Knowledge grows

Development of intrinsic kinetic model for SCR monolith catalysts

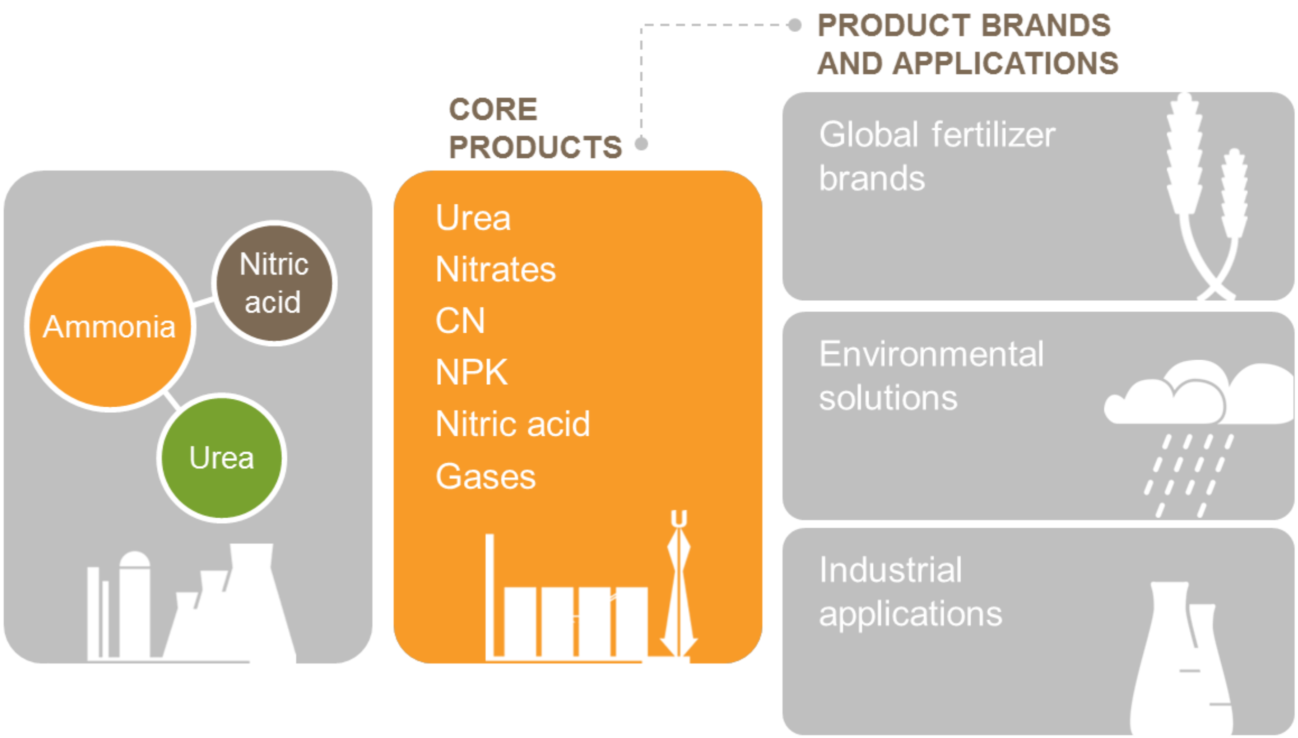
Sang Baek Shin (Yara International)
Štěpán Špatenka, Sreekumar Maroor (PSE UK)
In Seon Kim (PSE Korea)

Advanced Process Modelling Forum
20 April 2016
London, United Kingdom

Yara International

We deliver sustainable solutions for agriculture and the environment

- Yara International ASA is a Norwegian chemical company headquartered in Oslo, Norway.
- Established as Norsk Hydro – the world's first producer of mineral nitrogen fertilisers – in 1905, demerged in 2004.



Founder: Kristian Birkeland

Born in Norway

We have pioneered agricultural growth and production for over 100 years

1900-1905

Birkeland's Invention

Birkeland's discovery that hydroelectric power could be used to extract nitrogen from the air led to Norsk Hydro opening December 2, 1905.

1906-1939

Attracting Royal Attention

New large scale production plants opening and under construction in Notodden and Rjukan respectively are visited by King Chulalongorn of Siam. The plant at Herøya established in 1928. First production of regular NPK fertilizer in 1938.

1940-1959

Extending our Reach

Stockholm is home to a new sales office and the USA becomes a customer. The Glomfjord plant opens using hydroelectric power to upgrade ammonia to calcium nitrate and NPK.

1960-2003

Going Global

Qafco JV established in 1969. Yara acquires companies in the Netherlands, Sweden, Germany, the UK, France, Italy and China and establishes an office in Zimbabwe. Adubos Trevo is acquired in Brazil.

HYDRO

2004-2014

Going Public – Industry Shaper

March 25, 2004, Yara is listed on the Oslo Stock Exchange. The tagline 'Knowledge grows' introduced.

Yara offers solutions and work with public and private partners to create profitable and sustainable growth both for shareholders, stakeholders and society at large

YARA

Knowledge grows

2015 →

Knowledge grows - Providing shared value

Yara´s knowledge, products and solutions grow farmers', distributors' and industrial customers´ businesses profitably and responsibly while nurturing and protecting the earth´s resources, food and environment.

YARA

Knowledge grows

Today

we have a global impact

WE

Employ more than
13 000 people

Operate in more than
50 countries

Work with
15 mill. farmers

Sell to about
160 countries

OUR PRODUCTS HELP

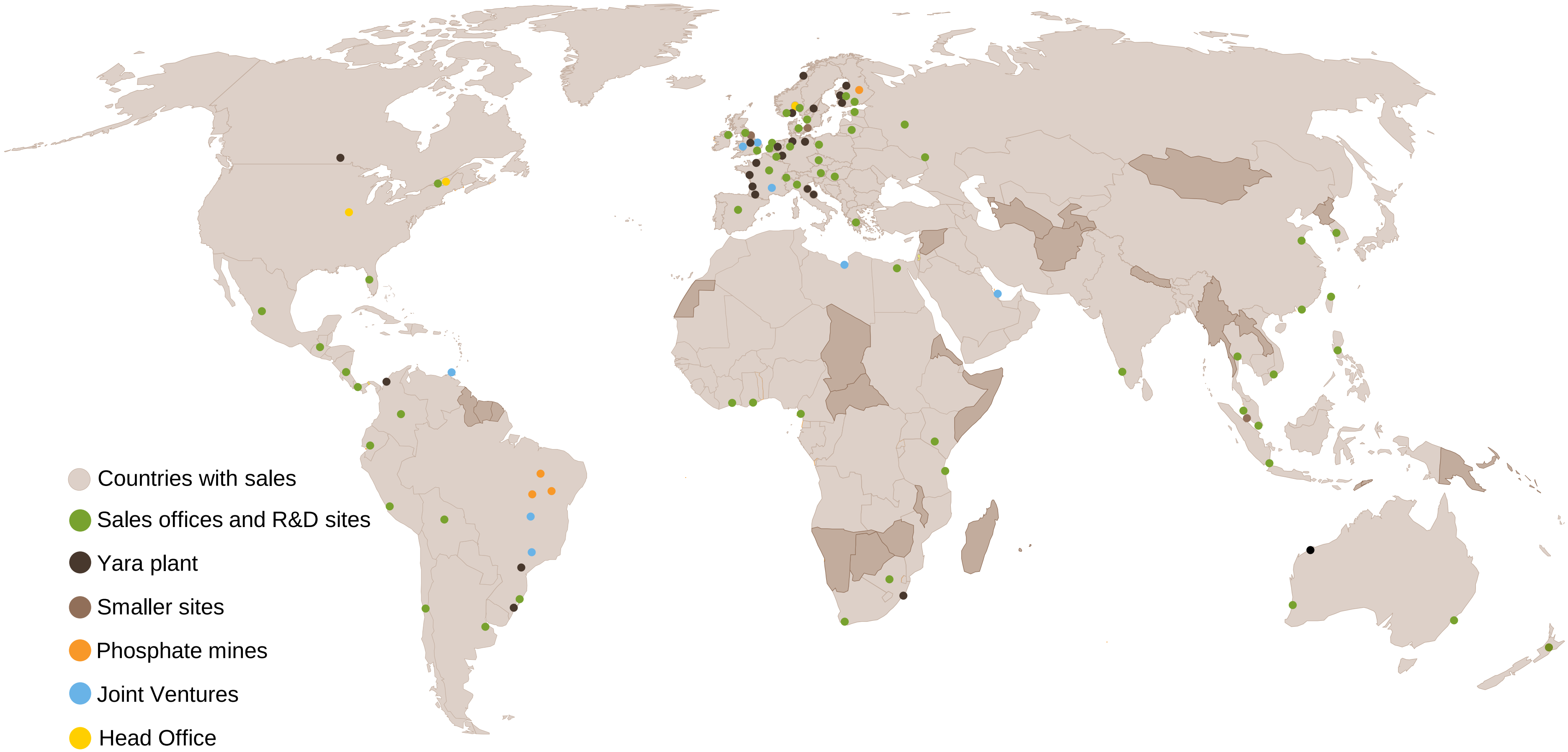
Produce
240 mill. tons of grains

Feed
240 mill. people

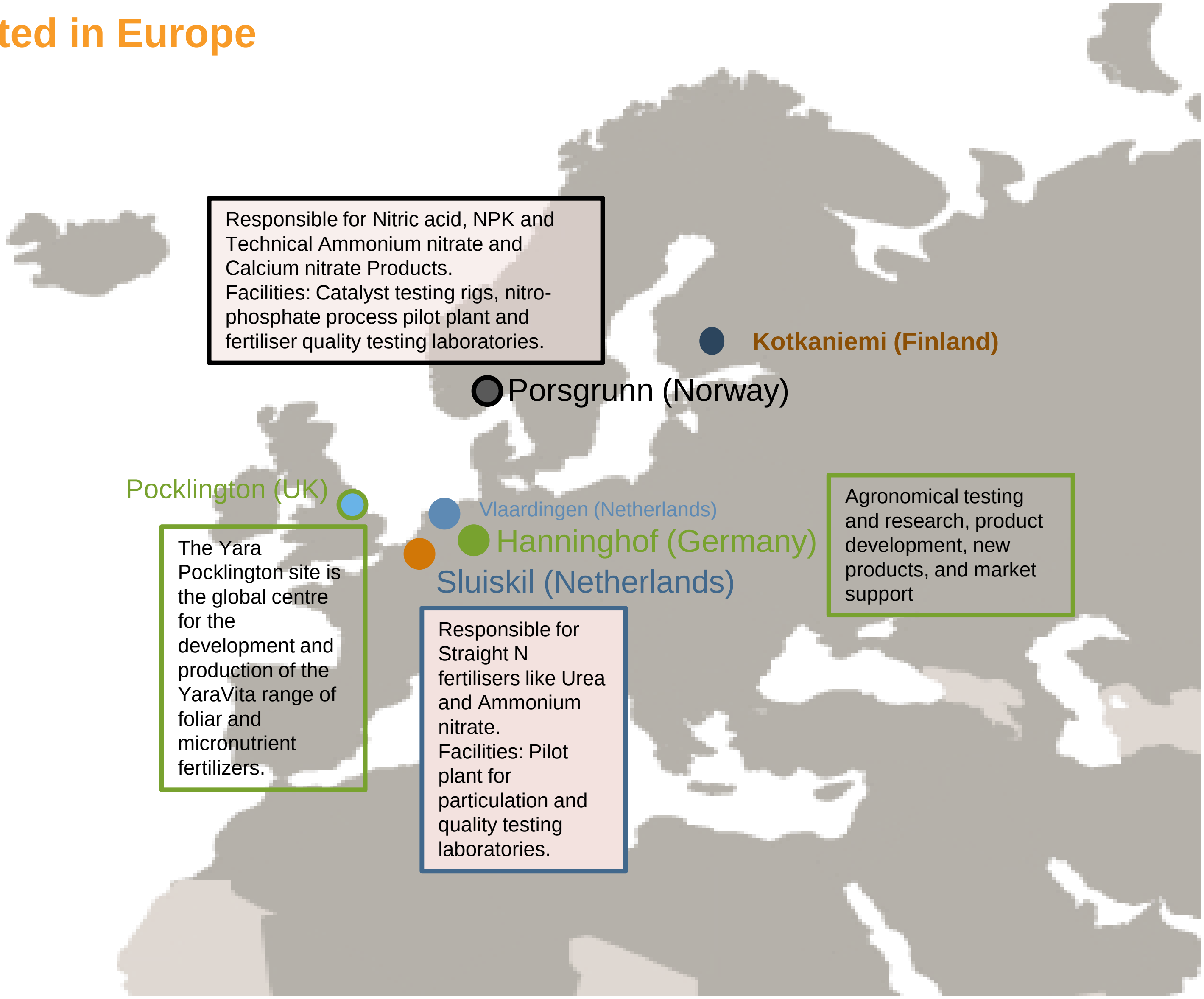
Deliver fresh air for
50 mill. citizens

Revenues and other income (2015)
NOK 112 Billion
(USD 14 Billion)

Our global presence
is growing



R&D units
are located in Europe



Background & objective

- Yara is a leading producer of complete **NOx abatement solutions,** including SCR and SNCR systems for industrial and maritime segment

- In order to enhance the SCR business, Yara is developing **novel designs of SCR deNOx catalyst monolith**
  - By applying model-based approach to reactor design
  - Requires intrinsic reaction kinetics for SCR

- **Kinetic experiments on a crushed SCR catalyst** were performed by Yara

- **Applied gPROMS Advanced Model Library for Fixed-Bed Catalytic Reactors (AML:FBCR) to extract Intrinsic kinetic parameters** by considering simultaneously catalytic chemical reactions and all relevant transport phenomena

Reaction scheme for SCR

NOx reduction reactions

1) $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ (standard SCR)
2) $6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$
3) $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$
4) $2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$
5) $NO + NO_2 + 2NH_3 \rightarrow 2N_2 + 3H_2O$ (fast SCR)

NH_3 oxidation reactions

6) $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$
7) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
8) $4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O$
9) $4NH_3 + 2O_2 \rightarrow N_2O + 3H_2O$
10) $2NH_3 + 8NO \rightarrow 5N_2O + 3H_2O$
11) $6NH_3 + 8NO_2 + 3O_2 \rightarrow 4N_2O + 6H_2O$
12) $4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O$
13) $16NH_3 + 12NO + 7O_2 \rightarrow 4N_2O + 24H_2O$

Additional reactions

14) $2SO_2 + O_2 \rightarrow 2SO_3$
15) $NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4$
16) $2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4$
17) $2NH_4HSO_4 \rightarrow (NH_4)_2SO_4 + H_2SO_4$
18) $NH_4HSO_4 + NH_3 \rightarrow (NH_4)_2SO_4$
19) $2NH_3 + H_2O + 2NO_2 \rightarrow NH_4NO_3 + NH_4NO_2$
20) $2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O$

- The number of reactions to be considered in gPROMS modelling was reduced:
  - Experiments with SO_2 and SO_3 were not performed → all **reactions involving SOx are excluded**.
  - NH_4NO_3 is not being measured and hence **reactions involving NH_4NO_3 are excluded**.
  - NO_2 could not be introduced in the feed → it was not possible to distinguish between some of the reactions
  - Experiments without NO do not show enough evidence to consider reaction 8 and 9

Reduced reaction scheme

NOx reduction reactions

1) $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ (standard SCR)
2) $6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$
4) $2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$

NH_3 oxidation reactions

6) $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$
7) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
10) $2NH_3 + 8NO \rightarrow 5N_2O + 3H_2O$
12) $4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O$

7 catalytic reactions

Gas phase reactions

1) $2NO + O_2 \rightarrow 2NO_2$
2) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
3) $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

3 thermal reactions

Reaction rate equations for gPROMS modelling

- Eley-Rideal mechanism is generally accepted for SCR reactions over V-W-Ti catalyst for temperatures > 200°C: NH_3 is strongly adsorbed on the catalyst surface and reacts with NO in the gas phase.
- Oxygen adsorbs on different active site. Adsorption of NO and NO_2 compete with O_2
- Catalytic reactions:

Catalytic Reaction #	Reaction rate
1	$r_1 = \dfrac{k_1 K_{NH_3} P_{NH_3} \; K_{O_2} P_{O_2} P_{NO}}{\left(1+K_{NH_3}P_{NH_3}\right)\left(1+K_{O_2}P_{O_2}+K_{NO}P_{NO}+K_{NO_2}P_{NO_2}\right)}$
2	$r_2 = \dfrac{k_2 K_{NH_3} P_{NH_3} \; P_{NO}}{\left(1+K_{NH_3}P_{NH_3}\right)}$
4	$r_4 = \dfrac{k_4 K_{NH_3} P_{NH_3} \; K_{O_2} P_{O_2} P_{NO_2}}{\left(1+K_{NH_3}P_{NH_3}\right)\left(1+K_{O_2}P_{O_2}+K_{NO}P_{NO}+K_{NO_2}P_{NO_2}\right)}$
6	$r_6 = \dfrac{k_6 K_{NH_3} P_{NH_3} \; K_{O_2} P_{O_2}}{\left(1+K_{NH_3}P_{NH_3}\right)\left(1+K_{O_2}P_{O_2}+K_{NO}P_{NO}+K_{NO_2}P_{NO_2}\right)}$
7	$r_7 = \dfrac{k_7 K_{NH_3} P_{NH_3} \; K_{O_2} P_{O_2}}{\left(1+K_{NH_3}P_{NH_3}\right)\left(1+K_{O_2}P_{O_2}+K_{NO}P_{NO}+K_{NO_2}P_{NO_2}\right)}$
10	$r_{10} = \dfrac{k_{10} K_{NH_3} P_{NH_3} \; P_{NO}}{\left(1+K_{NH_3}P_{NH_3}\right)}$
12	$r_{12} = \dfrac{k_{12} K_{NH_3} P_{NH_3} \; K_{O_2} P_{O_2} P_{NO}}{\left(1+K_{NH_3}P_{NH_3}\right)\left(1+K_{O_2}P_{O_2}+K_{NO}P_{NO}+K_{NO_2}P_{NO_2}\right)}$

- Gas phase reactions:

Gas phase reaction #	Reaction rate
1	$r_1 = k_1^{T_{ref}} \; e^{-\frac{E_1}{R}\left[\frac{1}{T}-\frac{1}{T_{ref}}\right]} C_{NO}^2 C_{O_2}^n$
2	$r_2 = k_2^{T_{ref}} \; e^{-\frac{E_2}{R}\left[\frac{1}{T}-\frac{1}{T_{ref}}\right]} C_{NH_3}^1 C_{O_2}^0$
3	$r_3 = k_3^{T_{ref}} \; e^{-\frac{E_3}{R}\left[\frac{1}{T}-\frac{1}{T_{ref}}\right]} C_{NH_3}^1 C_{O_2}^0$

- Reduced reaction scheme:

NOx reduction reactions

1) $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ (standard SCR)
2) $6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$
4) $2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$

NH_3 oxidation reactions

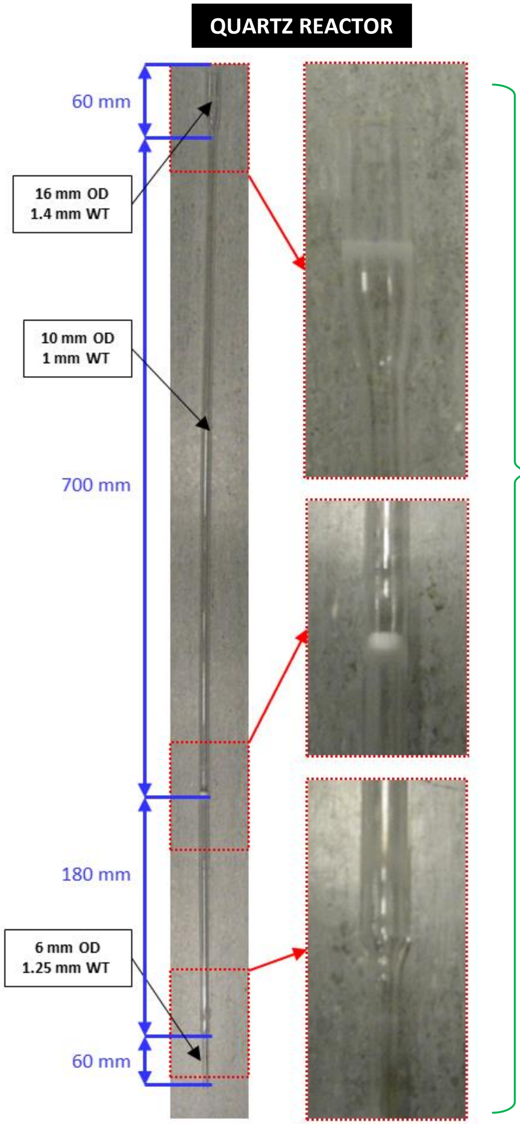
6) $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$
7) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
10) $2NH_3 + 8NO \rightarrow 5N_2O + 3H_2O$
12) $4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O$

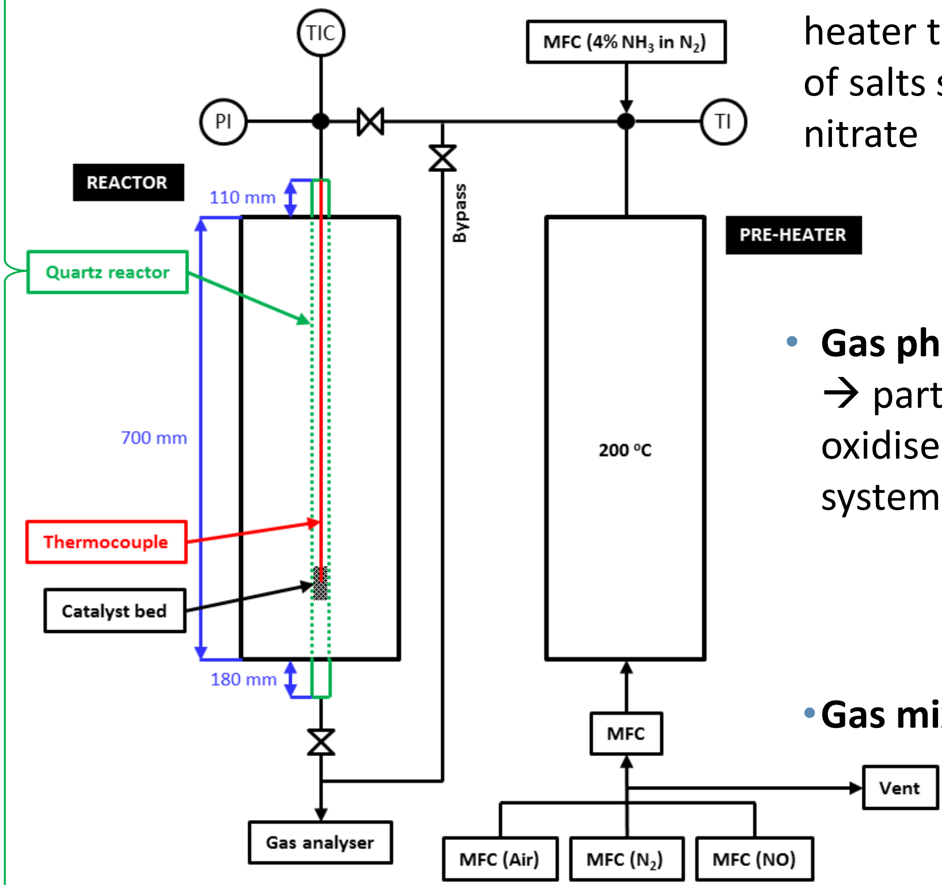
Gas phase reactions

1) $2NO + O_2 \rightarrow 2NO_2$
2) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
3) $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$

Experimental setup

- **Bypass line** is used to measure “inlet” concentrations of NO, NO_2 and NH_3
- **Thermocouple** tip is placed in the catalyst bed and reaction temperature is controlled based on this measurement





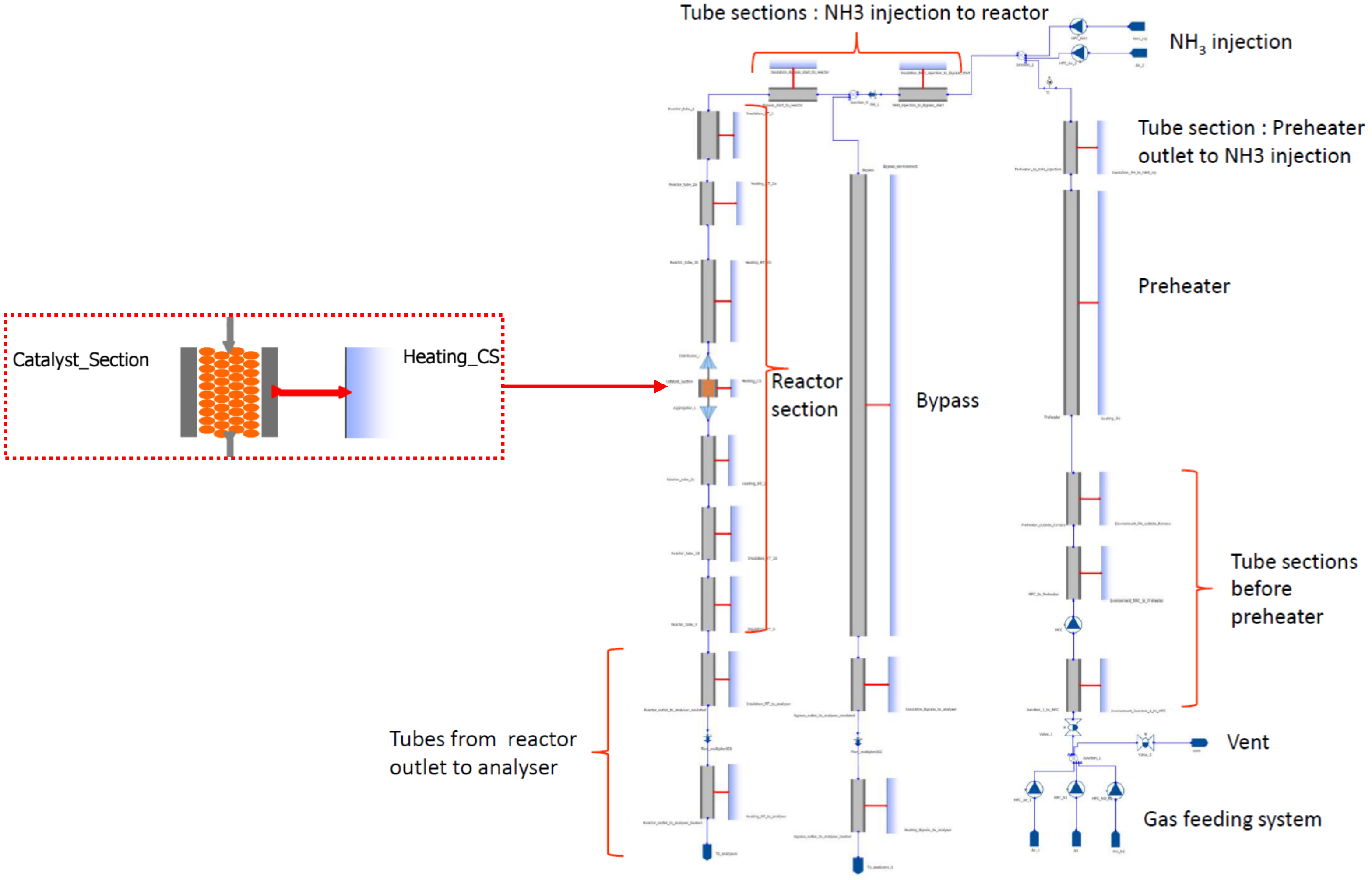
- **Ammonia** is added after pre-heater to minimise formation of salts such as ammonium nitrate

- **Gas phase reactions**
  → part of NO and NH3 is oxidised in the heated system

- **Gas mixture** (N_2, O_2, NO)

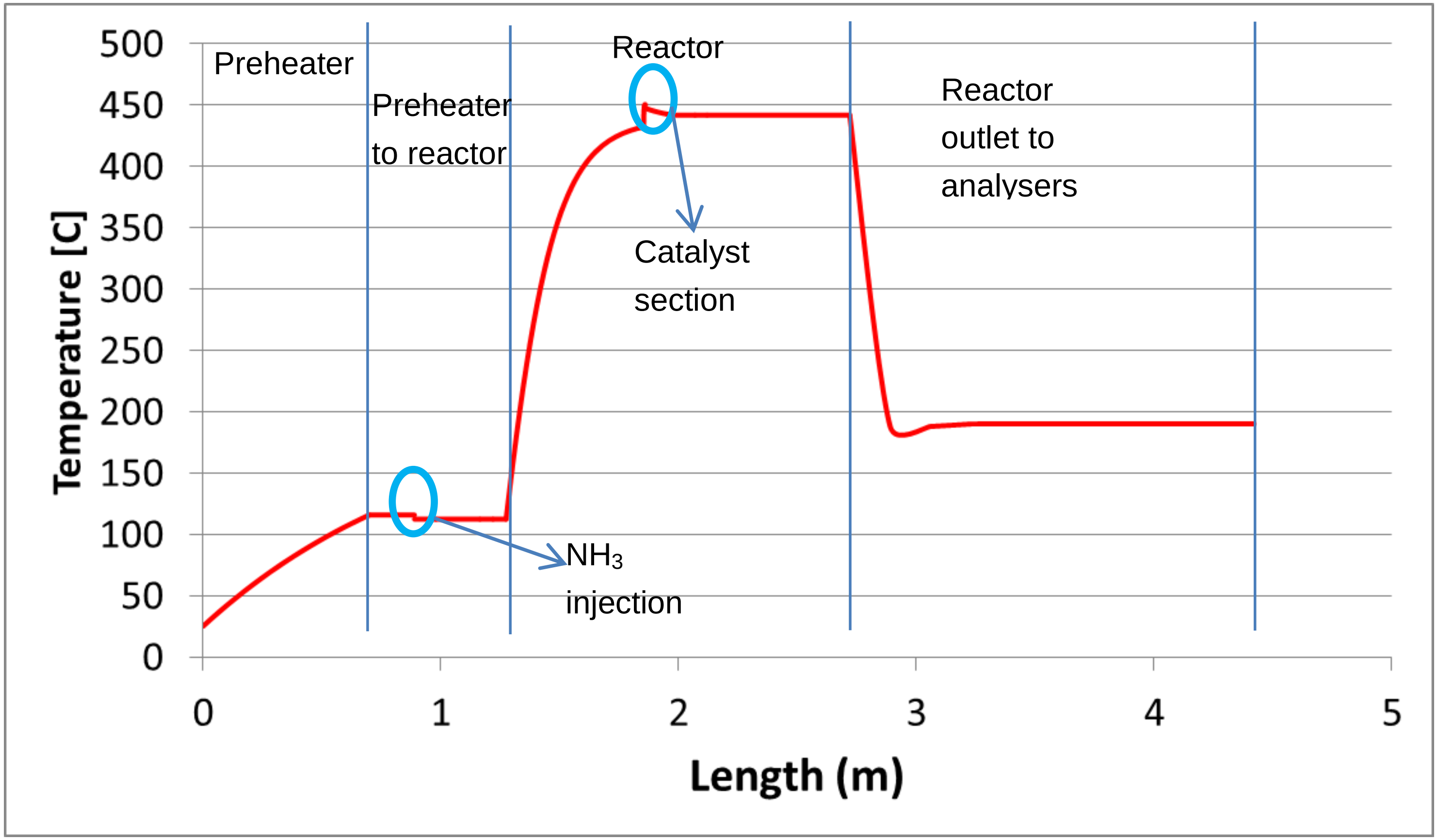
gPROMS model for experimental setup

- Model setup in gPROMS ModelBuilder using PSE's Advanced Model Library for Fixed-Bed Catalytic Reactors (AML:FBCR).



Example of results

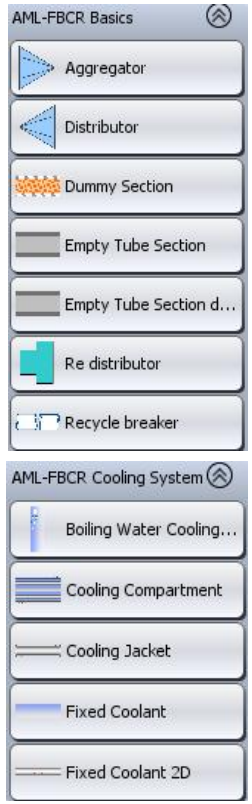
- Temperature profile in the whole experimental rig

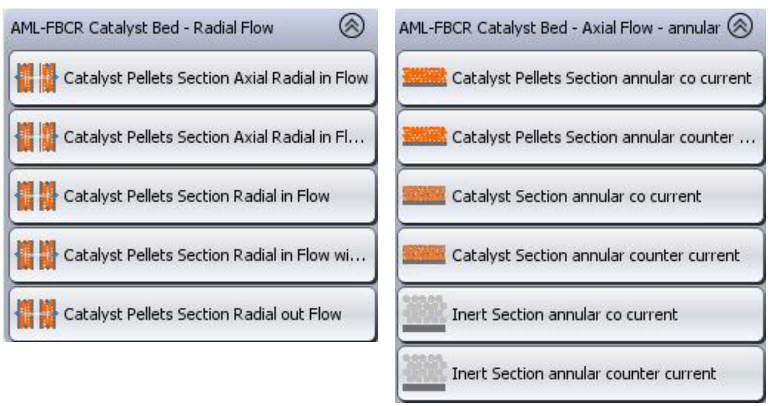


gPROMS AML:FBCR

Advanced Model Library for Fixed-Bed Catalytic Reactors

- Fundamental models
  - Catalyst pellet (1-D)
  - Tube (2-D)
  - Cooling side
  - ‘Utility models’
    - distribution, aggregation
- Multiple operation modes
  - Gas-phase or liquid-phase fluid
  - Homogeneous and inhomogeneous catalyst
  - Axial and radial flow beds
  - Multitubular designs
- Hybrid gPROMS-CFD multitubular modelling

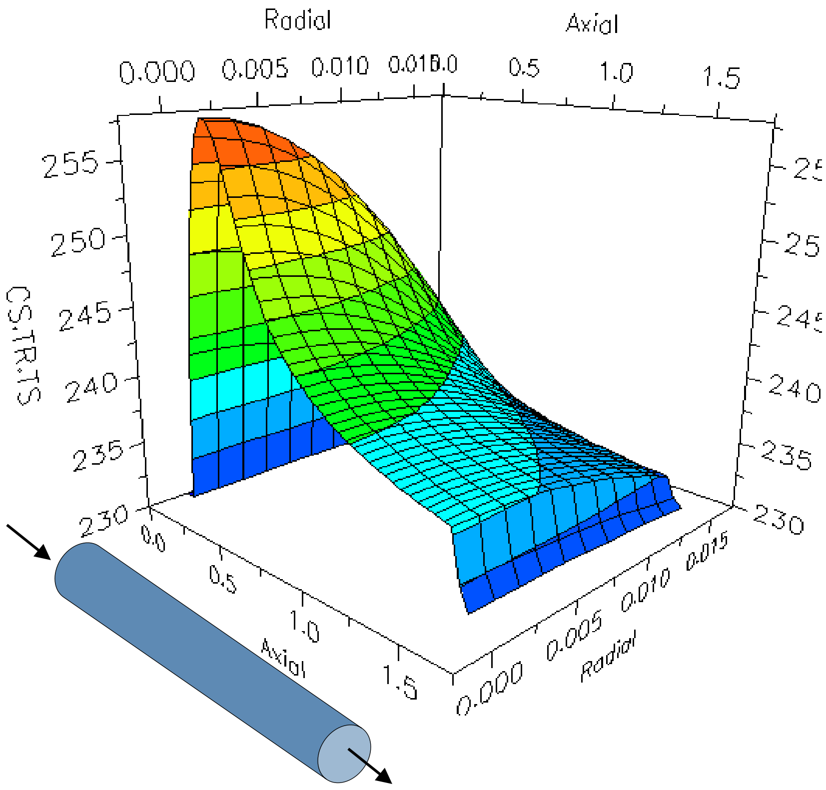


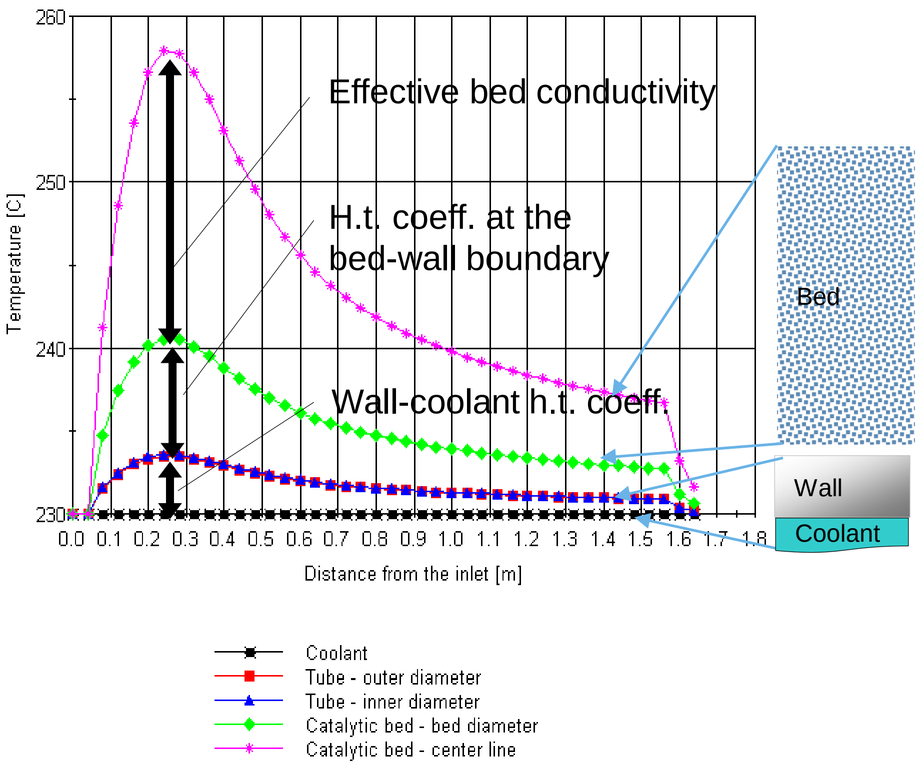


gPROMS AML:FBCR

Advanced Model Library for Fixed-Bed Catalytic Reactors

- 2-D mass and energy balances allow realistic predictions of temperature and concentration profiles inside the bed





gPROMS AML:FBCR
Catalyst pellet model

- 2 different AML:FBCR models employed:

	1-D distributed pellet model	Lumped pellet model
Fidelity	Simultaneous multicomponent diffusion and reactions Prediction of **temperature and composition profiles inside pellets.**	Simplified lumped approach with average reaction rate Requires catalyst effectiveness factor calculation
Complexity for catalyst bed model	Additional dimension to a 2-D bed model (→**3-D model**)	Not adding any more complexity to a 2-D bed model
Usability for modelling of <u>catalyst monolith</u>	Requires distributed model of catalyst layer in addition to a 3D model of a channel (e.g. when using CFD, it requires using **porous volume zones** to represent the catalyst)	Allows considering catalytic reaction as a **surface reaction** (e.g. when using CFD, only **surface zones** are needed to represent the catalyst)

Catalyst pellet model

When is lumped pellet model applicable?

a. **Catalytic reaction is very slow →** concentration profiles inside catalyst are uniform (*It could be the case at lower temperatures, but is it at higher?!*)

b. **Catalytic reaction is very fast →** all reactions take place in very thin catalyst layer at the surface (*It could be the case at higher temperatures, but is it at lower?!*)
- Units of reaction rates are effectively in [mol/s/$\mathbf{m^2}_{cat,external}$] instead of [mol/s/$\mathbf{kg}_{cat}$]

c. **When Fick diffusion applies** and effectiveness factor can be predicted reasonably well:
- Effective diffusivity of all components is similar AND reactions are pseudo-first order (i.e. only one reactant is limiting, concentration of others is constant)

In studied system: contents of reactants is <0.2%, similar diffusivities of main reactants in N_2, but pseudo-first order does not apply at all conditions

@1bar, 350°C:
$D_{NH3,N2}$ = 0.83cm²/s
$D_{NO,N2}$ = 0.87cm²/s
$D_{NO2,N2}$ = 0.70cm²/s
$D_{N2O,N2}$ = 0.54cm²/s
$D_{H2O,N2}$ = 0.95cm²/s

→ Lumped model needs to be applied with caution

- **Applied approach → use lumped model with effectiveness factor for obtaining the intrinsic kinetics, then validate the results using reactor model with distributed pellet model**

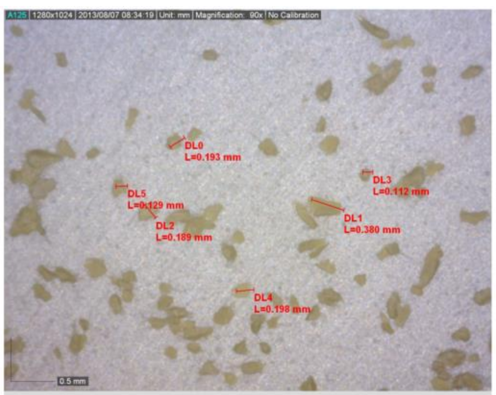
Estimated parameters

- Kinetic parameters
  - Rate constants: k, E
  - Adsorption constants: K_{ads}, ΔH_{ads}

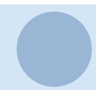
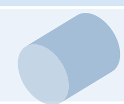
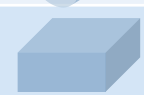
$$\mathrm{k}_j = \mathrm{k}_j^{T_{ref}} e^{\frac{-E_j}{R}\left[\frac{1}{T}-\frac{1}{T_{ref}}\right]} \qquad j = 1,2,3,4,6,7,10,12$$

$$\mathrm{K}_i = \mathrm{K}_i^{T_{ref}} e^{\frac{-\Delta H_i}{R}\left[\frac{1}{T}-\frac{1}{T_{ref}}\right]} \qquad i = NH_3, O_2, NO, NO_2$$

- Catalyst pellet tortuosity
  - Typically estimated from experiments with **different sizes of pellets** of <u>known well-defined shape</u>
  - However, crushed catalyst is a mixture of shapes:



mixture of
non-ideal shapes

Ideal shape	Characteristic length
	R/3
	R/2
	R = thickness/2

→ Estimated pellet tortuosity will depend on assumed average shape
→ it needs to be verified using experiments at fixed geometry
(e.g. monolith catalyst or catalyst pellets of a well-defined shape)

Lumped pellet model

- **Effectiveness factor model**
  - Thiele modulus $$\phi(z,r) = L\sqrt{\frac{k^{effective}(z,r)\rho_{cat}}{D_{NH_3,m}\left(\frac{\varepsilon_{cat}}{\tau}\right)}}$$
  - Pellet characteristic length $$L = \frac{R_{cat}}{L_{par}}$$
  - Pseudo-first order constant w.r.t. NH_3 $$k^{effective}(z,r) = \frac{\sum_{j=1}^{NR} -r_j^s(z,r)\nu_{NH_3,j}}{C_{NH_3}^s(z,r)}$$
  - Effectiveness factor $$\eta(z,r) = \frac{\tanh\left(\phi(z,r)\right)}{\phi(z,r)}$$

  (all variables local, i.e. at given axial and radial position in the bed)

➔ **Uncertain parameters in above equations for crushed catalyst: τ, L_{par}, (R_{cat})**

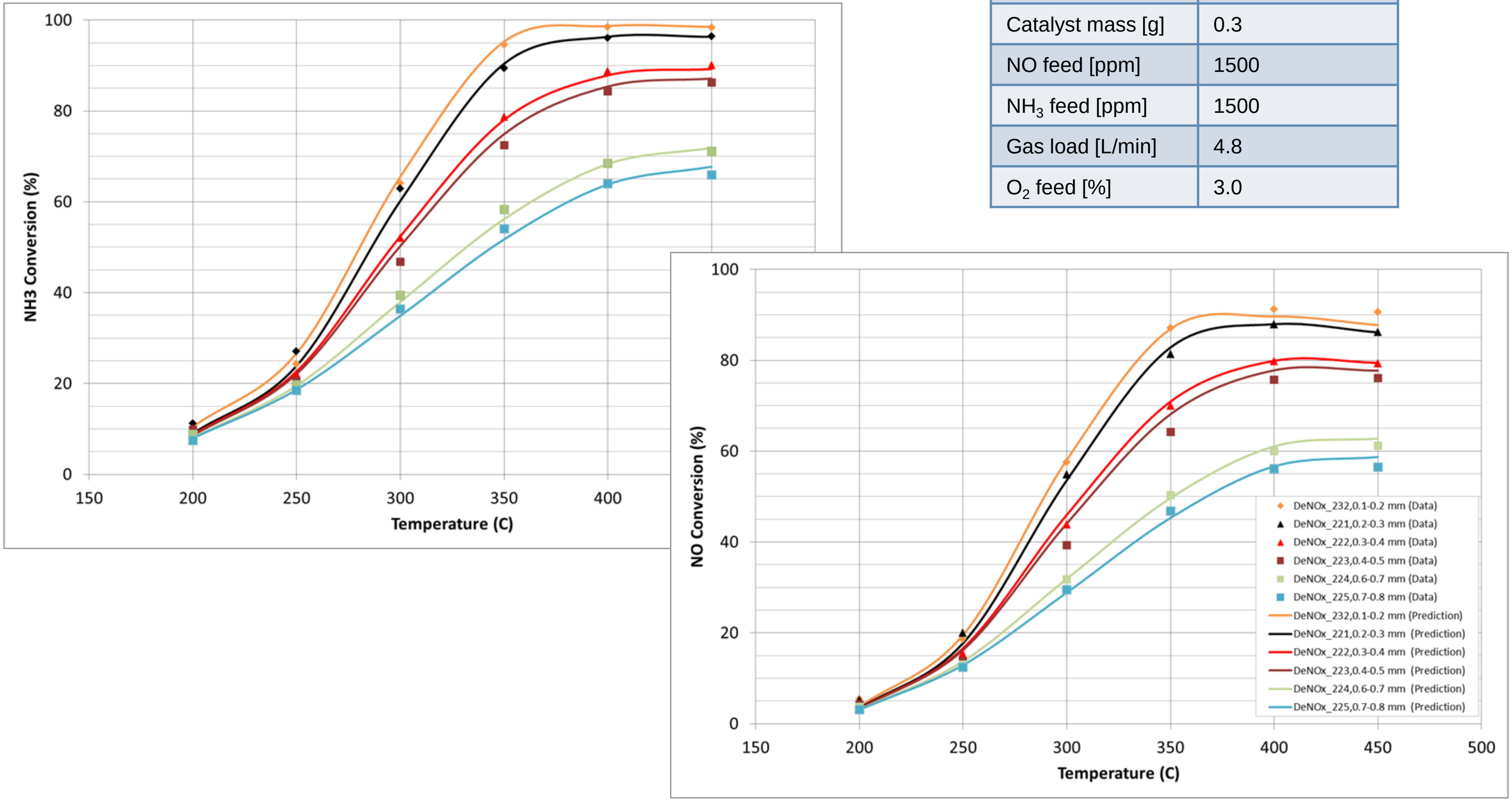
- However, they are all correlated, hence only one of them can be estimated.

$$R_{cat}\frac{\sqrt{\tau}}{L_{par}} = const.$$

Parameter estimation results – example:
Comparison to data at different temperatures

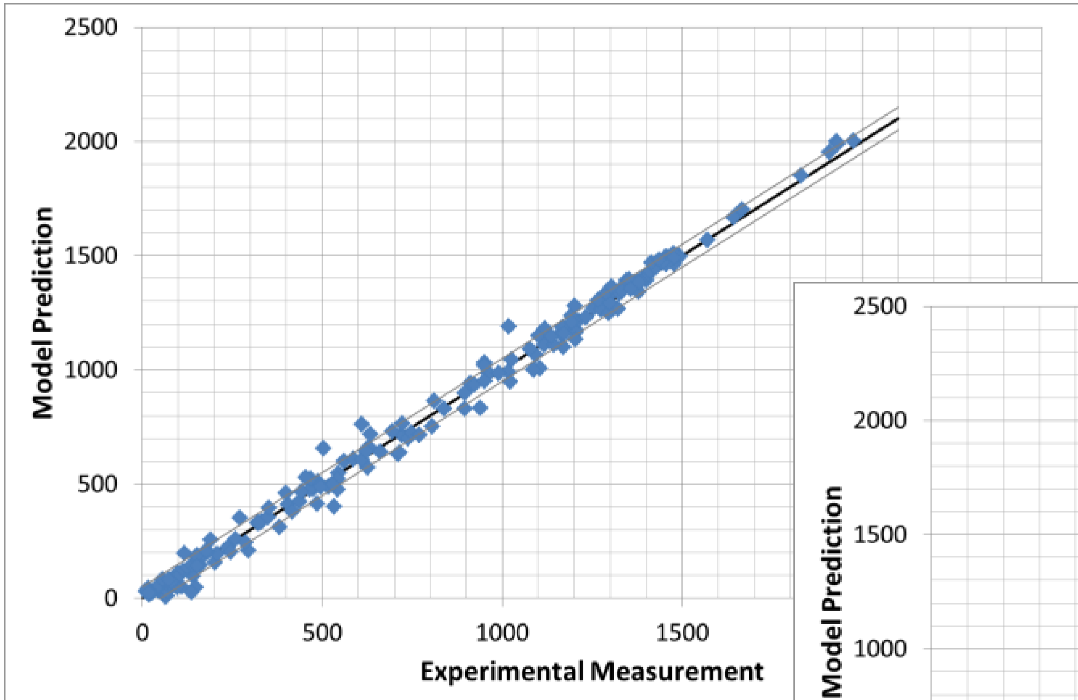
- Varying granule size

Experimental data set	
Pellet size [mm]	**0.1-0.8**
Catalyst mass [g]	0.3
NO feed [ppm]	1500
NH_3 feed [ppm]	1500
Gas load [L/min]	4.8
O_2 feed [%]	3.0

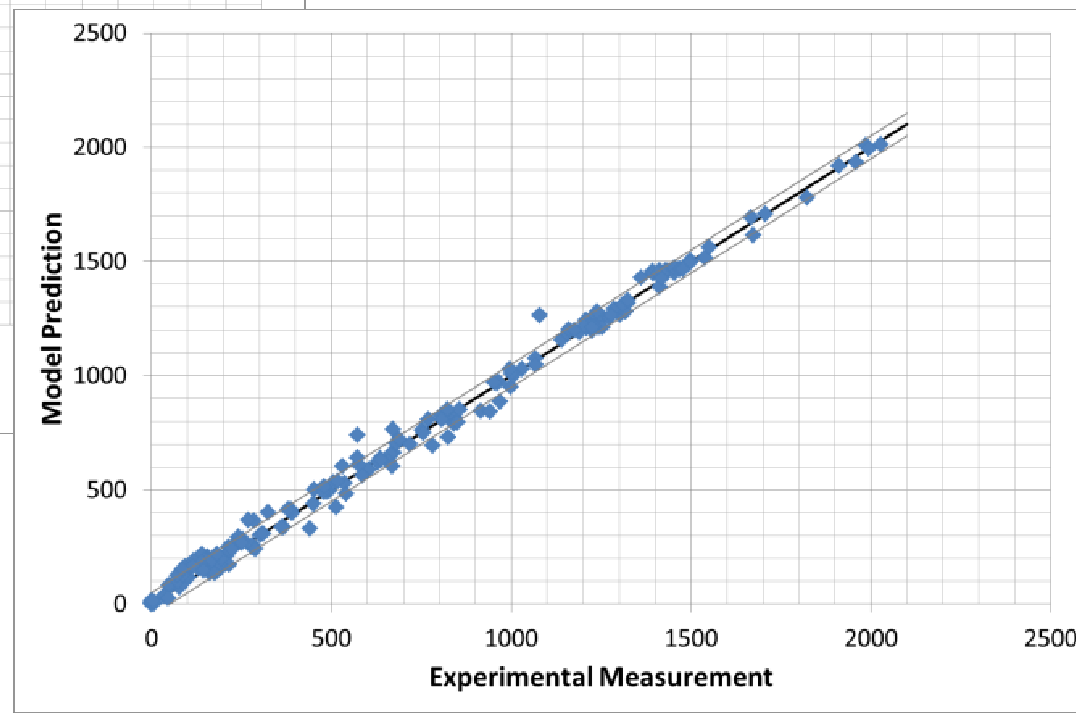


Parity Plots : NO and NH_3

Standard deviation plot = ±50 ppm



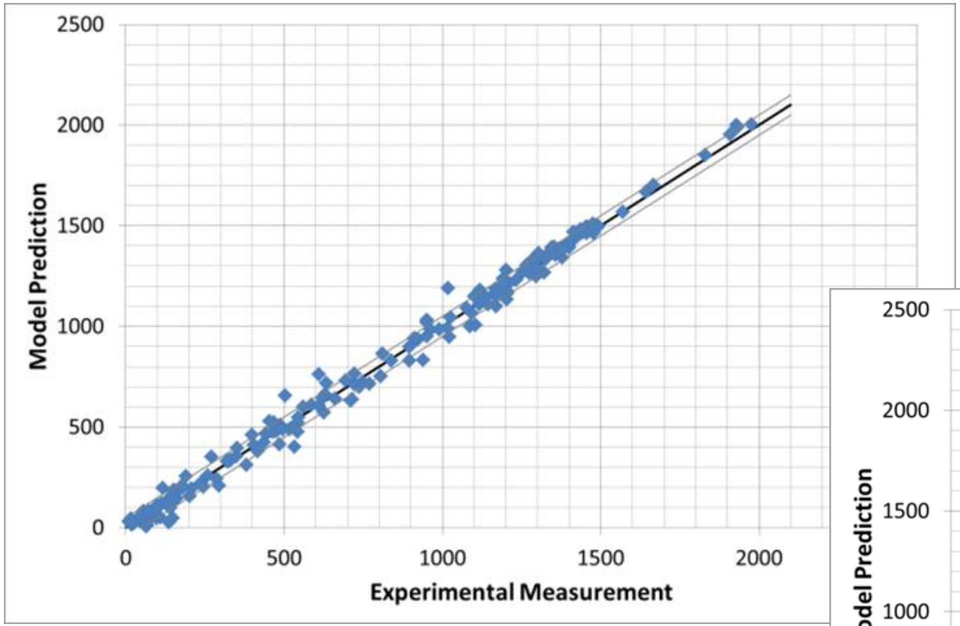
NH_3(ppm)



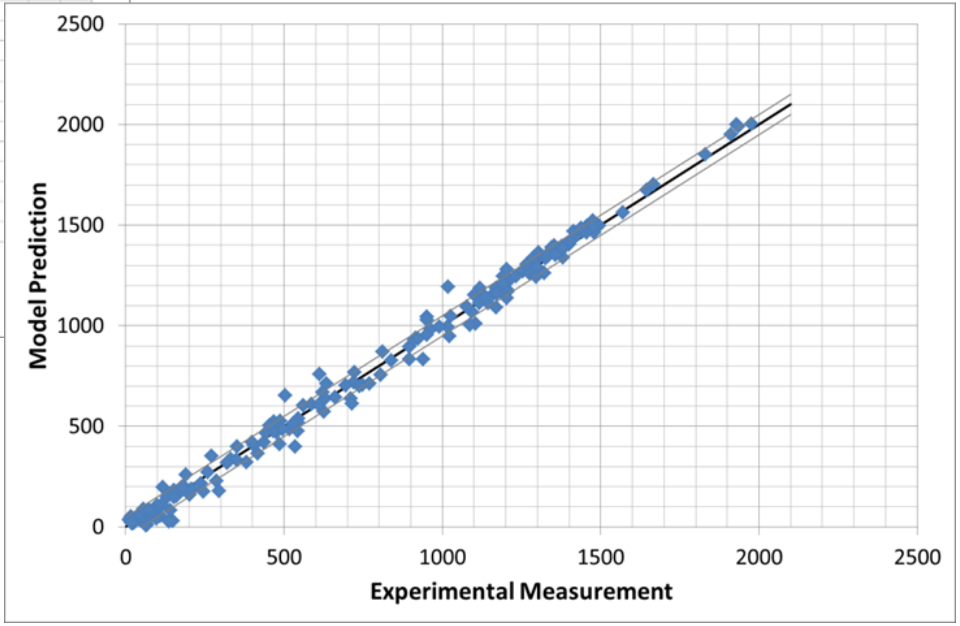
NO(ppm)

Surface reaction vs. 1-D pellet model
Parity plots : NH_3

Standard deviation plot = ±50 ppm



Surface reaction model



1-D pellet model

Surface reaction vs. 1-D pellet model
Comparison of estimated parameters

Parameter	Optimal Estimate	95% Confidence Interval	Optimal Estimate	95% Confidence Interval
	Surface reaction model		1-D pellet model	
$k_1^{T_{ref}}$ (T_{ref} = 400 °C)	**8.2378E-04**	8.4816E-05	**8.9436E-04**	9.8381E-05
$k_2^{T_{ref}}$ (T_{ref} = 400 °C)	**6.3373E-06**	1.4046E-06	**6.5450E-06**	1.4231E-06
$k_4^{T_{ref}}$ (T_{ref} = 400 °C)	**9.8026E-02**	2.5067E-02	**6.9919E-01**	6.7037E-01
$k_6^{T_{ref}}$ (T_{ref} = 400 °C)	**1.3743E-03**	2.6983E-04	**1.4310E-03**	2.7378E-04
$k_7^{T_{ref}}$ (T_{ref} = 400 °C)	**7.6008E-05**	4.2972E-05	**6.5711E-05**	4.1310E-05
$k_{10}^{T_{ref}}$ (T_{ref} = 450 °C)	**8.0206E-07**	1.6711E-07	**7.9037E-07**	1.6267E-07
$k_{12}^{T_{ref}}$ (T_{ref} = 450 °C)	**5.0465E-05**	8.7675E-06	**5.5904E-05**	1.0083E-05
$\ln\left(\frac{1}{K_{NH_3}^{T_{ref}}}\right)$ (T_{ref} = 400 °C)	**3.6960**	0.3192	**3.7363**	0.2783
$\ln\left(\frac{1}{K_{O_2}^{T_{ref}}}\right)$ (T_{ref} = 400 °C)	**5.7131**	1.0396	**5.7047**	1.0460
ΔH_{NH_3}	**-124215**	17545	**-110456**	13818
ΔH_{O_2}	**0**	Value fixed by user	**0**	Value fixed by user

NOx reduction reactions

1) $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ (standard SCR)
2) $6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$
4) $2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O$

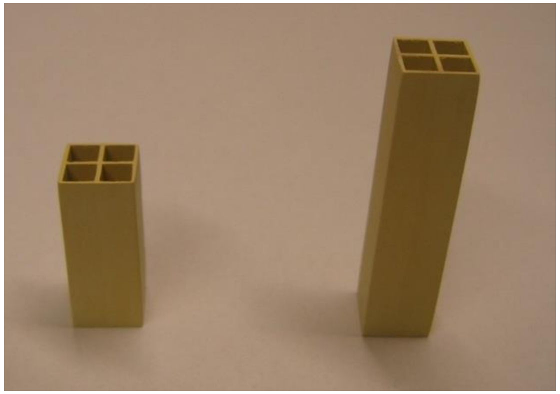
NH_3 oxidation reactions

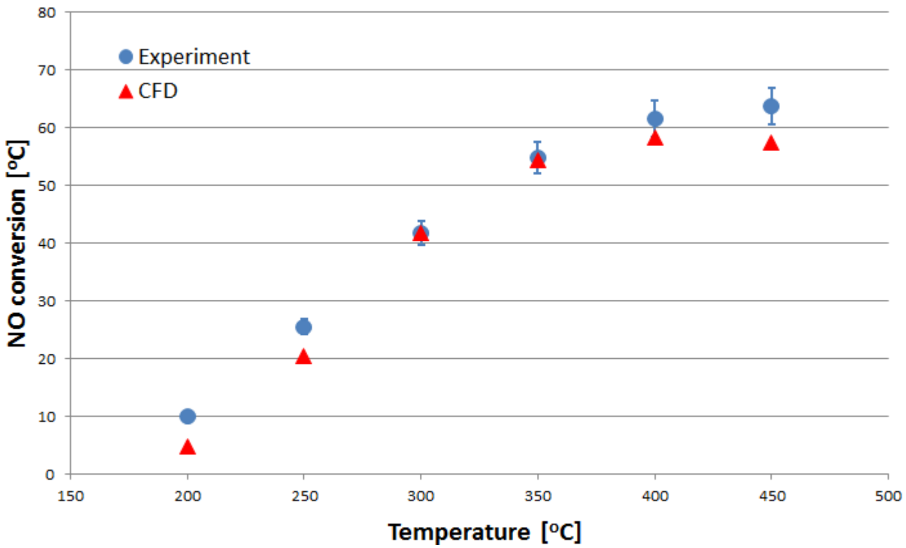
6) $4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O$
7) $4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$
10) $2NH_3 + 8NO \rightarrow 5N_2O + 3H_2O$
12) $4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O$

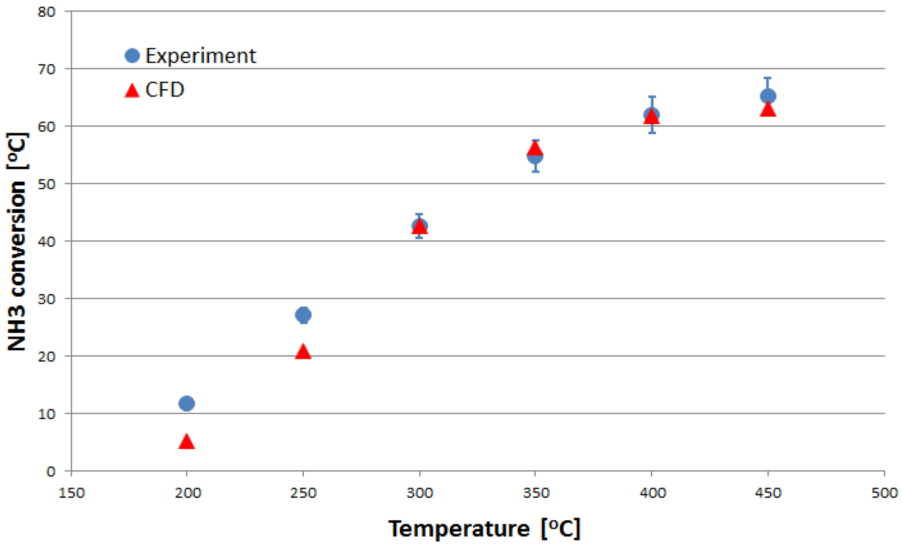
- Conclusion: **developed lumped pellet model is applicable for NH_3 and NO conversion.** Some inaccuracy can be expected for NO_2 conversion.

Monolith experiments for kinetic model validation

- 2.5cm and 5cm long mini-monolith catalysts are used.

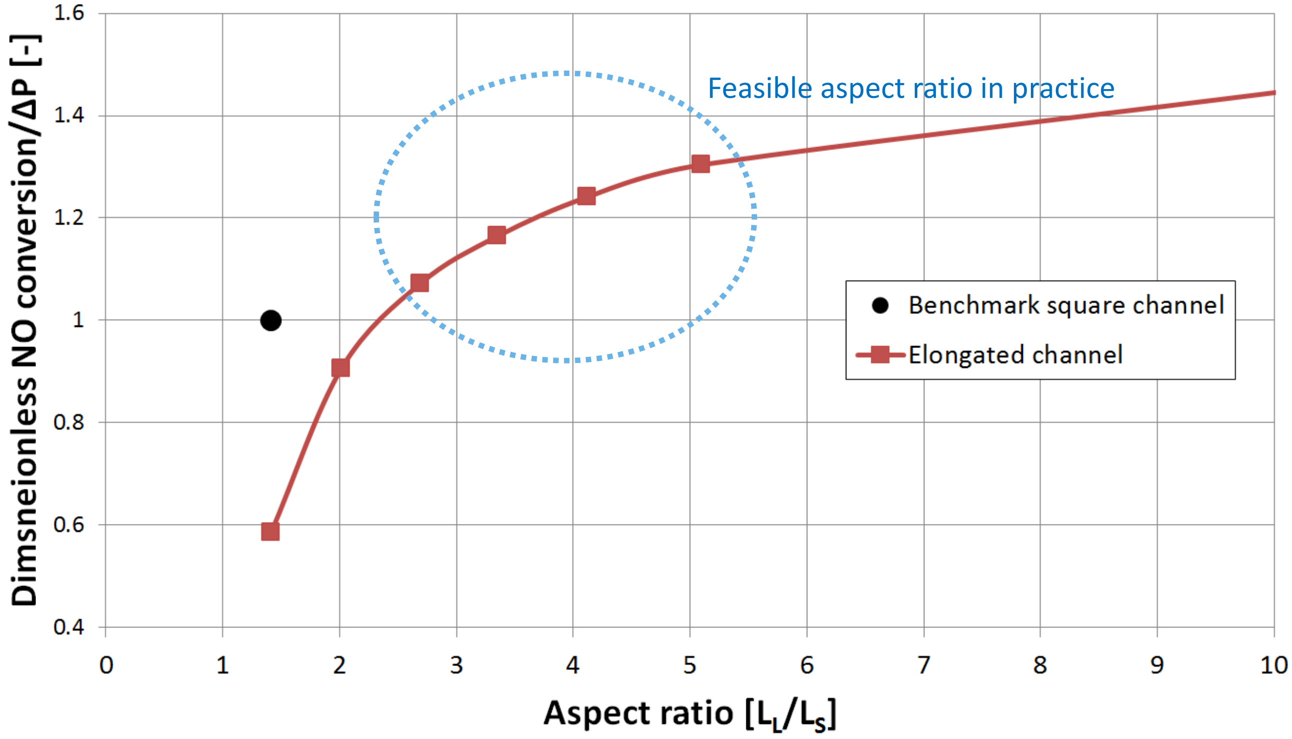


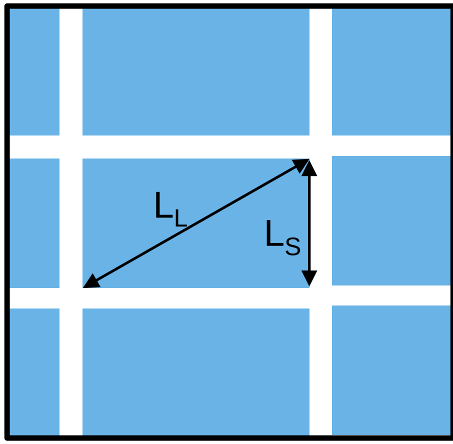




Application of kinetic model for new catalyst design

- Monolith catalyst simulation shows that adjusting the size and the aspect ratio of elongated channel allows to achieve lower ΔP and higher NO conversion than conventional square channel



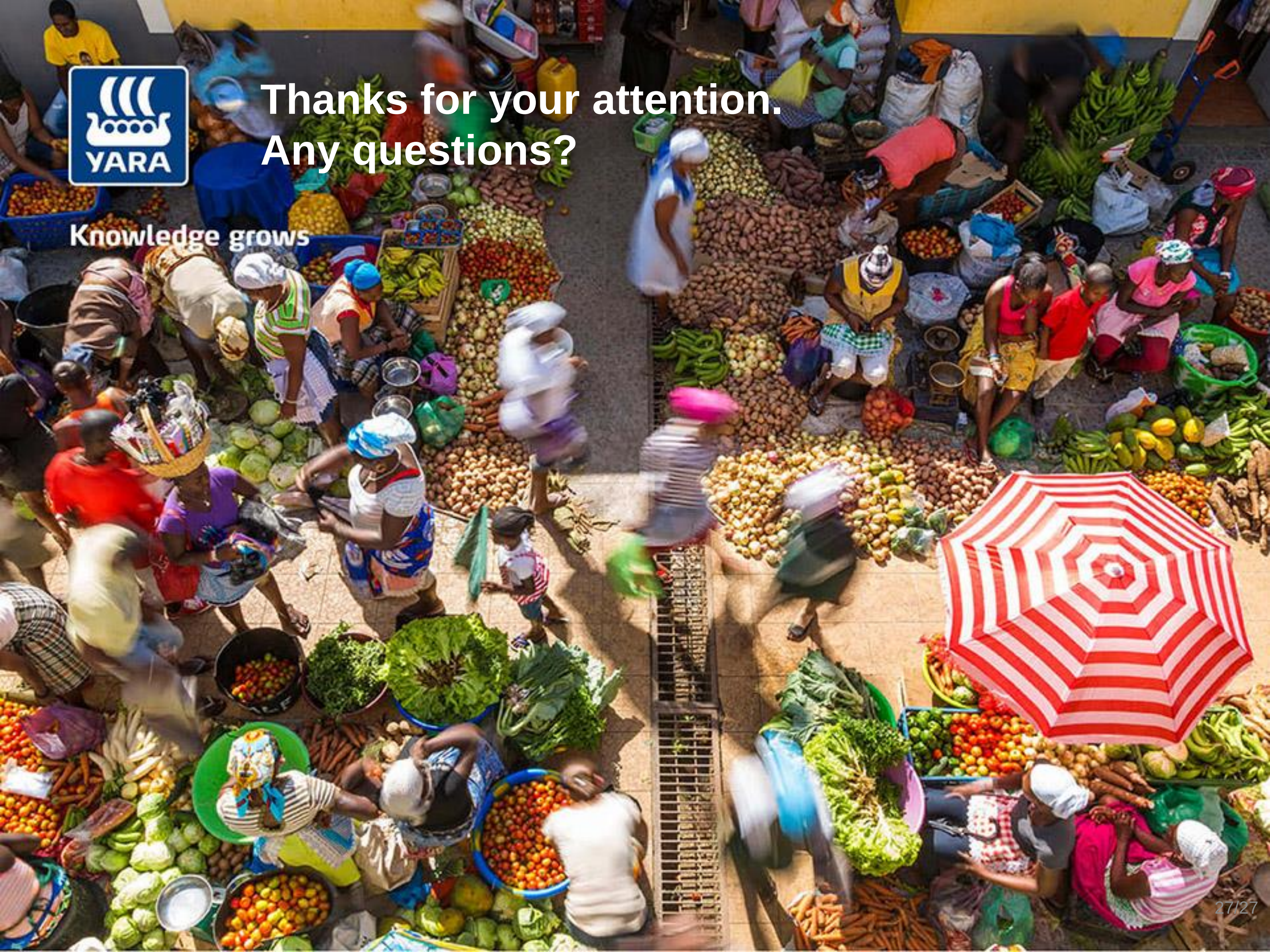


Concluding remarks

- PSE reviewed Yara's experimental plan and data and suggested modifications to the experimental setup and additional experiments with focus on validation of reaction kinetics
- Original reaction scheme was reduced based on analysis of experimental data
- Reaction rate expressions were identified from literature.

- Kinetic parameter estimation was performed using gPROMS AML:FBCR
- 1D-pellet model and surface reaction model were compared.
  - **Surface reaction model with predicted effectiveness factor seems to be adequate for prediction of NOx conversion**
- Kinetic model was validated by the comparison with mini-monolith experiments

- Project enabled Yara to obtain a new patent for a novel SCR monolith catalyst design



Thanks for your attention.
Any questions?

List of experiments

- 55 kinetic experiments were conducted under varying operating conditions:
  - Space velocity
  - Gas load
  - Granule size
  - Reactant concentration level at NH_3/NO ratio of 1
  - NH_3 concentration
  - NO concentration
  - O_2 concentration
- 4 experiments without catalyst
  ➔ investigate (non-catalytic) gas-phase reactions
- Temperature varied from 200°C to 450°C in all experiments

Run #	Factor	Particle size [mm]	Catalyst mass [g]	NO [ppmv]	NH3 [ppmv]	Gas load [L/min]	O2 [%]
1	Normal	0.1-0.2	0.3	1500	1500	4.8	13.0
2	S.V.1	0.1-0.2	0.3	1500	1500	3.6	13.0
3		0.1-0.2	0.3	1500	1500	4.8	13.0
4		0.1-0.2	0.3	1500	1500	6.0	13.0
5		0.1-0.2	0.3	1500	1500	7.2	13.0
6	S.V.2	0.1-0.2	0.3	1500	1500	4.8	3.0
7		0.1-0.2	0.3	1500	1500	4.8	3.0
8		0.1-0.2	0.3	1500	1500	4.8	3.0
9		0.1-0.2	0.3	1500	1500	6.6	3.0
10		0.1-0.2	0.3	1500	1500	8.4	3.0
11		0.1-0.2	0.3	1500	1500	9.6	3.0
12	Gas load	0.1-0.2	0.2	1500	1500	3.2	3.0
13		0.1-0.2	0.35	1500	1500	5.6	3.0
14		0.1-0.2	0.4	1500	1500	6.4	3.0
15		0.1-0.2	0.5	1500	1500	8.0	3.0
16		0.1-0.2	0.6	1500	1500	9.6	3.0
17	Granule size	0.2-0.3	0.3	1500	1500	4.8	3.0
18		0.3-0.4	0.3	1500	1500	4.8	3.0
19		0.4-0.5	0.3	1500	1500	4.8	3.0
20		0.6-0.7	0.3	1500	1500	4.8	3.0
21		0.7-0.8	0.3	1500	1500	4.8	3.0
22	Reactant conc. level	0.1-0.2	0.3	500	500	4.8	3.0
23		0.1-0.2	0.3	1000	1000	4.8	3.0
24		0.1-0.2	0.3	1250	1250	4.8	3.0
25		0.1-0.2	0.3	1750	1750	4.8	3.0
26	NO conc.	0.1-0.2	0.3	500	1500	4.8	3.0
27		0.1-0.2	0.3	1000	1500	4.8	3.0
28		0.1-0.2	0.3	2000	1500	4.8	3.0
29	NH3 conc.	0.1-0.2	0.3	1500	500	4.8	3.0
30		0.1-0.2	0.3	1500	1000	4.8	3.0
31		0.1-0.2	0.3	1500	2000	4.8	3.0
32	O2 conc.	0.1-0.2	0.3	1500	1500	4.8	0.0
33		0.1-0.2	0.3	1500	1500	4.8	6.0
34		0.1-0.2	0.3	1500	1500	4.8	9.0
35		0.1-0.2	0.3	1500	1500	4.8	17.0
36	Reproducibility test	0.1-0.2	0.3	1500	1000	8.4	3.0
37	modified run #15	0.1-0.2	0.5	1250	1500	8.0	2.0
38	modified run #25	0.6-0.7	0.3	1750	1750	9.6	3.0
39	modified run #24	0.4-0.5	0.3	1250	1250	4.8	3.0
40	Without NO	0.1-0.2	0.3	0	1500	4.8	3.0
41	Without NH3	0.1-0.2	0.3	1500	0	4.8	3.0
42	modified run #33	0.4-0.5	0.3	1500	1500	4.8	5.0
43	changed O2 injection*	0.1-0.2	0.3	1500	1500	4.8	3.0
44	Without O2	0.1-0.2	0.5	2000	2000	4.8	0.0
45	Increased gas load	0.1-0.2	0.3	1500	1500	12.0	3.0
46	modified case #240	0.1-0.2	0.3	1500	1500	12.0	6.0
47	modified case #247	0.1-0.2	0.3	0	1500	4.8	9.0
48	modified case #223	0.4-0.5	0.3	1500	1500	12.0	3.0
49	modified case #234	0.1-0.2	0.3	1000	1500	12.0	3.0
50	modified case #237	0.1-0.2	0.3	1500	1000	12.0	3.0
51	modified case #209	0.3-0.4	0.3	2000	2000	12.0	13.0
52	with quartz bed	0.1-0.2	0	2000	2000	4.8	3.0
53	with quartz bed	0.1-0.2	0	2000	2000	4.8	6.0
54	with quartz bed	0.1-0.2	0	0	2000	4.8	6.0
55	with quartz bed	0.1-0.2	0	2000	0	4.8	6.0