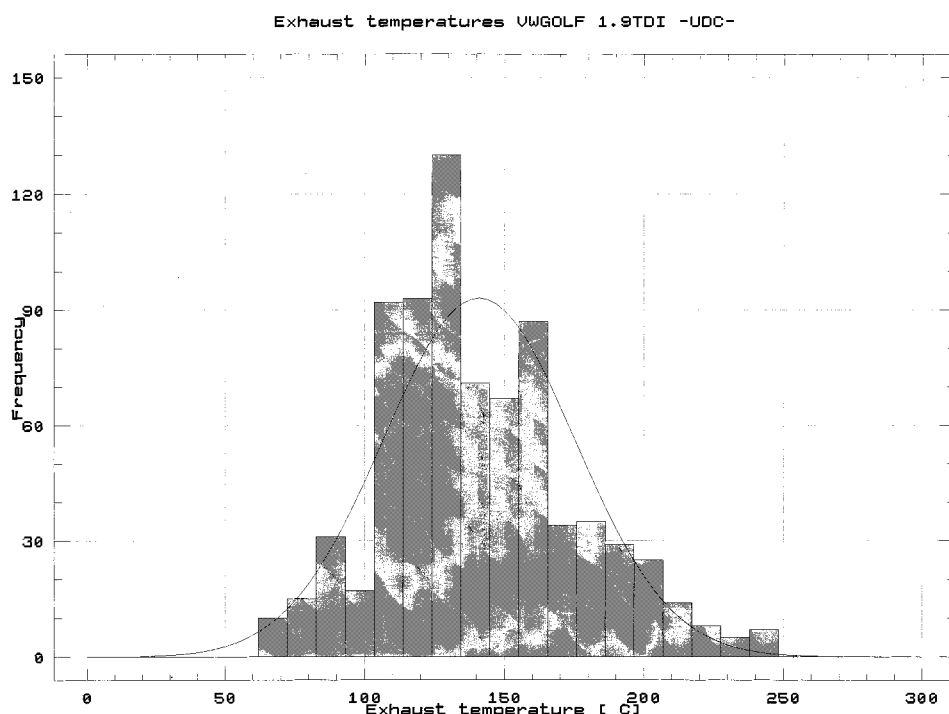**Figure 4.** Distillation curves of various diesel fuels.

Figure 5. Statistics for exhaust temperature levels of a diesel car driven in the European Urban Driving Cycle.

fuels (along with lubricating oil), could be drawn as arguments supporting the above crude assumption.

On the basis of this simplified assumption, we must then solve the problem of determining the VOF percentage present in diesel soot accumulated on a cellular ceramic filter installed on a diesel engine at a specific position along the exhaust line, after a certain vehicle driving history. This problem cannot be faced at present due to the above-mentioned complexities and the lack of experimental investigations of a real world situation.

The only possible approach here is to start the computation with accumulated soot of a specific hydrocarbon molar content, ζ, which will be assumed based

on empirical knowledge. The results from such computational investigations are then correlated with the measured filter loading history, based on full scale test results from steady-state tests and driving cycles,[3,11] (see for example the exhaust temperatures pertaining during Urban Driving of a VW Golf 1.9 TDI passenger car in Figure 5), the composition of particulate emitted at the respective operation points, and the filtering efficiency regarding dry particulate and VOF.

Once an initial ζ is reasonably assumed, we must regularly calculate the subsequent variation of ζ based on the composition of accumulated particulate and the filter temperature according to the soot oxidation and

hydrocarbon desorption and oxidation kinetics assumed. In this way, we may know, as function of time, the amount of hydrocarbon adsorbed in the dry carbon particulate, in the absence of oxidation.

The next step is the addition in the reaction scheme of the catalytic regeneration model, of the reaction of hydrocarbon oxidation by the catalyst oxides of the higher state. This leads to an improved catalytic regeneration model that takes into account hydrocarbon oxidation. This improved model is described in the next section.

Catalytic Regeneration Model with Adsorbed VOF Oxidation

As already explained above, the modeling approach presented here is based on the additional consideration of adsorbed hydrocarbon oxidation by the catalyst oxides inside the soot layer, as a triggering process for the ignition of the remaining dry particulate.

It is well-known that the commonly used metal additives for promoting filter regeneration form more than one type of oxides corresponding to the possible valent states they can assume. We can, therefore, distinguish between the metal being in "higher" or "lower" oxidation state. The fuel additive takes part in the combustion process, leaves the combustion chamber, and accumulates in the filter together with the emitted soot. Typical filtration efficiencies for additives in the trap are usually over 95%.[13,16] We can assume that during this process each metal additive particle adsorbs to an agglomerate of soot constituents, consisting of carbon and hydrocarbon molecules.

When the particle reaches the filter, a high percentage of the metal additive is actually in its higher oxidation state. Provided that the filter temperature exceeds a threshold on the order of 200 °C, the metal oxide in the deposit layer releases an oxygen atom to react with adsorbed hydrocarbons and thus assumes its "lower" oxidation state. The reduced oxides produced in this way may react at the same time with the oxygen contained in the flowing exhaust gas. This continuing oxidation/reduction process, which takes place at significantly lower temperatures than catalytic dry soot oxidation, results in reaction of adsorbed hydrocarbons and soot with oxygen from the exhaust gas via the fuel additive oxides, which act as catalysts.[17]

Starting point for the development of the modified mathematical model, which includes the process of adsorbed hydrocarbon oxidation, is the previously mentioned zero-dimensional catalytic regeneration model.[8] The basic features of the improved model are outlined below.

The exhaust gas is considered to flow through two layers: the particle deposit containing the fuel additive, which shrinks uniformly with time during regeneration, and the porous ceramic channel wall. A certain percentage of the dry particulate is in close contact with the catalyst oxide. Thus, the kinetics of dry soot oxidation by oxygen released by these oxides are significantly faster than the kinetics of dry particulate oxidation by exhaust oxygen. This mechanism was already present in the previous state of model development. However, at this stage we introduce also the oxidation of adsorbed hydrocarbons by oxygen released by the catalyst oxides. Due to the significantly better contact of the adsorbed hydrocarbons with the catalyst oxides, the kinetics of adsorbed hydrocarbon oxidation by the catalyst oxides

are even faster. However, as usual, the maximum hydrocarbon oxidation reaction rate is controlled by the available catalyst oxides of the higher state.

Following the previous model structure, we employ a single spatial variable x, whereas all variations in the direction perpendicular to x are neglected. The assumption of equal exhaust gas temperature entering the deposit layer over the monolith channels is realistic for sufficiently high exhaust flow rates related to the monolith volume, considering that the conductive heat transfer between the channel gas and the monolith walls is negligible compared to convective transport in the channels. As regards the kinetics of carbon oxidation, which in reality is a two step process (carbon oxidation to CO, followed by CO oxidation to CO_2), we follow the simplifying assumptions reported in,[8,18] and thus, the following incomplete carbon oxidation reaction is considered:

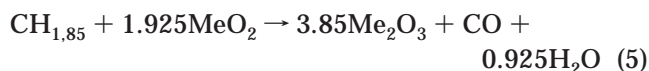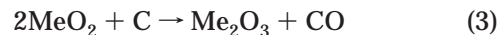$$C + \alpha O_2 \rightarrow 2(\alpha - 0.5)CO_2 + 2(1 - \alpha)CO \quad (1)$$

Here α is an index of the completeness of the reaction taking values from 0.5 to 0.9, depending on the reactor temperature levels. It must be mentioned that estimation of the value of index α can be performed with good accuracy based on the analysis of routine regeneration tests with simple temperature recordings, according to the methodology reported in ref **8**.

The following rate expression is used for carbon oxidation:

$$k_1 = kTe^{-E/RT} \quad (2)$$

For the apparent activation energy E appearing in this equation experimental evidence in ref **8**, it is implied that a value of 150 000 J/mol satisfactorily represents regeneration reaction behavior. Having adopted a value for the apparent activation energy, the factor k can be accordingly tuned to obtain good agreement between calculations and measurements.

Catalytic carbon oxidation is taken into account according to the approach of ref **8**, which uses the oxygen atoms exchange theory to describe the process. Additionally, catalytic oxidation of adsorbed hydrocarbons is taken into account, with significantly faster kinetics. During catalytic regeneration, the oxidation state of the metal oxides may be changed by reacting either with oxygen of the exhaust gas or with the carbon atoms and the hydrocarbon molecules of the deposit layer. Thus, if we assume that the metal additive Me forms oxides with both its three- and four-valent state the following redox-sensitive reactions take place:

$$2MeO_2 + C \rightarrow Me_2O_3 + CO \quad (3)$$

$$Me_2O_3 + \frac{1}{2}O_2 \rightarrow 2MeO_2 \quad (4)$$

$$CH_{1.85} + 1.925MeO_2 \rightarrow 3.85Me_2O_3 + CO + 0.925H_2O \quad (5)$$

The rates of the above three reactions are assumed to be an Arrhenius-type function of temperature. The metal additive reduction rate by dry soot (carbon) is then given by

$$R_{red} = k_{red}e^{-E_{red}/RT} \quad (6)$$

while the metal additive oxidation rate, which is assumed to be directly proportional to the availability of the exhaust gas oxygen as well as the lower oxidation state metal oxides, is calculated as follows:

$$R_{ox} = k_{ox}[O_2](1 - \psi)e^{-E_{ox}/RT} \quad (7)$$

Although any adsorbed hydrocarbons in the soot layer can be considered to react with the catalyst (catalytic oxidation) or directly with the exhaust gas oxygen (thermal oxidation), in fact, only the catalytic oxidation is important: For low exhaust gas temperatures (i.e. below approximately 250 °C), oxidation of hydrocarbons with the exhaust gas oxygen is negligible because it is limited by the reaction kinetics; for higher temperatures, adsorbed hydrocarbons are evaporated and leave the trap before reacting with either the catalyst or the exhaust gas oxygen. Therefore, the third reaction added to the model describes just the reduction of the metal additive by the adsorbed hydrocarbons. This reaction's rate is also expected to vary with temperature according to an Arrhenius type function similar to the one describing the metal additive reduction, that is

$$R_{red,HC} = \psi k_{red,HC}e^{-E_{red,HC}/RT} \quad (8)$$

Three quantities need to be defined to enable a complete description of the reactions' progress. The adsorbed hydrocarbons soot content is given by

$$\zeta = \frac{\text{moles of hydrocarbon present in soot}}{\text{carbon moles present in soot}} \quad (9)$$

As discussed above, an initial value of ζ is assumed, based on experimental evidence with the specific engine on the known filter operation history. The metal additive oxides are accumulated in the deposit soot layer and, following ref 8, we may define

$$\xi = \frac{\text{moles of metal oxides present in soot}}{\text{carbon moles present in soot}} \quad (10)$$

The fraction ξ is a function of the metal additive concentration in the fuel as well as the engine soot emissions produced during the trap loading operation. Metal additive oxides are generally present in the deposit layer in both the lower and the higher oxidation state. Again, following ref 8, we define

$$\psi = \frac{\text{"higher oxidation state" metal oxides present in soot}}{\text{total metal oxides present in soot}} \quad (11)$$

Mass exchange between exhaust gas flow and reactants or products is negligible compared to the exhaust flow itself. The conservation of mass for the exhaust gas can then be expressed as

$$\rho v = \frac{F(t)}{A} \quad (12)$$

Assuming that reaction 1 is first order in O_2 and that diffusion is negligible compared to convection the oxygen balance equation is

$$\frac{\partial}{\partial x}(\rho v y) = -s_j k_j \rho y \alpha \quad j = 1, 2 \quad (13)$$

where subscript j identifies regions 1 (deposit) and 2 (ceramic wall). Since there is no reaction in region 2 (porous wall), $k_2 = 0$.[8] The coefficient k_1 for region 1 is calculated from the above rate expression.

Assuming that the gas temperature equals that of the solid phase very near the entrance region of the deposit layer and considering negligible heat losses to the surroundings, the heat conservation equation can be formulated as follows:

$$\rho_j C_{pj} \frac{\partial T}{\partial t} = s_j\left(-\frac{\Delta H}{M_\alpha}\right)k_j \rho y + \frac{\partial}{\partial x}\left(\lambda_j \frac{\partial T}{\partial x}\right) - \rho v C_{pg} \frac{\partial T}{\partial x}$$
$$j = 1, 2 \quad (14)$$

ΔH indicates a combined reaction enthalpy resulting from the complete and incomplete oxidation of carbon, which is linked to α according to the relation

$$\Delta H = 2(\alpha - 0.5)\Delta H_{(i)} + 2(1 - \alpha)\Delta H_{(ii)} \quad (15)$$

The rate of shrinkage of the deposit layer is proportional to the rate of oxygen consumption and inversely proportional to the oxidation efficiency index α:

$$\rho_1 \frac{dw}{dt} = \frac{M_c}{M_\alpha} \frac{F(t)}{A}[y(x = 0) - y(x = -w)]\frac{1}{\alpha} \quad (16)$$

The initial conditions for the system eq 13, 14, and 16 are

$$T(x, t = 0) = T_b \quad (17)$$

$$w(t = 0) = w_b \quad (18)$$

The boundary conditions at $x = -w$ are

$$y = y_i(t) \quad (19)$$

$$\lambda_1 \frac{\partial T}{\partial x} = \rho v C_{pg}[T - T_i(t)] \quad (20)$$

where $F(t)$, $y_i(t)$, and $T_i(t)$ are the known conditions of the exhaust gas. At $x = w_s$

$$\frac{\partial T}{\partial x} = 0 \quad (21)$$

Using the dimensionless variables given in the Nomenclature section, the set of differential equations governing the reactor operation that was developed in ref 8 is transformed as follows.

The total rate of change of ψ may then be written as

$$\frac{d\psi}{dt} = R_{ox} - R_{red} - R_{red,HC} \quad (22)$$

By defining the dimensionless oxidation and reduction time constants as given in the Nomenclature section, we can rewrite eq 22 using nondimensional numbers in the following form:

$$\frac{d\psi}{dt} = \frac{1}{t_{ox}} - \frac{1}{t_{red}} - \frac{1}{t_{red,HC}} \quad (23)$$

A new equation must be added to the set to describe the change of volatile hydrocarbon molar content of the dry particulate, ζ.

$$\frac{d\zeta}{dt} = -\frac{\xi}{1.925\,\bar{t}_{red,HC}} - R_{boil,HC} \quad (24)$$

As seen in this equation, in addition to reaction kinetics, vaporization and desorption from the soot of its volatile organic fraction is considered in a simplified way, assuming that the VOF evaporates according to a typical diesel fuel boiling curve, (Figure 4). The VOF evaporation and desorption rate included in this equation, is assumed to be described by the following apparent kinetics,[19] which is tuned to produce the desired evaporation curve:

$$R_{boil,HC} = \zeta k_{boil,HC} e^{-E_{boil,HC}/RT} \quad (25)$$

The remaining equations describing the change of temperature and thickness of the dry particulate layer,[8] are modified as follows, to take into account adsorbed hydrocarbon oxidation:

$$\frac{dT_0}{dt} = \left[\bar{F}(\bar{t})\overline{\Delta H}y_i(\bar{t})\frac{1}{\alpha}\left(1 - \exp\left(-\frac{\bar{k}(T_0)w_0}{T_0\bar{F}}\alpha\right)\right) + \right.$$
$$\bar{F}(\bar{t})(T_i(\bar{t}) - T_0) + \frac{\xi w_0\overline{\Delta H}_{cat}}{2M\bar{t}_{red}} +$$
$$\left. \frac{\xi w_0\overline{\Delta H}_{HC}}{1.925\bar{M}_{HC}\bar{t}_{red,HC}} \right] \Big/ (\bar{C}_{p1}\bar{w}_0 + \bar{C}_{p2}\bar{w}_s) \quad (26)$$

$$\frac{dw_0}{d\bar{t}} = -\bar{M}\bar{F}(\bar{t})y_i(\bar{t})\frac{1}{\alpha}\left(1 - \exp\left(-\frac{\bar{k}(T_0)w_0}{T_0\bar{F}(\bar{t})}\alpha\right)\right) - \frac{\xi}{2\bar{t}_{red}} \quad (27)$$

Equations 23, 26, and 27 can be solved numerically by Runge–Kutta fourth-order techniques with the following initial conditions:

$$T_0 = w_0 = 1, \quad \psi = \psi_{eq}(y_i) \quad (28)$$

On the basis of the above-described model, a study of low-temperature regeneration of diesel filters under a variety of reactor conditions is to be conducted in the following sections.

Application to the Study of Low-Temperature Regeneration

The theoretical approach and the numerical model presented above will be applied in this section and the results will be discussed and compared with experimental results presented by other researchers.[7]

Table 1 contains the main data of the engine employed in the experiments presented in ref 13. Table 2 presents geometrical and thermophysical data of the filter type and catalyst under consideration. Table 3 presents the kinetics employed in the model, to describe hydrocarbon and soot oxidation and catalyst oxides oxidation. Catalyst dosimetry in fuel and VOF content in soot vary according to the specific application.

As already explained in ref 8 the determination of ξ (the molar fraction of catalyst oxides over dry soot) is based on a good knowledge, apart from the concentration of catalyst in fuel, of the following data: a statistical distribution of engine operation points, which represents the actual vehicle driving during trap loading, in terms of particulate emissions; a particulate emissions map

Table 3. Reaction Scheme and Kinetics Parameters Employed in the Model

reaction	rate law	activation energy E_i/R (K)	frequency factor A_i [mol K/(m²)s]
C/O$_2$	$k_1 = kTe^{-E/RT}$	1.8×10^4	0.1
Ce$_2$O$_3$/O$_2$	$R_{ox} = k_{ox}[O_2](1 - \psi)e^{-E_{ox}/RT}$	1.8×10^4	1.0×10^{11}
CeO$_2$/C	$R_{red} = k_{red}e^{-E_{red}/RT}$	1.8×10^4	5.0×10^{10}
CeO$_2$/CH$_{1.8}$	$R_{red,HC} = \psi k_{red,HC}e^{-E_{red,HC}/RT}$	1.2×10^4	3.0×10^{20}

(engine-out, solid part, volatile organic fraction) for the trap equipped engine. The particular catalyst-doped fuel must be used to produce this map, due to the significant effect of some fuel additives on the raw particulate emissions of diesel engines and their composition.

Also, as it should be clear from the model presentation, an estimation of the parameter ζ (the molar fraction of volatile organic matter over dry soot), which is essential to the prediction of real world trap operation, is also feasible based on the same two series of input data, with the addition of a statistical distribution of exhaust gas temperatures at filter inlet.

As an example, Figure 5 presents the statistical distribution of exhaust temperatures at filter inlet measured on a 1.9-liter-TDI engined car in the European Urban Driving Cycle. According to this figure, exhaust temperatures at filter inlet over UDC with a modern diesel car do not exceed 300 °C. Thus, a significant part of the VOF of the particulate emitted is expected to be collected on the filter, adsorbed on the dry particulate. However, the VOF content of the particulate emitted may vary considerably in the range 10–300%. On the basis of experience from measurements of VOF in dilution tunnels, we may project and assume that the VOF content of the particulate emitted by the specific car in the European Urban Driving Cycle is on the order of 50%, which, after filtration, could result in a molar hydrocarbon content in soot on the order of $\zeta = 0.15$ or even less (depending on overall soot loading).

On the other hand, for the indirect injection engine of Table 1, a significantly higher VOF content of the soot emitted is observed in low speed UDC driving, on the order of 300% (again, we may project from measurements on a Teflon-coated filter in a dilution tunnel). This, after filtration, could lead to a significantly higher molar hydrocarbon content in soot on the order of $\zeta = 1.0$ or even more, depending on overall soot loading. The so-called erratic regeneration behavior at low temperatures is observed mainly on this type of engine, so we may start the simulation with this order of magnitude for ζ.

Assuming $\zeta = 1$ for the set of experiments presented in Figure 2, we may tune the model to produce the low temperature, erratic regeneration behavior demonstrated in this figure. The results may be presented in the form of equilibrium dry soot loading as function of exhaust temperature at filter inlet. According to the description of the specific experiments presented in ref 7 the computation is assumed to simulate the performance, during a total of 50 000 s, of a o.d. 5.66 × 6 in. 100 cpi wall flow filter installed on the 1900 cm³ diesel engine of Table 1, running at 2000 rpm on 100 ppm cerium-doped fuel, with a steady filter inlet temperature that covers the range 150–450 °C. The results of the tuning process are presented in Table 3. If we simulate each of these time-consuming experiments with the model tuned according to the kinetics parameters of Table 3, we may produce a computational prediction of
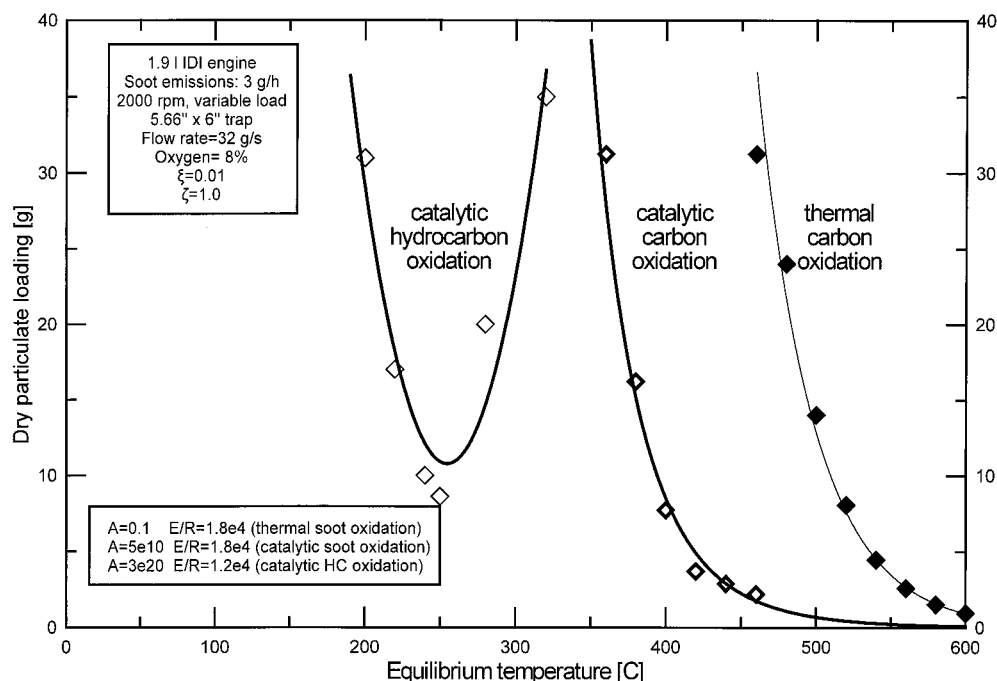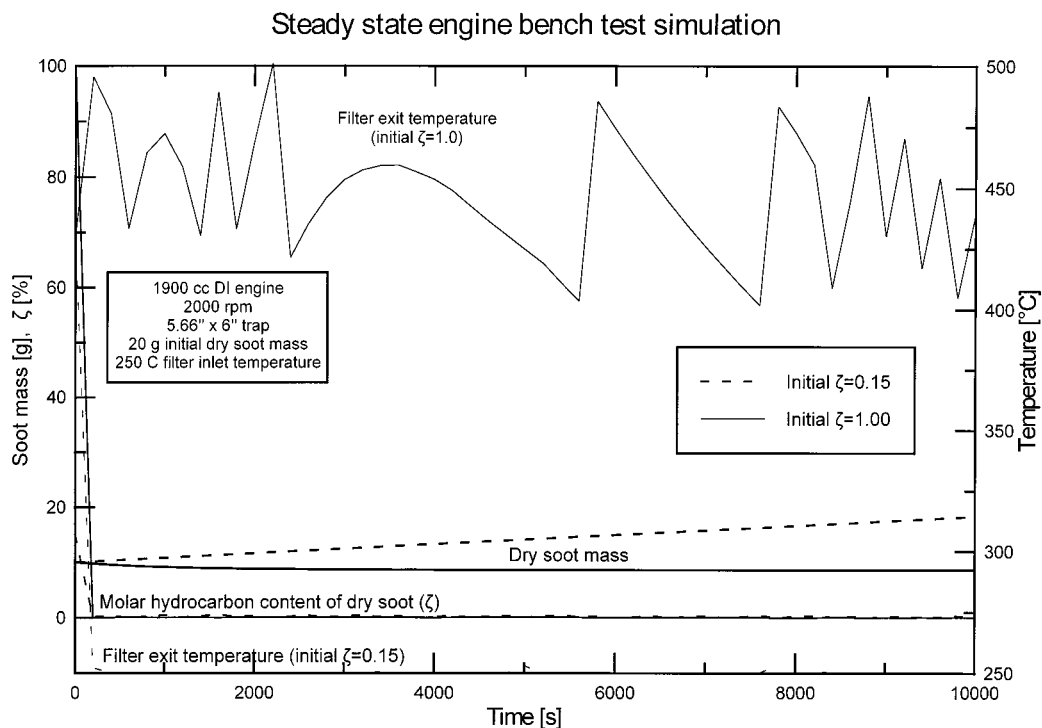
Figure 6. Computational prediction of equilibrium regeneration ranges during the steady-state experiments of Figure 2, with $\zeta = 1.0$ and 100 ppm concentration of cerium-based fuel additive.
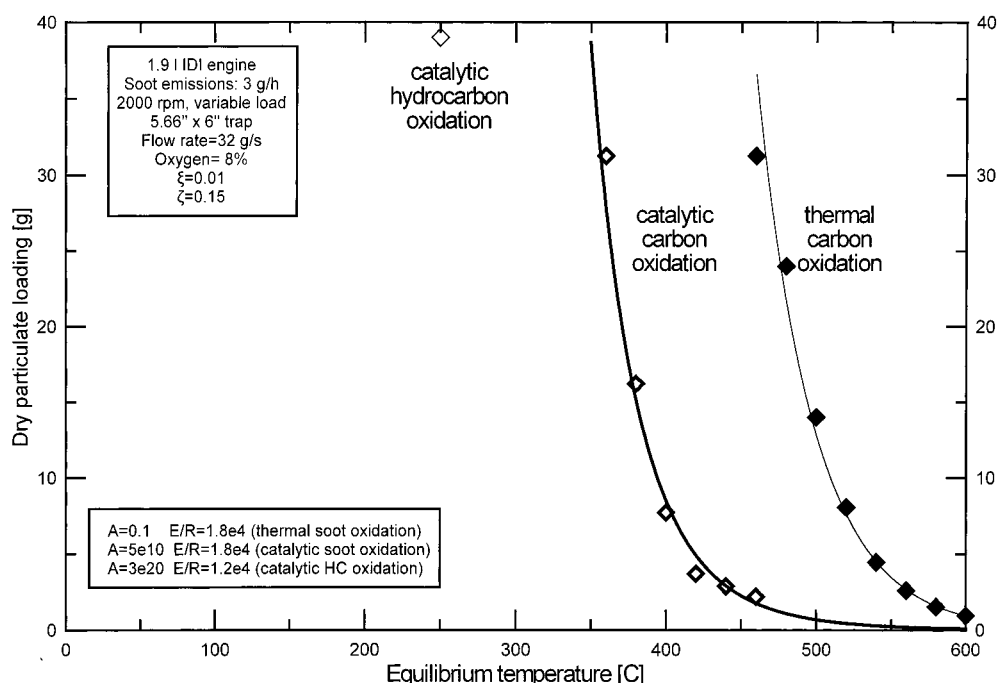
Figure 7. Computational prediction of equilibrium regeneration ranges during the steady-state experiments of Figure 2, with $\zeta = 0.15$ and 100 ppm concentration of cerium-based fuel additive.

the graph presented in Figure 2. Thus, we may observe in a clear manner the predicted catalytic activity in the filter, by means of the equilibrium filter loading attained for each different filter inlet temperature level. The results are presented in Figure 6. A comparison with the experimental results of Figure 2, shows that the improved model is able to predict the so-called erratic regeneration behavior at low temperatures, as well as the lack of regeneration in the range 300−380 °C. Also, it produces, with much better accuracy than the previous model (Figure 1), the deterministic regeneration behavior at higher temperatures.

A second series of model runs was carried out with a significantly lower value of molar hydrocarbon content in soot ($\zeta = 0.15$), to predict filter operation with an engine emitting particulate with very low VOF content, like the modern TDI diesel engines. The results are again plotted in Figure 7, where it is apparent that the computation does not predict any erratic regeneration range. According to the computational results, in this case we would observe an unsatisfactory filter performance, with high levels of filter loading that could eventually lead to filter overheating and melting. This is exactly what is known from the real performance of

Steady state engine bench test simulation

Figure 8. Computational prediction of the loading and regeneration behavior during the steady-state experiment of Figure 3. Filter inlet temperature is held constant at 250 °C. VOF content in soot: $\zeta = 1.0$.

filter systems installed on modern high injection pressure turbocharged direct injection diesel engines.

In addition to these overall results, it would be useful to present the evolution of dry particulate loading and molar hydrocarbon content (ζ) with time, during a typical experiment of the series that produced the results of Figure 6. This computation is assumed to simulate an experiment resembling to the one of Figure 3, with exhaust gas corresponding to 2000 rpm and a steady filter inlet temperature of 250 °C and 100 ppm cerium in fuel. On the basis of these assumptions, the model may simulate continuous steady-state operation of the filter-equipped engine with the results presented in Figure 8, assuming $\zeta = 1.0$ for the initial loading as well as for the continuous loading of the filter (3 g of total accumulated soot/h).

The computational prediction demonstrates a pattern that presents some similarity with the erratic regeneration patterns of Figure 3. Here one should mention that the computed evolution of ζ can only be indirectly experimentally checked.

To proceed with model predictions, one may mention that the continuous up-and-down shifts in engine operation (speed and load) points, associated with city driving, have been proven to be favorable to low-temperature regeneration by use of fuel additives, with IDI passenger car diesel engines and older DI heavy duty engines. This behavior could not be very well predicted by the previous mathematical models. Here we may simulate such an experiment containing a so-called sudden braking scenario, corresponding to a step increase in filter inlet temperature and flowrate, followed by a step decrease according to the pattern of Figure 9.

The results are presented in Figure 9, for two different levels of molar VOF content of dry particulate ($\zeta = 1.0$, $\zeta = 0.15$). According to these results, high VOF content in the particulate accumulated on the filter leads to low-temperature regeneration that may keep the filter almost clean during city driving at filter inlet temper-

atures less than 300 °C. However, a high filter loading that could be produced by prolonged operation in the range of 300−380 °C, and a subsequent enrichment of the particulate with VOF, could be followed by such a sudden vehicle braking scenario and lead to filter overheating and melting. This is exactly what is predicted by the computation of Figure 9 with $\zeta = 1.0$ where a maximum filter temperature of 1050 °C is predicted. Although statistically rare, this sequence of events is the main cause of the small or sever filter damages that are associated with fuel additive assisted filter systems and that limit filter durability. On the other hand, these dangerous situations are not predicted to happen with the relatively dry particulate emitted by modern TDI engines (Figure 9, $\zeta = 0.15$). However, in this case we also lack the favorable effects of erratic low-temperature regeneration. Thus, novel techniques should be sought to induce filter regeneration in these cases.

In this respect, one must also take into account that, in the ever changing conditions of real world low speed urban driving, we may observe a continuous and rather stochastic variation of volatile organic fraction content in the dry soot accumulated in the filter. This fact interacts very much with other nonuniformities regarding exhaust temperature and exhaust gas flow as well as soot and additive loading, to amplify the erratic occurrence of regeneration. Detailed study of low-temperature filter behavior should also include 3-D effects that further enhance the erratic character of low-temperature regeneration. However, this is a complex task that would require further experimental and computational effort. What we could see as a rational continuation of our work would be to conduct experimental work to support modeling of the real volatile organic fraction adsorption process in the particulate collected on a cellular ceramic filter under varying exhaust gas conditions and engine operation points.
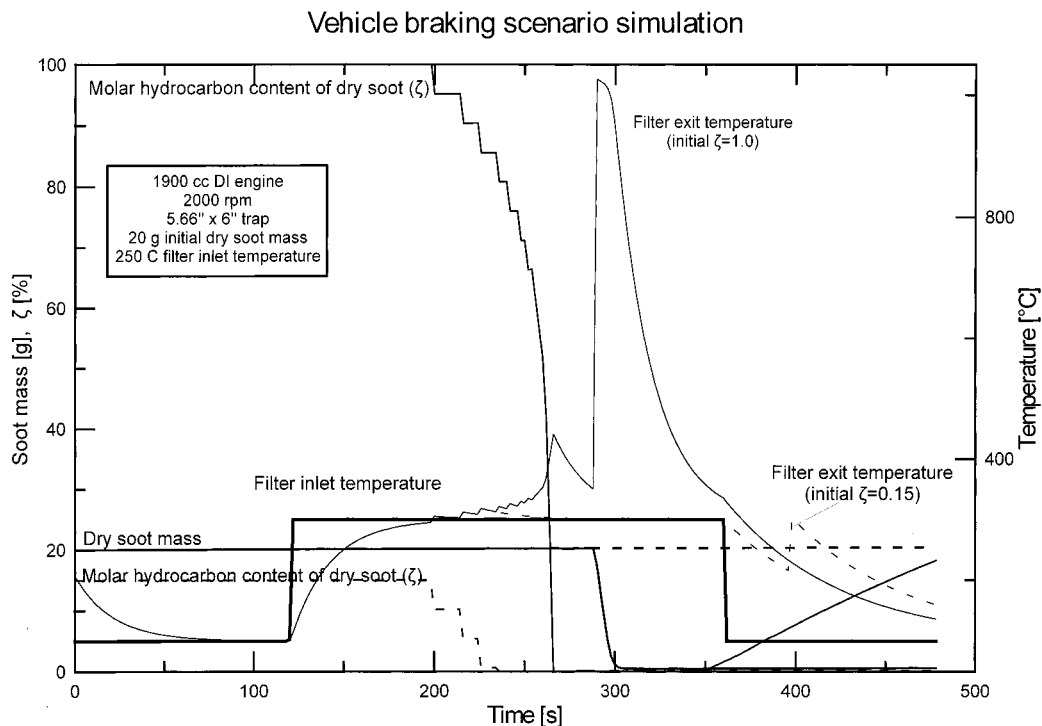
Figure 9. Computational prediction of the filter regeneration behavior during a step increase and decrease in exhaust temperature and flowrate (sudden vehicle deceleration scenario). VOF content in soot: $\zeta = 1.0$, $\zeta = 0.15$ (for comparison). Cerium based fuel additive was used, 100 ppm.

Concluding Remarks

More detailed study and modeling of the erratic nature of filter regeneration at low temperatures, corresponding to low speed city driving, is essential to the efficient support of the design of catalytic fuel additive-assisted diesel particulate filters.

This paper presents an improved 0-D catalytic regeneration model for the fuel additive assisted cellular ceramic diesel filter, which takes into account oxidation of the volatile hydrocarbons adsorbed in the soot.

The reaction scheme for this model is enhanced by additionally taking into account adsorbed hydrocarbons oxidation at low temperatures on the order of 200−350 °C, by the catalyst oxides present in the soot, originating from catalyst mixed in the diesel fuel, but also of the adsorbed hydrocarbons evaporation and desorption. However, the model is very empirical as regards the estimation of VOF adsorption in the filter soot layer under real exhaust gas conditions.

Even in this initial state of development, the model is demonstrated to predict, at least qualitatively, the low-temperature erratic regeneration behavior that is observed during real world city driving of diesel vehicles equipped with diesel filters and run on catalyst-doped fuel. This is a significant indicator of the validity of the reaction mechanism assumed.

Employing the improved model in the prediction of real world filter operation is expected to enhance model validity in supporting the design of filter systems with catalytic aids.

Furthermore, the results of the computations may be employed in the design of specific tests that will allow a valid experimental study of the process of adsorbed hydrocarbon oxidation and desorption at low temperatures, which is necessary in order to proceed in our understanding of this complex process.

Also, the model may be employed in the design of experiments necessary for better understanding and modeling of the VOF adsorption process in soot collected in diesel filters under varying raw (undiluted) diesel exhaust gas conditions.

Nomenclature

A: filtration area, m²

A/F: Air to fuel mass ratio

C_{pg}: specific heat capacity of exhaust gas, 1090 J/(kg K)

C_{p1}: specific heat capacity of soot deposit, 1510 J/(kg K)

C_{p2}: specific heat capacity of ceramic wall, 1120 J/(kg K)

C_{pj}: dimensionless heat capacity, $C_{pj}\rho_j/(C_{pg}\rho_1)$

Dam: Damkoehler number, $m_b/[F(0)t_{reaction}]$

E: apparent activation energy of soot oxidation, 150×10^3 J/mol

E_{ox}: activation energy for metal additive oxidation

E_{red}: activation energy for metal additive reduction with soot

$E_{red,HC}$: activation energy for metal additive reduction with adsorbed hydrocarbon

$\bar{F}$: dimensionless exhaust gas mass flow rate, $F(t)/F(0)$

$F(t)$: mass flow rate of exhaust gas, kg/s

$F(0)$: value of $F(t)$ at $t = 0$

ΔH: "combined" reaction enthalpy of soot oxidation, J/mol

$\Delta H_{(i)}$: enthalpy of reaction for CO_2 formation, 3.61×10^5 J/mol

$\Delta H_{(ii)}$: enthalpy of reaction for CO formation, 0.90×10^5 J/mol

ΔH_{cat}: enthalpy of reaction for soot oxidation by the catalyst oxides, J/mol

k_j: rate coefficient for the reaction in region j, m/s

k: collisions frequency factor, 6.0 m/(s K)

$\bar{k}_j$: dimensionless rate coefficient, $(s_1 w_b A_p M_a k_j)/[RT_b F(0)]$

M_a: molecular weight of exhaust gas, 29×10^{-3}

M_c: atomic weight of deposit, 12×10^{-3}

M_{HC}: molecular weight of adsorbed hydrocarbon, $13,85 \times 10^{-3}$

$\bar{M}$: soot−exhaust gas molecular weight ratio

m: accumulated soot mass, kg

p: exhaust gas pressure, 101×10^3 Pa

R: gas constant, 8.31 m³ Pa/(mol K)

s_1: specific area of deposit layer, 5.5×10^7 m⁻¹

T: temperature, K

$\bar{T}$: dimensionless temperature, T/T_b

T_b: temperature at $t = 0$, K

$T_i(t)$: inlet temperature, K

$\bar{T}_i$: dimensionless inlet temperature, T_i/T_b

T_{max}: maximum temperature developed during regeneration

$\bar{T}_{max}$: dimensionless maximum temperature developed during regeneration

t: time, s

$\bar{t}$: dimensionless time, $F(0)t/m_b$

t_{max}: dimensionless total regeneration duration

$t_{reaction}$: characteristic reaction time, $\rho_1/(s_1\rho_g k_j y_i)$, s

v: superficial velocity, m/s

w: thickness of the deposit layer, m

$\bar{w}$: dimensionless deposit layer thickness, w/w_b

w_s: channel wall thickness, m

$\bar{w}_s$: dimensionless wall thickness, w_s/w_b

x: distance, m

$\bar{x}$: dimensionless distance, x/w_b

y: oxygen concentration of the exhaust gas (mole fraction)

$y_i(t)$: mole fraction of oxygen at inlet

Greek Letters

α: index for the completeness of soot oxidation

ΔP: trap backpressure, Pa

ϵ: dimensionless group $C_{pg}F(0)w_b/A\lambda_1$

λ: bulk thermal conductivity

$\bar{\lambda}_j$: ratio of thermal conductivities, λ_j/λ_1

ξ: defined in eq 10

ρ: exhaust gas density, kg/m³

ρ_1: bulk density of the deposit layer, 550 kg/m³

ρ_2: bulk density of porous ceramic, 1400 kg/m³

ψ: defined in eq 11

Subscripts

b: initial condition

i: inlet condition

$j = 1,2$: indication of region 1 (deposit) or 2 (ceramic wall)

Literature Cited

(1) *FEA, HDV 2000: Requirements, Technical Feasibility and Costs of Exhaust Emissions Standards for Heavy Duty Vehicle Engines for the Year 2000 in the European Community*; Federal Environmental Agency, Berlin, June 1996.

(2) Koltsakis, G. C.; Stamatelos, A. M. Catalytic Automotive Exhaust Aftertreatment. *Prog. Energy Combust. Sci.* **1997**, *23*, 1−39.

(3) Moser, F. X.; Haas, E.; Schögl H. Zur Partikelemission von Nutzfahrzeug-Dieselmotoren. *Motortech. Z.* **1990**, *51* (5), 186−192.

(4) Montierth, M. Fuel Additive Effect upon Diesel Particulate Filters. *SAE Pap.* 1984, 840072.

(5) Wiedemann, B.; Doerges, U.; Engeler, W.; Poettner B. Regeneration of particulate Filters at Low Temperatures. *SAE Pap.* 1983, 830086.

(6) Wiedemann, B.; Neumann, K. Vehicular Experience with Additives for Regeneration of Ceramic Diesel Filters. *SAE Pap.* 1985, 850017.

(7) Lepperhoff, G.; Huethwohl, G.; Qin, L. Mechanismen zur Regeneration von Dieselpartikelfiltern durch Kraftstoffadditive. *Motortech. Z.* **1995**, *56* (1), 28−32.

(8) Koltsakis, G. C.; Stamatelos, A. M. Modeling Catalytic Regeneration in Wall-Flow Diesel Filters. *Ind. Eng. Chem. Res.* **1996**, *35*, 2−13.

(9) Koltsakis, G. C.; Stamatelos, A. M. Modes of Catalytic Regeneration in Diesel Particulate Filters. *Ind. Eng. Chem. Res.* **1997**, *36*, 4155−4165.

(10) Tan, J. C.; Opris, C. N.; Baumgard, K. J.; Johnson J. H. A Study of the Regeneration Process in Diesel Particulatte Traps using a Copper Fuel Additive. *SAE Pap.* **1996**, 960136.

(11) Pattas, K. N.; Stamatelos, A. M.; Koltsakis, G. C.; Kandylas, I. P.; Mustel, W. Computer Aided Engineering in the Design of Catalytically Assisted Trap Systems. *SAE pap.* **1997**, 970472.

(12) Wiedemann, B.; Doerges, U.; Engeler, W.; Poettner, B. Application of Particulate Traps and Fuel Additives for Reduction of Exhaust Emissions. *SAE pap.* **1984**, 840078.

(13) Lepperhoff, G.; Lueders, H.; Barthe, P.; Lemaire, J. Quasi-Continuous Particle Trap Regeneration by Cerium-Additives. *SAE pap.* **1995**, 950369.

(14) Clerc, C. J.; Johnson, J. H. A Computer Heat Transfer and Hydrocarbon Adsorption Model for Prediction Diesel Particulate Emissions in Dilution Tunnels. *SAE pap.* **1982**, 821218.

(15) Clerc, C. J. A Computer Model for predicting Temperature, Solids Concentration, and Adsorbed Hydrocarbon Concentration for Dilute Diesel Particulate Emissions. M.S. Thesis, MTU, Minneapolis, 1982.

(16) Simon, G.; Stark, T. Diesel Particulate Trap Regeneration Using Ceramic Wall-Flow Traps, Fuel Additives and Supplemental Electrical Ingiters. *SAE pap.* **1985**, 850016.

(17) De Soete, G. Combustion Catalytique des Suies Formées en Phase Gazeuse a Partir de Diesel-oils. Institut Français du Pétrole Techniques d'Applications Energétiques. *Rapport IFP* **1987**, June, No. 35378.

(18) Koltsakis, G. C.; Stamatelos A. M. Modeling Thermal Regeneration of Wall-Flow Diesel Particulate Traps. *AIChE J.* **1996**, *42*, 1662−1672.

(19) Satterfield, C. *Heterogeneous Catalysis in Practice*; McGraw-Hill Book Company: New York, 1980.