Catalytic Coatings for Diesel Particulate Filter Regeneration

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Abstract:
Diesel particulate filter can reduce nano-particulate emissions very efficiently.
The major challenge for all diesel particulate filter systems is their regeneration. Catalytic coatings can be used for diesel particulate filter system regeneration in several ways to enable or support filter regeneration by nitrogen dioxide or oxygen. Catalyst coatings can be placed on a catalyst substrate in front of the filter (CRT®), on the filter (CSF) or in a combined system (CCRT). Strategies and conditions for successful filter system regeneration of those systems are discussed.

Introduction:
Catalytic coatings are applied to clean up diesel emissions in millions of diesel oxidation catalysts, hundreds of thousands of diesel passenger car soot filter systems and tens of thousands commercial vehicle soot filter systems. Catalytic coatings have to meet several, sometimes conflicting targets like high activity and selectivity, a broad operational temperature window, high chemical and thermal durability as well as a minimum negative influence on exhaust backpressure. The main functions of catalytic coatings are catalysing oxidation reactions and (temporarily) trapping exhaust components.
In diesel applications catalytic coatings are used in oxidation catalysts, filter coatings and NOx storage catalysts or selective catalytic reduction (SCR) systems.
Regeneration is the key challenge for diesel particulate filter systems. While the use of fuel borne catalysts requires additional additive dosing equipment and adds to the amount of ash collected on filter systems, the use of catalytic coatings for particulate filter system regeneration does not require any additive dosing equipment and minimises the ash collected on filter systems to oil an fuel ash components. This is particularly important for HDD applications in order to minimise the required filter cleaning intervals.

Main conclusions:
Catalytic coatings can be utilised in many ways to enable particulate filter regeneration. Depending on the planned application, it can be chosen from a catalytic coating in front of a particulate filter (CRT®), on the filter (CSF) or in a combined system (CCRT). On the example of CRT® systems long-term durability of such systems has been demonstrated.
NO_2-slip, which has been associated with Pt-containing aftertreatment systems can be minimised by an optimised system design.
If the conditions are suitable, those systems can make use of the NOx content of the emissions and can be applied as passive systems. At low temperature applications, those systems may be applied in active systems, using the NOx- or oxygen content of the emissions. Active regeneration of such systems has been successfully demonstrated for NO_2 and O_2 based regenerations. 4-way systems are under development. They will allow the simultaneous reduction of CO, HC, PM and NOx emissions.

Catalytic Coatings for Diesel Particulate Filter Regeneration

Dr. Claus Görsmann, Dr Andy Walker

JOHNSON MATTHEY PLC, Royston/UK

Zurich, August 2003

Presentation Outline

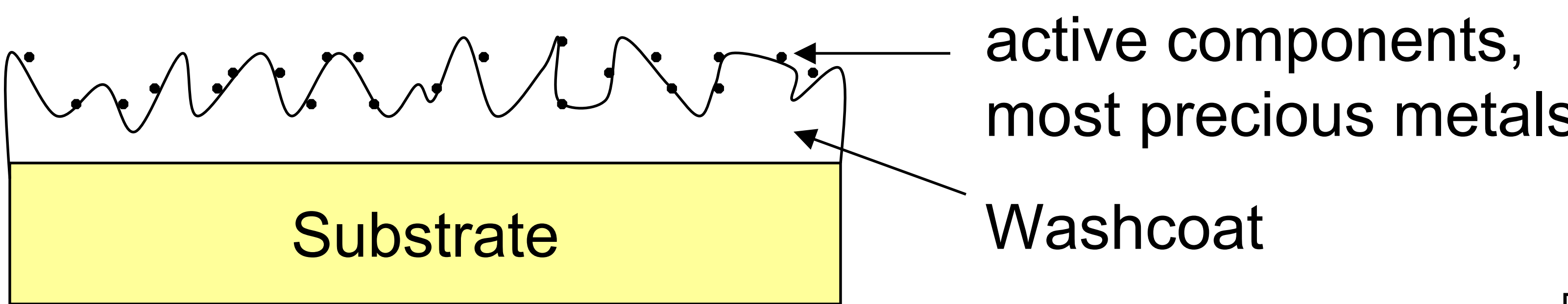
- **Introduction - catalytic coatings**
- **Diesel particulate filter – possibilities for regeneration**
- **Passive regeneration via NO_2**
  - CRT®
    - **Field experience**
  - CSF
  - CCRT
- **Active regeneration via NO_2 or O_2**
- **Overview DPF-systems / conclusions**
- **Outlook: 4-way-systems: simultaneous CO, HC, PM and NOx-reduction**

Catalytic Coatings...

- **are applied to clean-up diesel emissions in**
  - Millions of diesel oxidation catalysts (standard in modern diesel passenger cars)
  - Hundreds of thousands of diesel passenger car soot filter systems
  - Tens of thousands of commercial vehicle soot filter systems

- **are applied to surfaces in exhaust aftertreatment systems, usually on special support materials (catalyst substrates or soot filter)**
  - Typical catalyst support materials are cordierite (ceramic) or steel (metal)
  - Typical filter materials are silicon carbide (SiC), cordierite or sinter metal

- **consist of catalytic active components (often precious metals) and components, which enhance their efficiency and durability. Those components are called „Washcoat“**



General Requirements for Catalytic Coatings

1. High activity (and sometimes selectivity e.g. for SCR-catalysts) to operate in a broad temperature window
2. High chemical and thermal durability
3. Minimum negative influence on exhaust backpressure (especially for soot filter coatings)

Measures to meet those targets are often conflicting and require compromises and optimisations for the application

Catalytic Redox Reactions to Clean up Pollutants from Diesel Exhaust

Reductant + Oxidant → **Redox-Catalyst** → Products + Heat

Reductant	***Oxidant***	***Most imp. cat. property***	***Desired Product(s)***
CO	O_2	**Activity**	CO_2
HC	O_2	**Activity**	$CO_2 + H_2O$
C (PM)	O_2	**Activity**	CO_2
NO	O_2	**Activity**	NO_2 **f. C-oxidation**
HC	O_2	**Thermal Durabiliy**	**Heat**
HC	**NOx**	**Temperature Window**	$N_2 + CO_2 + H_2O$
Urea	**NOx** (+ O_2)	**Temperature Window**	$N_2 + CO_2 + H_2O$
NO_2	$BaCO_3$	**Activity**	$Ba(NO_3)_2$ **f. Storage**
HC	H_2O	**Activity**	H_2 **as reductant**
CO	H_2O	**Activity**	H_2 **as reductant**

“Non-Catalytic“ Redox Reactions to Clean up Pollutants from Diesel Exhaust

$$\text{Reductant} + \text{Oxidant} \longrightarrow \text{Products} + \text{Heat}$$

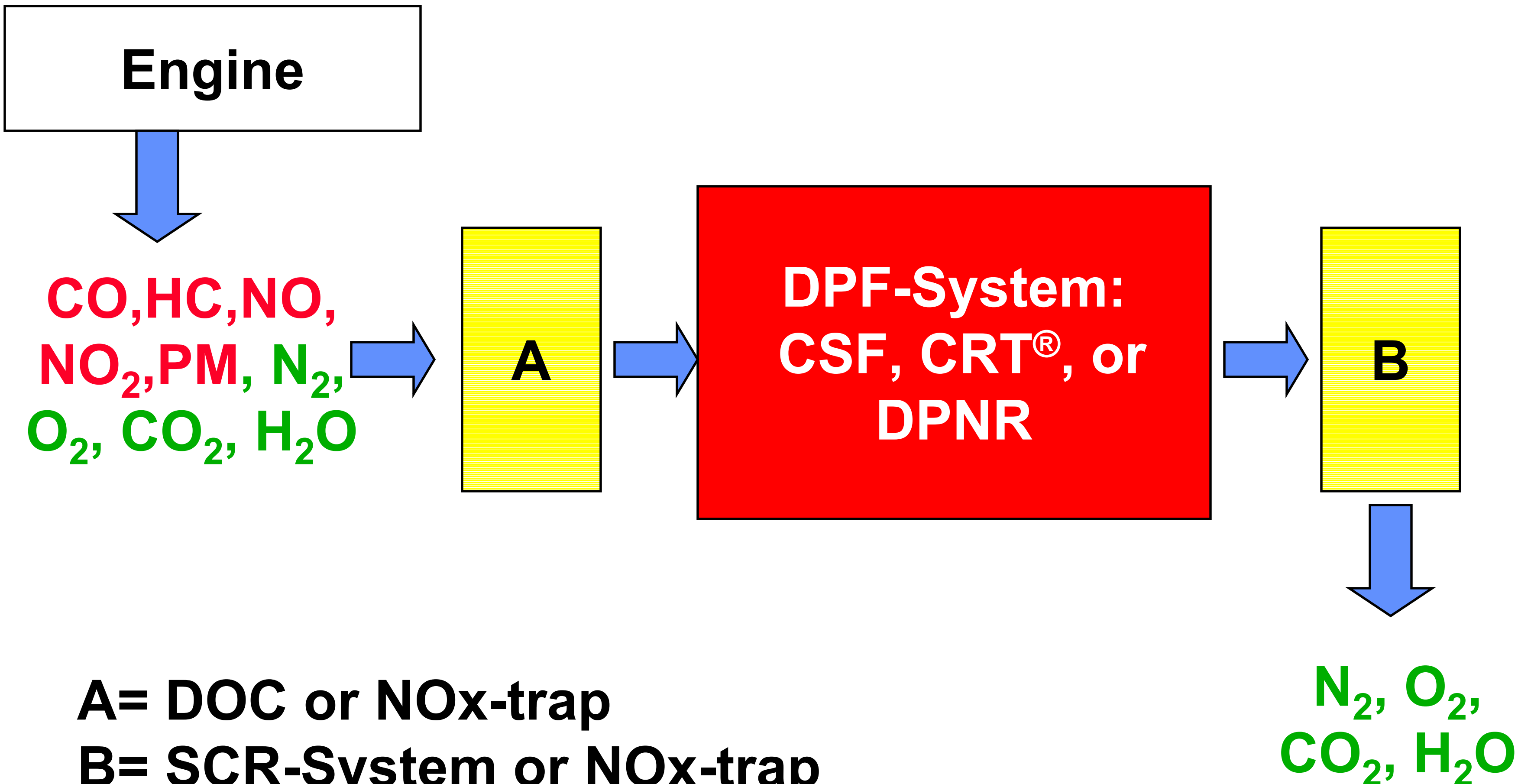
Reductant	*Oxidant*	*Desired Product(s)*
C (from PM)	O_2	CO_2
C (from PM)	NO_2	CO_2

Trapping of Components

- **Physical**
  - **Particulates** on (filter-) surfaces
  - HCs on zeolites (before catalyst light-off)

- **Chemical**
  - NOx trapping (and release)
    - **2 NO_2 (gas) + $BaCO_3$ → $Ba(NO_3)_2$ (solid) + CO_2**
    - **CO + $Ba(NO_3)_2$ (solid) → $BaCO_3$ + 2 NO_2 (gas) to be reduced to N_2 under rich engine conditions**

Catalytic Systems in Diesel Exhaust



A= DOC or NOx-trap
B= SCR-System or NOx-trap

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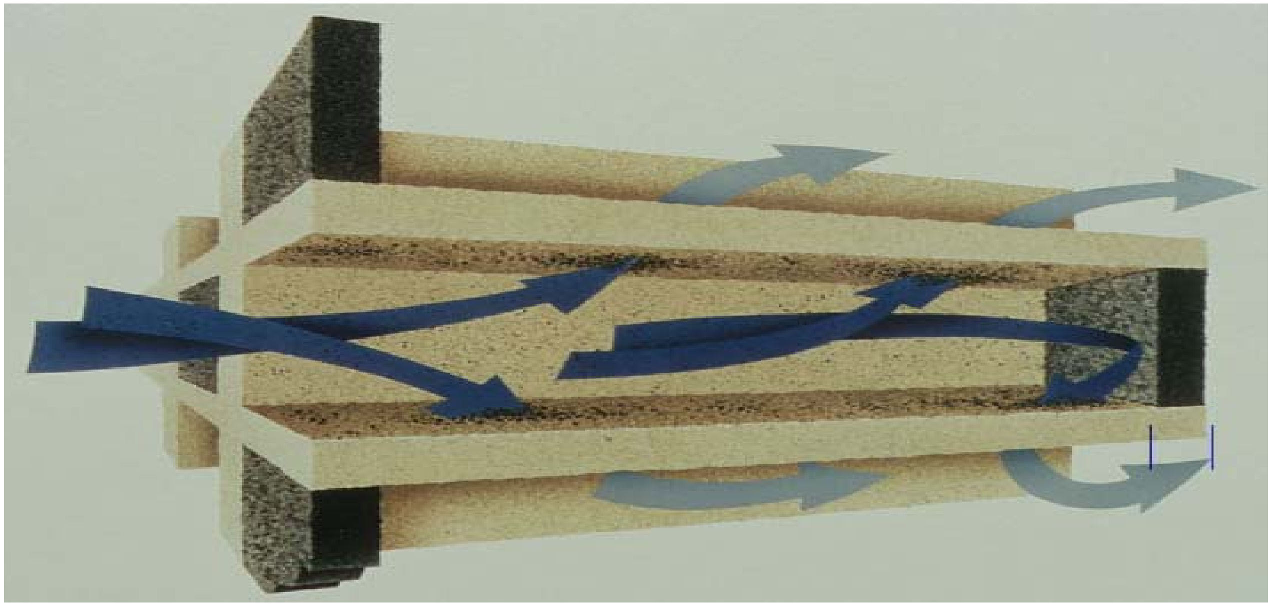
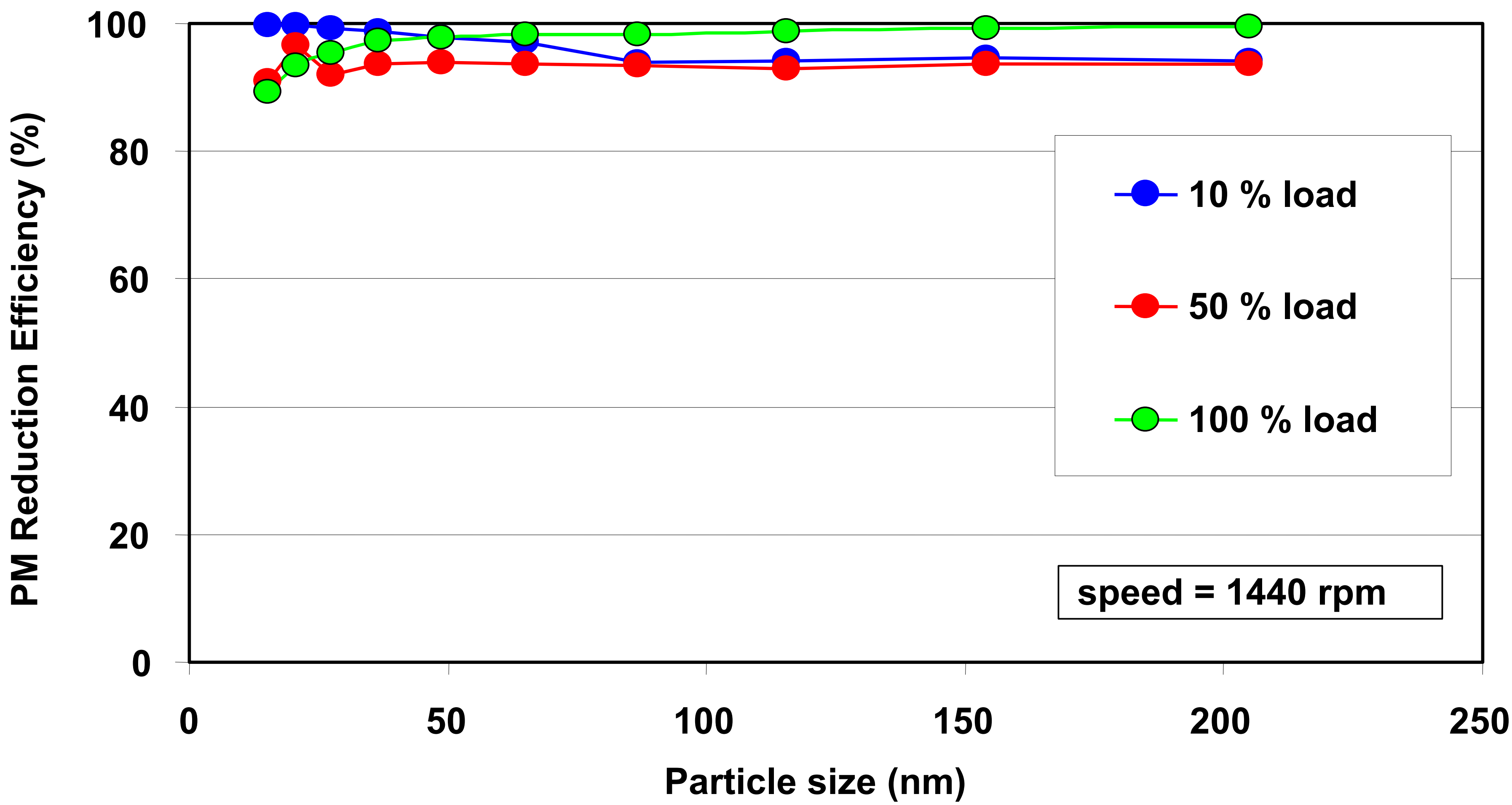
Trapping Particulates (DPF)



- **Typical filter materials of wall through filters are cordierite, silicon carbide or sinter metal.**
- **Typical soot filtration efficiency > 90% of PM mass.**

DPFs Control Nanoparticle Emissions



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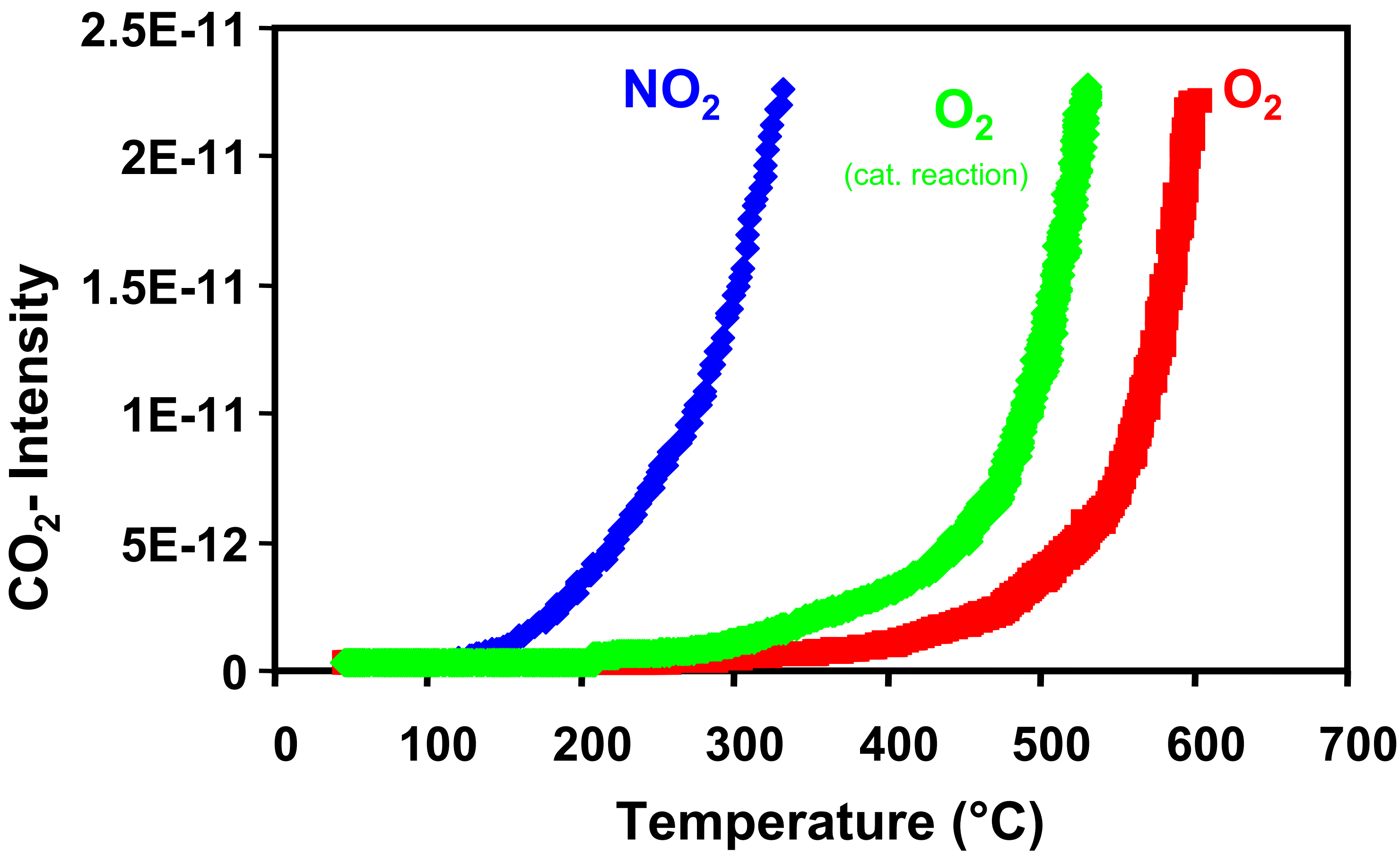
Temperatures at Which NO_2 and O_2 Combust Soot



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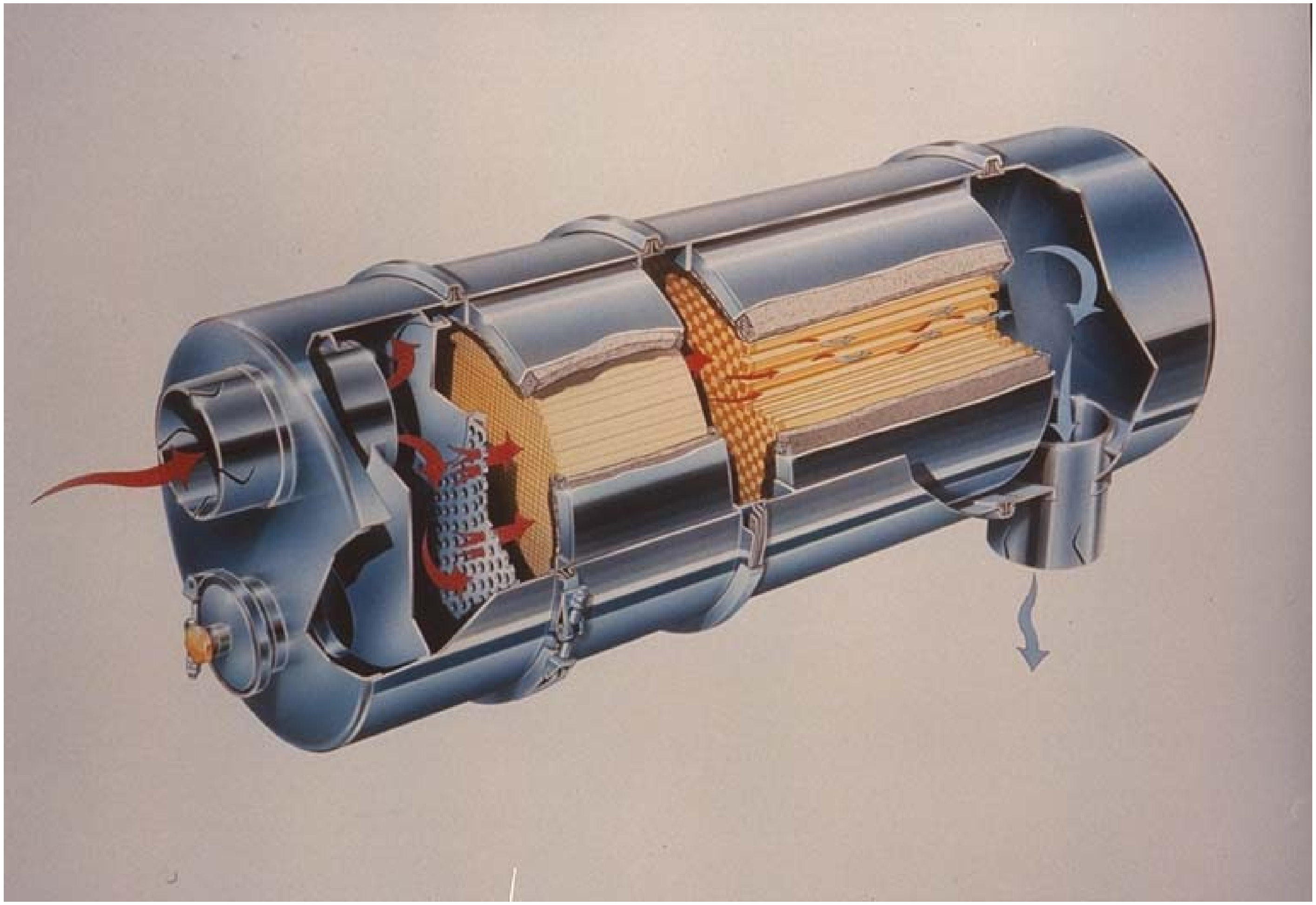
Carbon Combustion at Low Temperatures

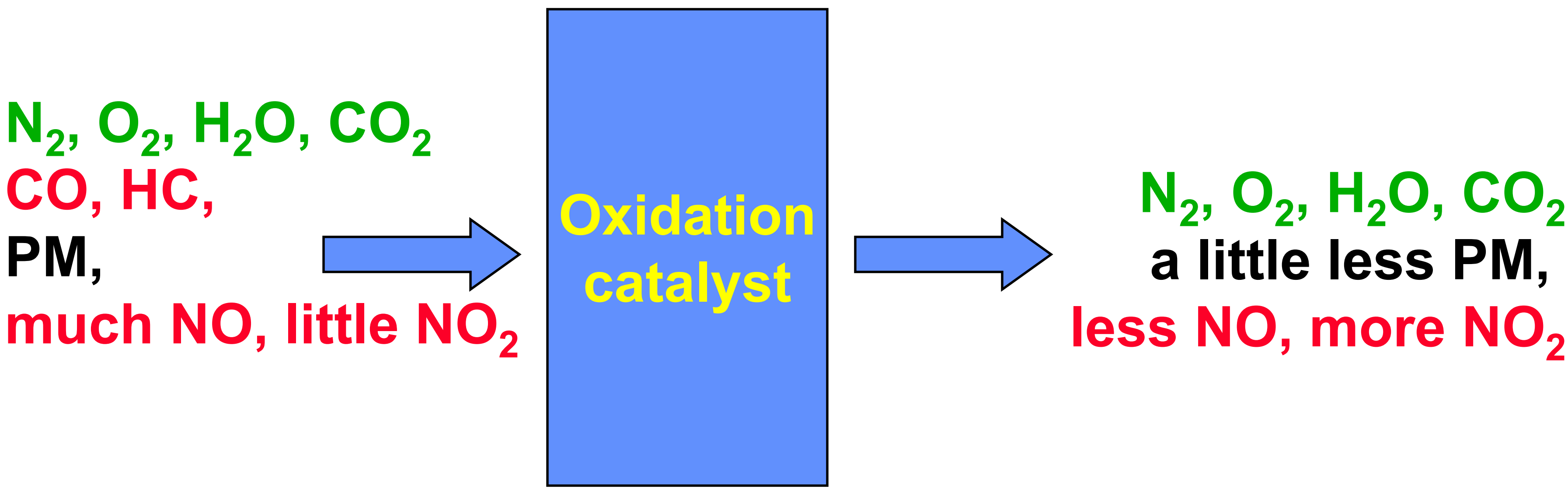
Nitrogen dioxide (NO_2)

- **oxidises carbon at low temperatures**
- **can be generated from NO**
  - by an oxidation catalyst upstream of the filter
    - **CRT® -system**
  - by a catalytic coating on the filter itself
    - **CSF (= CDPF), z.B. DPX™**

CRT® Schematic Diagram



Passive Regeneration by NO_2
- Effect of Oxidation Catalysts

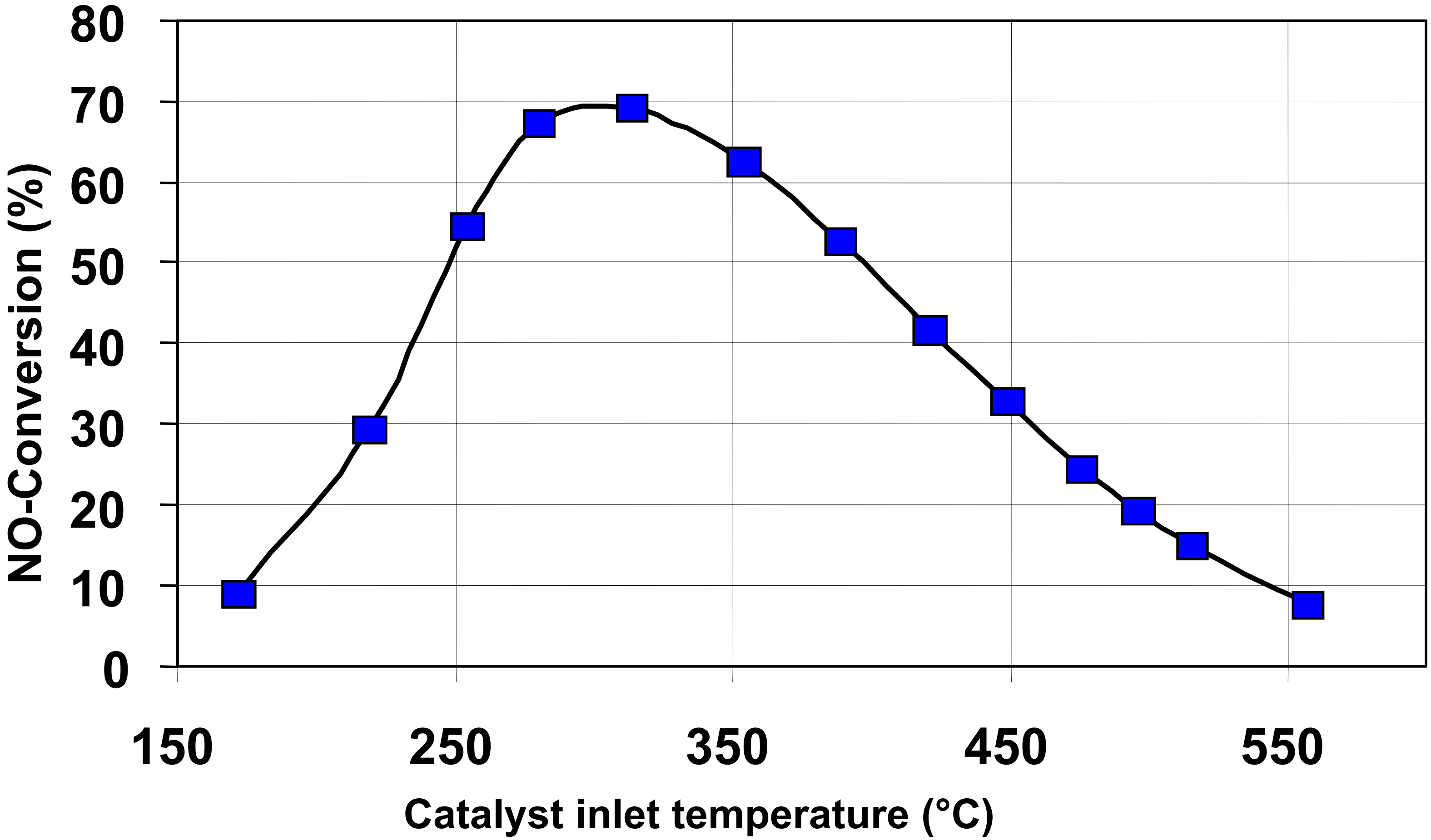


CO Oxidation at T > 150°C

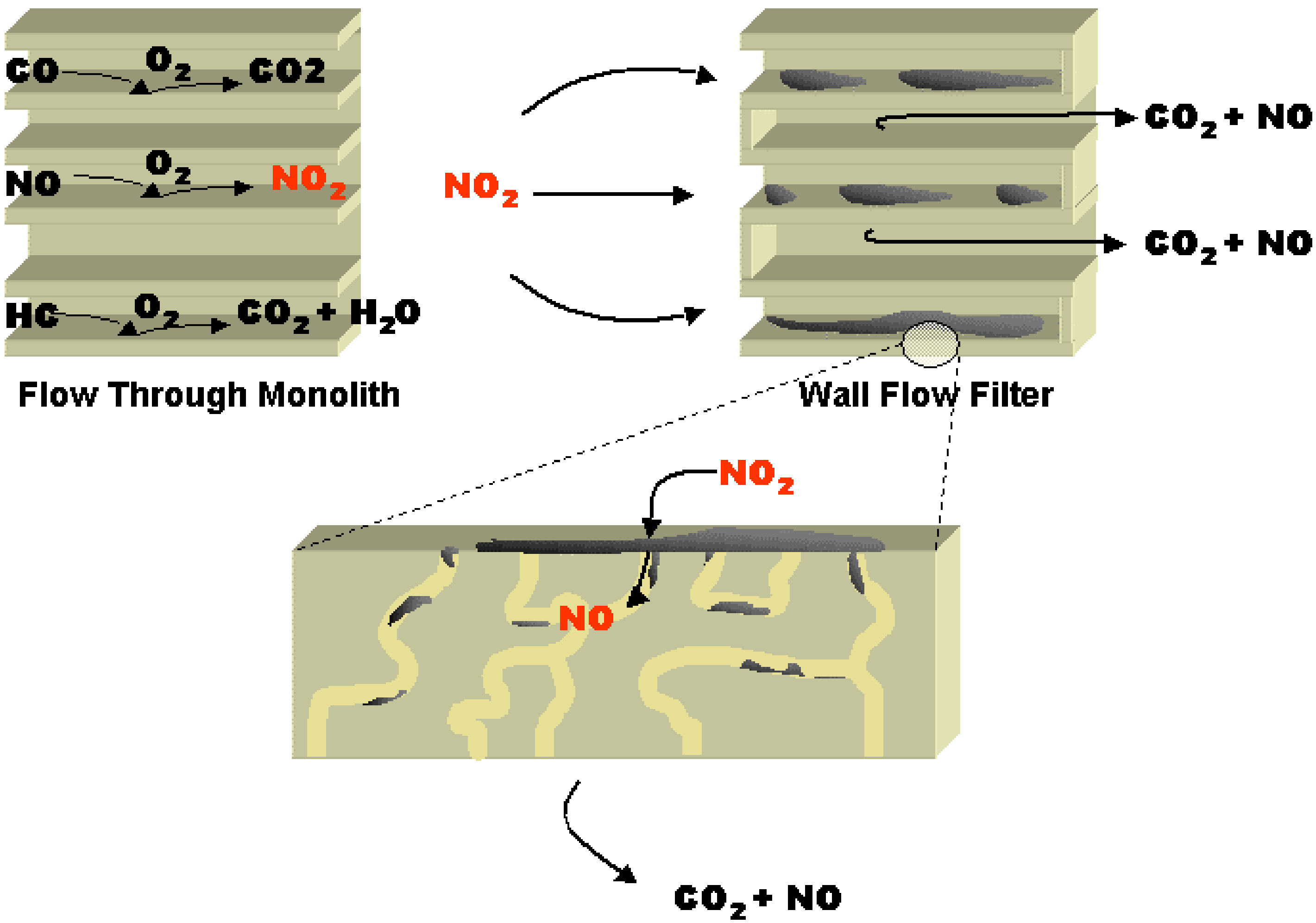
HC Oxidation at T > 200°C

NO Oxidation when CO and HC have been oxidised, typically at T > 230°C

NO Conversion to NO_2 Over an Oxidation Catalyst



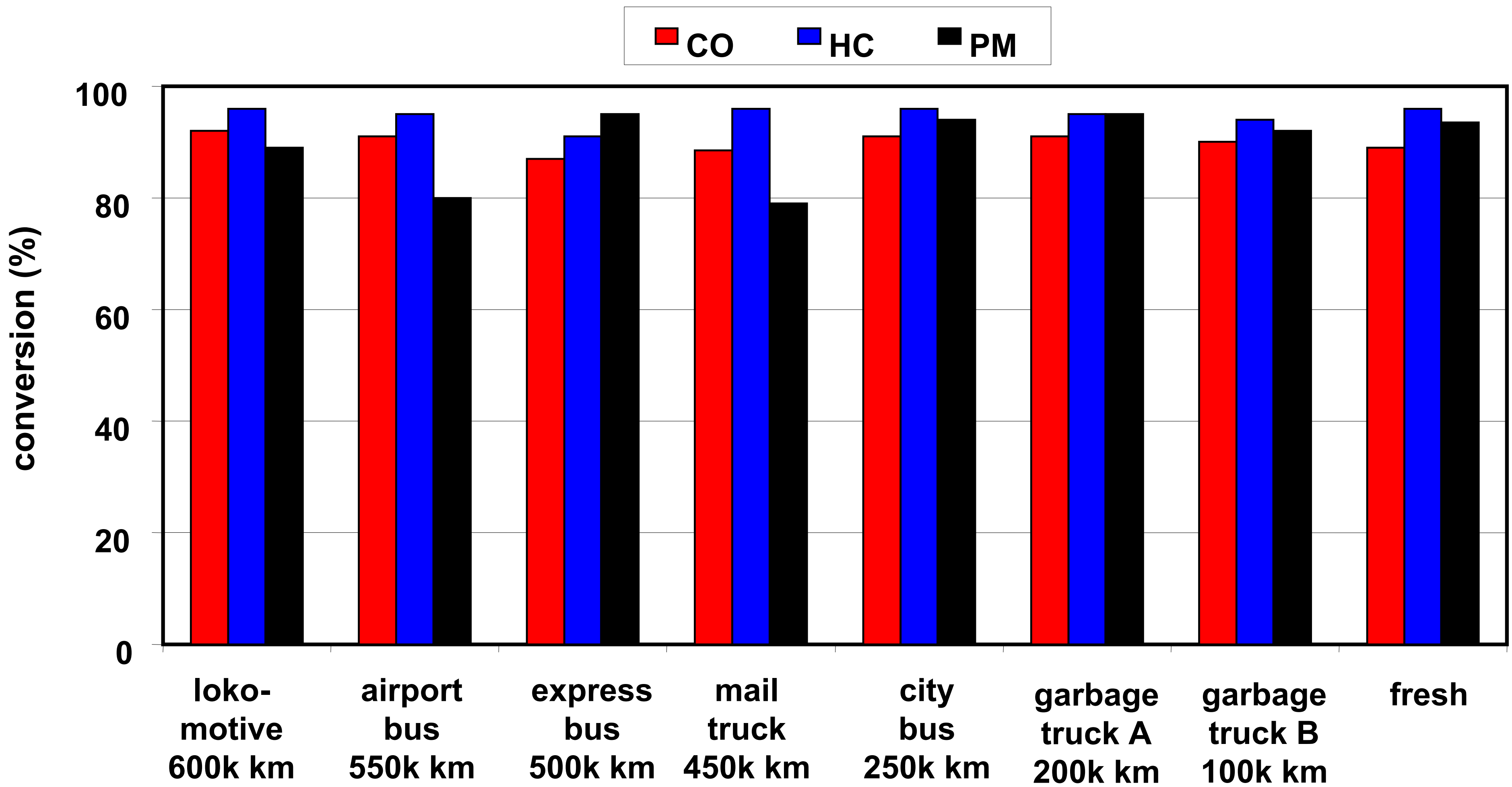
CRT® System Operation



CRT® Performance on Euro I Engine

	HC	CO	NOx	PM
Engine-Out	0.162	0.989	7.018	0.163
Engine+CRT	0.003	0.002	6.874	0.008
2005 Limits	0.460	1.500	3.500	0.020

Field Experience CRT®
- Pollutant Conversion



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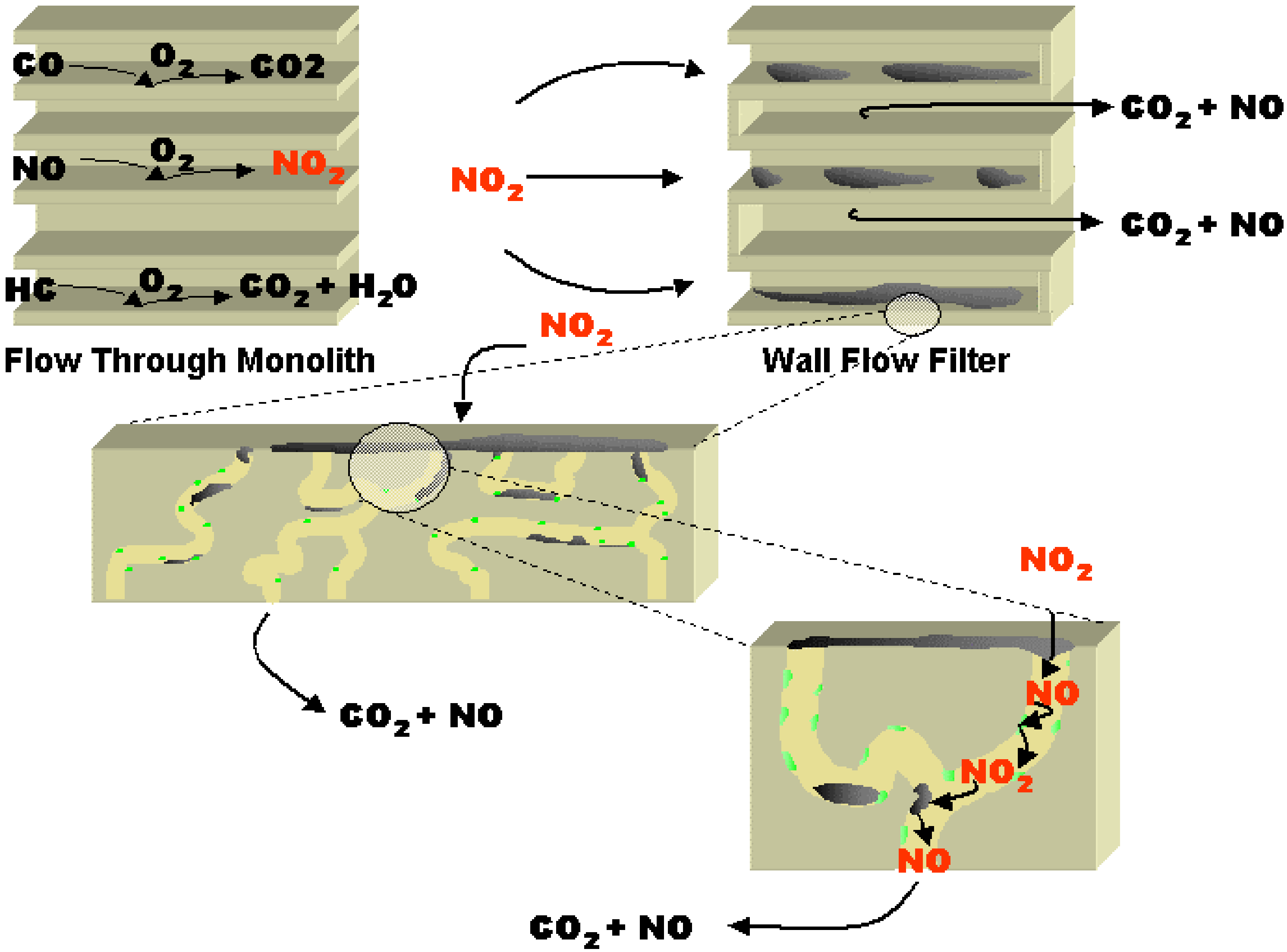
CSF and CCRT Operation



CRT® and CCRT Systems

- Within the CRT® system the reaction sequence is:

$$NO + \tfrac{1}{2}\,O_2 \longrightarrow NO_2 \qquad \text{(catalyst)}$$

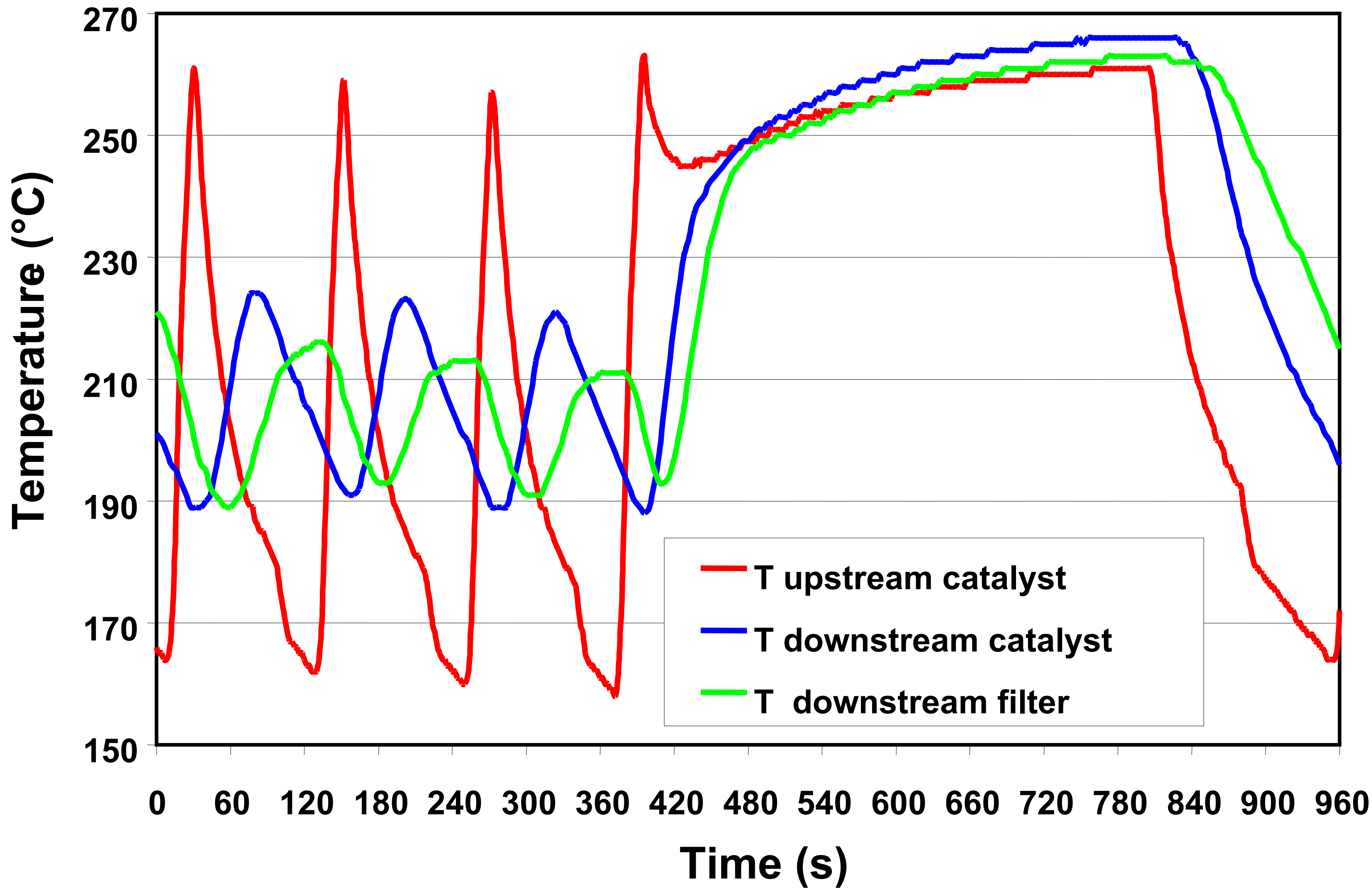
$$2\,NO_2 + C \longrightarrow 2\,NO + CO_2 \qquad \text{(filter)}$$

- Applying a catalyst coating to the DPF gives the possibility of re-use of NO:

$$NO + \tfrac{1}{2}\,O_2 \longrightarrow NO_2 \qquad \text{(Pt on filter)}$$

$$2\,NO_2 + C \longrightarrow 2\,NO + CO_2 \qquad \text{(filter)}$$

Low Temperature Cycle



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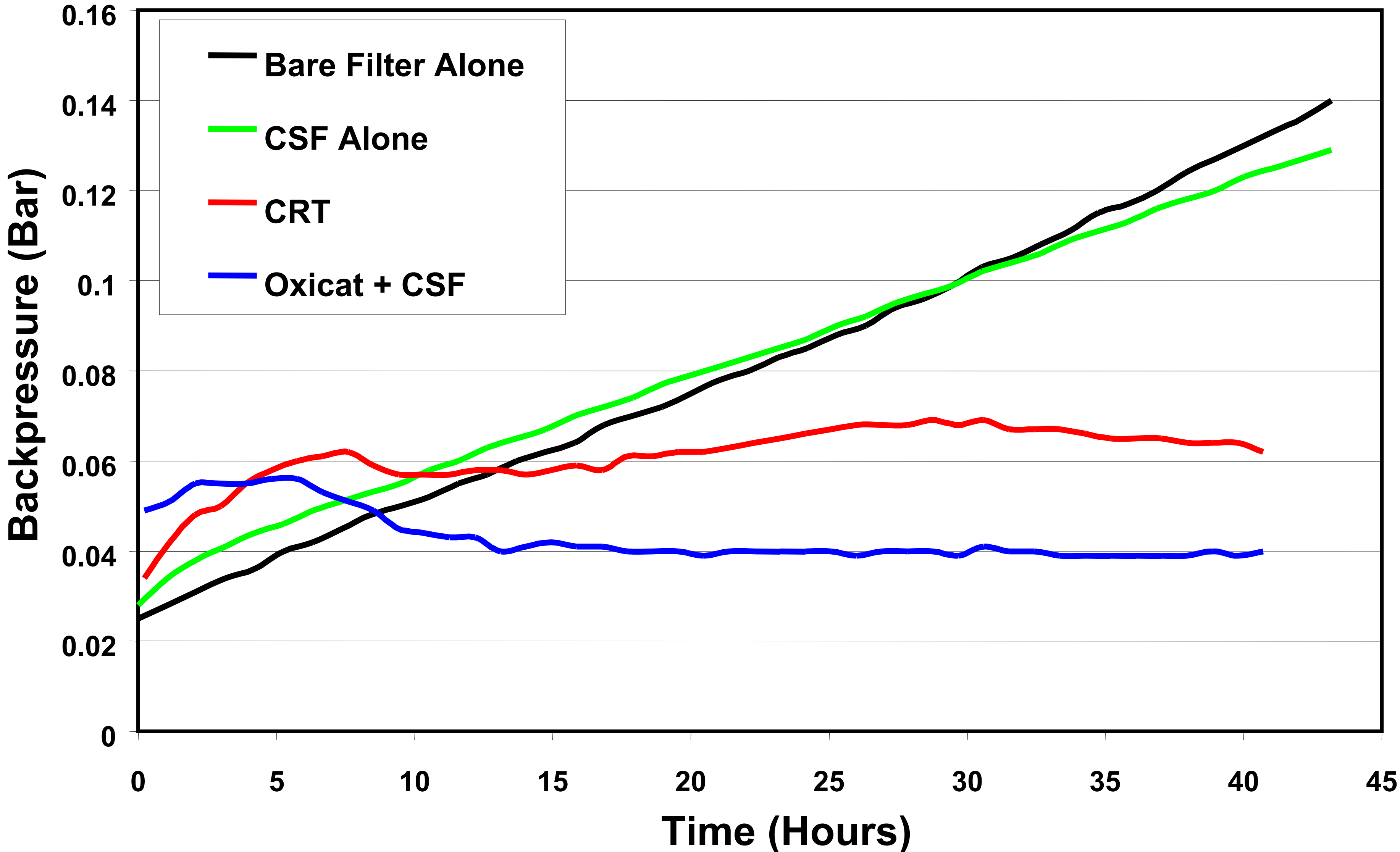
Low Temperature Cycle Performance



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The CCRT System...

- **combines the properties of CRT® and CSF**
- **allows a more efficient use of the emitted NOx for carbon combustion**
- **shows superior performance compared to CRT®- and CSF-only systems even at low CSF metal loadings, especially for**
  - low temperature applications
  - application with a low NOx/PM ratio

NO_2 slip can be minimised by optimising metal loading and distribution

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Active Filter Systems

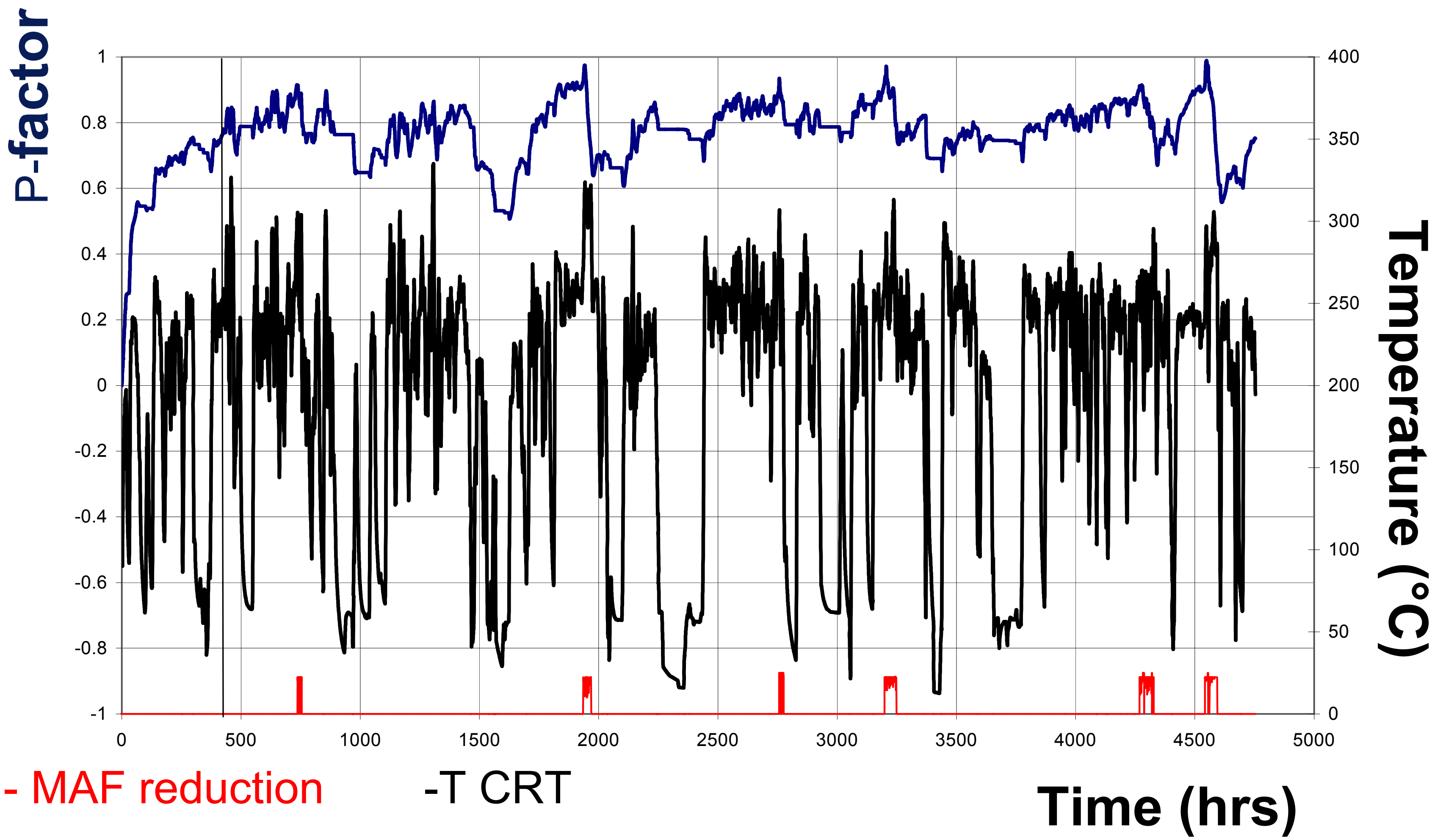
- **Where applications are too cold to ensure passive regeneration, active regeneration is required**
  – Passenger cars
  – Some garbage trucks, some city centre buses

- **This can take a number of forms:**
  – When engine-out NOx is high enough (e.g. HDD applications) the temperature can be raised to allow the stored soot to be combusted by NO_2
  – When engine-out NOx is low (e.g. passenger cars), oxygen-based combustion must be used

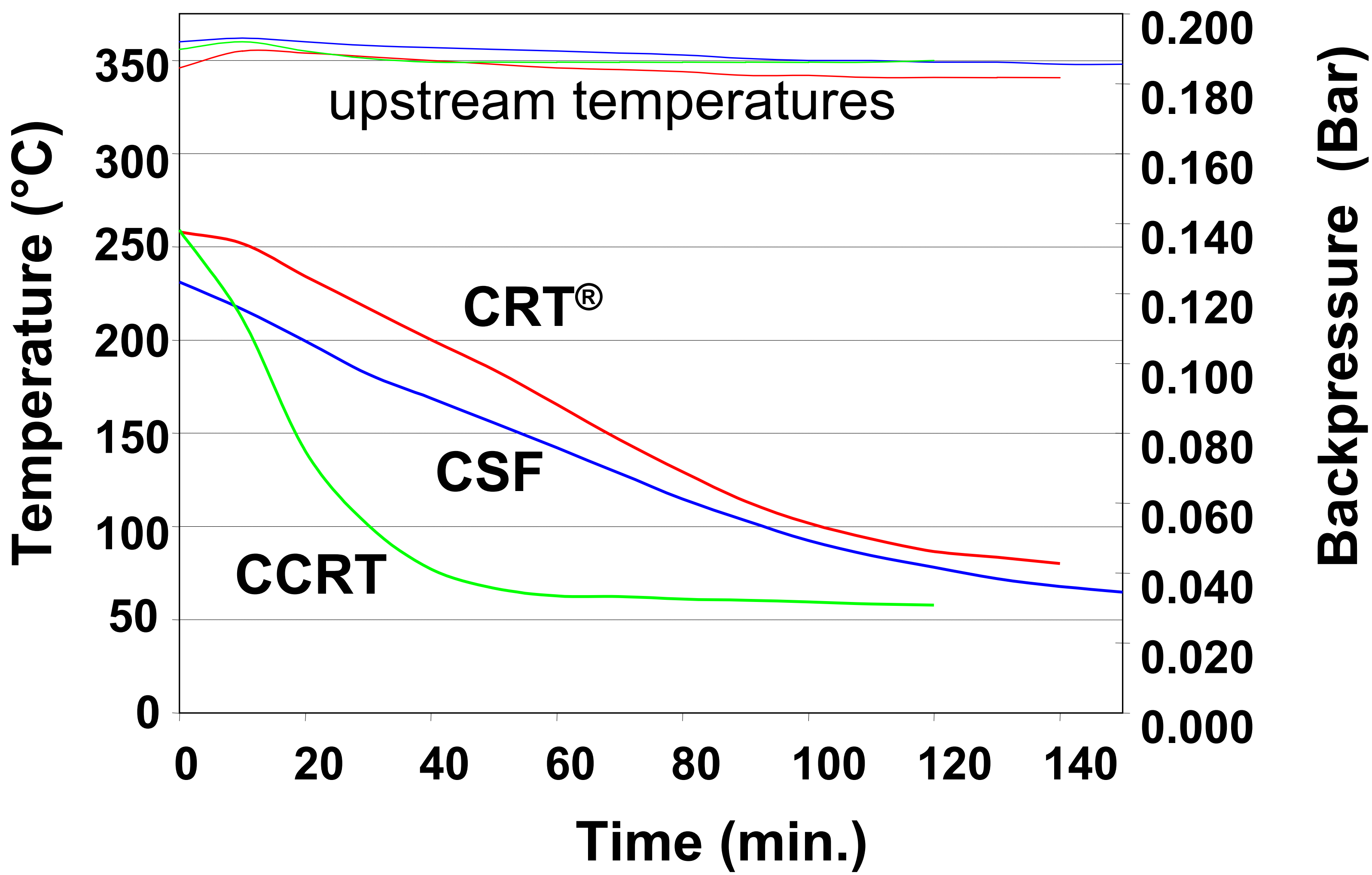
Active Regeneration in the Field

- **JM, TNO and DAF performed a field test to investigate active regeneration**
- **Strategy involved changing VGT position to control temperature**
- **Active regeneration was triggered when system back pressure (normalised for flow rate) reached a critical level (P factor = 1)**
- **Temperature rises and back pressure decreases during active regeneration periods**
- **Promising strategy**

Active CRT Regeneration by NO_2 in a field trial (JM/TNO/DAF)



Active Regeneration by NO_2 – Engine Test with CRT®-, CSF- and CCRT Systems



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Active Regeneration Using NO_2

- **Safe strategy**
- **Takes a long time, due to low mass flow of NOx**
- **Fuel injection suppresses NO oxidation reaction**
  - Not the best strategy
- **Engine modifications to increase temperature look more promising**
- **CCRT offers significant advantages over the CRT when using NO_2-based active regeneration**

Active Regeneration With O_2

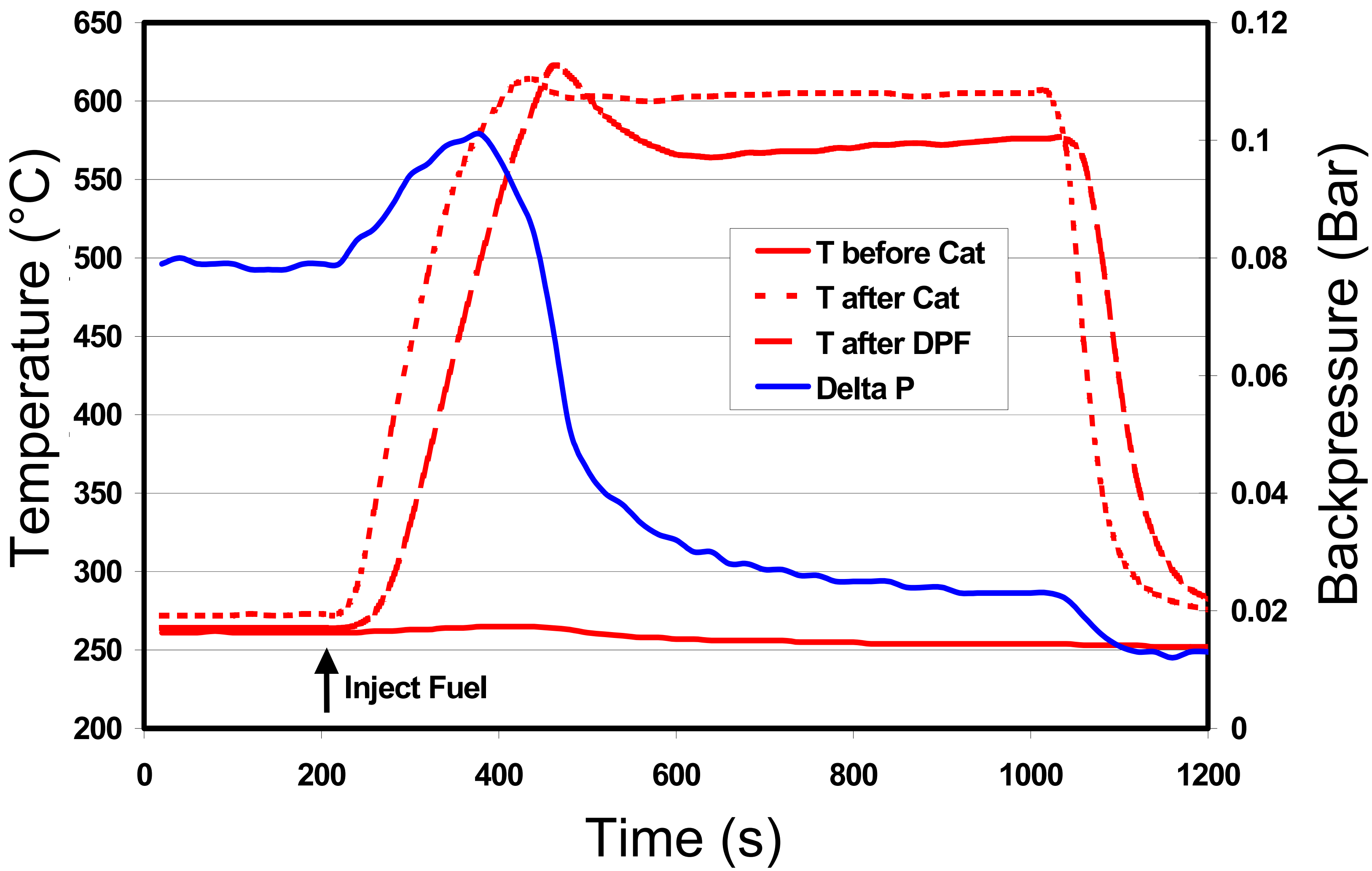
For un-catalysed reaction C + O_2 → CO_2 are 550-600°C required

Possibilities to use catalytic coatings

- **DOC as *catalytic burner*:**
  - To produce heat upstream of the filter
    - **CO, HC + O_2 → CO_2 , H_2O + heat**
    - **High thermal durability required**

- ***Filter coating***
  - To produce heat in the filter
    - **DOC function from precious metals (z.B. Pt)**
      - **CO, HC + O_2 → CO_2 , H_2O + heat**
    - **high thermal durability required**
  - For catalytic carbon oxidation
    - **through contact with e.g. Cerium oxide**

Active Regeneration of CRT With O_2 (105 g Soot on 17-litre DPF)



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Active regeneration via O_2

- **Active regeneration with O_2 is a fast process**
- **The combustion rate is similar for CRT® and CCRT**
  - The catalytic coating has no significant influence on the O_2-C-reaction
- **Very promising strategy**

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Overview Diesel Particulate Filter Systems

Passive systems (NO_2-based)

- CRT®
- CSF
- CCRT

Active systems

- **NO_2-based**
  - Engine means (EGR, air intake throttling, etc.)
- **O_2-based**
  - Additive supported
  - Catalyst. Burner
  - Engine means (post injection, etc.)

Conclusions

- Filter systems provide excellent filtration of all particles, including nanoparticles
- Catalytic coatings play a key role in soot filter regeneration
- Regeneration can be carried out by
  - **NO_2 from a pre-catalyst (low temperature, passive or active regeneration)**
  - **NO_2 from a catalyst on the filter (low temperature, passive or active regeneration)**
  - **O_2 using post injection (higher temperature, active regeneration)**

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4-way-systems: Simultaneous CO, HC, PM and NOx-reduction

Possibilities:

- **EGR + DPF system (-60% NOx-, >90% PM-, CO-, HC- reduction)**
- **DPF-system + NOx-trap (>90% NOx-, CO-, HC-, PM- reduction)**
  - DPF upstream of NOx-trap
    - **Uses synergy effects of the systems**
  - NOx-trap upstream of DPF:
    - **More efficient NOx storage at low temperatures**
    - **Unfavourable for filter regeneration**
  - NOx-trap on DPF (DPNR system)
    - **Compact**
    - **Issues: backpressure, NOx storage capacity, regeneration frequency**
- **DPF system + SCR (> 90% NOx-, PM-, CO-, HC- reduction)**
  - SCR upstream of filter
    - **Unfavourable for filter regeneration**
  - SCR downstream of filter (SCRT)
    - **Uses synergy effects of system**

Technical Terms and Abbreviations

- **HDD: heavy duty diesel**
- **LDD: light duty diesel**

- **PM: particulate matter**
- **HC: hydrocarbons**
- **NOx: sum of NO and NO_2, is calculated as NO_2 because NO is finally getting oxidised to NO_2 under atmospheric conditions**

- **DOC: diesel oxidation catalyst oxidises CO, HC, NO**
- **DPF: diesel particulate filter filters PM from exhaust stream**
- **CSF: catalysed soot filter or CDPF: catalysed diesel particulate filter**
- **CRT®: continuously regenerating trap contains DOC + DPF**
- **CCRT: catalysed CRT: CRT in which DPF is coated**
- **SCR: selective catalytic reduction of NOx with ammonia**
- **SCRT: CRT system followed by SCR-system (DOC + DPF + SCR-Kat.)**
- **NOx-storage catalyst or NOx-trap stores NOx under lean exhaust conditions and reduces stored NOx under rich exhaust conditions**
- **DPNR: diesel particulate NOx reduction emission control system (from Toyota)**

- **Washcoat: coating material, in which active components are bedded in. Washcoat enables a good dispersion and enhances the chemical and thermal durability of the active components**

How to Clean up Diesel Emissions?

Pollutant	*Desired Product(s)*	*Principle*	*Tool*
CO	CO_2	Oxidation	Oxidation catalyst
HC	H_2O, CO_2	Oxidation	Oxidation catalyst
PM	CO_2	1) PM filtration (trapping) 2) PM oxidation with NO_2 or O_2 3) NO oxidation to increase NO_2 4) Heat formation by HC oxidation	Particulate filter and Oxidation catalyst
NOx	N_2	a) (partly) selective reduction with CO, HC, H_2 b) non selective Reduction (SCR) with CO, HC, H_2 c) selective Reduction with Ammonia or Urea d) NOx storage (trapping)	Lean-NOx catalyst or NOx-trap or SCR-cat

Catalytic Systems for Diesel Emissions aftertreatment (I) - Components

- **DOC (diesel oxidation catalyst)**
  - Oxidise CO, HC, NO, SO2 (unwanted)
- **DPF (diesel particulate filter)**
  - Uncoated
    - **Hold back PM**
  - Coated (CDPF (“catalysed DPF“) or CSF (“catalysed soot filter“))
    - **Hold back PM and oxidise CO, HC, NO, SO2 (unwanted)**
- **NOx aftertreatment systems**
  - **Lean-NOx-catalysts**
    - **Oxidise CO and HC**
    - **Reduce NOx to N2**
    - **Have low efficiency**
  - **SCR** (selective catalytic reduction)
    - **Reduce NOx with ammonia or urea**
  - **NOx storage catalysts (NOx-traps)**
    - **Store NOx under lean and reduce it under rich conditions**

Catalytic systems for diesel emissions aftertreatment (II) – multi component particulate filter systems

- **CRT® = "continuously regenerating trap"**
  - Diesel oxidation catalyst (DOC) + uncoated particulate filter (DPF)
- **CCRT ("catalysed CRT")**
  - DOC + coated filter (CSF)
- **SCRT**
  - CRT followed by SCR system
- **DPNR ("diesel particulate NOx reduction" emission control system)**
  - Particulate filter coated with NOx-trap coating