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Soot oxidation kinetics from TG experiments

Can they be used reliably in diesel particulate filter modelling tools?

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Abstract Thermogravimetric analysis (TG) has been used extensively for soot oxidation studies. Its known experimental and computational difficulties, however, have led to extended criticism concerning the reliability of the extracted kinetics and their potential for reliable reaction modelling. This study explores if TG kinetics could lead to successful simulation results notwithstanding the related disputes. For this, TG and mini-scale soot oxidation experiments with oxygen (O_2) were conducted. The TG kinetics reliability was controlled through comparison with the corresponding mini-scale results and by the satisfactory simulation of the mini-scale experiments.

Keywords Kinetics · Modelling · Oxidation · Soot · TG

Introduction

Diesel particulate filters (DPF) are considered an effective measure to reduce particulate matter emissions as they have filtration efficiencies up to 100%. The gradual loading of the filter increases DPF pressure drop and induces a fuel penalty. For this reason, the periodical regeneration of the DPFs, i.e. the combustion of the accumulated particulates, is necessary (e.g. [1, 2]). For the optimization of this procedure and in order to create viable and cost-effective systems, the automotive industry necessitates fast and economical evaluation of regeneration strategies. This task cannot be accomplished based solely on experimental data. Such an approach would be uneconomical, time-consuming and impractical. Thus good validated DPF modelling tools are invaluable for this purpose. The development of these models is very challenging, since it is necessary to describe multiple phenomena, such as heat and mass transfer and chemical reactions which take place simultaneously in the filter. Accurate input data, i.e. DPF and soot properties, inlet temperature and species concentration etc., together with soot reaction kinetics are also necessary, for successful modelling. Therefore, the study of soot combustion for the extraction of reliable chemical kinetics data that can be coupled in DPF models is very important.

The two main soot reactions of interest are the reaction with oxygen (O_2) and nitrogen dioxide (NO_2). Despite the significant progress in soot oxidation studies and the extended literature, there is still high uncertainty concerning the corresponding kinetic equations. Great scatter is observed regarding the reported activation energy (E) of both reactions (100–300 kJ/mol for O_2 and 40–70 kJ/mol for NO_2) and the order of reaction with respect to both the oxidant (0.6–1) and the running soot mass (0–nth) [e.g. 3, 4]. The basic challenges, which lead to those discrepancies, are related with the sample and experimental setup characteristics. The commonly used synthetic soot samples are not necessarily equivalent to real diesel soot. Then again the quality of real soot is not constant and depends on engine and operational parameters. And, finally, the experimental setup itself may impose uncertainties, such as rate controlling mass transfer limitations, etc.

As far as the experimental possibilities are concerned, there are three main groups in this direction, namely full and mini-scale experiments and thermogravimetric

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analysis (TG). Each one of these setups has specific characteristics and limitations. From full-scale experiments to TG, the procedure is simplified and more easily controlled but the conditions deviate from real world applications.

In particular, TG is a fast, economical and easy to use process with the important advantage of the direct measurement of sample mass evolution (the variable on which kinetic calculations are basically based). On the other hand, the extracted kinetics seem to depend on the experimental conditions (initial sample mass, heating rate, etc.) [5] and the applied calculation method [6]. Furthermore, mass transfer limitations may exist, since the reaction gas is supplied to the solid sample through diffusion [3]. These known experimental and computational difficulties have led to extended criticism concerning the reliability of TG results [7].

Mini-scale reactors usually involve bed reactors while also ad hoc setups, which include, for example, the use of loaded filter substrate test species in the reactor, have been reported [4]. In these setups, the gas passes through the sample, similarly to real DPFs where the exhaust gas flows through the collected soot. Furthermore, effort is usually made to keep the beds very thin and to allow them to operate in a differential mode with negligible change in the oxidant concentration, in order to avoid mass transfer limitations [4]. Therefore, in contradiction to TG, such limitations are rarely reported [e.g. 8–10]. On the other hand, the necessary soot mass evolution is determined through the carbon mass balance in this case. Thus, carbon monoxide (CO) and carbon dioxide (CO_2) analyzers are necessary, something which renders these setups quite more complicated and less practical than TG.

However, when evaluating soot oxidation experiments for modelling purposes it should always be kept in mind that the rate equations used in these models describe only the chemical reaction. Therefore, the used kinetics should be intrinsic, i.e. they should be uncoupled from mass transfer limitations and deviations due to the setup characteristics and calculation steps. This means practically that the same reaction rate should be determined for the same sample independently of the used setup; something that is not always the case.

In this context, the goal of this study was to explore if TG kinetics could in fact lead to reliable soot oxidation simulation results notwithstanding the related abovementioned disputes concerning the method. For this purpose, soot oxidation with O_2 was studied separately in a TG and a mini-scale reactor in the temperature (up to 700 °C) and concentration (up to 22% O_2/N_2) range relevant to real DPF applications. As mentioned above, mini-scale experiments are generally accepted as a better means for determining reaction kinetics mainly because they allow better contact between soot and the reaction gas. Therefore, they were used to control the reliability of the TG extracted kinetics. First direct comparison of the measured rates with both setups was done. Then, it was explored if the extracted TG kinetic equations could be used successfully in a commercial DPF modelling tool for the simulation of the mini-scale experiments. For this purpose, the Axisuite (http://www.exothermia.com/) modelling platform was used. Axisuite is a modular simulation platform covering the complete range of engine exhaust components. The module Axifoam v3.210, which refers to the simulation of foam substrates, such as those used in the mini-scale study was used. The simulation scenarios were created based on the mini-scale experiments.

The study is focused on oxidation with O_2 because very slow reaction rates were observed when NO_2 concentrations (up to 1,000 ppm) and temperatures (up to 500 °C) close to those anticipated in typical diesel exhaust values were used in TG. The used NO_2 concentrations were very low, and they were apparently causing limitations to the transfer of the reactive species to the soot sample. For example, in an experiment at 400 °C with 475 ppm NO_2, a reaction rate of 0.002 min^{-1} was measured in the TG while a reaction rate of 0.02 min^{-1} (i.e. approximately 10 times higher) was measured in the mini-scale under the same conditions. These low reaction rates increased the necessary experimental time greatly, a fact that rendered the TG study of soot oxidation with NO_2 under the desired conditions unpractical.

Methodology

TG experiments

Details about the TG experimental setup are given elsewhere [11, 12]. Both real diesel soot from a loaded DPF and synthetic soot (Printex U) were used. Isothermal and non-isothermal tests were done at different O_2 concentrations (5–22% O_2/N_2), sample masses (0.5–10 mg), heating (5–20 °C/min) and flow rates (80–100 ml/min). The reaction stoichiometry was determined through CO/CO_2 measurements at the TG outlet. The used protocols and details about the TG experimental study are described in [12].

Mini-scale experiments

Details about the mini-scale reactor that has been developed and used are presented in [13]. Soot was sampled on metal foam discs under steady flow conditions. For the oxidation tests, the loaded discs were placed in a flow reactor which was externally heated in a high temperature

Table 1 Mini-scale experimental protocols

Protocol	Flow rate/l min^{-1a}	Mass/mg	Reaction gas	Temperature range/^{o}C
Isothermal	6	15–20	22% O_2	595, 620, 650
			10.1, 14.9% O_2	600
Step temperature increase	6	15–20	22% O_2	250, 350, 450, 550, 650
Non-isothermal	1.5–7	20–63	22% O_2	Up to 650 °C
	5^b	~90		
	7^c	60		

[a] All tests were done with foams [14] of 800 μm pore size except tests (b) and (c) where a combination of both foams and only foam with 580 μm were used, respectively

tube furnace. The flow rate and temperature through the stacked foams could be independently controlled. Three different temperature protocols (isothermal, non-isothermal and step temperature increase) were used. The rate of the reaction with O_2 was measured using all temperature protocols up to 650^{o}C and with O_2 concentration between 10.1 and 22% O_2/N_2. The experimental parameter influence was investigated through non-isothermal measurements with 22% O_2/N_2 and by varying the reaction gas flow rate (1.5–71 pm), the soot mass (up to 115 mg), the foam type [14] (pore size of 800 and 580 μm) and the disc number. The used protocols are described in Table 1.

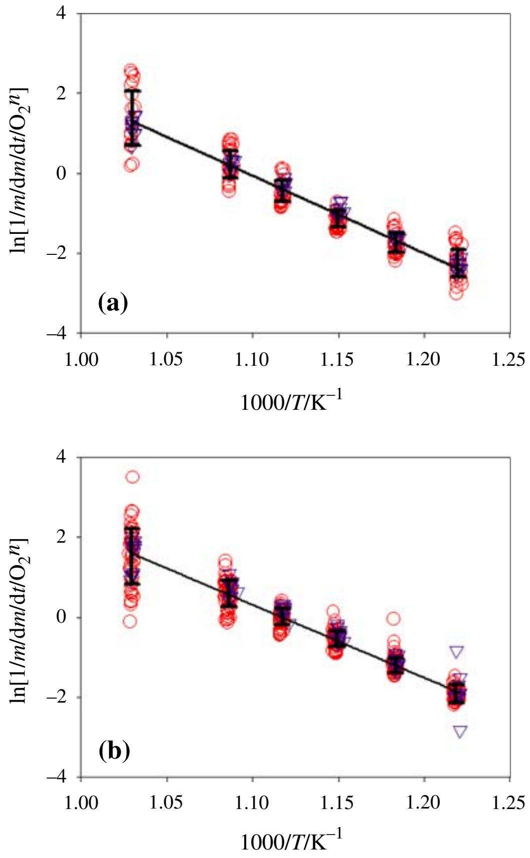


Fig. 1 Aggregated Arrhenius plots (*open inverted triangle* isothermal data, *open circle* non-isothermal data): **a** soot, **b** Printex U (the *error bars* correspond to ±standard deviation)

Kinetic formulations

Subsequently, the basic magnitudes which appear in this paper are defined. The conversion fraction (α) is defined as:

$$a = 1 - \frac{m}{m_0} \tag{1}$$

where m and m_0 are the running and the initial sample mass, respectively.

The reaction rate constant (k) is defined as follows:

$$\ln\left(\left(\frac{1}{m}\cdot\frac{\mathrm{d}m}{\mathrm{d}t}\right)\Big/[\mathrm{O}_2]^n\right) = \ln(k) = \ln A - \frac{E}{RT} \tag{2}$$

A, E and n are the pre-exponential factor, activation energy and reaction order with respect to O_2, respectively. $[O_2]$ is the

Table 2 The kinetic expressions derived from TG experiments

	Kinetic equation
TG (soot)	$1.72 \times 10^9 \cdot \exp\left(-\frac{161219}{R \cdot T}\right) \cdot [\mathrm{O}_2]^{0.75}$
TG (Printex U)	$6.72 \times 10^8 \cdot \exp\left(-\frac{151492}{R \cdot T}\right) \cdot [\mathrm{O}_2]^1$

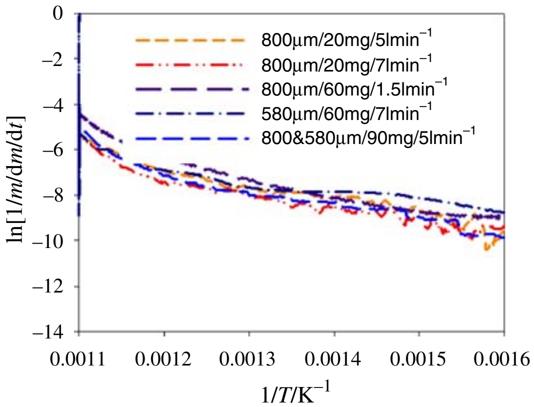


Fig. 2 Aggregated Arrhenius plots for the non-isothermal mini-scale experiments

molar fraction of O_2 in the reaction gas. R, T and t are the universal gas constant, temperature and time, respectively.

Results and discussion

TG experiments

Details about the TG kinetic study and the discussion of the kinetic results can be found in [12]. A short summary of the results is given here. Very good agreement between the k determined at 550–575–600–625–650 and 700 °C from the isothermal and non-isothermal experiments was observed both for soot and Printex U. The corresponding k can be found in Fig. 1 in the form of an Arrhenius plot. For the non-isothermal experiments the presented k correspond to the instantaneous values, that were measured at each specified temperature during the experiment. As discussed extensively in [12], the determined activation energy level ($\sim$160 kJ mol^{-1} for soot) is in the range reported in literature for experiments where kinetics control the reaction [9]. Furthermore, the calculated effectiveness factors (for soot they were in the majority greater than 0.9) and the fact that the pellet height remains unchanged during oxidation indicate also that chemical kinetics control the reaction (Regime I as defined for example in [15, 16]). The proposed kinetic equations extracted from the TG data can be found in Table 2 both for Printex U and real soot.

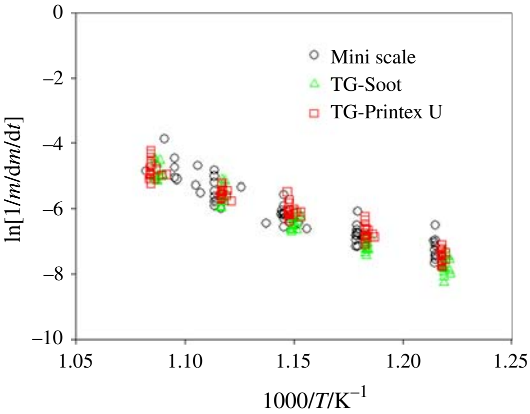


Fig. 3 Comparison of the reaction rates measured between 550–700 °C with 22% O_2/N_2 with the TG and the mini-scale reactor

Mini-scale experiments

The study of soot oxidation kinetics in the mini-scale reactor revealed that it assures practically isothermal conditions in the sample (the difference between the inlet and outlet temperature was generally better than 1%). As can be seen in Fig. 2, k was not found to depend either on the reaction gas flow rate or the sample mass, indicating that there are no mass transfer limitations and that the chemical kinetics control the reaction under the investigated conditions.

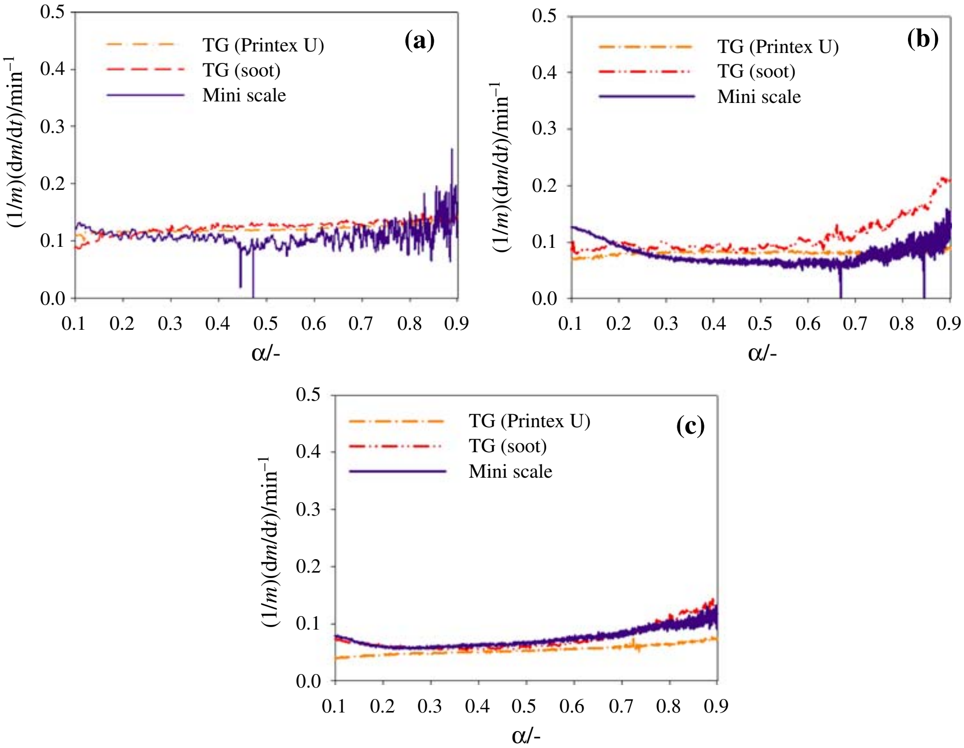
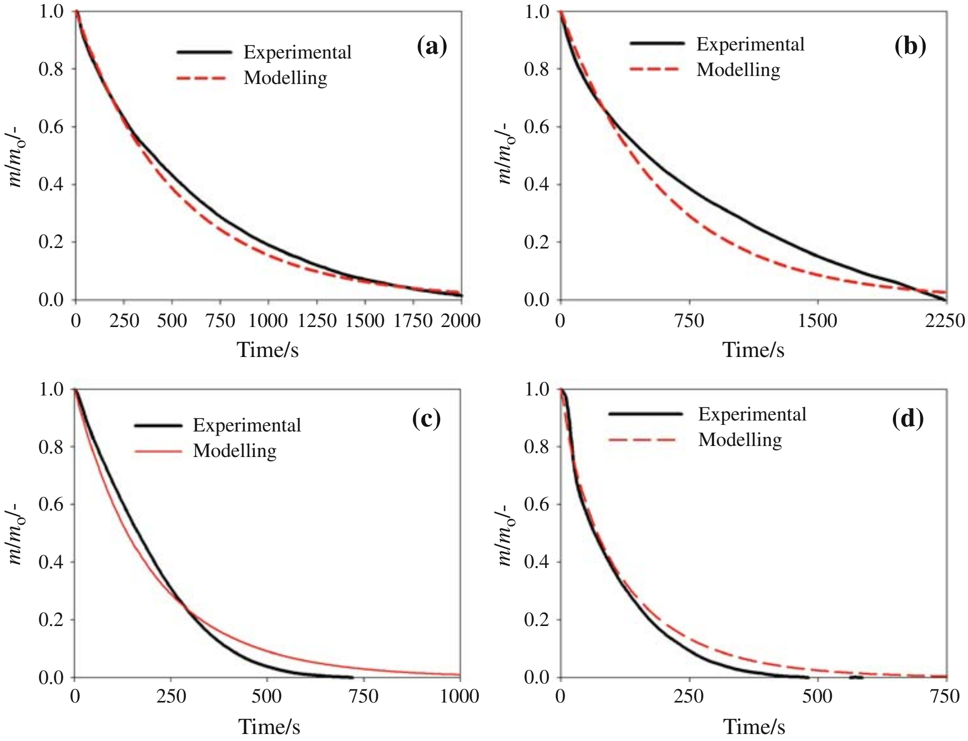


Fig. 4 Reaction rates measured by TG and mini-scale at 600 °C and **a** 22%, **b** 14.9% and **c** 10.1% O_2/N_2

Fig. 5 Experimental and simulated curves from isothermal experiments at: **a** 600 °C/22% O_2/N_2, **b** 600 °C/10.1% O_2/N_2, **c** 620 °C/22% O_2/N_2 and **d** 650 °C/22% O_2/N_2



Reaction rate comparison

First, the measured $(1/m)(dm/dt)$ values are compared. Figure 3 shows a comparison of the measured values in the form of an Arrhenius plot. The TG (both for soot and Printex U) and mini-scale data from experiments between 550–650 °C with 22% O_2/N_2 are presented. Figure 4 shows $(1/m)(dm/dt)$ evolution over α from experiments at 600 °C for three O_2 concentrations (22, 14.9 and 10.1% O_2/N_2). It is observed that both the levels and the tendencies of k for soot oxidation with O_2 were consistent for the tested conditions.

Modelling

As already mentioned above, in order to test the validity of the TG extracted kinetics, the mini-scale experiments were simulated using a commercial DPF modelling tool. Figure 5 shows the experimental and simulated curves from isothermal experiments at: (a) 600 °C/22% O_2/N_2, (b) 600 °C/10.1% O_2/N_2, (c) 620 °C/22% O_2/N_2 and (d) 650 °C/22% O_2/N_2, respectively. Figure 6 shows the experimental and simulated curves from a single non-isothermal experiment with 22% O_2/N_2. The TG kinetic equation determined for soot (Table 2) was used for these simulations. It is observed that the experimentally determined kinetics give reliable results in all investigated cases. Similarly good agreement was found when the kinetics determined by the TG experiments with Printex U (e.g. Fig. 6) were used.

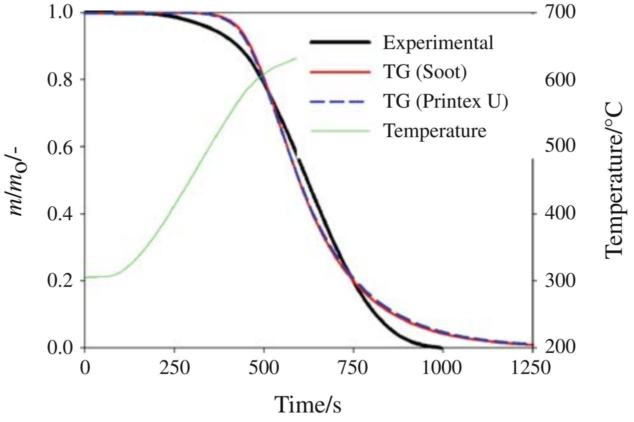


Fig. 6 Experimental and simulated curves from a non-isothermal experiment with 22% O_2/N_2

Conclusions

Soot oxidation was studied separately in a TG and a mini-scale reactor. Consistent reaction rates were determined by both experimental setups. Furthermore, the TG extracted kinetics led to reliable modelling of soot oxidation with O_2 under isothermal and non-isothermal conditions and for a wide range of temperatures (up to 650 °C) and concentrations (up to 22% O_2/N_2).

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