Modeling prompt NO formation: Impact of physical constraints to chemical pathways

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Overview

- Combustion of steel industry byproduct gasses – a case study in prompt NO formation
- Kinetic analysis
- Experimental results
- Why does model prediction differ form data (kinetic analysis revisited)

NOx Formation pathways

- Thermal NOx (Zeldovich)
  - Direct N_2 oxidation
  - High temperature required (> 1800 K)
- Prompt NOx (Fenimore)
  - $N \equiv N$ bond scission by flame radicals
  - Occurs only in flame fronts
- N_2O Pathway
  - Through $N_2 + O + M \rightarrow N_2O + M$
  - Relevant under elevated pressures
- Fuel NOx
  - NO formation from N-containing fuel fragments (CN, NH)
  - Relevant if fuel contains chemically-bound nitrogen

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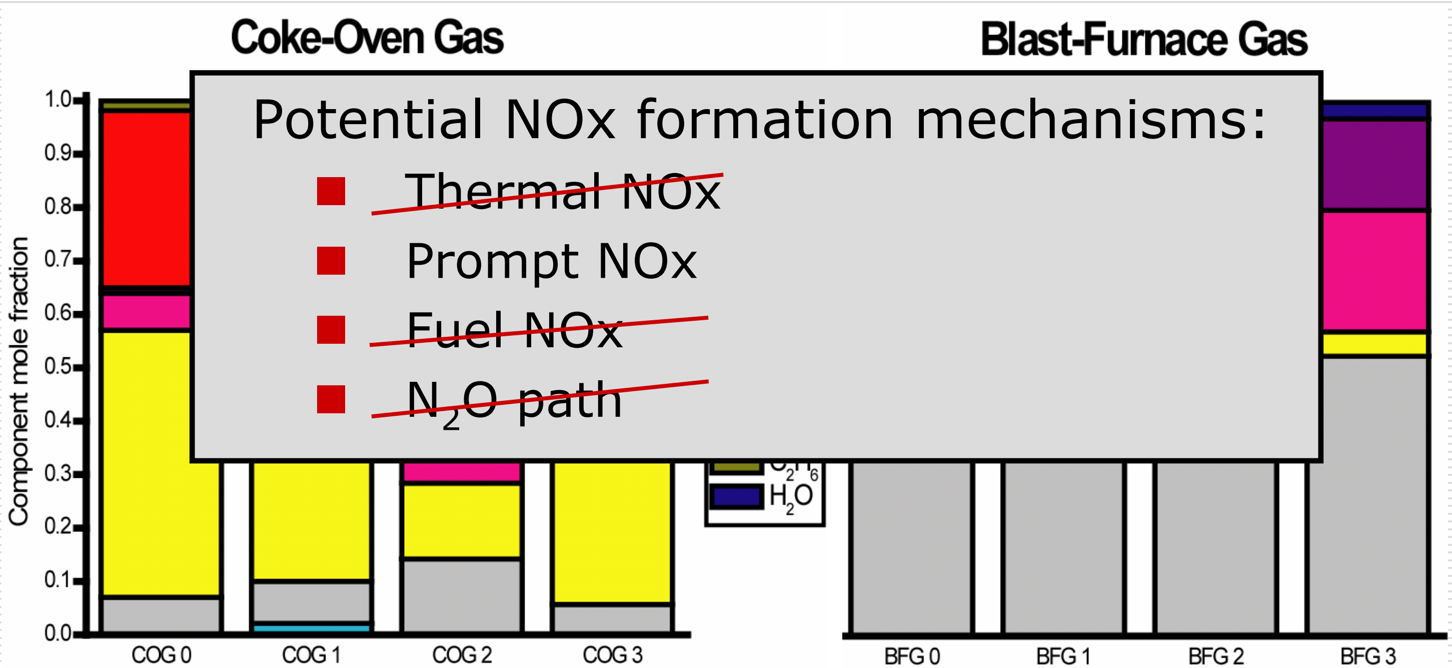
Case study:
NOx from steel-making by-product fuels

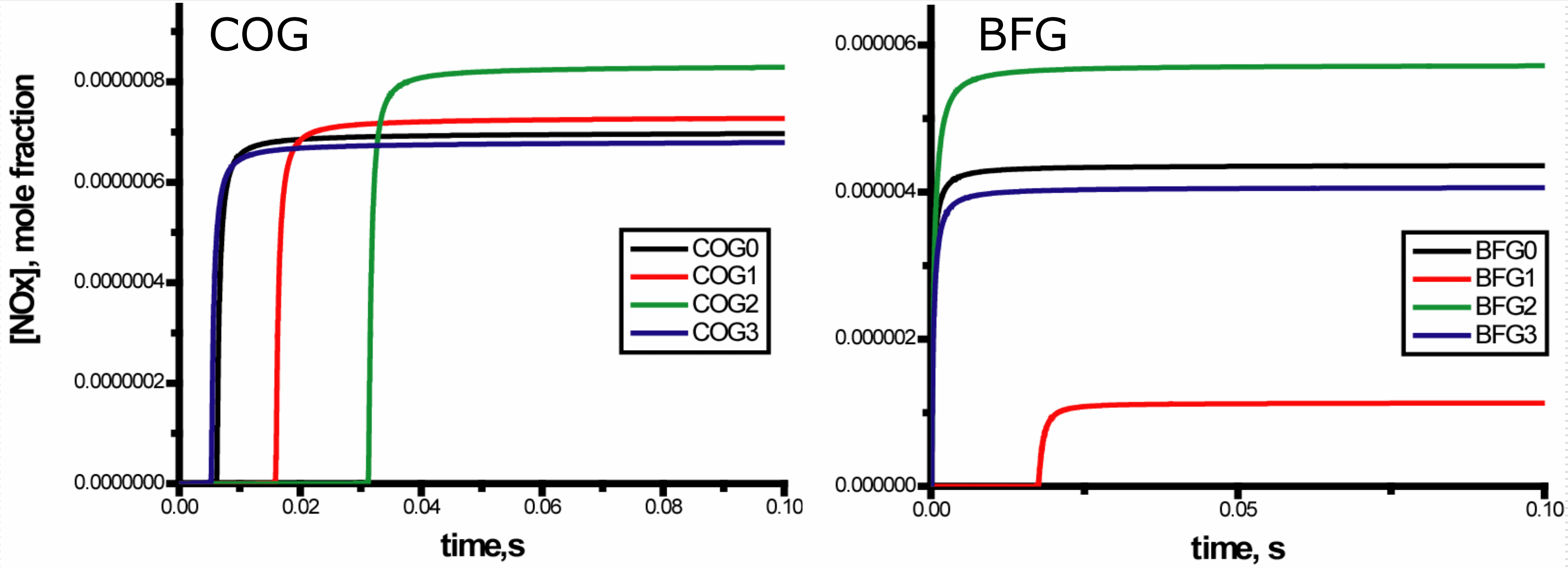
By-product fuels composition variability



Potential NOx formation mechanisms:

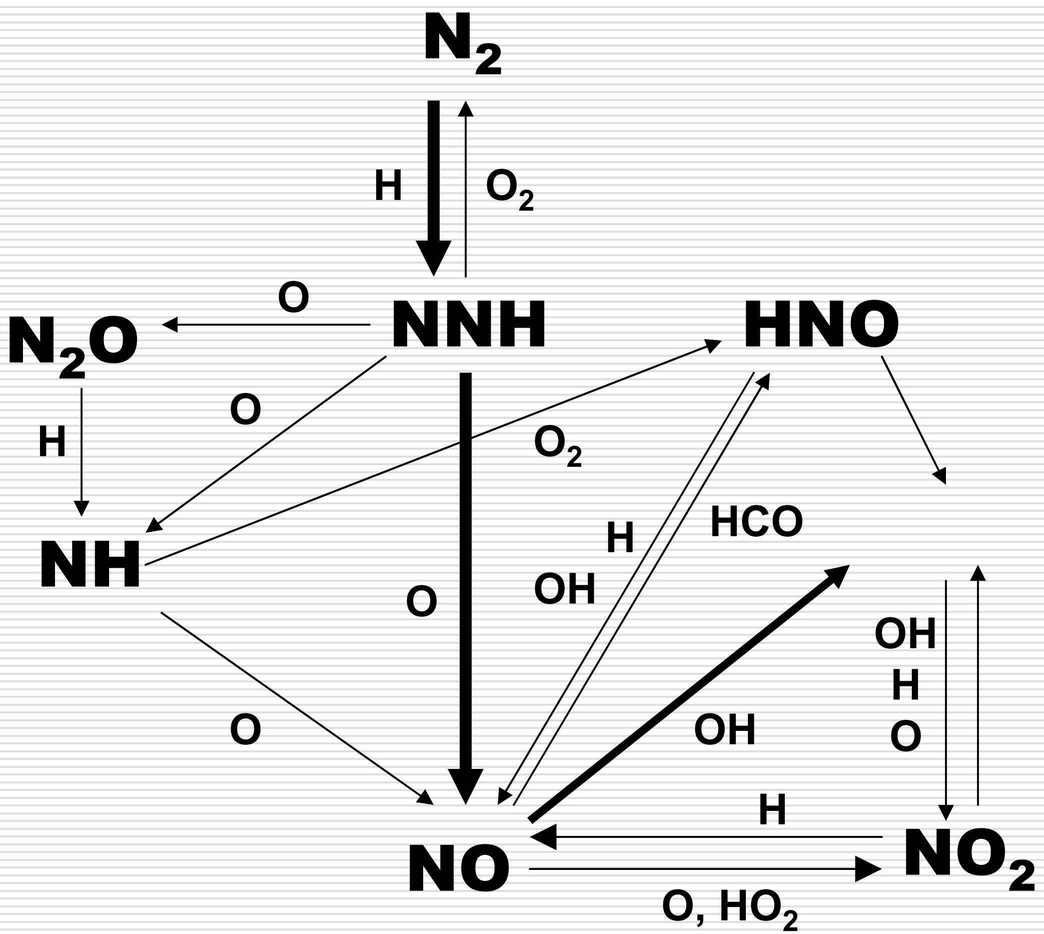
- ~~Thermal NOx~~
- Prompt NOx
- ~~Fuel NOx~~
- ~~N_2O path~~

Resulting NOx emissions variability



Predicted NO emissions for stoichiometric oxidation in plug-flow reactor at 1200 K and 1 atm

NOx formation pathway analysis



What about Fenimore's N_2+CH path?

- No N_2 + CH measurements were free of H atoms

- HCN is not the product of N_2 + CH
(Moskaleva and Lin, 2000)

- New calculations indicate:
  - Lower rate for N_2 + H
  - higher rate for N_2 + H

than currently accepted values

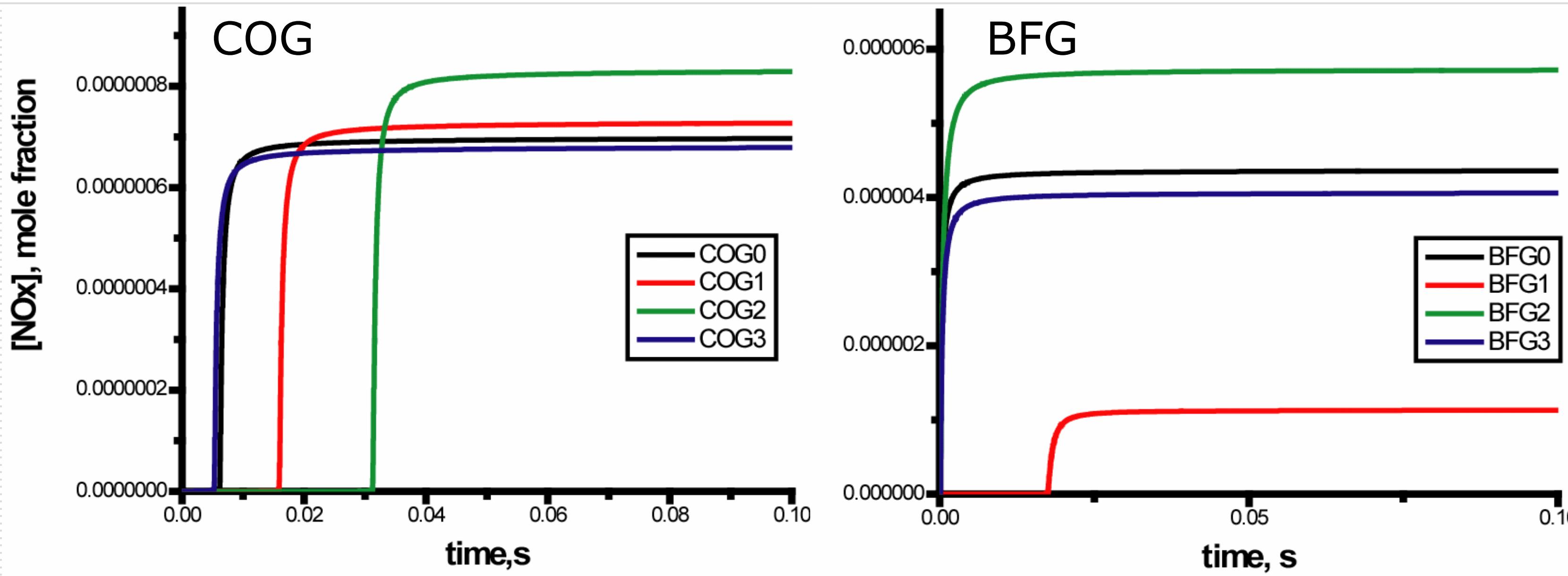
Prompt NOx control chemistry

- Initial step: $N_2 + H \rightarrow NNH$

  NNH oxidation to NO is relatively fast and easy

- Competing process: any H scavenging process
  - $CH_4 + H \rightarrow CH_3 + H_2$
  - $C_2H_6 + H \rightarrow C_2H_5 + H_2$
  - $C_2H_5 + H \rightarrow C_2H_4 + H_2$

Resulting NOx emissions variability



Predicted NO emissions for stoichiometric oxidation in plug-flow reactor at 1200 K and 1 atm

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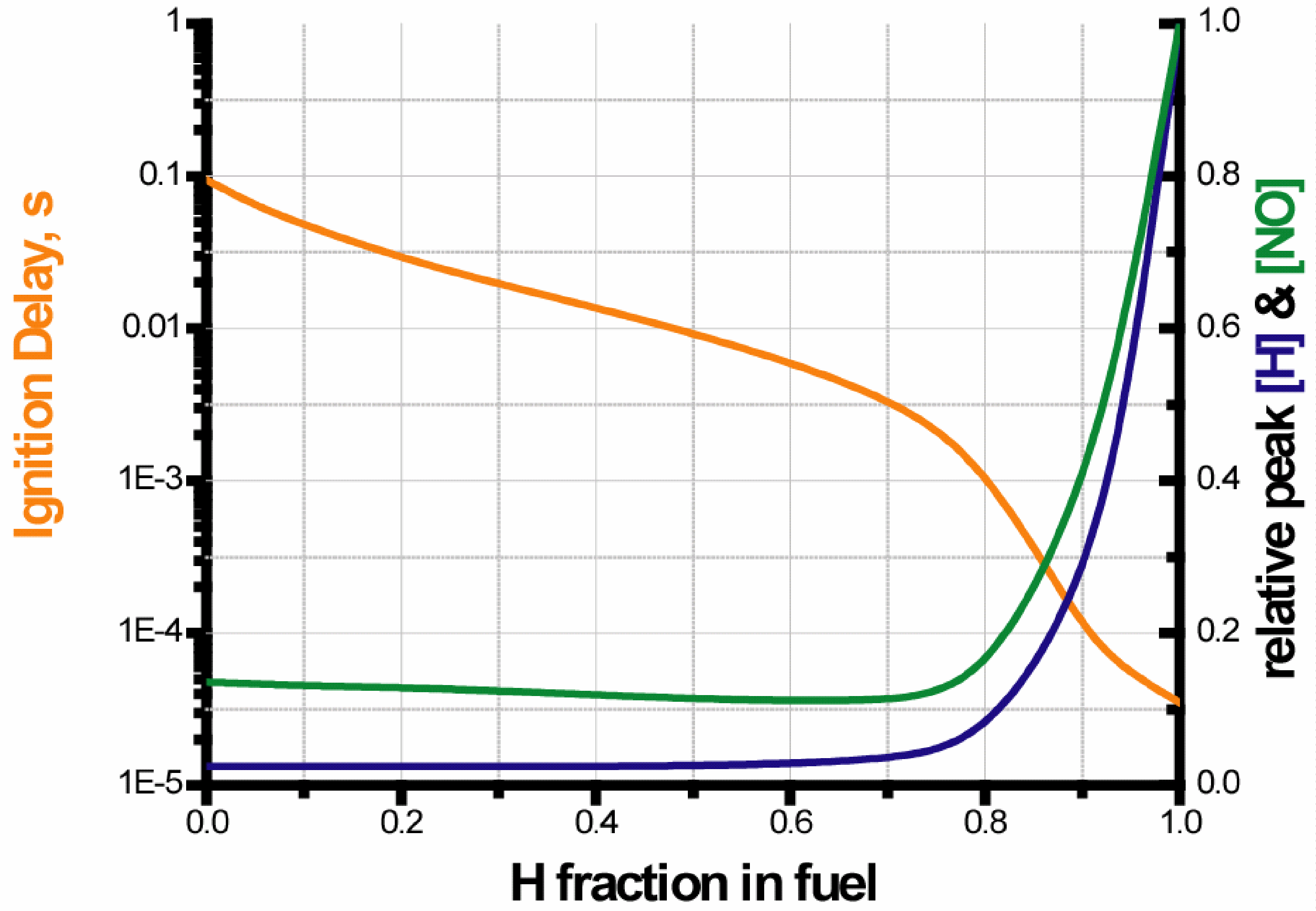
Minimizing NOx emissions from hydrogen-containing fuels



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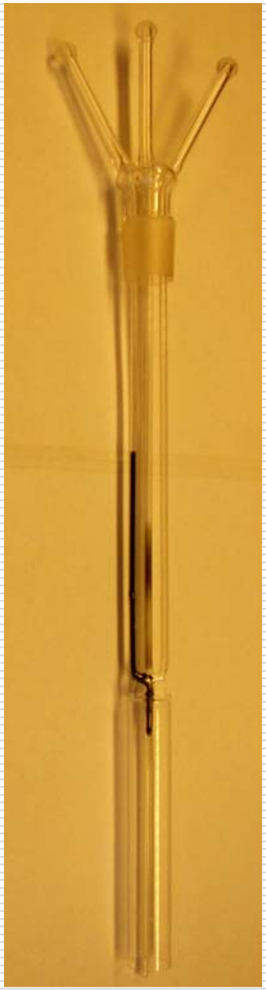
Experimental efforts

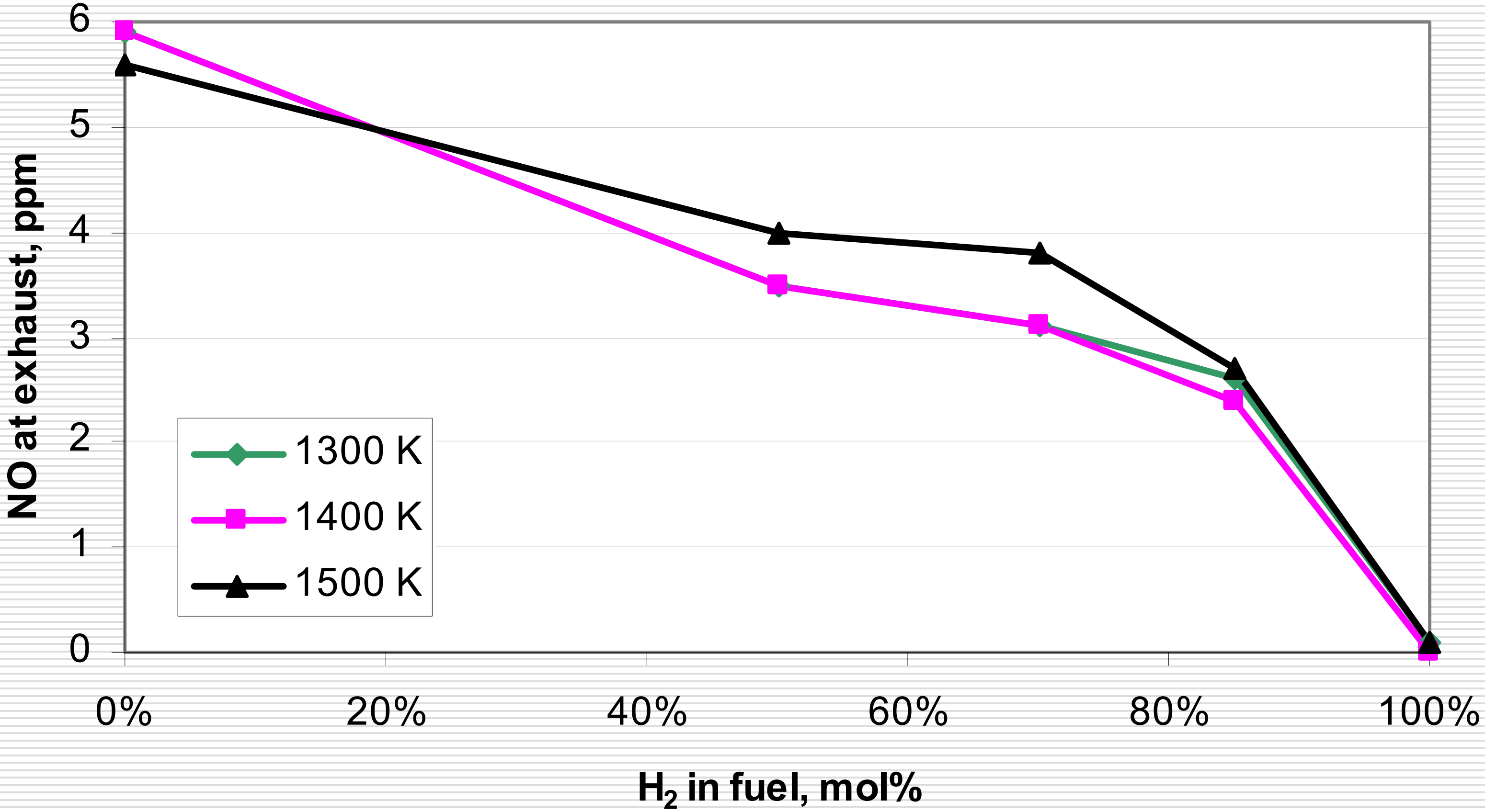


“Traditional” approach:
- preheat fuel components (CH_4, C_2H_6, H_2, CO) separately
- mix fuel components
- inject preheated fuel into N_2/O_2 stream

Problem:
- Mixing time 3-7 ms
- Ignition delay:2-10 ms

Solution:
- Premix cold gases, let them heat up together
  (drawback: some reactions may occur during heatup)

Experimental results



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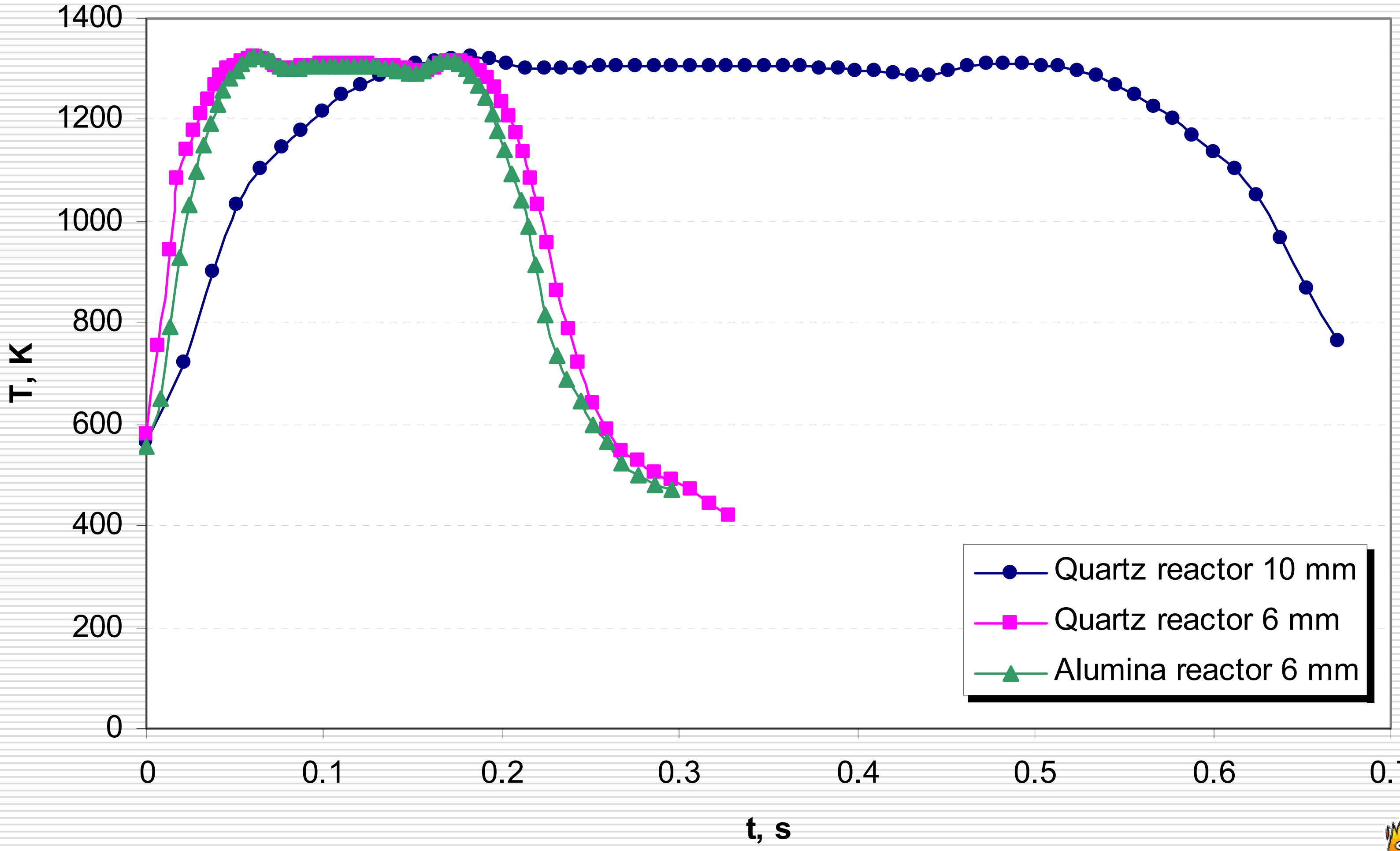
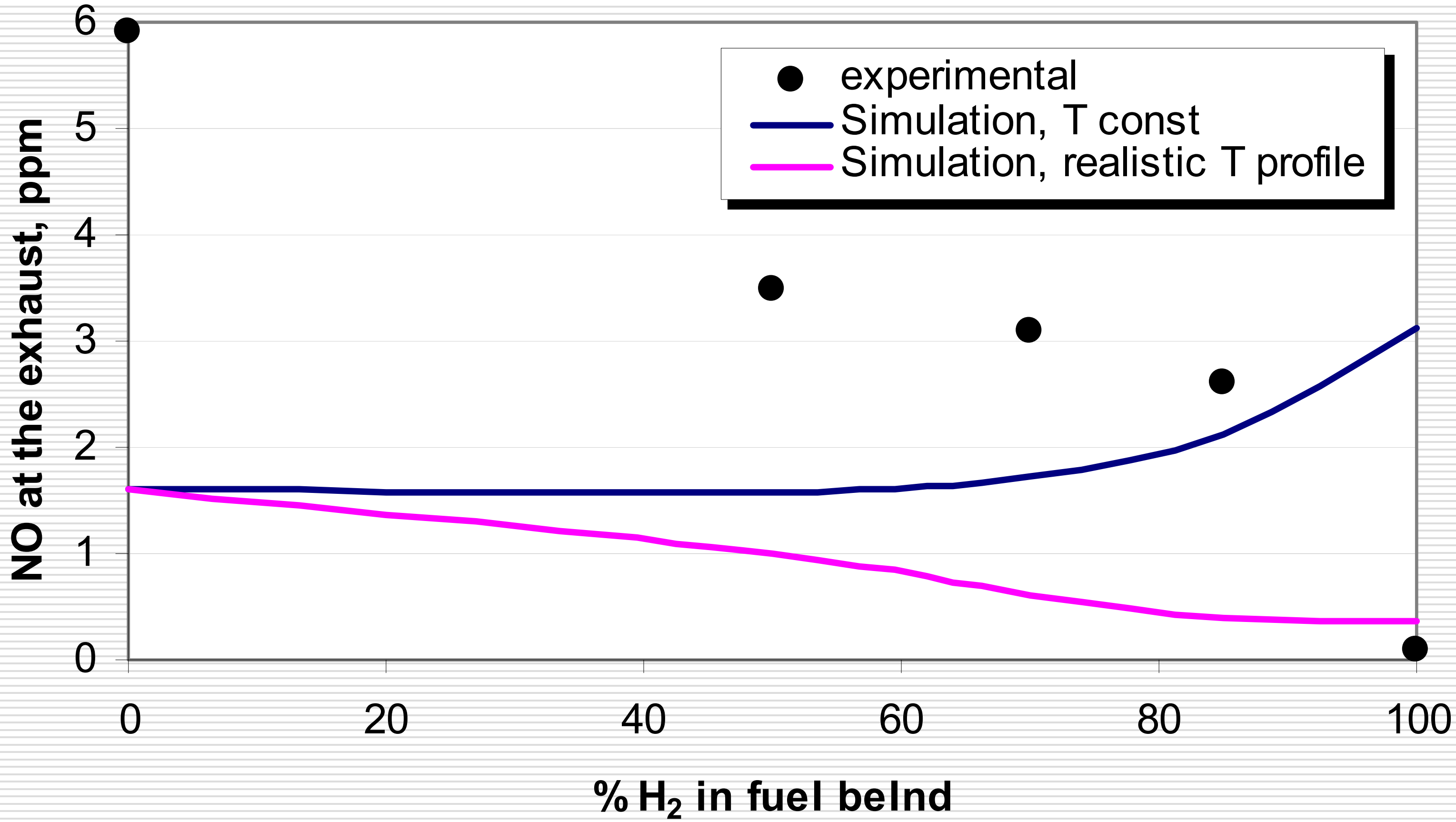
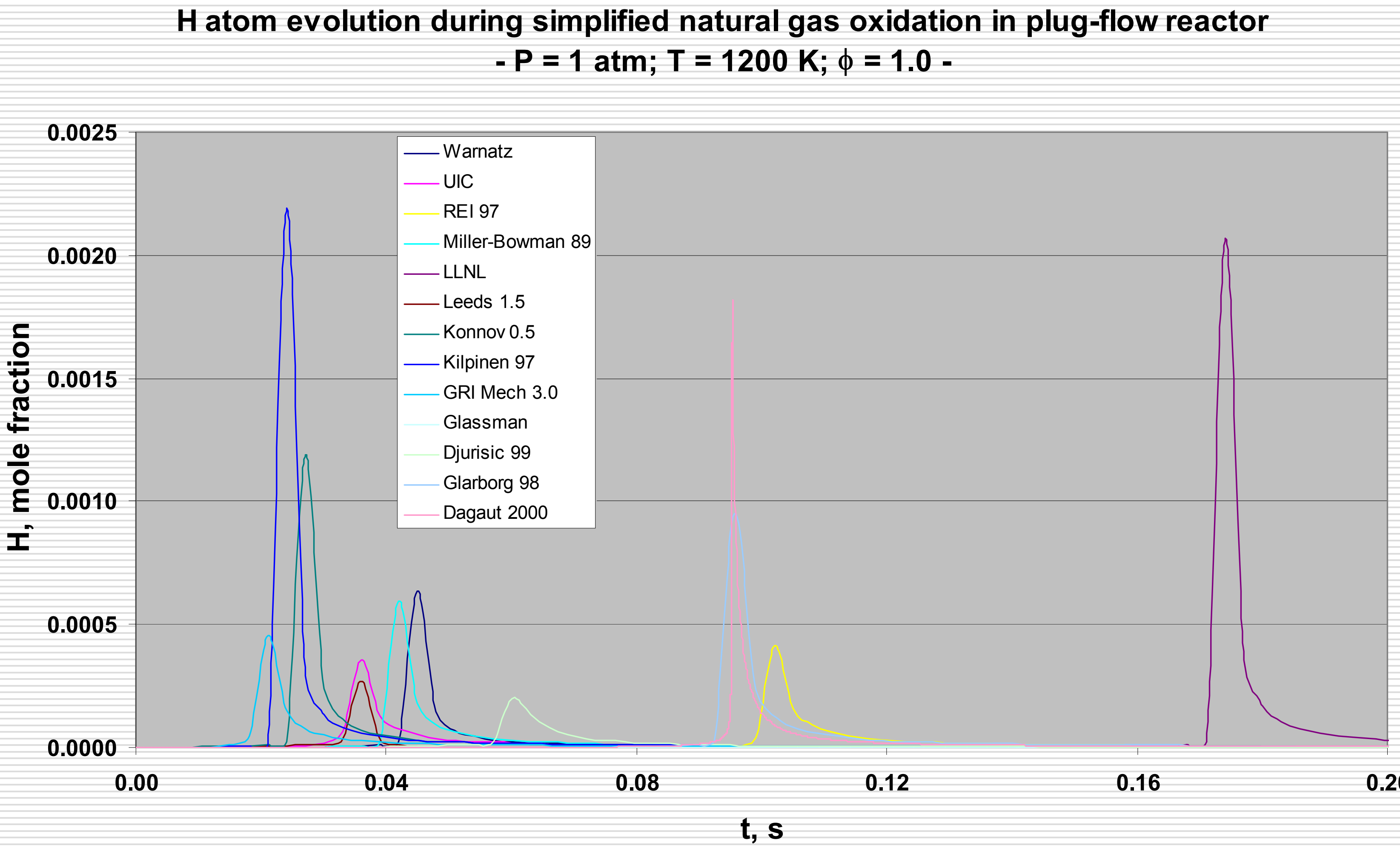
Experimental temperature profiles



Numerical simulations revisited



State of the art in understanding of H evolution



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Summary

- Prompt NO emissions in experiments appear to be independent on temperature
- In hydrogen-loaded fuels, accurate heatup modeling necessary
- N_2 + H is the dominant pathway to prompt NO formation
- Accurate modeling of H availability necessary for accurate prompt NO modeling

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