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Evaluation of three different gas phase chemistry mechanisms for predicting NOx emission formation in recovery boilers

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Conclusions (1)

- Recovery boiler measurements and model predictions using detailed chemistry show NO, NH_3, and HCN to be relevant species in NO emission formation.
- HCN in recovery boilers is the result of NO-reburning (NO + CxHy → HCN +...)
- A detailed chemistry mechanism (ÅA mechanism) that describes fuel nitrogen chemistry, predicts the overall trends and concentration levels of NO, NH_3, and HCN in good agreement with in-furnace measurements data (boiler oxidizing or reducing conditions)
- A skeletal mechanism (ÅA, 32 elementary reactions) developed for description of NH_3-NO chemistry, predicts boiler NH_3 trends and concentrations in agreement with detailed mechanism. NO is overpredicted, consistent with skeletal mechanism not including NO-reburning (the pathway for NO to react further / be reduced)
- **Based on the boiler measurements and chemical kinetics calculations it is concluded that NO-reburning chemistry is important to take into account in mathematical modeling (e.g. CFD) of recovery boiler NO emission formation**

Conclusions (2)

- The 2-step mechanism (De Soete) underpredicts to considerable degree the NH_3-to-NO conversion chemistry.
- The De Soete chemistry is based on data at flame temperatures >1700 °C, which is considerably higher than temperature levels in recovery boilers. This means that in RB simulations the De Soete chemistry is used outside its range of validity.
- **De Soete mechanism is concluded to not be suitable for simulations of recovery boiler N chemistry**

Background

- Detailed understanding of boiler NOx emission formation and emission formation dependence on different process parameters is key to meeting tightening emission limits or for providing insight into NO reduction levels achievable using primary measures. Mathematical modeling offers a tool for understanding and studying boiler NOx formation.

- Chemistry mechanisms with different levels of complexity are currently available. The most detailed ones consider tens or hundreds of species involved in several hundreds of reactions. These mechanisms describe hydrocarbon and nitrogen chemistry and their interactions. These mechanisms are usually applied in simulations using so-called ideal reactors (plug flow and perfectly stirred tank reactors and modifications of these) and are suitable for studying detailed chemistry. In the other end of the spectrum are simplified chemistry mechanisms, which typically consist of a few species and reactions. One benefit of the simplified reactions mechanisms is that they can be incorporated into models based on Computational Fluid Dynamics (CFD). The lower number of species and reactions usually translates into shorter simulation times and better performance in terms of solution convergence. An intermediate class of reaction mechanisms is called skeletal or reduced. These consist of a larger number of species and reactions than the simplified ones but the number of species and reactions is considerably smaller than in the detailed ones. However, these mechanism often include radical species which in practice means issues with solution convergence and stability.

- The current standard approach for CFD engineering calculations of gas phase combustion and NO formation in black liquor recovery boilers usually involves calculating hydrocarbon chemistry using a five-step mechanism (Jones-Lindstedt), whereas NO chemistry is typically modeled using a two-step mechanism considering NO formation (unbalanced reaction R1) and reduction (unbalanced reaction R2).

$$NH_3 + O_2 \rightarrow NO + H_2O \qquad (R1)$$
$$NO + NH_3 \rightarrow N_2 + H_2O \qquad (R2)$$

Objectives

- Obtain better understanding about how boiler NOx predictions depend on chemistry mechanism
  - Benefits, suitability, accuracy, limitations,...
  - How well does 2-step chemistry describe RB NOx chemistry, or should a more detailed chemistry mechanism be used instead?

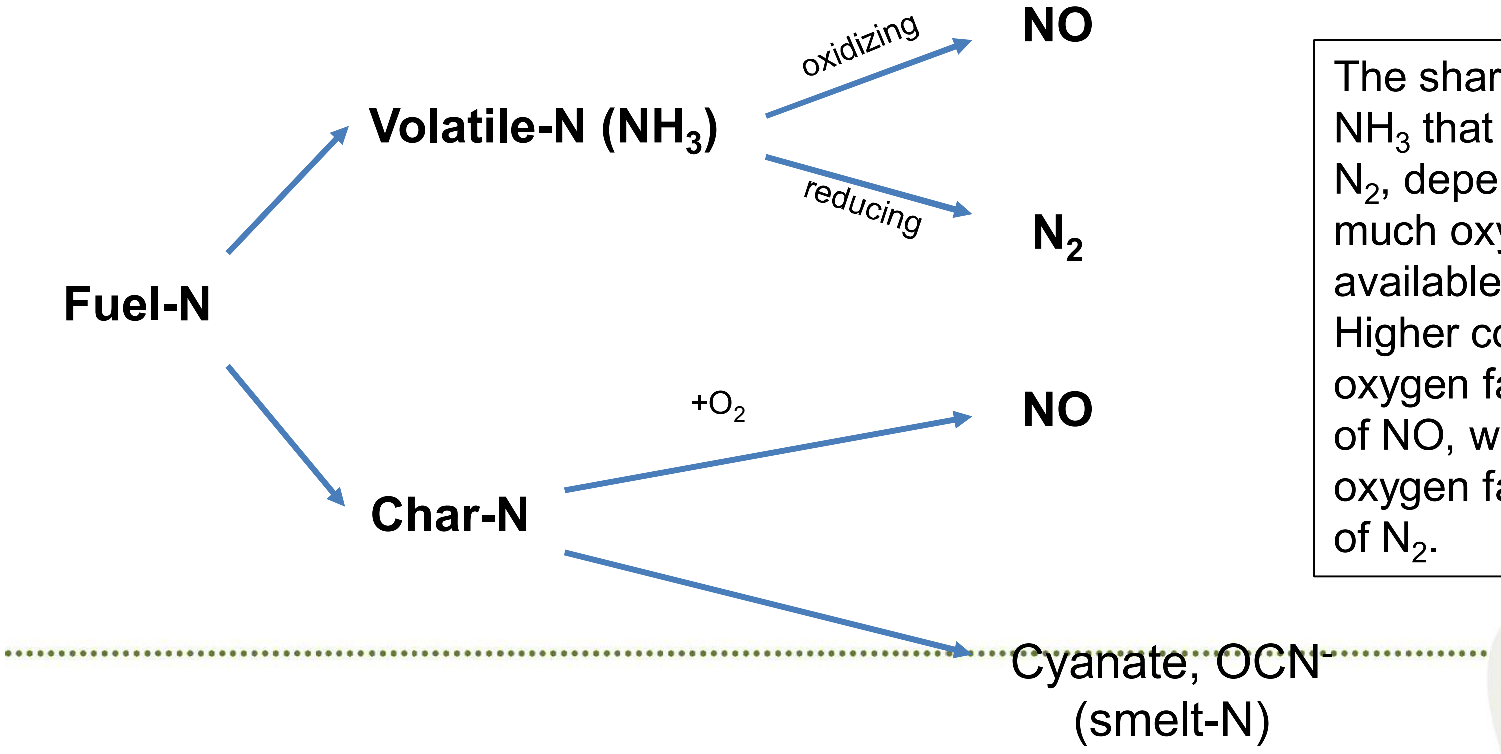
- Simulations using
  - **ÅA Detailed chemistry mechanism** – reference to which other simulations are compared to
  - **ÅA Skeletal mechanism** – detailed chemical kinetics but without NO-reburning (HCN) chemistry, this provides information about how predictions differ with full detailed mechanism vs skeletal (no HCN) mechanism and shows the impact of NO-reburning chemistry on predicted boiler NOx
  - **De Soete 2-step mechanism** - this is a standard model available in commercial CFD software (e.g. Fluent), how does this predict boiler NOx?

Black liquor fuel-N chemistry relevant for present work

From a historical perspective, the below description of gas (volatiles) and in general solid fuel (including BL) nitrogen chemistry has been the basis for the description of chemistry overall using two global reactions and skeletal mechanisms focusing on NH_3/NO chemistry. The approach is understandable from the point of view that NO and N_2 are the final products e.g. exiting a boiler. However, as dicussed in this work, HCN is an important intermediate species (is not emitted from a boiler).

Global: $NH_3 + O_2 \rightarrow NO$
$NO + NH_3 \rightarrow N_2$

Skeletal: **elementary reactions describing NH_3/NO chemistry**



Fuel-N

Volatile-N (NH_3)

oxidizing

NO

reducing

N_2

Char-N

$+O_2$

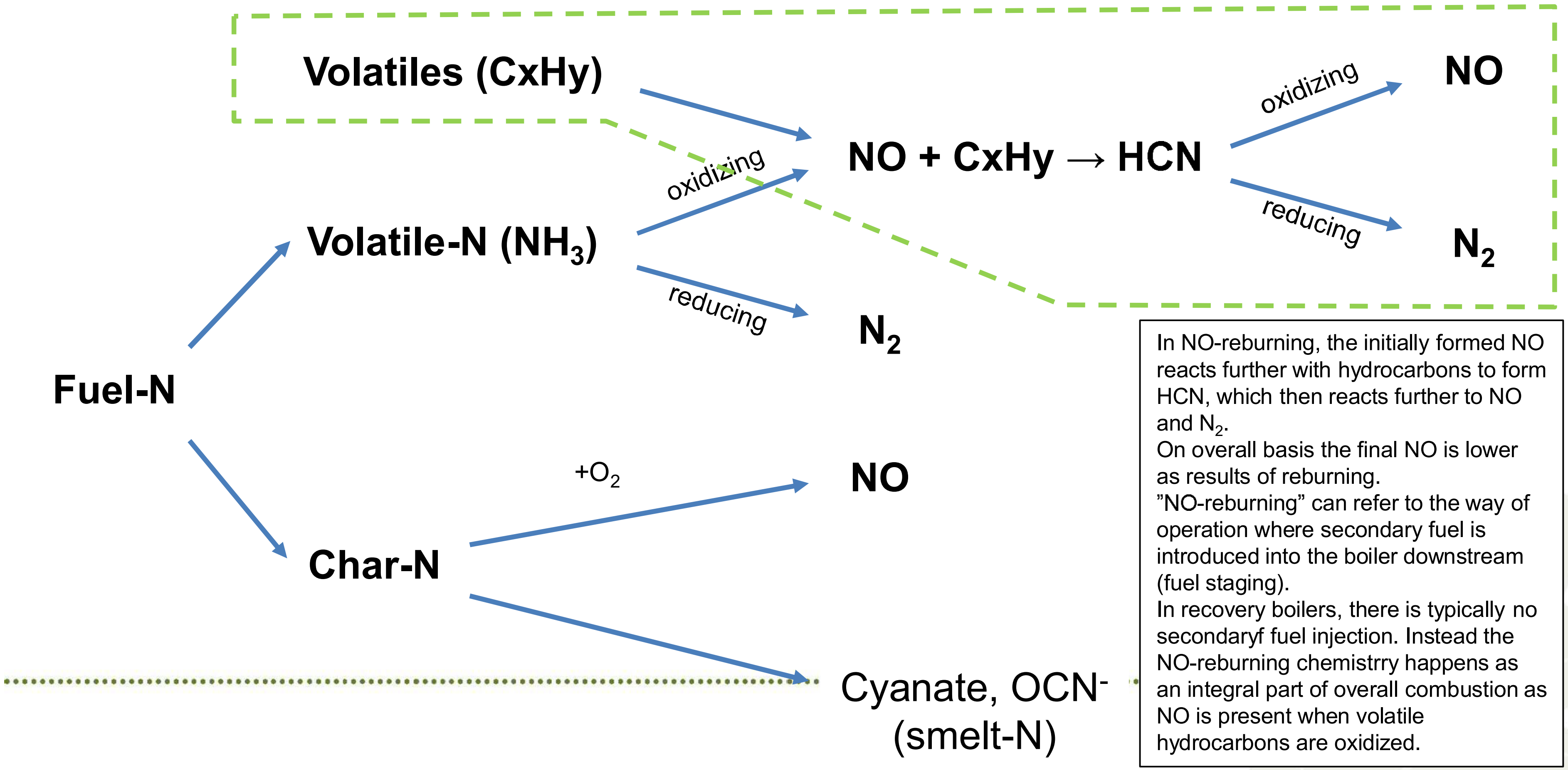
NO

Cyanate, OCN^-
(smelt-N)

The share of volatile NH_3 that forms NO vs N_2, depends on how much oxygen is available.
Higher concentrations of oxygen favor formation of NO, whereas lack of oxygen favors formation of N_2.

Black liquor fuel-N chemistry relevant for present work

Boiler measurements (2009) and detailed chemistry calculations (present work) show that NO-reburning takes place in recovery boilers
→ **important to include NO-reburning in modeling**

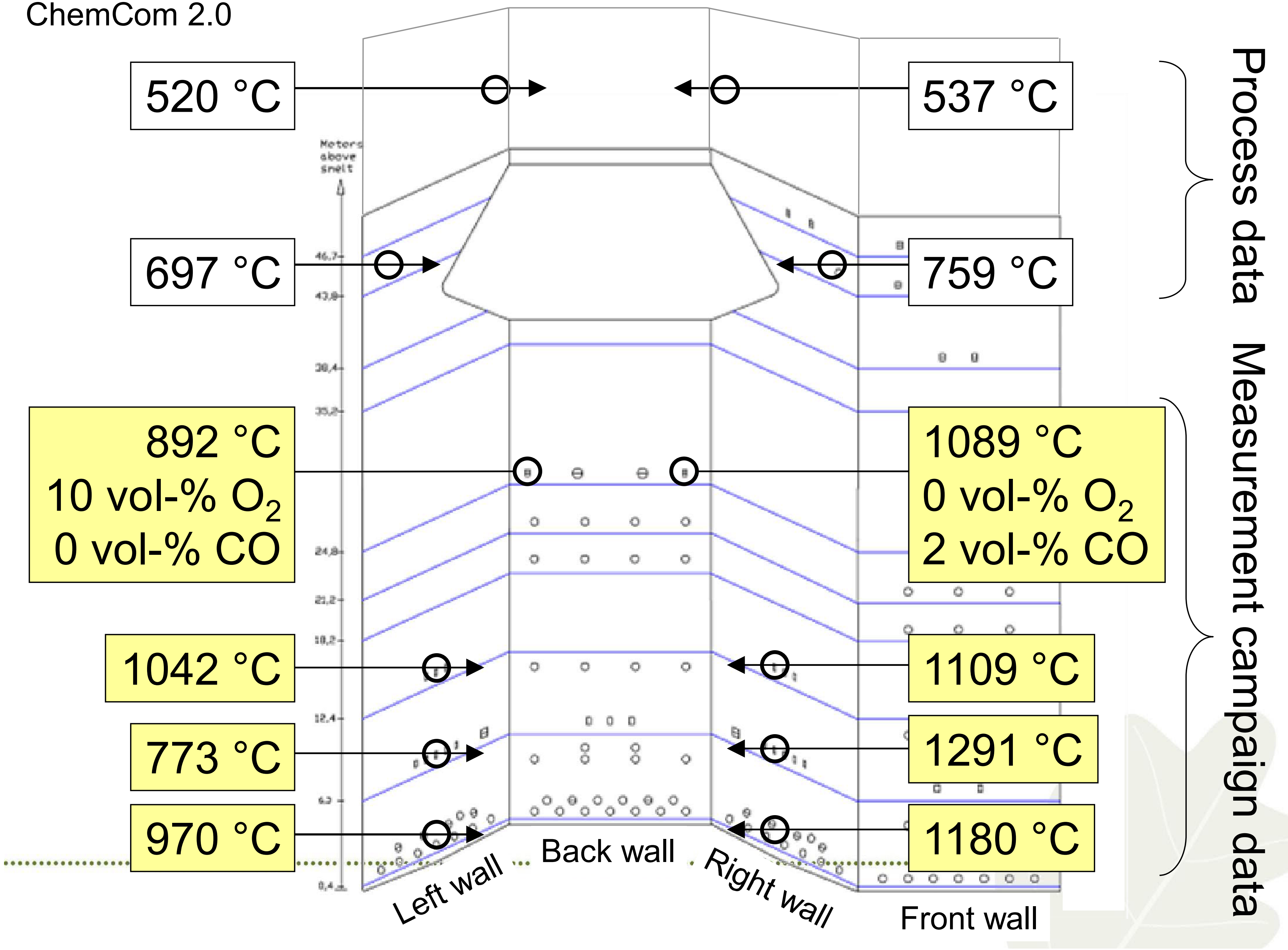


In NO-reburning, the initially formed NO reacts further with hydrocarbons to form HCN, which then reacts further to NO and N_2.
On overall basis the final NO is lower as results of reburning.
”NO-reburning” can refer to the way of operation where secondary fuel is introduced into the boiler downstream (fuel staging).
In recovery boilers, there is typically no secondaryf fuel injection. Instead the NO-reburning chemistrry happens as an integral part of overall combustion as NO is present when volatile hydrocarbons are oxidized.

Wisaforest case

- ChemCom 2.0 measurement campaign (2009)
- 70% MCR
- In-furnace temperatures and gas concentrations were measured
- Due to low load, boiler was running in an asymmetric way (not intentional) where the liquor spraying was set up symmetrically (left vs right), but the droplets were not evenly distibuted/mixed with combustion air.
  Instead, oxidizing conditions (left boiler side) and reducing conditions (right boiler side) were created, giving rare in-furnace data on combustion chemistry for oxidizing and reducing conditions.

ChemCom 2.0



520 °C

537 °C

697 °C

759 °C

892 °C
10 vol-% O_2
0 vol-% CO

1089 °C
0 vol-% O_2
2 vol-% CO

1042 °C

1109 °C

773 °C

1291 °C

970 °C

1180 °C

Left wall

Back wall

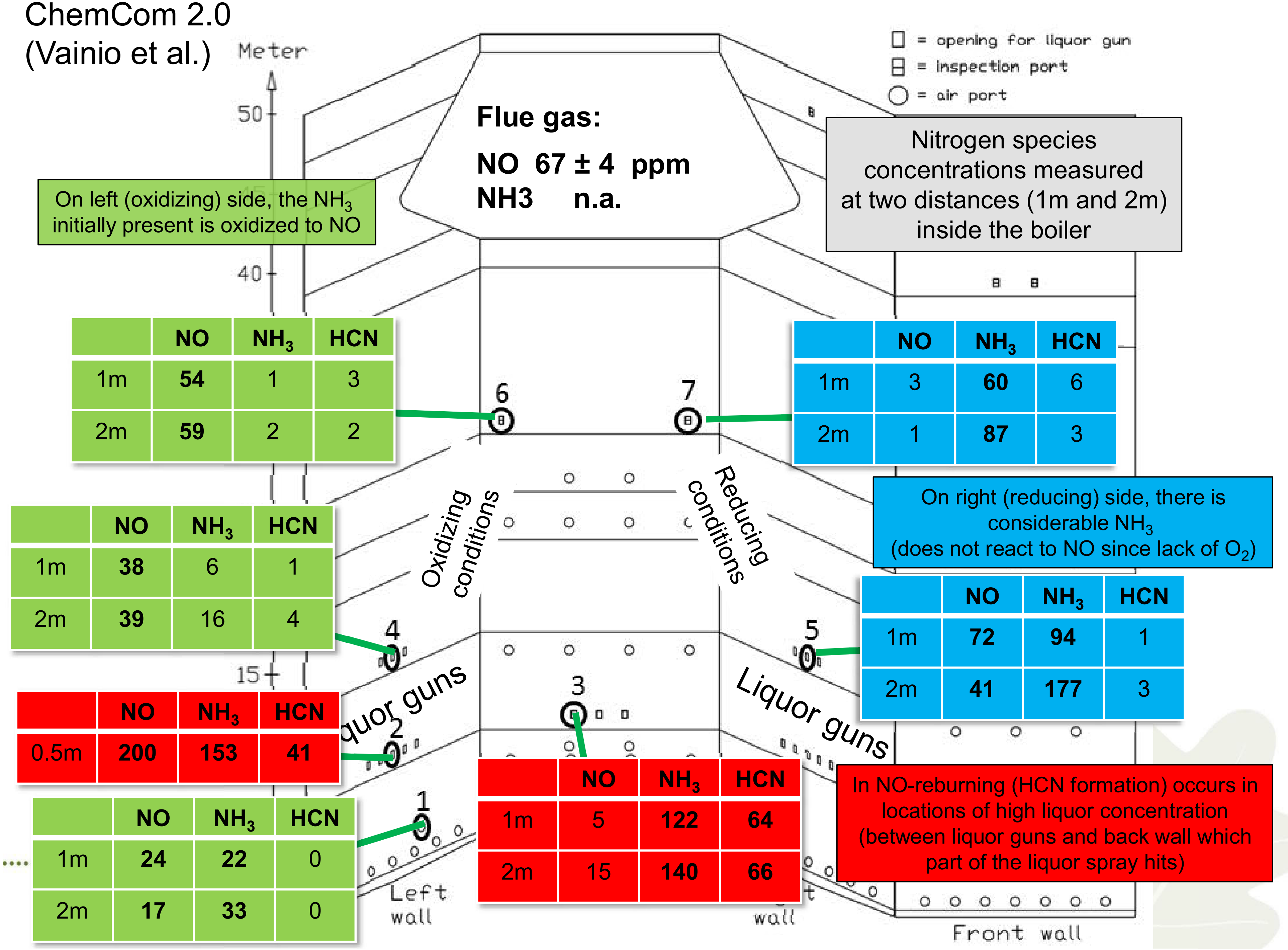
Right wall

Front wall

Process data

Measurement campaign data

ChemCom 2.0
(Vainio et al.)



Flue gas:

NO 67 ± 4 ppm
NH_3 n.a.

On left (oxidizing) side, the NH_3 initially present is oxidized to NO

Nitrogen species concentrations measured at two distances (1m and 2m) inside the boiler

	NO	NH_3	HCN
1m	**54**	1	3
2m	**59**	2	2

	NO	NH_3	HCN
1m	3	**60**	6
2m	1	**87**	3

On right (reducing) side, there is considerable NH_3
(does not react to NO since lack of O_2)

	NO	NH_3	HCN
1m	**38**	6	1
2m	**39**	16	4

	NO	NH_3	HCN
1m	**72**	**94**	1
2m	**41**	**177**	3

	NO	NH_3	HCN
0.5m	**200**	**153**	**41**

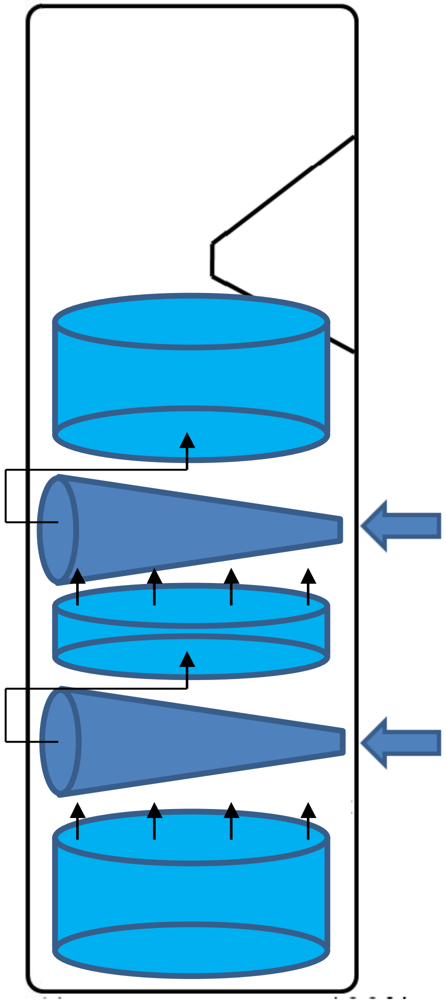
	NO	NH_3	HCN
1m	5	**122**	**64**
2m	15	**140**	**66**

....

	NO	NH_3	HCN
1m	**24**	**22**	0
2m	**17**	**33**	0

In NO-reburning (HCN formation) occurs in locations of high liquor concentration (between liquor guns and back wall which part of the liquor spray hits)

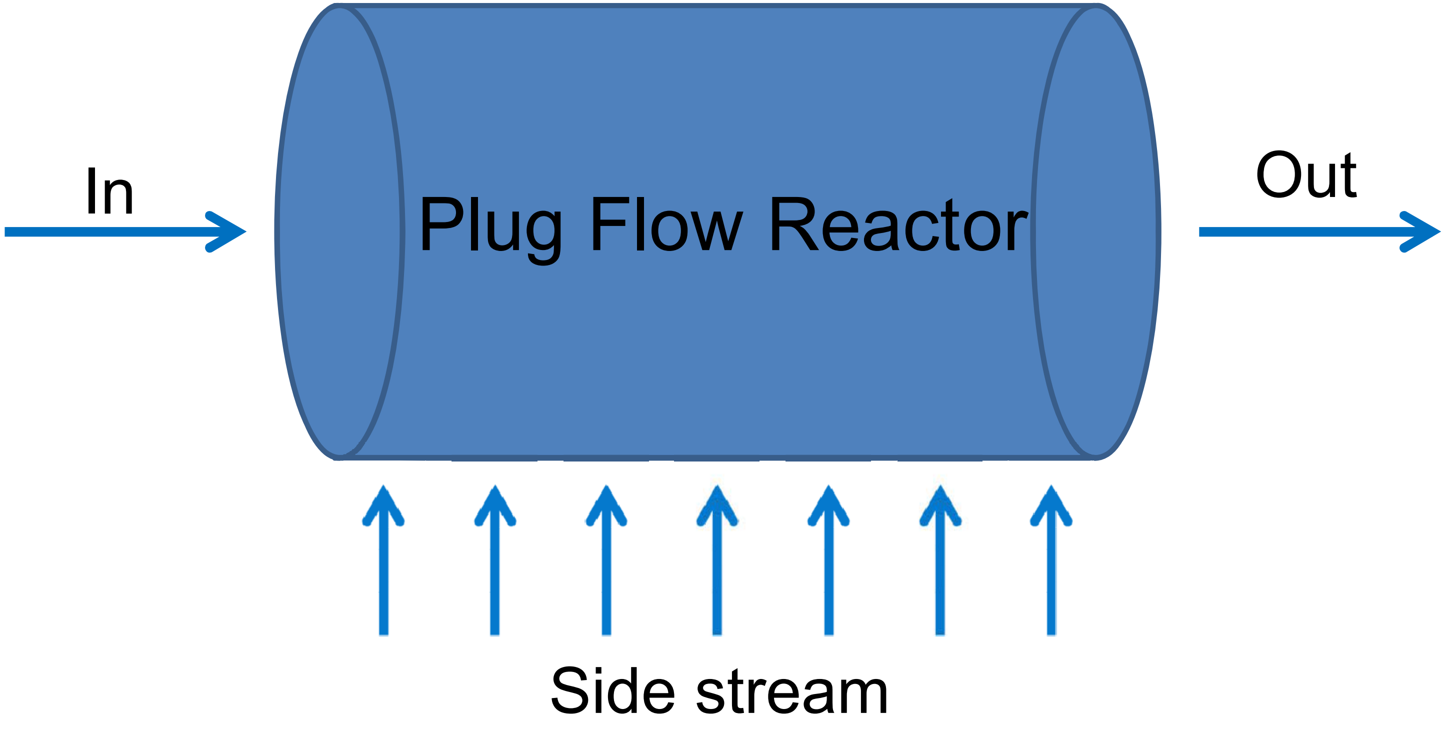
”Jet-NOx” model



- Simplified fluid dynamics
  - Furnace sections and air jets described as a network of reactors (see image)
- Detailed kinetics can be included
- Droplet conversion input taken from a CFD calculation of the boiler: vertical profiles of boiler temperature, drying, pyrolysis, char carbon conversion, and nitrogen release (volatiles and char nitrogen)
- See next slides for more details

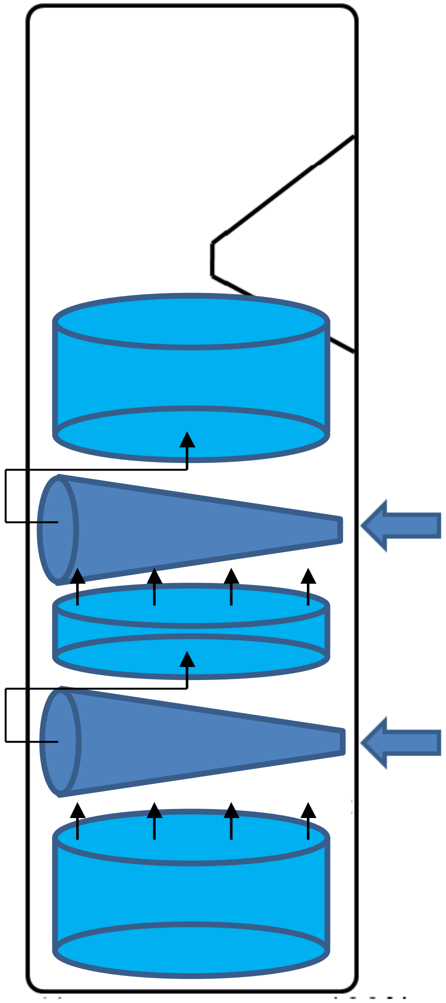
Arrows indicate the flow of gas from one reactor to next.
Furnace gas is gradually entrained into combustion air jets,
and gas from the end of the air jet moves to a furnace section between air levels

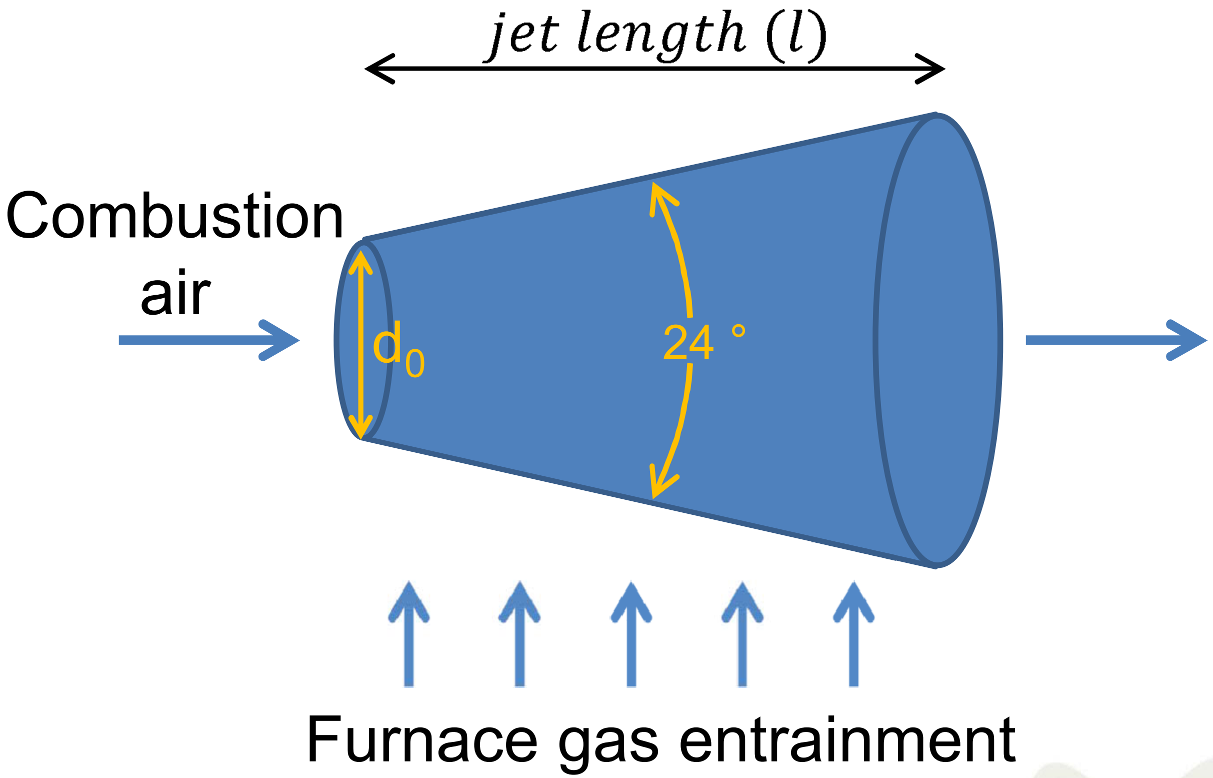
Zwietering reactor



The Zwietering reactor can be described as a plug flow reactor with a leaking wall.
In the Jet-NOx model, this reactor type is used to describe furnace gas entrainment (the side stream) into combustion air jets, as well as the release of moisture, volatiles, and char conversion gas phase products (e.g. CO and NO) as the side stream in furnace sections between air levels.
The applications to describe air jets and furnace sections is illustrated on next slides

Zwietering reactor – Air Jet





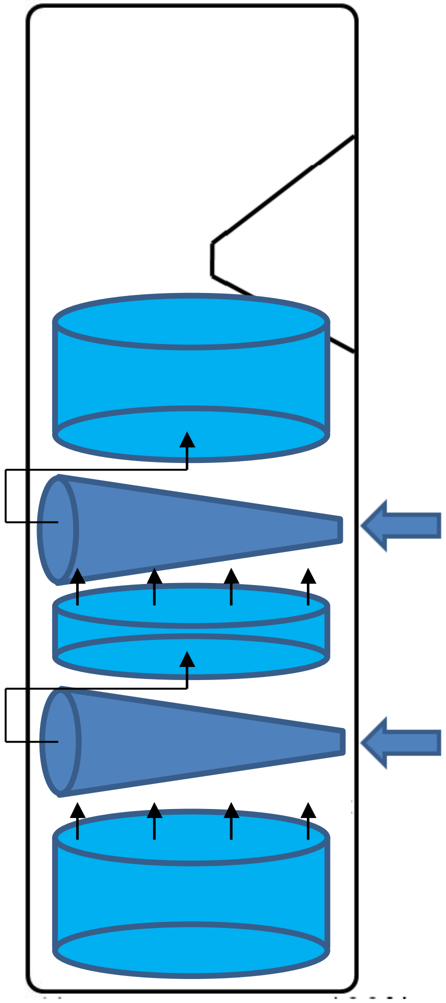
$jet\ length\ (l)$

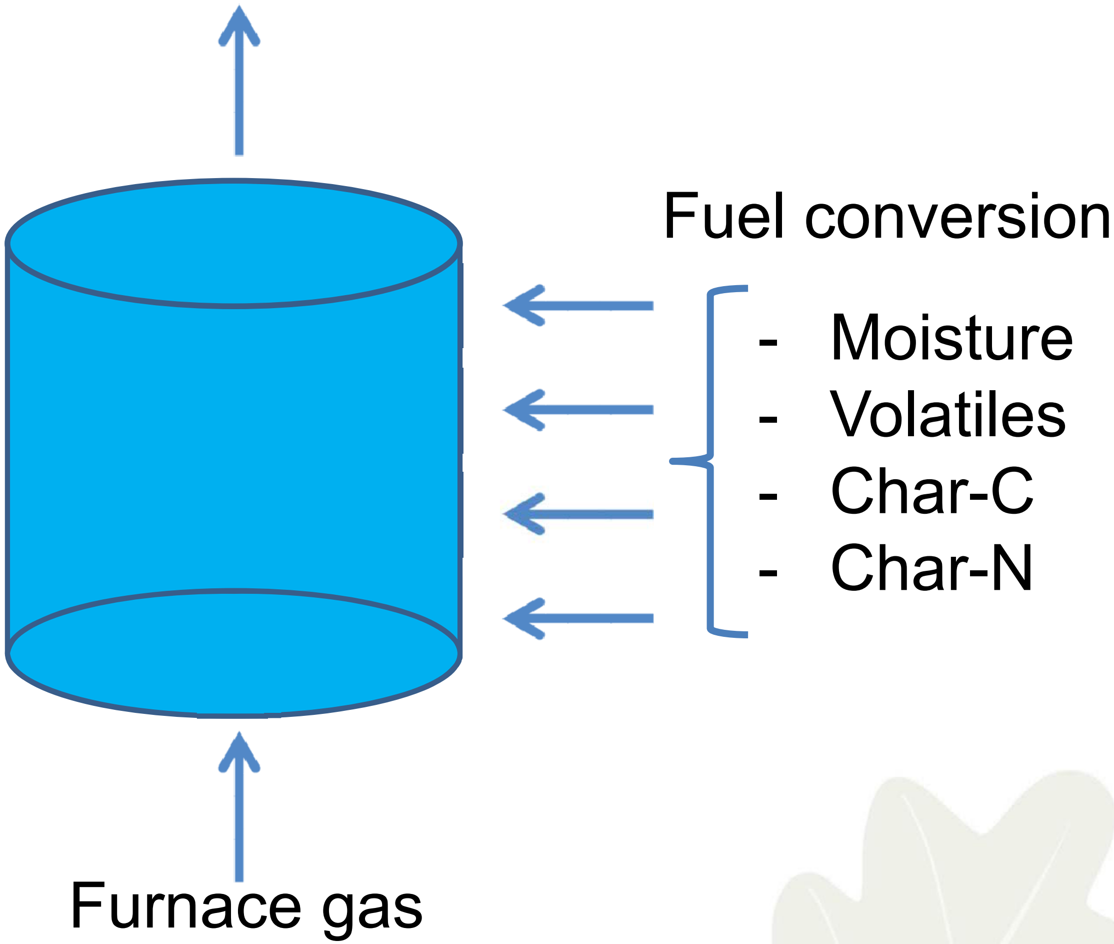
Combustion air

Furnace gas entrainment

$$\frac{\dot{m}}{\dot{m}_0} = 0.25\frac{l}{d_0}\left(\frac{\rho_0}{\rho_{furnace\ gas}}\right)^{1/2}$$

Zwietering reactor – Furnace section



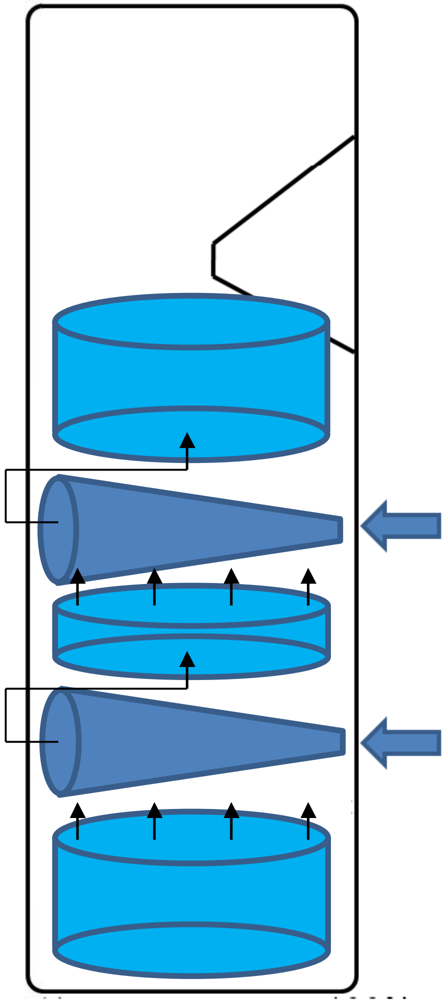


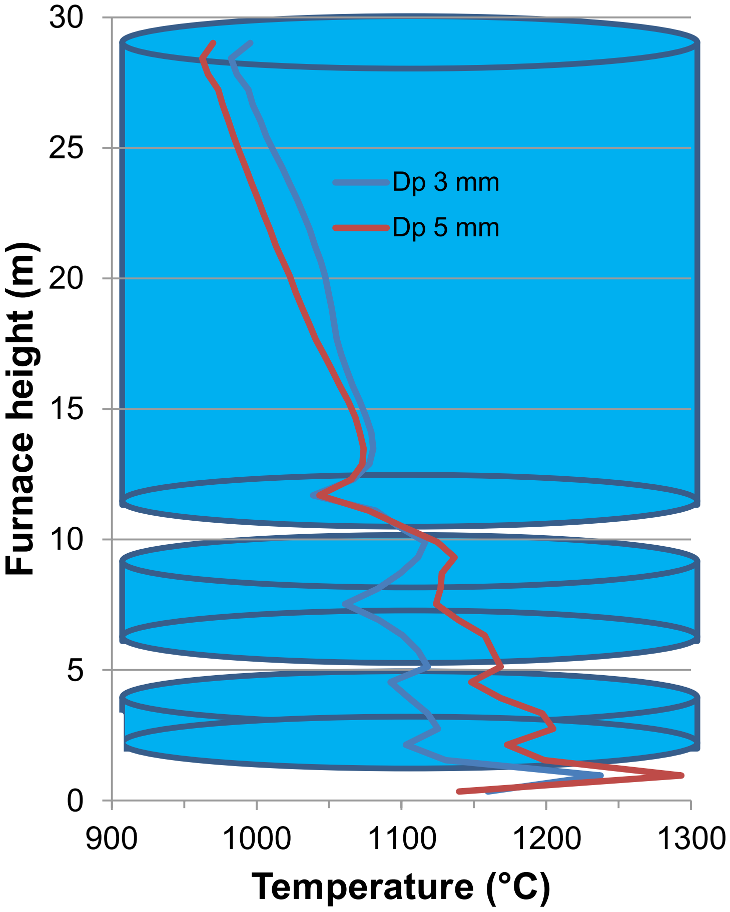
Fuel conversion

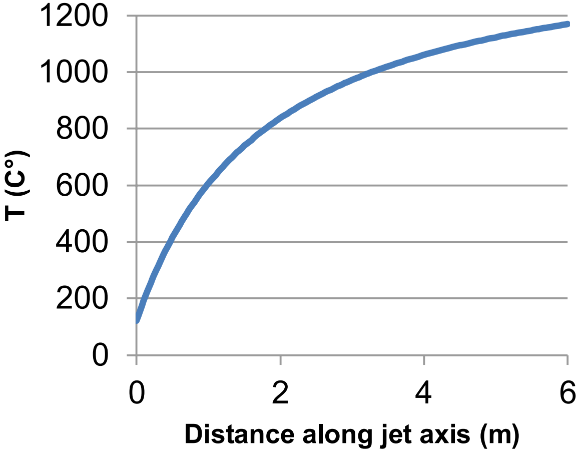
- Moisture
- Volatiles
- Char-C
- Char-N

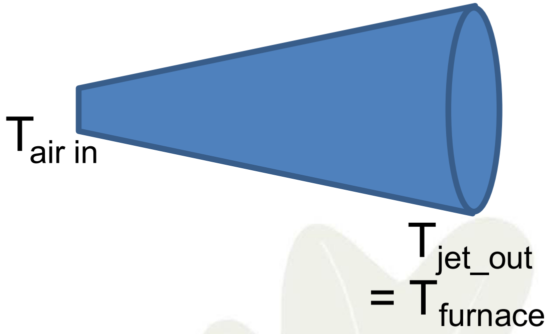
Furnace gas

Temperature profiles



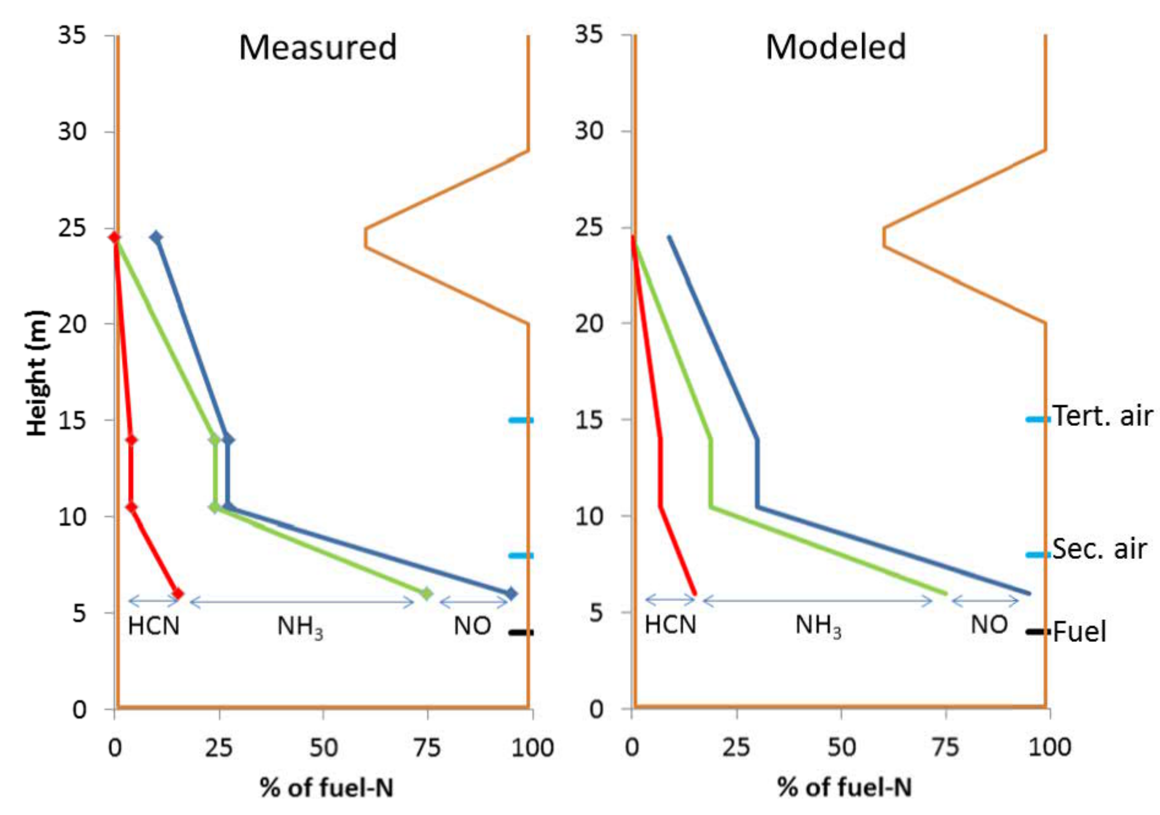




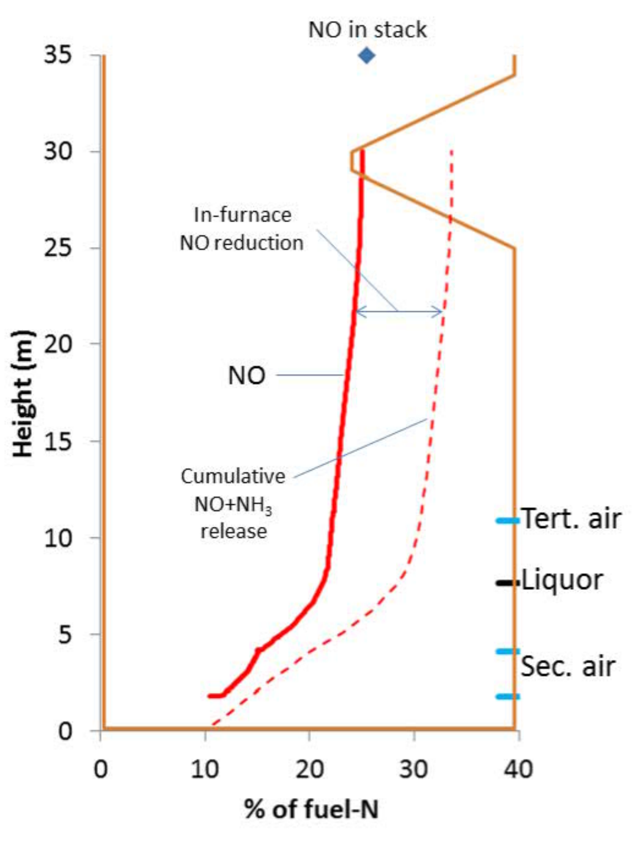


”Jet-NOx” prediction examples

Bubbling Fluidized Bed boiler

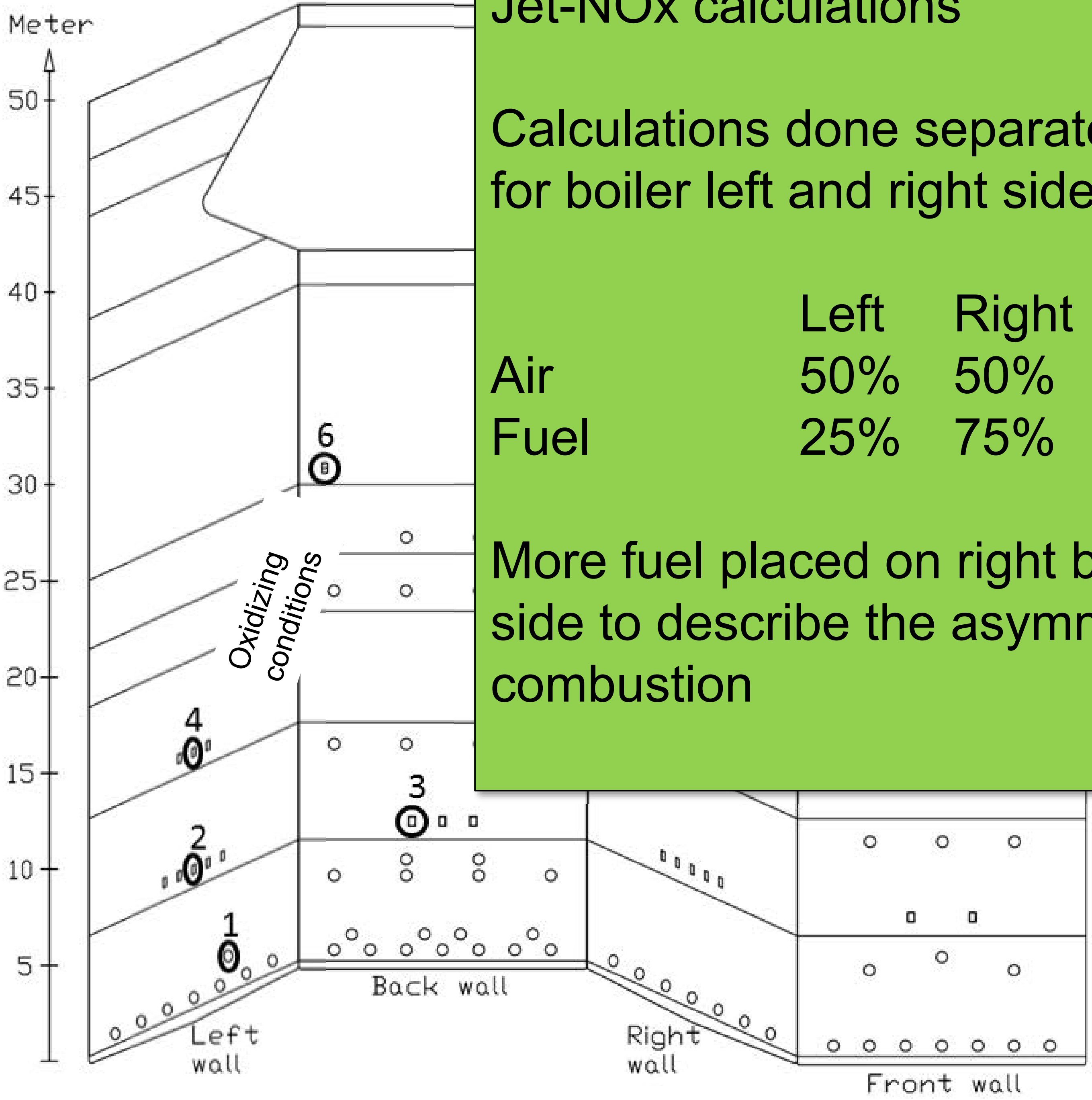


Kraft recovery boiler



Wisaforest Jet-NOx calculation setup

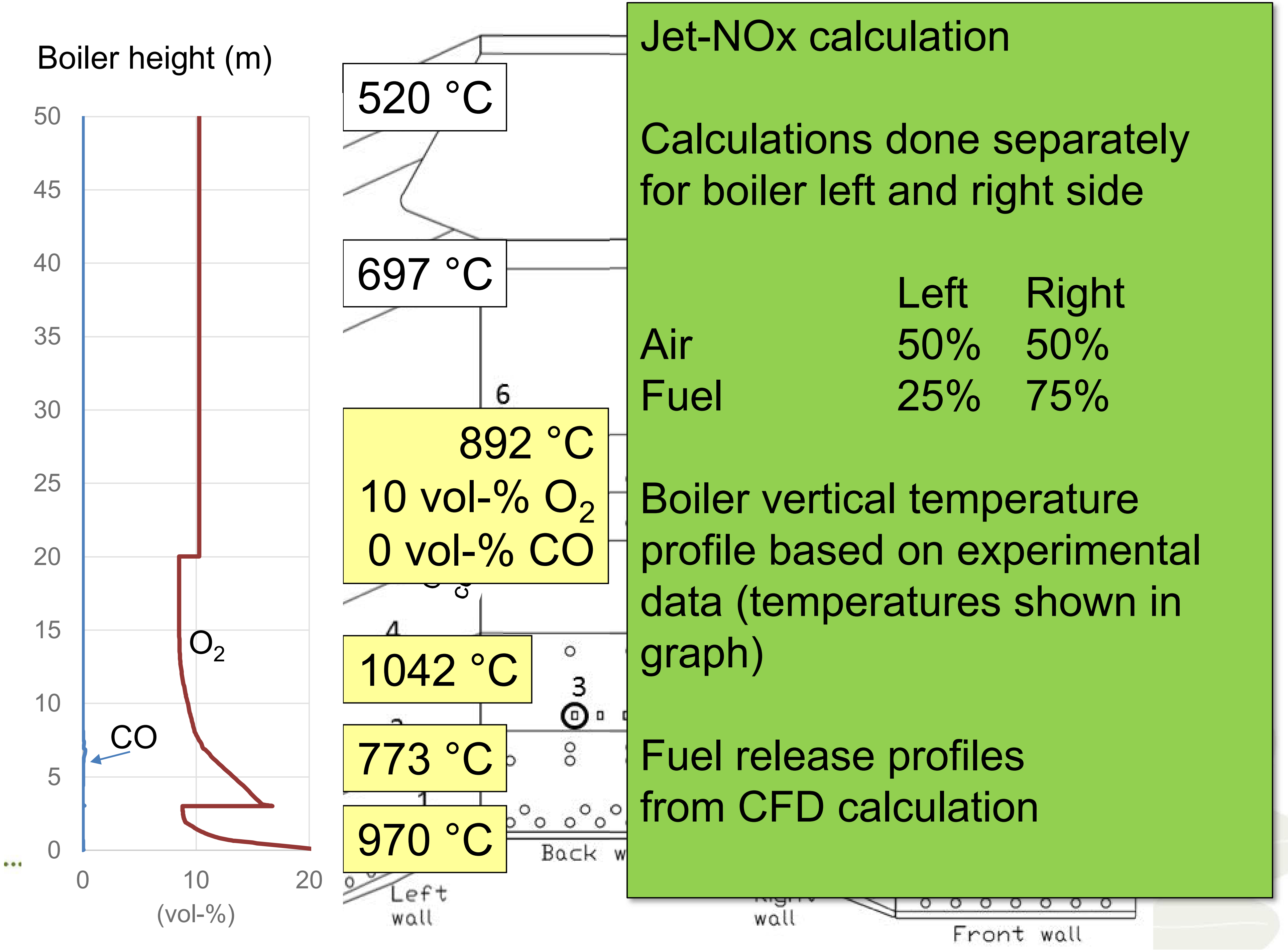
Jet-NOx calculations



Calculations done separately for boiler left and right side

	Left	Right
Air	50%	50%
Fuel	25%	75%

More fuel placed on right boiler side to describe the asymmetric combustion



520 °C

697 °C

892 °C
10 vol-% O_2
0 vol-% CO

1042 °C

773 °C

970 °C

Jet-NOx calculation

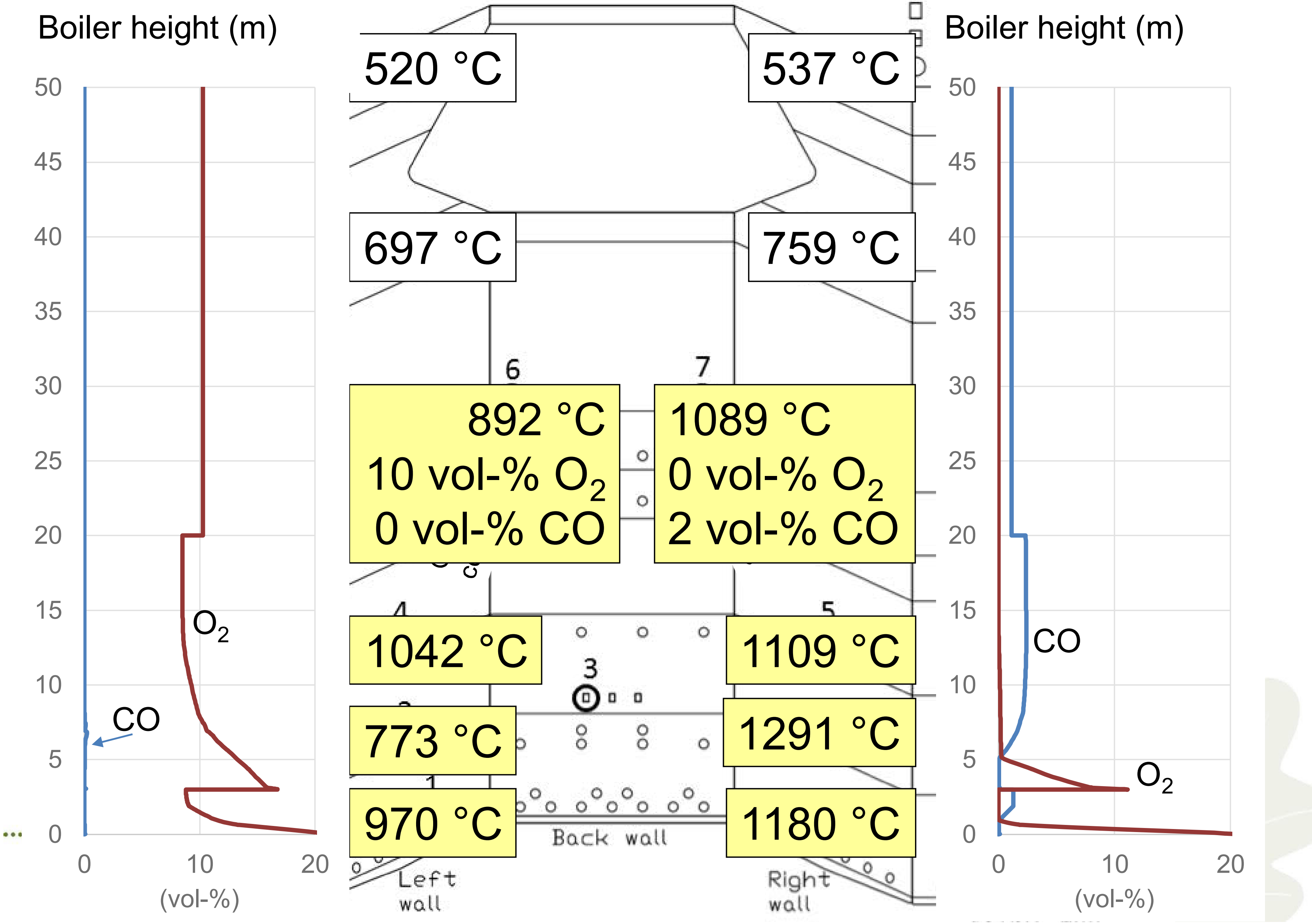
Calculations done separately for boiler left and right side

	Left	Right
Air	50%	50%
Fuel	25%	75%

Boiler vertical temperature profile based on experimental data (temperatures shown in graph)

Fuel release profiles from CFD calculation

Resulting Chemkin model CO and O_2 profiles on boiler left and right side.
Model CO and O_2 consistent with measurements, meaning the oxidizing vs reducing boiler conditions are captured in the model



Wisaforest Jet-NOx

Results
using ÅA detailed chemistry mechanism

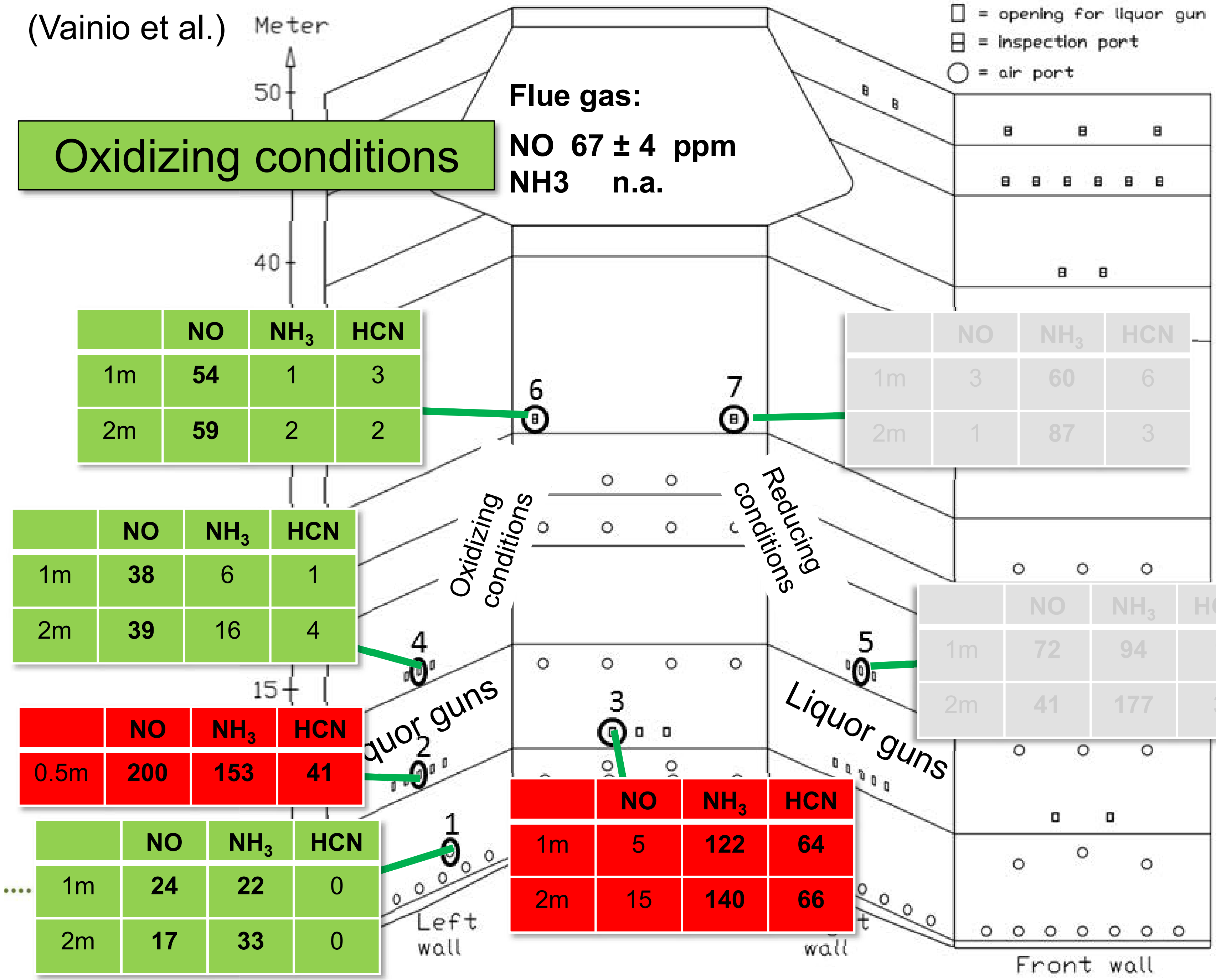
ChemCom 2.0
(Vainio et al.)

Oxidizing conditions

Flue gas:

NO 67 ± 4 ppm

NH3 n.a.



Port 6:

	NO	NH_3	HCN
1m	**54**	1	3
2m	**59**	2	2

Port 7:

	NO	NH_3	HCN
1m	3	**60**	6
2m	1	**87**	3

Port 4:

	NO	NH_3	HCN
1m	**38**	6	1
2m	**39**	16	4

Port 5:

	NO	NH_3	HCN
1m	**72**	**94**	1
2m	**41**	**177**	3

Port 2:

	NO	NH_3	HCN
0.5m	**200**	**153**	**41**

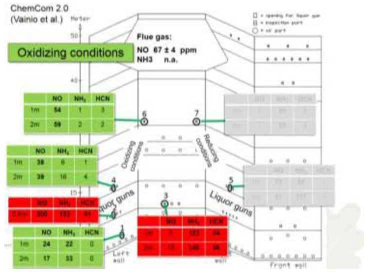
Port 3:

	NO	NH_3	HCN
1m	5	**122**	**64**
2m	15	**140**	**66**

Port 1:

	NO	NH_3	HCN
1m	**24**	**22**	0
2m	**17**	**33**	0

Modeled boiler left side - Oxidizing conditions



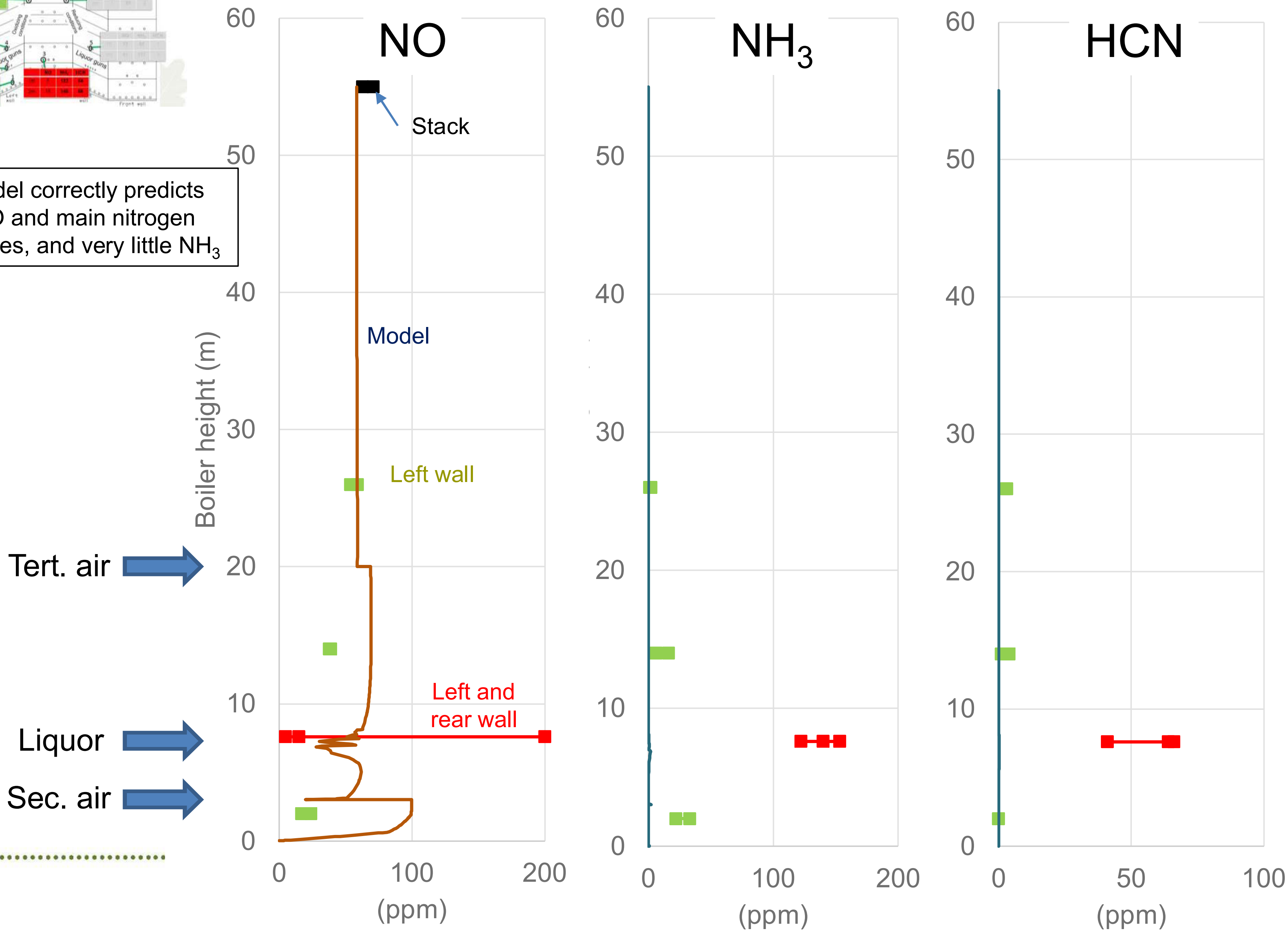
	NO	NH_3	HCN
1m	54	1	3
2m	59	2	2

	NO	NH_3	HCN
1m	38	6	1
2m	39	16	4

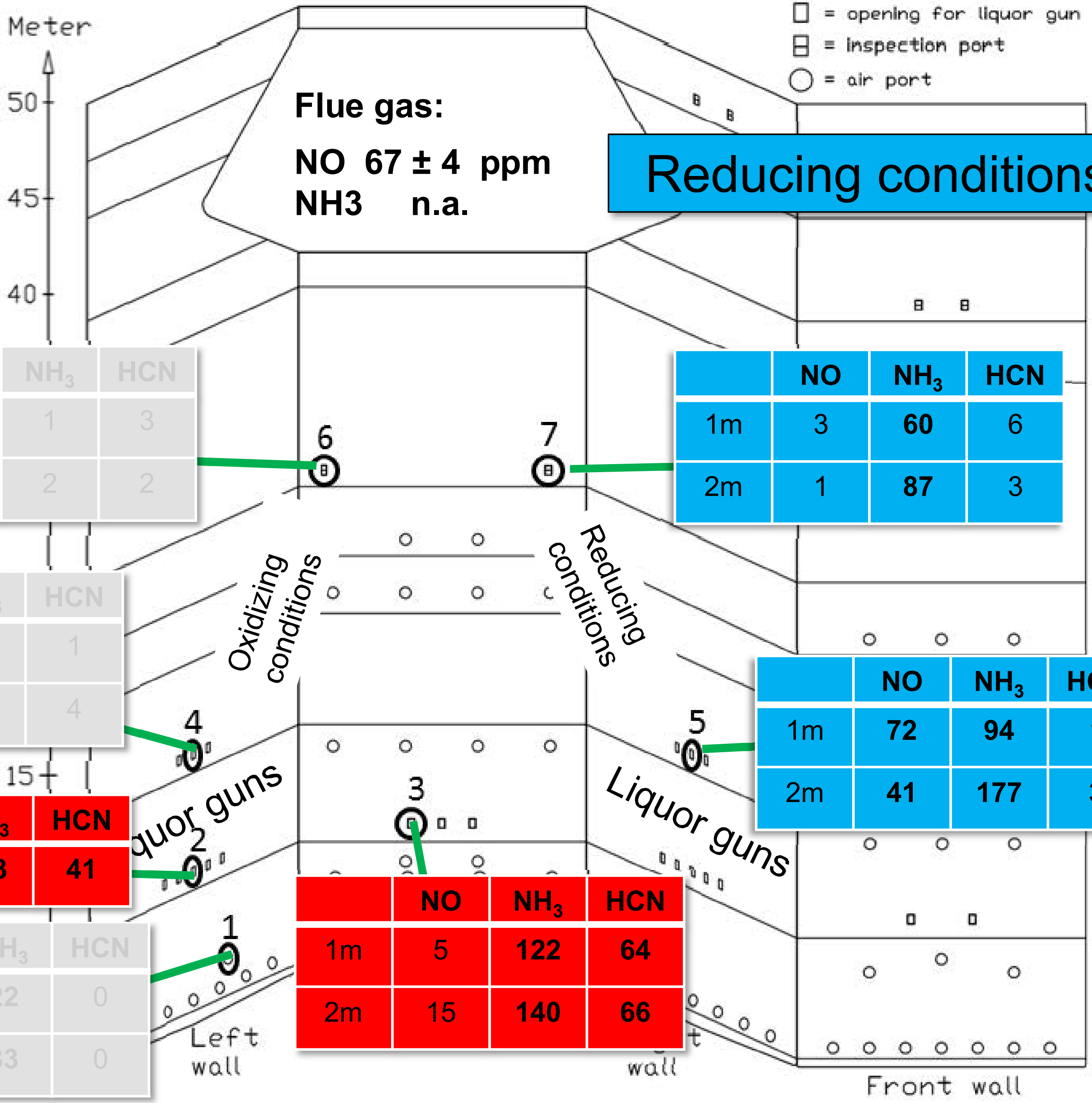
	NO	NH_3	HCN
0.5m	200	133	41

	NO	NH_3	HCN
1m	24	22	0
2m	17	33	0

Model correctly predicts NO and main nitrogen species, and very little NH_3



ChemCom 2.0
(Vainio et al.)



Flue gas:

NO 67 ± 4 ppm
NH3 n.a.

Reducing conditions

	NO	NH_3	HCN
1m	**54**	1	3
2m	**59**	2	2

	NO	**NH_3**	**HCN**
1m	3	**60**	6
2m	1	**87**	3

	NO	NH_3	HCN
1m	**38**	6	1
2m	**39**	16	4

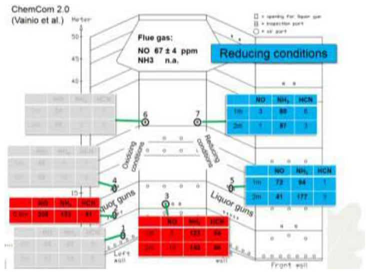
	NO	**NH_3**	**HCN**
1m	**72**	**94**	1
2m	**41**	**177**	3

	NO	**NH_3**	**HCN**
0.5m	**200**	**153**	**41**

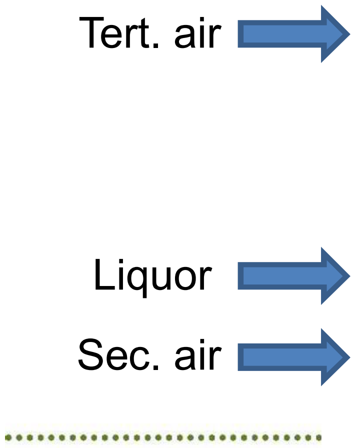
	NO	**NH_3**	**HCN**
1m	5	**122**	**64**
2m	15	**140**	**66**

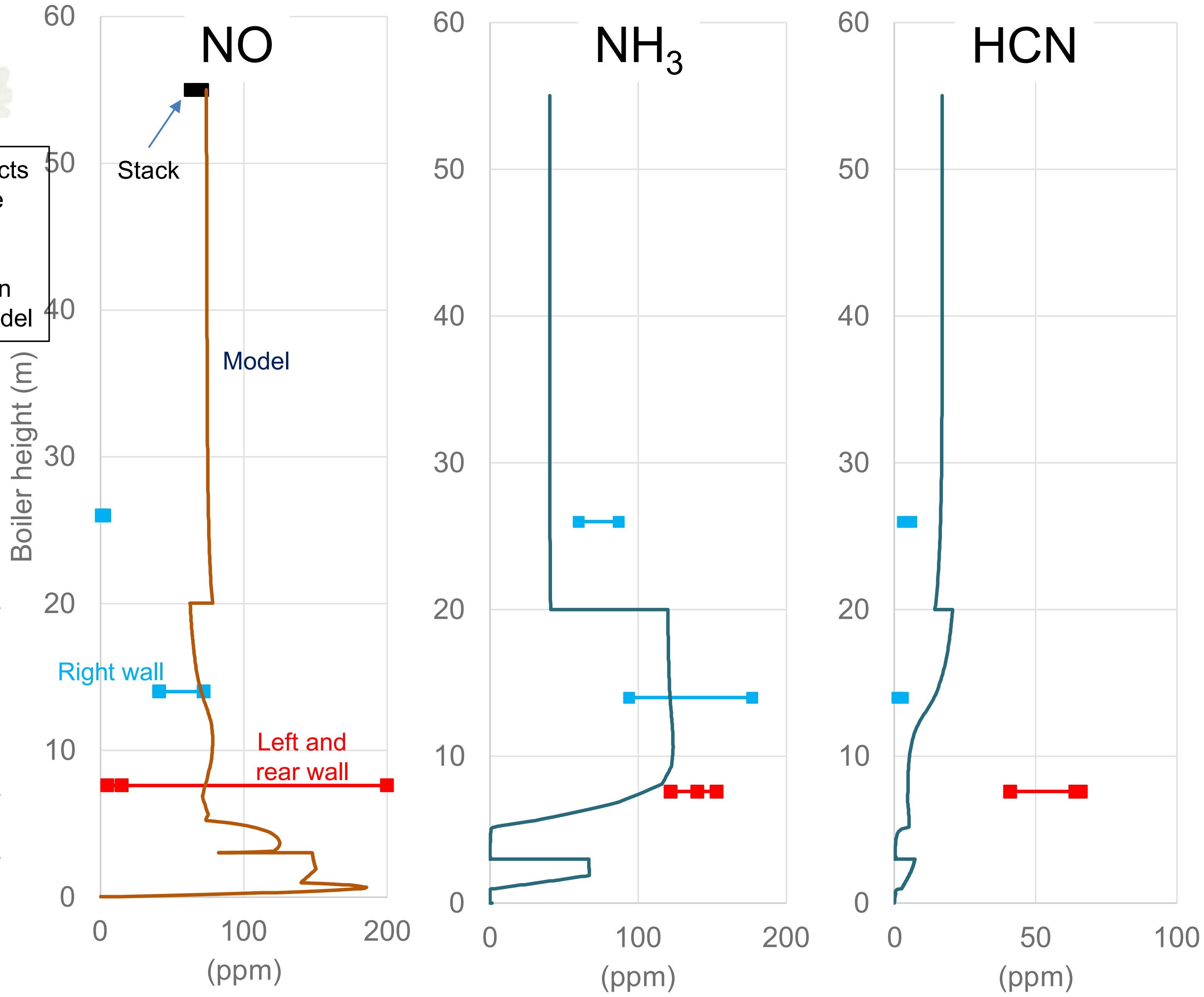
	NO	NH_3	HCN
1m	**24**	**22**	0
2m	**17**	**33**	0

Modeled boiler right side - Reducing conditions



Model correctly predicts NO and NH_3 as the main nitrogen species.
Also, HCN formation is captured by the model





To note

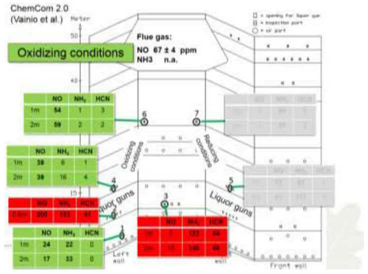
- Jet-NOx simulations are for boiler left and right side respectively and on average
- Local (high/low) values of NO, NH_3, and HCN will not be captured. This should be taken into consideration when addressing model validity
- While chemistry mechanisms should be evaluated by how well they describe the NOx formation chemistry, i.e. they should reproduce the correct trends, including ideally correct/reasonable final NOx, ***the main focus in this work is on the similarities/differences between mechanisms.***
  Of particular interest for CFD modeling is if/how much predictions differ when using detailed vs simplified chemistry

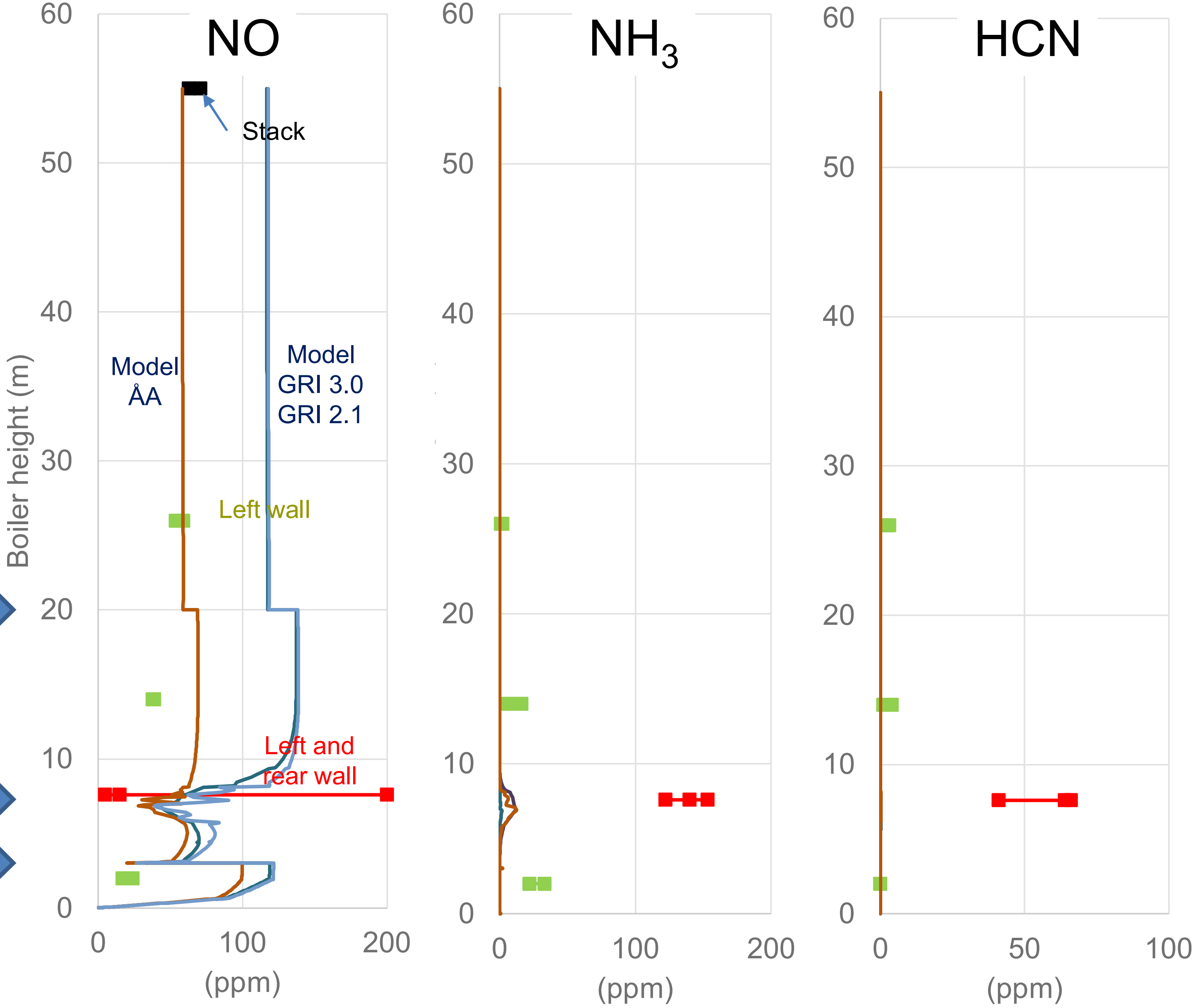
Wisaforest Jet-NOx

Results using three detailed chemistry mechanisms ÅA, GRI 3.0, GRI 2.1

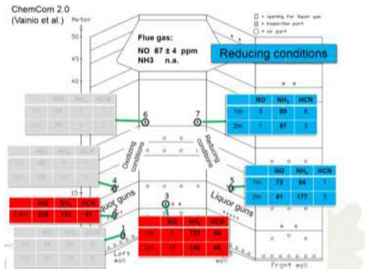
This is outside the original project plan.
The GRI mechanisms were included
to see if and how much predictions differ
when using different detailed mechanisms

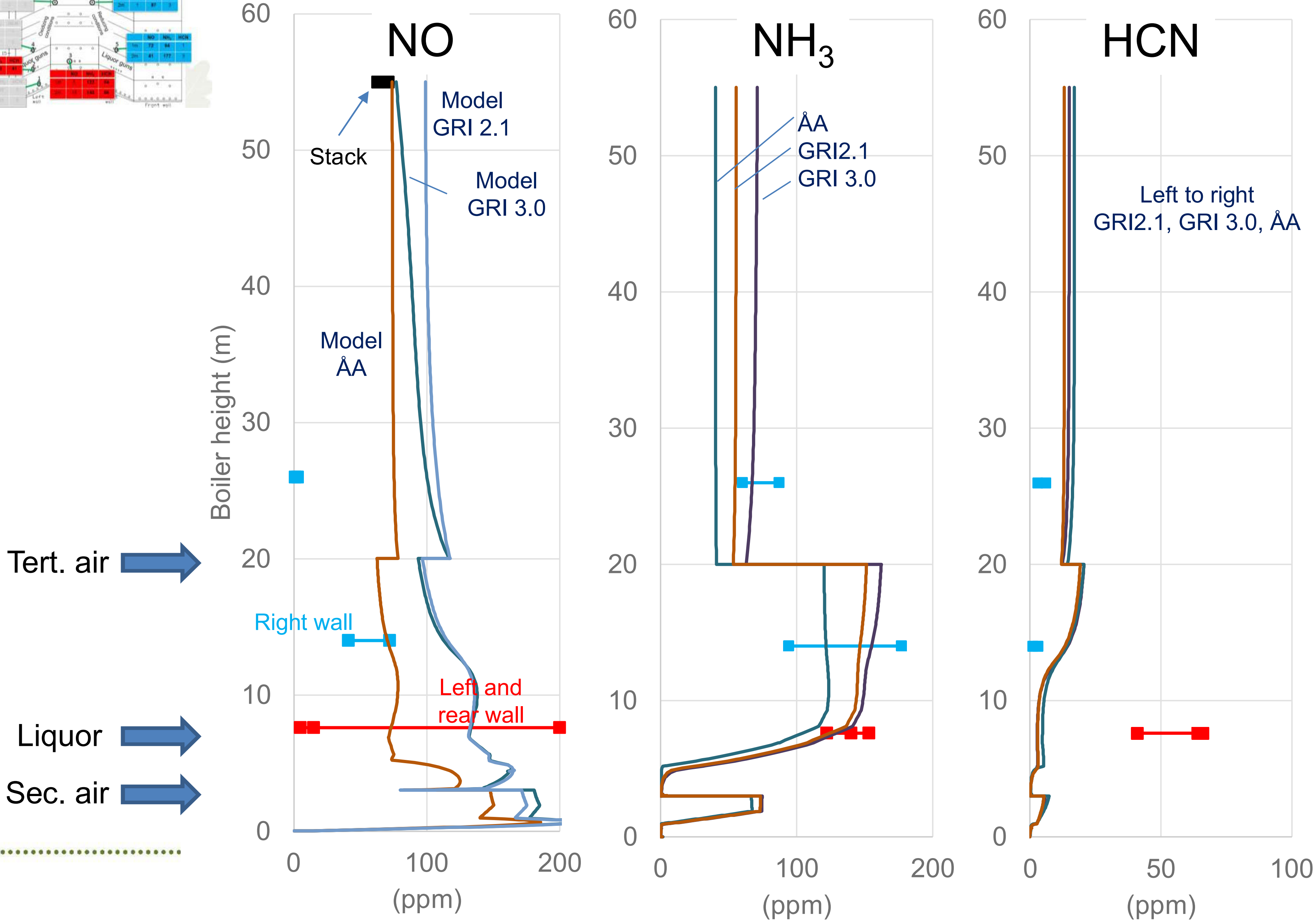
Modeled boiler left side - Oxidizing conditions





Modeled boiler right side - Reducing conditions





Detailed mechanisms - conclusions

- In general GRI 2.1 and GRI 3.0 predict higher NO than ÅA mechanism
  - ÅA developed for fuel-nitrogen chemistry, whereas GRI mechanisms are known to predict higher NO
  - GRI 3.0 reducing conditions, upper furnace NO chemistry/profile needs to be investigated further
- Some differences in NH_3 profiles
- HCN profiles relatively similar

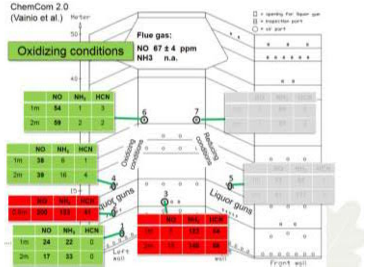
Wisaforest Jet-NOx

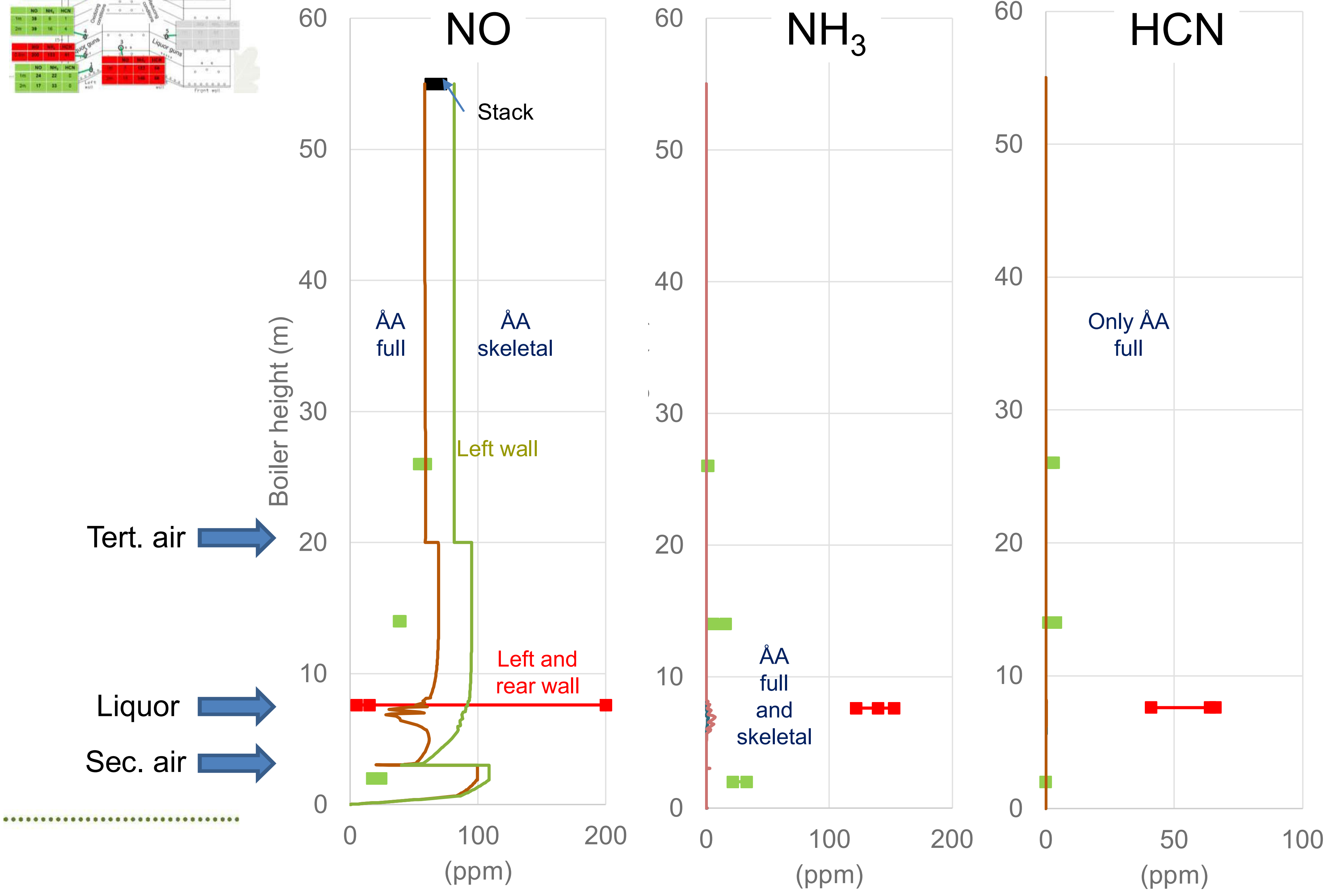
ÅA detailed chemistry vs ÅA skeletal

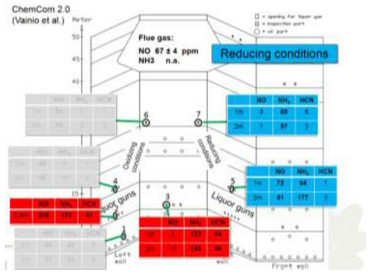
ÅA skeletal mechanism

- Based on the full detailed mechanism, with HCN chemistry removed
  - In skeletal mechanism 32 reactions describing N chemistry
  - Elemental reactions, include radical species
- The skeletal mechanism was originally developed with the objective to describe NH_3-NO chemistry
  - This is in-line with the general idea that NH_3 reacts in different proportions to NO and N_2, depending on conditions ”oxidizing” vs ”reducing”. This same idea is used in global (2-step) NH_3-NO chemistry, but there using only the two reactions.
  - As seen in the results of the present work, NO prediction using the skeletal mechanism differs from prediction using full detailed mechanism, this indicating the importance of including NO-reburning/HCN in recovery boiler modeling

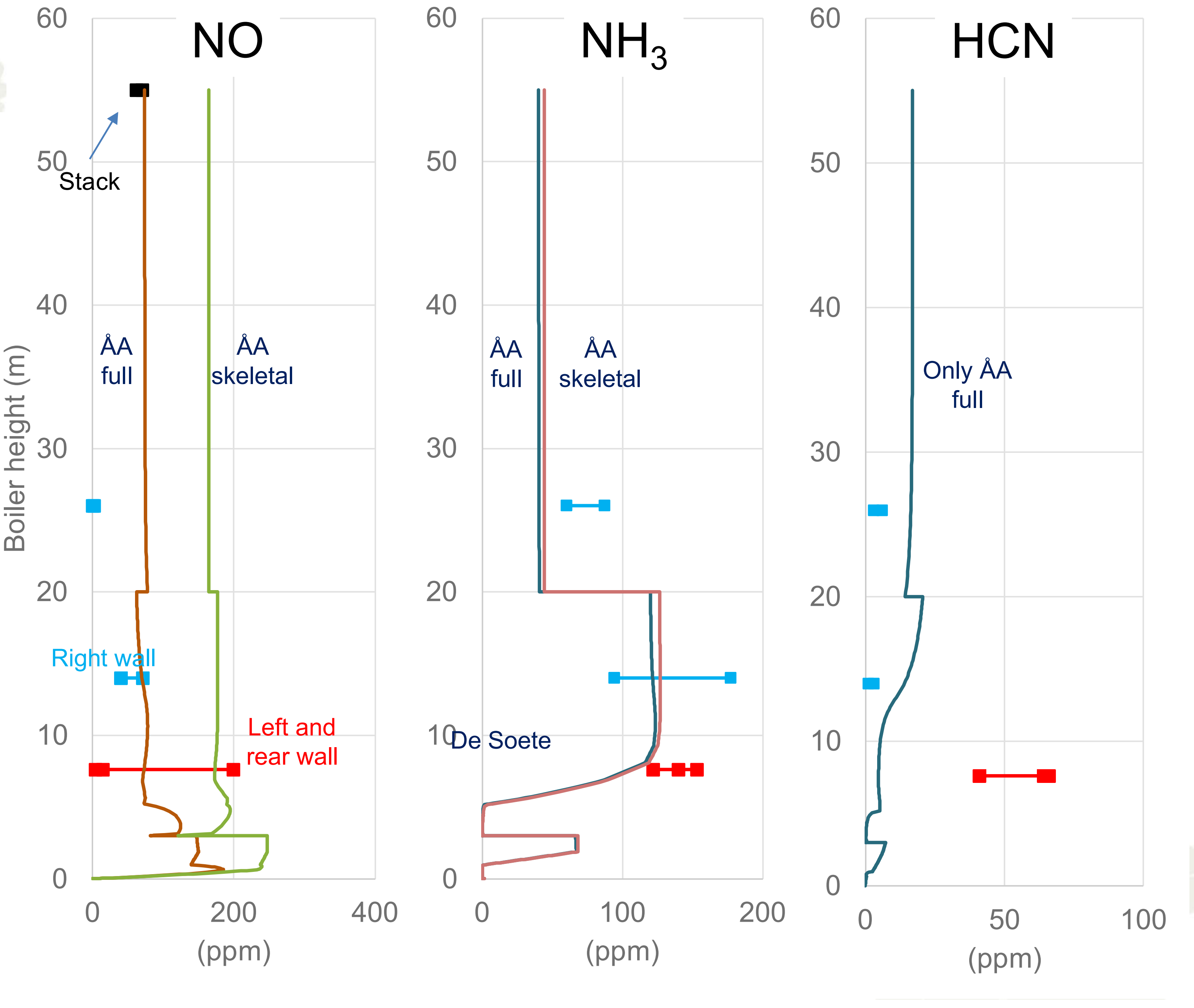
Modeled boiler left side - Oxidizing conditions

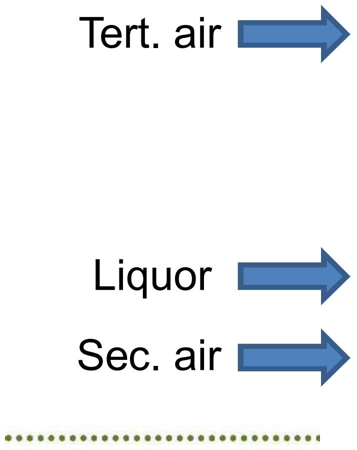






Modeled boiler right side - Reducing conditions





ÅA skeletal mechanism conclusions

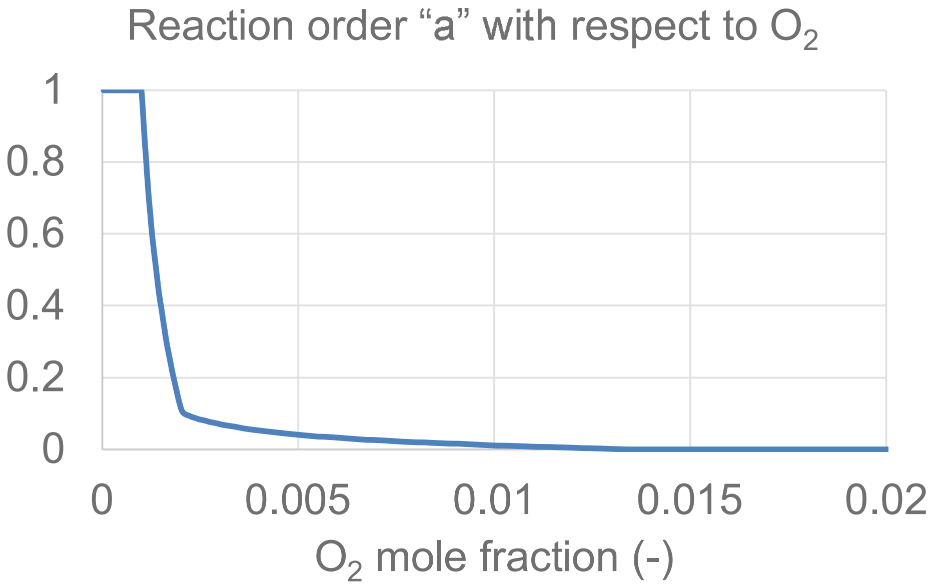
- The skeletal mechanism predicts very well the trends and levels of NH_3
    - Practically zero NH_3 in oxidizing conditions (boiler left side)
    - Considerable NH_3 concentration in reducing conditions (boiler right side)
- NO is overpredicted
    - The difference to full mechanism is greater on the right (reducing) boiler side, where skeletal predicted NO is twice the NO predicted by full mechanism
    - This overprediction of NO is in-line with the skeletal mechanism not including NO-reburning chemistry ($NO + CxHy \rightarrow HCN + ...$)
    - The full mechanism and boiler measurements show NO-reburning to take place, and omitting NO-reburning chemistry affects predicted NO level

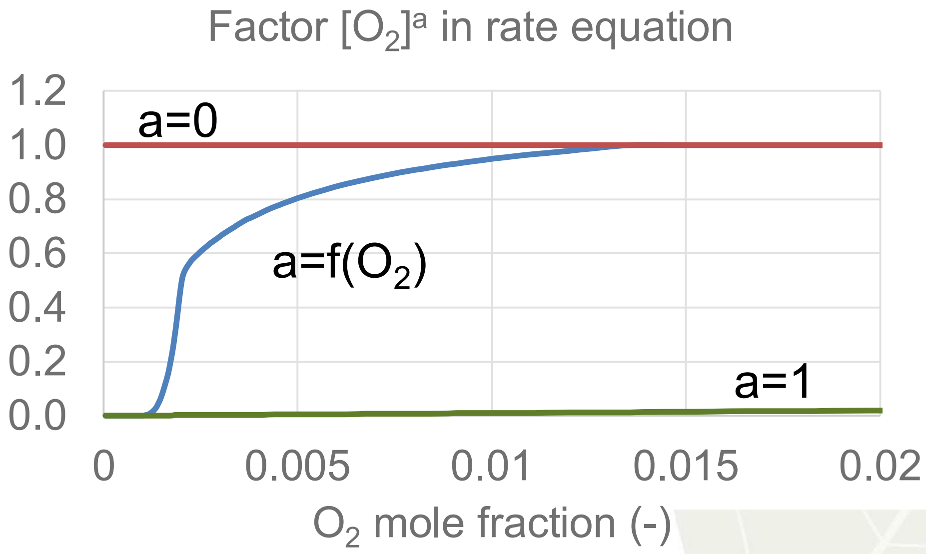
Wisaforest Jet-NOx

ÅA detailed chemistry vs 2-step

De Soete 2-step chemistry

- $NH_3 + O_2 \rightarrow NO$
  - $R = k\,[NH_3]^1\,[O_2]^a$, $a=f(O_2)$
- $NO + NH_3 \rightarrow N_2$
  - $R = k\,[NO]\,[NH3]$



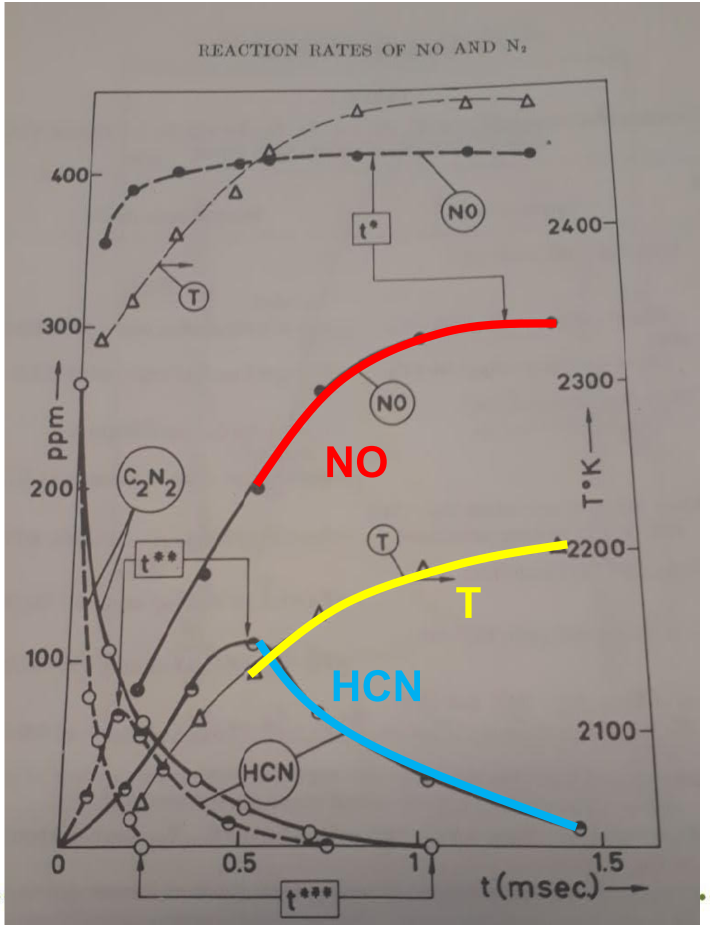


Implementing reaction order ”a”
as function of O_2
requires
adding own (user-supplemental)
code to Chemkin

Checking De Soete 2-step chemistry implementation

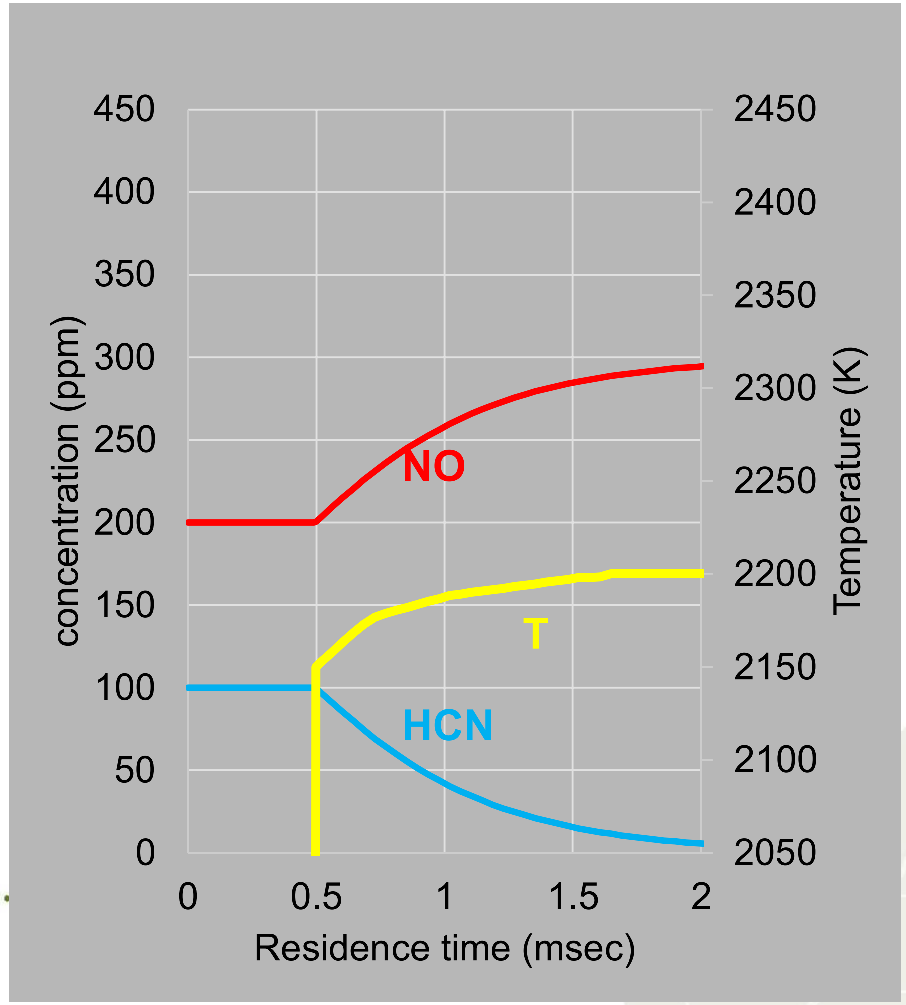
Simulations were set up to represent HCN-NO chemistry as shown in below pictures.
Model predictions agree well with experimental data, indicating code is correctly implemented.

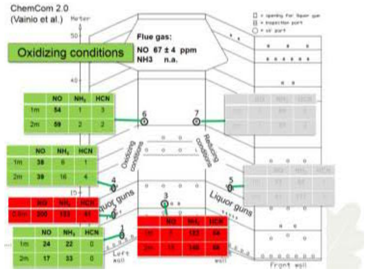
Example profiles for two burner flow rates:
198 cm3/s (continuous lines)
441 cm3/s (dashed lines)



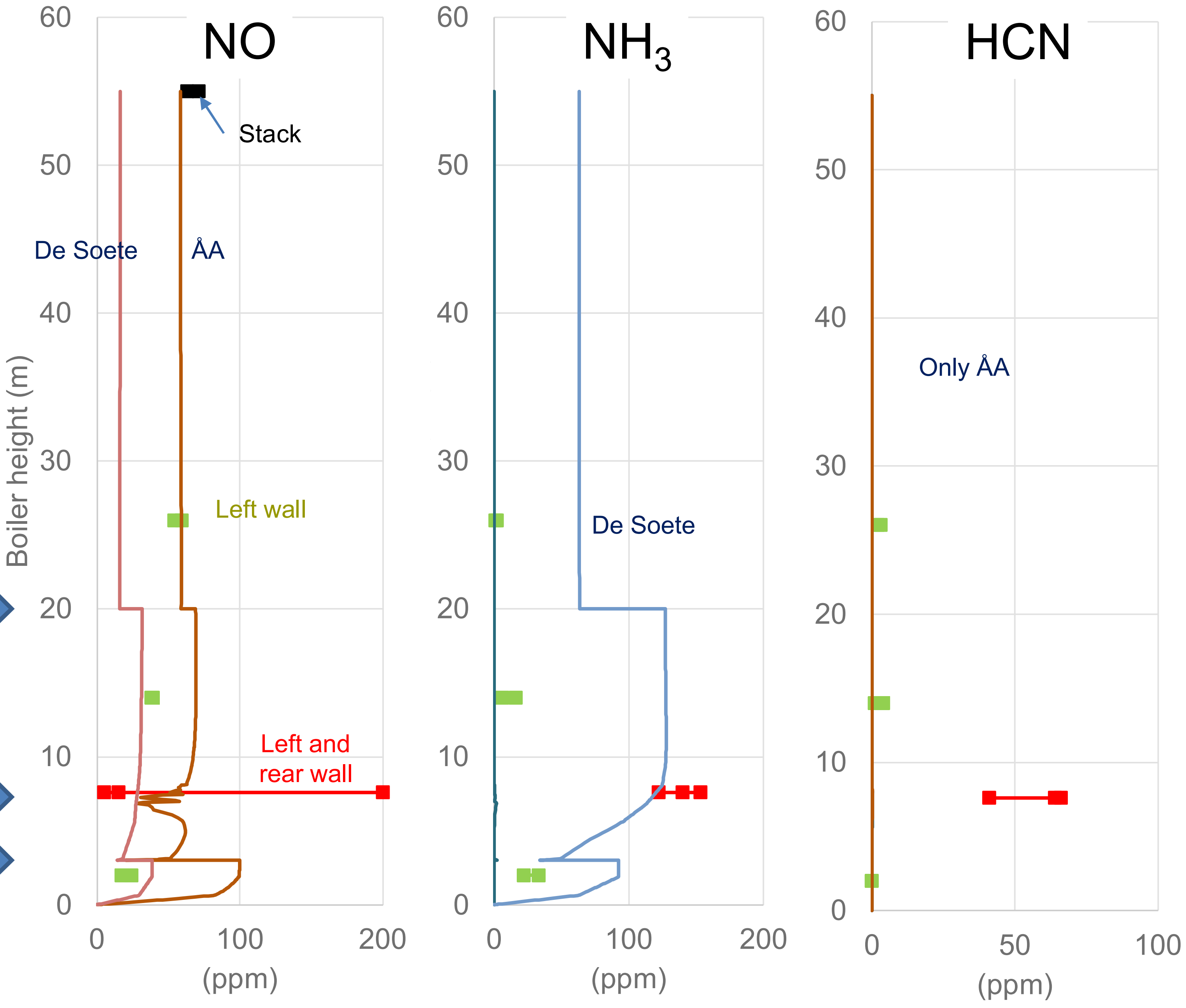
(De Soete, 1975)

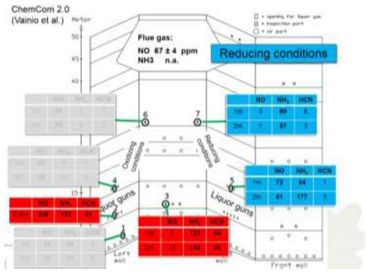
Chemkin calculation





Modeled boiler left side - Oxidizing conditions



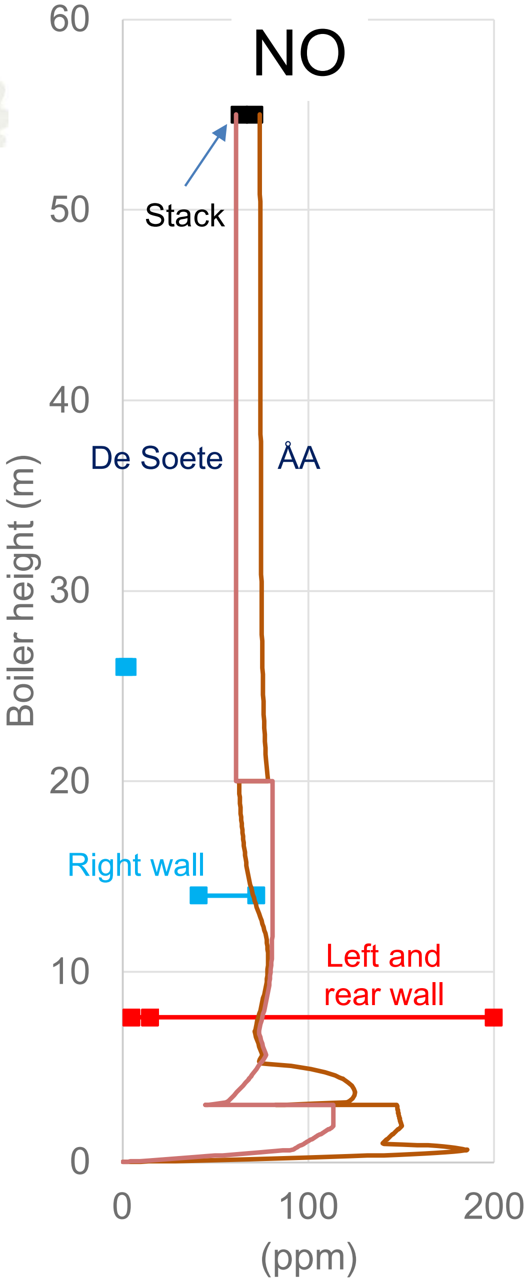


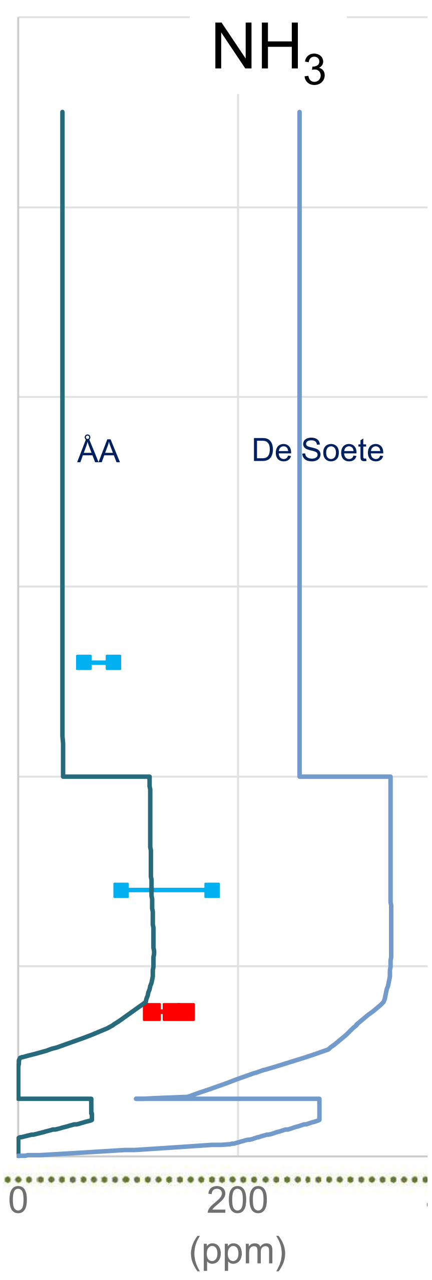
Modeled boiler right side - Reducing conditions

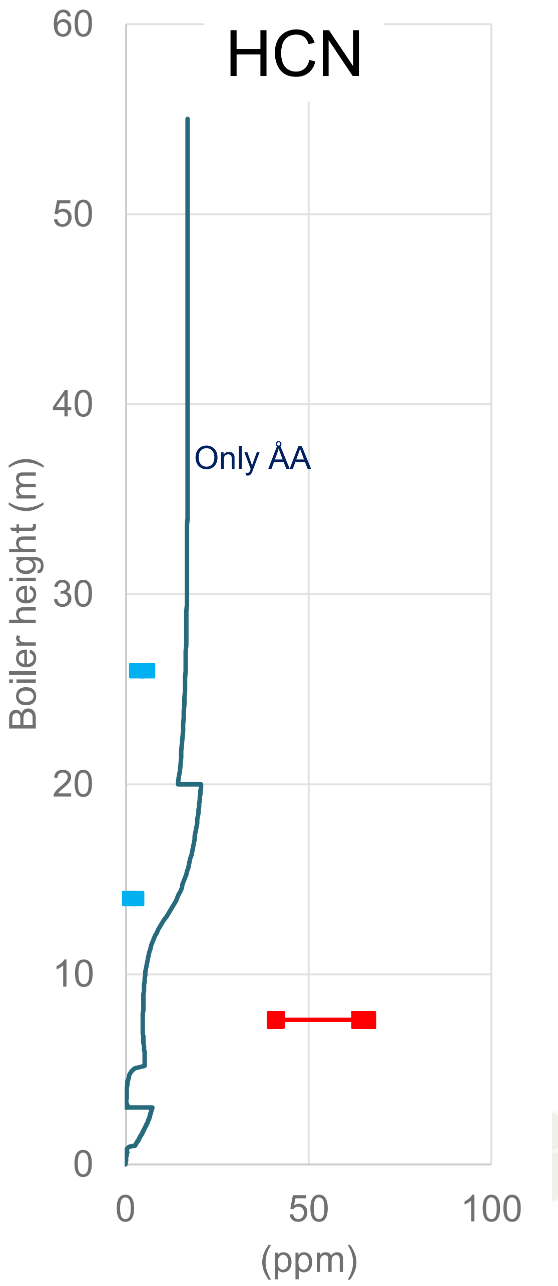
Tert. air

Liquor

Sec. air







De Soete 2-step chemistry conclusions

- Reactions are very slow compared to full mechanism; this results in
    - Oxidizing boiler side: low NO and high NH_3 (which is unreacted)
    - Reducing boiler side: NO similar to NO by detailed mechanism, but reason is the too high NH_3 (unreacted) compared to detailed mechanism

- The De Soete 2-step mechanism does not correctly describe recovery boiler N chemistry

Conclusions (1)

- Recovery boiler measurements and model predictions using detailed chemistry show NO, NH_3, and HCN to be relevant species in NO emission formation.
- HCN in recovery boilers is the result of NO-reburning (NO + CxHy → HCN +...)
- A detailed chemistry mechanism (ÅA mechanism) that describes fuel nitrogen chemistry, predicts the overall trends and concentration levels of NO, NH_3, and HCN in good agreement with in-furnace measurements data (boiler oxidizing or reducing conditions)
- A skeletal mechanism (ÅA, 32 elementary reactions) developed for description of NH_3-NO chemistry, predicts boiler NH_3 trends and concentrations in agreement with detailed mechanism. NO is overpredicted, consistent with skeletal mechanism not including NO-reburning (the pathway for NO to react further / be reduced)
- **Based on the boiler measurements and chemical kinetics calculations it is concluded that NO-reburning chemistry is important to take into account in mathematical modeling (e.g. CFD) of recovery boiler NO emission formation**

Conclusions (2)

- The 2-step mechanism (De Soete) underpredicts to considerable degree the NH_3-to-NO conversion chemistry.
- The De Soete chemistry is based on data at flame temperatures >1700 °C, which is considerably higher than temperature levels in recovery boilers. This means that in RB simulations the De Soete chemistry is used outside its range of validity.
- **De Soete mechanism is concluded to not be suitable for simulations of recovery boiler N chemistry**

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Soodakattila-alan yhteistoiminta
Pöytäkirja. Vuosikokous 26.4.2018, Helsinki Congress Paasitorni
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Soodakattilapäivä 25.10.2018
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