Kinetics, changes in particle size and internal structure of two Diesel soots and a carbon black during oxidation in oxygen or nitrogen dioxide

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Presentation Overview

- Introduction
- Characteristics of the soots and the oxidants
- Description of the oxidation experiments
- Effect of heat-treatment
- Results of the oxidation experiments
- Comparison of physical models of burning soot
- Pore evolution during oxidation of a carbon black (Printex U)
- Conclusions

Introduction

- This presentation juxtaposes two studies of the oxidation of two Diesel soots:
  - $20 – 880$ ppm NO_2, $300 – 550°C$ [1]
  - $2.7 – 24.4$ vol.% O_2, $450 – 550°C$ [2]
- Conditions approaching those in a regenerating Diesel particulate filter (DPF).
- Both studies used the same samples of soots from a Diesel engine fuelled by:
  - Ultra low sulphur Diesel (ULSD soot)
  - A mixture of 90% biodiesel and 10% ULSD (B90 soot)
- The oxidation of a carbon black (Printex U) by O_2 was also studied.

[1] Tighe, C.J., Hayhurst, A.N., Twigg, M.V., Dennis, J.S., 2012. The kinetics of oxidation of Diesel soots by NO_2, *Combust. Flame* 159, 77-90.

[2] Tighe, C.J., Hayhurst, A.N., Twigg, M.V., Dennis, J.S., 2016. The kinetics of oxidation of Diesel soots and a carbon black (Printex U) by O_2 with reference to changes in both size and internal structure of the spherules during burnout, *Carbon* 107, 20-35.
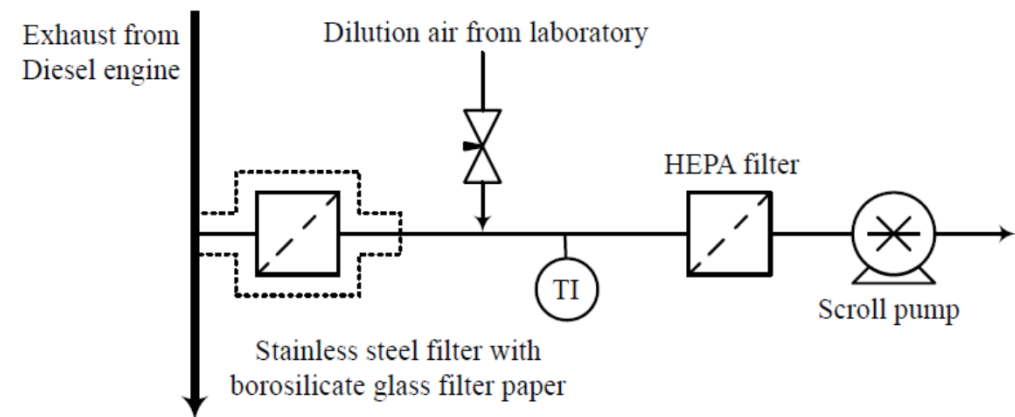
Characteristics of the Soots – Preparation

- Soots collected from exhaust of 4-stroke, 2.1 l Ford Mondeo Diesel engine.
- Air flow reduced during B90 runs to allow for oxygen in fuel (~ 10 wt.%).
- Borosilicate glass filter heated to 200°C.
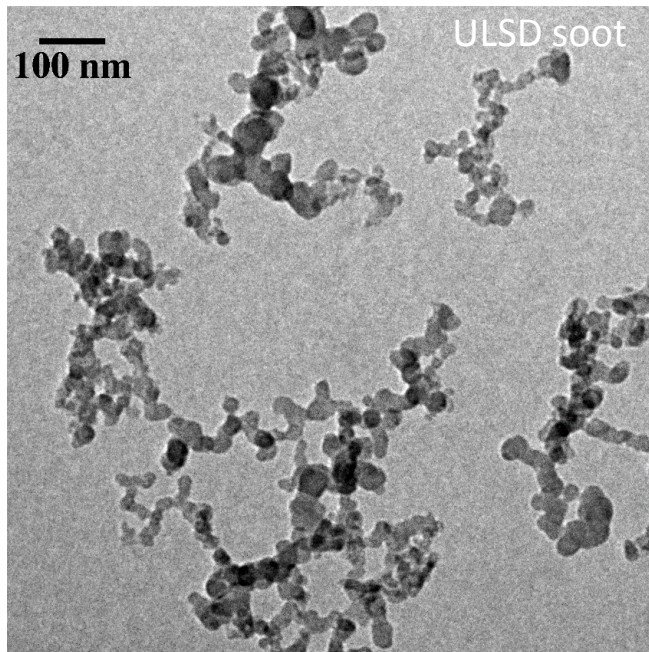- Printex U supplied by Degussa, produced by combustion of natural gas

Operating characteristic	ULSD	B90
Equivalence ratio, f	0.24	0.23
Exhaust temperature (°C)	230	234
Filter Smoke Number (FSN)	1.5	1.1
Engine speed (rpm)	1500	
Load[a] (bar)		3.5
Oil pressure (bar)		260
Fuel injection timing[b] (°)/injected mass (mg)		5/7.5
Pilot injection timing[b] (°)/injected mass (mg)		5/7.5

[a] Brake mean effective pressure.
[b] Crank angle before top dead centre.

Exhaust from Diesel engine

Dilution air from laboratory

HEPA filter

TI

Scroll pump

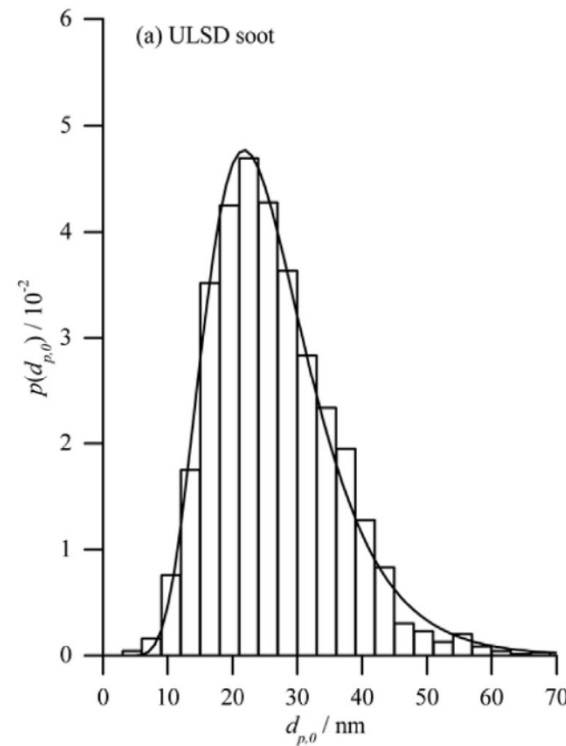Stainless steel filter with borosilicate glass filter paper

Characteristics of the Soots – Size Distributions

ULSD soot

100 nm

N particles measured by TEM were described by log-normal distribution:
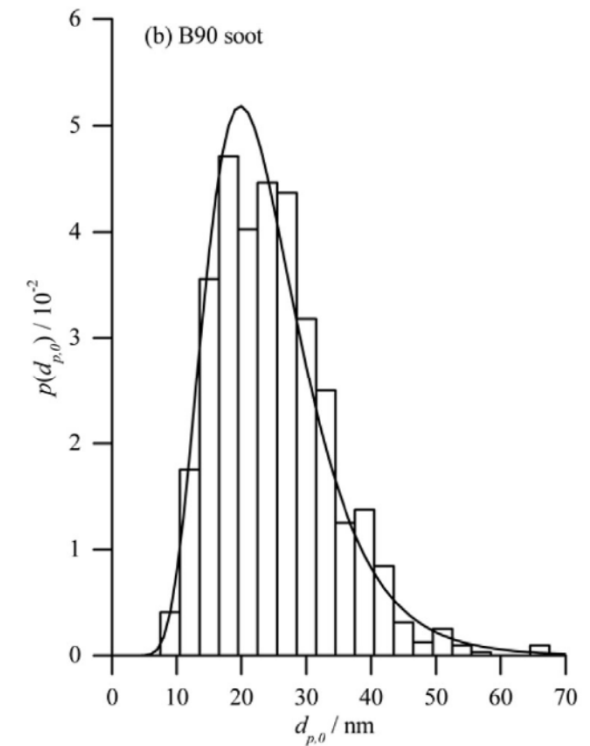
$$p(d_{p,0}) = \frac{1}{d_{p,0}\ln(\sigma_{gm})\sqrt{2\pi}}\exp\left\{-\frac{\left[\ln\left(d_{p,0}\big/(d_{p,0})_{gm}\right)\right]^2}{2\left[\ln(\sigma_{gm})\right]^2}\right\}$$ Eq. (1)

(a) ULSD soot

$p(d_{p,0})\,/\,10^{-2}$

$d_{p,0}\,/\,\mathrm{nm}$

$N = 2329$
$\ln(\sigma_{gm}) = 0.36$
$(d_{p,0})_{gm} = 24.8$

(b) B90 soot

$p(d_{p,0})\,/\,10^{-2}$

$d_{p,0}\,/\,\mathrm{nm}$

$N = 1068$
$\ln(\sigma_{gm}) = 0.38$
$(d_{p,0})_{gm} = 21.8$

Characteristics of the Soots – N_2 Adsorption

- Surface area (BET method) and pore diameters (BJH) measured by N_2 adsorption
- Volumetric mean diameter of "pores" similar to diameters of spherules.
- No evidence for micropores less than 2 nm:
  - Interplanar distance between lamellae in soot is ~ 0.36 nm [3].
- Sauter mean diameters determined using either S_{BET} or size distributions by TEM:
  - Very close agreement between these values for both Diesel soots.
  - *i.e.* the soots may be treated as separate, tiny spherules.

Morphological measurements. Here, S_{BET} is the BET area, S_{pore} is the surface area in pores with ID between 2 and 200 nm, as determined by the BJH model, $d_{pore} = 4V_{pore}/S_{pore}$, where V_{pore} is the volume in pores narrower in diameter than 200 nm from the BJH model.

Sample	S_{BET} (m^2 g^{-1})	S_{pore} (m^2 g^{-1})	d_{pore} (nm)
ULSD soot	108 ± 5	116 ± 6	18.7 ± 1
B90 soot	103 ± 5	110 ± 6	21.6 ± 1
Printex U	73 ± 4	76 ± 4	20.7 ± 1

[3] O.I. Smith, 1981. Fundamentals of soot formation in flames with application todiesel engine particulate emissions, Prog. Energy Combust. Sci. 7, 275–291.

Characteristics of the Soots – Composition

- Elemental analysis of carbon (C), hydrogen (H) and nitrogen (N).
- Mass remaining after combustion in O_2 at 950°C was the ash content.
- Hydrocarbon fraction ~ 7H assuming long alkane with ratio C:H as in CH_2.
- Deficit in the elemental analysis is mostly adsorbed oxygen.
- $w_{O,mono}$ is an estimate of the mass fraction of a monolayer of oxygen on area S_{BET}.

Elemental composition of soots and Printex U (% by mass), together with errors, and the fraction of oxygen (% by mass), $w_{O,mono}$, constituting a monolayer adsorbed on the BET surface area

Sample	C (±0.5)	H (±0.1)	N (±0.1)	Ash (±0.5)	Deficit (±1.0)	$w_{O,mono}$
ULSD soot	89.3	1.2	0	1.8	7.7	23
B90 soot	84.0	1.6	0	3.3	11.1	22
Printex U	91.8	0.6	0	0.1	7.5	16

Characteristics of the Oxidants

	O=N–O	O=O
Bond energy[4] (red) / kJ mol^{-1}	305	498
Kinetic diameter / nm	0.40 – 0.51[5]	0.35[6]
Molecular diffusivity[7] in N$_2$ at 500 °C / cm^2 s^{-1}	0.83	1.04
Molecular weight, M / g mol^{-1}	46	32
Knudsen diffusivity[8] in 1 nm pore at 500 °C / cm^2 s^{-1}	2.0×10^{-3}	2.4×10^{-3}

- Most significant differences are in energy required to abstract O and kinetic diameter.

[4] Lide, D. R. (ed.), 1996. Handbook of Chemistry and Physics, 77th edn, CRC Press.
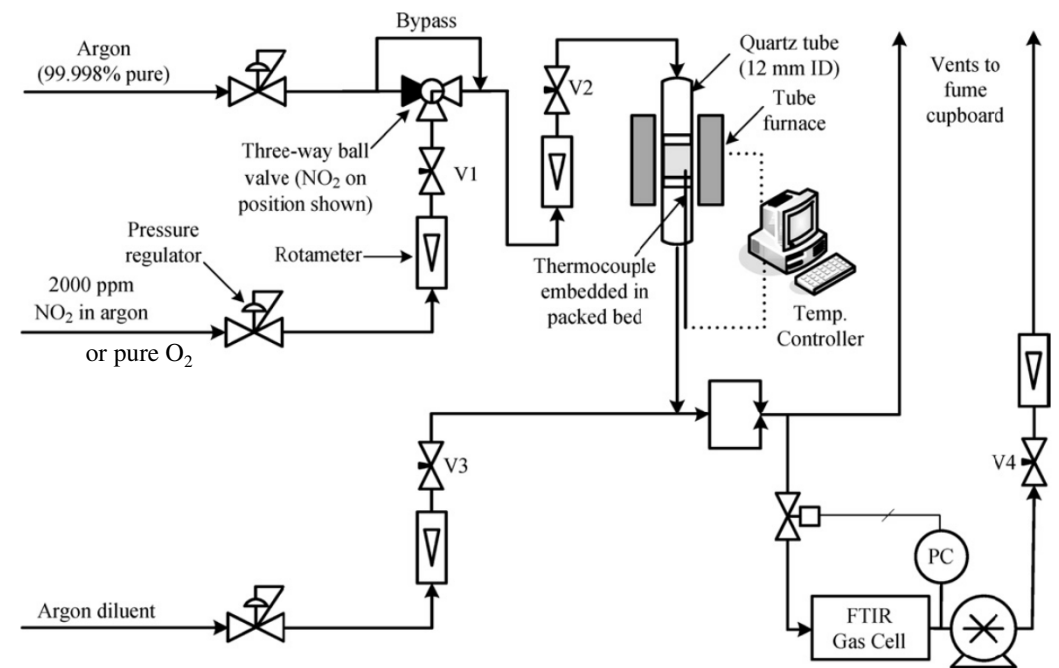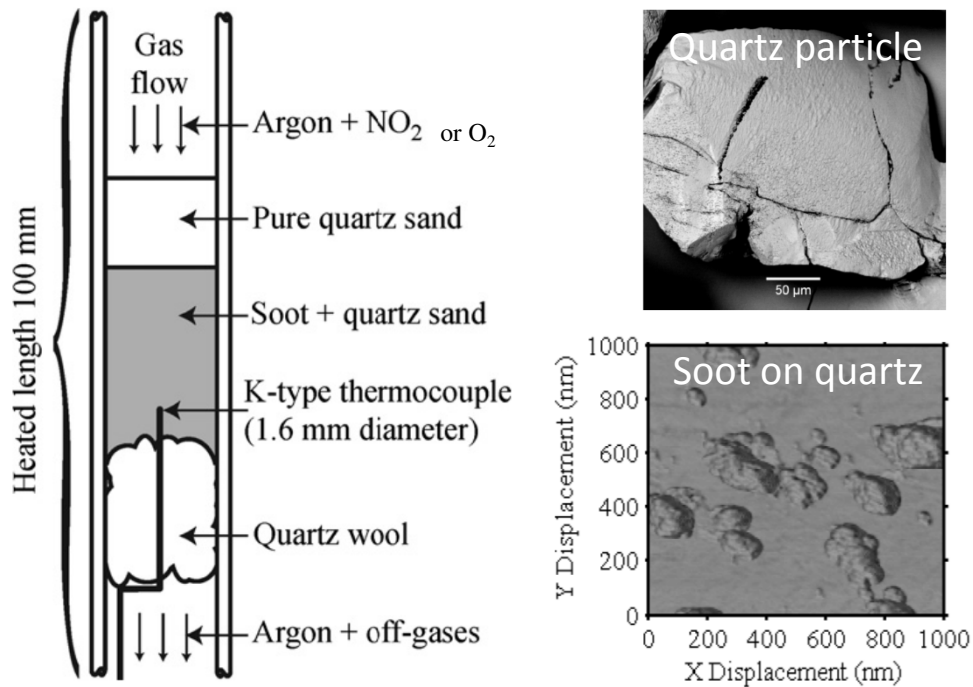[5] Xie, L., Liu, F., Liu, K., Shi, X., He, H., 2014. Catal. Sci. & Technol 4, 1104 – 1110.
[6] Breck, D.W., 1974. Zeolite Molecular Sieves: Structure, Chemistry and Use, John Wiley & Sons,
[7] Yaws, Carl L., 2003. Yaws' Handbook of Thermodynamic and Physical Properties of Chemical Compounds, Knovel.
[8] Ruthven, D. M., 1984. Principles of Adsorption and Adsorption Processes, 1st edn, John Wiley & Sons. $D_K = 4850 d_{pore}(T / M)^{0.5}$

Description of Oxidation Experiments

Gas flow

Argon + NO$_2$ *or O$_2$*

Pure quartz sand

Soot + quartz sand

K-type thermocouple (1.6 mm diameter)

Quartz wool

Argon + off-gases

Heated length 100 mm

Quartz particle

50 µm

Soot on quartz

Y Displacement (nm)

X Displacement (nm)

Bypass

Argon (99.998% pure)

Three-way ball valve (NO$_2$ on position shown)

Pressure regulator

2000 ppm NO$_2$ in argon *or pure O$_2$*

Rotameter

V1

V2

Quartz tube (12 mm ID)

Tube furnace

Thermocouple embedded in packed bed

Temp. Controller

Vents to fume cupboard

V3

V4

Argon diluent

PC

FTIR Gas Cell

1. A known mass of soot was widely dispersed over particles of quartz sand (typically 0.008 wt.%)

2. The mixture of soot and sand was placed in a quartz reactor (O.D. 12.5 mm), forming a packed bed.

3. [CO$_2$], [CO], [NO$_2$] and [NO] in off-gases continuously measured.

4. Packed bed heated to 550 °C with only Ar flowing over it.

5. Held for at 1 h then cooled to desired oxidation temperature.

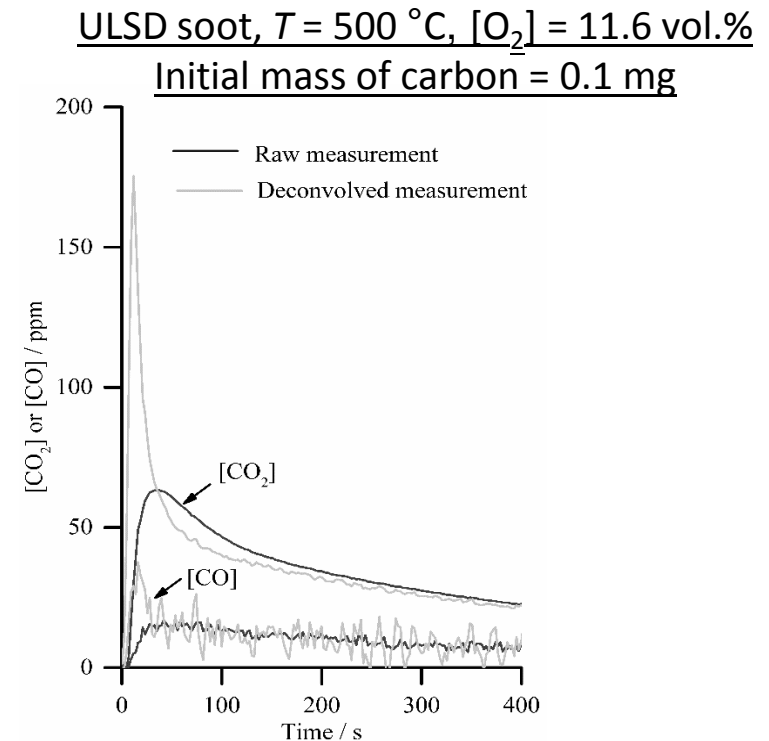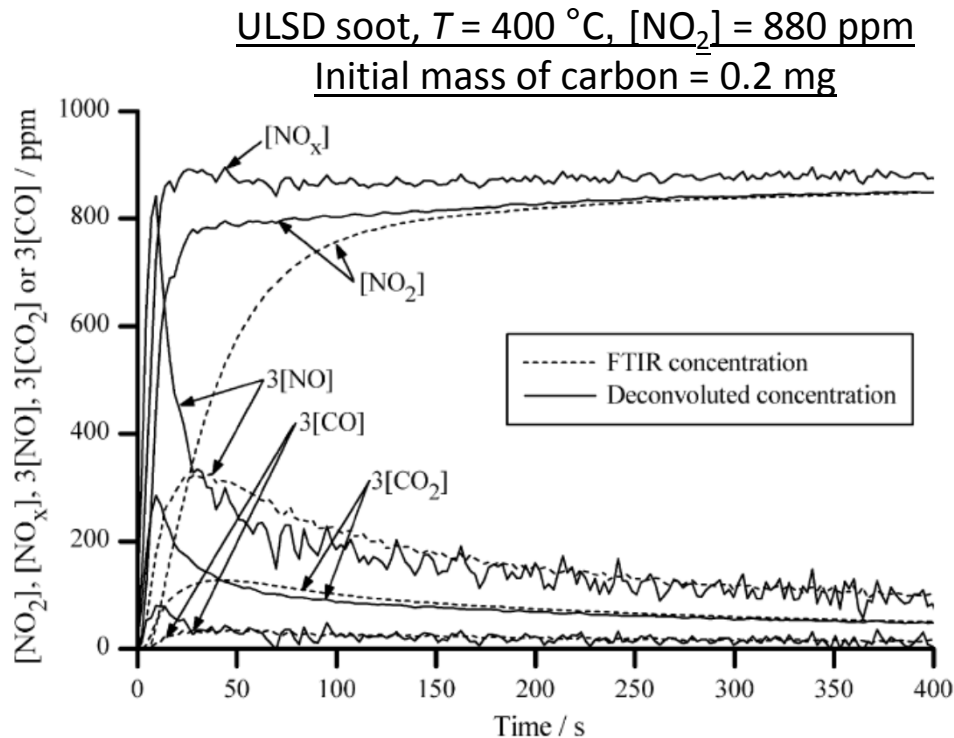6. Oxidant switched on, defined as t = 0, until burnout complete

Effect of Heat-Treatment

Heavy duty Diesel soot, initial mass = 10 mg
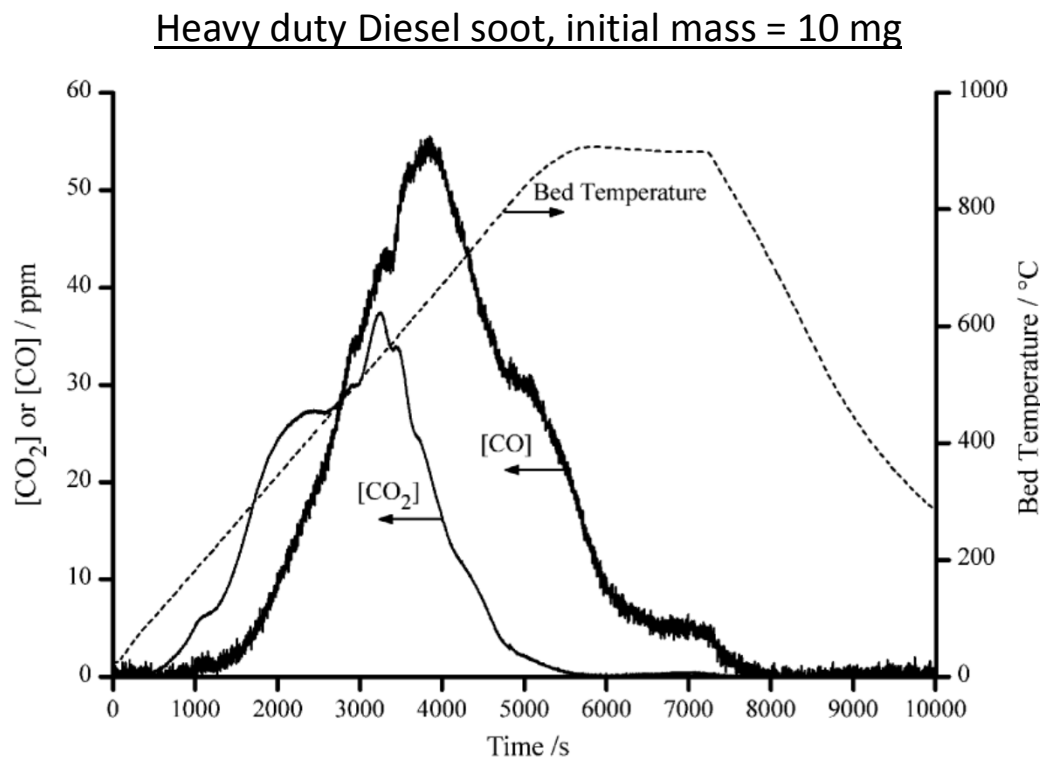
- Diesel soots were heated at 550°C in argon, prior to oxidation in NO_2 or O_2.
- Small (ppm) concentrations of CO and CO_2 were detected:
  - Loss of carbon between measurements i, interval Δt (= 2.3 s), given by:
  $$\Delta m_{C,i} = 1.2 \times 10^{-2} F([CO]_i + [CO_2]_i)\Delta t \,/\, \text{kg}$$
  - Molar flowrate, $F = 1.91 \times 10^{-4}$ mol s^{-1}
  - Heat-treatment resulted in loss of ~ 5% of the initial mass of carbon.
- Printex U heat-treated at 900°C, resulting in loss of ~ 1.5% of initial mass of carbon.
- No water vapour or hydrocarbons were detected during heat-treatment.
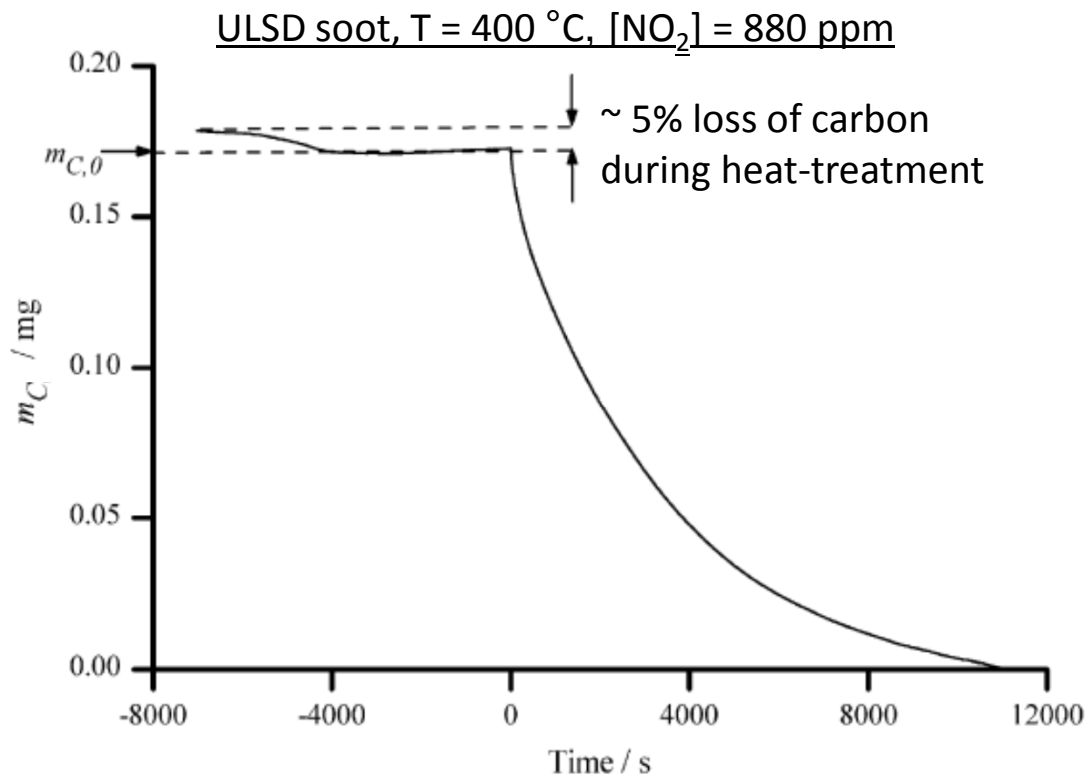
Products of Oxidation of the Soots

ULSD soot, T = 400 °C, $[NO_2]$ = 880 ppm
Initial mass of carbon = 0.2 mg

ULSD soot, T = 500 °C, $[O_2]$ = 11.6 vol.%
Initial mass of carbon = 0.1 mg

- There were two stages of burning in either NO_2 or O_2:
  - Initial, rapid transient reactions, which consumed ~ 20 % of the Diesel soots.
  - A second, slower stage of burning, which is the focus of subsequent analysis.
- The heat-treatment reduced the initial rate, but the second stage was unaffected.

Overall Oxidation Reactions

- No water vapour detected during oxidation.
  - Hydrocarbons most probably pyrolysed to C and H_2 during heat-treatment.
- For oxidation by NO_2:
  - $C_{(s)} + NO_{2(g)} \rightarrow NO_{(g)} + CO_{(g)}$ and $C_{(s)} + 2NO_{2(g)} \rightarrow 2NO_{(g)} + CO_{2(g)}$.
  - Ratio [CO]/[CO_2] increased from 0.2 at 350 °C to 0.5 at 500 °C in 880 ppm NO_2.
- For oxidation of carbon by O_2:
  - $2C_{(s)} + O_2 \rightarrow 2CO_{(g)}$ and $C_{(s)} + O_2 \rightarrow CO_{2(g)}$.
  - Ratio [CO]/[CO_2] increased from 0.25 at 450 °C to 0.40 at 550 °C in 24.4 vol% O_2.
- Ratio [CO]/[CO_2] lower than a fundamental study [9] of oxidation of carbon:
  - Possible further reaction $2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$ in gas phase or surface-mediated.
  - However, [CO] + [CO_2] and therefore rate of oxidation of carbon unchanged.

[9] L. Tognotti, J.P. Longwell, A.F. Sarofim, 1991. Products of the high temperature oxidation of a single char particle in an electrodynamic balance, Proc. Combust. Inst. 23, 1207–1213.
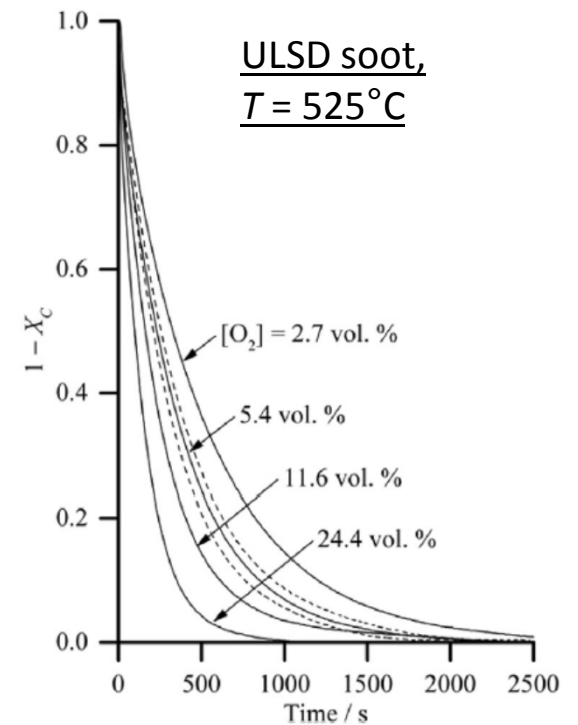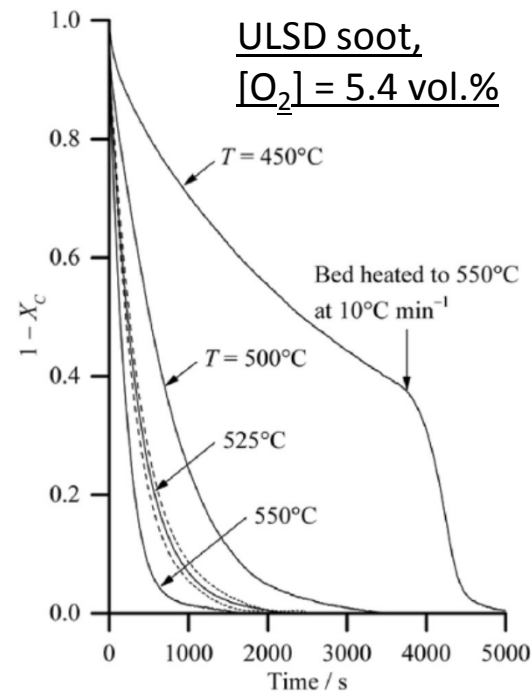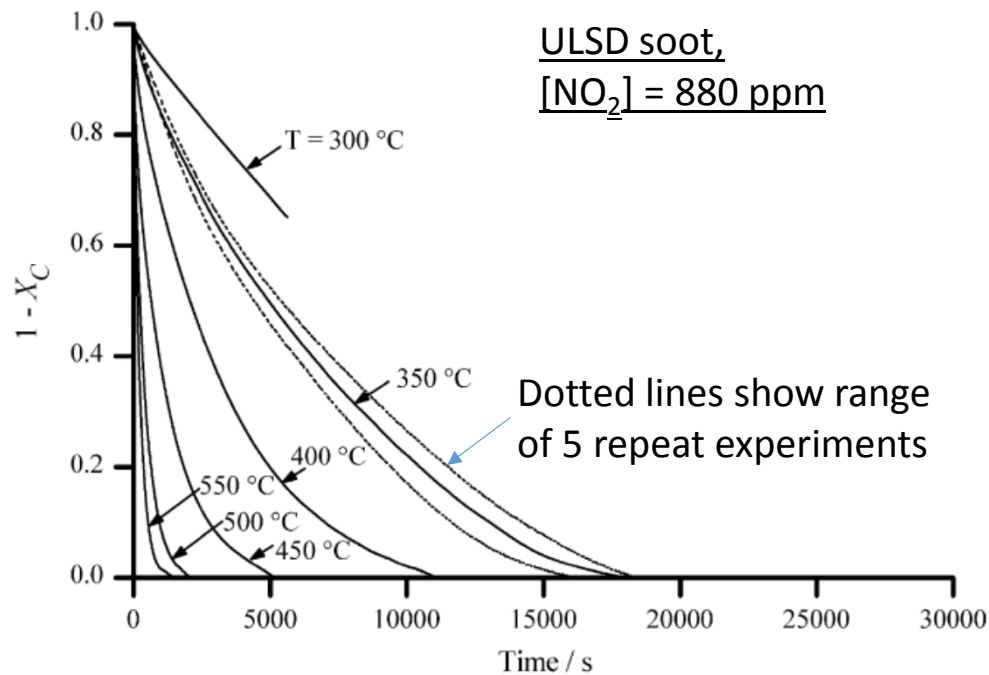
Plots of Decrease in Mass of Carbon with Time

ULSD soot, T = 400 °C, $[NO_2]$ = 880 ppm

$m_{C,0}$

~ 5% loss of carbon during heat-treatment

m_C / mg

Time / s

- Initial mass of carbon determined by:
  - (i) Known initial mass of soot multiplied by C fraction from elemental analysis.
  - (ii) Sum of all $\Delta m_{C,i}$ during heat-treatment and complete oxidation.
- These methods agreed to within ±5% for all the oxidation experiments.
- All of the carbon initially in the packed bed was oxidised to CO and CO_2:
  - Supports theory of pyrolysis of hydrocarbons during heat-treatment.
- Define conversion of carbon:

$$X_C = \frac{m_{C,0} - m_C}{m_{C,0}}$$

Plots of X_C against time

ULSD soot, [NO$_2$] = 880 ppm

T = 300 °C

350 °C

400 °C

550 °C

500 °C

450 °C

Dotted lines show range of 5 repeat experiments

$1 - X_C$

Time / s

ULSD soot, [O$_2$] = 5.4 vol.%

T = 450°C

Bed heated to 550°C at 10°C min^{-1}

T = 500°C

525°C

550°C

$1 - X_c$

Time / s

ULSD soot, T = 525°C

[O$_2$] = 2.7 vol. %

5.4 vol. %

11.6 vol. %

24.4 vol. %

$1 - X_C$

Time / s

- These look like first order exponential decays, so plot $\ln(1 - X_C)$ against time.
- Gradient is the specific rate of oxidation of carbon $r = \dfrac{1}{m_C}\dfrac{dm_C}{dt}$ kgC s^{-1} kgC^{-1}

Plots of $\ln(1 - X_C)$ Against Time
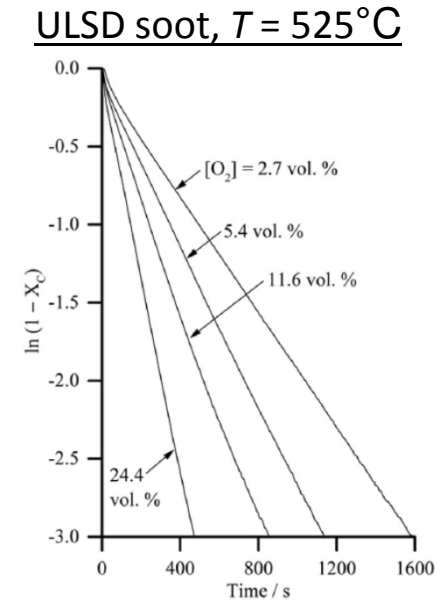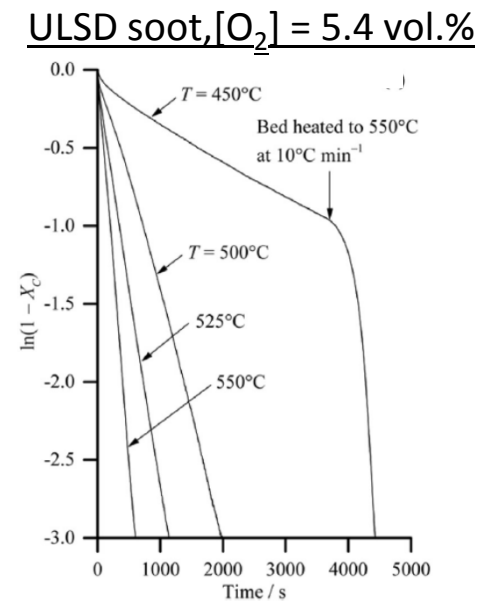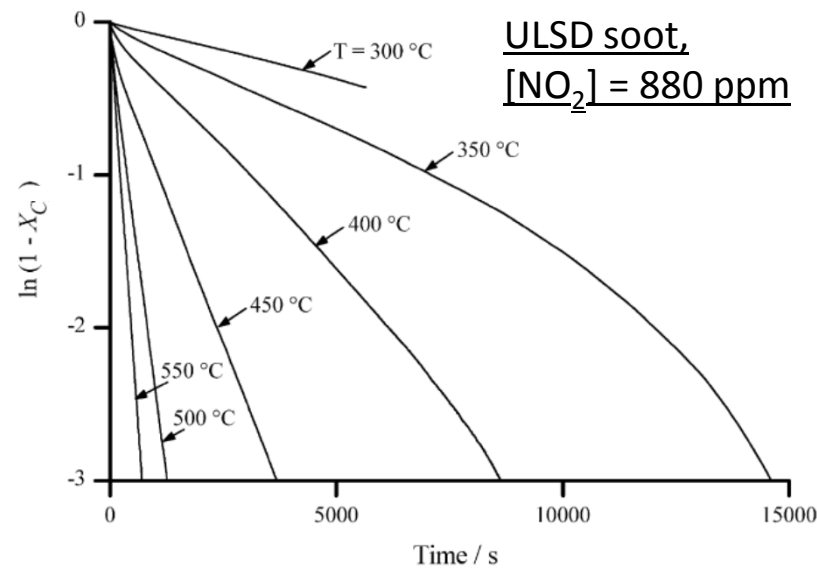
- These plots were strikingly linear for oxidation by O_2, but not for NO_2
- Gradient of plots like the ones above were use to determine r:
  - For NO_2, the gradients were taken from the linear parts of the curves up to $X_C = 0.65$.
- Define n^{th} order rate equation $-r = k_v C_A{}^n$, where A is NO_2 or O_2
  - The physical significance of k_v will be discussed later.

Orders of Reaction
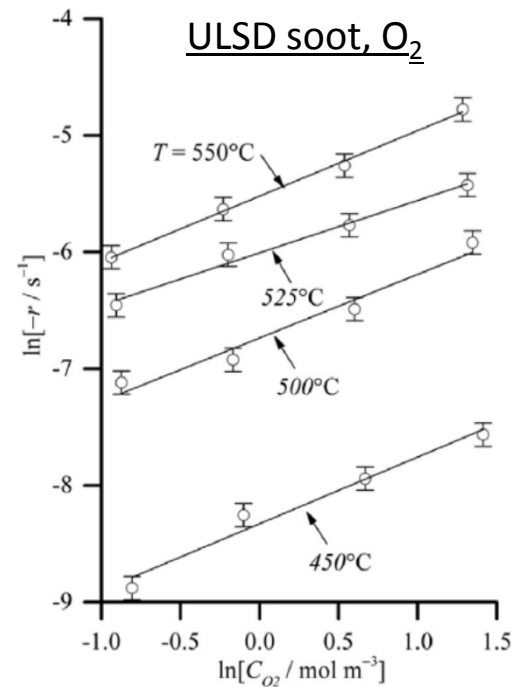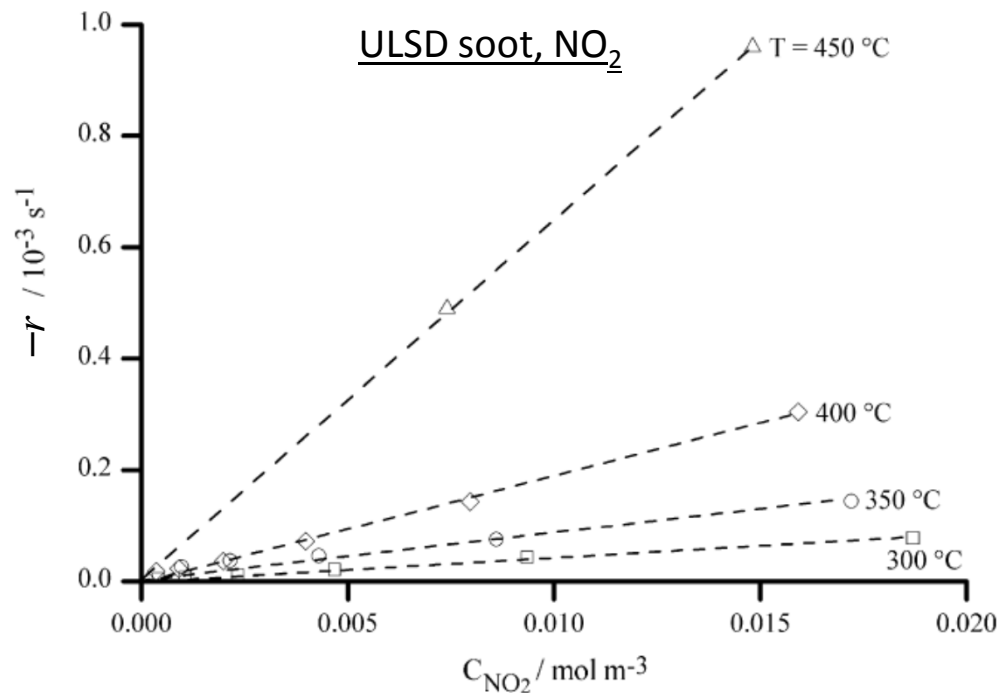
- The oxidation of the carbon in both the ULSD and B90 soots was:
  - First order with respect to NO_2 ($n = 1.0 \pm 0.1$)
  - Half order with respect to O_2 ($n = 0.50 \pm 0.07$)

Arrhenius Plots
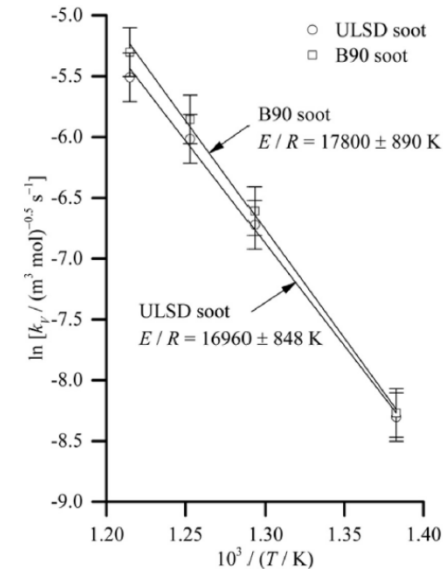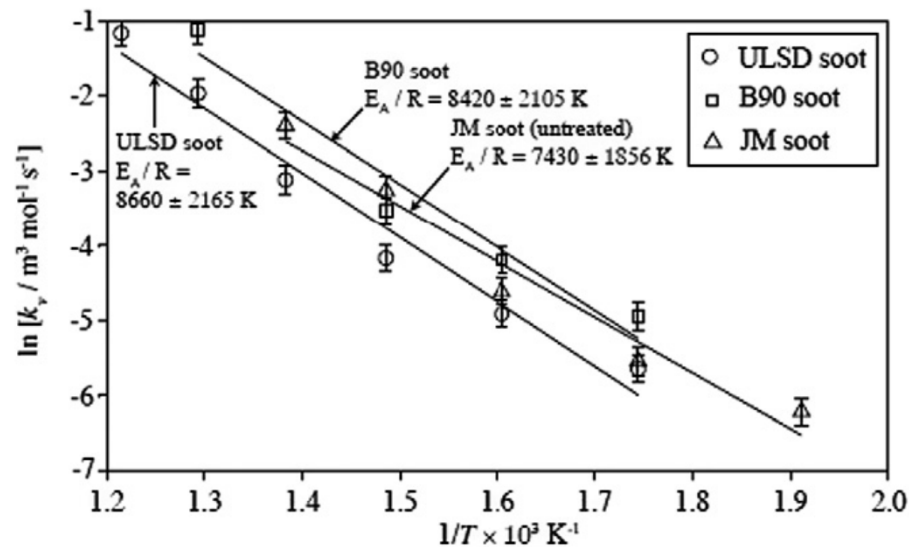
- The rate of oxidation by NO_2 of B90 soot was twice that of ULSD soot
- Surprisingly, there was no discernible difference in the rates of oxidation by O_2.
- Activation energies, E, were determined:
- When diffusion through pores controls overall rate:

$$E_{obs} \approx \frac{E_{true}}{2} \text{ and } n_{obs} \approx \frac{n_{true}+1}{2}$$

E / kJ mol^{-1}	NO_2	O_2
ULSD soot	72 ± 18	141 ± 7
B90 Soot	70 ± 18	148 ± 7

Comparison of Physical Models of Burning Soot

- Pseudo-homogeneous burning:

$$\ln(1 - X_C) = -k_v C_A{}^n t \qquad \text{Eq. (2)}$$

- Shrinking particles, initially of uniform size:

Rate constant for surface reaction

$$1 - \left(1 - X_C\right)^{1/3} = \frac{2k_s C_A{}^n}{d_{p,0}\rho_M} t \qquad \text{Eq. (3)}$$
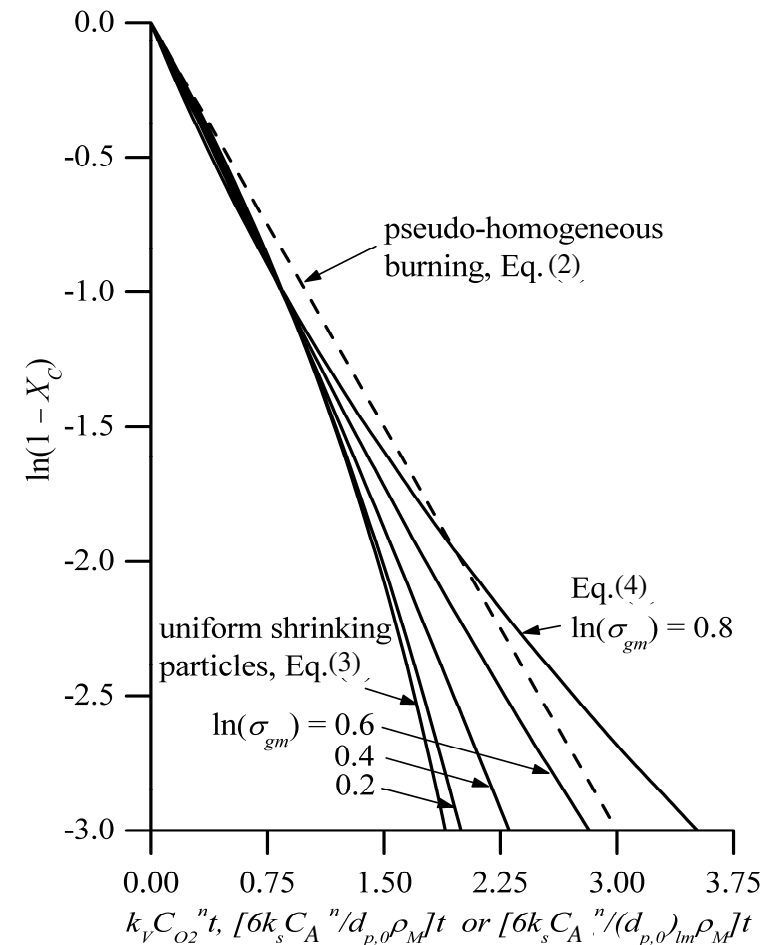
Molar density of carbon

- Shrinking particles, sizes initially distributed log-normally, with $p(d_{p,0})$ given by Eq. (1):

$$1 - X_C = \int_{d_{p,t}}^{\infty} \left(1 - \frac{2k_s C_A{}^n}{d_{p,0}\rho_M} t\right)^3 p(d_{p,0})\, \mathrm{d}d_{p,0} \qquad \text{Eq. (4)}$$

where $d_{p,t} = [2k_s C_A{}^n / \rho_M]t$

- Mechanisms can be confused when $\ln(\sigma_{gm}) = 0.6$

pseudo-homogeneous burning, Eq. (2)

Eq.(4) $\ln(\sigma_{gm}) = 0.8$

uniform shrinking particles, Eq.(3)

$\ln(\sigma_{gm}) = 0.6$
0.4
0.2

$\ln(1 - X_C)$

$k_v C_{O2}{}^n t,\ [6k_s C_A{}^n / d_{p,0}\rho_M]t\ $ or $\ [6k_s C_A{}^n/(d_{p,0})_{lm}\rho_M]t$

Test for Pore Diffusion Control

- Direct evidence that spherules burn on the inside in O_2, but on outside in NO_2 [10, 11].
- Could rate of oxidation be controlled by diffusion of NO_2 within porous spherules?
- Levenspiel [12] provides a criterion, which demonstrates negligible pore resistance:

Rate of oxidation per unit volume of solid → $\dfrac{(-r''')_{obs} L^2}{D_e C_{NO2}} < 1$ ← Length scale

Effective diffusivity →

$(-r''')_{obs} = \rho_M (-r) = \rho_M k_V C_{NO2}$

Molar density of carbon →

$\boxed{\dfrac{\rho_M k_V L^2}{D_e} < 1}$ Eq. (5)

- For ULSD soot at T = 550 °C and [NO_2] = 880 ppm (C_{NO2} = 0.013 mol m^{-3}), k_V = 0.35 m^3 mol^{-1} s^{-1}.
- For an individual spherule, initial diameter 25 nm, $L = d_{p,0} / 6 = 25 \times 10^{-9} / 6 = 4 \times 10^{-9}$ m.
- D_e assumed to be equal to the molecular diffusivity of NO_2, $D = 8 \times 10^{-5}$ m^2 s^{-1}.
- Molar density $\rho_M = \rho_p / M_C = 1800 / 1.2 \times 10^{-2} = 1.5 \times 10^5$ mol m^{-3}.
- Left hand side of Eq. (5) is equal to 1.1×10^{-8} *i.e.* criterion for negligible pore resistance easily met.

- Therefore the rate of oxidation in NO_2 is <u>not</u> controlled by molecular diffusion in pores.

[10] H. Seong, S. Choi, 2015. Oxidation-derived maturing process of soot, dependent on O_2-NO_2 mixtures and temperatures, Carbon 93, 1068 – 1076.
[11] A. Strzelec, R.L. Vander Wal, T.N. Thompson, T.J. Toops, C.S. Daw, 2016. NO_2 Oxidation Reactivity and Burning Mode of Diesel Particulates, Top. Catal. 59, 686 – 694.
[12] O. Levenspiel, 1972, Chemical Reaction Engineering, John Wiley & Sons.

Pore Evolution in Printex U

[13] S.K. Bhatia, D.D. Perlmutter, 1980. A random pore model for fluid-solid reactions 1. isothermal, kinetic control, AlChE J. 26 379–386.
[14] E.E. Petersen, Reaction of porous solids, AlChE J. 3 (4) (1957) 443–448.

$[O_2]$ = 11.6 vol.%
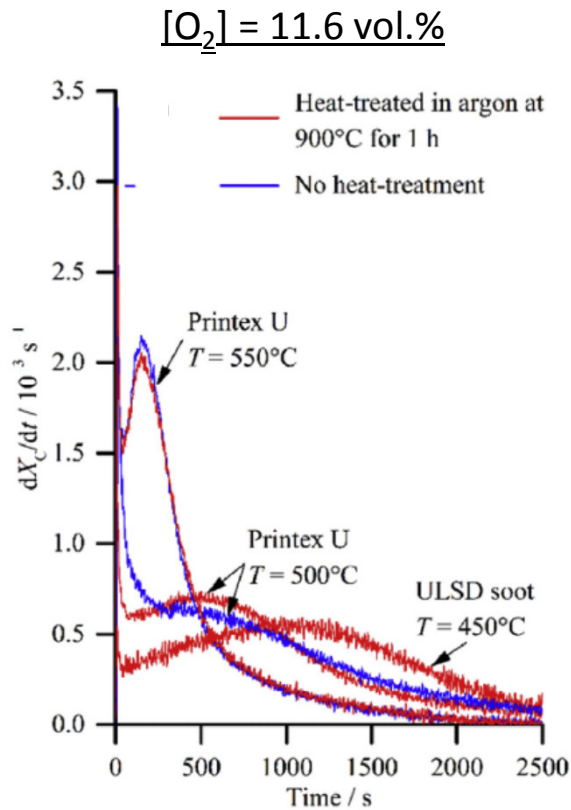
- Initial, rapid reactions consumed ~ 6 % of heat-treated Printex U.

- Unlike the Diesel soots, the rate rose to a second maximum.

- Second maximum also observed with ULSD soot heat-treated at 900°C.

- Consistent with models of the evolution of pores in a burning particle:

(i) Bhatia & Perlmutter [13], allowing for intersection of growing pores:

$$\frac{dX_C}{d\tau'} = \left[\left(1 - \frac{\tau'}{s}\right)^3\left(1 + \frac{\psi\tau'}{2}\right) + \frac{3}{s}\left(1 - \frac{\tau'}{s}\right)\right]\exp\left[-\tau'\left(1 + \frac{\psi\tau'}{4}\right)\right]$$

Initial porosity

- where $\tau' = [k_s C_{O2}{}^n / \rho_M(1 - \varepsilon_{p,0})]t$ and $s = d_{p,0}S_{p,0} / 2(1 - \varepsilon_{p,0})$ and ψ is a parameter, which represents the initial structure of the pores.

(ii) Petersen [14], with no allowance for the intersection of pores:

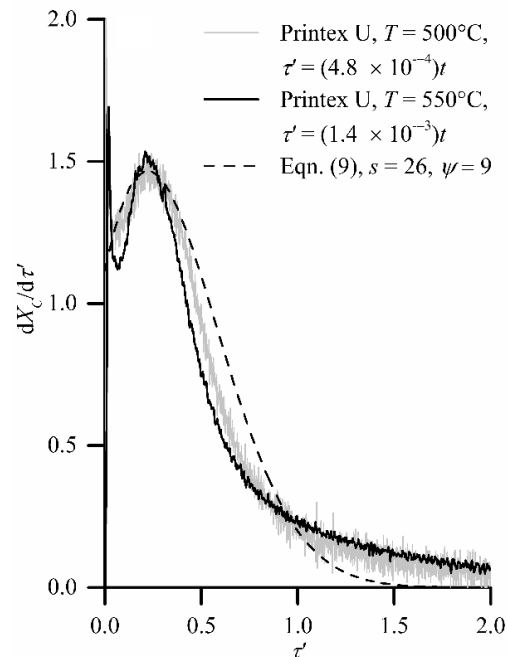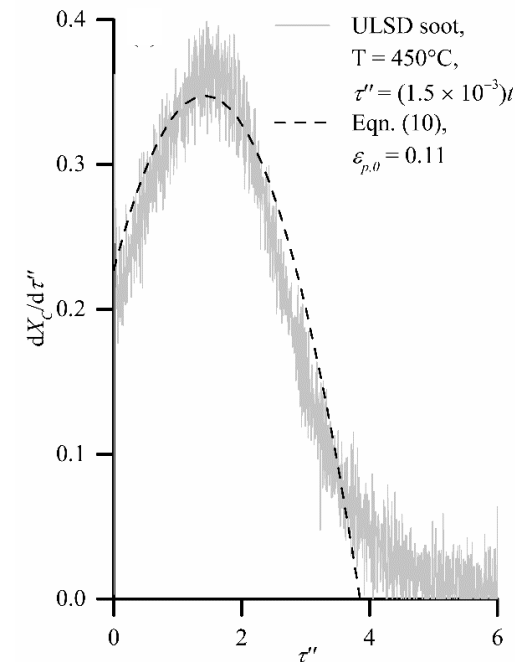$$\frac{dX_C}{d\tau''} = \frac{\varepsilon_{p,0}}{1 - \varepsilon_{p,0}} \frac{2G(1 + \tau'') - 3(1 + \tau'')^2}{G - 1}$$

- where $\tau'' = [2k_s C_{O2}{}^n / d_{p,0}\rho_M]t$ and G is a root of $(4\varepsilon_{p,0}/27)G^3 - G + 1 = 0$

Fitting the Models of Pore Evolution

Printex U – Bhatia & Perlmutter [13]

ULSD soot – Petersen [14]

- Two adjustable parameters: s and ψ.
- For pores, which are of initially uniform diameter, $\psi = \ln(\varepsilon_{p,0}) = 9 \rightarrow \varepsilon_{p,0} = 0.1$.
- However, there is an inconsistency with s.

- One adjustable parameter: $\varepsilon_{p,0} = 0.11$.
- Bhatia & Permutter's model did not fit the second maximum for ULSD soot.

Conclusions

- Rates of oxidation of ULSD and B90 soots were measured in NO_2 or O_2.
- The rate of oxidation of B90 soot by NO_2 was twice that of ULSD soot.
- Surprisingly, in O_2 there was negligible difference in the reactivities of the soots.
- Similar orders of reaction and activation energies were determined for both soots:
  - First order with respect to NO_2, $E \approx 70$ kJ mol^{-1}.
  - Half order with respect to O_2, $E \approx 140$ kJ mol^{-1}.
- Plots of $\ln(1 - X_C)$ against t were compared to physical models of burning spherules:
  - Demonstrated pseudo-homogeneous burning of the two soots in O_2.
  - Suggested that the particles of soot burned mainly on their outsides in NO_2.
- The rates of oxidation of the soots by NO_2 were not controlled by pore diffusion.
- A second maximum in the rate of oxidation of Printex U by O_2 was consistent with a model of pores, growing and intersecting within the spherules.
- The insides of the spherules of the two Diesel soots and Printex U must have been accessible to O_2 as they burned.

Acknowledgements