



UNIVERSITY OF
CAMBRIDGE

Department of Chemical Engineering



THE HETEROGENEOUS REACTION OF OXIDES OF NITROGEN WITH CARBONACEOUS PARTICLES

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Cambridge Particle Meeting

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REACTIONS OF NITROGEN DIOXIDE (NO_2) WITH DIESEL SOOT

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OUTLINE

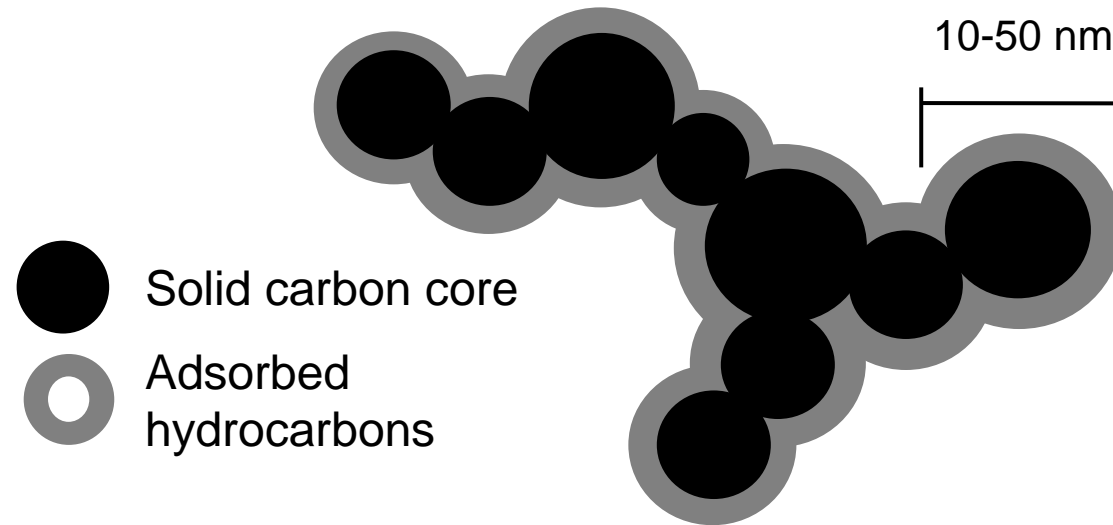
- Background.
- What is Diesel soot?
- Experimental.
- Reactions of NO_2 with Diesel soot.
- Determination of a soot's reactivity.
- The effect of pyrolysis on the reactivity of soot.
- Conclusions.

BACKGROUND

- The oxidation of Diesel soot by NO_2 typically occurs above 200°C .
- Oxidation by O_2 typically occurs above 500°C .
- Consequently, NO_2 may be used to burn out particles of soot from the exhaust of a Diesel engine, at exhaust temperatures (below $\sim 400^\circ\text{C}$).
- This method is employed in e.g. the Johnson Matthey Continuously Regenerating Trap (CRT).
- The objective of this project is to study this reaction and the reactivities of various soots.

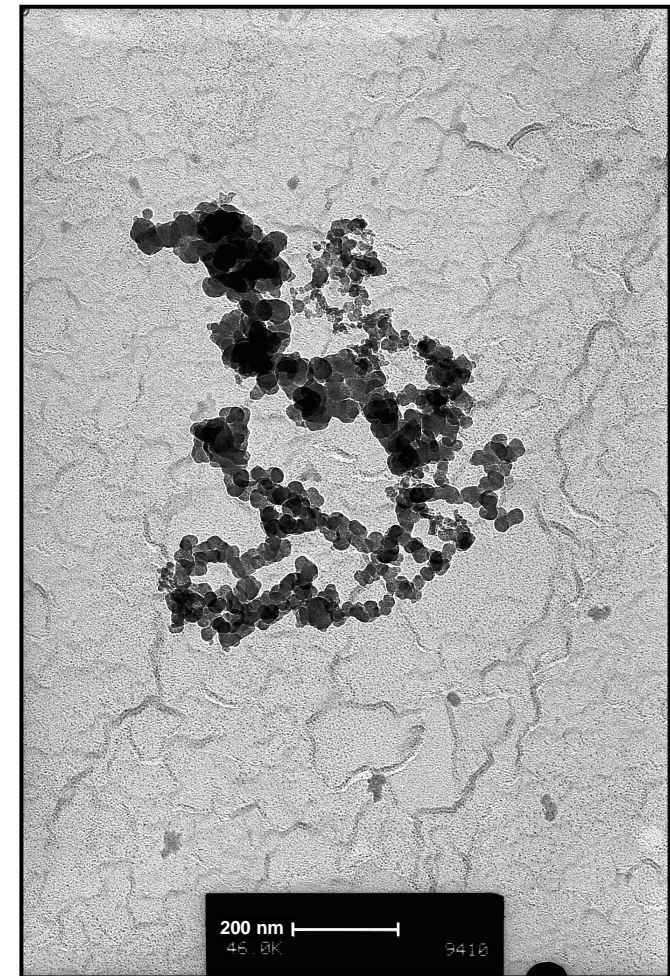
WHAT IS DIESEL SOOT?

- Diesel soot is more complex than a particle of solid carbon.



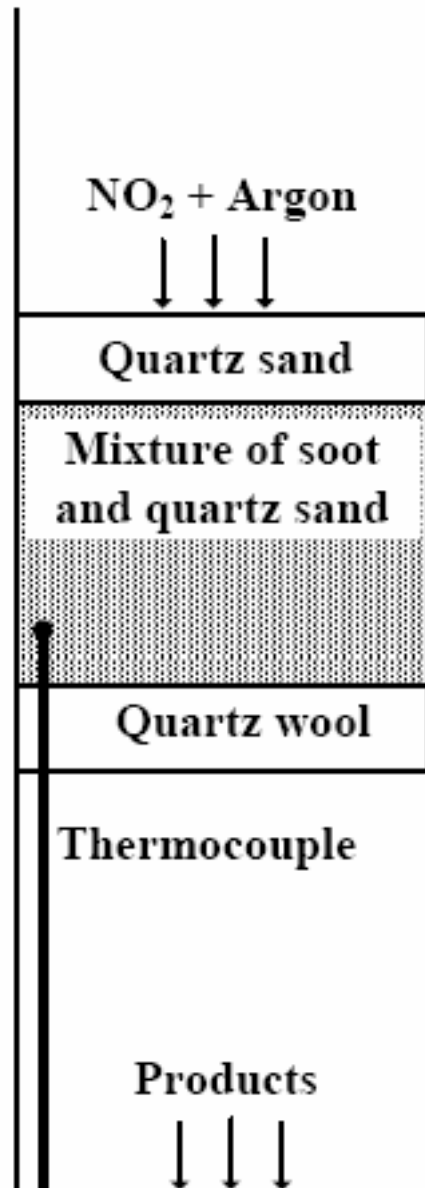
- Solid carbon core encapsulated by a layer of adsorbed hydrocarbons.
- Specific surface area $126 \text{ m}^2 \text{ g}^{-1}$ (BET)

C	H	O	N	Sulphur, ash
83	1.6	~12	0.1	balance



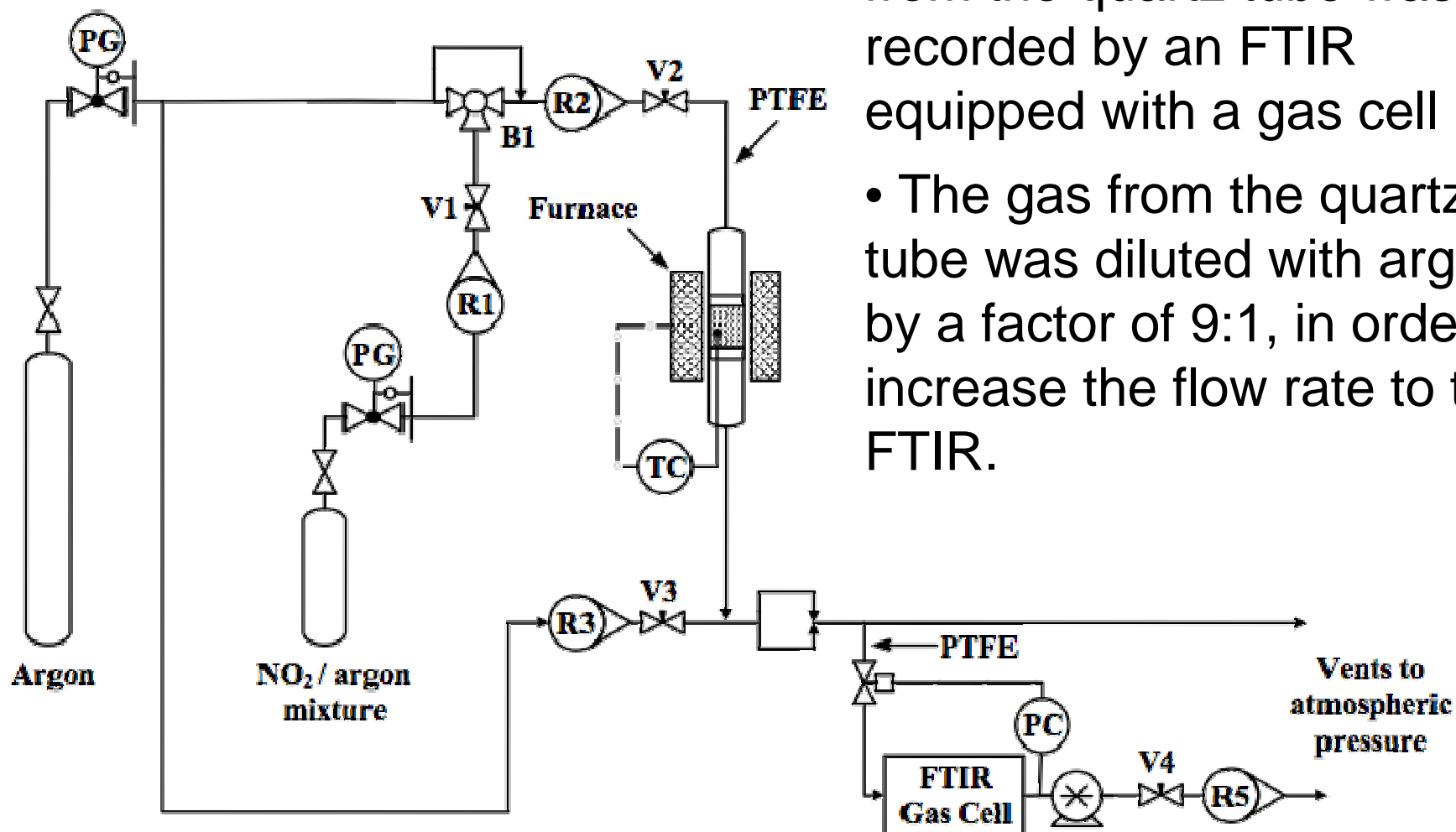
TEM image of Diesel soot

EXPERIMENTAL



- Diesel soot was dispersed in quartz sand (sieved to 150-212 μm).
- A mixture of soot and quartz sand (known masses) was supported on a plug of quartz wool, inside a quartz tube (12 mm OD).
- Argon (0.998%) flowed continuously through the packed bed (flow rate = 275 cc min^{-1} at 25°C and 1 atm., giving a typical residence time = 0.25 s at 300°C).
- The bed was heated to the desired temperature (20 - 500°C) by a surrounding furnace.
- NO_2 was then added to the argon to yield $[\text{NO}_2]_{\text{in}} = 25 - 900$ ppmv.

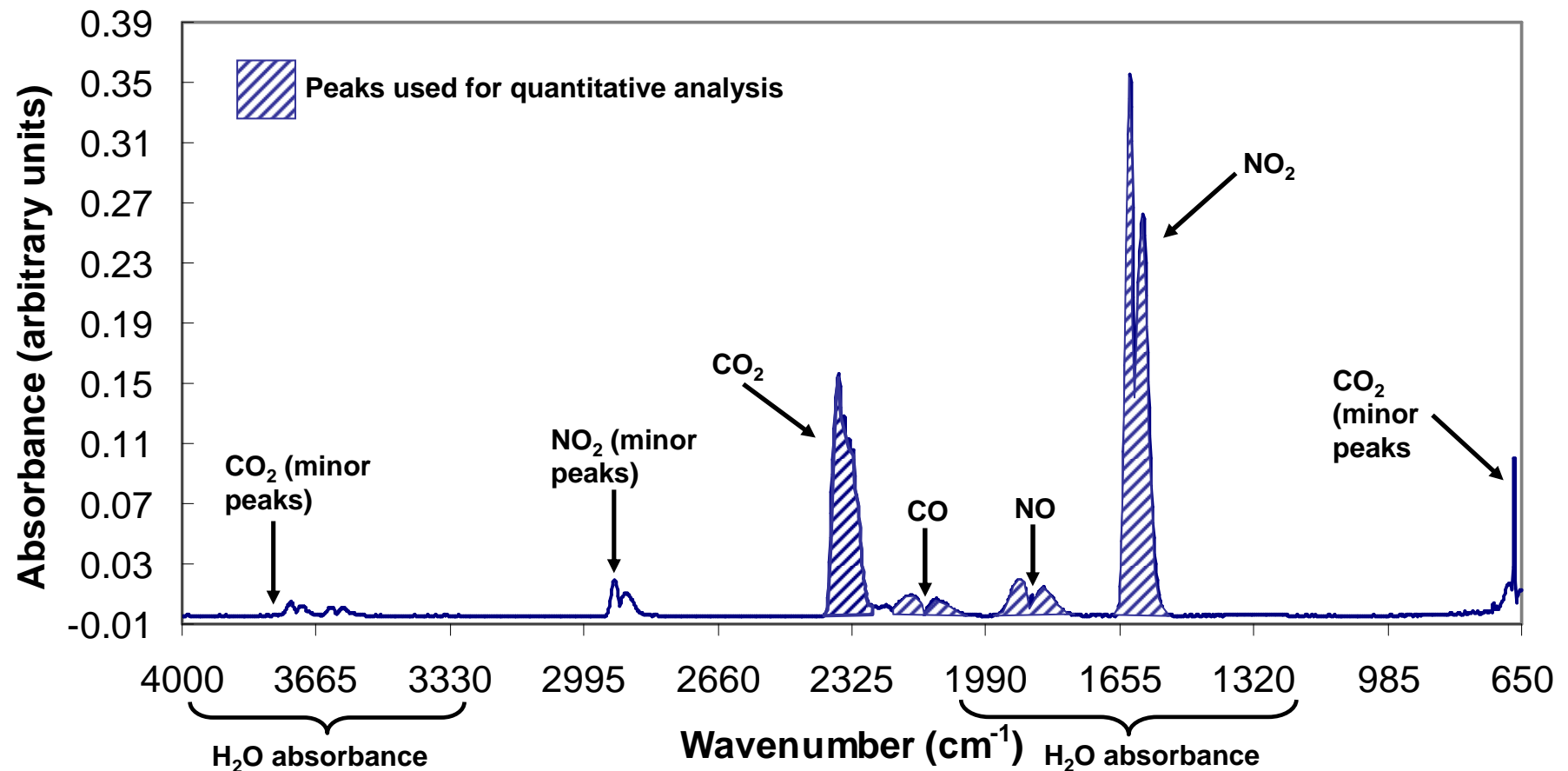
EXPERIMENTAL



- An IR spectrum of the gas from the quartz tube was recorded by an FTIR equipped with a gas cell
- The gas from the quartz tube was diluted with argon by a factor of 9:1, in order to increase the flow rate to the FTIR.

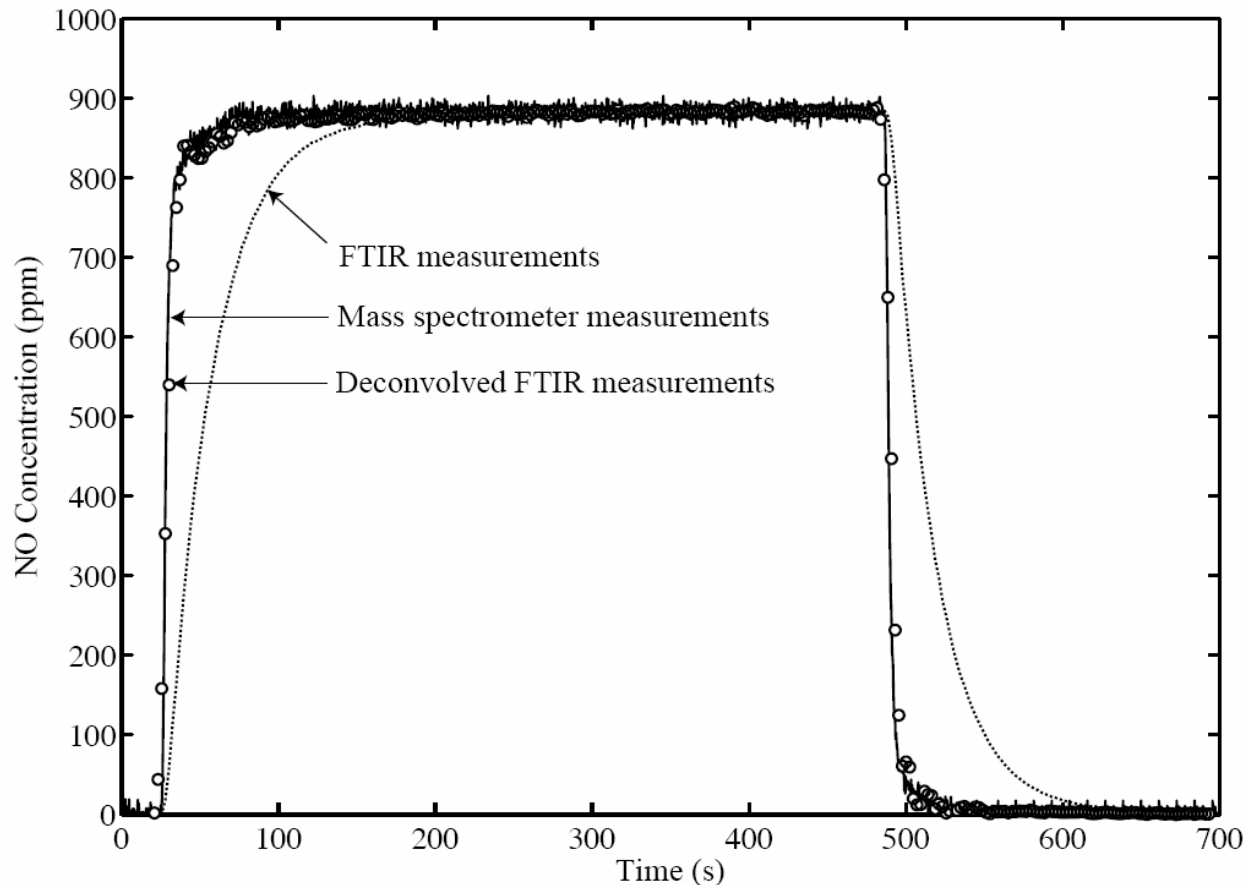
DETERMINATION OF CONCENTRATIONS FROM IR SPECTRA

- Concentrations of NO_2 , NO , CO and CO_2 were determined using the shaded regions of the IR spectrum below. A five point calibration was routinely performed for these species.



DECONVOLUTION OF CONCENTRATION MEASUREMENTS

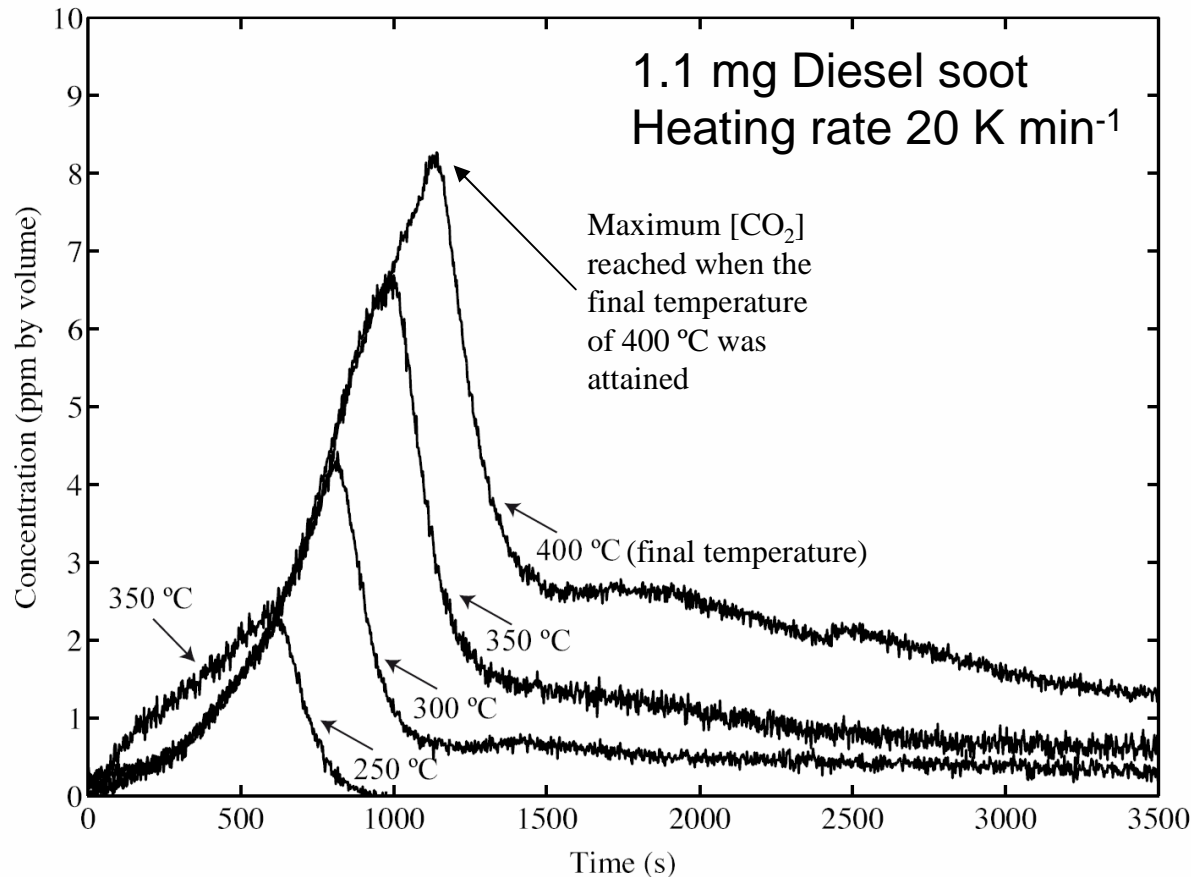
- When the concentration of *e.g.* NO₂ is changing rapidly, the concentration in the gas cell is different from that entering it.



- The response of the sampling system to a step change in NO₂ was used to determine a transfer function.
- Concentration measurements were corrected by deconvolution with this transfer function.

EVOLUTION OF CO₂ ON HEATING DIESEL SOOT IN ARGON

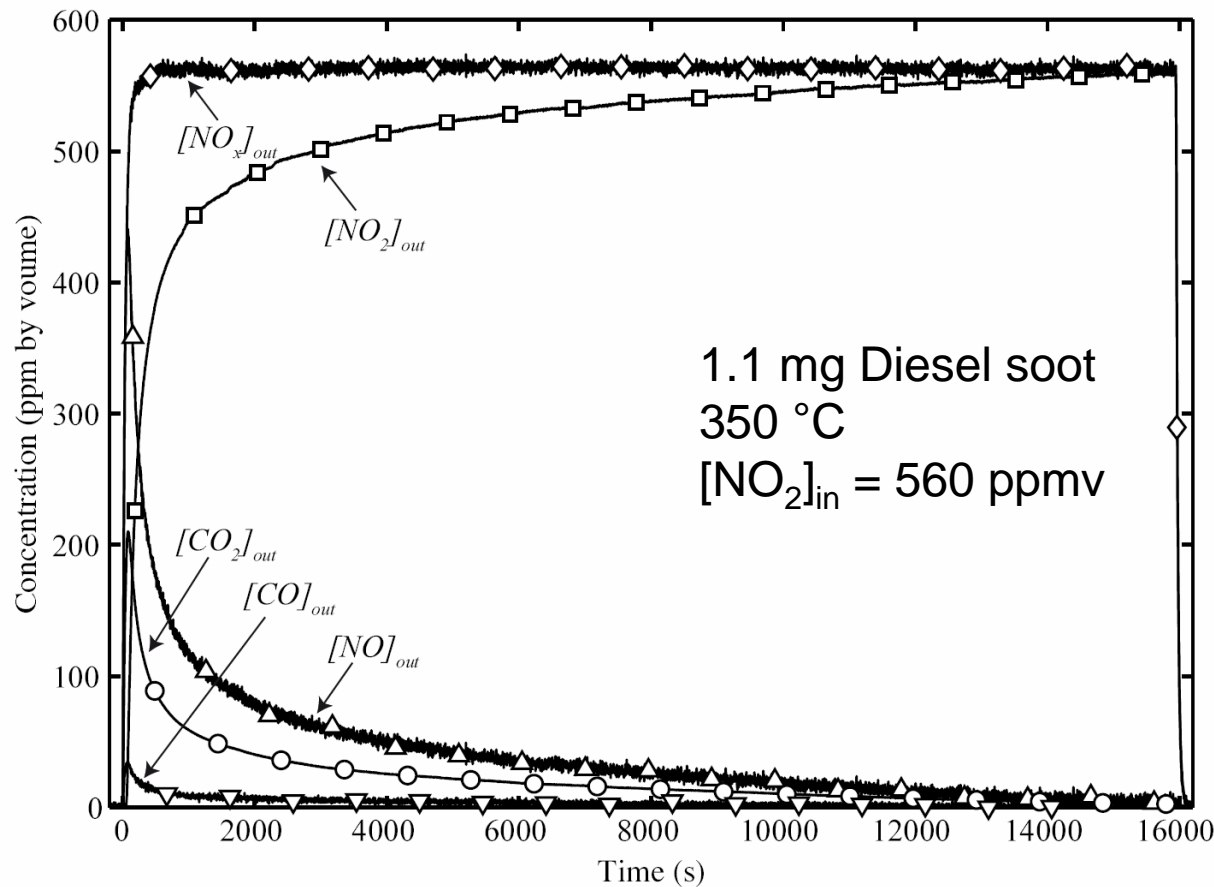
- Diesel soot was heated from ambient to *e.g.* 350°C at a constant rate in a continuous flow of argon.
- Small concentrations of CO₂ were measured (<8 ppm).



- CO₂ originates from the decomposition of labile oxygen adsorbed on the soot.
- This phenomenon was observed when using other soots (*e.g.* Degussa Printex U).
- At > 100°C H₂O from moisture released

THE REACTION OF DIESEL SOOT WITH MIXTURES OF NO_2 AND ARGON

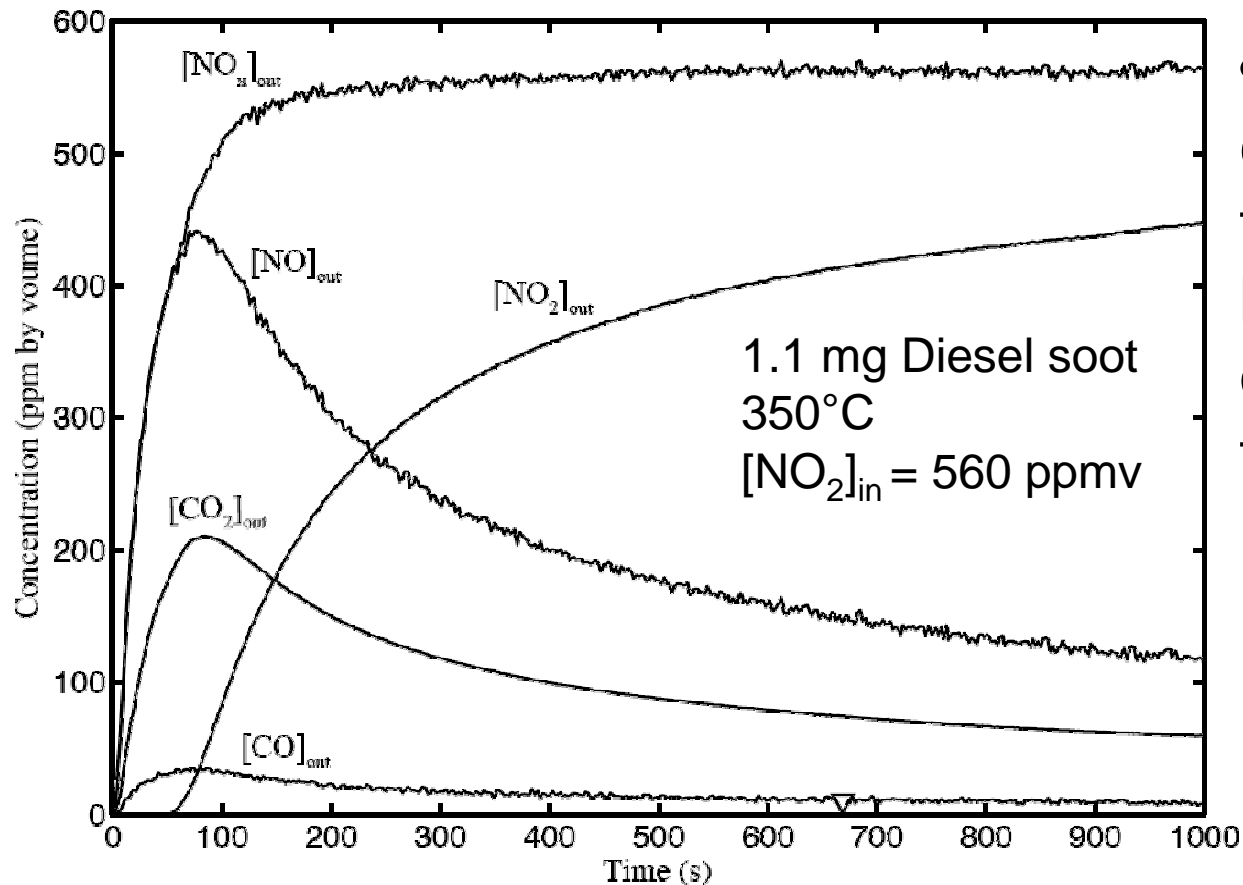
- Diesel soot was first heated to *e.g.* $350\text{ }^\circ\text{C}$ in a continuous flow of argon.



- NO_2 was then introduced to give *e.g.* $[\text{NO}_2]_{in} = 560\text{ ppmv}$.
- The conversion of NO_2 fell from an initial value of unity.
- $[\text{CO}] / [\text{CO}_2]$ was 0.15 *i.e.* CO_2 was the major product.

THE REACTION OF DIESEL SOOT WITH MIXTURES OF NO_2 AND ARGON

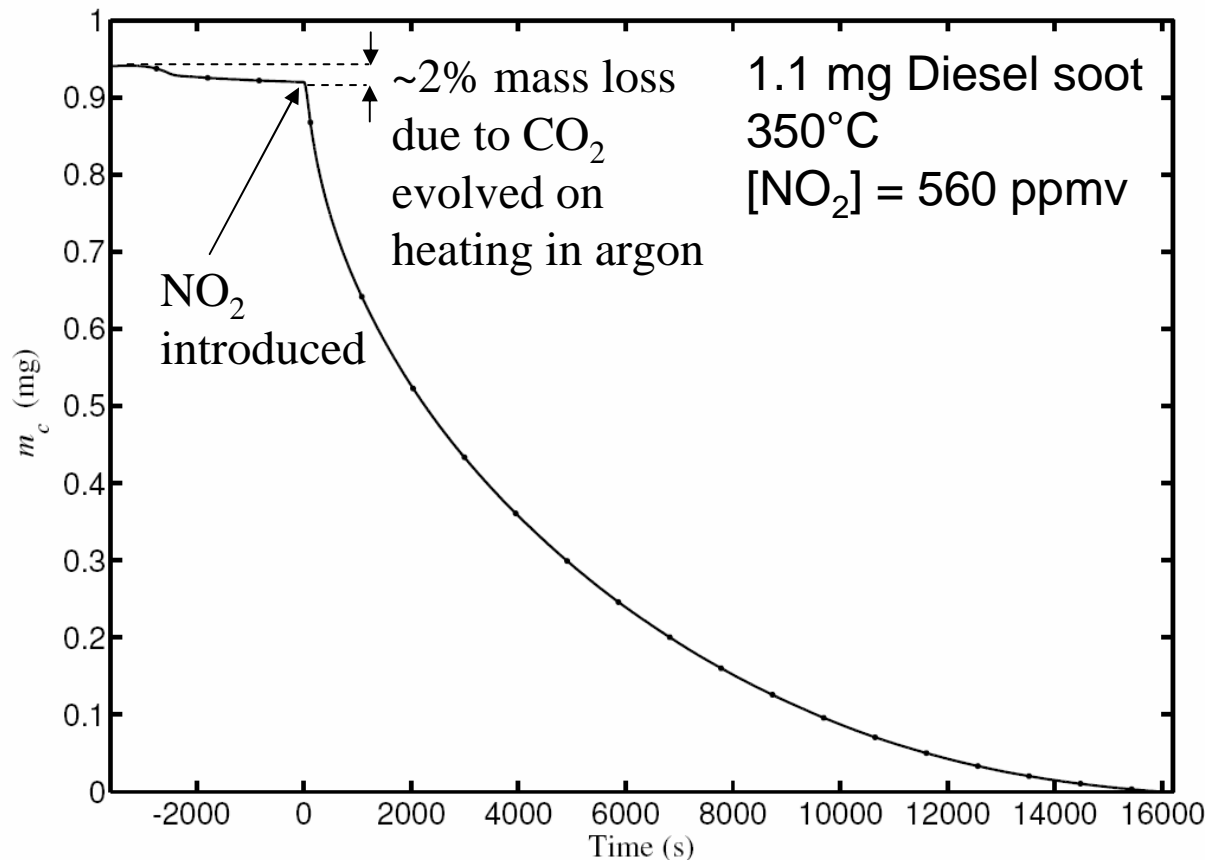
- For $t < 50$ s, no NO_2 was detected in the gas leaving the reactor.



- The mass of carbon consumed up to a time, t , was calculated by integrating the plot of $[\text{CO}_2] + [\text{CO}]$ against time.

DETERMINATION OF THE MASS OF CARBON REMAINING

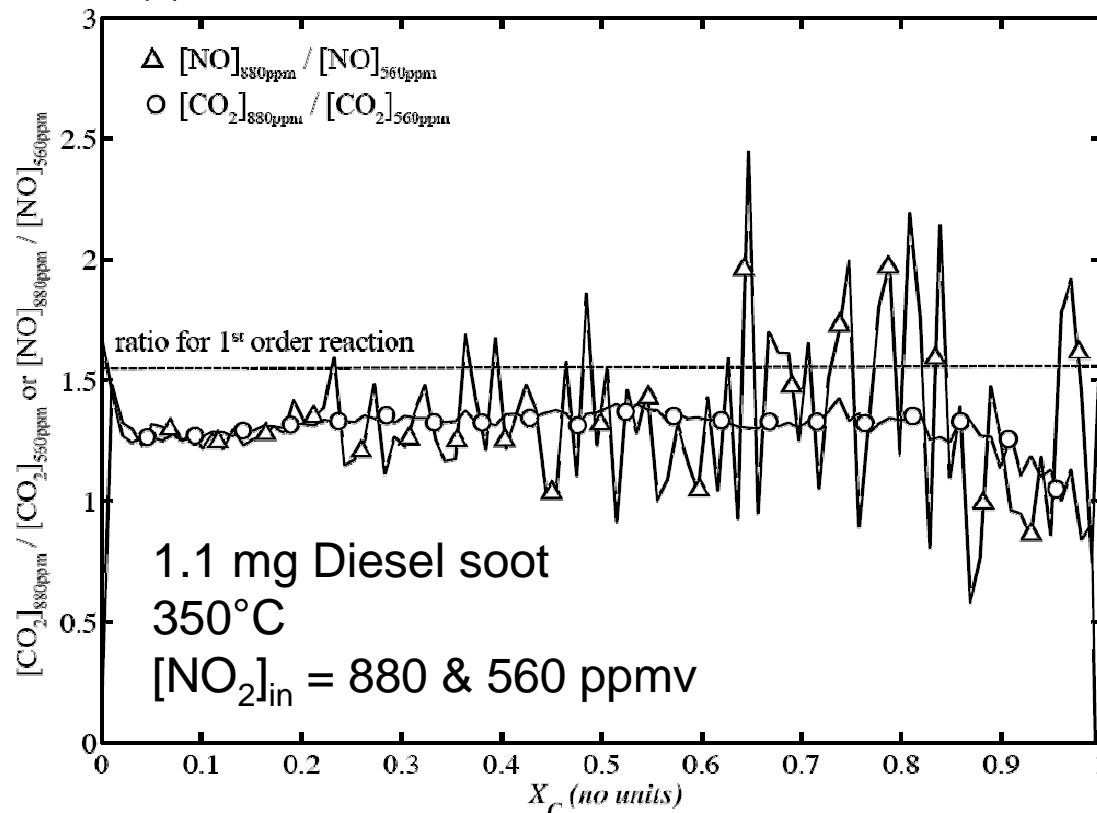
- The total mass of carbon reacted during an experiment was:-
- Derived from the total area under the measured profiles of [CO₂] and [CO].



- Generally within $\pm 10\%$ of the known initial mass of carbon in the packed bed *i.e.* all of the carbon in the soot reappears as CO and CO₂.

OVERALL REACTIONS AND ORDER OF REACTION WITH RESPECT TO NO_2

- The measured concentrations are consistent with the overall reactions:



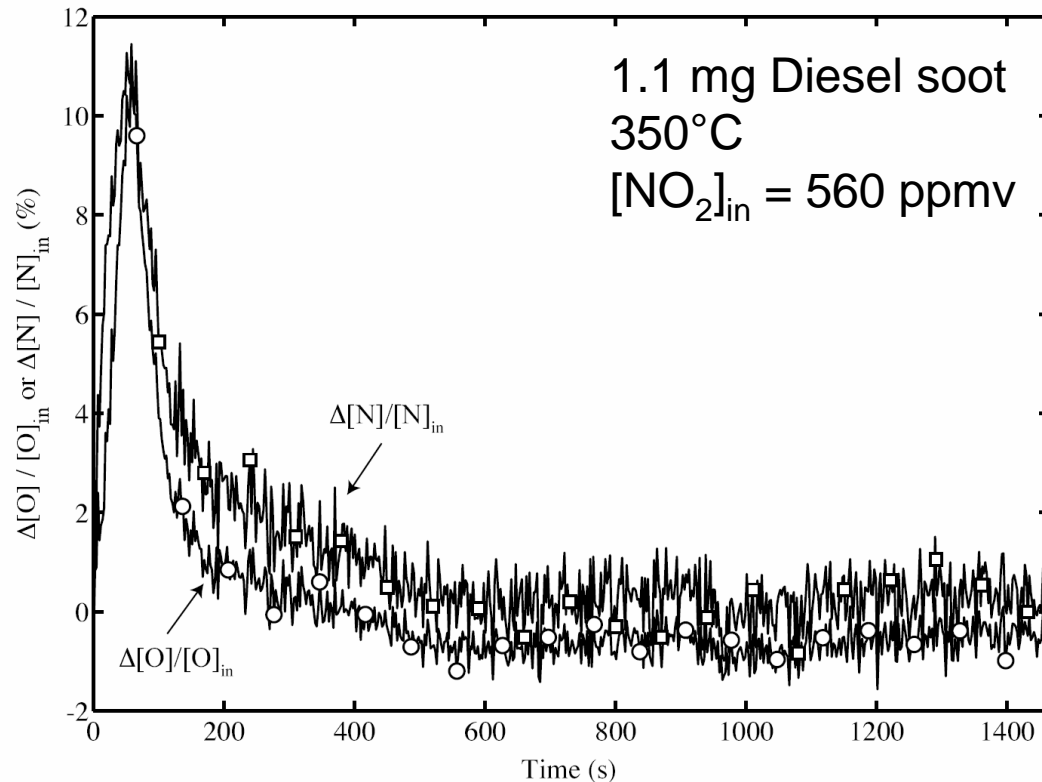
- Below 600°C, Diesel soot does not react with CO_2 or NO .
- Experiments at different $[\text{NO}_2]_{\text{in}}$ indicate that reaction (1) is ~1st order with respect to NO_2 .

MASS BALANCES FOR NITROGEN AND OXYGEN

The changes in the amounts of atomic nitrogen (N) and oxygen (O) during the reaction may be expressed as:

$$\Delta N = [\text{NO}_2]_{\text{in}} - [\text{NO}_2]_{\text{out}} - [\text{NO}]_{\text{out}}$$

$$\Delta O = 2[\text{NO}_2]_{\text{in}} - 2[\text{NO}_2]_{\text{out}} - [\text{NO}]_{\text{out}} - 2[\text{CO}_2]_{\text{out}} - [\text{CO}]_{\text{out}}$$



- For $t < 200$ s there was a net loss of up to 10% N and O, suggesting that NO₂ was adsorbed.
- For $t > 200$ s, $\Delta N = 0 \pm 3\%$ and $\Delta O = -2 \pm 3\%$.
- NO₂ was then converted totally to NO and oxidation of soot was only by NO₂.

DETERMINATION OF A SOOT'S REACTIVITY

- NO_2 was consumed when passing over Diesel soot. Therefore the soot at the top of the bed was exposed to a higher $[\text{NO}_2]$ than the soot at the bottom.
- Also, as the mass of soot decreased, less CO_2 and CO were produced *i.e.* less NO_2 was converted to NO .
- We want a measure of a soot's reactivity which takes into account both the conversions of NO_2 and of soot.
- We can define an effective rate coefficient for reaction (1), $k_{\text{CO}_2,m}$, based on the mass of carbon. For reaction (1), first order in $[\text{NO}_2]$, the local rate of consumption of carbon is:

$$-r_C = k_{\text{CO}_2,m} w_C C_{\text{NO}_2}.$$

where C_{NO_2} is the local concentration of NO_2 and w_C is the local mass of carbon per unit volume of the bed.

DETERMINATION OF A SOOT'S REACTIVITY (2)

- Reaction (1) was modelled by two coupled partial differential equations, representing the gas and solid phases. The behaviour of the system was investigated by solving these equations numerically with representative rate constants.
- Assuming plug flow in the gas phase and that the rate of change of X_C with time is slow (pseudo-steady state with respect to the soot), a simplified differential equation governing the conversion of NO_2 over the packed bed, X_{NO_2} , is

$$\frac{\partial X_{\text{NO}_2}}{\partial Z} = \frac{2k_{\text{CO}_2,m}m_{\text{C},0}}{Q}(1 - X_{\text{NO}_2})(1 - X_C).$$

where Z is the dimensionless length of the bed, Q is the total flow rate of gas, $m_{\text{C},0}$ is the total mass of carbon at $t = 0$ and

$$X_{\text{NO}_2} = \frac{[\text{NO}_2]_{\text{in}} - [\text{NO}_2]_{\text{out}}}{[\text{NO}_2]_{\text{in}}} = \frac{2[\text{CO}_2]_{\text{out}}}{[\text{NO}_2]_{\text{in}}}, \quad X_C = \frac{W_{\text{C},0} - W_C}{W_{\text{C},0}}.$$

DETERMINATION OF A SOOT'S REACTIVITY (3)

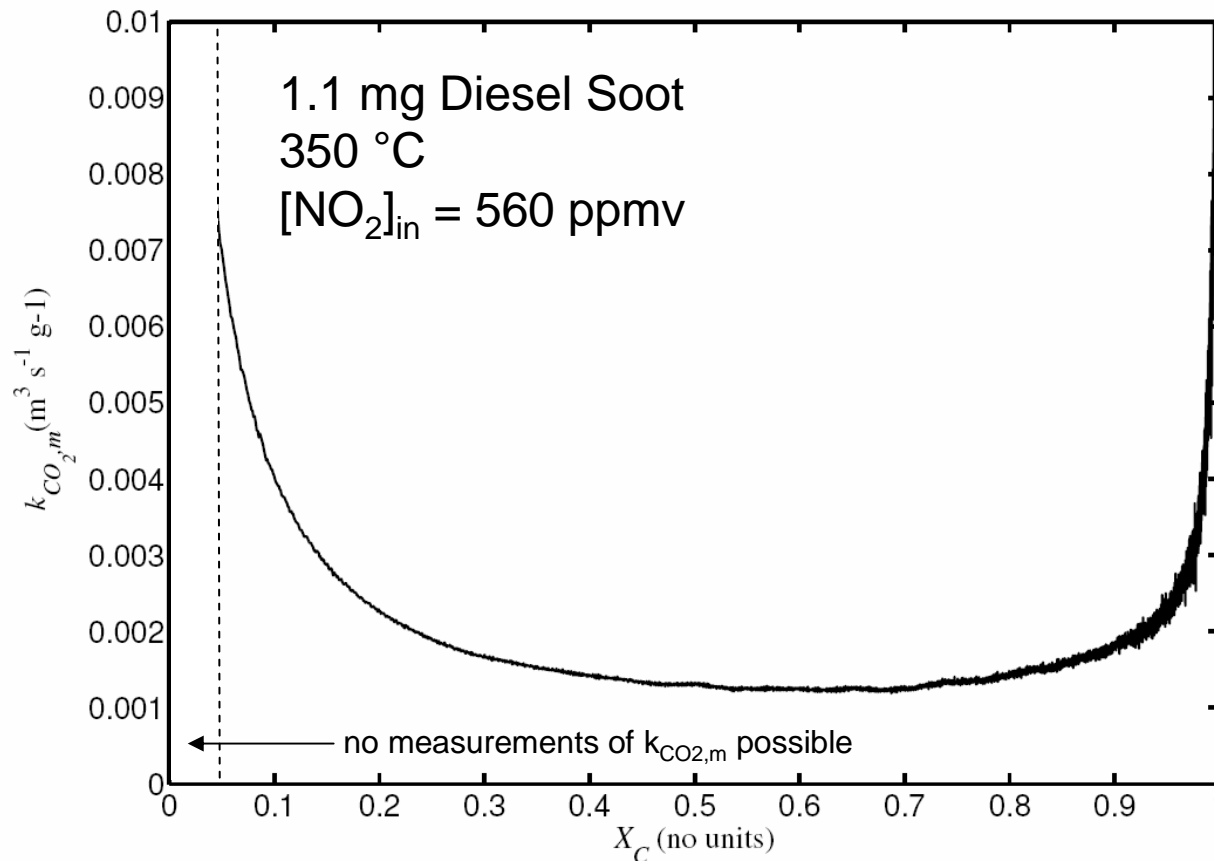
- The numerical results showed that with representative rate constants, X_C is spatially uniform to within $\pm 10\%$. In this case, the simplified differential equation may be integrated over the length of the packed bed to give

$$k_{CO_2,m} = -\frac{Q}{2m_{C,0}} \frac{\ln(1 - X_{NO_2})}{(1 - X_C)}. \quad X_C = \frac{m_{C,0} - m_C}{m_{C,0}}.$$

- X_{NO_2} and X_C were determined from measured concentrations.
- Therefore $k_{CO_2,m}$ was derived for each measurement point.
- This method is not applicable for $[NO_2]_{out} = 0$.

CHANGES IN REACTIVITY OF DIESEL SOOT WITH CONVERSION

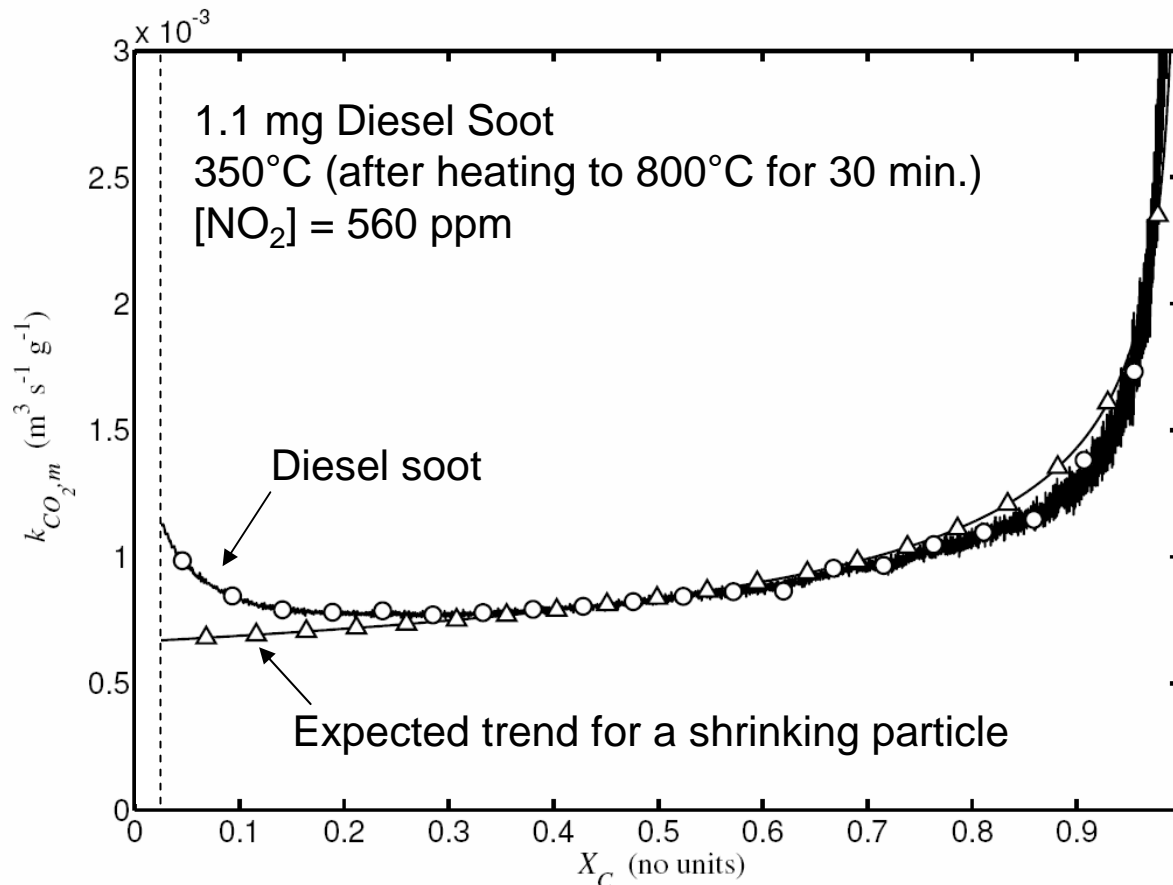
- The value of $k_{CO_2,m}$ at $X_C = 0.05$ was ~ 5 times higher than at $X_C = 0.5$, *i.e.* the reactivity of the Diesel soot is initially high.



- $k_{CO_2,m}$ was constant between $X_C = 0.3$ and 0.8
- $k_{CO_2,m}$ increased rapidly at conversions approaching 1.
- The specific surface area of the soot particles increases whilst they shrink.

THE EFFECT OF PYROLYSING SOOT PRIOR TO REACTING IT WITH NO_2

- Diesel soot was first heated in argon to $800\text{ }^\circ\text{C}$ for 30 min, then cooled to $350\text{ }^\circ\text{C}$ before exposure to NO_2 .

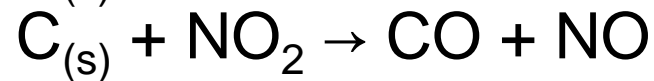
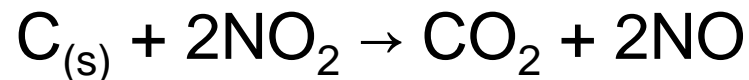


- $k_{\text{CO}_2,m}$ at $X_C = 0.02$ was only ~ 1.5 times higher than at $X_C = 0.5$ *i.e.* pyrolysing the soot reduces its reactivity in the earliest stages.
- Reactivity increases at $X_C > 0.2$ and more rapidly at $X_C > 0.8$ *cf.* shrinking particle.

CONCLUSIONS

- Above 200°C, NO₂ oxidises soot to form NO, CO₂ and, to a lesser extent, CO.

- In spite of the complex nature of Diesel soot, the consumption of carbon in the soot is described by only two overall reactions:



- The reactivity of Diesel soot is initially high, because of the adsorbed hydrocarbons being burned. The reactivity of Diesel soot at $X_C = 0.05$ is ~ 5 times higher than at $X_C = 0.5$.

- Pyrolysis of Diesel soot at 800 °C prior to reaction with NO₂ at 350°C reduces the initial high reactivity and leads to behaviour consistent with that of a shrinking particle.

ACKNOWLEDGEMENTS

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