Technical Challenges in the Integration of DPF and SCR Aftertreatment on a Single Substrate – Review from a Systems and Modeling Perspective

Maruthi N. Devarakonda
Institute for Interfacial Catalysis
Pacific Northwest National Laboratory, Richland, WA

Co-Authors: Mark Stewart, Ken Rappé, Jonathan Male and Darrell Herling

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Presentation Outline

- Review of Integrated Systems for NOx/PM control
- Technical Challenges and Approach to Integration
- Modeling and Control System Design Challenges
- Summary

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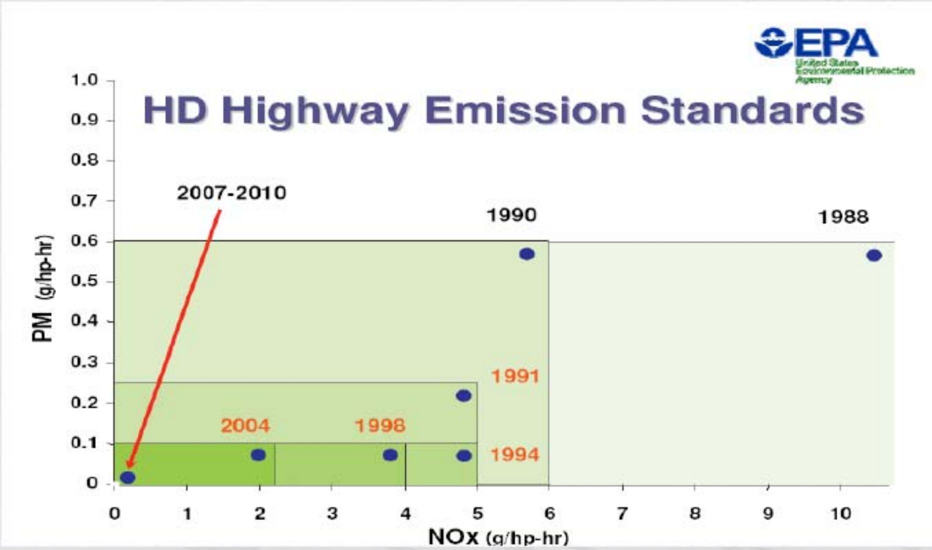
Simultaneous NO_x and PM Regulations

- US EPA emission regulations for on-road vehicles running on HD diesel engines: NO_x of 0.2 gm/bhp-hr and PM of 0.01 gm/bhp-hr.
- Urea-SCR and DPFs are considered as the core technologies to meet these regulations because of their proven efficiency in controlling NO_x and PM from HD diesel exhaust.
- Following a SCR-DPF network, a minimum of 3 catalytic converters (DOC-DPF-SCR) is necessary for simultaneous control of HC, CO, NO_x and PM and to meet the 2010 EPA regulations.
- Overall volume and precious metal costs associated with such a network motivate the research of integration of catalytic converters into a single device.



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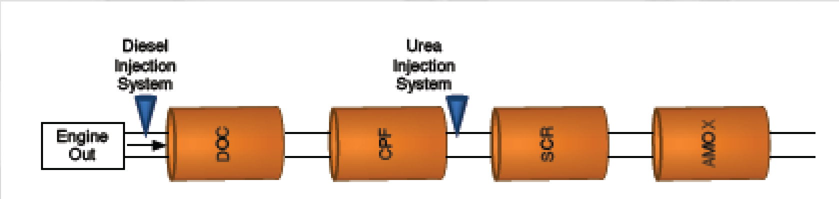
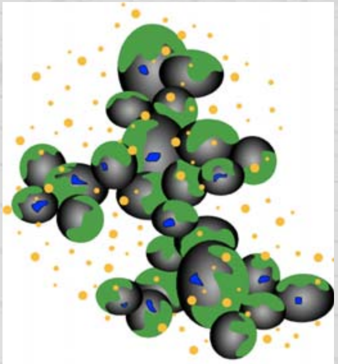
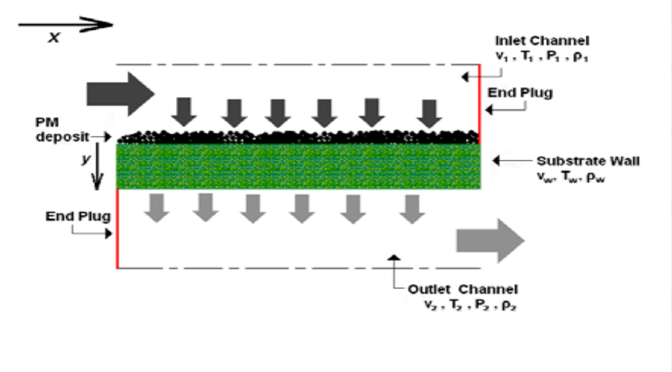


Diesel Particulate Filters (PM Control)

- DPFs are devices that oxidize the particulate matter (soot) from the diesel exhaust.
- A wall flow reactor where the alternate channels are plugged.
- Soot accumulates over time as the exhaust is passed through the filter and needs to be regenerated at regular intervals to avoid back pressure on the engine.
- Soot is represented as black globules, HC/SO_4 as green mass, imbedded metallic ash as blue streaks and nucleation mode as yellow dots in this artistic representation (Maricq, 2007).
- Soot can be regenerated through NO_2 (passive) or through the addition of diesel fuel (active) either upstream of the DOC or post-cylinder injection.
- Several models of DPFs exist in literature starting from thermal regeneration (Bissett, 1983), pressure drop and filtration (Konstandopoulos and Johnson, 1989), etc which have been used to understand the science in the filters.

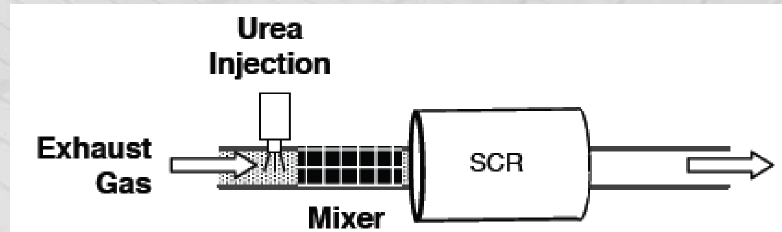




Images taken from References : G. Koltsakis, CLEERS 2007
M. Maricq, Journal of Aerosol Science, 2007
K. Premchand, SAE 2007-01-1123

Selective Catalytic Reduction (Urea-SCR)

- SCR catalysts reduce NO_x by selectively reducing them to N_2 and H_2O through the use of NH_3 as reductant.
- A flow through reactor, similar to a diesel oxidation catalyst.
- Various catalyst formulations have been tested for mobile SCR applications. Vanadium seems to be a promising candidate in Europe, base-metal exchanged zeolites are favored in US.
- Urea-SCR technology stands as a proven technology in reducing NO_x in Europe and in US for both light duty and heavy duty diesel engines.
- Cu-zeolite shows better NO_x conversion at low temperatures and is a favorite for light duty, whereas Fe-zeolite is preferred for high temperature heavy duty applications.
- Issues such as incomplete urea decomposition and droplet evaporation, HNCO hydrolysis and formation of melamines still exist which affect the NO_x conversion performance.



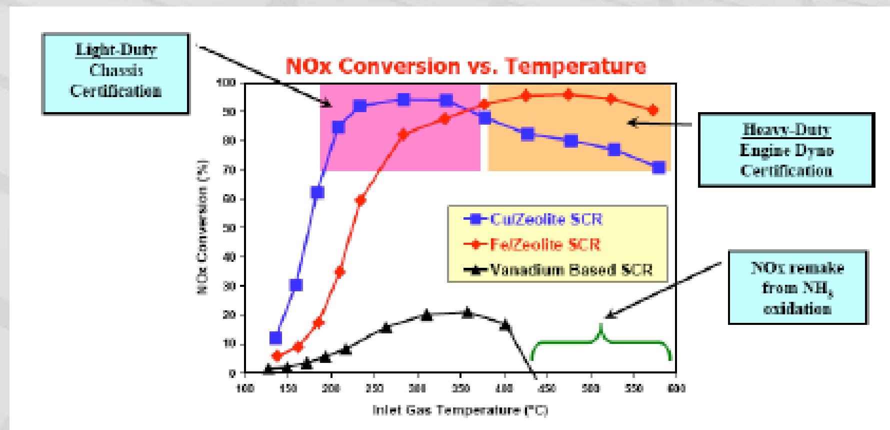
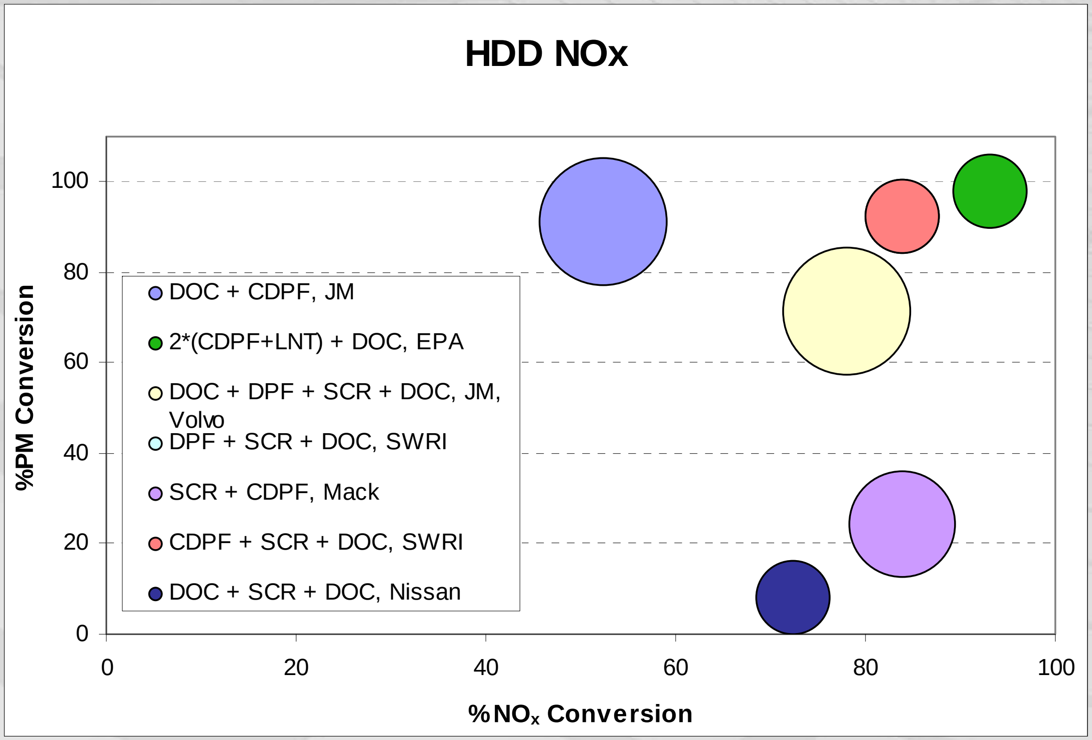


Image taken from Reference : G. Cavataio, CLEERS 2007

4-Way Systems for HDD



Ref:
JM, SAE 2003-01-0048
EPA, SAE 2001-01-1351
JM, Volvo: SAE 2003-01-0778
SWRI: DEER 2000
Mack: SAE 2005-01-1861
SWRI: DEER 2004
Nissan: SAE 2005-01-1860

Image Courtesy: Jonathan Male

- Various 4-way catalyst formulations from the literature were evaluated and shown in the chart.
- Ideal scenario is to be on the upper right hand side of the chart., i.e. 90% NO_x reduction and > 90% PM filtration efficiency.
- 2*(DPF+LNT) tested by EPA looks promising (green bubble).
- Size of the bubble represents the number of studies done using that system.

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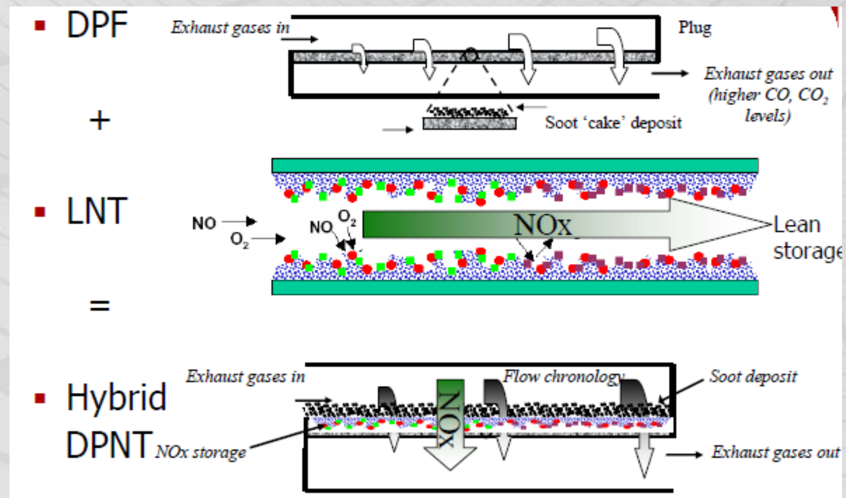
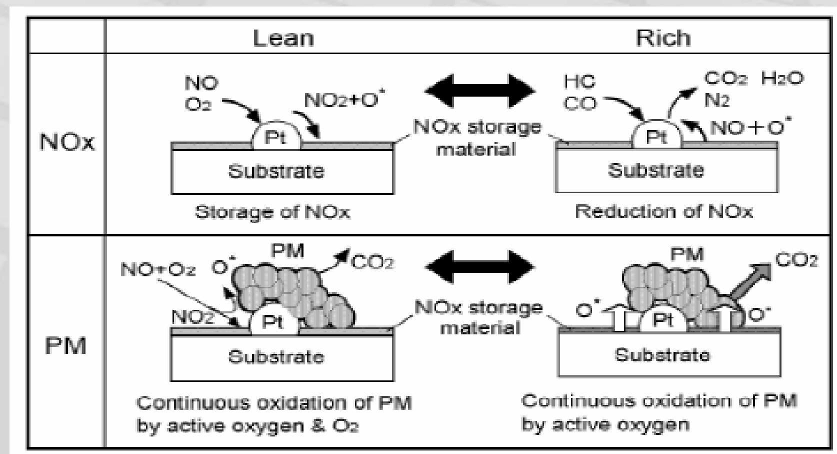
Integrated Systems – Diesel Particulate NO_x Reduction (DPNR) Catalyst

- First introduced by Toyota by combining elements of LNT and DPF in 2003.
- The device is a wall flow monolith with NO_x trapped on the catalyst washcoated onto the monolith.
- The catalyst is regenerated in a way such that both the PM oxidation and NO_x reduction occur.
- Limitations include sulfur discharge and an abnormal rise in bed temperature if forced PM oxidation is not conducted uniformly, thus harming the NOx reduction and PM capabilities of the device.





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Integrated Systems – NO_x/PM Control (Materials)

- Integrated systems using catalyst elements are researched from a materials perspective to clean NO_x and PM from flue gases.
- Schaub et al. perfomed kinetic analysis of NO_x reduction in a catalytic filter on a multi-functional reactor filled with ceramic filter materials doped with compounds of transition metals.
- CeO_2 and Ce-Zr mixed oxides with different Ce:Zr ratios were characterized by Raman spectroscopy, XRD, TEM, N_2 adsorption at -196C and H_2-TPR. $Ce_{0.76}Zr_{0.24}O_2$ showed the best performance.
- A detailed kinetic study was conducted by Fino et al. on layered type Perovskite catalysts $La_{1.8}K_{0.2}Cu_{0.9}V_{0.1}O_4$ by FTIR analysis and temperature programmed isothermal tests. Vanadium ion in the perovskite lattice enhanced NO conversion.

Ref: Fino et al., Applied Cat B., 2003
Schaub et al., Chemical Engineering & Processing, 2003
Atribak et al., Journal of Catalysis, 2008.

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Integrated Systems – SCR/DPF Technology (Vehicle Tests)

- Lee et al. evaluated a Cu-SCR/DPF technology on a Chevy Silverado pick-up truck equipped with a prototype 4.9 L 6 cylinder diesel engine.
- A/T system included a closed-coupled DOC, underfloor DOC and a 2-way SCR/DPF catalyst.
- NO_x reduction performance was found comparable to a standard Cu-based flow through SCR catalyst during FTP and US06 tests and is independent of soot loading in the filter (5 g/l).
- Significant performance degradation observed following multiple filter regenerations because of deactivation of both DOC and SCR catalysts.

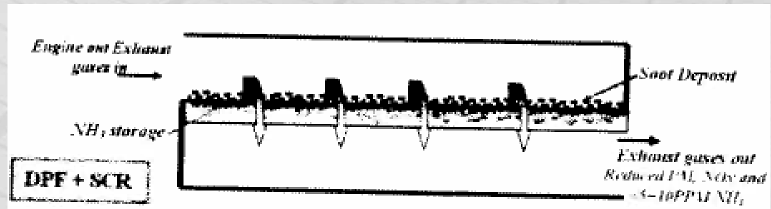

Image taken from Lee, 2008

- Dobson et al. studied durability of a SCR/DPF system for a light duty truck. Catalyst loading was limited on the combined device to avoid excessive backpressure.
- Lower soot loadings were maintained so as to avoid damage to the filter during forced regeneration.
- No reactions between soot and NH_3 and no solid deposits were observed from incomplete HNCO hydrolysis.

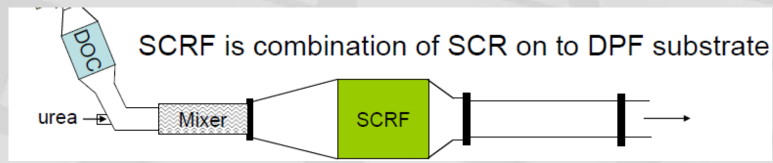

Image taken from Dobson, 2008

Ref: Lee et al., SAE Paper 2008-01-0072
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Integrated Systems – SCR/DPF Technology (Vehicle Tests)

- Oladipo et al. investigated an SCR filter whose performance was evaluated using both NH_3 and urea as reductants.
- Large mixing length between the urea injection point and SCR catalyst allows for greater residence time of the gas and thus complete decomposition/hydrolysis of urea.
- Back-to-back tests with NH_3 and urea reveal that urea decomposition is not a limiting factor and the NO_x conversion remains the same in both the cases.
- Steady state tests at 250°C and SV = 21k/hr resulted in a 12% reduction in NO_x conversion at a soot loading of 2.5 g/l. One possible reason might be soot plugging in the catalyst pores.
- Comparison between flow-through and wall-flow SCR catalysts show that the flow through catalyst has a NO_x conversion advantage.
- The authors suggest incorporating flow through SCR components in the integrated device for better NO_x conversion.

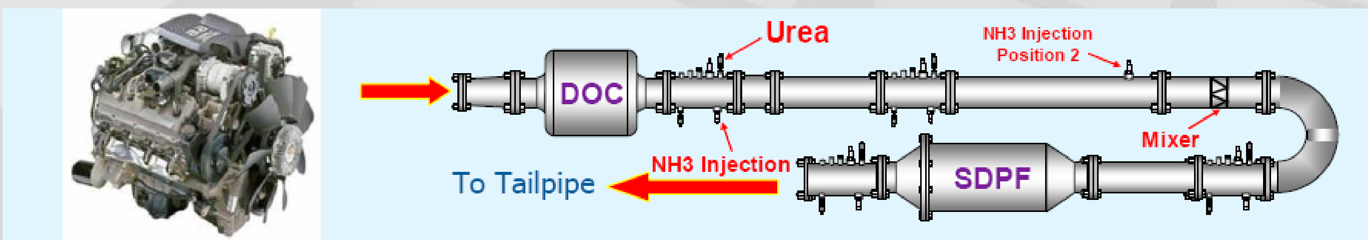

Image taken from Oladipo, 2008

Ref: Oladipo et al., DEER Conference, 2008.

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Technical Challenges from a Systems Perspective

- Accumulation of soot decreases NO_x conversion.
  - Soot plugging, blocking active sites?
  - Increased resistance to mass transfer?
- Flow through SCR performs better when compared to a wall flow SCR
  - Bypass active sites in the catalyst?
- How does NH_3 store on a wall flow device?
  - A very important control variable for control systems design. Essential to know the storage patterns as a function of temperature, axial length etc.
  - Helps in the control strategy during thermal excursions seen in FTP tests and for adaptation during aging conditions.
- How does soot interact with the reductant and its by-products?
  - soot + urea, soot + HNCO, soot + NH_3
- Hydrocarbon poisoning of the device during active regeneration of the filter.
  - High concentrations of hydrocarbons enter the particulate filter during active regeneration.
  - How to address the HC poisoning of the SCR catalyst?
- A filter with oxidation catalyst consumes the reductant (oxidize NH_3) and thus less NO_x conversion
  - Can we afford to have an oxidation catalyst between the injection point and the SCR catalyst in the device?
- Practical mixing length etc..

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Approach to Integration (Structure)

- The integrated systems reviewed, perform the basic functionalities such as NO_x conversion, PM filtration and NH_3 storage, etc.
- However, there are issues that need to be addressed such that the integrated device performs similar to conventional de-coupled devices.

- Diesel particulate filters with wall flow monolith exhibit superior particulate filtration efficiency when compared to a flow through monolith.
- The wall flow structure enables effective soot contact with the catalyst that promotes passive regeneration of soot.
- In addition, as the soot traverses through the cake and deep-bed layers formed on the substrate, the residence time of the particles is high in the wall flow monoliths thus providing high filtration efficiencies.

✓ This is an important consideration in down-selecting a wall flow monolith for the integrated device.

NO_2 - A Key Player

- NO_2 plays an important role in NO_x reduction in an SCR catalyst and in passive regeneration of soot in a particulate filter.
- NO_2 promotes high NO_x conversion efficiency on vanadium catalysts through the fast SCR (NO/NO_2 = 1:1) and on base-metal exchanged zeolite catalysts through the fast (NO/NO_2 = 1:1) and NO_2-SCR reactions.
- In order to utilize NO_2 for the passive regeneration of soot in the integrated system, a catalyzed filter is desirable to promote passive regeneration if it is determined that it doesn't affect the system performance (NH_3 oxidation).
- NO_2 emissions from the tailpipe should also be minimized for various environmental concerns.

✓ Thus NO_2 is envisioned as a key player in the integrated system, irrespective of the ordering of the catalysts.

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Approach to Integration (Ordering)

- Ordering of the catalysts is the most important aspect in the design of integrated aftertreatment systems for simultaneous NO_x and PM control.
- The down-selected integrated system should exhibit positive synergies in all the four functionalities (NO_x reduction, catalytic oxidation of NO to NO_2, PM filtration and oxidation and NH_3 slip control) while minimizing reductant (diesel and urea) slip.
- Choice of SCR catalyst formulation is an important step. Vanadium is not recommended for environmental concerns.
- Base-metal exchanged zeolites are a promising option, out of which Fe-zeolites exhibit greater thermal stability to withstand active regeneration temperatures, without losing any catalytic activity.
- Unique oxidation abilities of NO to NO_2 on a Fe-zeolite can also be exploited for passive regeneration of soot in the filter, without a precious metal catalyst.
- ✓ Therefore, Fe-zeolite formulation is recommended for an SCR catalyst.

A Couple of Scenarios for Catalyst Ordering

A. Uncatalyzed filter with Fe-zeolite catalyst

B. Catalyzed filter with Fe-zeolite catalyst

The following objectives have to be considered while choosing the appropriate scenario:

1. To determine the contribution of NO_2 to overall NO_x conversion and the passive regeneration of soot in the filter.
2. To evaluate the integrated system and improve fuel economy by eliminating frequent active regenerations (using passive regeneration) and
3. To determine if an oxidation catalyst can be avoided thus reducing the overall cost of the integrated system and possibly wasting NH_3 through oxidation.

✓ Combination of Cu and Fe zeolites (1:2 ??) can be considered so as to enhance the low temperature NO_x conversion.

Importance of Modeling in Understanding Integrated Aftertreatment Systems

- Modeling has been an important tool to understand the science of diesel particulate filters and other catalytic converters.
- Though there is room for more research in understanding the nonlinear relationship between the pressure drop-soot loading in the filter, modeling efforts have illuminated the filtration and oxidation mechanisms of soot and other important characteristics in the filter.
- A similar modeling oriented path can be chosen for the integrated device.
- ✓ Incorporating SCR kinetics into a device level CPF model might be an interesting bench-marking exercise to evaluate the raw performance of the integrated system.

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Modeling Challenges

- Level of complexity for accurate model predictions.
- Incorporating competitive adsorption and inhibition between species (NH_3, HC).
- Axial (and radial??) storage of NH_3.
- Heat transfer/flow/filtration effects on the SCR catalyst.
- Reduction of higher fidelity models to lower order models for control system design.
  - How do we reduce while maintaining the accuracy?
  - What performance metrics do we consider?
- Test protocols for step-wise system identification
- System identification of such a complex device which includes
  - SCR (a minimum of 6 reactions including 3 SCR, 1 NH_3 oxidation, 2 surface reactions. Can include N_2O formation and NH_4NO_3 decomposition).
  - DPF (thermal and catalytic oxidation of soot)
  - Oxidation catalyst (HC, CO and reversible NO oxidation reactions, HC storage, etc)

Control System Design Challenges – Model Based Control

- From a control engineering standpoint, the integrated system can be considered as a multiple input, multiple output (MIMO) dynamic system with two actuators (diesel and urea injectors) and two sensors for feedback purposes.
  - DeltaP sensor
  - NO_x/NH_3 sensor
- Open loop optimal control (Pontryagin's minimum principle) or closed-loop optimal control following HJB theory can be used.
- Optimal trajectory generation of urea and diesel injection rates to exploit the inherent coupled dynamics between the SCR, oxidation catalyst and the filter for optimal performance of such device.
- How do we adapt such a system for catalyst aging and poisoning scenarios?
  - Tunable parameters
  - Adaptive control algorithm

$u_1,\ u_2 : [t_a,\ t_b] \rightarrow R^m$ such that the constraints

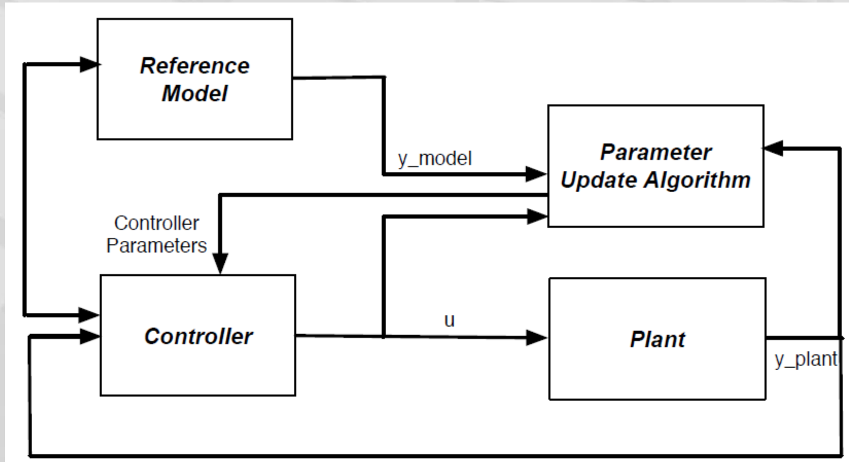
$$x(t_a) = x_a$$

$$\dot{x}(t) = f(x(t), u_1(t), u_2(t), t) \text{ for all } t \in [t_a, t_b]$$

are such that and the cost functional J is minimized

$$J(u_1, u_2) = K(x(t_b), t_b) + \int_{t_a}^{t_b} L(x(t), u_1(t)u_2(t), t)dt$$

is minimized



Ref: J.B. Burl, "Linear Optimal Control"

Summary

- A wall flow ceramic filter is considered as an appropriate substrate for the combined aftertreatment system.
- To utilize passive regeneration of soot in the filter, a catalyzed filter is desirable if NH_3 oxidation is avoided.
- NO_2 is expected to play a key role in the integrated device irrespective of the ordering of catalysts.
- Fe-zeolite is recommended as SCR catalyst formulation in the device because of its superior thermal stability and NO oxidation characteristics that can support the passive regeneration of soot.
- Ordering of the catalysts is the key for greater systems performance.
- Various technical challenges such as soot plugging, thermal aging, etc exist from a systems perspective and need to be understood.
- Modeling of such a device might lead to better understanding of the science.

References on SCR, DPF and 4-way catalysts

SCR

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DPF

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