A reduced chemical kinetics mechanism for NOx emission prediction in biomass combustion

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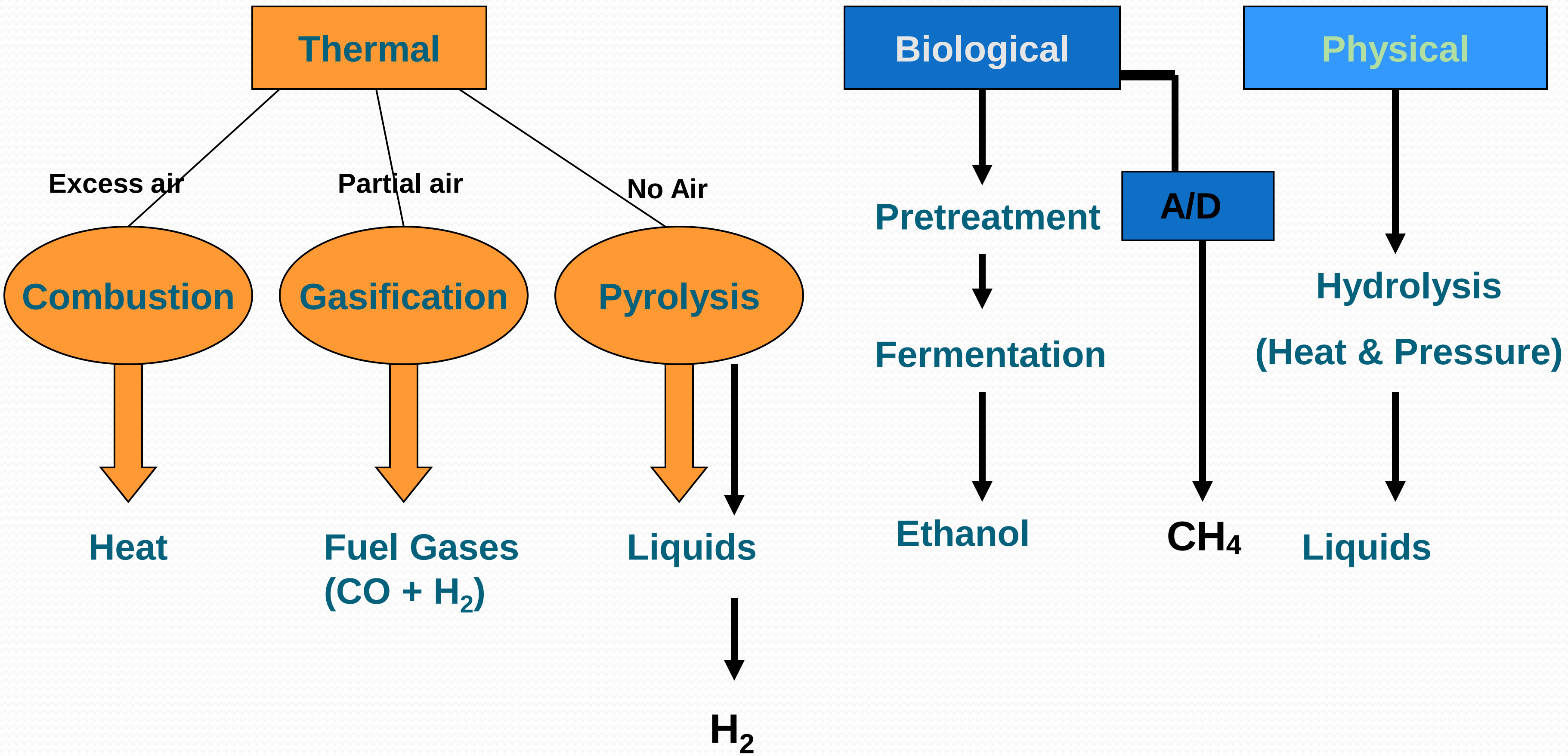
Outline

- Introduction
- NOx formation mechanisms
- Modeling approach
- Reduction procedure
- Results and discussion
- Concluding remarks

Biomass Conversion Pathways



Emissions from biomass combustion

- Biomass furnaces exhibit relatively high emissions of NOx and particulates in comparison to furnaces with natural gas or light fuel oil
- LCA studies shows that the contribution of NOx to the biomass emissions is around 40%

Table 1. Environmental Impact Points (EIP) According to the Ecological Scarcity Method for Heating with Wood Chips (base case for greenhouse effect)[a]

	[EIP/GJ]	[%]
NO_X	13 030	38.6%
PM 10	12 600	36.5%
CO_2	670	2.0%
SO_X, NH_3, CH_4, NMVOC, primary energy, residues, and others	8 200	22.9%
Total	34 500	100%

Reduction technologies overview

- Based on the elemental composition of the biomass fuel, the important emissions/problems and the proper emission reduction technology are defined

Element	Guiding concentration in the fuel wt% (d.b.)	Limiting parameter	Fuels affected outside guiding ranges	Technological methods for reducing to guiding ranges
N	< 0.6	NO_x emissions	Straw, cereals, grass, olive residues	Primary measures (air staging, reduction zone)
	< 2.5	NO_x emissions	Waste wood, fibre boards	Secondary measures (SNCR or SCR process)
Cl	< 0.1	Corrosion	Straw, cereals, grass, waste wood, olive residues	– fuel leaching – automatic heat exchanger cleaning – coating of boiler tubes – appropriate material selection
	<0.1	HCl emissions	Straw, cereals, grass, waste wood, olive residues	– dry sorption – scrubbers – fuel leaching
	< 0.3	PCDD/F emissions	Straw, cereals, waste wood	– sorption with activated carbon
S	< 0.1	Corrosion	Straw, cereals, grass, olive residues	See Cl
	< 0.2	SO_x emissions	Grass, hay, waste wood	See HCl emissions
Ca	15–35	Ash-melting point	Straw, cereals, grass, olive residues	Temperature control on the grate and in the furnace
K	< 7.0	Ash-melting point, depositions, corrosion	Straw, cereals, grass, olive residues	Against corrosion: see Cl
	–	Aerosol formation	Straw, cereals, grass, olive residues	Efficient dust precipitation, fuel leaching
Zn	< 0.08	Ash recycling, ash utilization	Bark, woodchips, sawdust, waste wood	Fractioned heavy metal separation, ash treatment
	–	Particulate emissions	Bark, woodchips, sawdust, waste wood	Efficient dust precipitation, treatment of condensates

Emission reduction control measures

- **Primary measures**

  These measures are dealing with the combustion zone and improvements to this area to avoid creation of these emissions

- **Secondary measures**

  secondary measures look at the exit of combustion chamber, i.e. the flue gas, to remove the emissions from the exhaust gas and reduce the emission levels - possibility up to 99% reduction

Primary emission reduction measures

- Modifications to the fuel:
  - the fuel composition;
  - the moisture content of the fuel;
  - the particle size of the fuel;
- Combustion chamber:
  - selection of the type of combustion equipment;
  - improved construction of the combustion application;
  - combustion process control optimization;
- staged-air combustion;
- staged-fuel combustion and reburning.

NOx formation mechanisms

NO from N_2:

1- occurs primarily by <u>thermal NO formation</u>

or Zeldovich mechanism

$$O + N_2 \leftrightarrow N + NO$$
$$O_2 + N \leftrightarrow O + NO$$
$$OH + N \leftrightarrow H + NO$$

High activation energy, slow, and rate limiting

@ temperatures above 1600-1800K

2- <u>prompt mechanism (Fenimore)</u>

Important in rich combustion

(hydrocarbons radicals exist)

$$CH + N_2 \leftrightarrow HCN + N$$
$$C + N_2 \leftrightarrow CN + N$$
$$N + OH \leftrightarrow NO + H$$

3- <u>N_2O mechanism</u>

Important in fuel lean, low temperature condition

$$O + N_2 + M \leftrightarrow N_2O + M$$
$$H + N_2O \leftrightarrow NO + NH$$
$$O + N_2O \leftrightarrow NO + NO$$

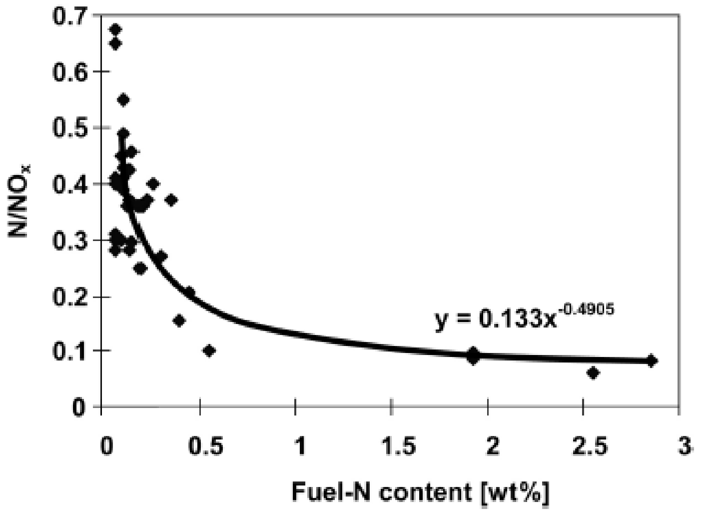
NOx formation mechanisms

In solid fuel systems

- 80%: NO from oxidation of fuel-N
- 20%: thermal NO
- Other NO formation mechanisms are usually negligible

Typical nitrogen content in selected fuels [3,12,20,21,29]

Fuel	N content (wt%)
Straw	0.3–1.5
Other agricultural residues	0.4–3.5
Wood	0.03–1.0
Peat	0.5–2.5
Coal	0.5–2.5
Paper	0.1–0.2
RDF	0.8
Tires	0.3
Household waste	0.5–1.0
Plastic waste	0.0
Sewage sludge	2.5–6.5



- Combustion of biomass and waste is mostly carried out on a grate or in a fluidized bed combustor; systems with comparatively low combustion temperatures. In these systems the yields of thermal NO can be considered to be small or negligible

Modelling

- Complex composition of biomass: the chemical model mechanism contains many different species and therefore a large number of reactions.

$$CH_mO_n + \lambda(1 + m/4 - n/2)(O_2 + 3.76N_2)$$
$$\rightarrow \text{intermediate}\,(CO, H_2, CO_2, CH_4,\ char, \ldots)$$
$$\rightarrow CO_2 + m/2H_2O + (\lambda - 1)O_2 + \lambda 3.76N_2$$

- Biomass combustion gas phase kinetics is fairly well researched and understood, the proposed mechanisms are yet complex and need very long computational time.

Modelling

- The selected detail mechanism: 81 species and 703 elementary reactions
- The mechanism includes C, H, O, and N while S, Cl, and the other trace elements are not included
- the primary (pyrolysis) gas composition (vol%):

H_2	H_2O	CH_4	C_2H_2	C_2H_4	C_2H_6	CO	CO_2
14.45	8.22	11.73	0.23	2.88	1.58	39.14	21.77

- with an addition of (NH3 and HCN) to predict NOx

Mechanism Reduction

- **reaction flow analysis**: identify the major reaction paths by performing an element flux analysis
- **sensitivity analysis**: to ensure that important species involved in only minor reaction flows are indeed kept in the model
- **time scale analysis**: many chemical reactions occur for time scales much shorter than the physical processes. These fast reactions can be treated in less detail by the numerical solver without considerable loss of accuracy
- **Necessity analysis**: (flow + sensitivity analysis)

species such as NOx, CO, and SOx can be defined as the target species of the combustion products and the analysis aims at finding which species and reactions are necessary for the formation of the defined gases

Reactor condition

- the reactor temperature of 700-1100 °C,
- residence time 1, 0.1, 0.01, 0.001 sec.,
- The equivalence ratio of 0.3-1 (excess air ratio of 1-3.3)
- isothermal condition
- a single PSR
- total fuel-N content: 1000 ppm
- The HCN/NH_3 ratio is 0.65

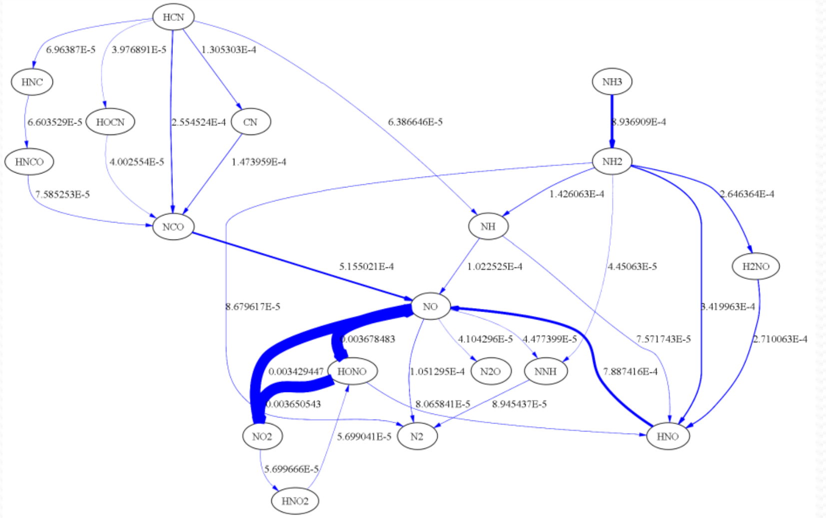
Necessity analysis

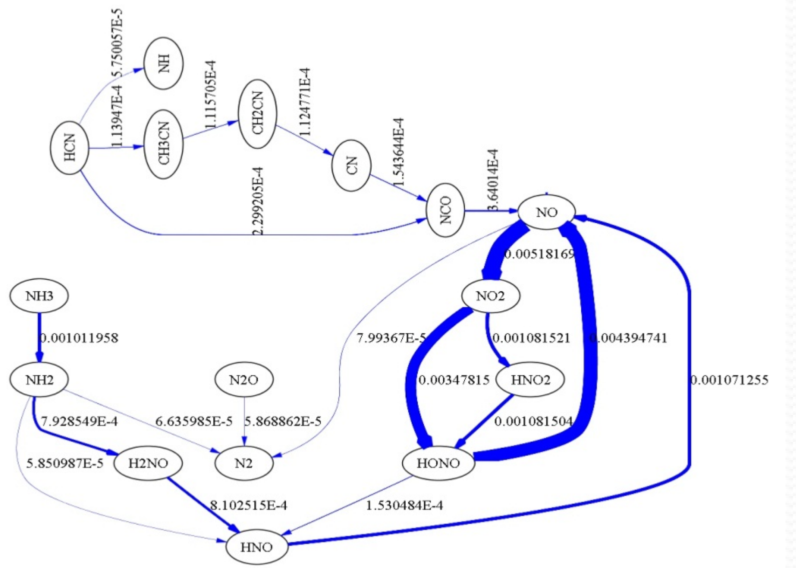
- H_2, N_2, H_2O, C_2H_2, C_2H_4, C_2H_6, NH_3, HCN, CO, CO_2, CH_4, O_2 are assumed as the necessary species

- the necessity analysis targets are set to NO, NO_2, O_2, H_2O, and temperature

Results

- Reaction flow analysis limited to 1% of max flux for nitrogen at an overall excess air ratio of 1.7. Fuel-N content=1000 ppm, T=850 °C (upper graph) and T=700 °C (lower graph), residence time=1 sec





- Importance of NH_2/HNO radicals for NH_3 conversion path, and NCO for HCN

- Sensitive: HONO, NH2, NNH, HNO2, HNC, and NCO

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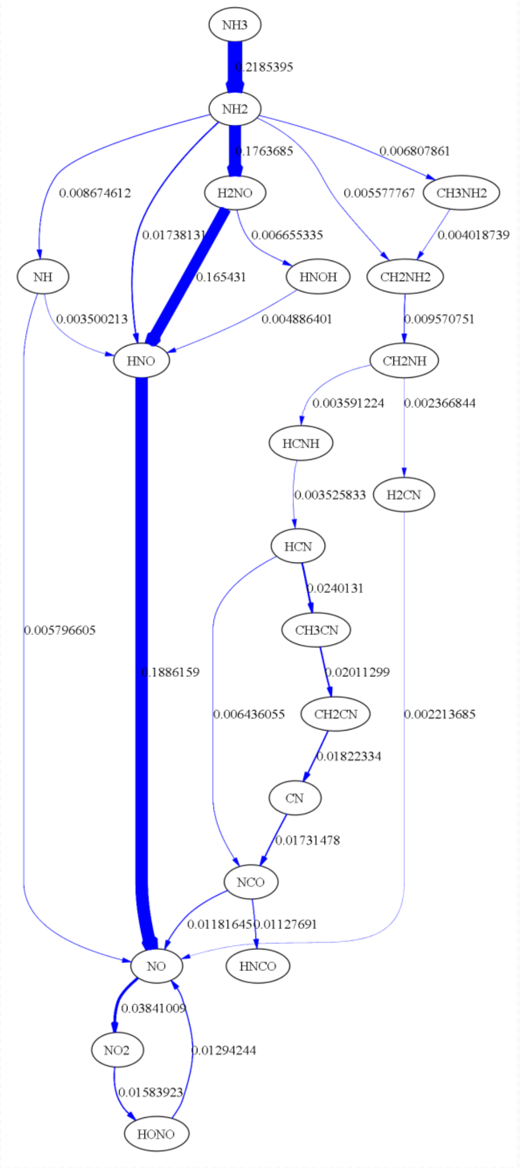
Short residence time

- Reaction flow analysis limited to 1% of max flux for nitrogen at an overall excess air ratio of 1.7. T=850 °C, residence time=0.001 sec
- N2O is not appearing in the flow which indicates high dependency of N2O on residence time



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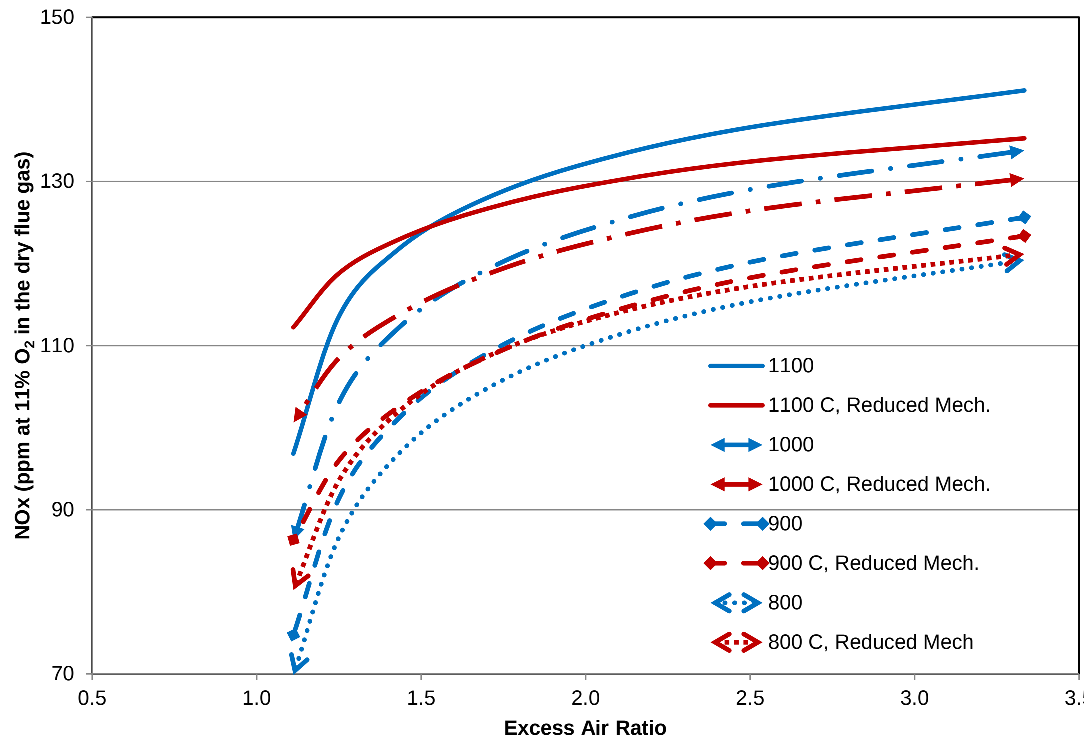
Effect of excess air ratio

- Comparison of reduced and detailed mechanism on NOx at different overall excess air ratios and temperatures. Residence time=1 sec
- increasing level of NOx as the excess air ratio increase
- Higher error at higher temp.



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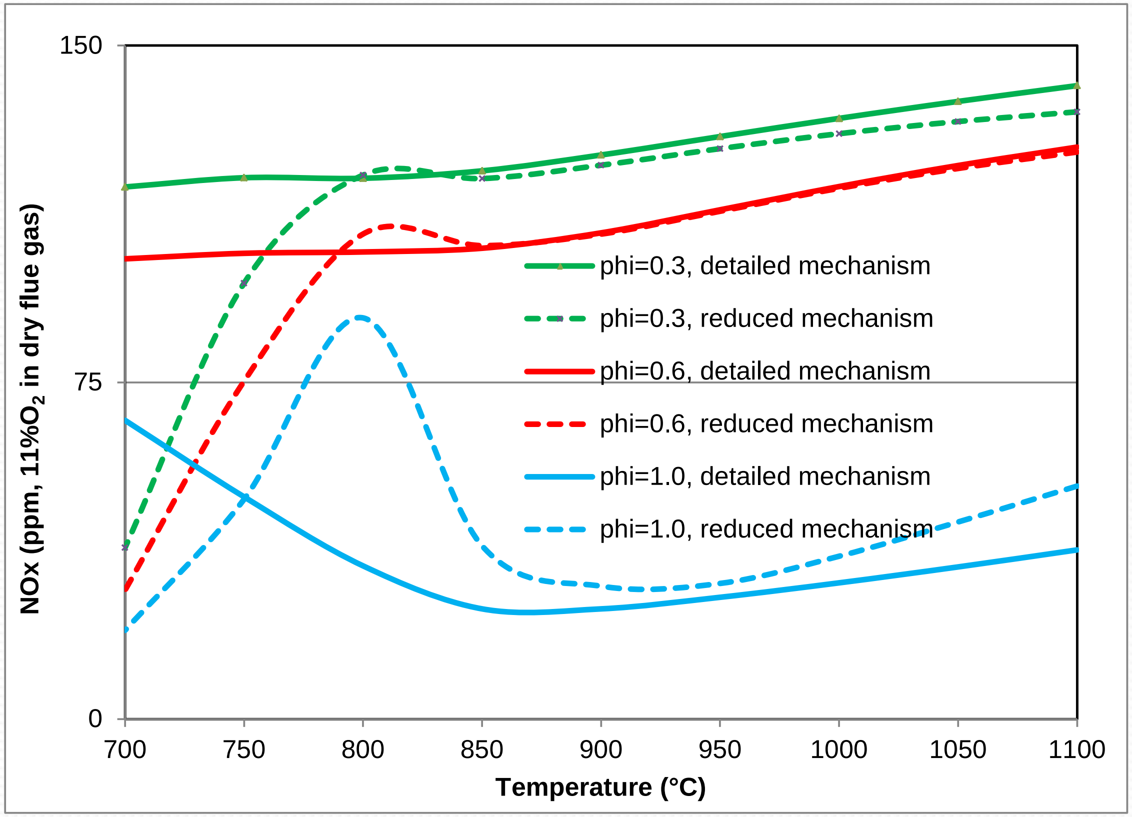
Temperature effect

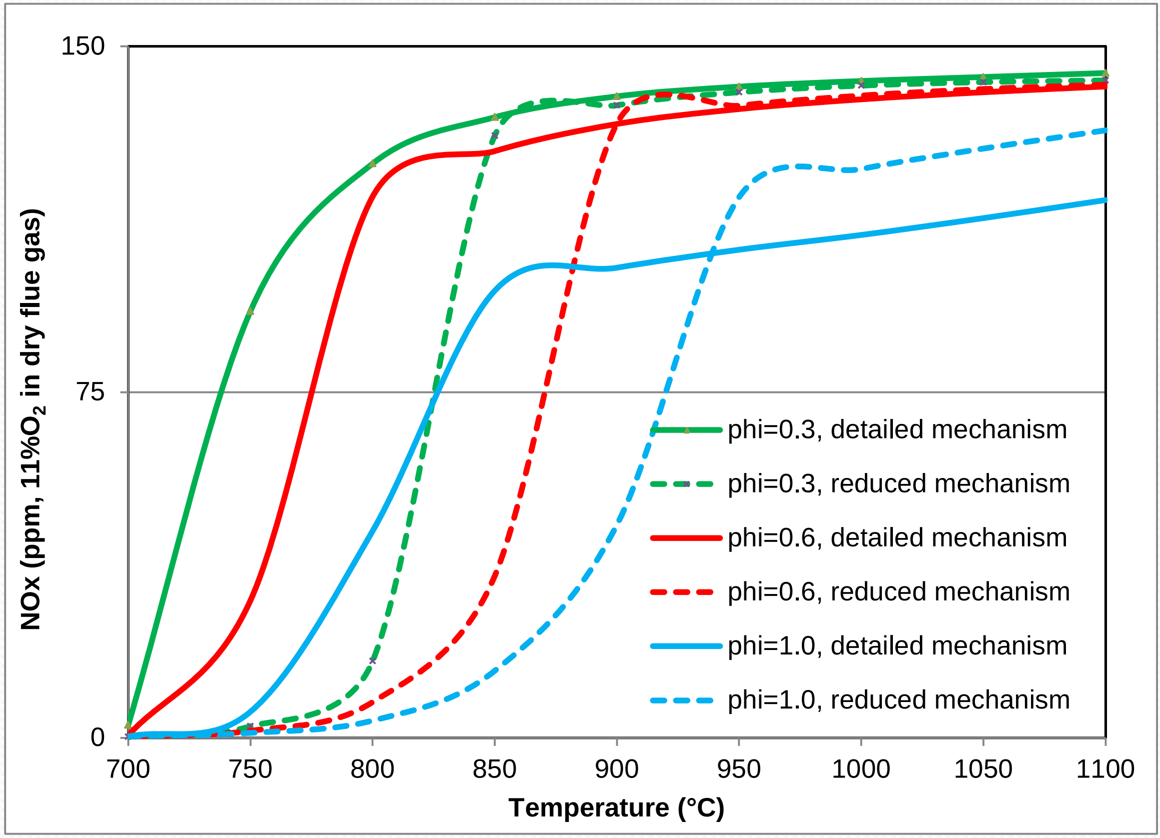
- NOx emission level, residence time=1 sec
- at temperatures above 780 °C, the reduced mechanism has an error range of less than 4%
- nitrogen conversion path for HCN is carried out through $CH_3CN/CH_2CN/CN$ in 700 °C, while these species are removed from the mechanism in the reduction procedure



Residence time=0.01 sec

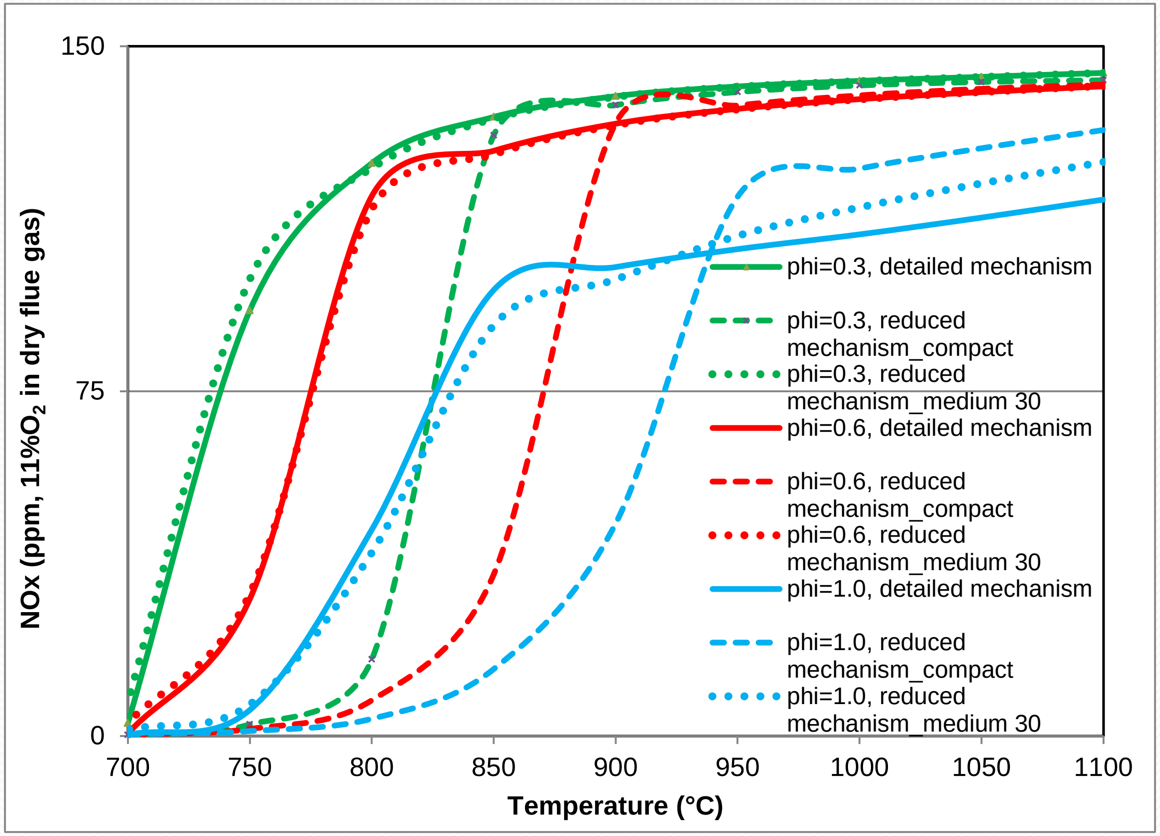
- NOx emission, residence time=0.01 sec

- At moderate and very fuel lean combustion the NOx level is well predicted by the compact mechanism (moderate and high temperatures)



Medium reduced mechanism

- Comparison of three mechanism; NOx emission at residence time=0.01 sec
- The <u>medium</u> reduced mechanism : 51 species
- >> if the lower temperature range, i.e. 700-850 °C, is important for any simulation, the highly reduced mechanism is not applicable



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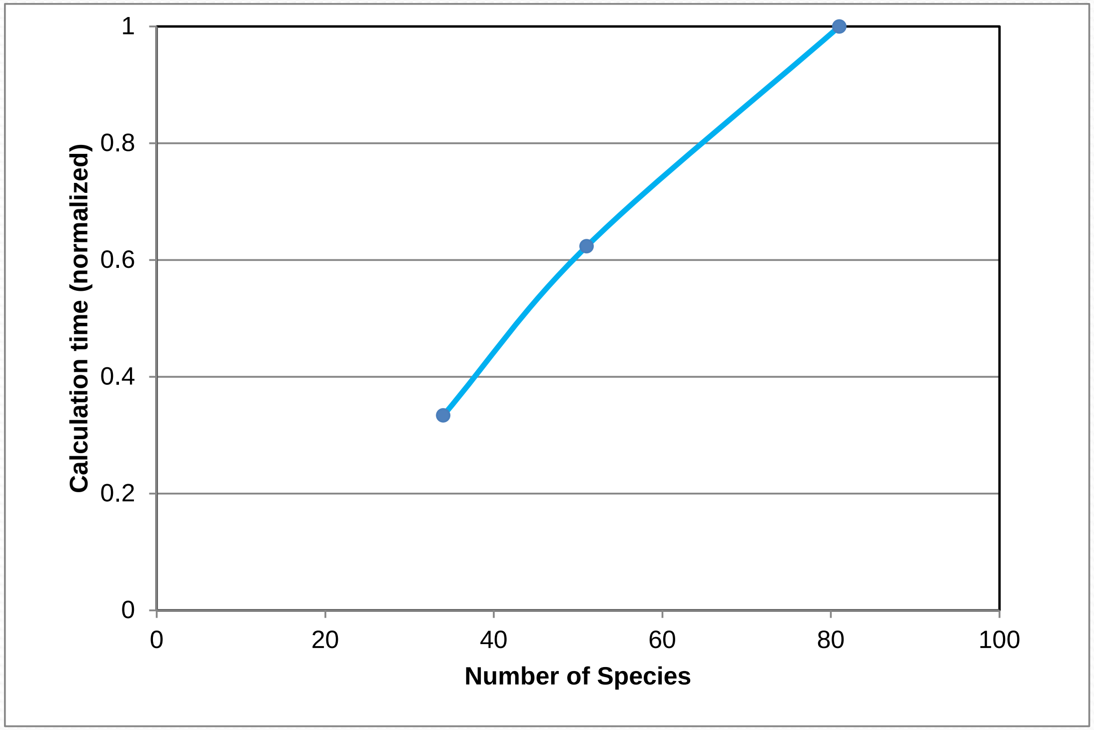
Computational time

- Comparison of three mechanism; computational time to perform analysis for a PSR

- The compact mechanism shows almost 70% reduction in the computational time for the single PSR



Conclusion

- A reduced mechanism has been developed for gas phase biomass combustion.
- The chemical kinetics mechanism for biomass combustion is very sensitive to the combustion conditions (temperature, excess air ratio, and residence time showed large effect on the NOx level).
- The reduced mechanism, as a result of necessity analysis, has 35 species and 198 reactions (compared with 81 species and 703 reactions in the detailed mechanism), which minimized the size of detailed mechanism by almost 70% corresponding to the same amount of reduction in the time needed for such modeling/simulation works.
- The reduced mechanism predicts concentrations of NOx very close to those of the complete mechanism in the range of reaction conditions of interest. Temperatures above 800 °C and excess air ratios of above 1.5 give acceptable NOx results corresponding to errors less than 10%, although the very low residence time conditions have more narrow satisfactory range.
- The medium reduced mechanism (51 species) predicts NOx very well
- The most reduced model was not able to capture the low temperature reactions of NOx formation, thereby underpredicting NOx concentrations at temperatures below 800 °C.

Thank you for your attention!