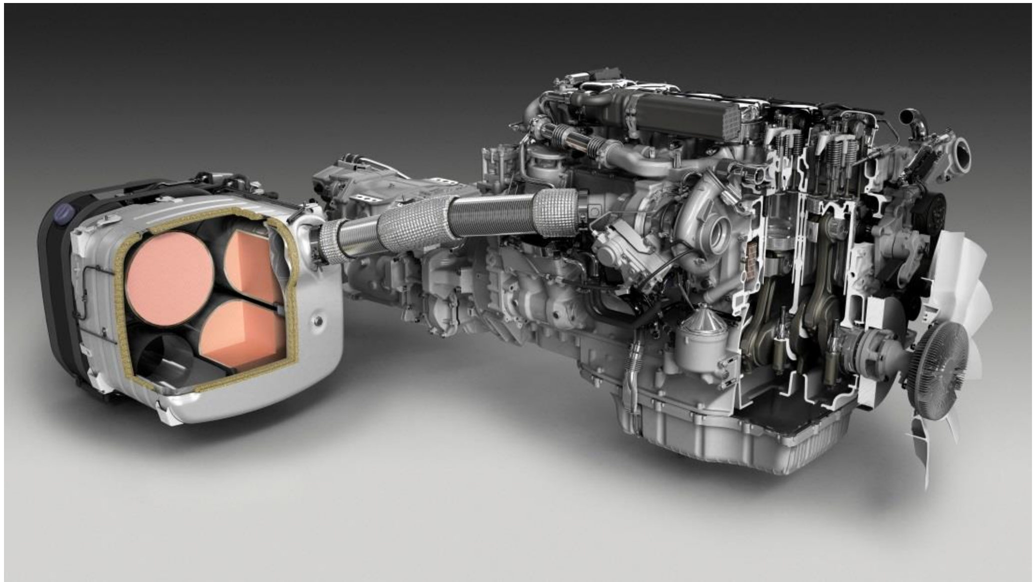
KTH ROYAL INSTITUTE
OF TECHNOLOGY

Optimizing the diesel oxidation catalyst for fuel diversification

Jonas Granestrand, August 2014

Agenda

- Background
- My project
- Main takeaways from literature study
- Experimental approach



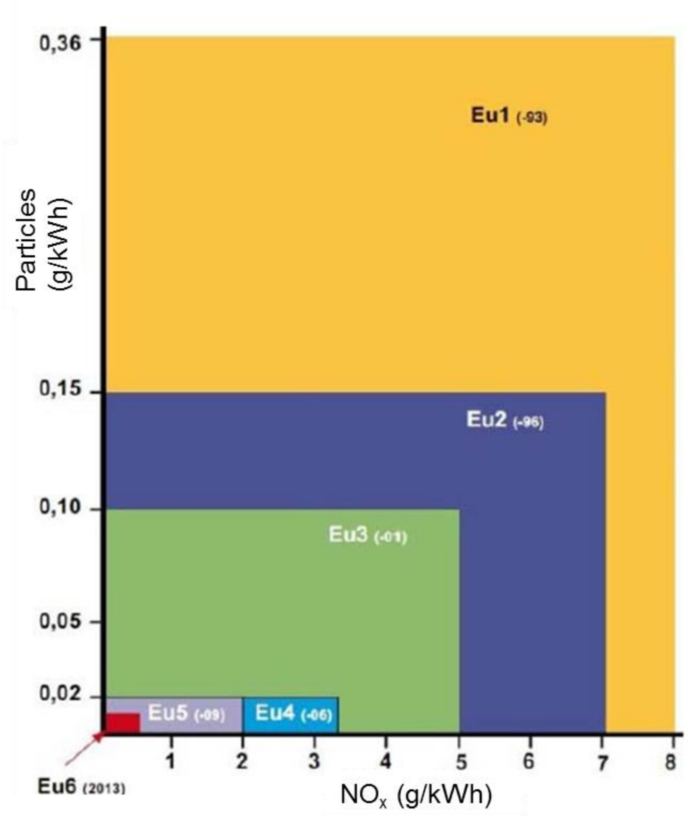
Pollutants from diesel trucks

- Nitrogen oxides (NO_x)
- Particulates
- Hydrocarbons
- CO
- CH_4
- CO_2
- N_2O

Regulated pollutants

Greenhouse gases

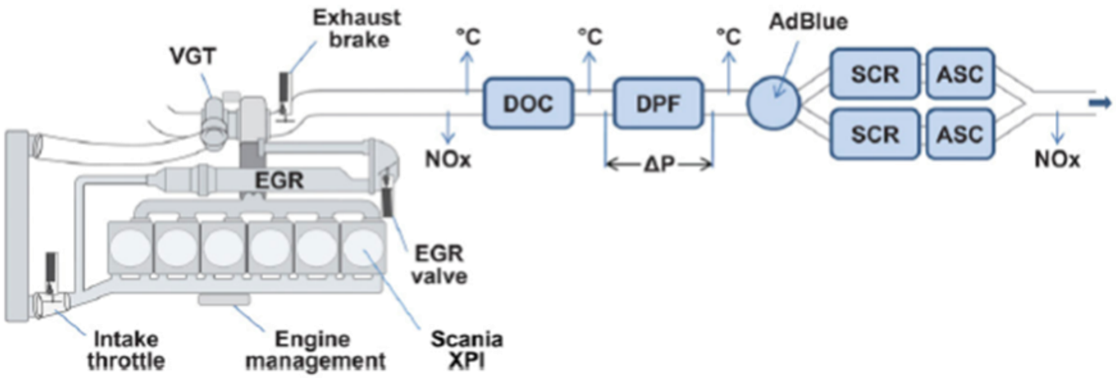
European emission legislation



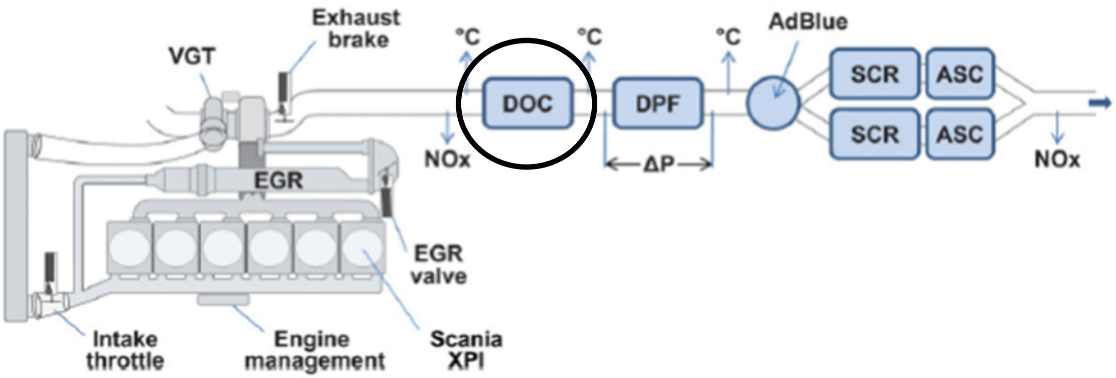
Emissions cut by over 90 % compared to 2000

Euro 6 introduces particle number limits

Scania's aftertreatment – summary



Example of a Euro 6 aftertreatment system

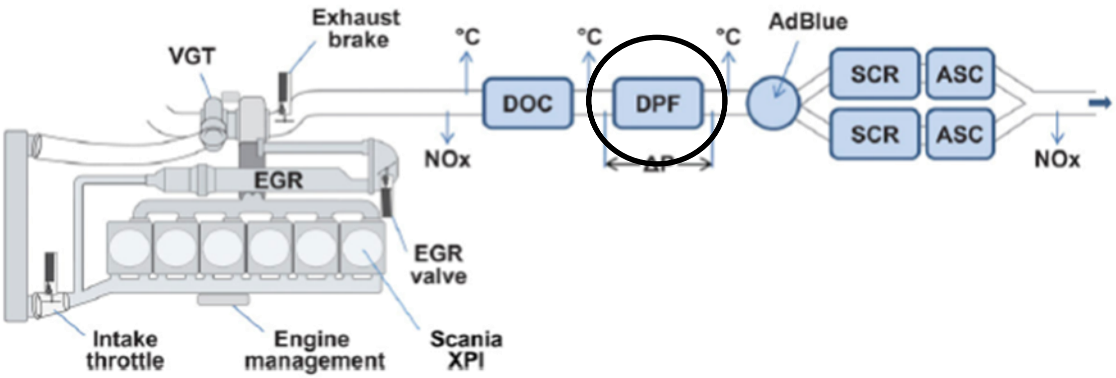


DOC Oxidizes hydrocarbons and CO into CO_2 and H_2O

Oxidizes NO into NO_2

Pt-Pd/Al_2O_3 typically used

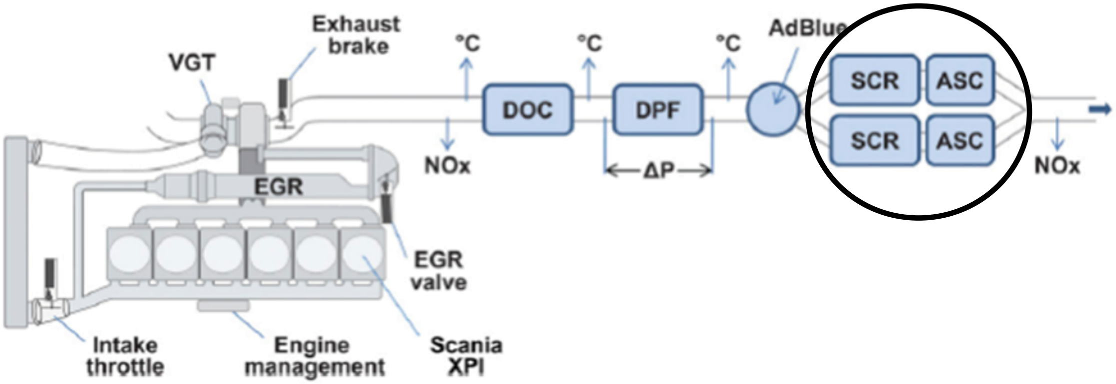
Example of a Euro 6 aftertreatment system



DPF traps particulates

NO_2 generated in the DOC helps burn away trapped soot

Example of a Euro 6 aftertreatment system



In the SCR catalyst NO_x reacts with NH_3

Increasing the NO_2/NO_x ratio from engine-out levels increases activity

Excess NH_3 is taken care of in the ASC

The DOC plays a central role in the system

- Takes care of CO and hydrocarbons
- Oxidizes NO into NO_2
- Facilitates particle filter regeneration
- Increases NO_x removal activity
- However, its position close to the engine exposes it to various poisons
  - Is performance and longevity affected by fuel substitution?

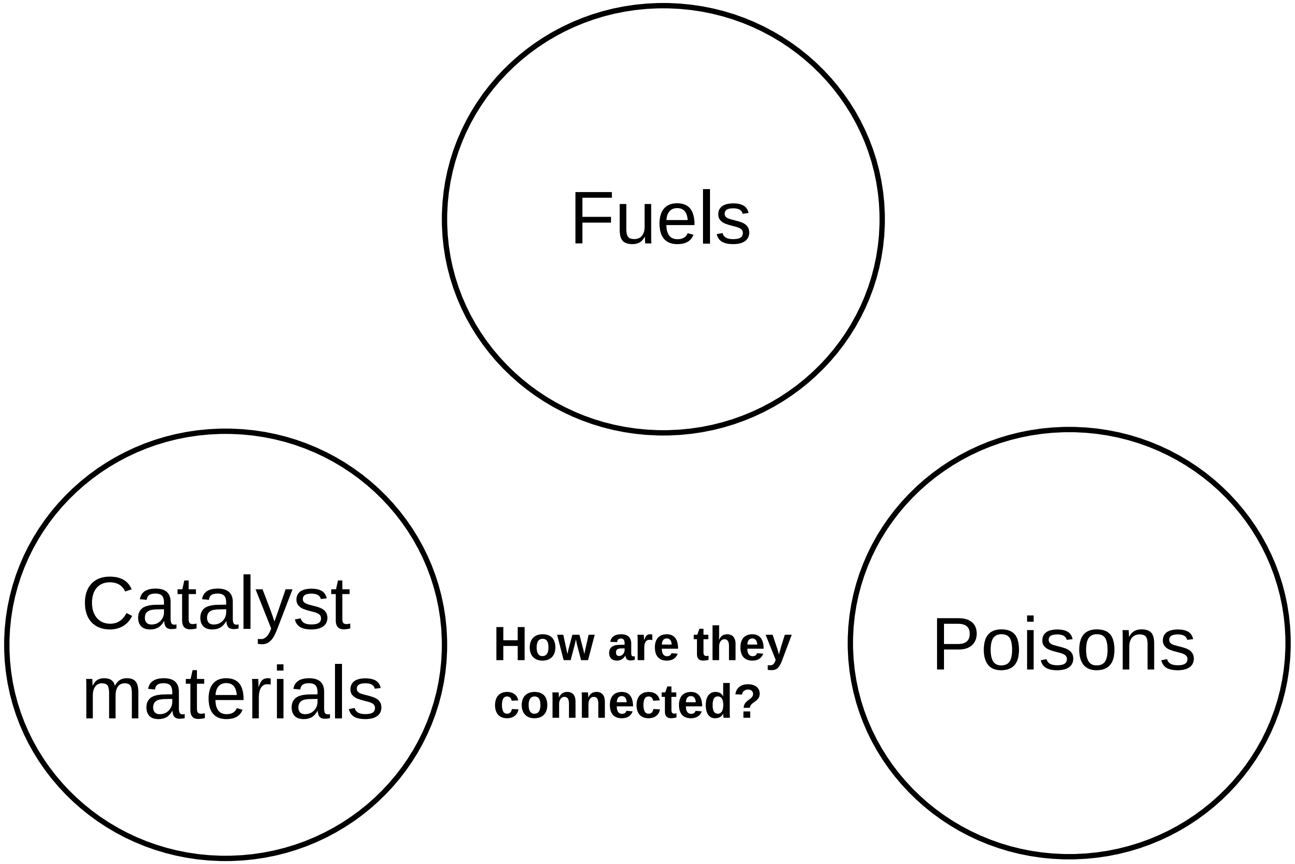
How does fuel substitution affect exhaust chemistry?

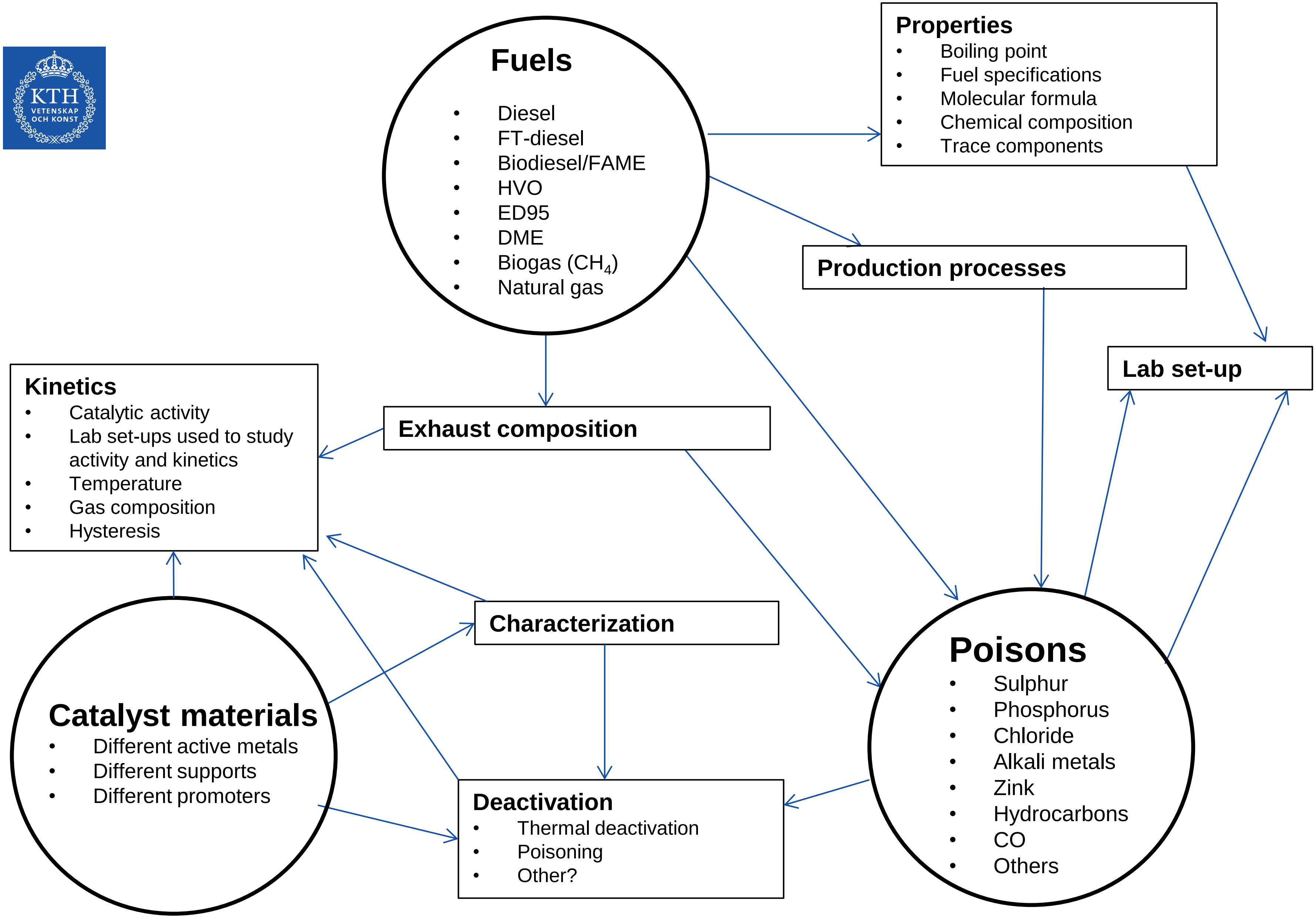
- Changed relative composition of main components
- Other hydrocarbons
- Trace elements that may act as catalyst poisions
  - From feedstock
  - From catalysts used in production process

My project

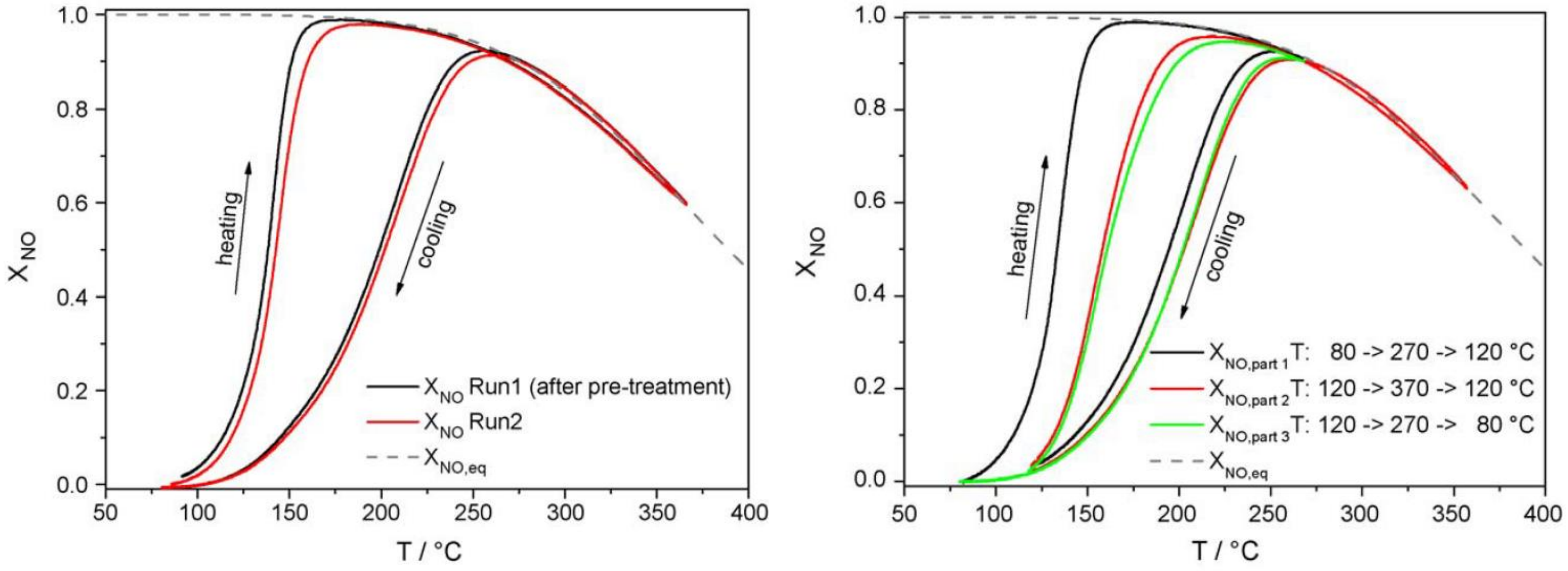
- Development of an oxidation catalyst
  - which optimizes the performance of the entire aftertreatment system
  - Which is optimized for fuel diversification
- Verify on lab scale its effect on the rest of the aftertreatment system
- Map the effects of poisoning on catalyst performance for different fuels

Three main areas to study




Fuels
Diesel
FT-diesel
Biodiesel/FAME
HVO
ED95
DME
Biogas (CH_4)
Natural gas
Properties
Boiling point
Fuel specifications
Molecular formula
Chemical composition
Trace components
Production processes
Lab set-up
Kinetics
Catalytic activity
Lab set-ups used to study activity and kinetics
Temperature
Gas composition
Hysteresis
Exhaust composition
Characterization
Catalyst materials
Different active metals
Different supports
Different promoters
Deactivation
Thermal deactivation
Poisoning
Other?
Poisons
Sulphur
Phosphorus
Chloride
Alkali metals
Zink
Hydrocarbons
CO
Others

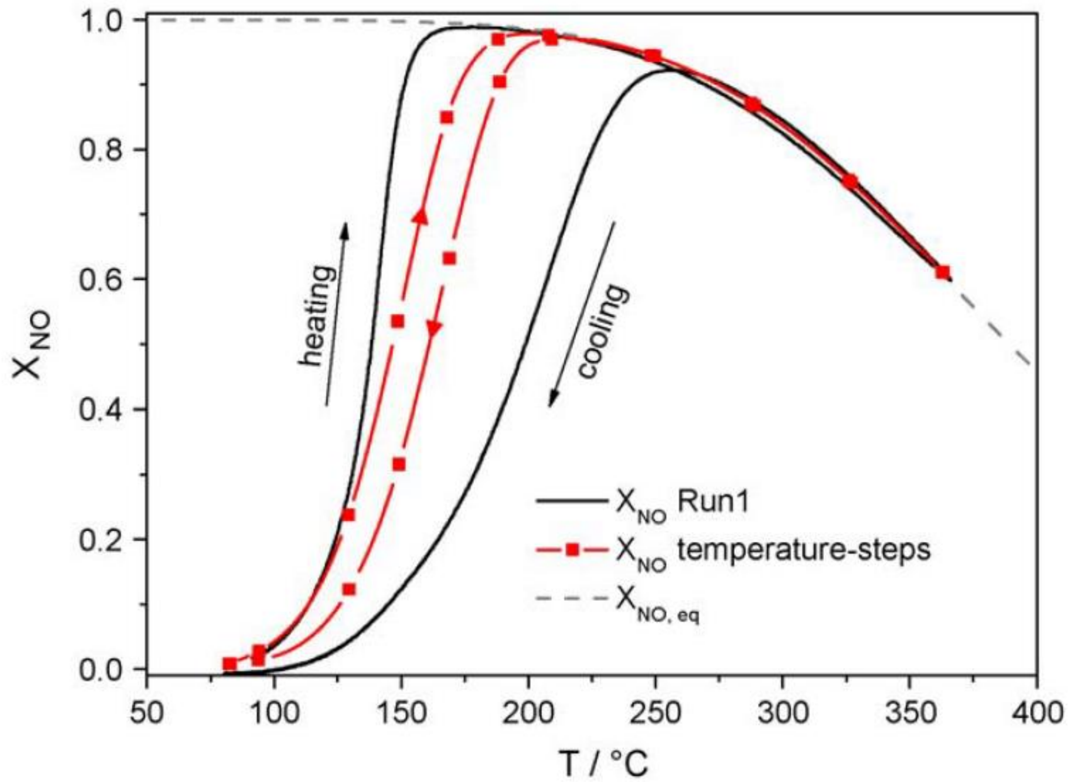
Hysteresis effect for NO oxidation



The catalyst is reversibly deactivated at high temperatures due to oxide formation from reaction with formed NO_2.

Hauptmann, W., et al., *Inverse hysteresis during the NO oxidation on Pt under lean conditions.* Applied Catalysis B: Environmental, 2009. **93**(1–2): p. 22-29.

NO oxidation: reverse hysteresis



The reverse hysteresis effect is a transient effect.

Hauptmann, W., et al., *Inverse hysteresis during the NO oxidation on Pt under lean conditions.* Applied Catalysis B: Environmental, 2009. **93**(1–2): p. 22-29.

DOC kinetics

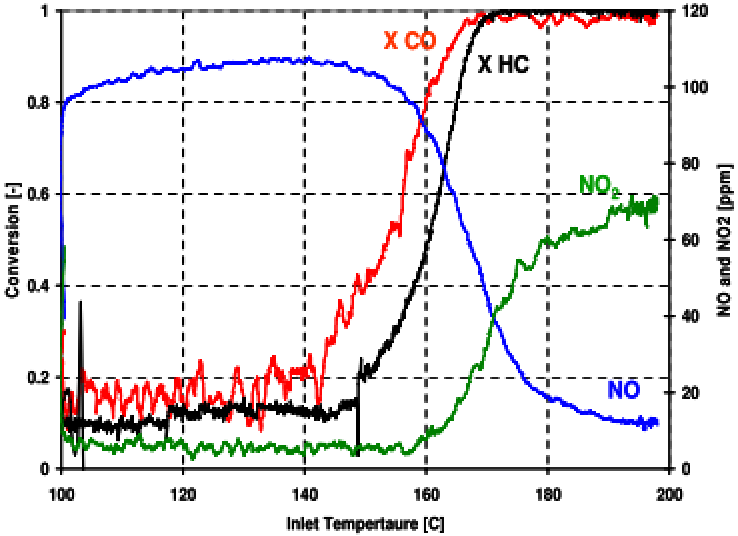
$$CO + \frac{1}{2} O_2 \rightarrow CO_2$$

$$NO + \frac{1}{2} O_2 \rightarrow NO_2$$

$$HC + O_2 \rightarrow CO_2 + H_2O$$

The different reactions influence each other

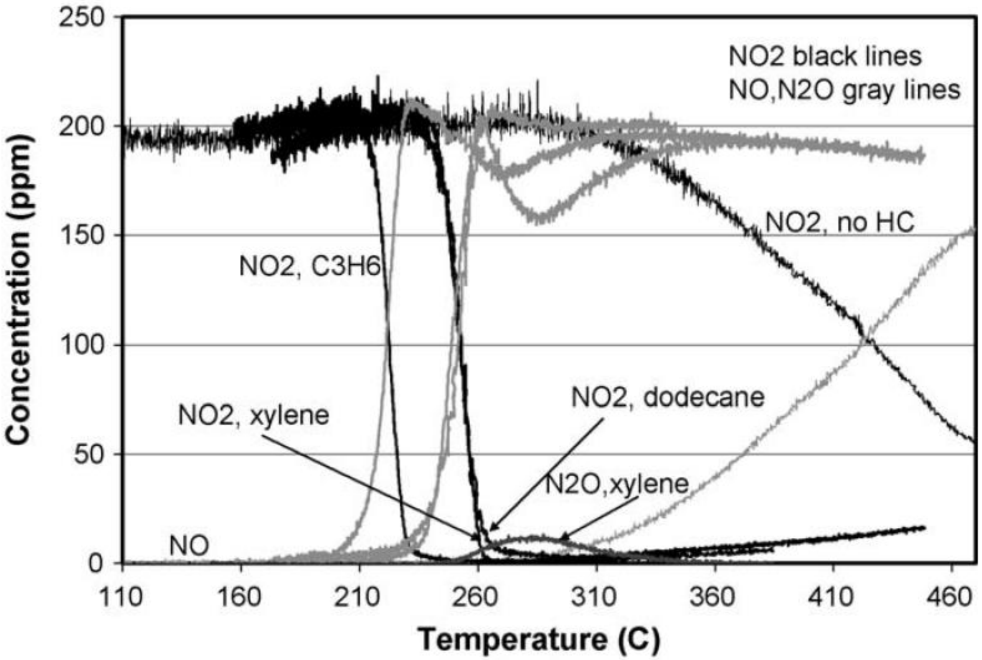
Reactant mixture effects: NO, CO and HC co-oxidation



NO oxidation starts after CO and HC have already been oxidized

Katare, S., Patterson, J., and Laing, P., "Aged DOC is a Net Consumer of NO2: Analyses of Vehicle, Engine-dynamometer and Reactor Data," SAE Technical Paper 2007-01-3984, 2007, doi:10.4271/2007-01-3984.

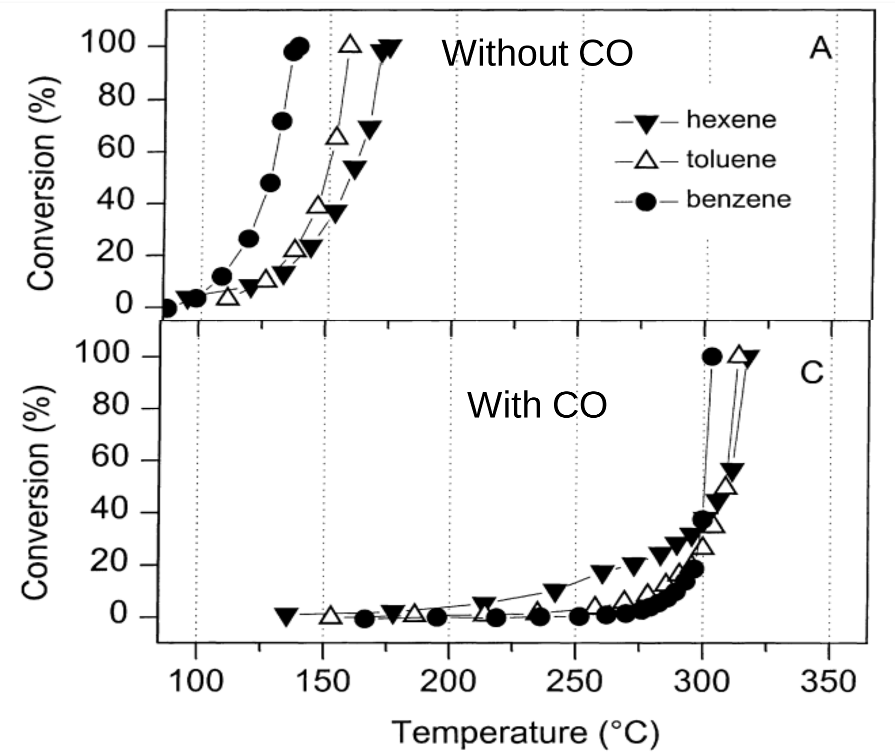
Reactant mixture effects: HC and CO can act as reductants of NO_2



Because of oxidation of HC and CO by NO_2, with high NO_2 outputs from the engine, the DOC may actually be a net consumer of NO_2

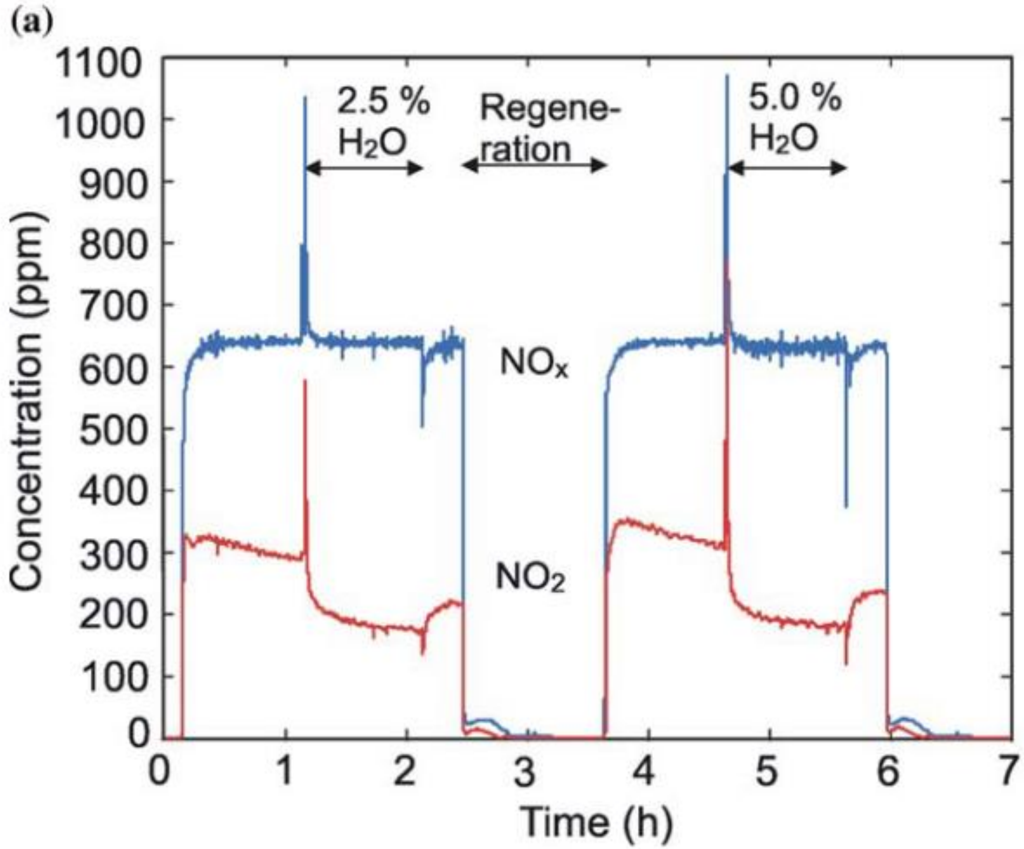
Irani, K., W.S. Epling, and R. Blint, *Effect of hydrocarbon species on no oxidation over diesel oxidationcatalysts.* Applied Catalysis B: Environmental, 2009. **92**(3–4): p. 422-428.

CO inhibition



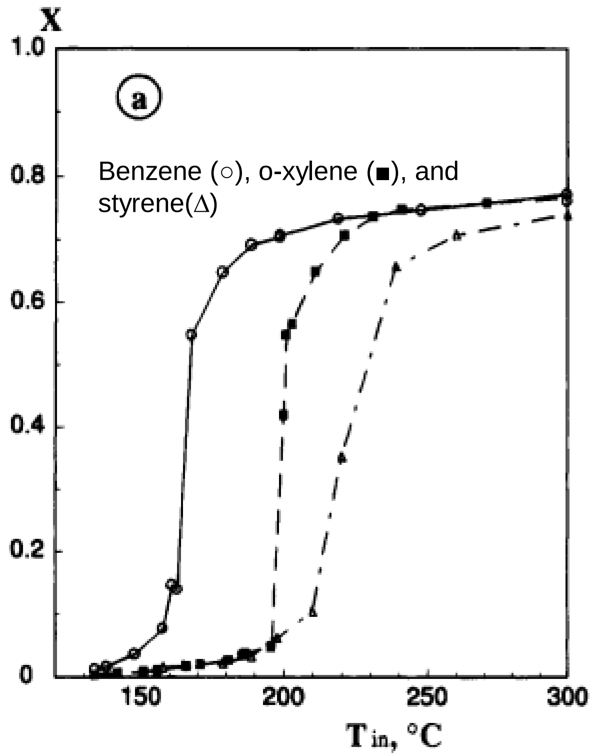
Patterson, M.J., D.E. Angove, and N.W. Cant, *The effect of carbon monoxide on the oxidation of four C6 to C8 hydrocarbons over platinum, palladium and rhodium.* Applied Catalysis B: Environmental, 2000. **26**(1): p. 47-57.

Inhibition by water

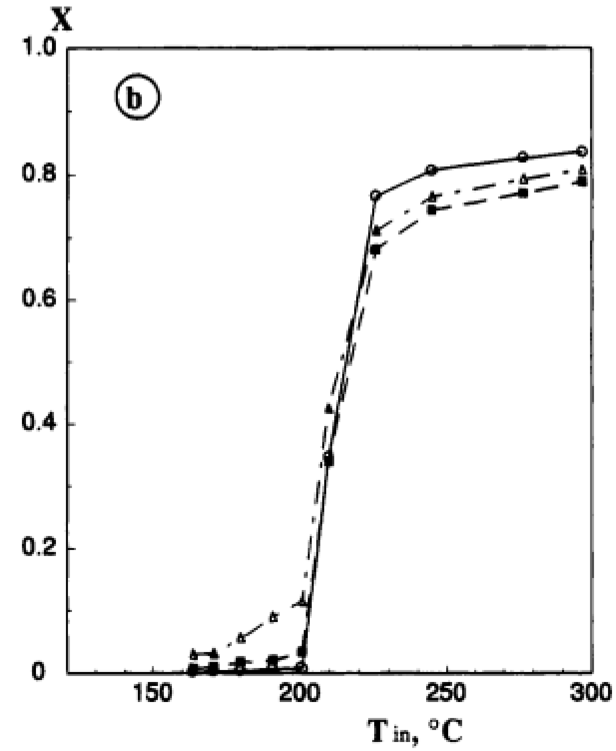


Olsson, L., et al., *The effect of a changing lean gas composition on the ability of NO2 formation and NO x reduction over supported Pt catalysts.* Topics in Catalysis, 2004. **30-31**(1-4): p. 85-90.

HC oxidation: reactant mixture effects



Individual HCs



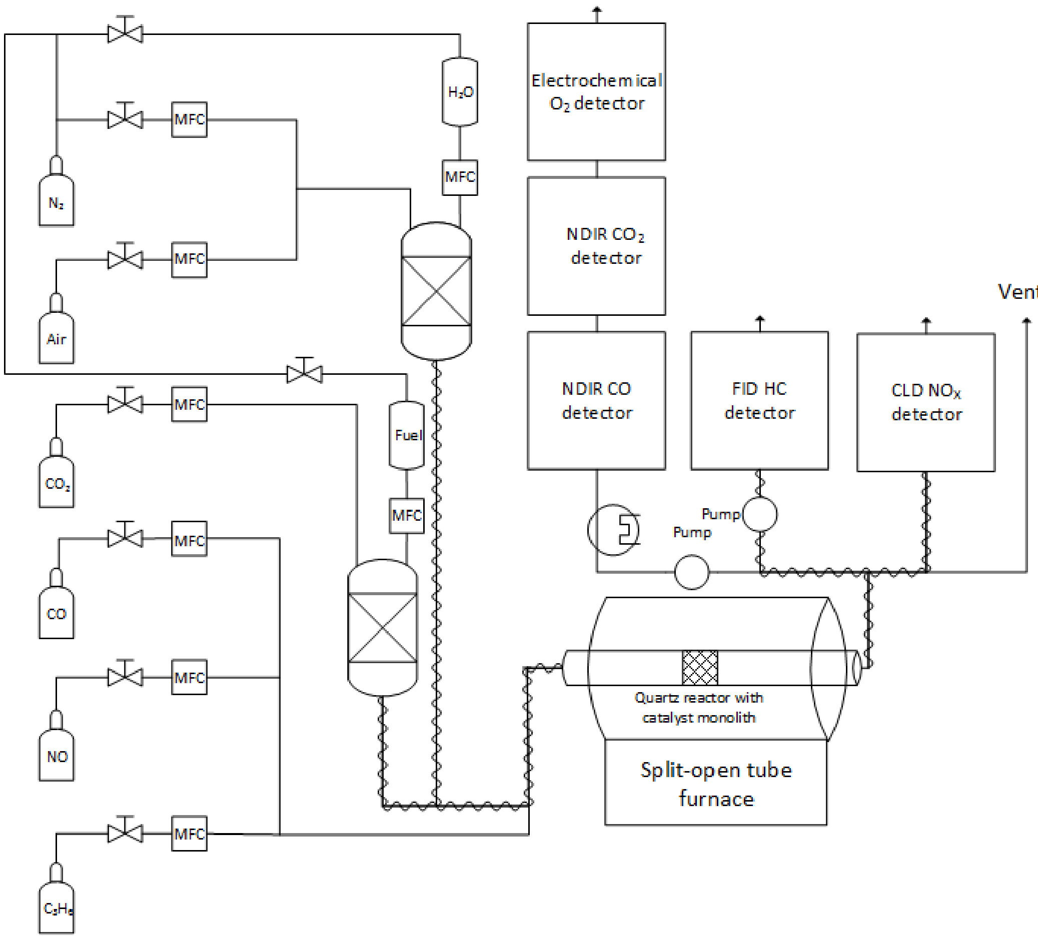
HC mixture

Barresi, A.A. and G. Baldi, *Deep Catalytic Oxidation of Aromatic Hydrocarbon Mixtures: Reciprocal Inhibition Effects and Kinetics.* Industrial & Engineering Chemistry Research, 1994. **33**(12): p. 2964-2974.

Conclusions

- There are considerable inhibition effects between the different reactants
- A decrease in oxidation activity for one reactant may affect conversion of the other reactants
- To understand the deactivation process you want to be able to study oxidation of each reactant individually
- Using only C_3H_6 to model all hydrocarbons may not give accurate results
- Flexibility in mind when designing the experiment rig

Experimental set-up



Monolith dimensions:
D = 2 cm, L =3 cm

Space velocity:
80000 – 200000 h^{-1}

Acknowledgements

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Thank you for your attention!