EXPERIMENTAL DETERMINATION OF THE ACTIVATION ENERGY OF SOOT OXIDATION DURING REGENERATION PROCESS IN DIESEL PARTICULATE FILTER

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Abstract

In the models of regeneration of diesel particulate filters the reaction rate of soot oxidation is assumed to be of Arrhenius type temperature dependence. In that form reaction rate has two characteristic coefficients: an activation energy and pre-exponential coefficient. The activation energy determines the increase of the rate of reaction with temperature in the reaction region. The pre-exponential factor depends on model and gives the unit of reaction rate. In the literature, there are many different values of the activation energy, which were determined at different test conditions.

Our experimental studies were focused on creating test conditions very close to the real diesel particulate filter. The test bed consists of the ceramic plate covered with soot, which was put in the hot gas flow. The hot gas setups almost adiabatic condition for the reaction region. The flowing gas was the mixture of oxygen and nitrogen. During the experiments, the temperature above the plate and weight of the plate with soot were measured. For different temperatures of gas, we received various rates of soot depletion. The mass fraction of oxygen was changed too. Based on the collected data, the activation energy was calculated.

***Keywords**: particulate, soot, filter, rate of reaction*

1. Experimental test bed

The comparison between activation energy values in the papers on simulations and experiments gives disagreement. The authors of simulations articles assume activation energy between 140 kJ/kmol and 160 kJ/kmol. The researchers, who measure that parameter in experiments give energy from 45 kJ/kmol to 180 kJ/kmol. During our first simulations, we looked very carefully for the appropriate value. Another question was an influence of ceramic and particulate filter channel geometry on activation energy. The activation energy is measured in calorimeter, which has conditions not similar to filter channel. A ratio of gas to soot and availability of oxygen in calorimeter are higher than in filter, as a consequence of channel geometry. Determination of the activation energy requires building at the suitable test bed.

The special test bed was build and the new approach to the measurement of activation energy was tested. Specific conditions of filter require use of special materials. Figures 1 and 2 show the schematics of test bed.

1.1. The block of electric heaters

The heater consists of special designed compact electric heaters. Their power is about 3 x 1000 W. They are in a heat-resistance pipe. Thermal insulation material was put between the heaters and pipe. Radiation shields are used for better gas heating and reduction of heat loss. Problem of heat loss is very important because the temperature in the heater can reach up to1000 C, the second thing is the temperature of the heat-resistance pipe (health and safety at work problem). The addition of thermal insulation mats are used to reduction outside surface temperature.

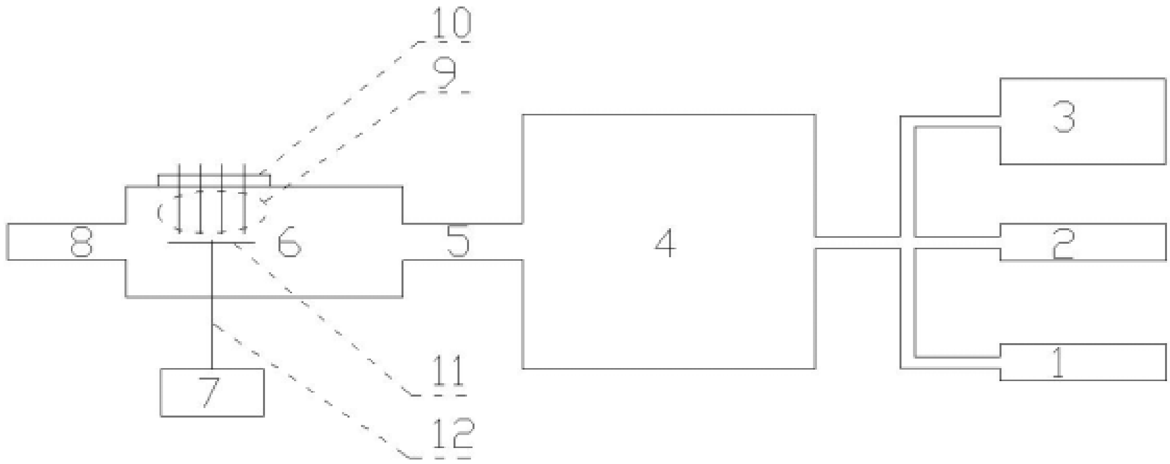

Figure 1. Schematic of test bed; 1 - cylinder with Nitrogen ; 2 - cylinder with Air; 3 - compressor of air; 4 - the block of electric heaters; 5 - connective channel; 6 - test region; 7 - lab scale; 8 - outlet channel; 9 – thermocouples; 10 - cover with thermocouples; 11 - plate with soot; 12 - stick, connector between scale and plate

1.2. Test region

Test chamber consists of two layer of acid resistance steel, between them thermal insulation material is placed. High temperature and small flow rate give large down stream temperature loss. The test bed was modified after a few experiments. Special insert was build. It consists of two thermal insulation mats between the layers of heat-resistance steel. The insert has a narrowing at measuring space. In the next step, outdoor thermal isolation was installed on the chamber. Character of heater work requires a flow channel modification. The heat accumulator straightens non-linear temperature lines (delay temperature fluctuation).

Thermocouples were installed in the nearest possible place for high accuracy. They hardly touch soot. Thermocouples can’t touch the plate. Every touch disturbs measurement.

1.3 Block of rotameters

The repeatability experiment is assured by constant flow rate of gas. Fixed gases ratio (ratio of nitrogen to oxygen) is controlled by rotameters. Use of rotameters is easier and allows cost reduction. Preparation of gases mixture in cylinder would be more expensive. What is more, preparation of gases mixture time consuming and would increase experiment time.

1.4. Plate with soot

During experiment, soot covered the ceramic plate. The use of ceramics gives good approximation test conditions to real filter conditions. Corundum plates were chosen to the experiments because only that material can be bought in reasonable time and price. After a few tests, way of plate was changed. There were sides build and connected with the plate. It reduced side-flow and removed indirect combustions.

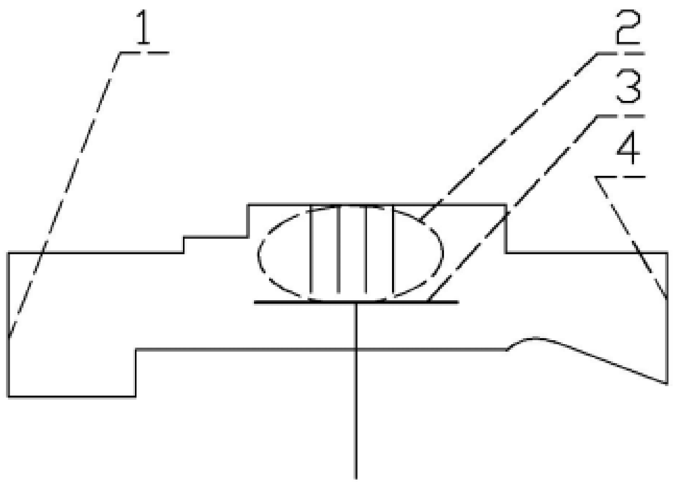

Figure 2. Scheme of measuring space; 1 - outlet of gases; 2 – thermocouple; 3 - plate with soot; 4 - inlet of heat gases from the heat accumulator

2. Experimental measurements

Measurement of temperature is based on a few thermocouples. They are situated in a few planes at longitudinal direction (average 3 planes) and radial (3-4 radiuses from symmetry axis). That solution is adequate when one verifies simulation model, but is not appropriate for finding the activation energy. In general, a lot of parameters, is assumed. All model's parameter influence one another, thus finding the most important one is very difficult.

In the approach presented in the article, we concentrate on soot combustion. Main measurements are the reaction region temperature and mass of soot during oxidation. Continues measurement of the soot mass is the most complicated experimental task. Many technical solutions were motivated by this measurement. Measurements were carried out at the same flow rate and gas mixture.

The following equipment was used:
- Weight: balance Radwag WPS-720/C2, repeatability 1 mg
- Temperature: thermocouple K, exposed junction .
- Flow rate: rotameters

According to filter conditions and measuring space geometry, the flow rate is assumed at the level of 5 m^3/h. Only few experiments were carried out at the lower flow rate set at 3 m^3/h.

3. Experiments

The test bed was heated during the 2-3 hours. The heating time and little volume of technical gases require a specific working procedure:
1. heat up test bed to a necessary temperature (gas - compressed air)
2. stabilization of temperature field in measurement region (gas - compressed air)
3. carry out of the measurements: temperature and mass decrease
   a) gas is changed (from air to nitrogen)
   b) plate with soot is putted in the place
   c) soot is heated up
   d) nitrogen flow rate is reduced and air flow rate is increased to suitable ratio
   e) combustion parameters are recorded
   f) after burn off, gas is changed to nitrogen

4. after carrying out a few experiments were carried out, the heater is turned off and test bed is cooling by flowing air.

Compressed air is chosen as a main gas during heat up and heat down, because this medium is accessible and gases in cylinders are more uncomfortable.

4. Data analysis

The Arrhenius equation parameters are based on experimental data. Experimental parameters are presented in the figures 3. The figures show the changes of the temperature and soot mass.

The Arrhenius equation has the form:

$$k = k_0[O_2]\exp\left(-\frac{E}{RT}\right) \qquad [1]$$

where:

E activation energy

T temperature

R gas constant

$[O_2]$ mass ratio

k_0 pre-exponential factor

The log of two sides gives:

$$\ln(k) = \ln(k_0[O_2]) + \left(-\frac{E}{R}\right)\left(\frac{1}{T}\right) \qquad [2]$$

The above equation is similar to the first order polynomial of the form:

$$y = a_0 + a_1 x$$

where:

$y = \ln(k)$

$a_0 = \ln(k_0[O_2])$

$a_1 = \left(-\frac{E}{R}\right)$

$x = \frac{1}{T}$

There are only two experiments needed to find a_0 and a_1. The needed parameters are taken from a figure. Explanation of the approach is presented below.

The figures were useful to determine *y* and *x*, which could be calculate from *k* and *T*. Temperature *T* is the temperature of reaction region T_2 in the figure. Pre-exponential factor *k* is calculated in a following way:

$$k = \frac{m1 - m2}{t2 - t1} \qquad [3]$$

where:

m1 soot mass at the beginning of the process in given period

m2 soot mass at the end of process in given period

t1 initial time of given period

t2 final time of given period

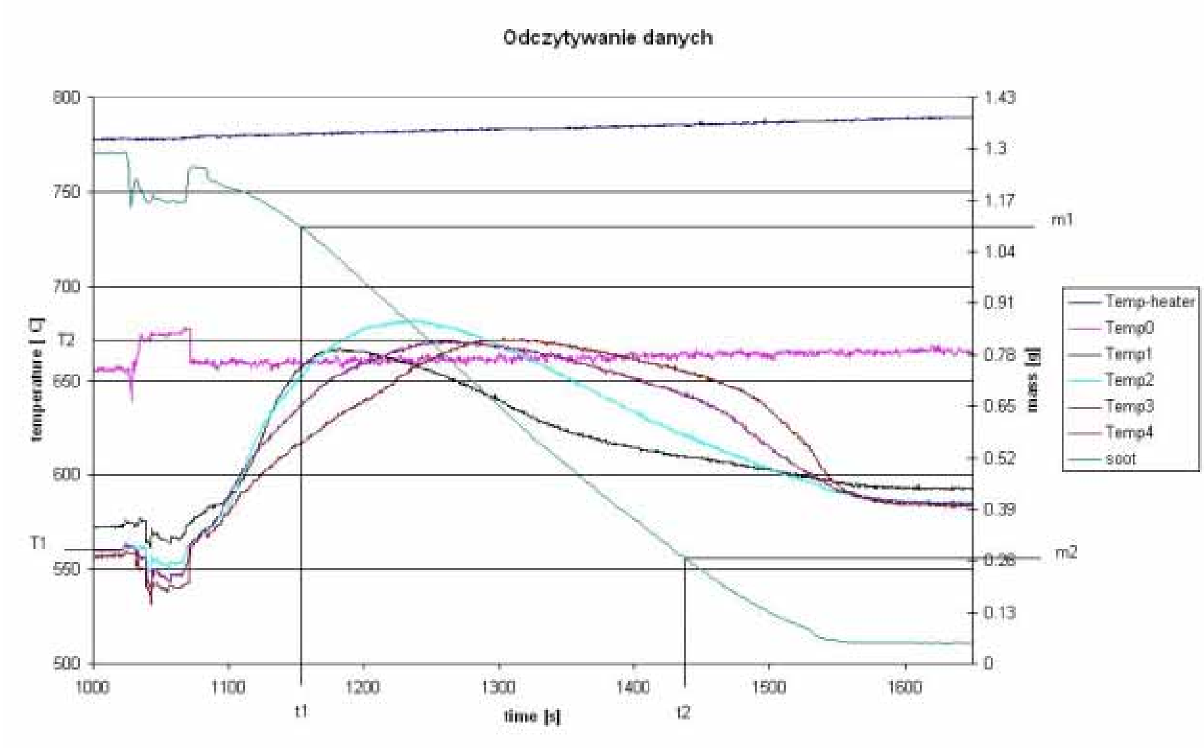

Figure 3. Data analysis procedure

Thus only five parameters from sample figures are needed to find the activation energy and the pre-exponential factor. If more then the two figures were used to find needed parameters, would be better adjusted. Researcher may change reaction zone temperature, for better adjustment.

5. Results and discussion

Most of experiments were carried out with technical soot N-772. Some of them were carried out with engine soot. The source of soot were the Warsaw city buses. The soot was collected from inside surface at buses exhaust pipes.

The N-772 parameters: bulk mass 460 kg/m^3, Mean diameter 60-100 nm.

Diesel engine soot has lower density about 3-4 times than the technical one. Main challenge during experiment was lightness (volatility). If flow rate is too high, soot is flown out from the ceramic plate. Maximal safe flow rate should be determined before experiments. Figure 1 shows a verifying test for N-772 soot. The flow out is unimportant at flow rate equal 5 m^3/h and temperature higher than 650 C.

Engine soot has higher lightness, so boundary flow rate is lower. The acceptable flow rate is equal to 3 m/h.

Figures 5,6,7 present the experiments and a reaction rate based on the experiments. The figures show the reaction rate for:

- technical soot N-772 at 21 % oxygen
- technical soot N-772 at 21 % oxygen
- diesel soot at 21 %

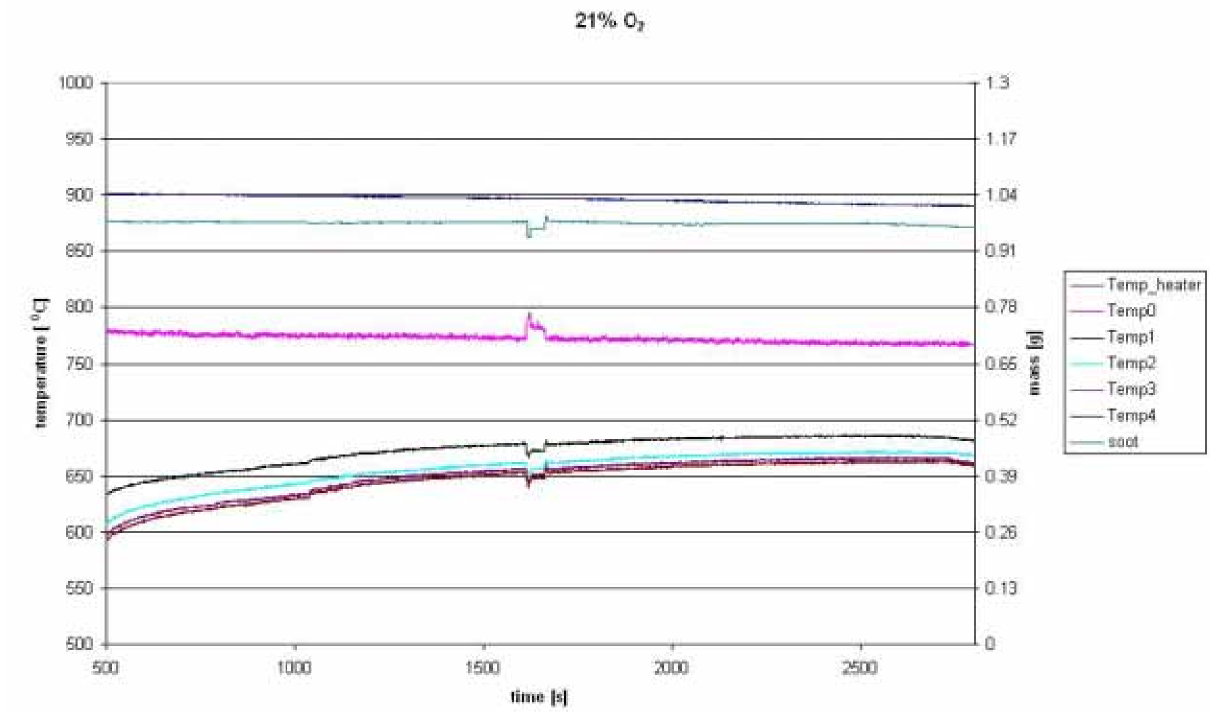

Figure 4. Soot mass loss during experiment with temperature over 650 C and flow rate 5m3/h

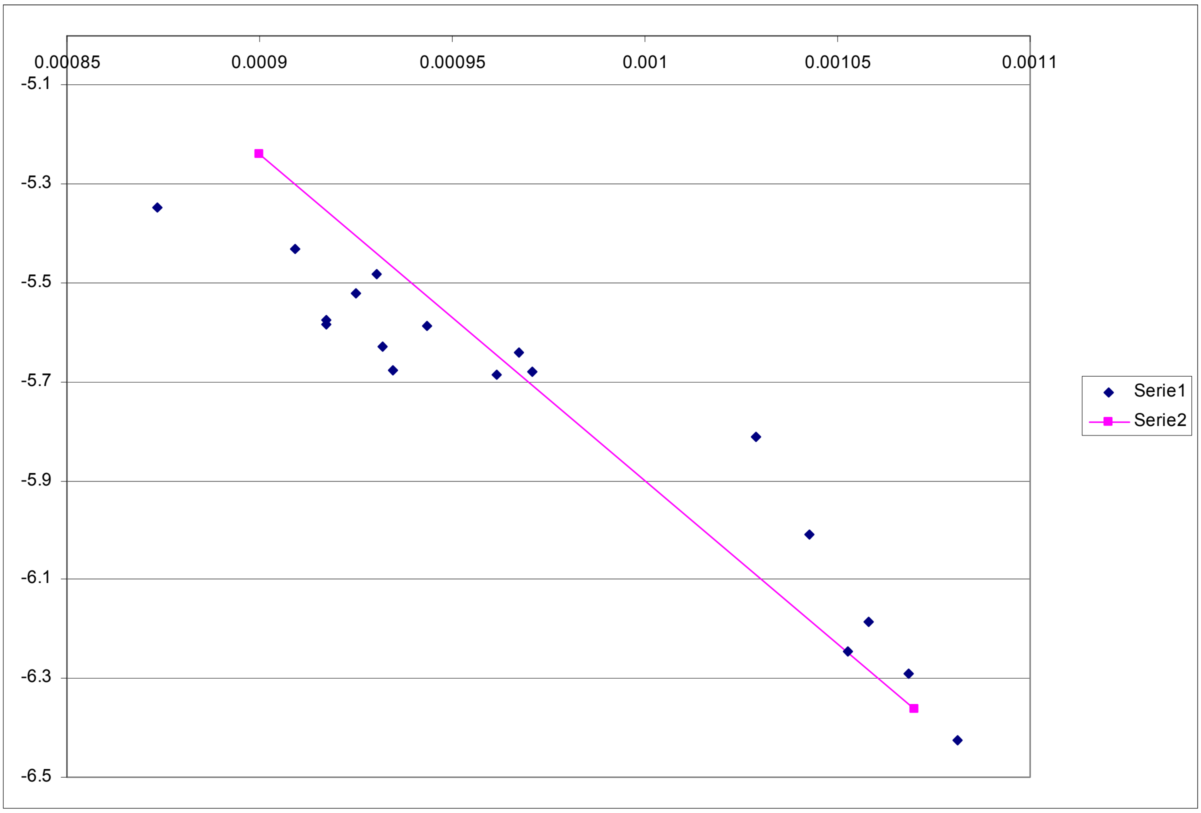

Figure 5. Experiments with technical soot N-772 at 21% oxygen

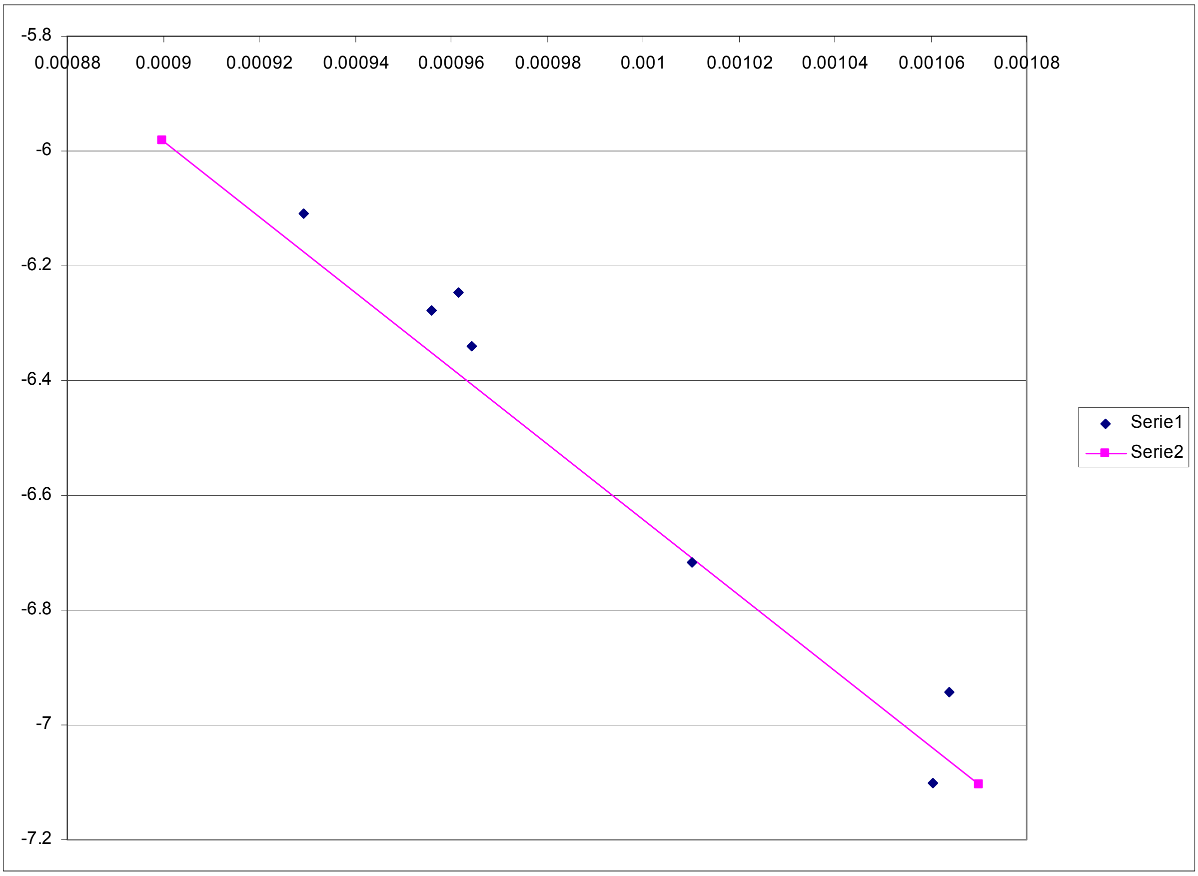

Figure 6. Experiments with technical soot N-772 at 10% oxygen

Figure 7. Diesel engine soot experiments at 21% oxygen

The Arrhenius parameters of presented reaction rates are as follows:

	N-772 21%	N-772 10%	Diesel 21%
k [1/s]	9.589299	9.589299	4.30875
E[kj/kmol]	54872.4	54872.4	45727

It should be noted, that the activation energy is on the low range as is presented in the literature of the subject. The technical soot arises in specific facility not in a diesel engine. The soot is complex particulate and it consists of chemical compounds of different reaction rates characteristics. The soot reaction rate is a result of a few reaction rates so the activation energy is an averaged value as well. Low value engine soot is a result of conditions in the exhaust pipe. The temperature is low inside, so the chemical reactions are stopped,. Many unburned organics components deposit on the soot particulates. The organics components usually are low value of the activation energy.

The soot complexity has been observed during experiments. There are remainders of the soot after combustion at the low temperature. If temperature increases, unburned soot burns off. The above observations can be done during a test of the minimal ignition temperature. The minimal ignition temperatures have been determined at the level of about 530-540 C for N-772 soot and 335C for diesel engine soot. These values have been checked for 21 % oxygen concentration in flowing gas. As the following figure shows, oxidation is possible at the lower temperature, but it does not give visible temperature increase.

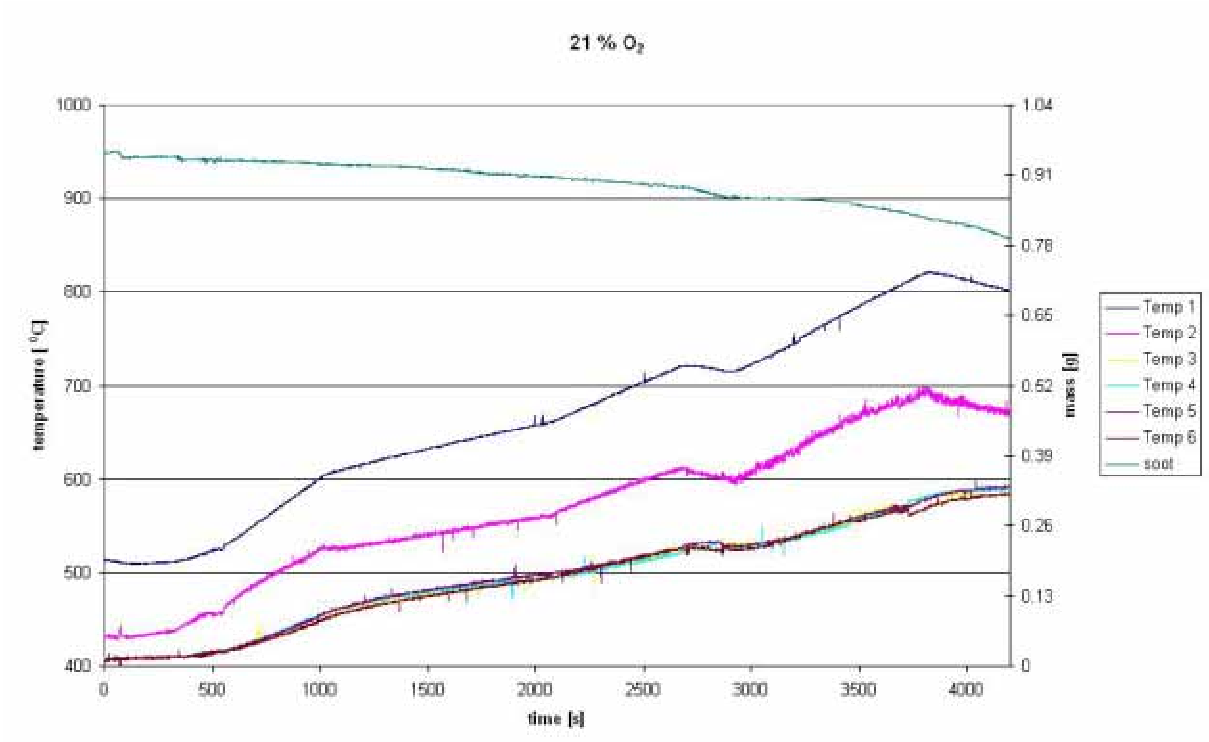

Figure 8. Slow oxidation of soot

The temperatures given above are not useful in the particulate filters. The conditions in the filter and on a test bed are different. Small dimensions of the filter channel and a little value of heat exchange coefficient generate high temperature increase during regeneration. Thus the initial temperature can be lower in the filter than on the test bed.

When the soot remaining is significant, the determined reaction rate is only the reaction rate of the oxidized part of the soot. Our aim has been to determine the activation energy of the whole soot (not part of it), thus activation energy has been determined based on experiments without soot or with little amount of soot after combustion. The experiments that have been chosen were the ones with suitable range of temperature.

Our experiments have shown that the second important parameter, which determines reaction rate and process temperature is the mass fraction of oxygen. The influence of oxygen concentration is shown below:

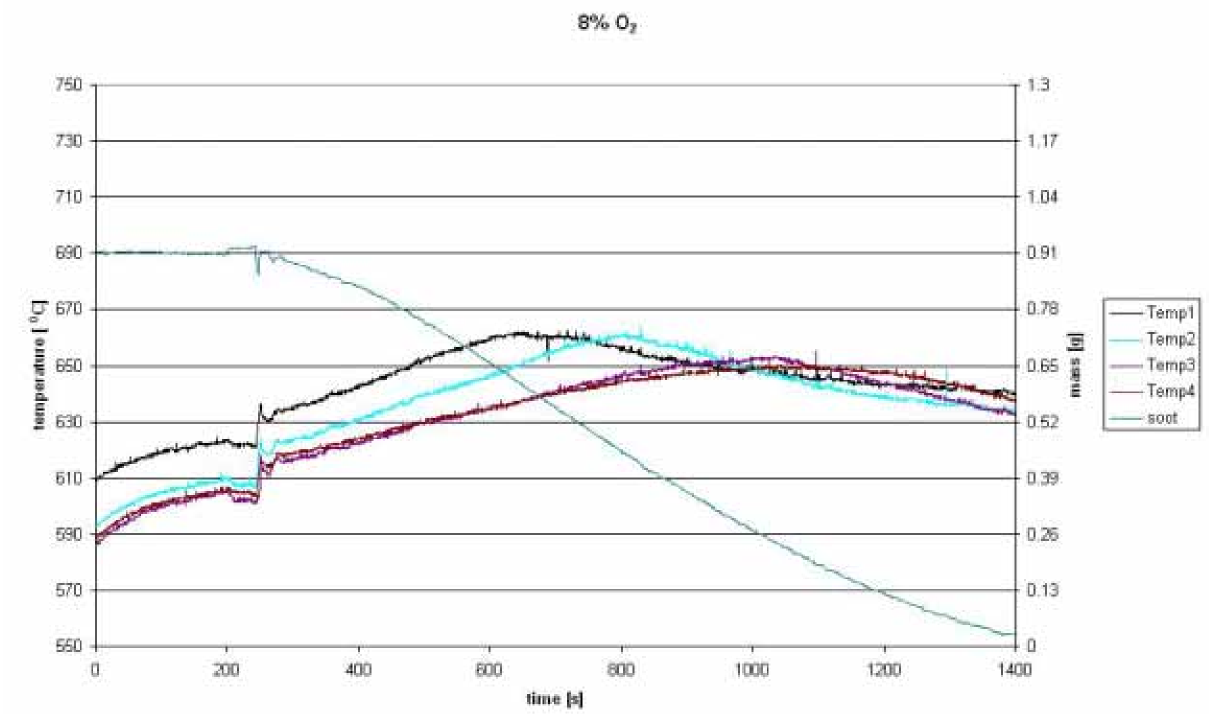

Figure 9. Experiment with technical soot N-772 at 8% oxygen

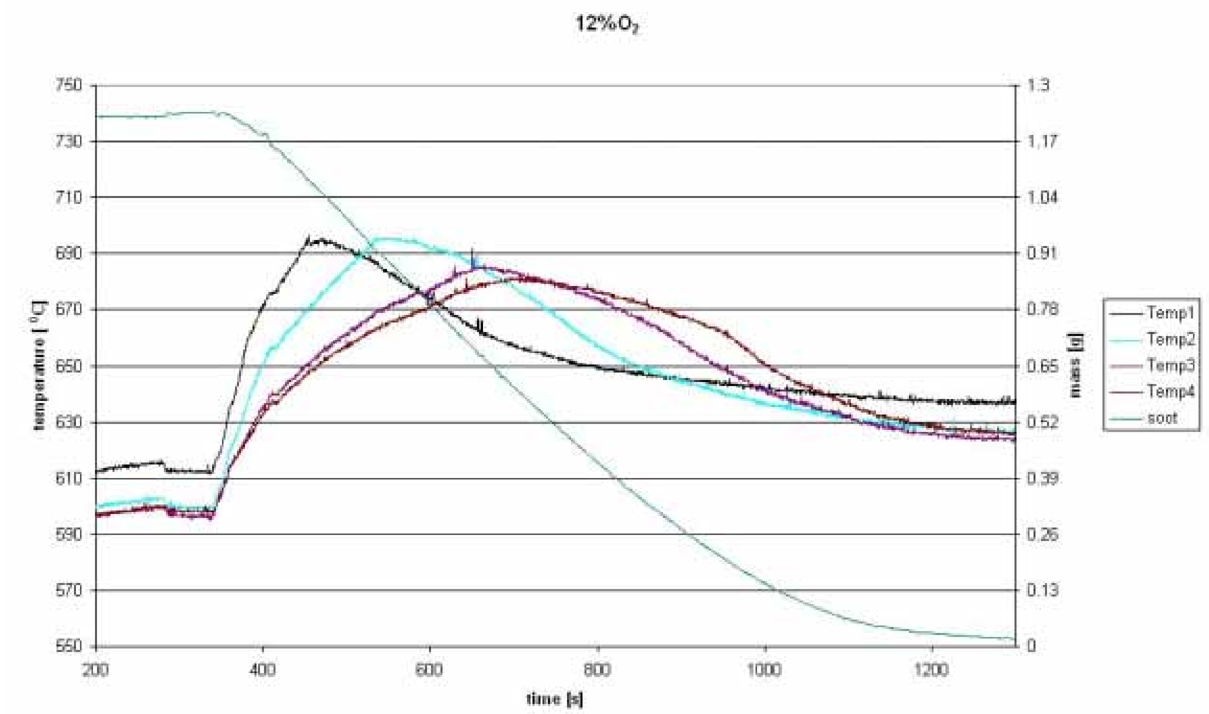

Figure 10. Experiment with technical soot N-772 at 12% oxygen

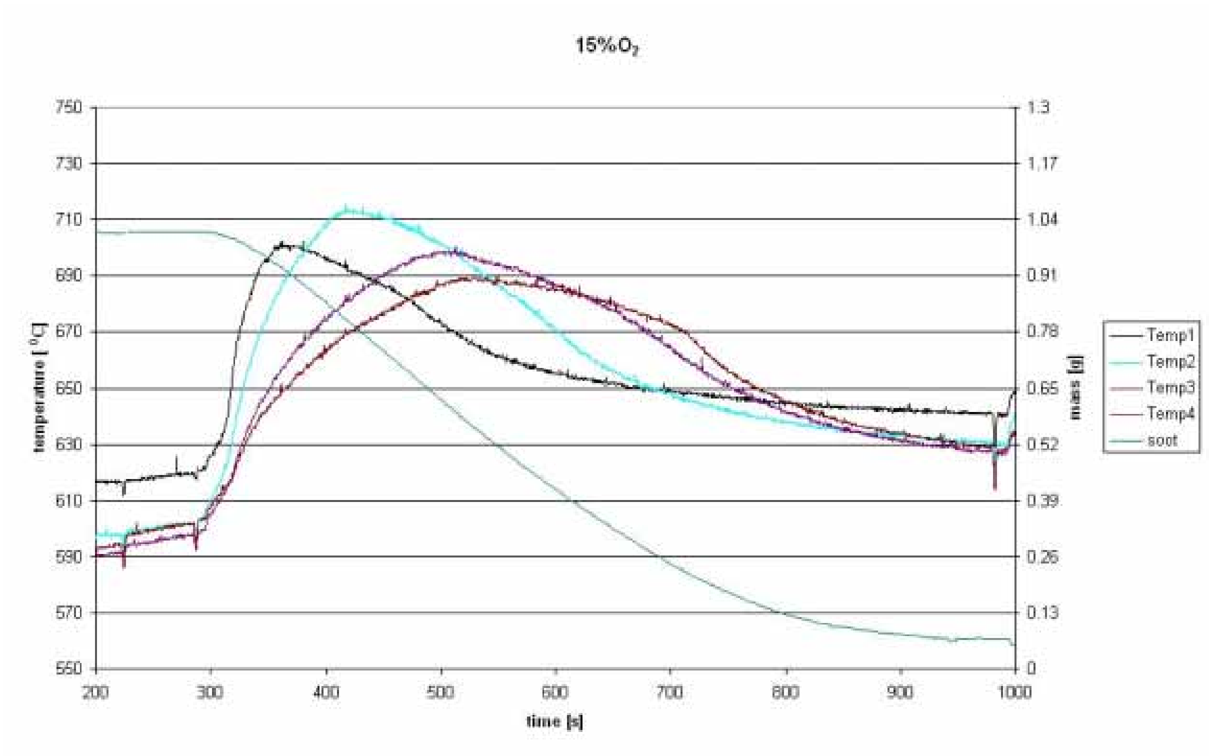

Figure 11. Experiment with technical soot N-772 at 15% oxygen

Figures 12 and 13 present oxygen influence for the experiment at the maximal temperature of the test bed (without overheat heaters).

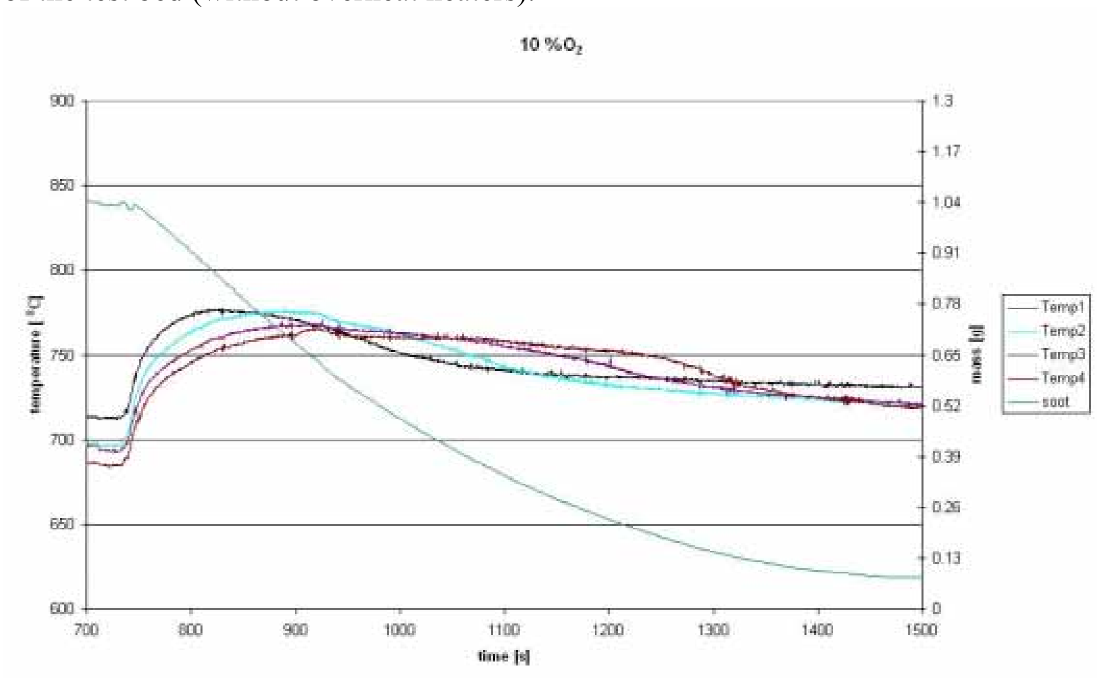

Figure 12. Experiment with technical soot N-772 at 10% oxygen

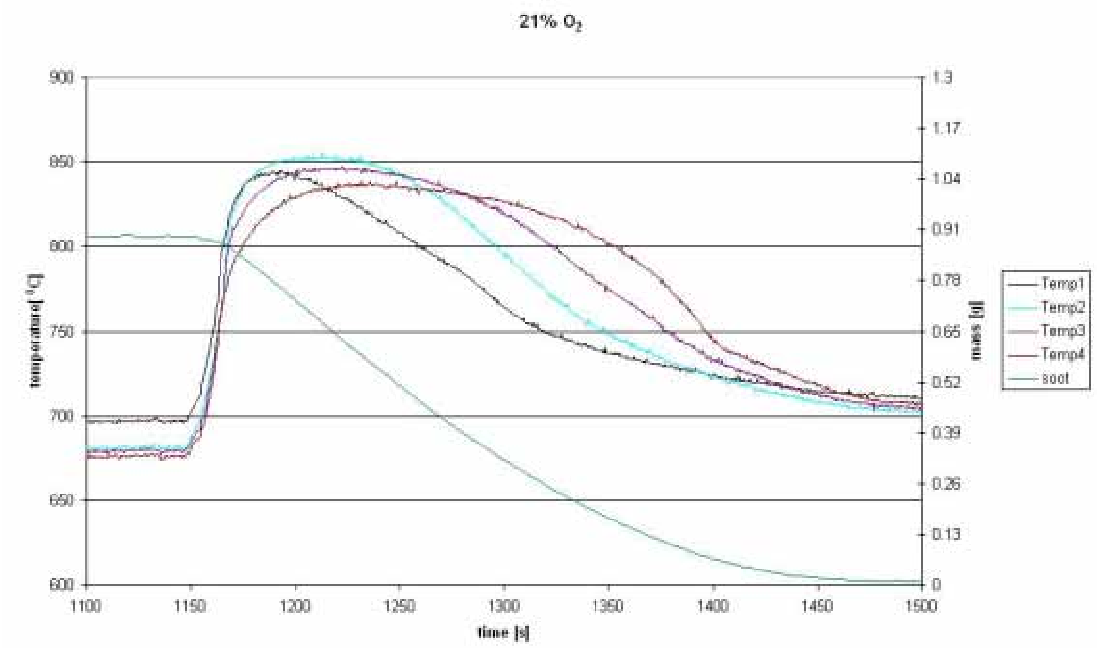

Figure 13. Experiment with technical soot N-772 at 21% oxygen

The parameters of above experiments are collected in the following table:

Initial temp.	*600 ℃*			*680℃ -700℃*	
Oxygen concentration	*8%*	*12%*	*15%*	*10%*	*21%*
Max temp	*661*	*695*	*712*	*775*	*852*
Rate of temperature increase1/s	*0.0586*	*0.815*	*1.49*	*2.26*	*6.23*

The figures 9.10.11.12.13 show real influence of oxygen fraction on regeneration process. When oxygen ratio increases, reaction zone temperature increases as well. When oxygen fraction increases too, growth rate of temperature increases rapidly, but burning time decreases.

The high temperature and a high growth rate of temperature can lead to filter failure. The high temperature can melt the ceramic, whereas the rapid temperature increase can break the filter monolith. Designer should reduce disadvantageous influence of the temperature and the growth rate of temperature on the filter. A low oxygen concentration is one of the best solution for solving above problems.

6. Conclusions

1. The original test bed was developed for better determination of the rate of soot oxidation at the conditions similar to the particulate filter.
2. The test bed gives possibility of the soot mass measurements. This measurement further enables to find the Arrhenius equation parameters.
3. For the better determination of reaction rate of oxidation, it is needed to check out the monographic test program. Our experiments were limited by the gases costs, so we were not able to study all cases.
4. Presented results show influence the oxygen concentration on a oxidation process.

References

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[2] Yezerets A., Currier N. W., Eadler H. A., *Experimental Determination of the Kinetics of Diesel Soot Oxidation By OD2 - Modelling Consequences*, SAE 2003-01-0833