



Urea water solution selective catalyst reduction mixer multi- objective optimization

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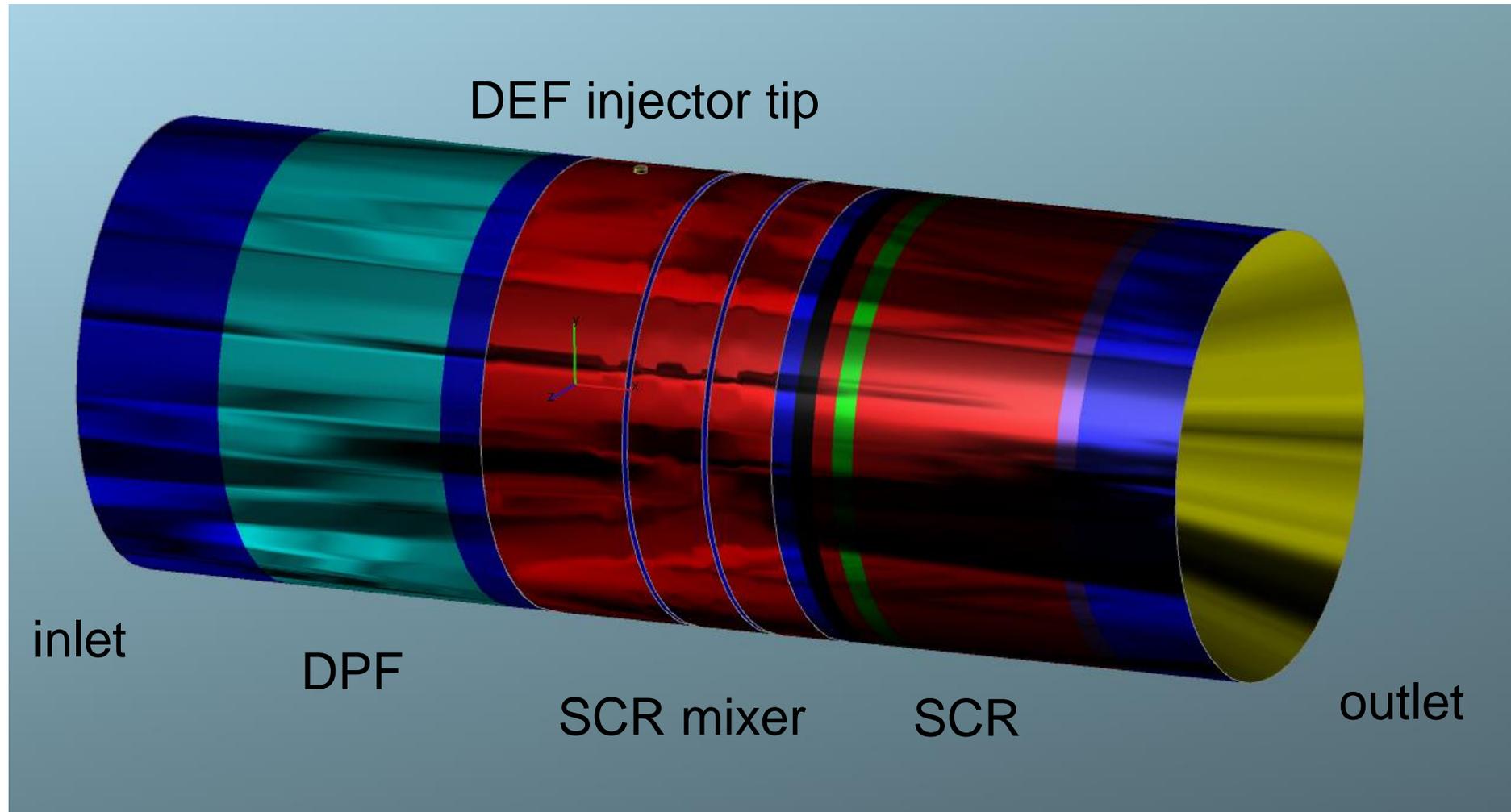
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Public information

Abstract

- The purpose of this article is to present the integration of an automotive applications specialized computational fluid dynamics package (AVL FIRE) with an optimization platform (modeFRONTIER) applied to a urea water solution selective catalyst reduction mixer multi-objective optimization
- Ammonia is needed to reduce the nitrogen oxides resulted from the diesel combustion. For automotive applications, due to its toxicity, ammonia is made on demand from a non-toxic precursor: urea. The resulting ammonia must be presenting itself uniformly at the inlet of the SCR catalyst – reductant uniformity index (Appendix I). Urea decomposition can lead to solid deposits given the condition in the SCR mixer
- In developing an SCR mixer, we take into consideration the optimization of the following parameters: minimize the pressure drop across the mixer, maximize the exhaust flow distribution uniformity at the face of the SCR catalyst, maximize the reductant uniformity, and minimize the amount of solid deposits formed as a result of DEF spray impingement on different mixer components. This optimization is at the core of the analysis led design and validation process. Until now this was done one case at a time since the analysis is complex and typically takes days to complete.
- The recent progress done in accelerating the run time in AVL FIRE without sacrificing the accuracy of the results, and the availability of the optimization platform modeFRONTIER raised the possibility of integrating FIRE with modeFRONTIER. With the accelerating procedures in place and the seamless integration among the CAD, CFD, and optimization platforms we can run about a hundred cases, in the same time as it took to run a single case
- The integration of the FIRE with modeFRONTIER will be exemplified on the simple concept mixer with generic input data, pertinent to the automotive applications.

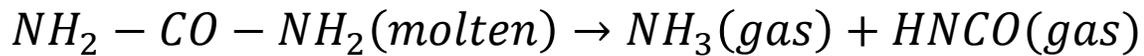
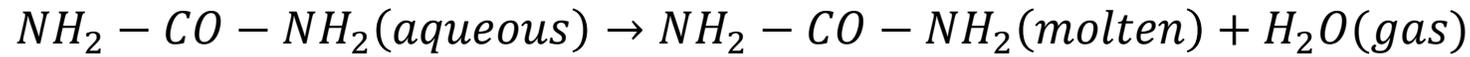
Generic SCR mixer



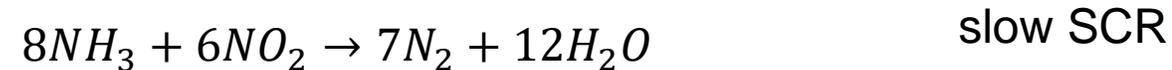
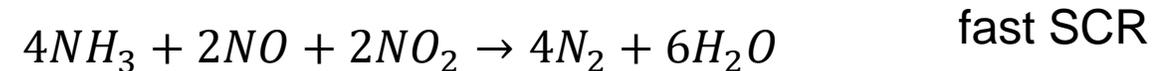
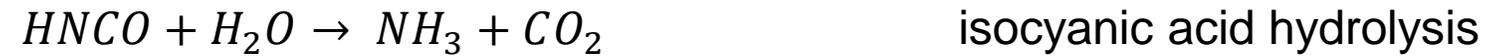
The generic SCR mixer is characterized by three parameters: two diameters DIA1 and DIA2 and one angle ALFA

SCR chemistry

Urea water solution spray water evaporation followed by urea thermolysis



Steady state SCR reactions (see appendix IV for generic reactions kinetics rate)

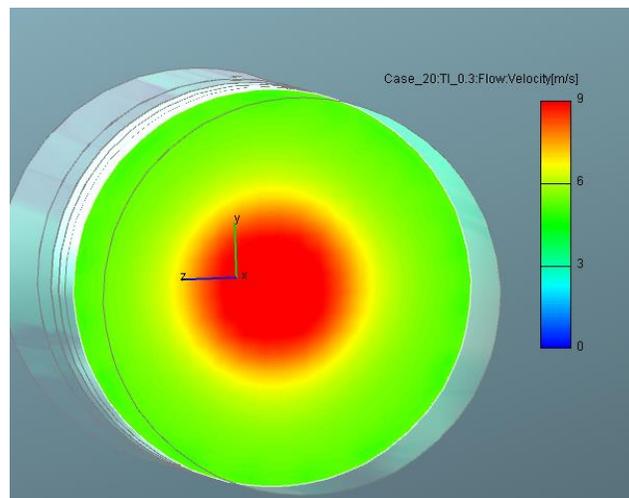


For the solid deposits reactions and kinetics see the appendices II, III, and IV

Baseline

DS_DIA1	Real Nu...	110.000000
DS_DIA2	Real Nu...	150.000000
DS_ALFA	Real Nu...	70.000000

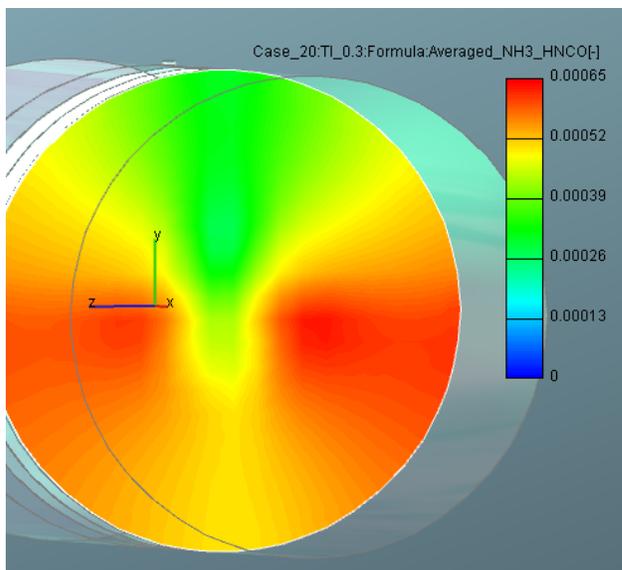
Baseline input parameters



delta P=1.921 kPa
FDI=0.930

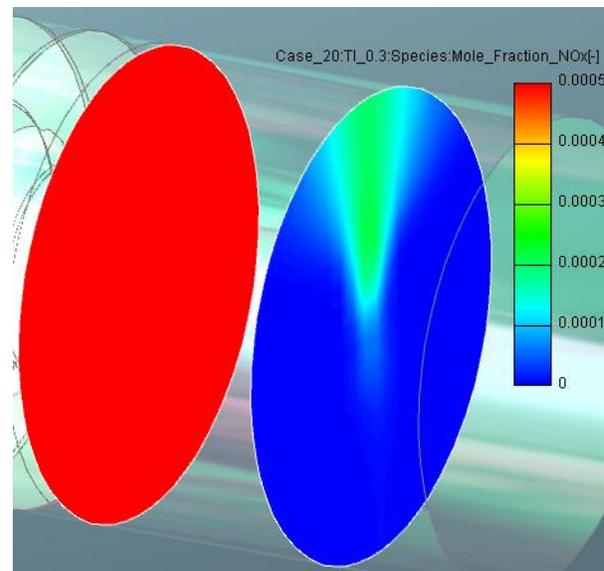
Exhaust flow velocity inside the SCR catalyst. The flow uniformity is 0.930 and the pressure drop across the mixer is 1.921 kPa

At the end of the simulation 0.14% of the injected urea water solution is in form of wall-film on the mixer's walls



UI=0.934

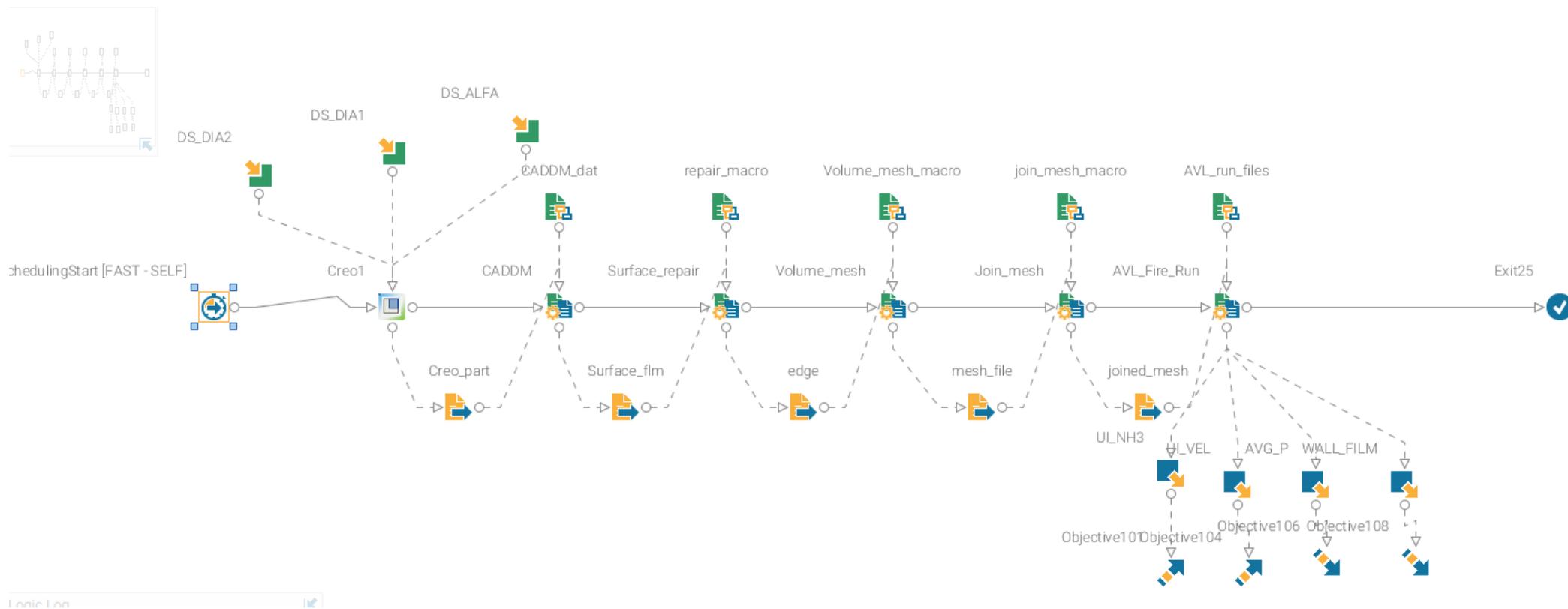
The time averaged reductant molar fraction (ammonia and isocyanic acid) at the inlet of the SCR catalyst. The reductant uniformity index is 0.934



deNOx=93.6%

The NOx molar fraction (NO and NO₂) at the inlet and outlet of the SCR catalyst. The deNOx efficiency for the baseline is 93.6%

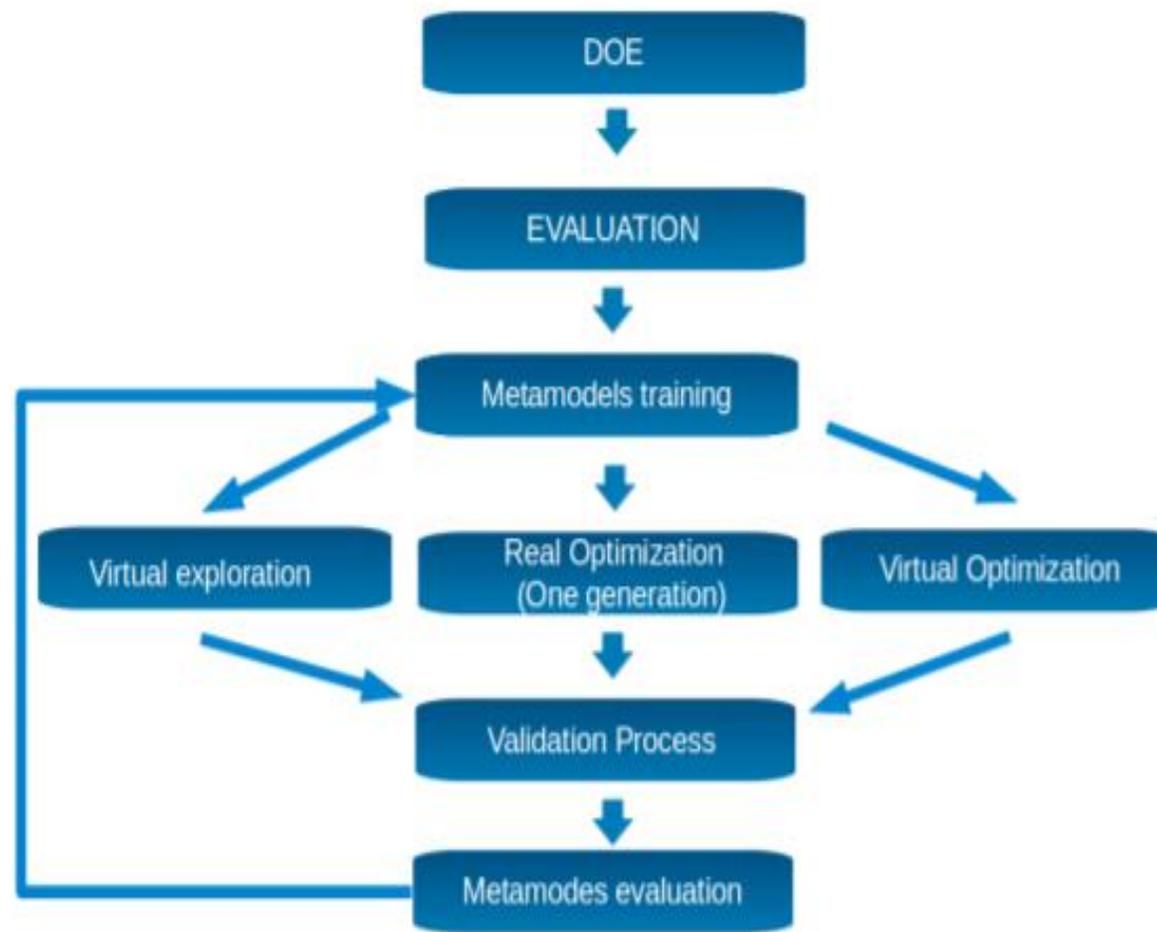
The optimization workflow



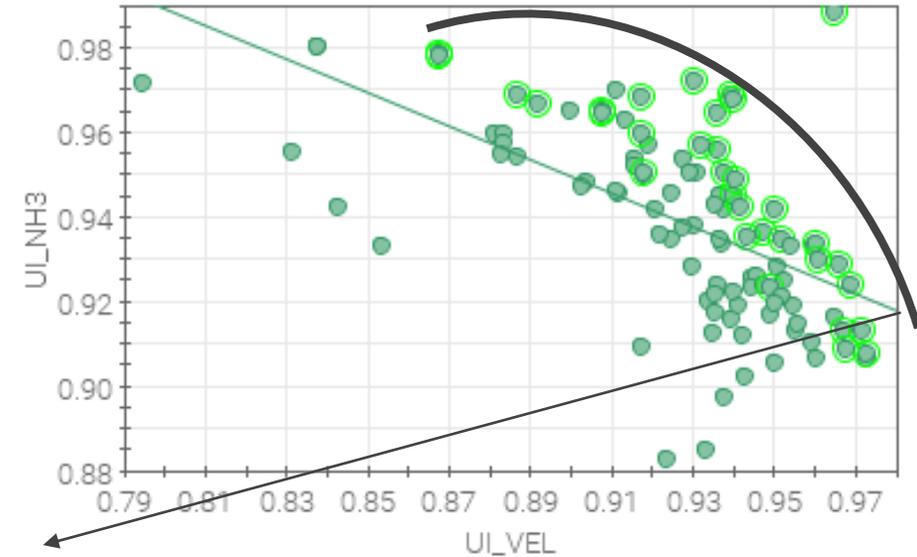
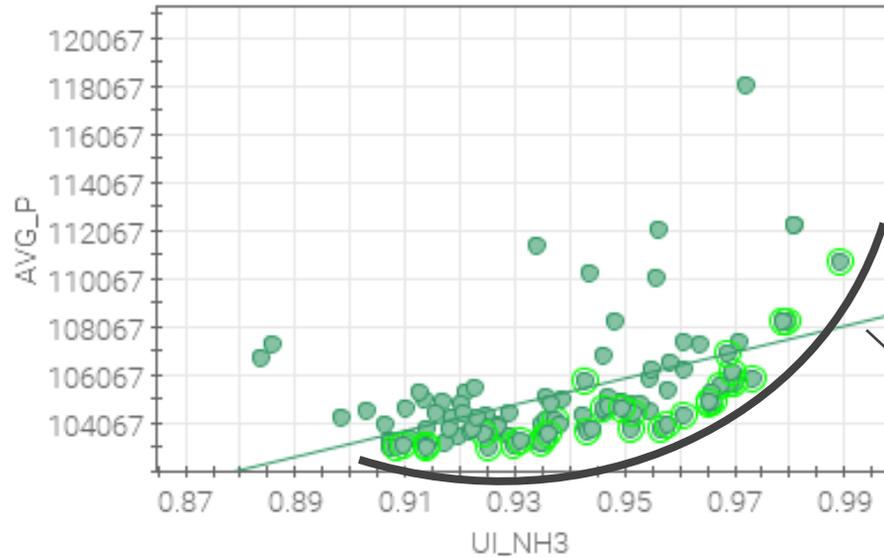
The optimization workflow starts with the list of input parameters from the CAD model. The CAD model is imported into AVL Fire, and the surface and edge meshes are generated. Based on a prescribed recipe the volume mesh is created and attached to an extruded flow domain corresponding to the porous region of the DOC and SCR. Once these meshes are joined seamlessly the resulting mesh is used for the advanced CFD analysis in AVL Fire. This contains all the model settings for the flow, spray, wall-film formation, chemical reactions for the spray decomposition, solid deposits formation and decomposition, and steady state SCR catalyst reactions. Once the case is completed the output of the simulation is stored and the process repeats until the number of prescribed cases is reached.

7 Optimization using FAST optimizer

- Inputs:
 - DS_DIA1
 - DS_DIA2
 - DS_ALFA
- Objectives:
 - average pressure drop ↓
 - ammonia uniformity ↑
 - exhaust flow uniformity ↑
 - wall-film mass ↓
- FAST is an optimization algorithm combining real and virtual optimization strategies.
- Default settings of FAST optimizer has been used to evaluate 200 designs with initial database of 27 DOE design points.

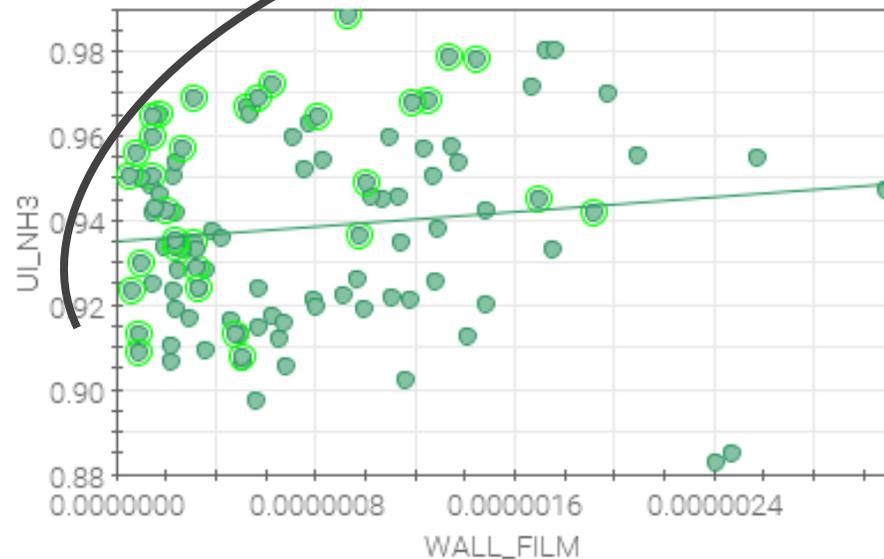


Pareto Designs

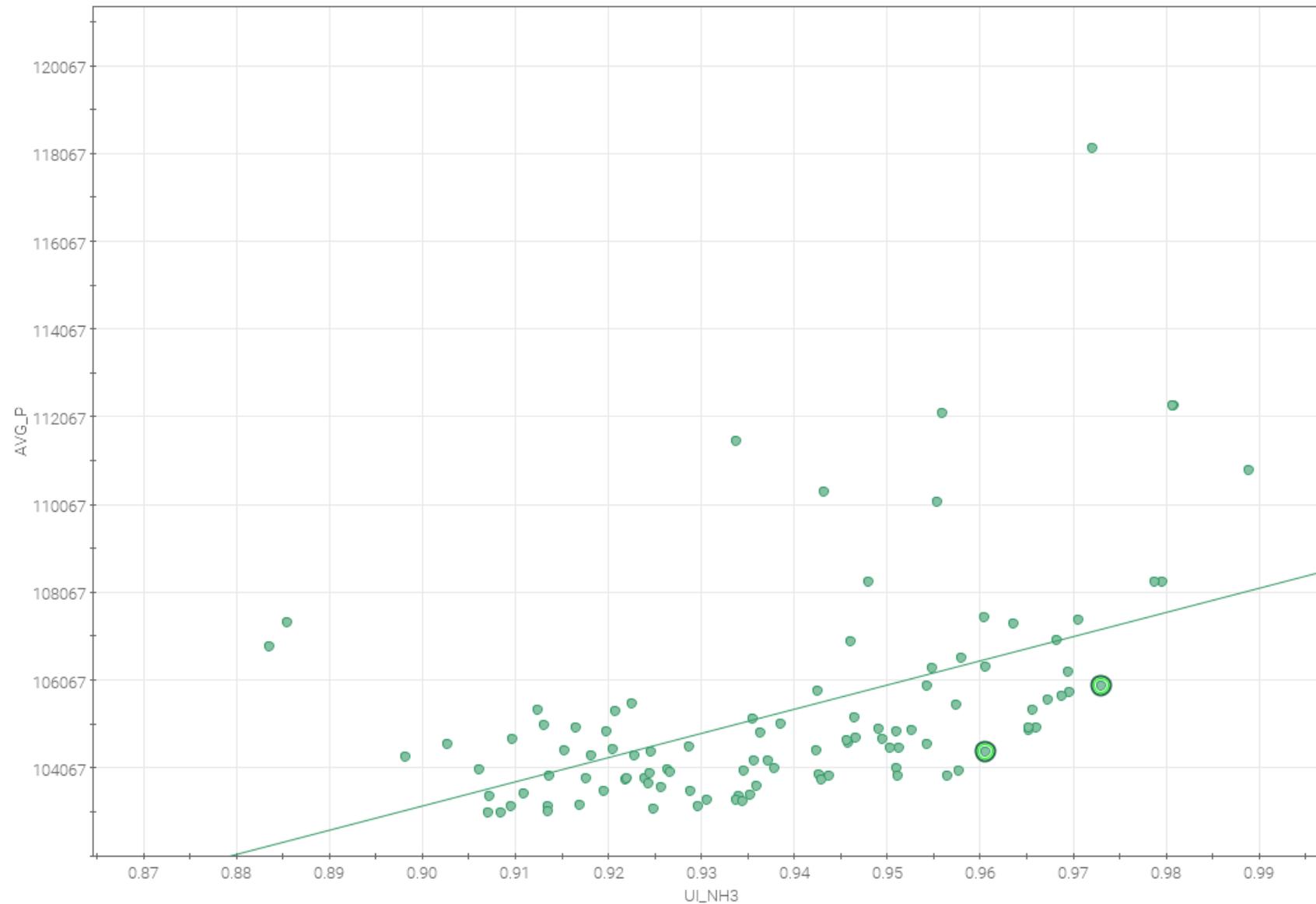


The Pareto Frontier

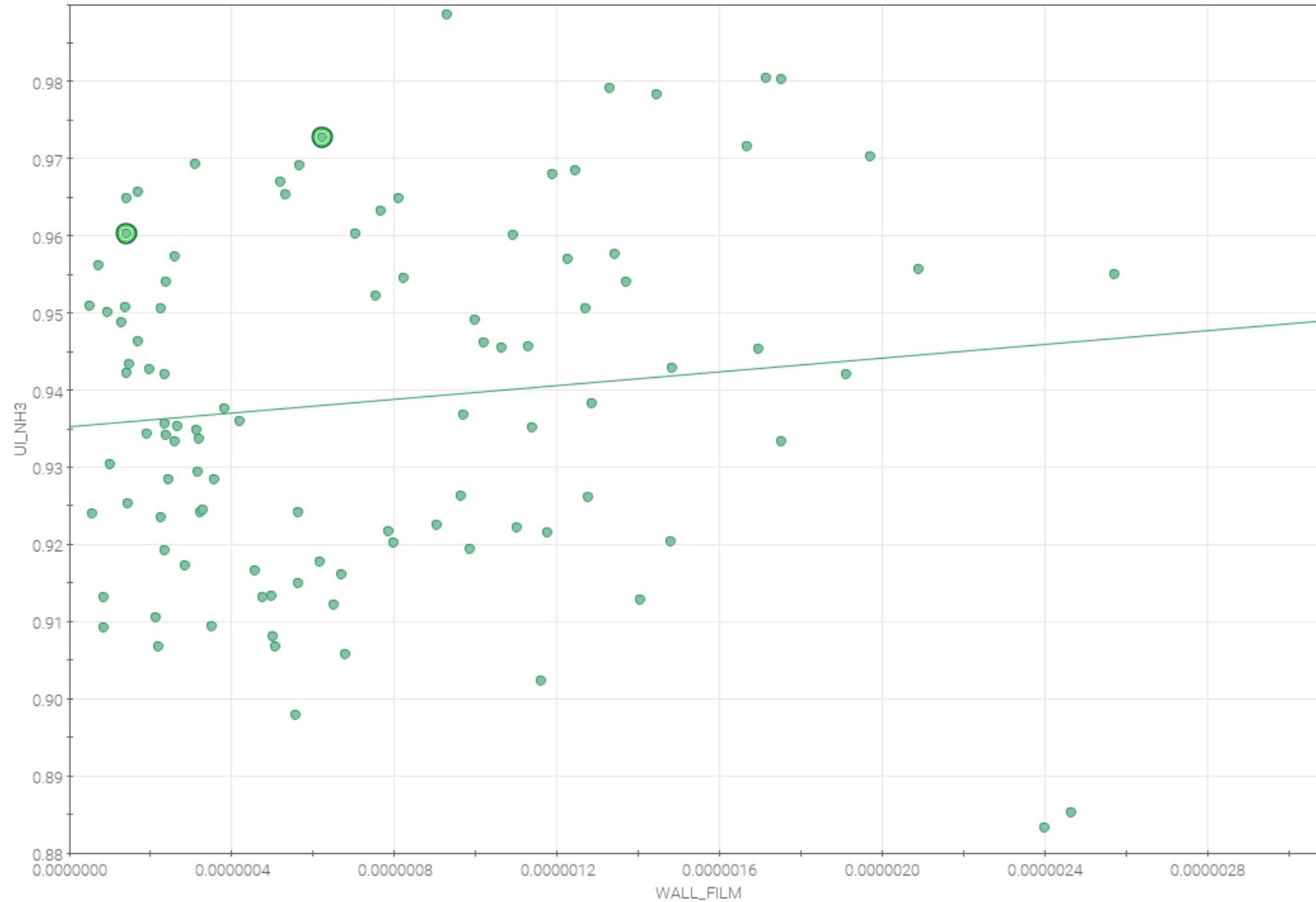
- A solution belongs to the Pareto Frontier when none of the objectives can be improved without degrading the others. All Pareto Frontier solutions are considered equally good (Pareto optimal)
- The highlighted designs in the scatter charts are Pareto Designs



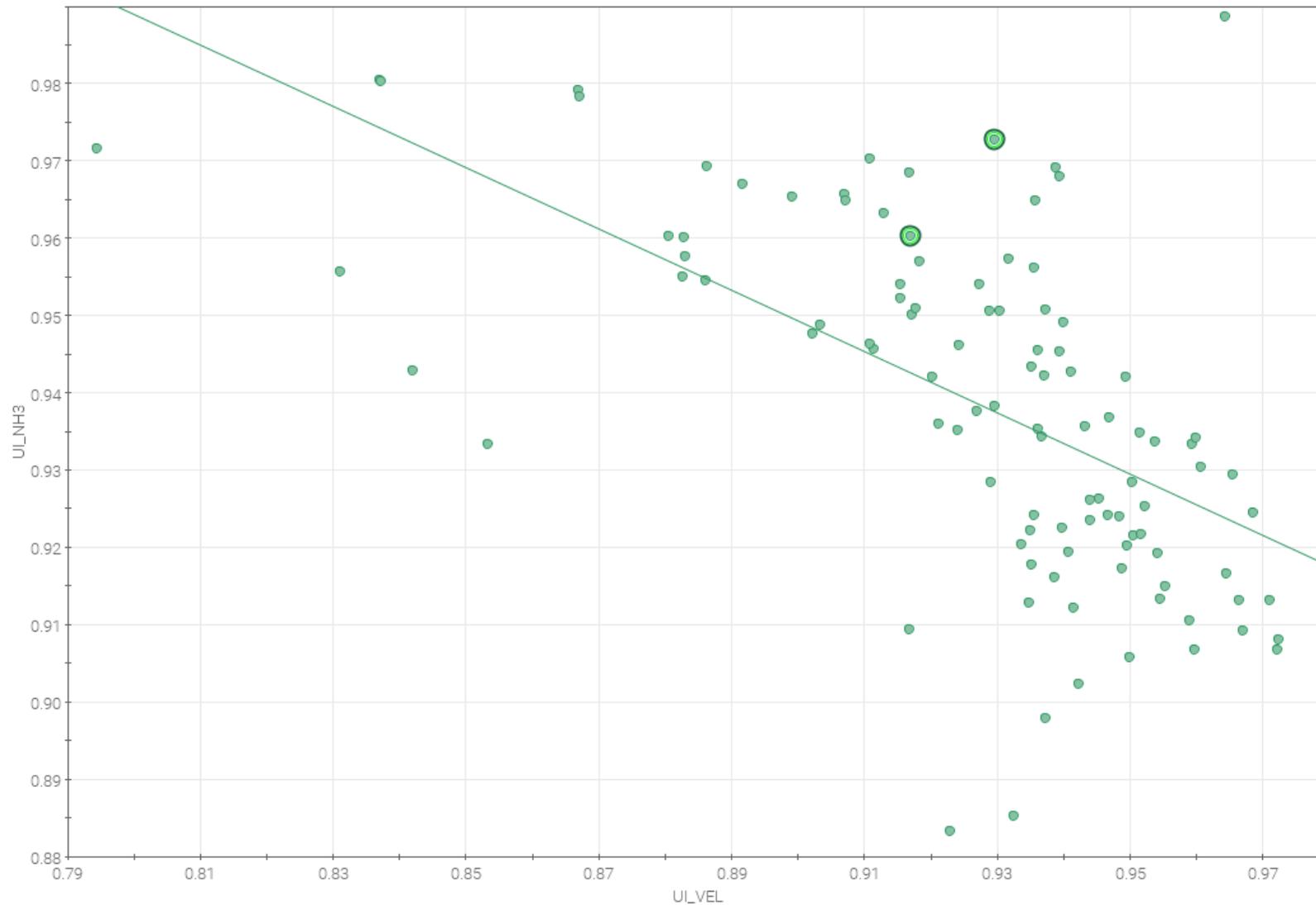
Design trade-offs: reductant uniformity vs. pressure drop



Design trade-offs: reductant uniformity vs. DEF wall-film mass



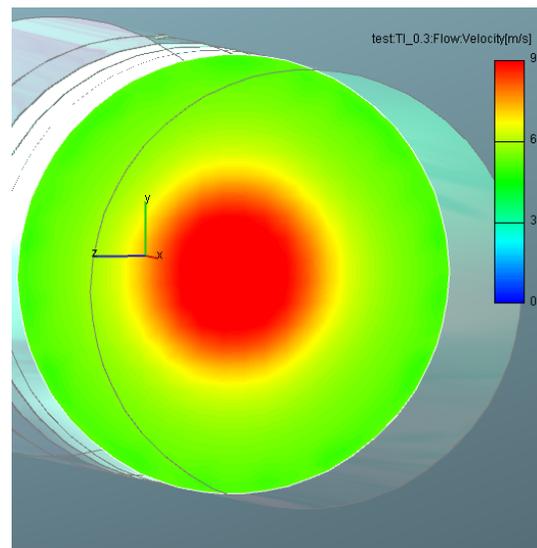
Design trade-offs: reductant uniformity vs. flow uniformity



Winner design

DS_DIA1	Real Nu...	94.622000
DS_DIA2	Real Nu...	161.459250
DS_ALFA	Real Nu...	77.894600

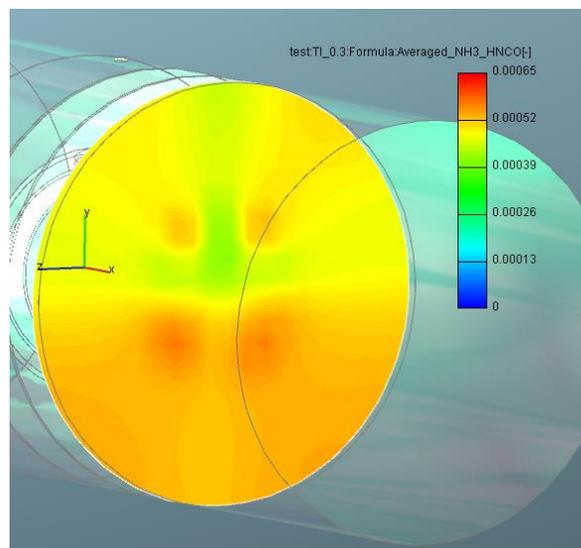
“Winner” input parameters



delta P=3.430 kPa
FDI=0.929

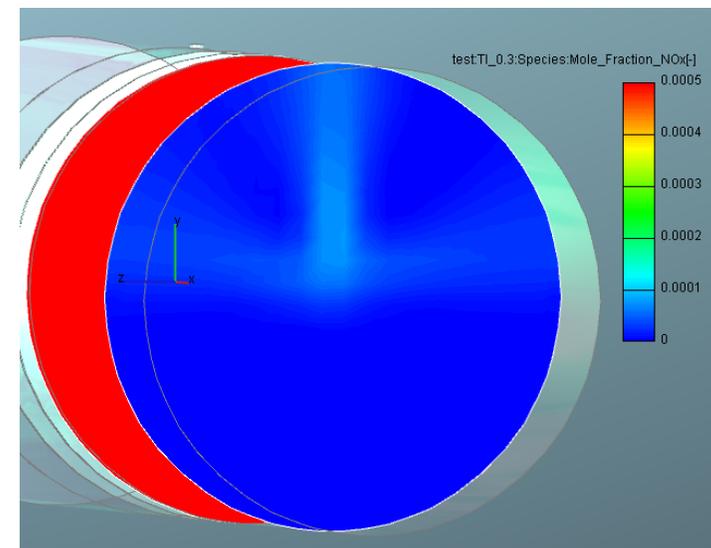
Exhaust flow velocity inside the SCR catalyst. The flow uniformity is 0.929 and the pressure drop across the mixer is 3.430 kPa

At the end of the simulation 0.51% of the injected urea water solution is in form of wall-film on the mixer's walls



UI=0.973

The time averaged reductant molar fraction (ammonia and isocyanic acid) at the inlet of the SCR catalyst. The reductant uniformity index is 0.973



deNOx=97.3%

The NOx molar fraction (NO and NO₂) at the inlet and outlet of the SCR catalyst. The deNOx efficiency for the winner is 97.3%

Conclusions and future work

- We were successful in integrating AVL Fire with modeFRONTIER and applied it to a urea water solution selective catalyst reduction mixer multi-objective optimization
- The baseline was created using our best engineering judgment. The design has had three parameters (two diameters and one angle) and we populated the inputs with a Latin hypercube technique on a 50% range centered on the baseline values. Some of the cases were not successfully realized due to inferences in the design
- The CFD model incorporates all the chemical reactions that describe the urea water solution spray decomposition, homogeneous reactions, transformation from wall-film to solid deposits and decomposition of the solid deposits, and finally the SCR catalyst reactions
- The results of the model for each case fully describe the performance of the SCR mixer: pressure drop, exhaust flow uniformity at the entrance in the SCR , reductant uniformity at the same location, amount of the wall-film, and deNOx efficiency
- The analysis of the overall results can lead to useful and insightful design guidelines and possible tradeoffs between different mixer performances
- From the resulting realized cases we took the case with the highest deNOx efficiency as the winner of the design of experiment. Comparing to the baseline where the deNOx efficiency was 93.6%, the winner design had 97.3% deNOx efficiency
- We intend to use deNOx efficiency as output parameter of the model that need to be maximized and solid deposits mass to be minimized therefore the outcome can be readily compared with the test cell results

Appendix I Exhaust flow and reductant uniformity indices at the inlet face of the SCR

$$FDI = 1 - \frac{1}{2} \sum_{k=1}^n \frac{A_i}{A_{tot}} \frac{|v_i - v_{avg}|}{v_{avg}}$$

FDI- flow distribution index

n- number of finite volume elements at the inlet face of the SCR

A_i - surface area of each individual finite volume element belonging to the SCR face

A_{tot} - total surface area of the SCR face

v_i - axial velocity in the finite volume element i^{th}

v_{avg} - average axial velocity at the face of the SCR

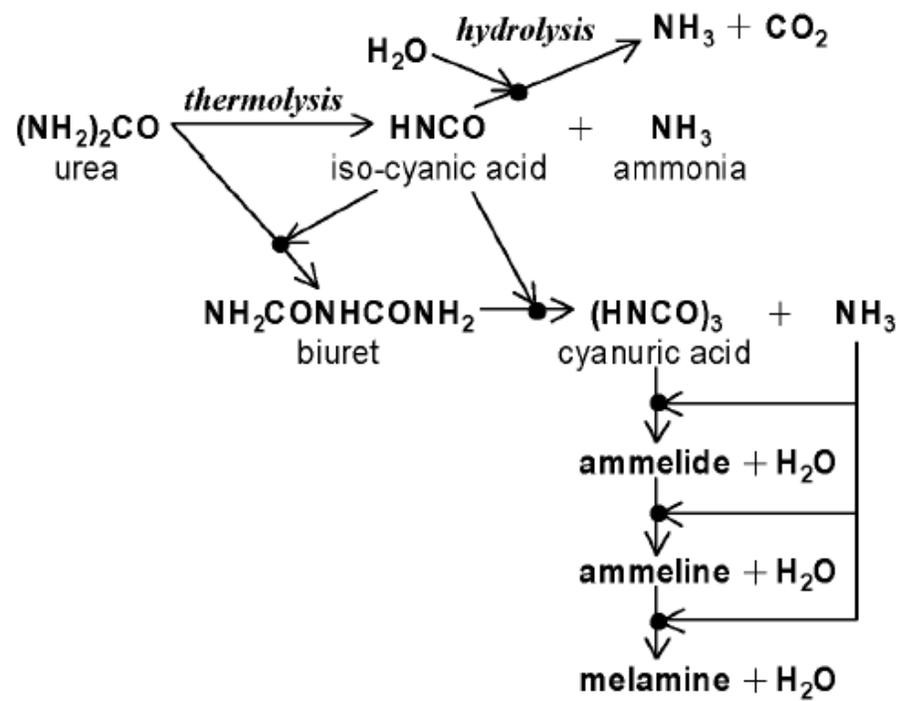
UI- reductant uniformity index

$[NH_3]_i$ - reductant molar concentration in the i^{th} finite volume element

$[NH_3]_{avg}$ - average molar concentration at the face of the SCR

$$UI = 1 - \frac{1}{2} \sum_{k=1}^n \frac{A_i}{A_{tot}} \frac{|[NH_3]_i - [NH_3]_{avg}|}{[NH_3]_{avg}}$$

Appendix II Urea decomposition reactor chemical reactions*

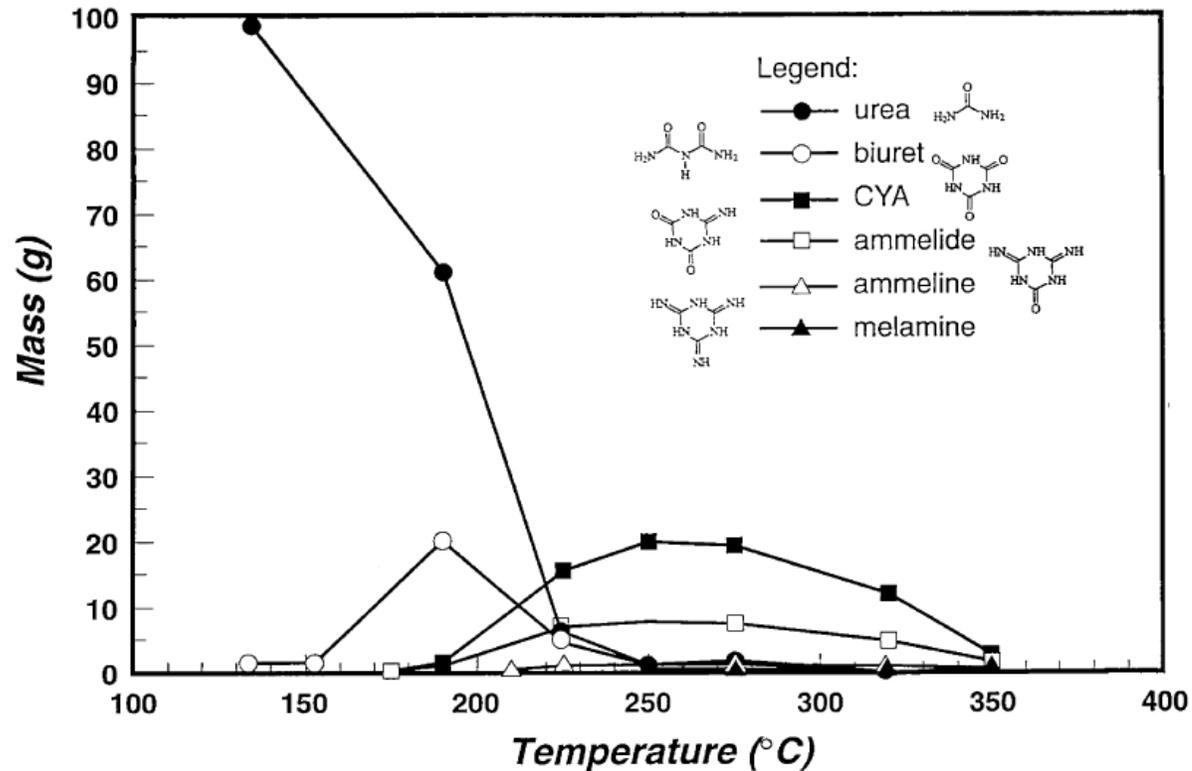


Reaction scheme of urea

The desired decomposition for urea is through thermolysis, however if the temperature and pressure increase are suitable the urea can turn into solids. Typically, this pathway is favored in wall-film resulting from spray mixer walls interaction. The two pathways can coexist, and the resulting compounds have higher decomposition temperature as seen from TGA data

*Nishioka A. "A study of a new aftertreatment system (2): control of urea solution spray for urea-SCR", SAE paper 2006-01-0644 (2006)

Appendix III SCR solid deposits conversion with temperature*



The thermo gravimetric analysis (TGA) of the urea indicate the components seen in urea solid deposits from SCR applications. As the temperature increases and time progresses the resulting components have lower mass, but higher decomposition temperature.

*Schaber P. M. et al. "Thermal decomposition (pyrolysis) of urea in an open reaction vessel ", *Thermochimica Acta* 424 (2004) 131-142

Appendix IV Kinetic modeling of urea solid deposits*

$$\frac{dn_i}{dt} = \sum_{r=1}^N \nu_{i,r} \frac{dn_r}{dt} + j_i$$

$$\frac{dn_r}{dt} = k_r V_R \prod_j c_j^{\nu_j}$$

$$j_i = \frac{1}{4} \alpha_0 \nu c_{i,l}^s a$$

$$k_r = A_0 e^{-\frac{E_A}{RT}}$$

$$\nu = \sqrt{\frac{8RT}{\pi M}}$$

$$h = \frac{C_{liq}^{eq}}{C_{gas}^{eq}} = \frac{\rho_{liq}}{p_{vap}} \frac{M}{RT}$$

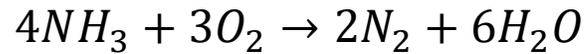
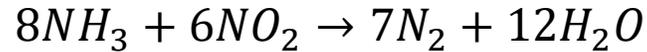
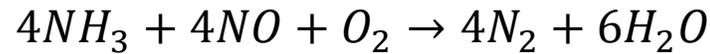
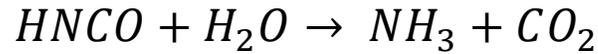
n mole number
 ν stoichiometric factor
 j evaporation source term
 k reaction rate
 V reactor volume
 c concentration of educt species
 γ reaction order
 A pre-exponent factor
 a surface area

E activation energy
 R universal gas constant
 T temperature
 ν gas thermal velocity
 α accomodation factor
 ρ density
 M molar mass of dissolved species
 p vapor pressure of dissolved species

	Reaction	γ_j	A	E_A (kJ/mol)
I	$CYA_{(s)} \rightarrow 3HNCO_{(g)}$	0	$1.001 \times 10^3 \text{ mol/s}$	118.42
II	$biuret_{(m)} \rightarrow urea_{(m)} + HNCO_{(l)}$	1	$1.107 \times 10^{20} \text{ 1/s}$	208.23
III	$urea_{(m)} + HNCO_{(l)} \rightarrow biuret_{(m)}$	1 / 1	$3.517 \times 10^{11} \text{ ml/mol s}$	75.45
IV	$urea_{(m)} \rightarrow HNCO_{(l)} + NH_3_{(g)}$	0.3	$2.000 \times 10^4 \text{ mol}^{0.7} / \text{ml}^{0.7} \text{ s}$	74.00
V	$2biuret_{(m)} \rightarrow ammelide_{(s)} + HNCO_{(l)} + NH_3_{(g)} + H_2O_{(g)}$	2	$3.637 \times 10^{26} \text{ 1/s}$	257.76
VI	$biuret_{(m)} + HNCO_{(g)} \rightarrow CYA_{(s)} + NH_3_{(g)}$	1 / 1	$9.397 \times 10^{20} \text{ ml/mol s}$	158.68
VII	$biuret_{(m)} + HNCO_{(g)} \rightarrow triuret_{(s)}$	1 / 1	$1.091 \times 10^{15} \text{ ml/mol s}$	116.97
VIII	$triuret_{(s)} \rightarrow CYA_{(s)} + NH_3_{(g)}$	1	$1.238 \times 10^{18} \text{ 1/s}$	194.94
IX	$urea_{(m)} + 2HNCO_{(l)} \rightarrow ammelide_{(s)} + H_2O_{(g)}$	1 / 2	$1.274 \times 10^{20} \text{ ml}^2 / \text{mol}^2 \text{ s}^2$	110.40
X	$biuret_{(m)} \rightarrow biuret_{(matrix)}$	1	$8.193 \times 10^{26} \text{ 1/s}$	271.50
XI	$biuret_{(matrix)} \rightarrow biuret_{(m)}$	1	$3.162 \times 10^{09} \text{ 1/s}$	122.00
XII	$biuret_{(matrix)} \rightarrow 2HNCO_{(g)} + NH_3_{(g)}$	1	$5.626 \times 10^{24} \text{ 1/s}$	266.38
XIII	$urea_{(s)} \rightarrow urea_{(m)}$	1	$1.000 \times 10^{15} \cdot T^{1.5} \text{ 1/s}$	160.00
XIV	$ammelide_{(s)} \rightarrow ammelide_{(g)}$	1	$1.000 \times 10^{14} \text{ ml/mol s}$	201.67
XV	$HNCO_{(l)} \rightarrow HNCO_{(g)}$	Herz-Knudsen-equation		

*Brack W. et al. "Kinetic modeling of urea decomposition based on a systematic thermogravimetric analyses of urea and its most important byproducts", Chemical Engineering Science 106 (2014) 1-8

Appendix V Kinetic modeling of SCR steady state reactions



HNCO Hydrolysis

$$\text{HNCO} + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{CO}_2$$

Frequency Factor: K m⁴/(kmol.s)

Activation Temperature: E K

$$\dot{r} = K \cdot \exp\left(\frac{-E}{T_s}\right) \cdot c_{\text{HNCO}}^L \cdot c_{\text{H}_2\text{O}}^L$$

NO2 Reduction (slow SCR)

$$8\text{NH}_3 + 6\text{NO}_2 \rightarrow 7\text{N}_2 + 12\text{H}_2\text{O}$$

Frequency Factors: K_1 m/s, K_2 m³/kmol

Activation Temperatures: E_1 K, E_2 K

$$\dot{r} = K_1 \cdot \exp\left(\frac{-E_1}{T_s}\right) \cdot c_{\text{NO}_2}^L \cdot \frac{K_2 \cdot \exp\left(\frac{-E_2}{T_s}\right) \cdot c_{\text{NH}_3}^L}{1 + K_2 \cdot \exp\left(\frac{-E_2}{T_s}\right) \cdot c_{\text{NH}_3}^L}$$

NO Oxidation (Steady-State Approach)

Rate Approach 1 Rate Approach 2

$$\text{NO} + \frac{1}{2}\text{O}_2 \leftrightarrow \text{NO}_2$$

Temperature Dependency (A) [1]

Frequency Factor: K m^(2.5)K/(kmol^(0.5).s)

Activation Temperature: E K

$$\dot{r} = K \cdot T_s^A \cdot e^{\left(\frac{-E}{T_s}\right)} \cdot \left[c_{\text{NO}} \cdot c_{\text{O}_2}^{1/2} - \frac{c_{\text{NO}_2}}{K_{\text{Equ},2}(T_s)} \right]$$

NO Reduction (standard SCR)

$$4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$$

Frequency Factors: K_1 m/s, K_2 m³/kmol

Activation Temperatures: E_1 K, E_2 K

$$\dot{r} = K_1 \cdot \exp\left(\frac{-E_1}{T_s}\right) \cdot c_{\text{NO}}^L \cdot \frac{K_2 \cdot \exp\left(\frac{-E_2}{T_s}\right) \cdot c_{\text{NH}_3}^L}{1 + K_2 \cdot \exp\left(\frac{-E_2}{T_s}\right) \cdot c_{\text{NH}_3}^L}$$

NH3 Oxidation 1

$$4\text{NH}_3 + 3\text{O}_2 \rightarrow 2\text{N}_2 + 6\text{H}_2\text{O}$$

Frequency Factor: K m/s

Activation Temperature: E K

$$\dot{r} = K \cdot \exp\left(\frac{-E}{T_s}\right) \cdot c_{\text{NH}_3}^L$$

NOx Reduction (fast SCR)

$$4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$$

Frequency Factors: K_1 m⁴/(kmol.s), K_2 m³/kmol

Activation Temperatures: E_1 K, E_2 K

$$\dot{r} = K_1 \cdot \exp\left(\frac{-E_1}{T_s}\right) \cdot c_{\text{NO}}^L \cdot c_{\text{NO}_2}^L \cdot \frac{K_2 \cdot \exp\left(\frac{-E_2}{T_s}\right) \cdot c_{\text{NH}_3}^L}{1 + K_2 \cdot \exp\left(\frac{-E_2}{T_s}\right) \cdot c_{\text{NH}_3}^L}$$

