

EVOLUTION OF MORPHOLOGY AND REACTIVITY OF DIESEL SOOT WITH PROGRESSIVE OXIDATION

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Introduction

Emissions of diesel particulate matter (soot), produced by diesel engines due to diffusion flame combustion process, are regulated to a very low level by the US EPA. Soot removal from the exhaust stream is accomplished using a mature filtration technology. However subsequent regeneration of diesel particulate filter (DPF) requires oxidation of accumulated soot, which represents substantial practical challenge.

The two oxidants available in the diesel exhaust to oxidize soot are NO_2 and O_2 . The former is very reactive at the temperatures typically found in the diesel exhaust and therefore allows soot to be oxidized mostly in a passive fashion, i.e. at normal engine operation. However, NO_2 is becoming increasingly scarce in the exhaust due to dramatically reduced legislated NO_x emission levels, and therefore regeneration is increasingly reliant on oxidation by O_2 . The latter requires temperatures substantially higher than those typically found in the diesel exhaust. Such conditions are created on a periodic basis by artificial heating of the DPF. Optimization of such fuel-intensive regeneration events requires detailed, quantitative understanding of diesel soot oxidation process. The reported study has been focused on characterizing oxidation of diesel soot samples and a model soot sample (Printex-U) by O_2 under conditions relevant to DPF operation, i.e. in the range of temperatures between ~ 400 and 600°C . This paper brings together our individual earlier publications covering various aspects of soot oxidation into a single analysis, covering evolution of soot reactivity with progressive oxidation.

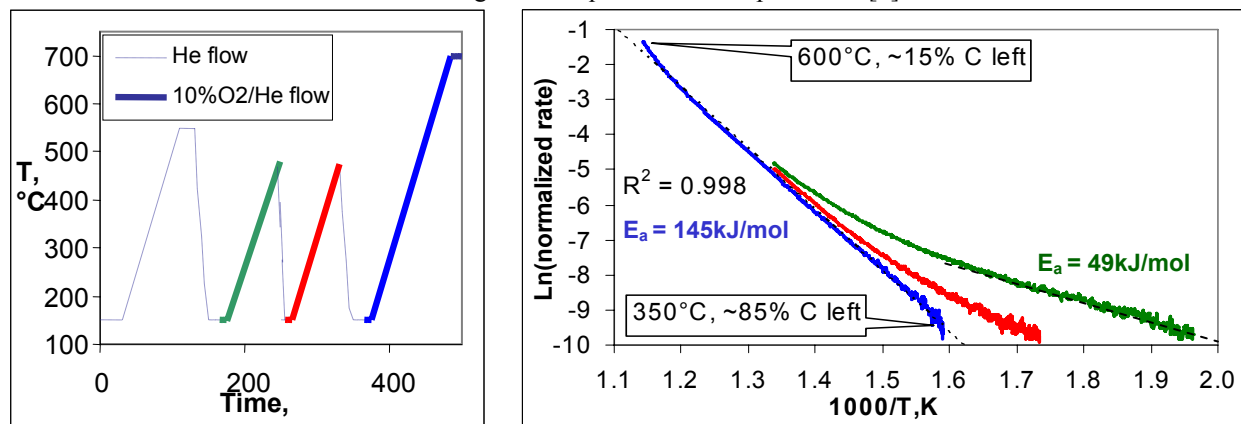
Experimental

Diesel particulate matter was collected from a Cummins ISB engine using DPF, as described in [1,2]. The experimental apparatus and conditions for soot oxidation experiments was described in [3,4].

Results and Discussion

It was found that upon first exposure of carbon samples to the target oxidation conditions, the initial rate (or normalized rate, i.e. the first order rate constant) was quite high, and rapidly declining with the oxidation. The experiment shown in Figure 1 was undertaken to better investigate this effect. The sample was first heated in the flow of inert gas to 550°C to remove adsorbed hydrocarbons, which would affect the oxidation rate measurements. After that the sample was cooled down to 150°C and subjected to Temperature-Programmed Oxidation (TPO).

Figure 1. Sequential TPO experiments [2]



Upon reaching 450°C, the gas composition was switched to inert to quench the oxidation process, the sample was cooled back to 150°C, re-exposed to the oxidizing environment and heated again. The last oxidation test did not stop at 450°C, but rather proceeded to a higher temperature until complete oxidation of carbon was achieved, confirmed by an excellent carbon mass balance. As shown in Figure 1, oxidation of the initial ~15% of carbon has been accomplished by a progressive increase in the activation energy. The final segment of the experiment showed excellent linearity of the Arrhenius curve in the range from ~15% to ~85% of carbon conversion.

Subsequent study reported in [3] has demonstrated that such initial high reactivity effect was not specific to an un-oxidized soot conditions, but can be repeatedly re-created by prolonged (days) exposure of soot samples, both diesel and model, to the ambient conditions. No such reactivity enhancement was achieved under inert conditions. It was therefore postulated that prolonged exposure to ambient conditions leads to the development of highly reactive functional group coverage which can not be achieved under the more vigorous oxidation conditions. However, attempts to identify these groups via XPS analysis did not prove successful, as no systematic change in the form of density or oxygenated groups on the carbon surface was observed with progressive ambient aging (see Figure 2 and Table 1).

Figure 2. Example of XPS spectra of carbon sample (C_{1s} and O_{1s} regions)

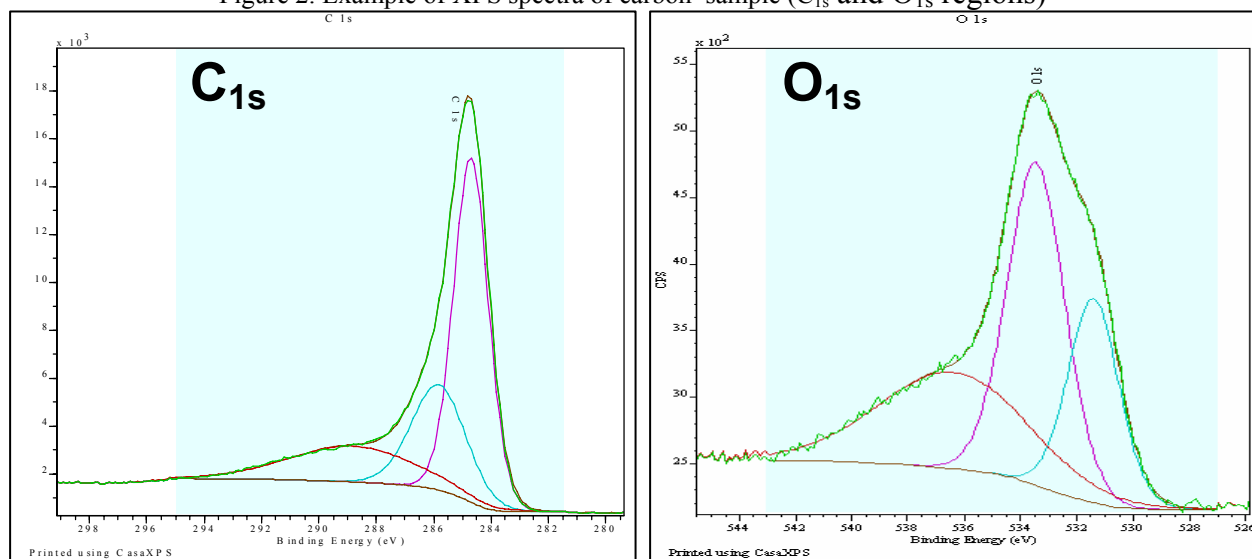


Table 1. Density of oxygenated groups as measured by XPS

	O/C (%)
As-received	15.6
After TPD	4.3
Immediately after 375C oxidation	17.7
Air aging– 3 days	16.8
Air aging– 7 days	17.2
Air aging–14 days	16.4
Air aging–23 days	16.0

In all the subsequent experiments, the first 15-20% of carbon were removed *in-situ* by oxidation and sample was subsequently maintained under the inert flow, to prevent the initial high reactivity effect from impacting the detailed kinetic studies.

In order to investigate changes in the kinetics of carbon oxidation, a step-response experimental technique was developed [4]. As illustrated in Figure 3, the sample has been kept under the oxidant-free flow, except for short periods when it was exposed well defined “pulses” of the oxidizing gas of desired composition. The oxidation rate is determined from CO_x concentration resulting from carbon oxidation. As a result, an oxygen composition sweep can be obtained while consuming only differentially small amounts of carbon. Similarly, temperature dependence can be obtained while also consuming only differentially small amounts of carbon [4].

Figure 3. Mass-spectrometer traces of O₂ and CO₂ in the reactor outflow during step-response experiments.

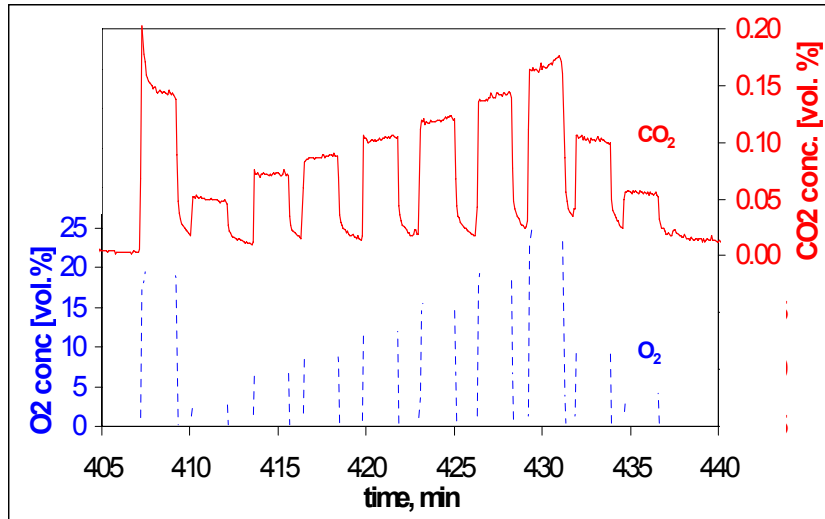
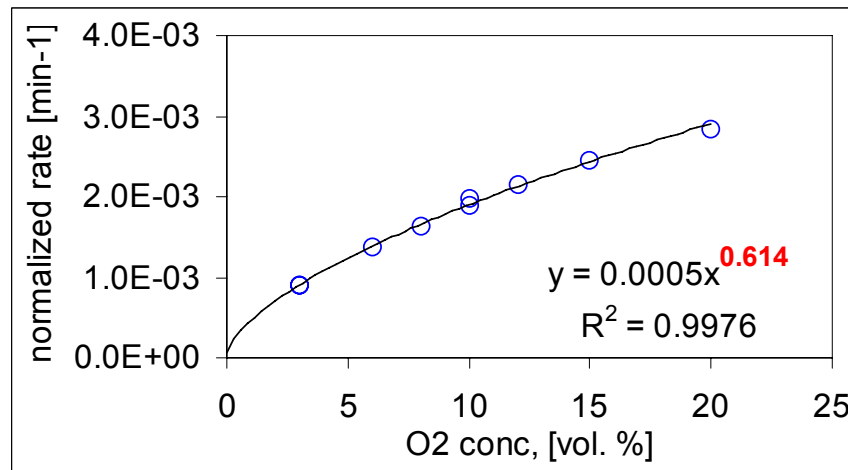


Figure 4. Reaction order in O₂ analysis from the data reported in Figure 3.



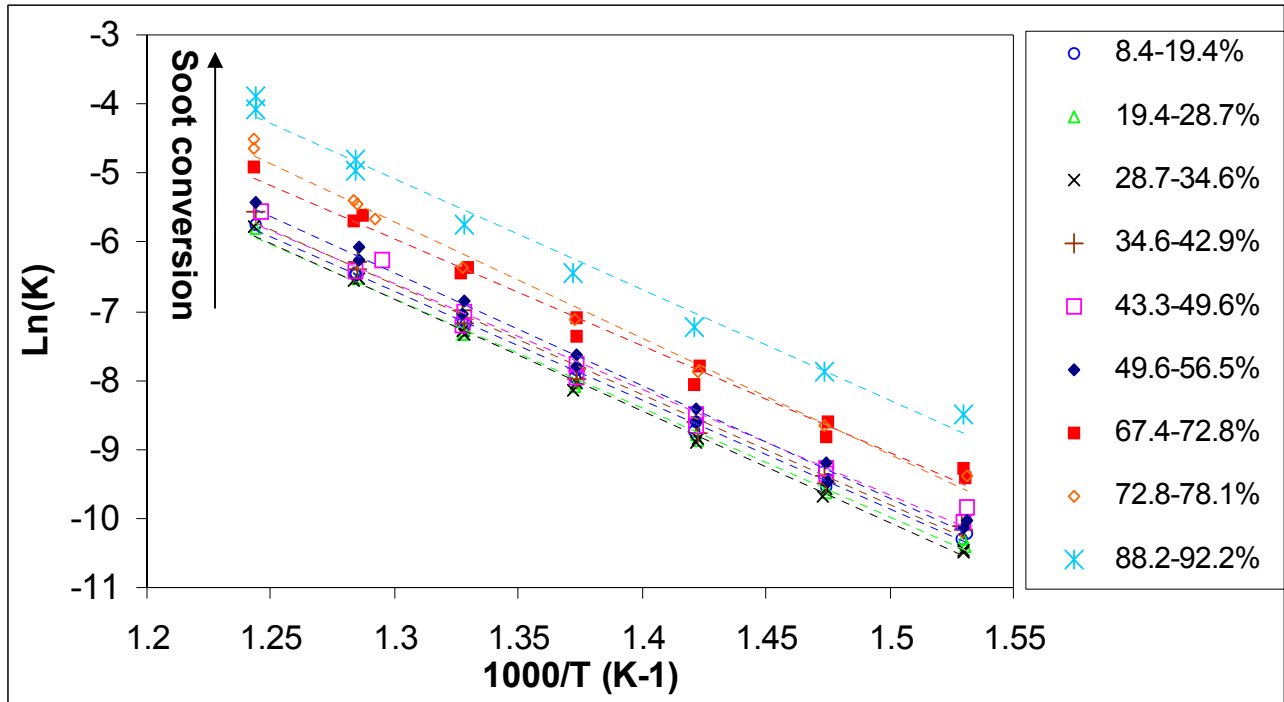
The important implication of the step-response technique is that it allowed us to probe such key kinetic parameters as reaction order with regards to oxygen and activation energy at different stages of carbon oxidation. The data reported in Table 2 illustrate this capability, from the perspective of determining the reaction order in O₂. Two aliquots of the same soot sample have been pre-oxidized to remove 14.2 or 24.5% of carbon, respectively and then subjected to step-response experiments similar to those described in Figures 3 at different temperatures. The carbon conversion was tracked by integrating the total amount of CO_x evolved, reported in Table 2 for each oxygen sweep. Analysis of the data reported in Table 2 shows no systematic dependence between the reaction order in oxygen and degree of carbon conversion or temperature. The independence from temperature is particularly remarkable, indicating that fractional reaction order is not due to a mixed kinetic control.

Table 2. Results of step-response experiment for diesel soot [4].

sample #	Series	T, °C	Soot conv. %		Order	R ²
			Beginning of the series	End of the series		
1	1	405	14.2	15.1	0.65	0.998
1	2	454	15.7	18.6	0.57	0.980
1	3	504	20.6	31.3	0.58	0.996
1	4	529	33.4	43.5	0.60	0.973
1	5	479	44.1	48.1	0.58	0.998
1	6	430	48.1	49.3	0.61	0.998
1	7	553	51.6	67.3	0.63	0.971
1	8	455	71.0	72.6	0.61	0.996
2	9	461	24.5	28.2	0.55	0.998
2	10	535	28.5	49.1	0.63	0.963
2	11	510	50.3	59.2	0.60	0.998
2	12	485	59.8	63.5	0.61	0.998
2	13	461	63.5	65.3	0.57	0.998
2	14	510	69.0	74.5	0.62	0.993
2	15	485	74.8	77.3	0.63	0.996
2	16	461	77.4	79.5	0.65	0.999
average order					0.61	
standard deviation					0.03	

The results of a similar experiment focused on the temperature dependence of soot oxidation are reported in in Figure 5. As one can see, the slope of individual temperature sweeps was not systematically changing with progressive oxidation, while the absolute reactivity was increasing.

Figure 5. Results of step-response oxidation experiments in the Arrhenius coordinates. The legend indicates the initial and final soot conversion values for each temperature sweep

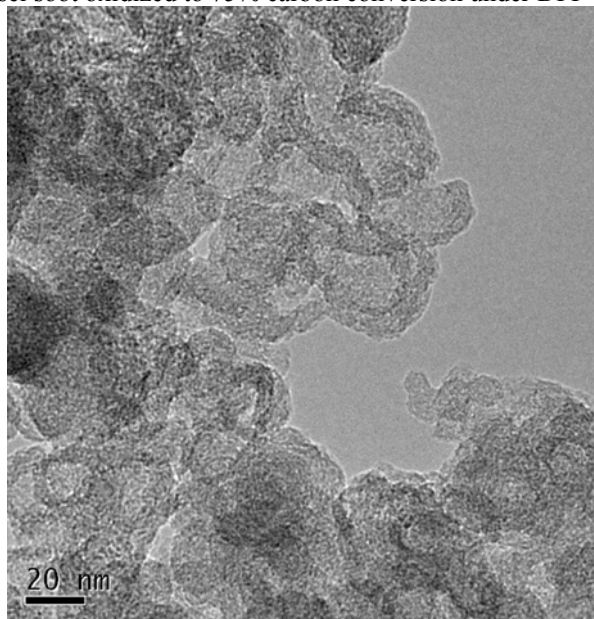


The above information indicates that such key kinetic parameters as reaction order in oxygen and activation energy remain constant with progressive oxidation of carbon, and that therefore the underlying chemical process does not change, while the density of reactive sites is increasing with carbon conversion.

Attempts to correlate changes in reactivity of carbon to such gross morphological characteristics as surface area and porosity proved unsuccessful [4].

A more detailed study of soot nano-structure and morphology evolution with oxidation has been initiated to better understand evolution of soot reactivity, and more specifically the density of reactive sites, with progressive oxidation. The initial results were reported in [5]. In particular, it was established that oxidation of diesel soot under the conditions typical for DPF applications, leads to a progressive formation of voids inside primary nano-particles, contrary to any existing literature information for regular diesel soot. This explains why such kinetic formalisms as shrinking core or dense sphere models did not fit the experimental data.

Figure 6. HRTEM of diesel soot oxidized to 75% carbon conversion under DPF-relevant conditions.



Summary

We have found that reactivity of diesel and model soot samples evolved quite noticeably with progressive oxidation of a given population of carbon particles, and varied between different populations. The developed step-response technique allowed us to quantitatively characterize changes in carbon reactivity with progressive oxidation and decouple chemical and morphological factors controlling the carbon reactivity changes. On-going HRTEM study provided the first insights into the changes of primary particles morphology under the DPF regeneration-relevant conditions, including the development of internal voids. Further work in this direction is currently underway and additional results will be reported in the meeting.

References

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