Department of Chemistry, Materials, and Chemical Engineering
Politecnico di Milano (Italy)

POLITECNICO DI MILANO





Alberto Cuoci

Numerical simulation of NOx formation in turbulent flames through the Kinetic Post-Processing (KPP) technique

Université Libre de Bruxelles

March 5th, 2014 – Bruxelles (Belgium)

Outline

1. The CRECK Modeling Group @ Politecnico di Milano
2. Introduction
3. The Kinetic Post Processing (KPP) Technique for NOx
   - ✓ Kinetic mechanisms for CFD applications
   - ✓ Reactor networks from CFD
   - ✓ Effects of temperature fluctuations on NOx formation
   - ✓ Solution of reactor networks
4. Applications to lab-scale and industrial flames
   - ✓ Lab-scale flames
   - ✓ Industrial cases
5. Extension to other pollutants
6. Conclusions

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The CRECK Modeling Group

People

Full Professors

Eliseo Ranzi

Tiziano Faravelli

Assistant Professors

Alessio Frassoldati

Alberto Cuoci

PhD Students

Mattia Bissoli

Matteo Pelucchi

Chiara Saggese

Alessandro Stagni

Giancarlo Gentile

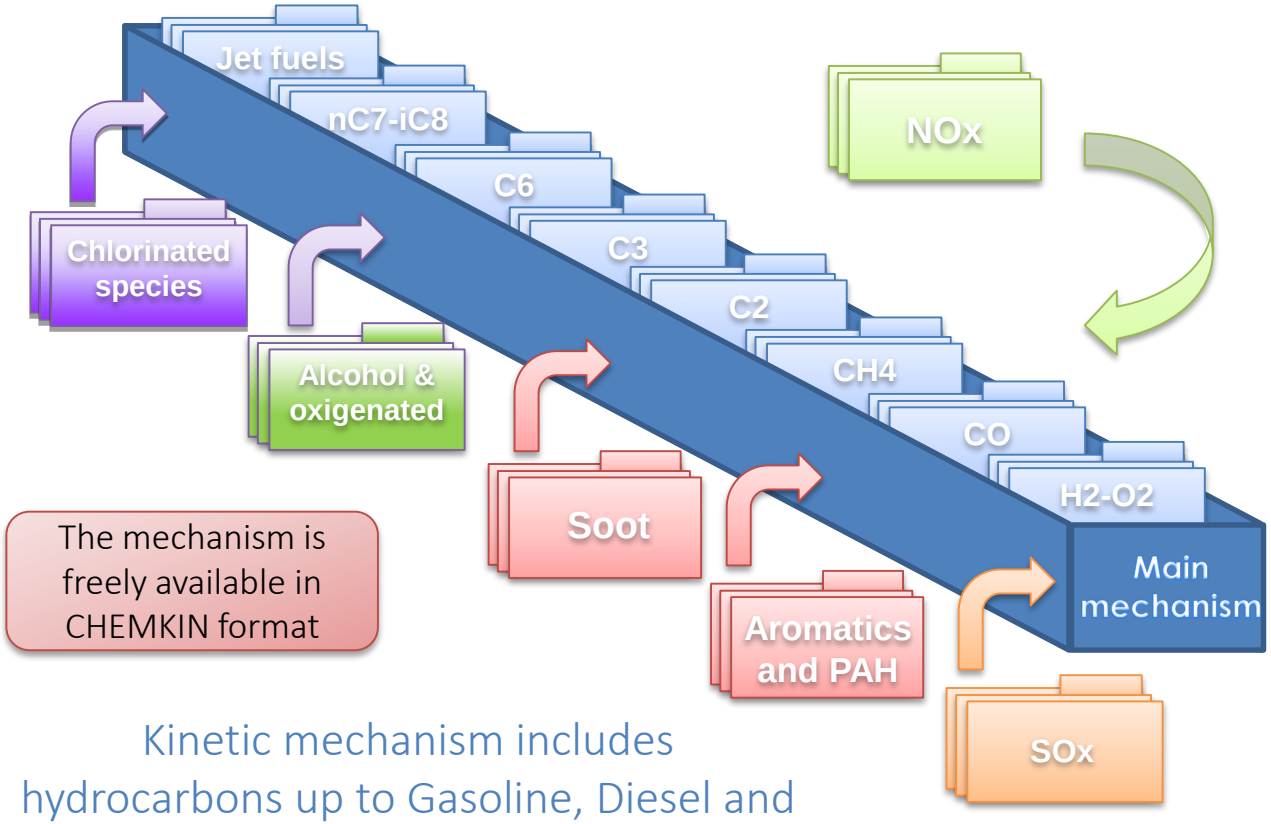
Paulo De Biagi

Permanent Staff

Dipartimento di Chimica, Materiali e Ingegneria Chimica *"Giulio Natta"*
Politecnico di Milano

http://creckmodeling.chem.polimi.it/

Detailed kinetic mechanism



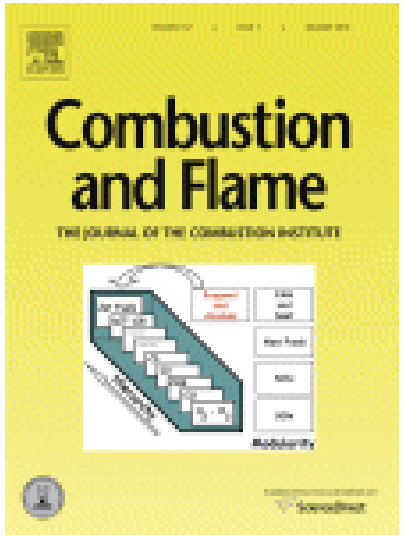
The mechanism is freely available in CHEMKIN format

Kinetic mechanism includes hydrocarbons up to Gasoline, Diesel and jet fuels, as well as several pollutants

- Hierarchy
- Modularity
- Generality

~ 500 species

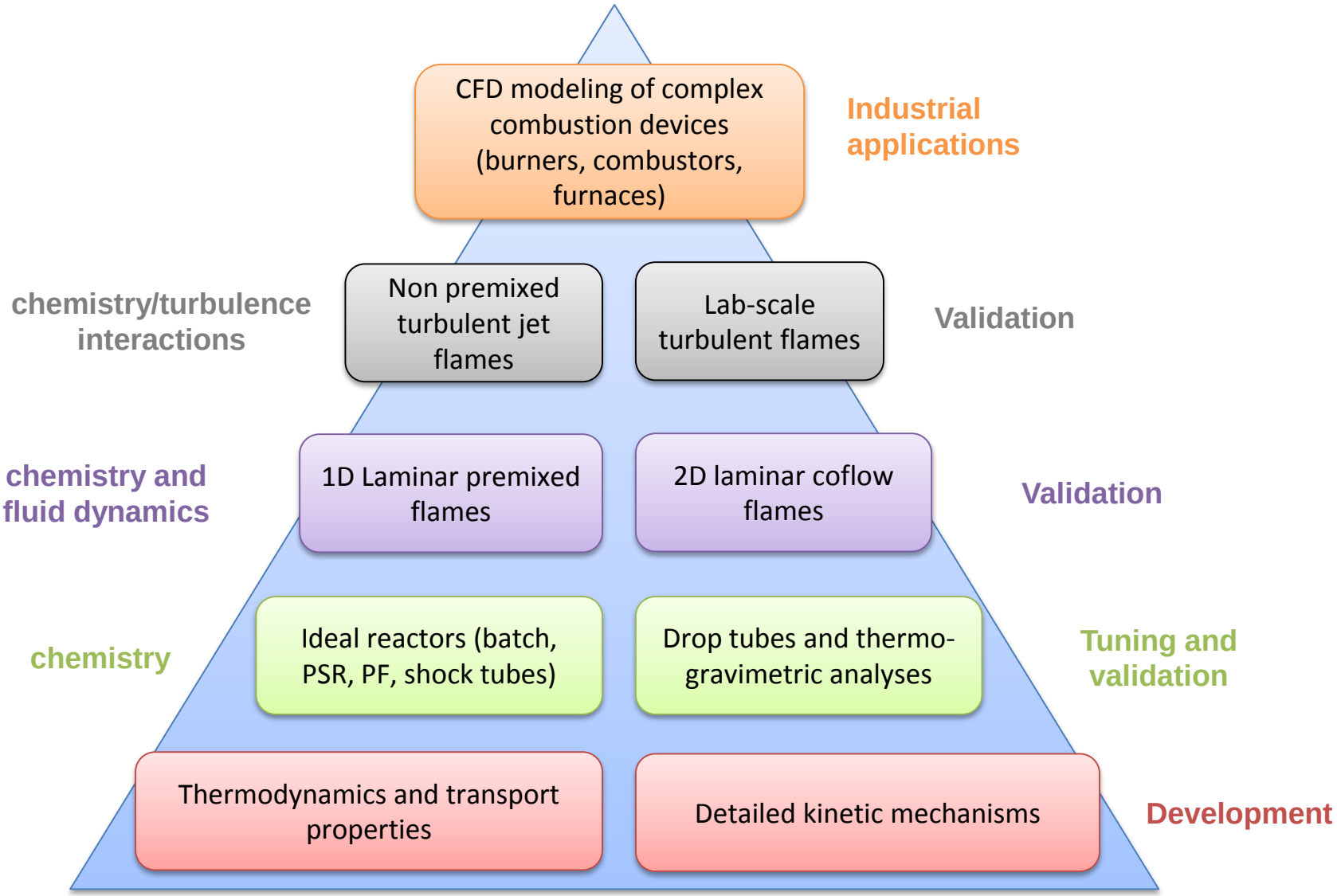
~ 15,000 reactions



A. Frassoldati, A. Cuoci, Faravelli T., Niemann U., Ranzi E., Seiser K., Seshadri K., Combustion and Flame 157(1), 2-16 (2010)

Ranzi, E., Frassoldati, A., Grana, R., Cuoci, A., Faravelli, T., Kelley, A.P., Law, C.K, Progress in Energy and Combustion Science, 38 (4), pp. 468-501 (2012)

From molecules to furnaces

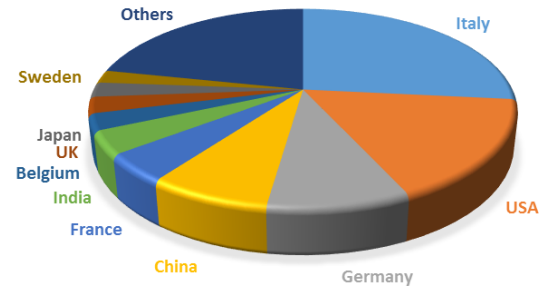


The CRECK Modeling Group on the web

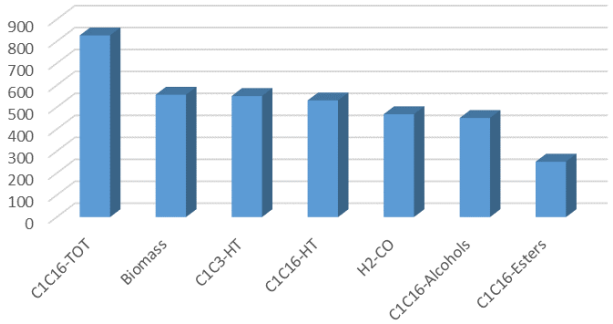
The kinetic schemes can be freely downloaded in CHEMKIN format from our web site:

http://creckmodeling.chem.polimi.it/

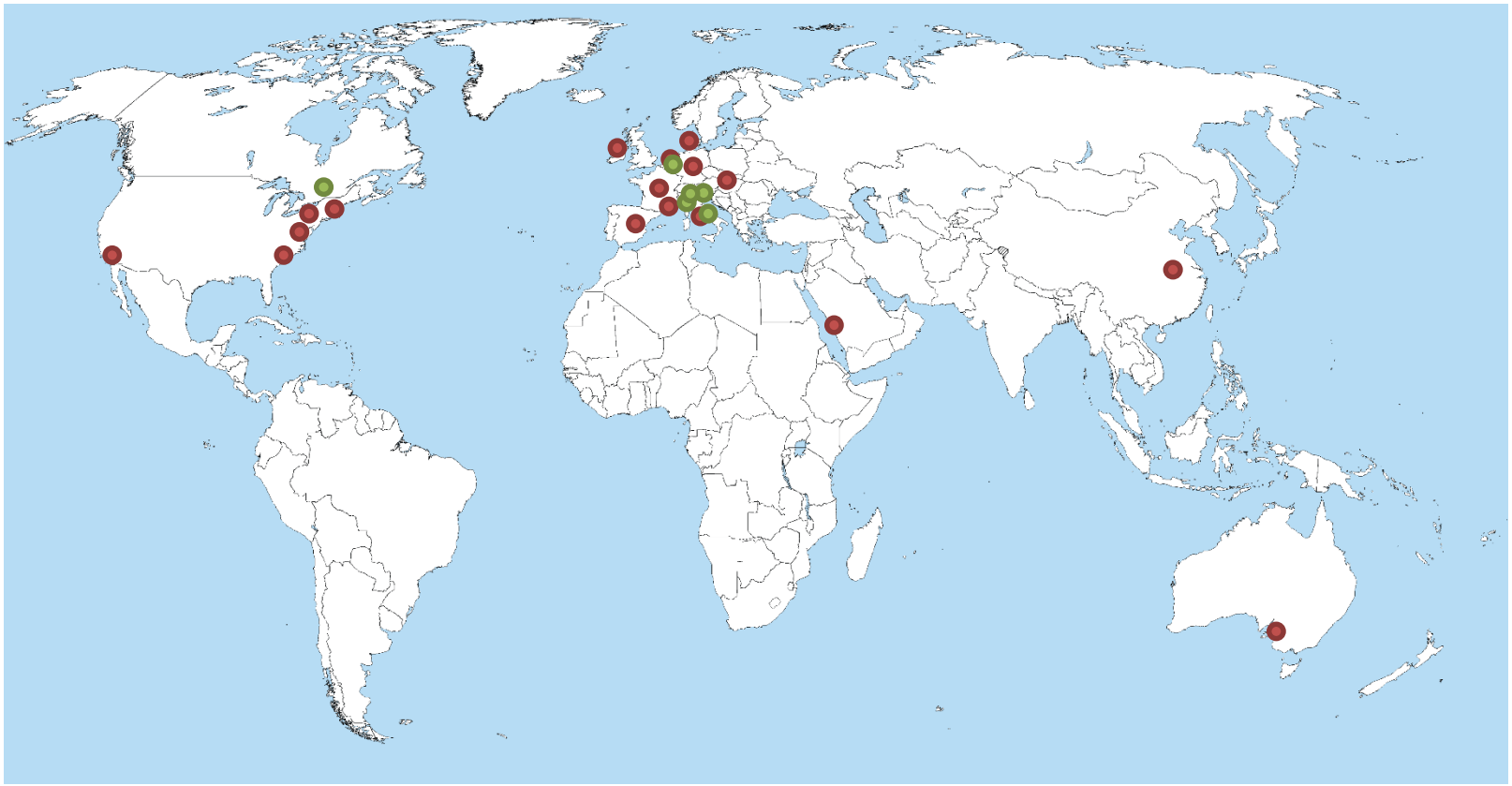
Statistics since January 2013
Unique visitors: 9,600
Visits: 12,000 (~28 per day)
Visits from 97 countries



The kinetic schemes were downloaded more than 3,600 times since Jan 2013



Academic and Industrial Collaborations



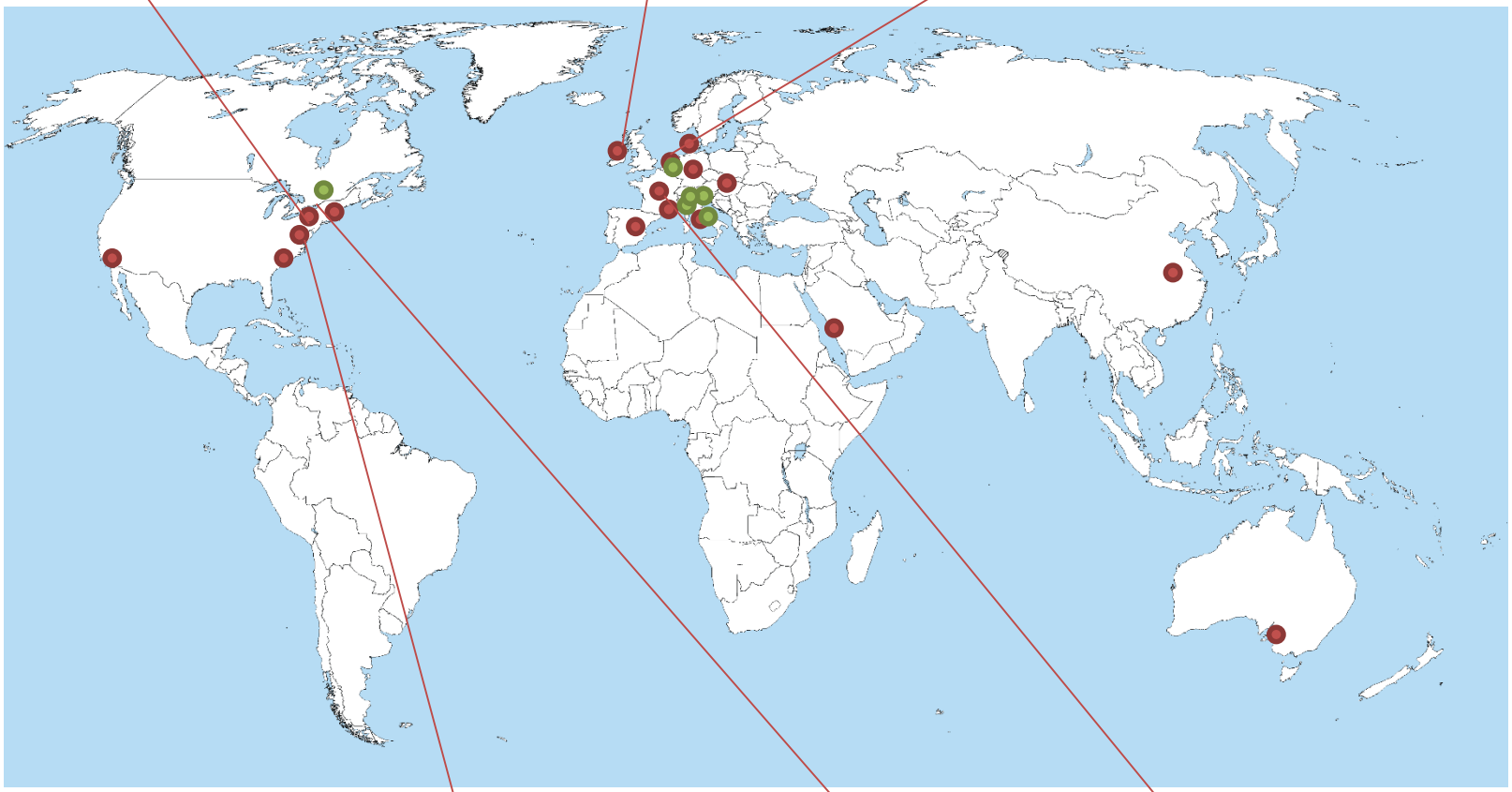
Academic Industrial

Academic collaborations (I)

Rensselaer Polytechnic Institute
M. Oehlschlaeger
Decalin ignition

University of Galway
H. Curran
Oxygenated fuels

Université Libre de Bruxelles
A. Parente
Reduction of kinetic mechanisms



University of Yale
S. Gomez
Kinetics of real fuels

Northeastern University
Y.A. Levendis
Coal

CNRS Orléans
P. Dagaut
Large fuels

Academic collaborations (II)

University of San Diego
K. Seshadri, F.A. Williams
Kinetics of real fuels
Droplet combustion

North Carolina University
P. Westmoreland
Alcohol kinetics

DTU
P. Glarborg
Kinetics of bromine and chlorine

University of Princeton
C.K. Law
Flame speeds

Cornell University
B. Fischer
Biomass kinetics

University of Zaragoza
M. Alzueta
Soot

Academic collaborations (III)

University of Bielefeld
K. Kohse-Höinghaus
Alcohols kinetics

University of Ostrava
V. Nevrly
Pulsating flames

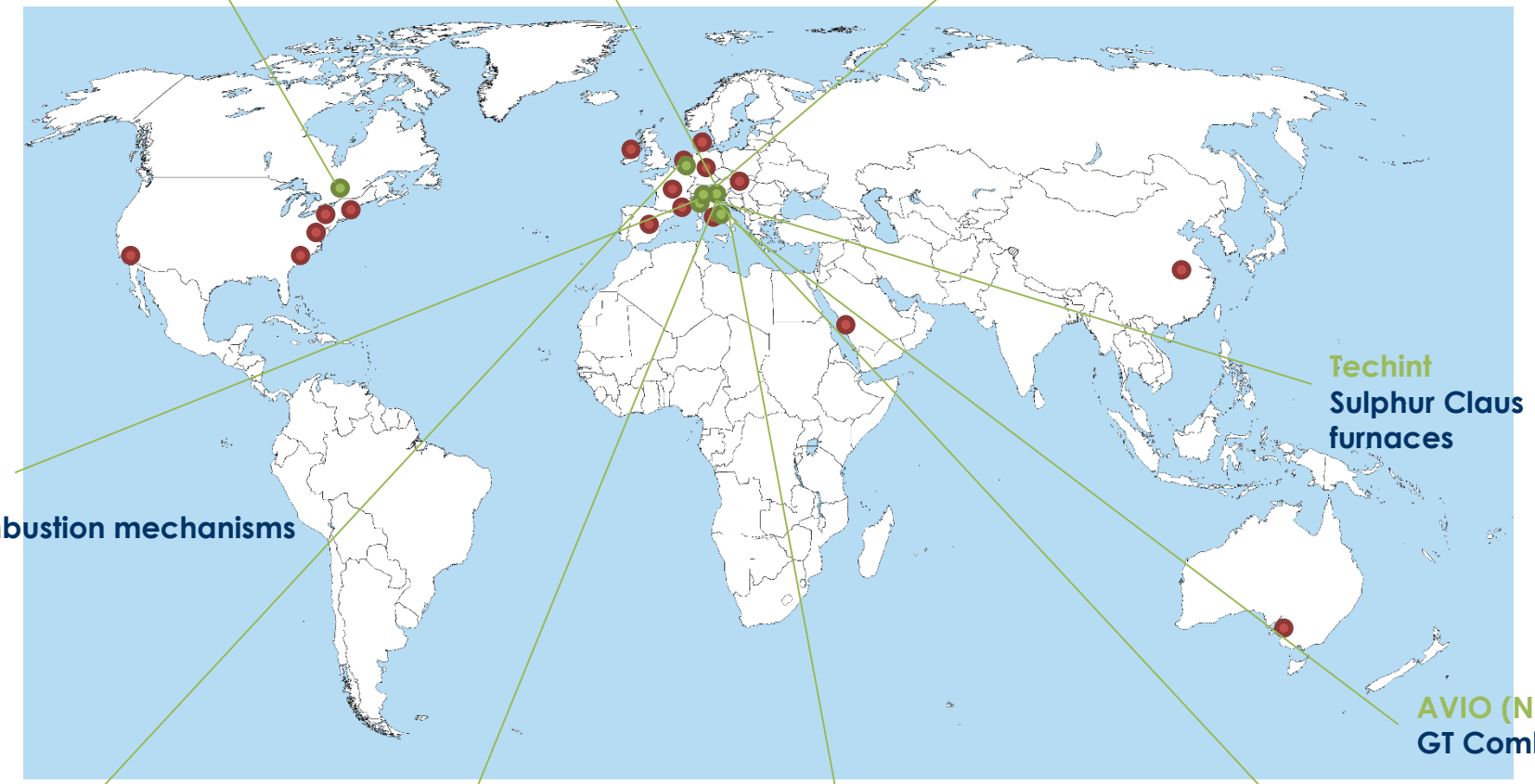
University of Hefei
F. Qi
Laminar, coflow flames

University of Nancy
F. Battin-Leclerc
Kinetics of large methyl-esters

KAUST University
M. Sarathy
PRIME Project

University of Adelaide
P. Medwell
MILD combustion

Industrial collaborations



Rolls-Royce Canada
NOx modeling

Danieli
Industrial burners (flameless)

MORE
Oxy-combustion burners and NOx

Techint
Sulphur Claus furnaces

CSM
Combustion mechanisms

AVIO (Napoli)
GT Combustors

Technip
NOX from furnaces

Agusta-Westland
NOX from helicopters

Riello
Domestic burners

ENGITEC
Oxy-combustion

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Reduction of pollutant emissions (I)

Increasingly stringent regulations for pollutant emissions in furnaces, power plants, gas turbines, burners etc.

Pollutant	Health Effect
CO – **Carbon Monoxide**	• Cardiovascular effects, especially in those persons with heart conditions
HC – **Unburned Hydrocarbons** (a primary component of Volatile Organic Compounds, or VOC)	• Eye and respiratory tract infection • Headaches • Dizziness • Visual disorders • Memory impairment
NO_x – **Nitrogen Oxides**	• Lung irritation • Lower resistance to respiratory infections
PM – **Particulate Matter** (smoke is a primary component of PM.)	• Premature mortality • Aggravation of respiratory and cardiovascular disease • Changes in lung function • Increased respiratory symptoms • Changes to lung tissues and structure • Altered respiratory defence mechanisms

Reduction of pollutant emissions (II)

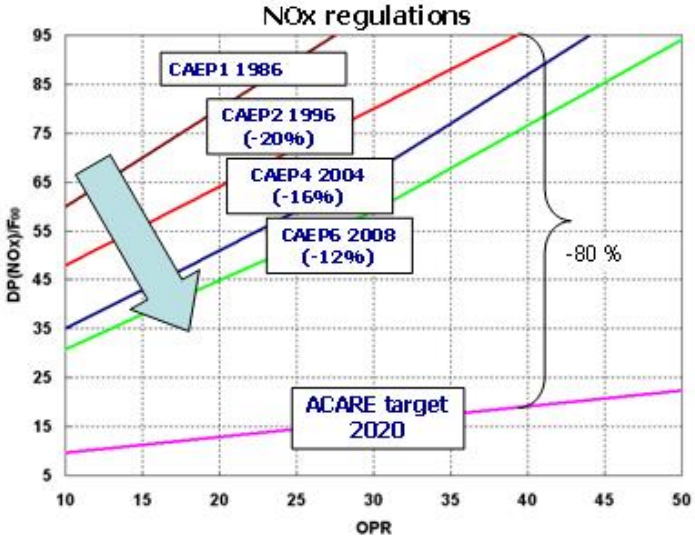
Environmental Targets for 2020*

Reduce noise by 50%

Reduce NOx emissions by 80%

The ACARE targets represent a doubling of the historical rate of improvement...

Reduce fuel consumption and CO_2 emissions by 50%

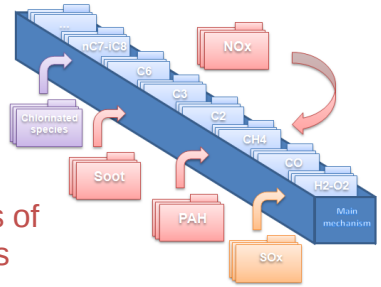


Advisory Council for Aeronautics Research in Europe.
Targets are relative to year 2000

Coupling detailed kinetics and complex CFD

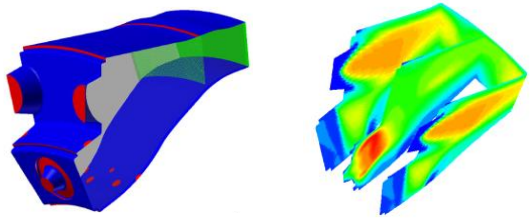
Combustion is a complex process that involves hundreds of species and thousands of chemical reactions.

Detailed kinetic schemes



hundreds of species

CFD simulations



millions of computational cells

Jet fuels and surrogate mixtures

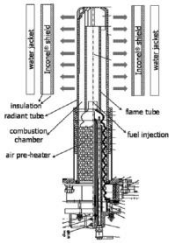
need of modeling synergistic effects between the different components

Biofuels

bioalcohols, biodiesel, green diesel, bioethers

Oxyfuel combustion

need of including radical species (O, H, OH, etc.)

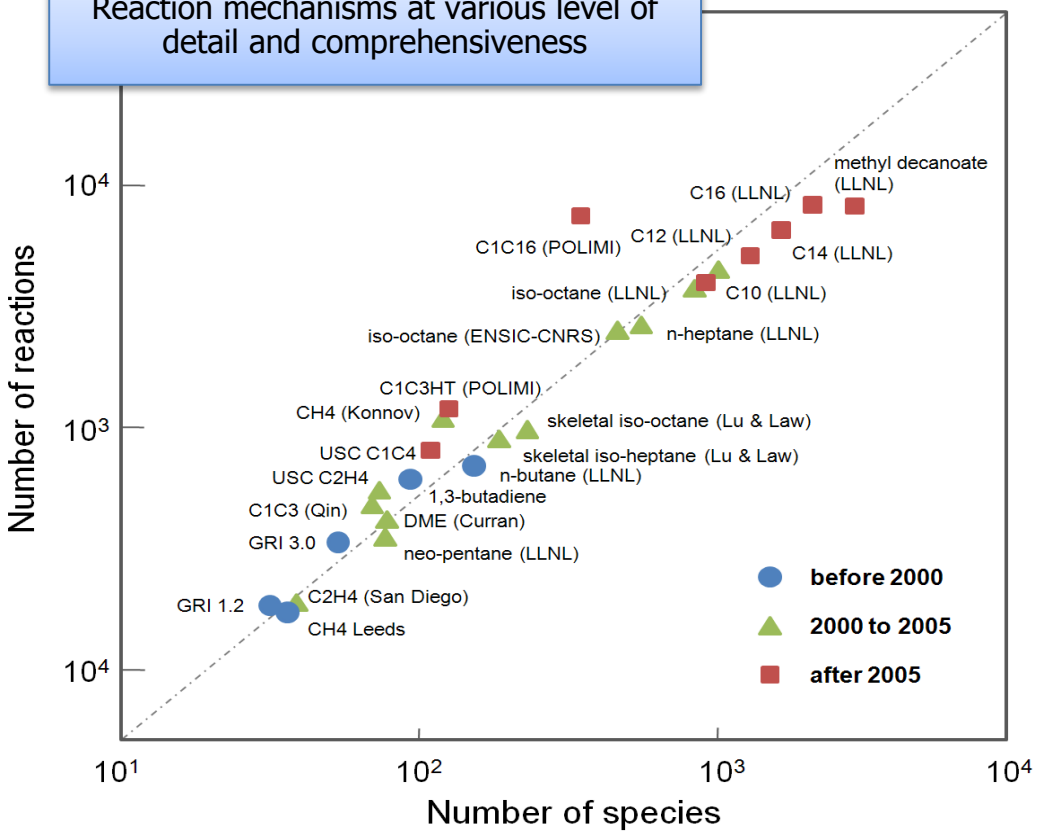


Flameless combustion

(low Damkholer number, slow chemistry)

Detailed kinetic mechanisms

Reaction mechanisms at various level of detail and comprehensiveness



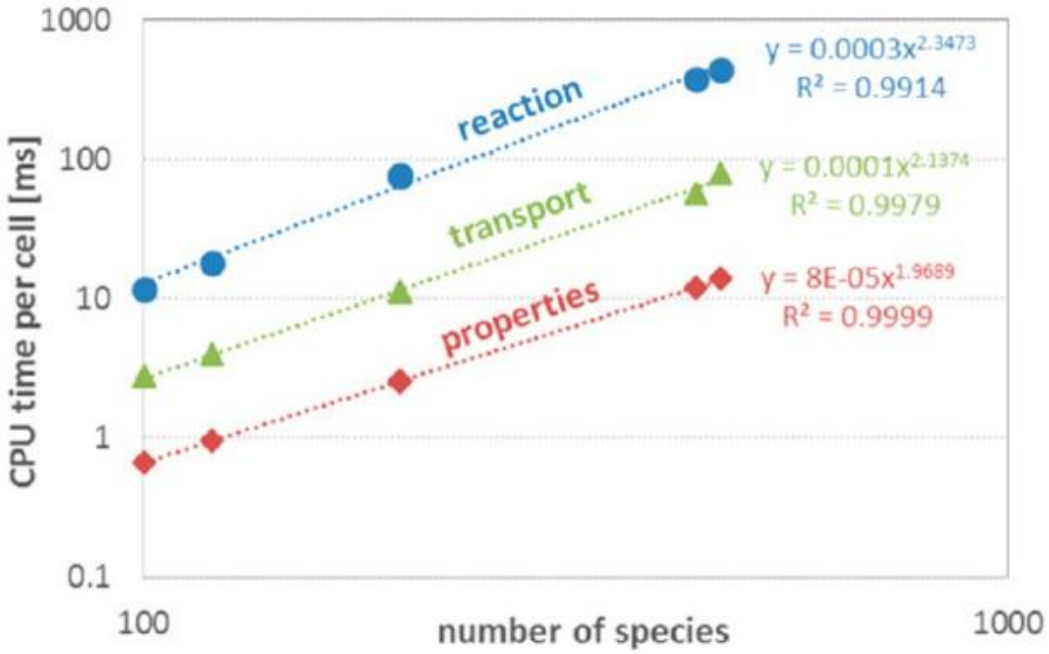
Adapted from:
***T.F. Lu, C.K. Law**, Prog. Energy Comb. Sci., 35 (2009)*

increasing effort to incorporate **more complex reaction mechanisms** in simulation of combustion processes and this has led to the development of reaction mechanisms with different levels of detail and comprehensiveness

computational cost associated with such mechanisms is usually very high

need of **computational tools** to make computationally efficient the management of large kinetic schemes and easy their **integration** in new and/or existing numerical codes

Computational cost of kinetics



Simulation of laminar, coflow flames fed with ethylene (2D, structured grid, in-house code)

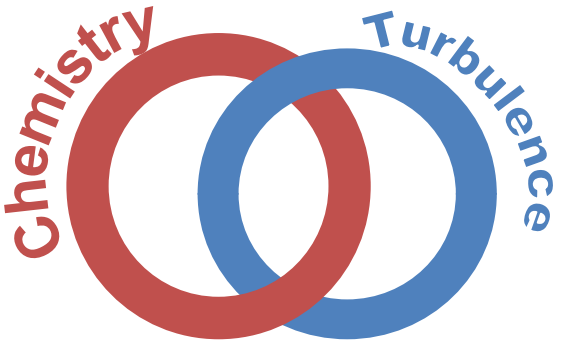
Usually the computational cost of multi-dimensional CFD simulations increases **more than quadratically** with respect to the number of species

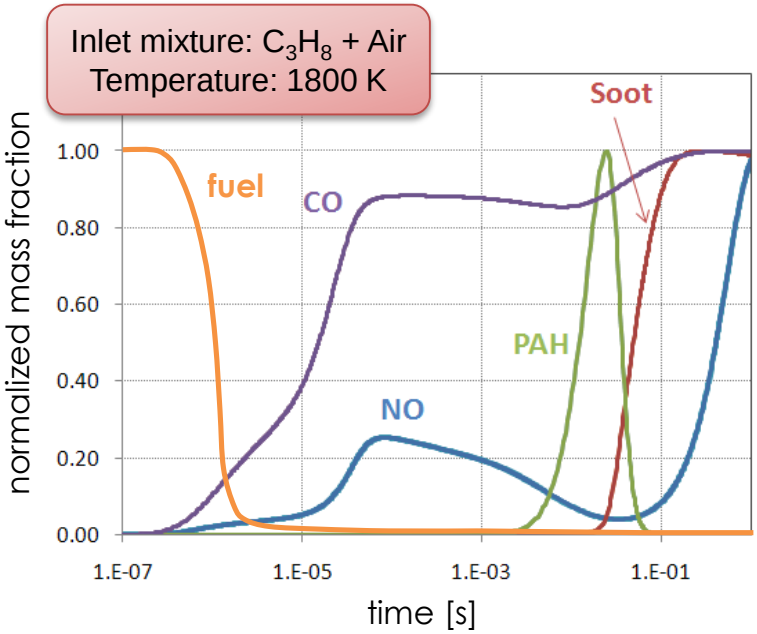
$$C \approx N^{2.5}$$

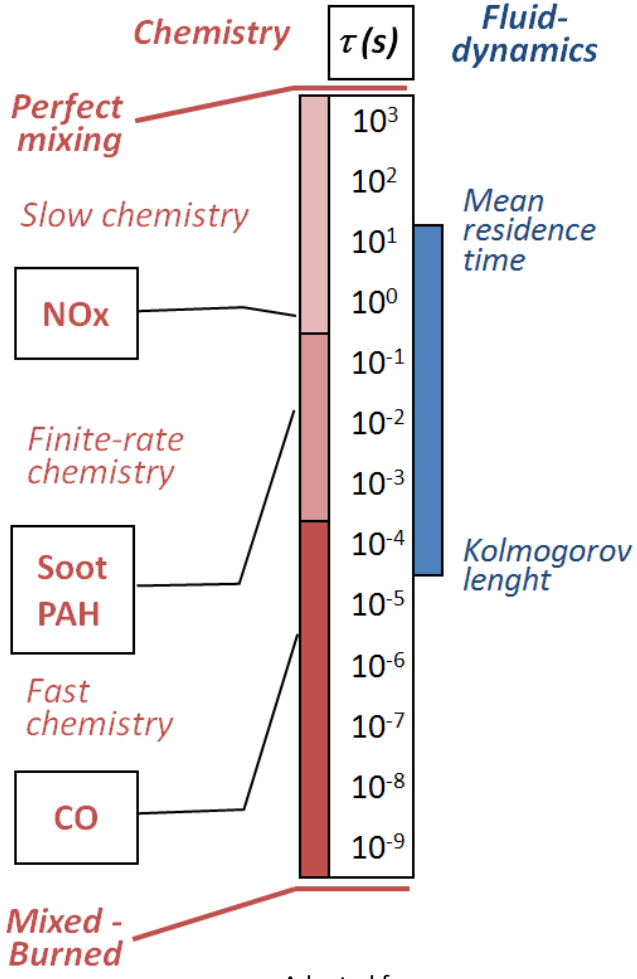
Cuoci, A. Frassoldati, T. Faravelli, E. Ranzi, "Numerical Modeling of Laminar Flames with Detailed Kinetics Based on the Operator-Splitting Method", Energy & Fuels, 27 (12), p. 7730-7753 (2013), DOI: 10.1021/ef4016334

Coupling between turbulence and chemistry

Strong coupling between chemistry and turbulence in combustion processes







Adapted from:
R. Fox, *"Computational models for turbulent reacting flows"*, Cambridge University Press (2002)

Coupling detailed kinetics and complex CFD

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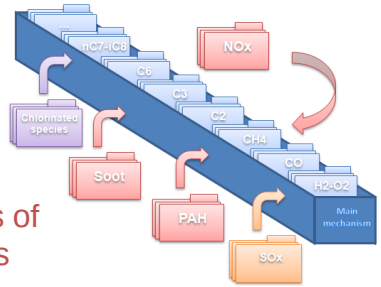
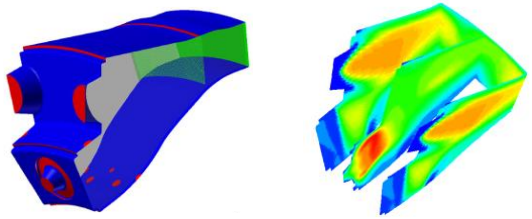
Detailed kinetic schemes



hundreds of species

CFD simulations



millions of computational cells

Jet fuels and surrogate mixtures

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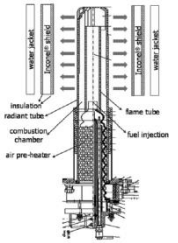
Flameless combustion

(low Damkholer number, slow chemistry)

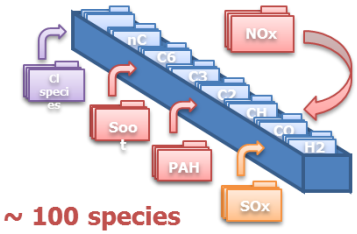


Segregated vs Coupled Algorithms

Fully segregated algorithms

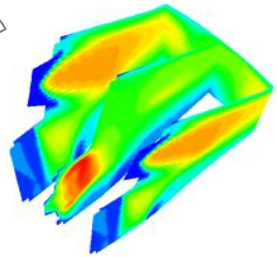
☺ easy to implement and computationally efficient
☹ unfeasible when large, stiff kinetic mechanisms are used

Detailed kinetic schemes



~ 100 species
~ 1000 reactions

Complex geometries



Strong non linearity of reaction terms
High stiffness

Fully coupled algorithms

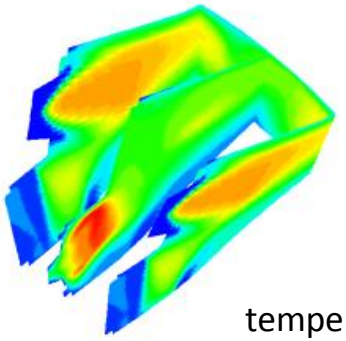
☺ all the processes and their interactions are considered simultaneously
☺ natural way to treat problems with multiple stiff processes
☹ the resulting system of equations can be extremely large and the computational cost prohibitive

Operator-splitting methods

☺ usually avoid many costly matrix operations
☺ allow the best numerical method to be used for each type of term or process
☹ the resulting algorithms can be very complex and usually differ from term to term

The Kinetic Post Processing technique

CFD simulation

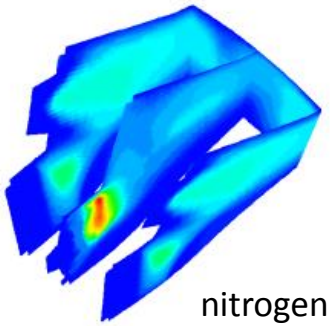


temperature

a steady state CFD simulation of the combustion device is performed using a **global kinetic mechanism**, which allows for the correct prediction of **thermal and flow fields**, but which cannot give us information on pollutant species

pollutant species usually affect only marginally the main combustion process and consequently do not influence the overall temperature and flow field

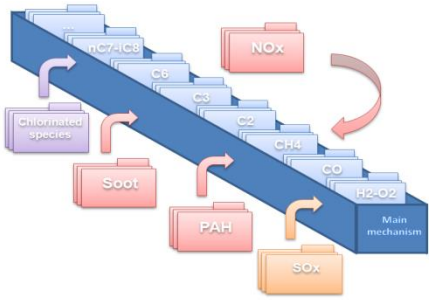
Post-Processing



nitrogen oxides

"slow" pollutant species

Detailed chemistry



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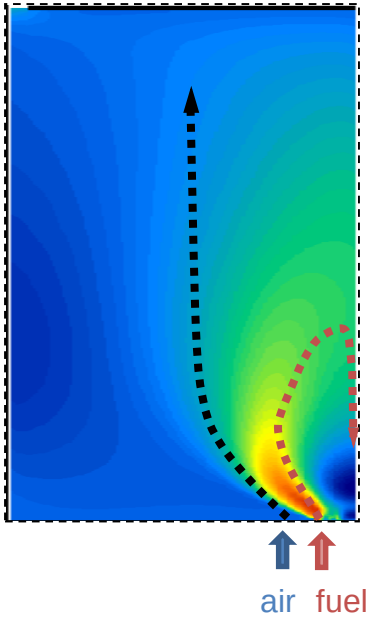
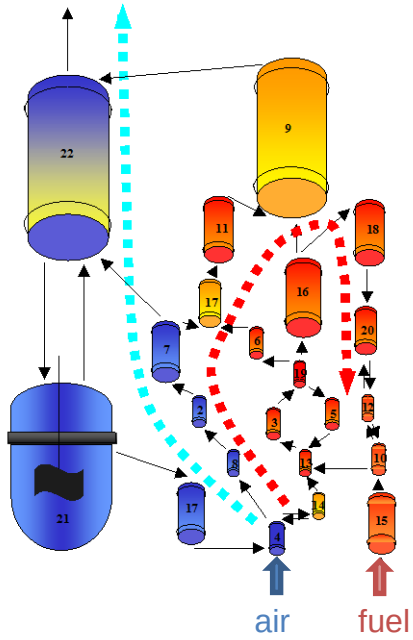
The Kinetic Post Processing technique

1. CFD Simulation



2. Clustering and network construction



✓ The clustering reduces the overall dimensions of the problem

✓ According to the clustering, a complex reactor network is constructed

3. Interactions with the turbulence

✓ In each reactor a fixed temperature is assumed

✓ These temperature is corrected to take into account the effects of turbulent fluctuations on the mean reaction rates

4. Network solution

✓ A very detailed kinetic scheme is used

✓ High number of non linear equations

example: 100 species x 50,000 reactors = 5,000,000 eqs

✓ Specifically conceived numerical method

Kinetic Post Processing in the literature

Ehrhardt et al. (1998)

were **the first** to propose and apply the post-processing technique. A simplified network of ideal PSRs or plugflow reactors. The proposed zone model was restricted only to flows without recycling zones and with downstream convection much larger than upstream diffusion.

Falcitelli et al. (2002)

a **general algorithm to construct the reactor network**, and application to practical industrial systems, such as glass melting furnaces and pilot- and full-scale boilers.

Skjøt-Rasmussen et al. (2003)

retained all of the individual cells in the computational domain, which were treated as PSRs, with fixed temperature and mass flow rates, as predicted by the CFD simulation. The reactors were modeled using DKM and the effects of turbulent fluctuations were accounted for.

Fichet et al. (2010)

post-processing a gas turbine flame fed with natural gas. Attention was devoted to the **splitting criteria** to minimize the number of equivalent reactors the reactor **temperature was not assumed fixed** from CFD results, but the energy balance was solved during the post-processing phase.

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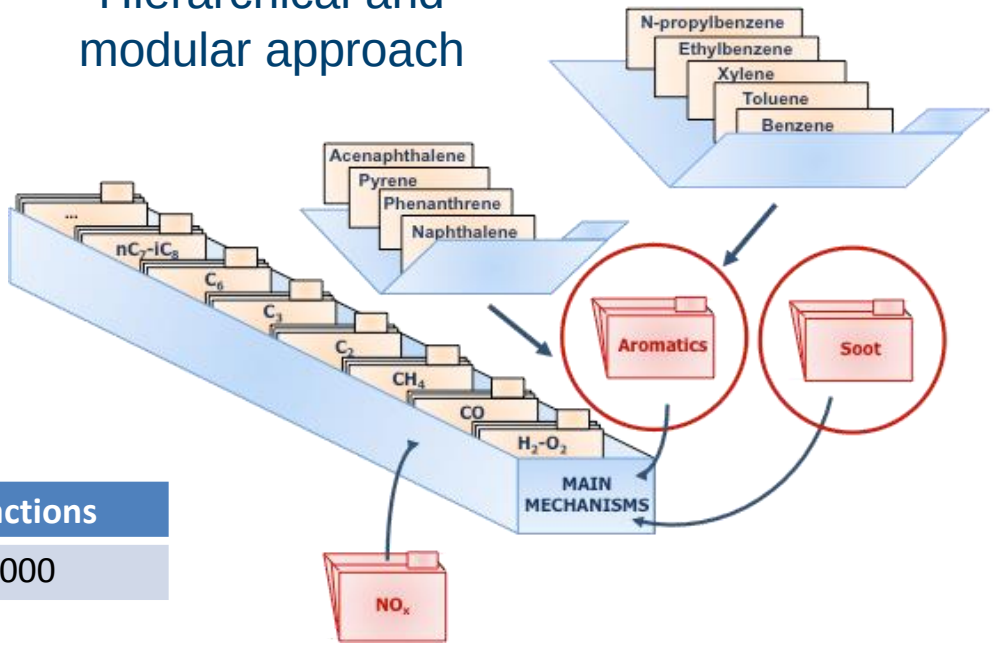
Kinetic mechanisms for CFD

- ✓ Detailed mechanisms for hydrocarbon combustion may include thousands of species
- ✓ Lumping methodology is able to significantly reduce its number
- ✓ A further reduction is needed for their use in multidimensional models

Hierarchical and modular approach



Mechanism	# Species	# Reactions
Polimi_C1C16	500	15000

Detailed kinetics → **Skeletal schemes** → **Global schemes**

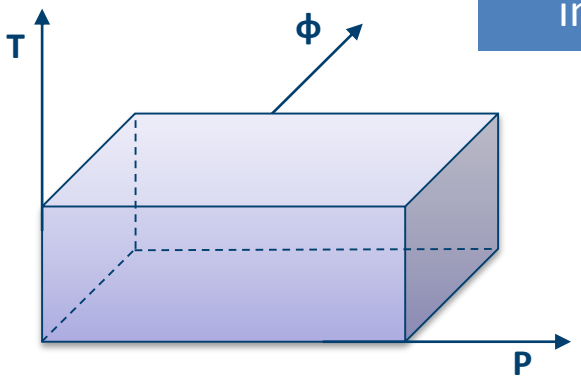
Reacting Flux Analysis method (RFA)

1.

Selection of testing conditions:
- ✓ Temperature: 700 – 2000 K
- ✓ Pressure: 1 – 50 atm
- ✓ Equivalence Ratios: 0.5 – 2

2.

- ✓ Progressive reduction of detailed kinetics.
- ✓ Analysis of Reacting fluxes in sample PFRs reactors



3.

Validation of reduced kinetics through comparison with experimental data and detailed mechanism:
- ○ Shock Tube Reactor
- ○ Laminar Flame Speed
- ○ Perfectly Stirred reactors

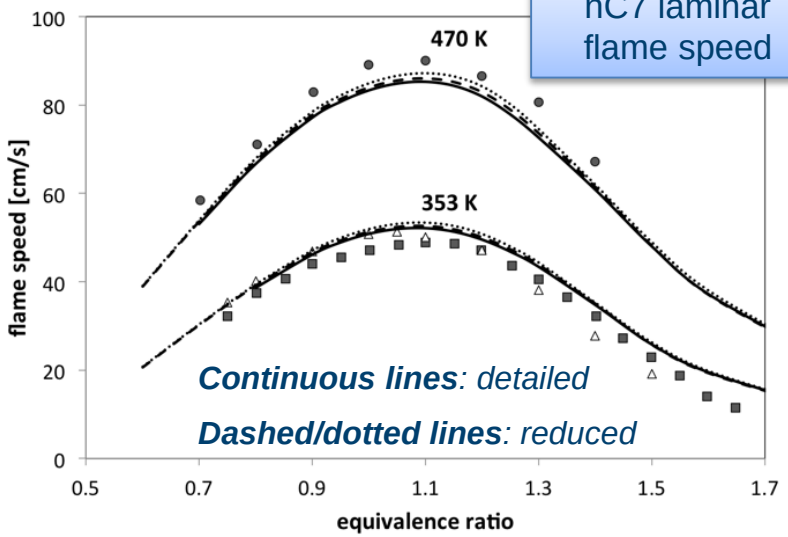
4.

Application to multi-dimensional codes

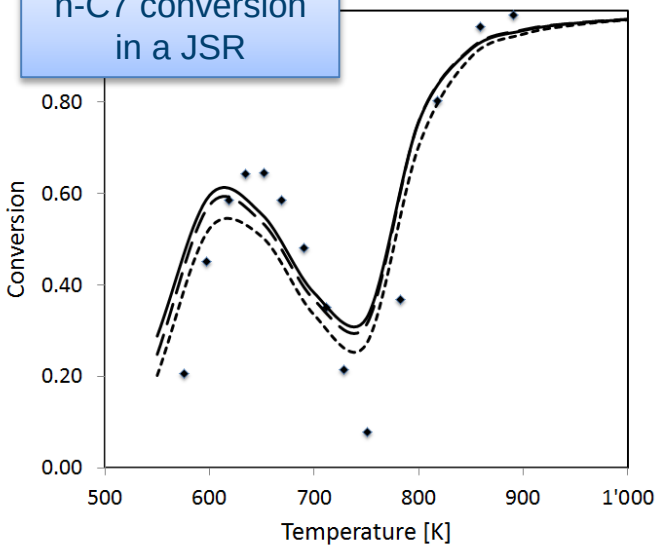
Stagni A., Cuoci A., Frassoldati A., Faravelli T., Ranzi E., Industrial & Engineering Chemistry Research, Accepted, In press (2014), DOI: 10.1021/ie403272f

Reduced kinetic schemes

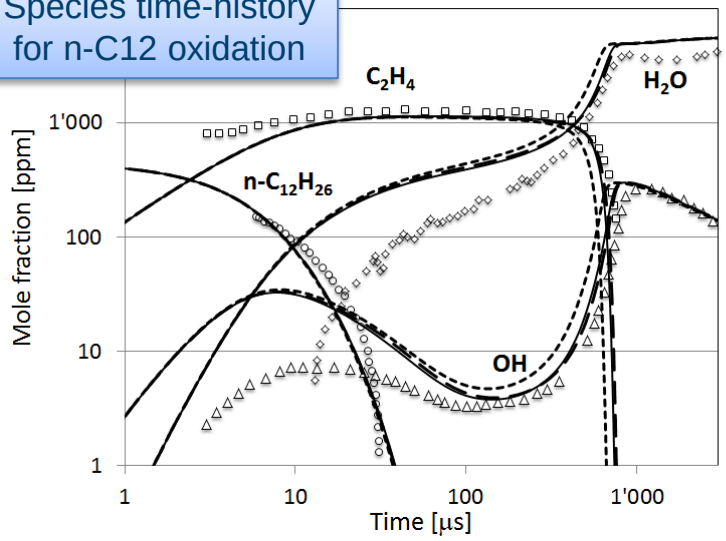
nC7 laminar flame speed



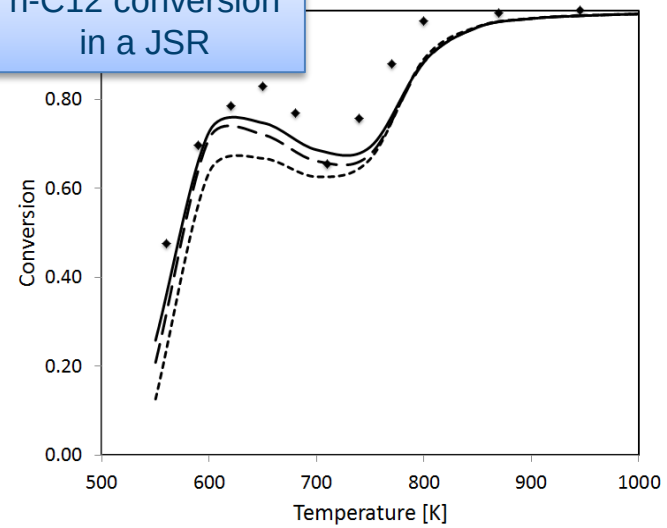
n-C7 conversion in a JSR



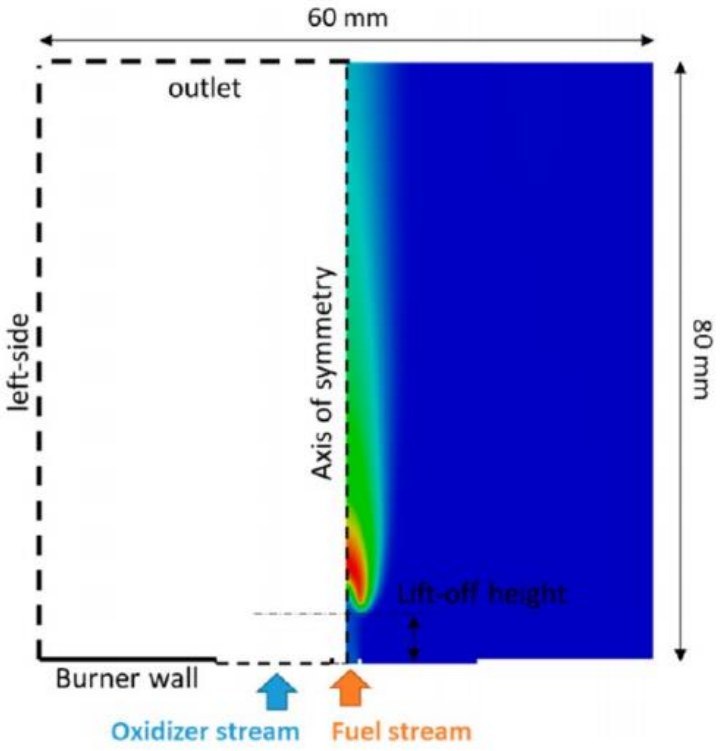
Species time-history for n-C12 oxidation

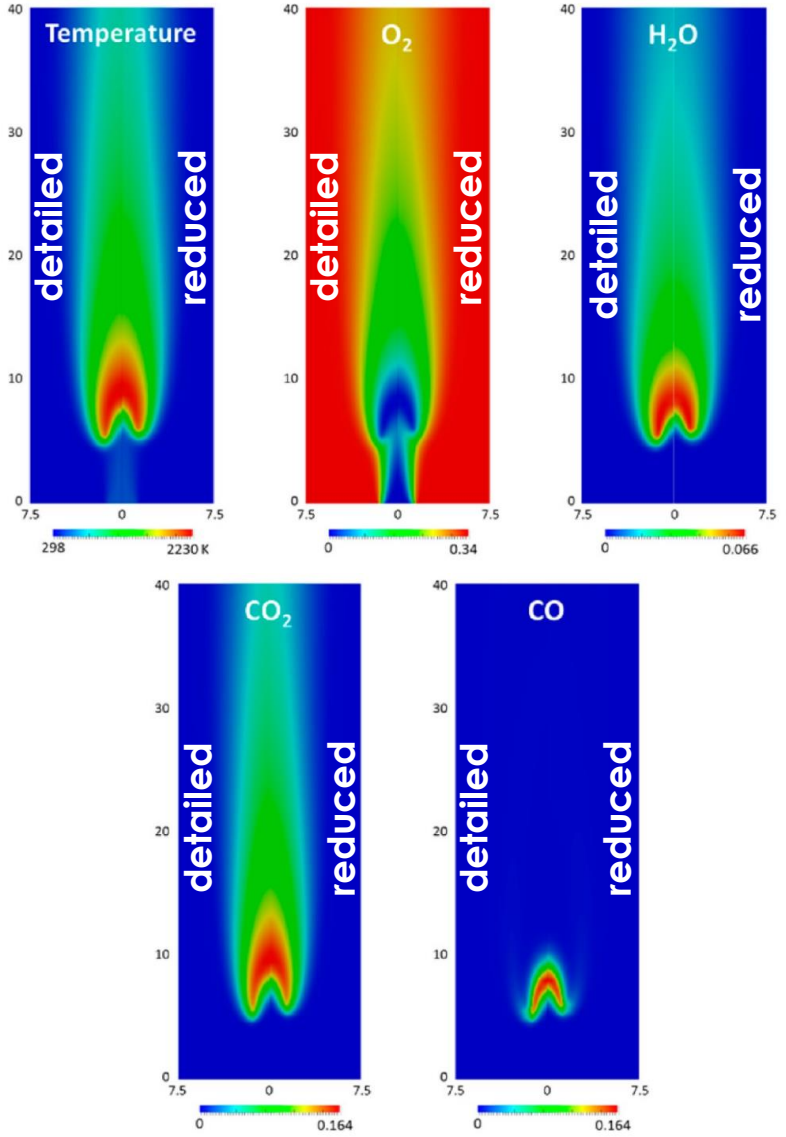


n-C12 conversion in a JSR



Validation in coflow flames





Fuel: 3.67% NC7 96.33% N2 (vol.) @ 470K

Oxidizer: 31% O2 69% N2 (vol.) @ 300K

Velocities: 79 cm/s (F) and 68.7 cm/s (O)

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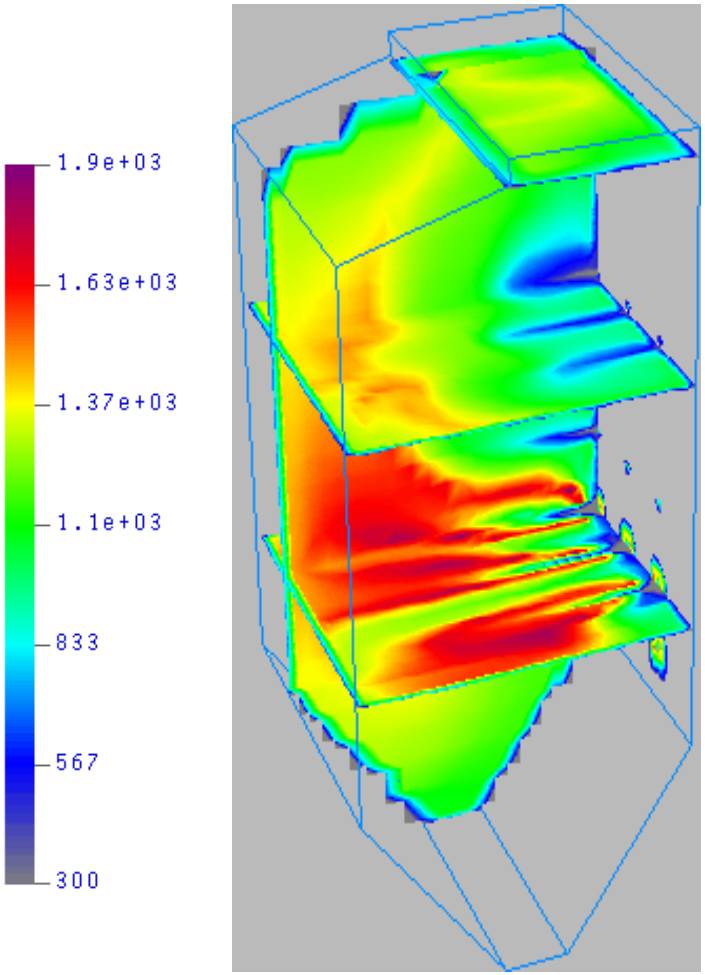
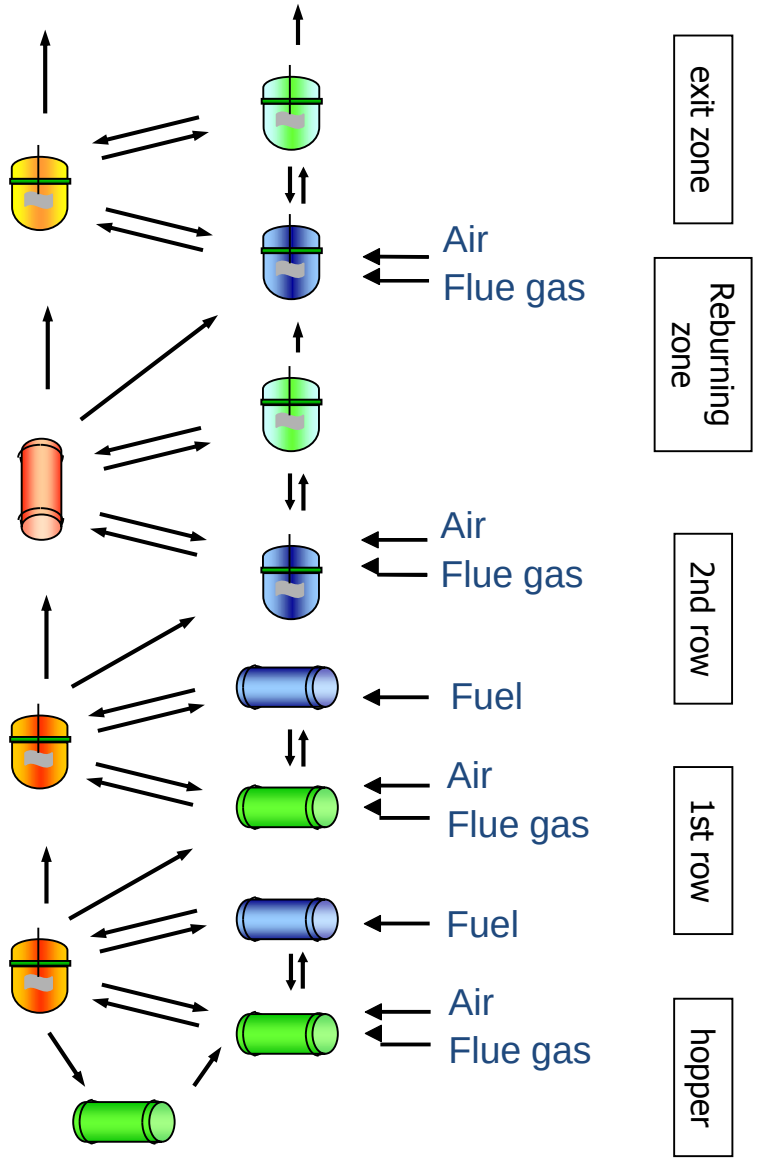
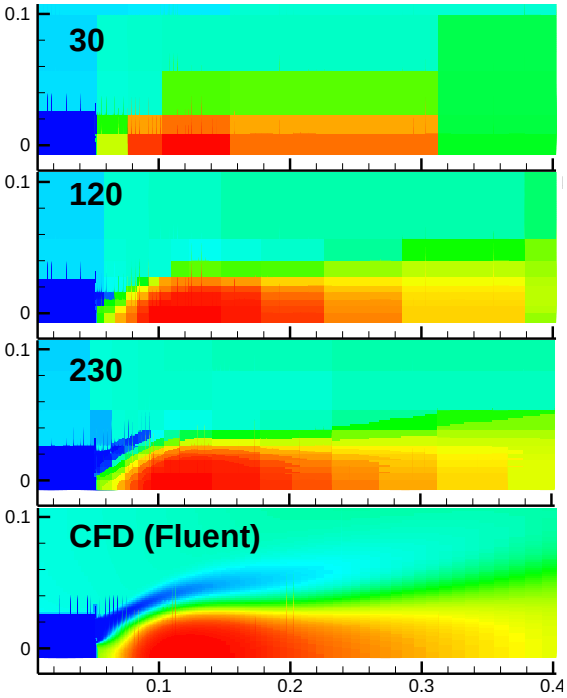
From the CFD simulation to the Reactor Network

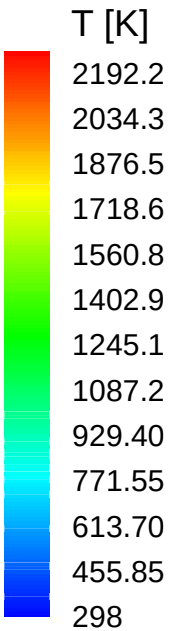
Industrial furnace (Cassano d'Adda, 75 MW)

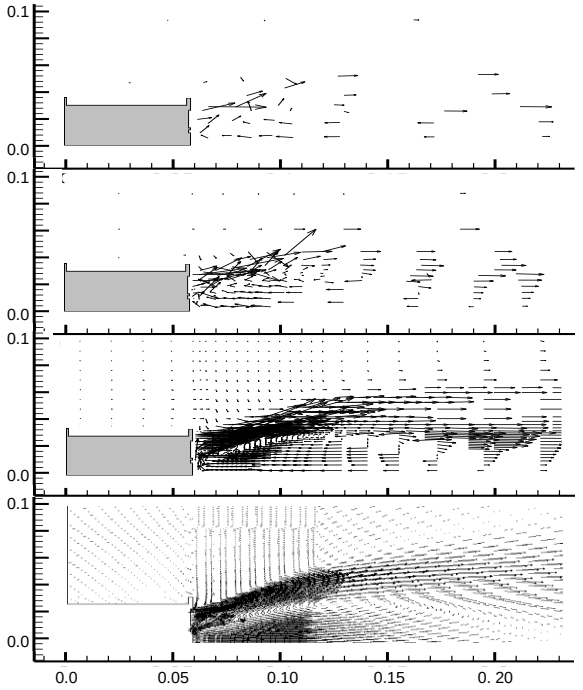




The clustering procedure (II)





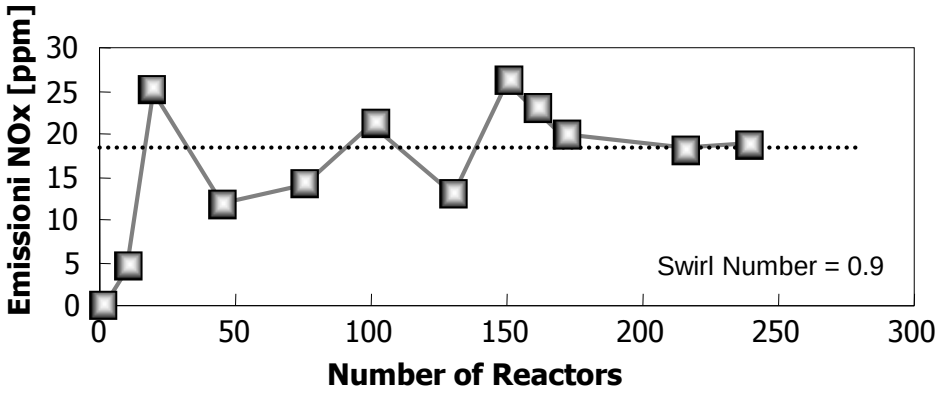


70 reattori

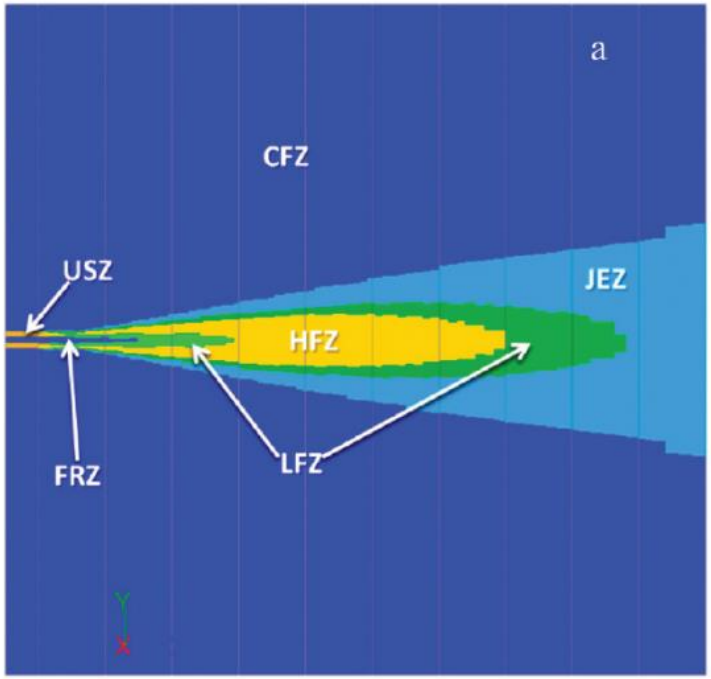
300 reattori

1000 reattori

Fluent



Clustering criteria for diffusion flames (I)



upstream zone (USZ):
region between the furthest upstream part of the domain and the outlets of the jet and pilot

fuel-rich zone (FRZ):
where initial mixing and fuel decomposition occurs

low- and high-temperature flame zones (LFZ and HFZ):
where heat release rates are highest (i.e., the flame brush)

jet expansion zone (JEZ):
the region of combustion products at elevated temperatures

co-flow zone (CFZ):
region of low-temperature, slow-moving air

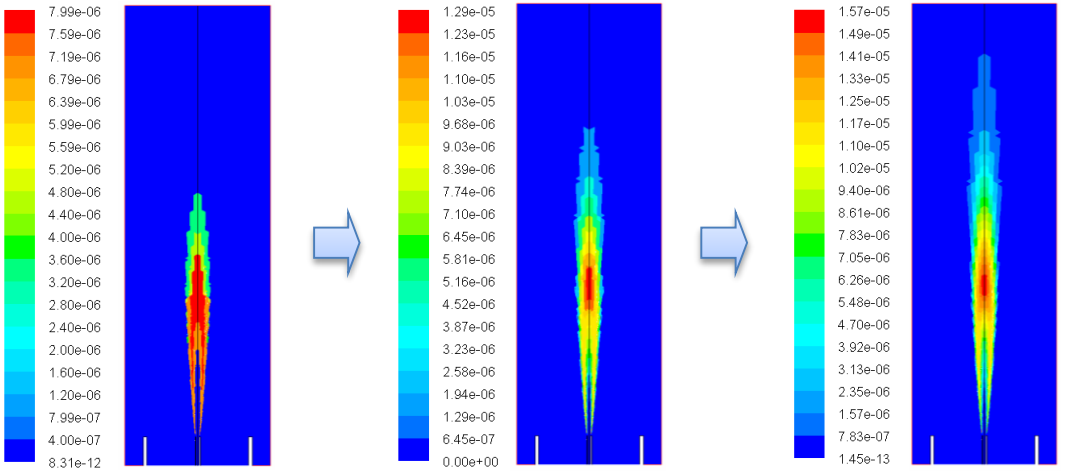
Consider neighboring computational cells, whose z coordinates, temperatures, and mixture fractions place them within the limits of the same zone. If the differences in properties between the cells are less than those defined for their assigned zone (Δf, ΔT, and Δz), they are considered to be the same reactor in the CRN.

Monaghan, R.F.D., et al., *Detailed multi-dimensional study of pollutant formation in a methane diffusion flame* (2012) Energy and Fuels, 26 (3), pp. 1598-1611, DOI: 10.1021/ef201853k

Clustering criteria for diffusion flames (II)

zone	zone limits	reactor criteria
upstream zone (USZ)	$z < 0$ m	n/a
fuel-rich zone (FRZ)	$z > 0$ m, $0.9 < f < 1.0$	$\Delta f = 0.01$, $\Delta z = 0.01$ m
low-temperature flame zone (LFZ)	$z > 0$ m, $0.1 < f < 0.9$, $T < 1400$ K	$\Delta T = 100$ K
high-temperature flame zone (HFZ)	$z > 0$ m, $0.1 < f < 0.9$, $T > 1400$ K	$\Delta T = 100$ K ($T < 1800$ K), $\Delta T = 50$ K (1800 K $< T < 2000$ K), $\Delta T = 2$ K ($T > 2000$ K)
jet expansion zone (JEZ)	$z > 0$ m, $0.01 < f < 0.1$	$\Delta T = 100$ K
co-flow zone (CFZ)	$z > 0$ m, $0 < f < 0.01$	$\Delta z = 0.2$ m

NO mass fraction fields



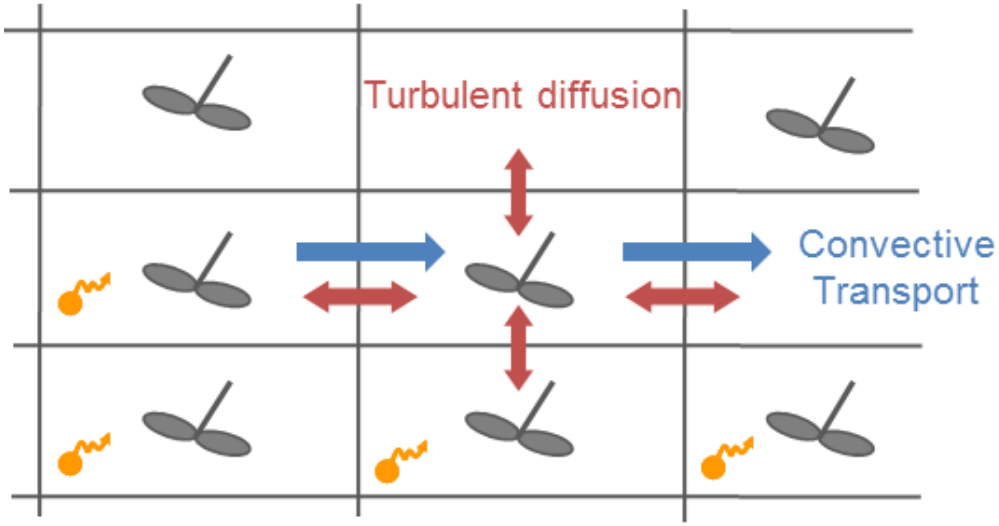
40/42000 reactors | 270/42000 reactors | 1400/42000 reactors

✓ In the first guesses, coarse meshes with a high level of clustering are adopted

✓ The calculations are then iteratively performed using a progressively increased number of cells up to convergence, i.e without further grid sensitivity

✓ The NOx-Postprocessor typically reduces the number of the original grid-cells with a factor of ~10

The mass balance equations



Diffusion flux due to concentration gradients and velocity fluctuations of the turbulent flow

$$\vec{J}_i = -\frac{\mu_t}{Sc_t} \cdot \nabla \omega_i$$

$$\left[\sum_{n=1}^{Ns} W_n \omega_{i,n}^{out} - W \cdot \omega_i^{out} \right] + \sum_{n=1}^{Ns} J_{i,n} S_n + V^* \tilde{\Omega}_i + \Pi_i = 0$$

Convection

Diffusion

Chemical reactions

Vaporization
Devolatilization

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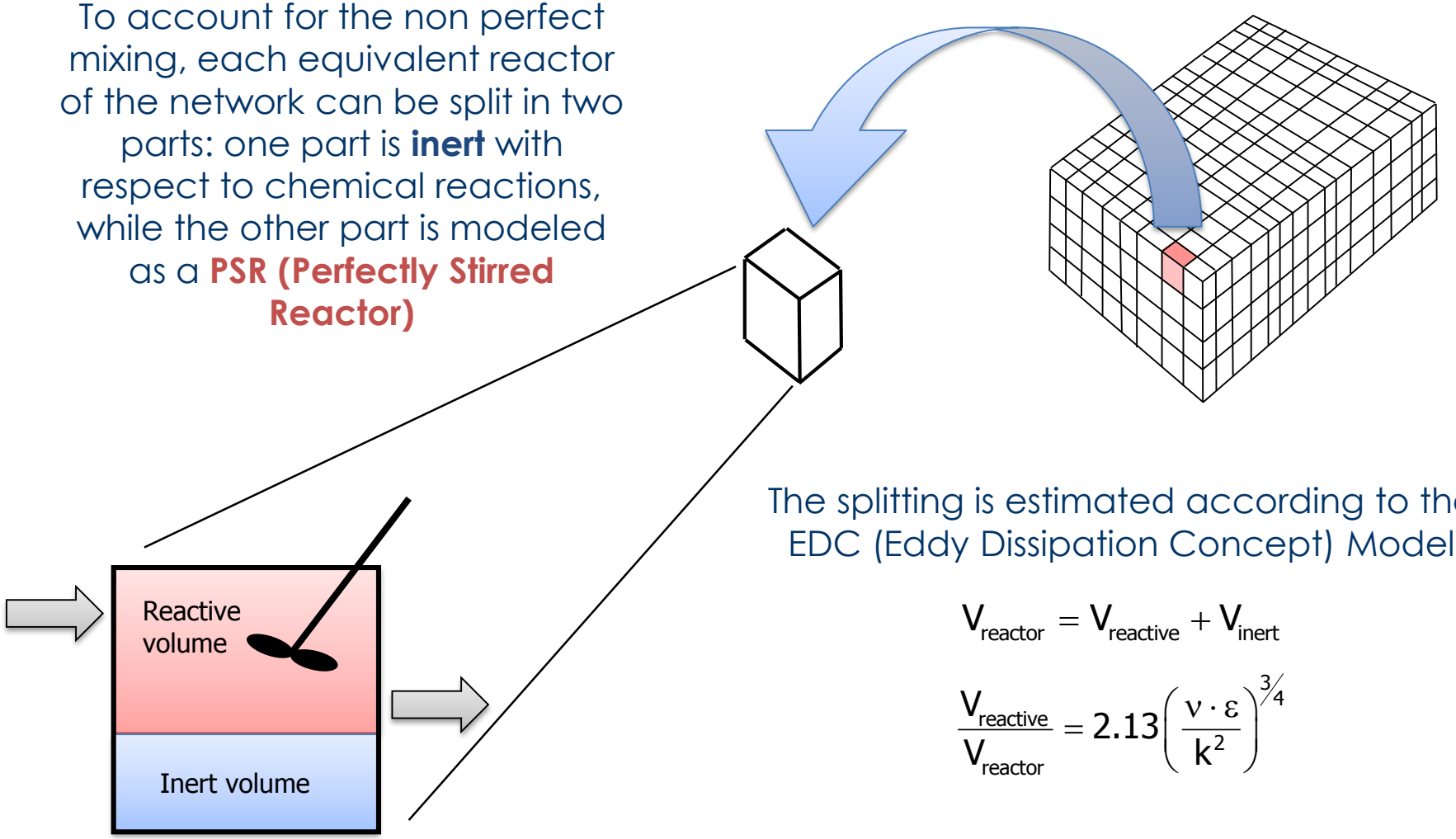
Effective volume of reaction

To account for the non perfect mixing, each equivalent reactor of the network can be split in two parts: one part is **inert** with respect to chemical reactions, while the other part is modeled as a **PSR (Perfectly Stirred Reactor)**

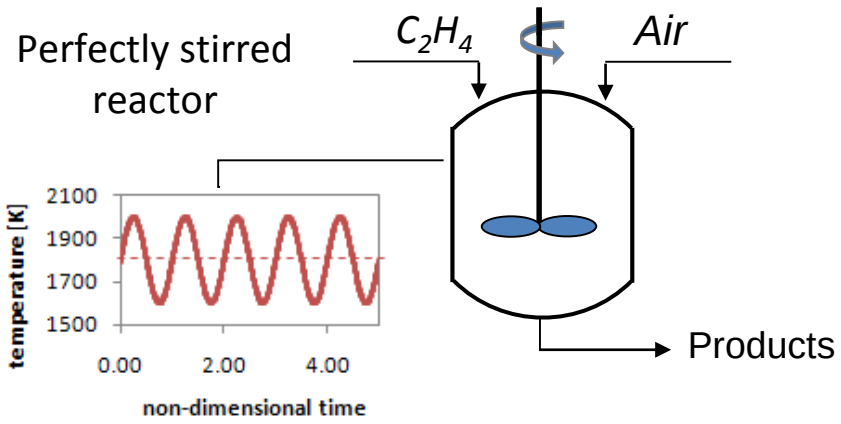


The splitting is estimated according to the EDC (Eddy Dissipation Concept) Model

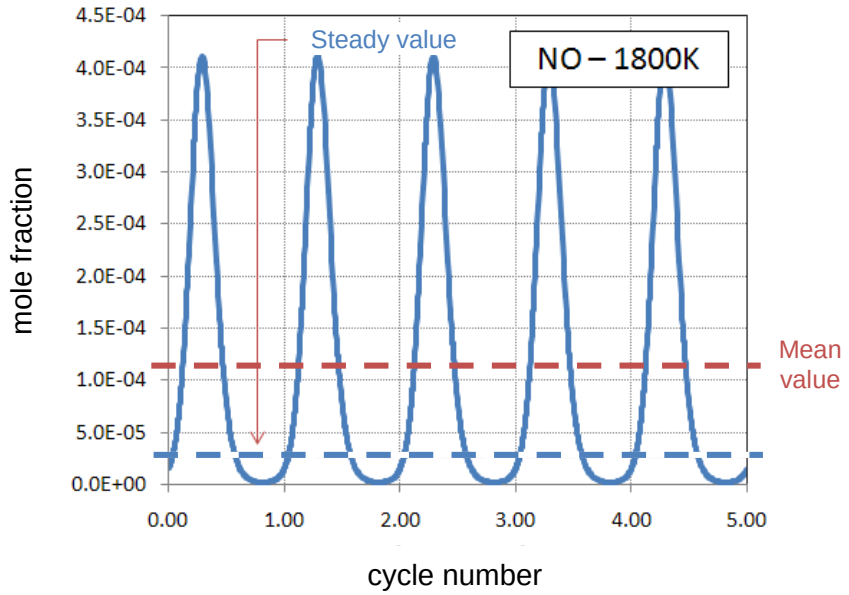
$$V_{reactor} = V_{reactive} + V_{inert}$$

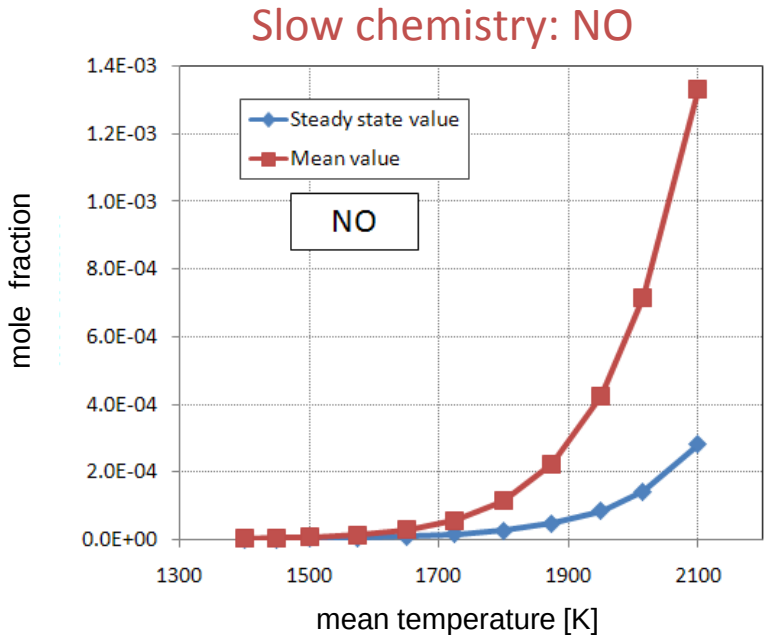
$$\frac{V_{reactive}}{V_{reactor}} = 2.13\left(\frac{\nu \cdot \varepsilon}{k^2}\right)^{3/4}$$

Fluctuations of temperature and NOx



The fluctuations of temperature have a strong impact on the formation of NOX because of the high activation energy of the thermal path





Correction coefficient for reaction rates (I)

Rate constant is highly non linear function of temperature

$$k(T) = A \cdot T^{\beta} \cdot \exp\left(-\frac{E_{att}}{RT}\right)$$

Introduction of a proper probability distribution function p(T)

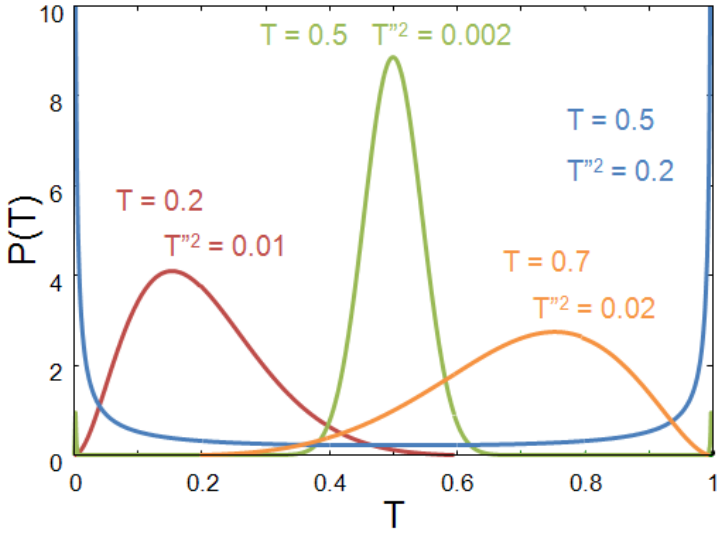
$$\tilde{k}(T) = \int_{T_{min}}^{T_{max}} k(T)\,p(T)\,dT = C_C\,k\left(\tilde{T}\right)$$

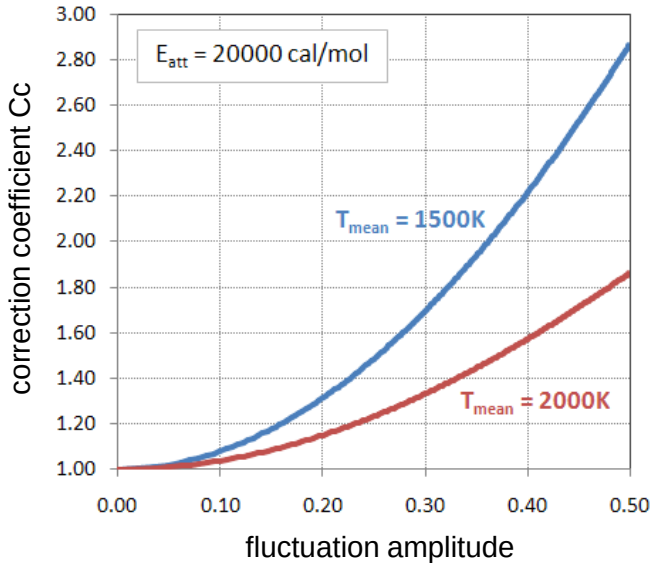
Correction coefficient

$$C_C = \frac{\int_{T_{min}}^{T_{max}} k(T)\,p(T)\,dT}{k\left(\tilde{T}\right)}$$

Requires the knowledge of the variance of temperature

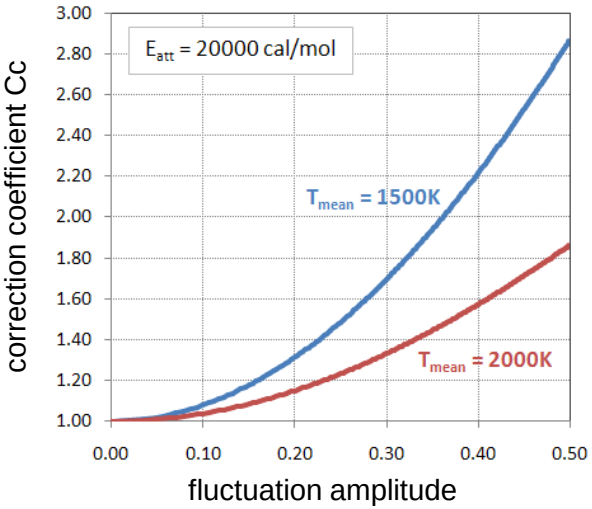
β-PDF

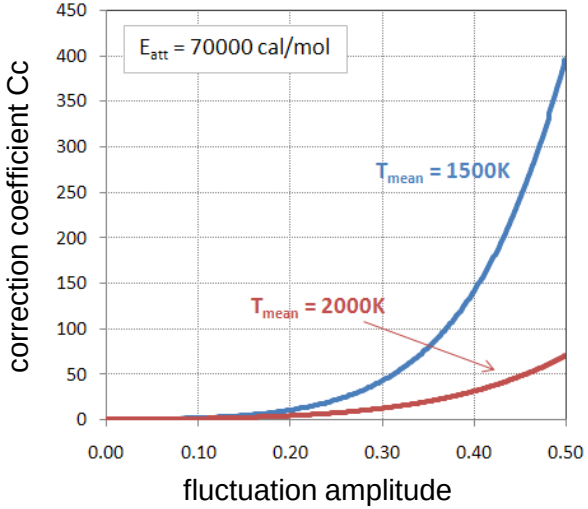




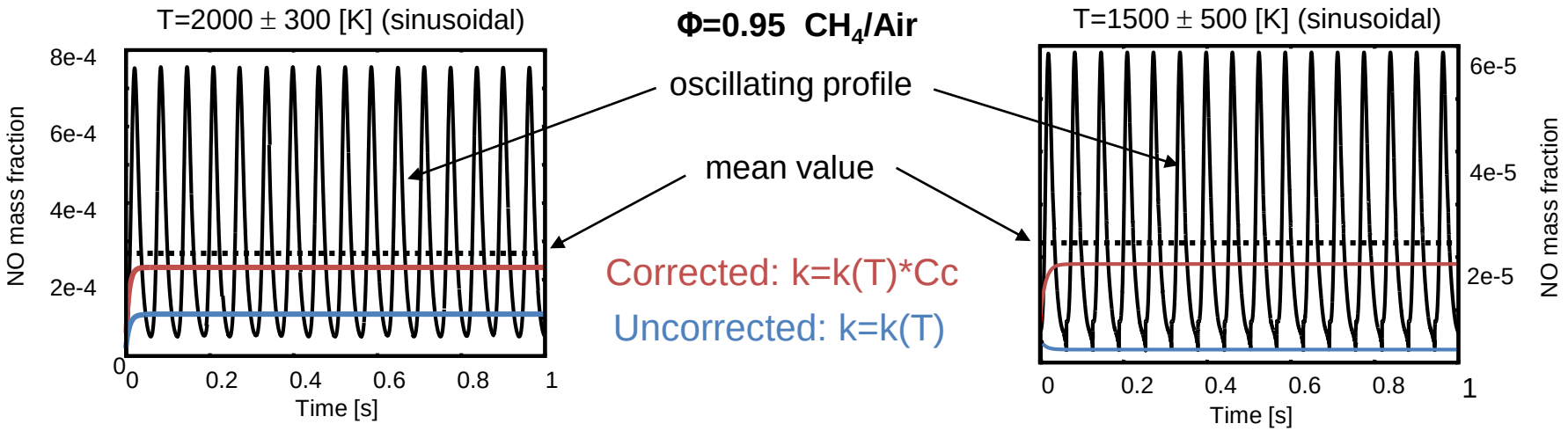
A. Cuoci, A. Frassoldati, G. Buzzi Ferraris, T. Faravelli, E. Ranzi, International Journal of Hydrogen Energy (32), p. 3486-3500 (2007)

Correction coefficient for reaction rates (II)





The correction Coefficient is significantly > 1 for high activation energies (Thermal NOx)

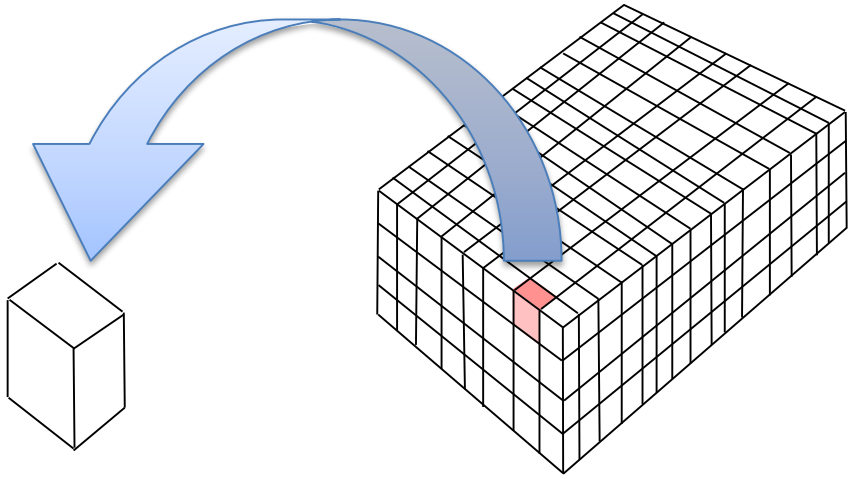


The error (<15%) is due to the fluctuations of composition (neglected)

Calculation of correction coefficients

The correction coefficient must be calculated for each reaction in each reactor

$$C_C = \frac{\int_{T_{min}}^{T_{max}} k(T)p(T)dT}{k(\tilde{T})}$$



Tabulation of Correction Coefficients

Since during the post-processing phase the temperature is fixed in each reactor, the correction can be pre-calculated and stored in memory (i.e. it is always the same, since it is independent of the composition)

Transport equation for the variance of temperature

$$\frac{\partial}{\partial t}\left(\bar{\rho}\widetilde{T''^2}\right) + \nabla\left(\bar{\rho}\tilde{\mathbf{v}}\widetilde{T''^2}\right) = \nabla\left(\frac{\mu_T}{Sc_T}\nabla\tilde{T}\right) + 2\frac{\mu_T}{Sc_T}\nabla\tilde{T}\nabla\tilde{T} - C\bar{\rho}\frac{\varepsilon}{\kappa}\widetilde{T''^2}$$

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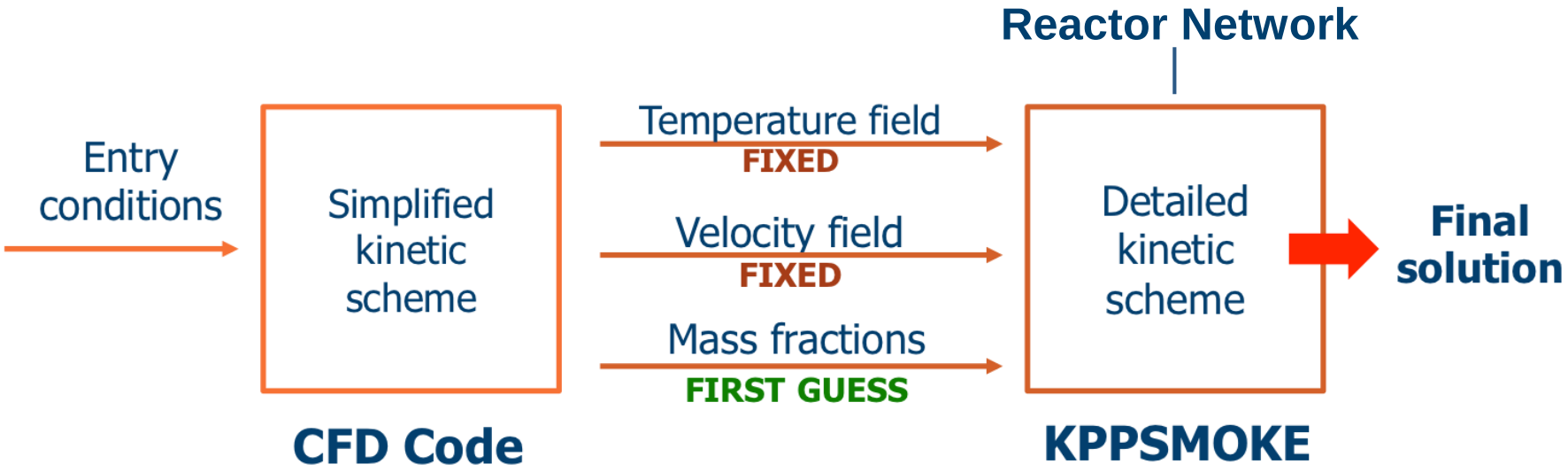
Numerical solution of the reactor network

HYPOTHESIS

Negligible influence of minor species on temperature and velocity fields → **Skeletal** kinetics to assess CFD

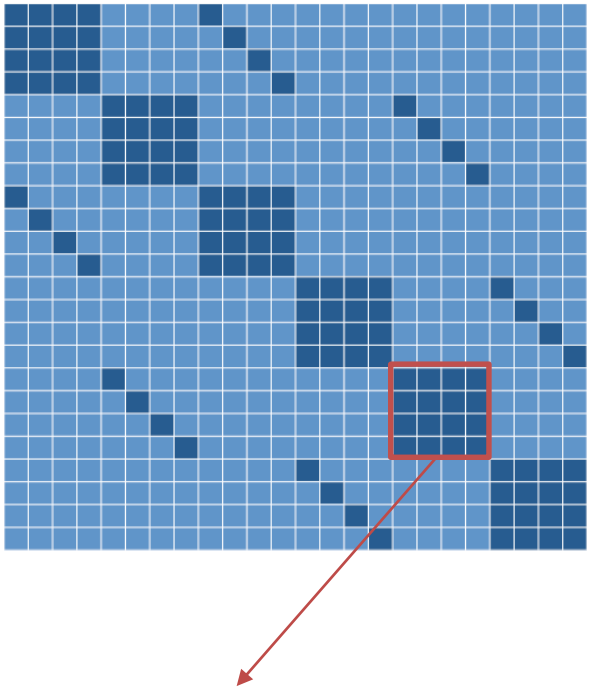
Multi-technique solution strategy

Only **mass** balances are solved in CRN



Non Linear System (NLS) of equations

Jacobian sparsity pattern



Single reactor

$$\left(\sum_{k=1}^{N_{AD}} \dot{m}_{k,j}\omega_{k,j,i} - \dot{m}_j\omega_{j,i}\right) + \sum_{k=1}^{N_{AD}}\left(J_{j,k,i}\cdot S_{j,k}\right) + V_j^*\tilde{\Omega}_{j,i} + \Pi_{j,i} = 0$$

Linear

$$J_i = -\frac{\mu_t}{Sc_t}\cdot\nabla W_i$$

Linear

Non Linear (Power Law)

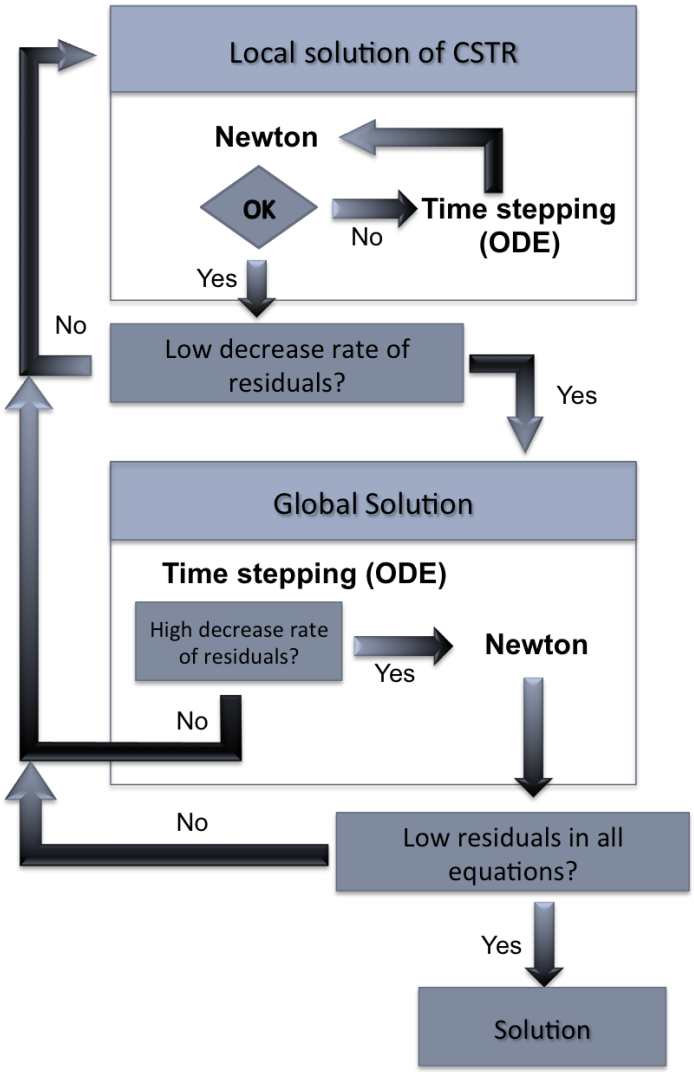
- Jacobian is **sparse** and **block-unstructured**
- High degree of **accuracy** is sought

A **fully coupled** resolution is implemented

$$\mathbf{C}(\boldsymbol{\omega}) + \mathbf{R}(\boldsymbol{\omega}) + \mathbf{f} = \mathbf{0}$$

Linear **Non-Linear** **External feeds**

Numerical procedure



the numerical procedure combines different techniques to obtain the final solution, because the global Newton's method (or modified Newton's methods) can be successfully applied only if the first-guess solution is close to the real solution.

Remember that the first-guess solution (from CFD) could account only for a few species, while the KPP solution for hundreds of species

1. Global Newton's Method
2. Global ODE (Backward Euler)
3. Direct Substitutions (Local solution)
   a. Local Newton's Method
   b. Local ODE system (stiff solver)

Local solution

The individual reactors are solved sequentially to take the whole system closer to the solution. This means that each reactor is solved using a **local Newton's method**.

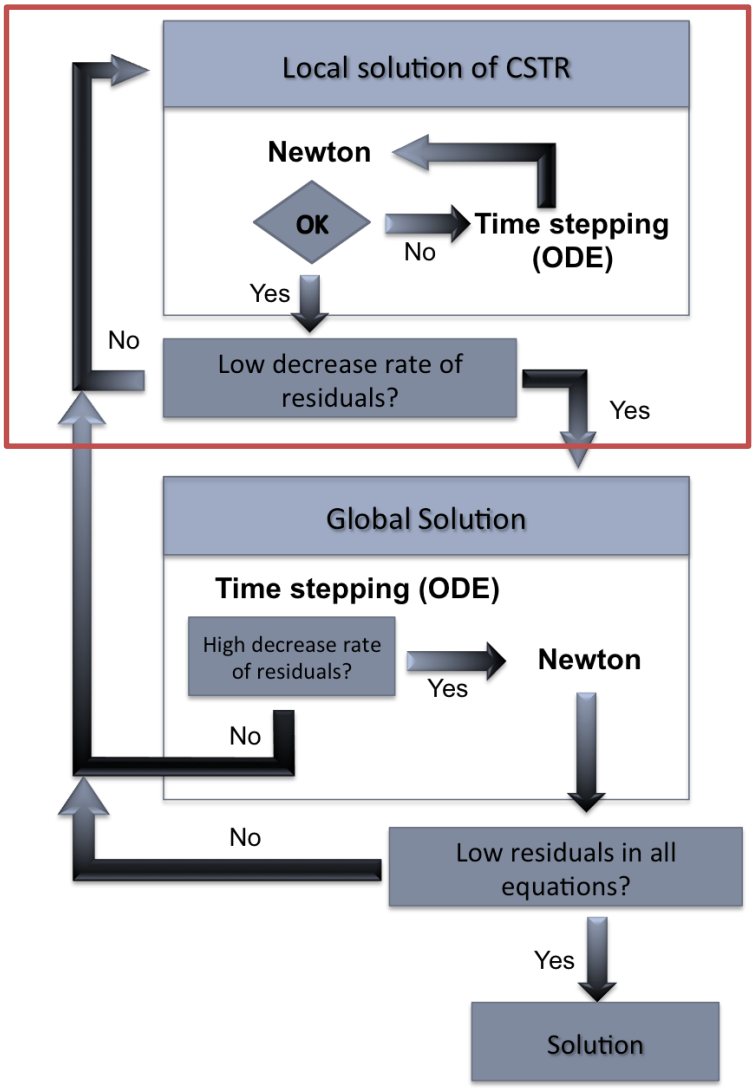
$$\left[\mathbf{C}_{in}\left(\boldsymbol{\omega}\right)+\mathbf{f}\right]_{old}+\mathbf{C}_{out}\left(\boldsymbol{\omega}\right)+\mathbf{R}\left(\boldsymbol{\omega}\right)=\mathbf{0}$$

To improve the robustness, especially in the first iteration, a **false transient method** is used to solve the single reactors. The NLS is transformed into a ODE system by adding the unsteady term

$$\mathbf{m}\frac{d\boldsymbol{\omega}}{dt}=\left[\mathbf{C}_{in}\left(\boldsymbol{\omega}\right)+\mathbf{f}\right]_{old}+\mathbf{C}_{out}\left(\boldsymbol{\omega}\right)+\mathbf{R}\left(\boldsymbol{\omega}\right)$$

Stiff ODE solvers

CVODE, DVODE, LSODE, RADAU5, BzzMath



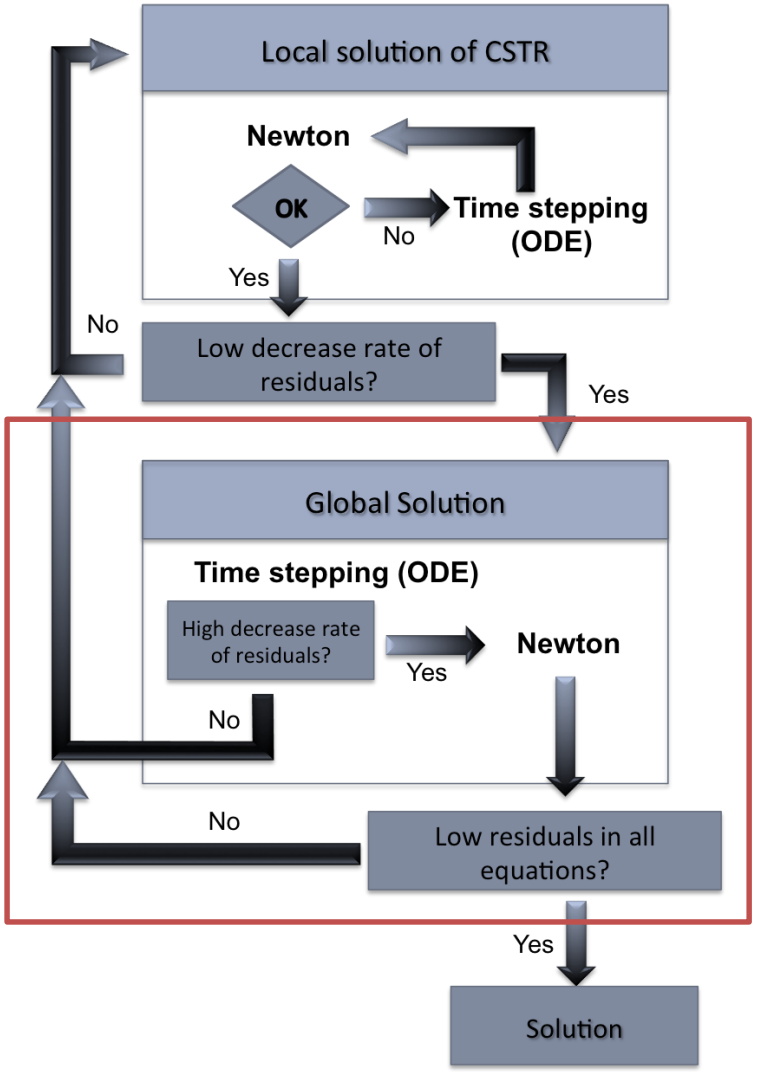
Global solution

the **global Newton's method**, to ensure the accuracy needed to correctly predict chemical species present in very small amounts (ppm or smaller)

$$\mathbf{C}(\boldsymbol{\omega}) + \mathbf{R}(\boldsymbol{\omega}) + \mathbf{f} = \mathbf{0}$$

When complex flows are investigated, the sequential approach (i.e., direct substitutions) could not be enough to reduce the residuals of equations to sufficiently small values to successfully apply the global Newton's method. In such a case, a **global time-stepping** procedure must be taken into account.

$$\mathbf{m}_{tot} \frac{\boldsymbol{\omega}^{n+1} - \boldsymbol{\omega}^{n}}{\Delta t} = \mathbf{C}\left(\boldsymbol{\omega}^{n+1}\right) + \mathbf{R}\left(\boldsymbol{\omega}^{n+1}\right) + \mathbf{f}$$

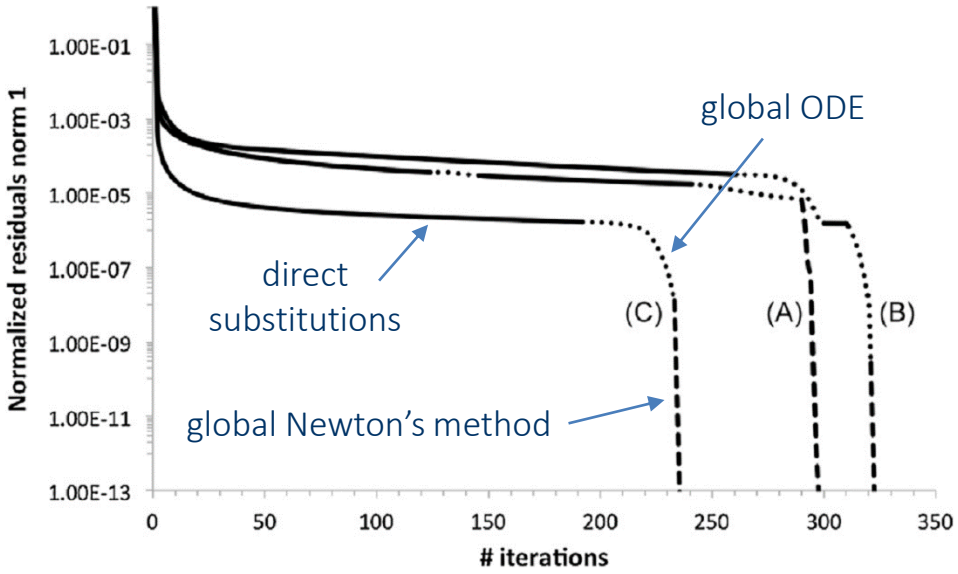


Linear System solvers

MUMPS 4.10 (Direct Solver)

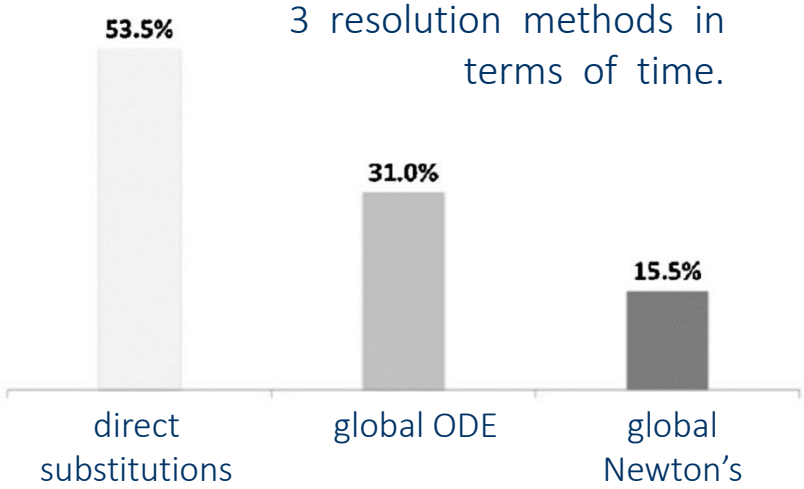
LIS 1.24 (Iterative Solver)

Numerical performances



Residuals norm 1 trends, normalized with respect to their initial value (set equal to 1)

Relative importance of the 3 resolution methods in terms of time.



A: a tubular combustor (56,150 reactors, 4.8M equations)
B: an aircraft combustor (252,885 reactors, 22M equations)
C: an aircraft combustor (290,764 reactors, 25M equations)

POLIMI NC7 kinetic mechanism
86 species and 1427 reactions

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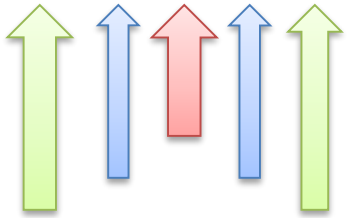
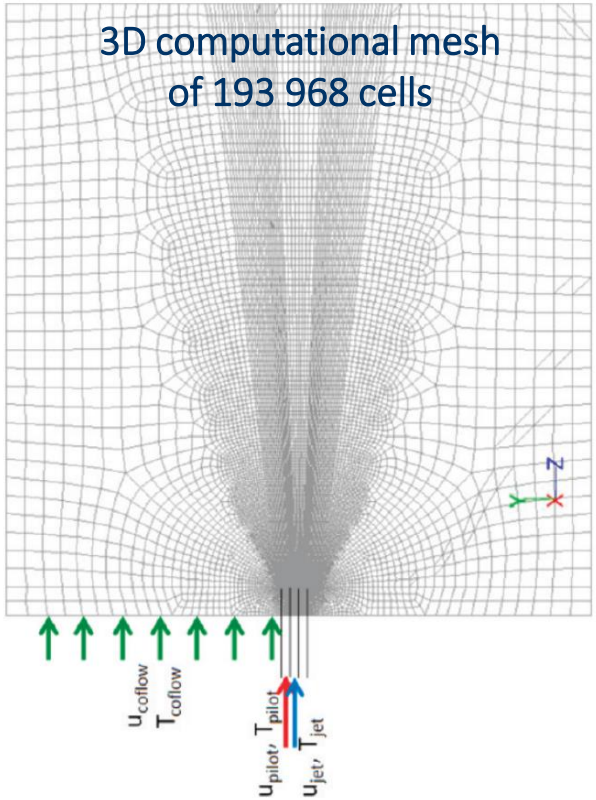
Validation: Sandia Flame D



Barlow, R. S. and Frank, J. H., *Proc. Combust. Inst*. 27:1087-1095 (1998)

Nozzle diameter = 7.2mm
Pilot diameter = 18.2mm
Re = 22,400

Fuel: 25% CH4 + 75% Air (vol.)
Pilot: equilibrium composition of a mixture of CH4/air (Φ=0.77)
Oxidizer: air



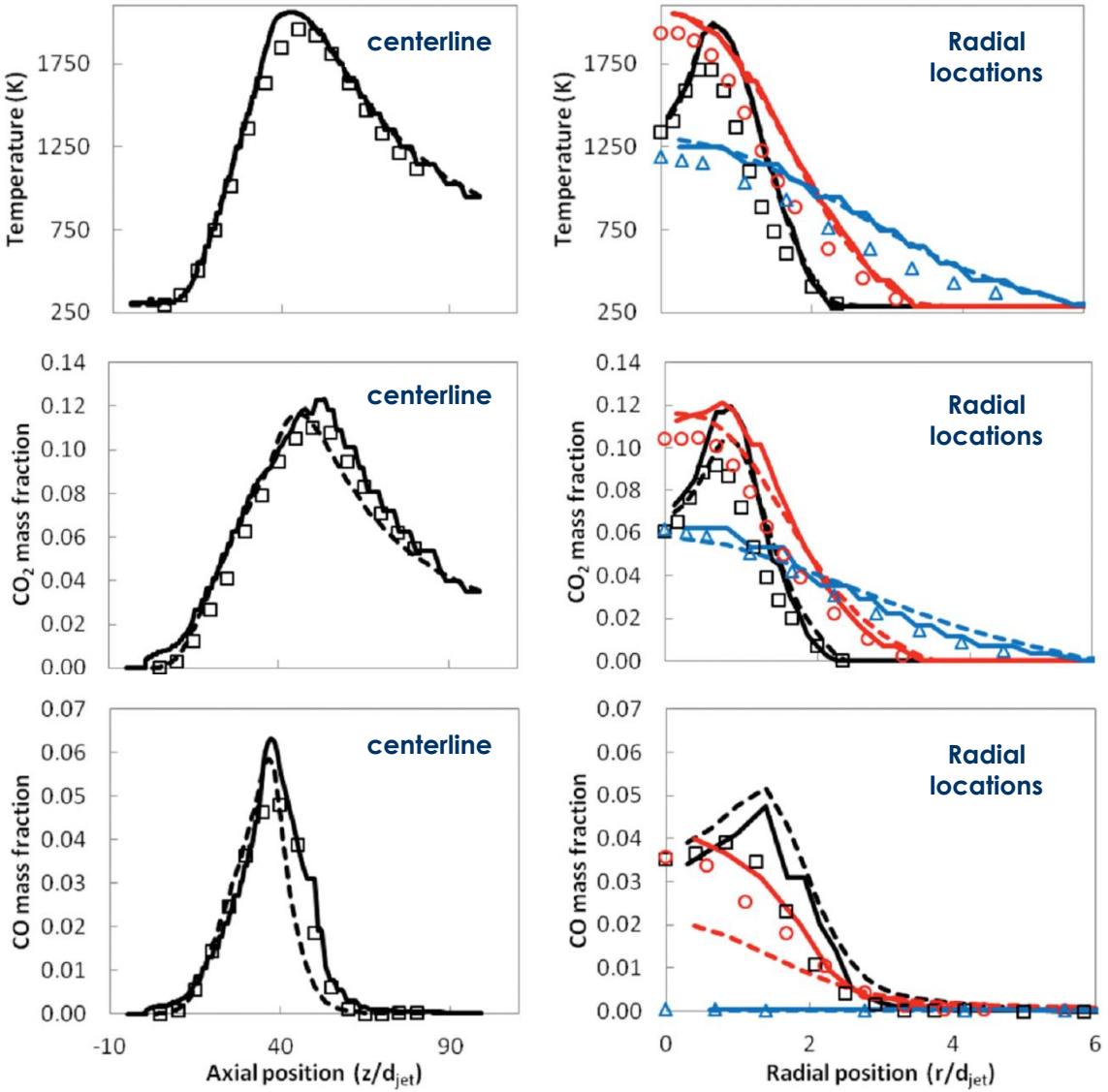
NUI Galway
OÉ Gaillimh

Monaghan, R.F.D., et al., Detailed multi-dimensional study of pollutant formation in a methane diffusion flame (2012) Energy and Fuels, 26 (3), pp. 1598-1611, DOI: 10.1021/ef201853k

RANS Simulations performed using the DRM22 kinetic scheme:

- 22 species
- 104 reactions

CFD results vs KPP results



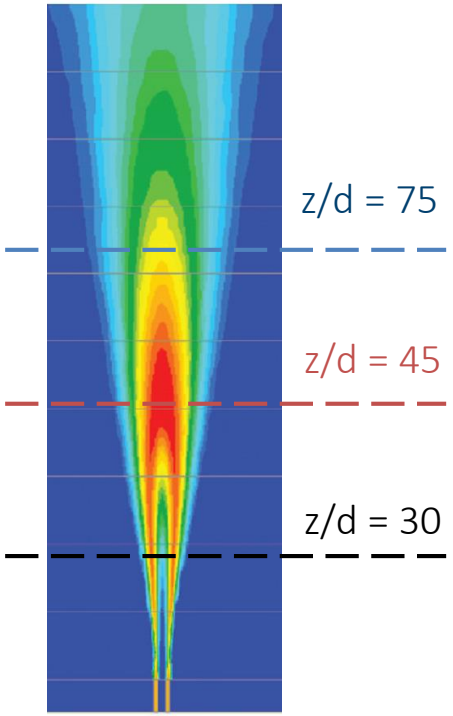
***Continuous lines**: KPP predictions*

***Dashed lines**: CFD predictions*

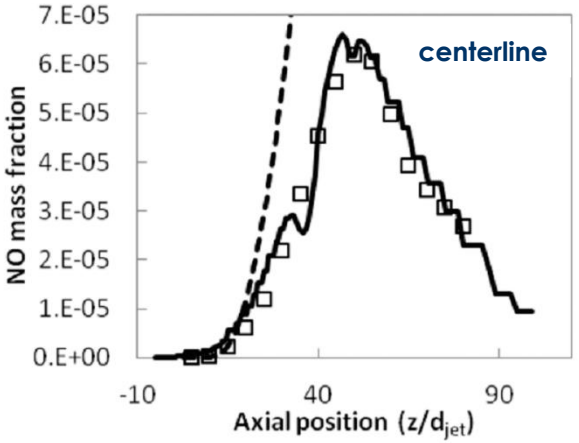
1114 Reactors

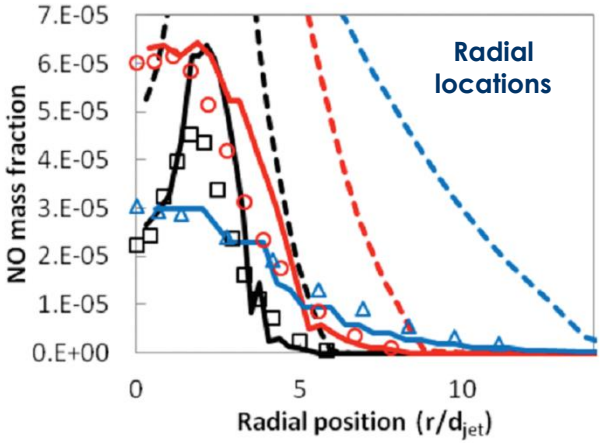
(less than 1% of the original cells)

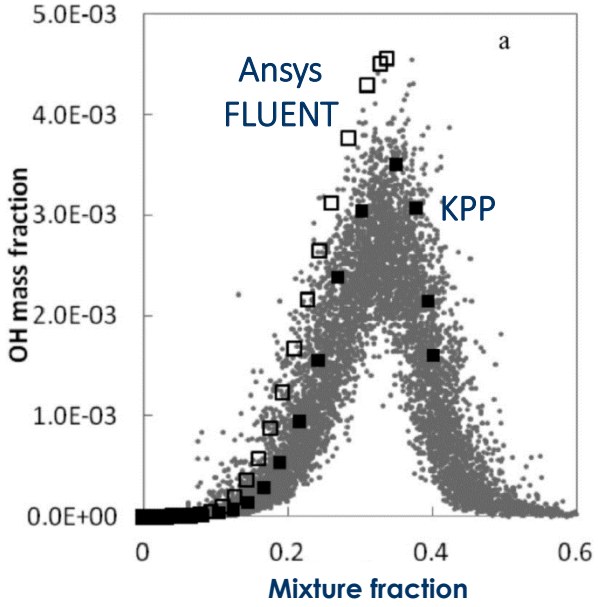
103 species and 582 reactions

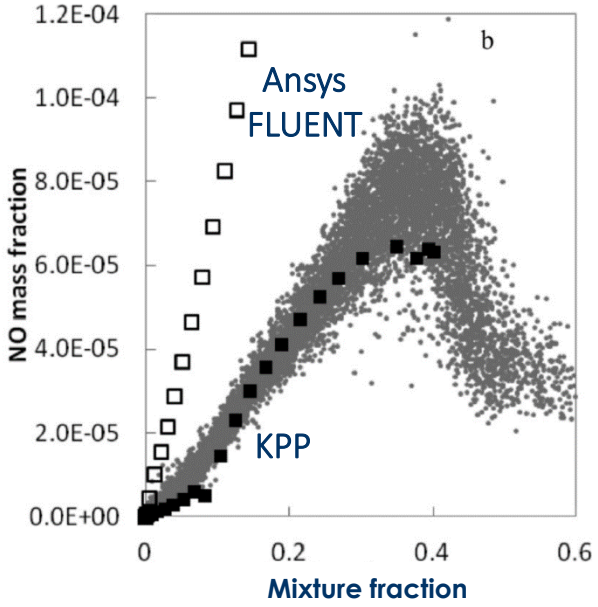


NOx predictions









***Continuous lines**: KPP predictions*

***Dashed lines**: Ansys FLUENT NOX post-processor*

The Ansys FLUENT NOx post-processor has the following configuration:

- ✓ thermal, prompt, and N2O pathways activated
- ✓ instantaneous thermal [O] and [OH] models, quasi-steady N2O model
- ✓ temperature-only β-PDF turbulence interaction with 10 PDF points
- ✓ temperature variance with a global maximum temperature.

Numerical performances

CRN size	mechanism	time to solution (h:min:s) CHEMKIN PRO	time to solution (h:min:s) KPP	improvement factor
108 PSRs	GRI 1.2	0:14:20	0:00:06	143
108 PSRs	GRI 3.0	0:25:11	0:00:30	50
108 PSRs	NUIG C2	failed	0:00:39	
211 PSRs	GRI 1.2	0:23:45	0:00:16	89
211 PSRs	NUIG C2	failed	0:00:26	
255 PSRs	GRI 1.2	1:57:48	0:00:16	442
255 PSRs	NUIG C2	failed	0:01:28	
372 PSRs	NUIG C2	failed	0:01:48	
411 PSRs	NUIG C2	failed	0:02:04	
523 PSRs	NUIG C2	failed	0:02:26	
617 PSRs	NUIG C2	failed	0:02:38	
722 PSRs	NUIG C2	failed	0:03:20	
809 PSRs	NUIG C2	failed	0:03:50	
1114 PSRs	NUIG C2	failed	0:09:30	

NUIG C2

103 species

582 reactions

GRI 3.0

53 species

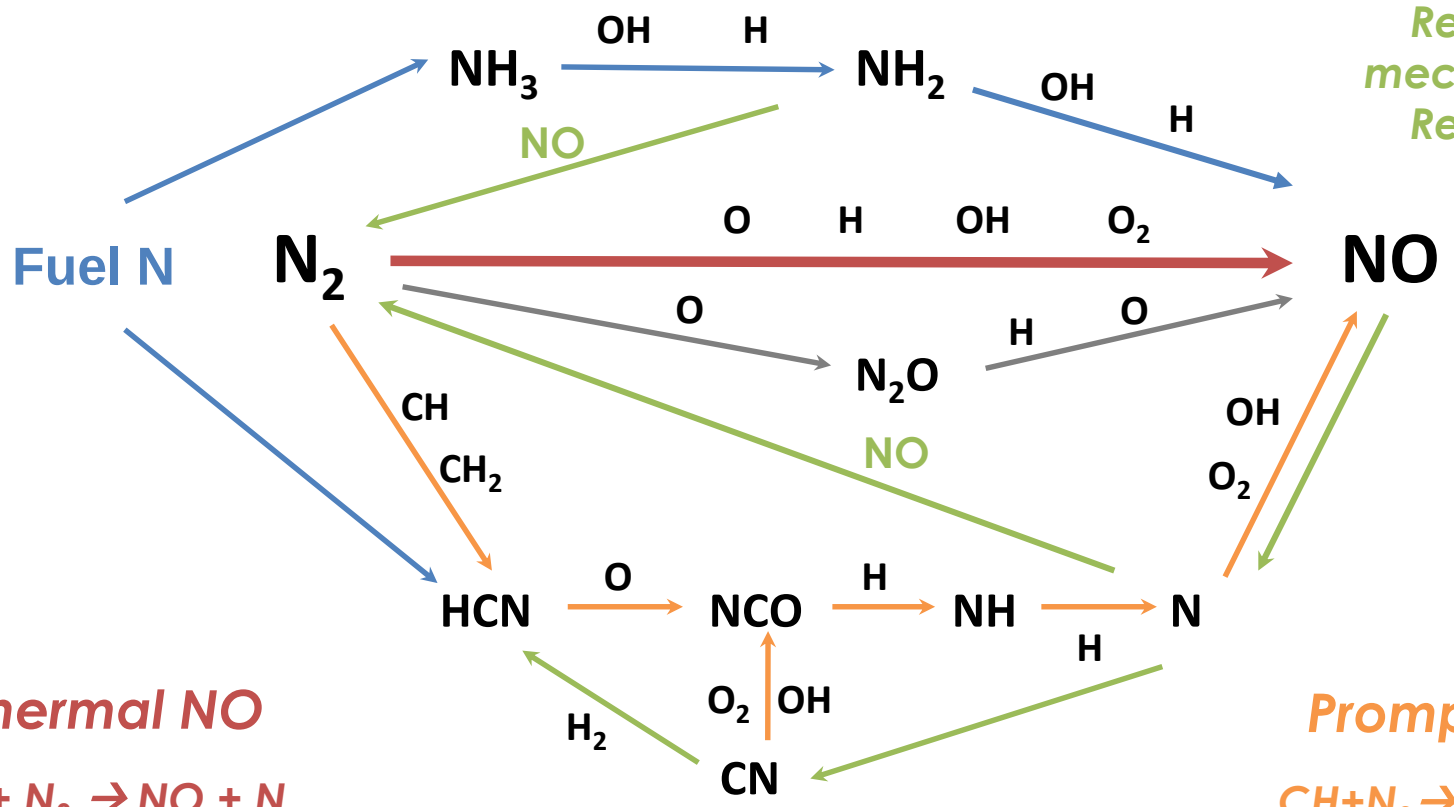
325 reactions

GRI 1.2

32 species

279 reactions

NOx formation pathways (I)



Thermal NO

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

High T and τ

$\lambda > 1$

N_2O Mechanism

$N_2 + O \rightarrow N_2O$

High P and $\lambda >> 1$

Prompt NO

$CH + N_2 \rightarrow HCN + N$
$CH_2 + N_2 \rightarrow HCN + NH$
$C + N_2 \rightarrow CN + N$

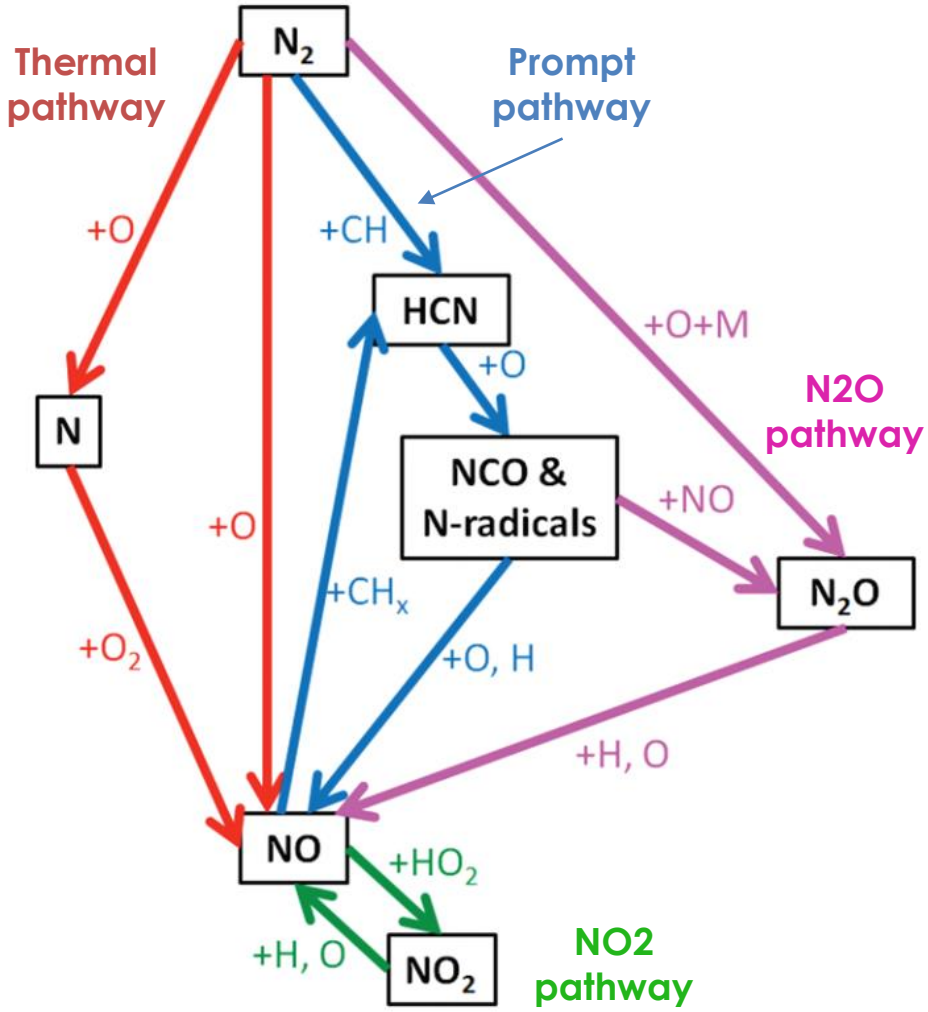
Low T and τ

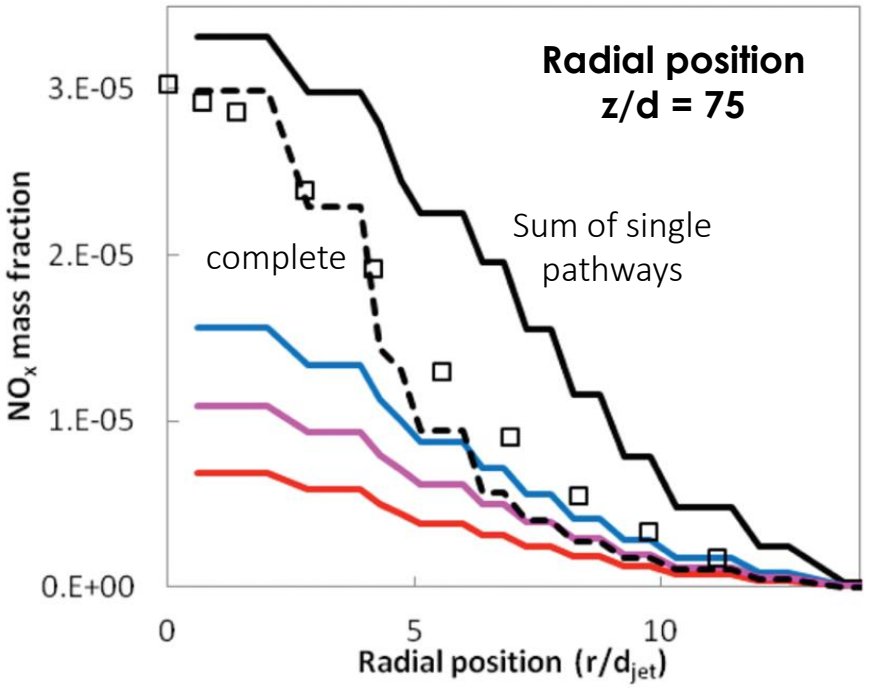
$\lambda < 1$

NOx formation pathways (II)

- Thermal NOx (Zeldovich)
  - Direct N_2 oxidation.
  - High temperature required (> 1800 K). Highly temperature dependent
- Prompt NOx (Fenimore)
  - N≡N bond scission by fuel radicals ($CH+N_2=HCN+N$).
  - Occurs in flame fronts. Not significantly temperature dependent
- N_2O Pathway
  - Through $N_2 + O + M \rightarrow N_2O + M$.
  - Relevant under elevated pressures and lean combustion (gas turbines)
- Fuel NOx
  - NO formation from N-containing fuel fragments (CN, NH).
  - Relevant if fuel contains chemically-bound nitrogen.

NOx Pathway Analysis

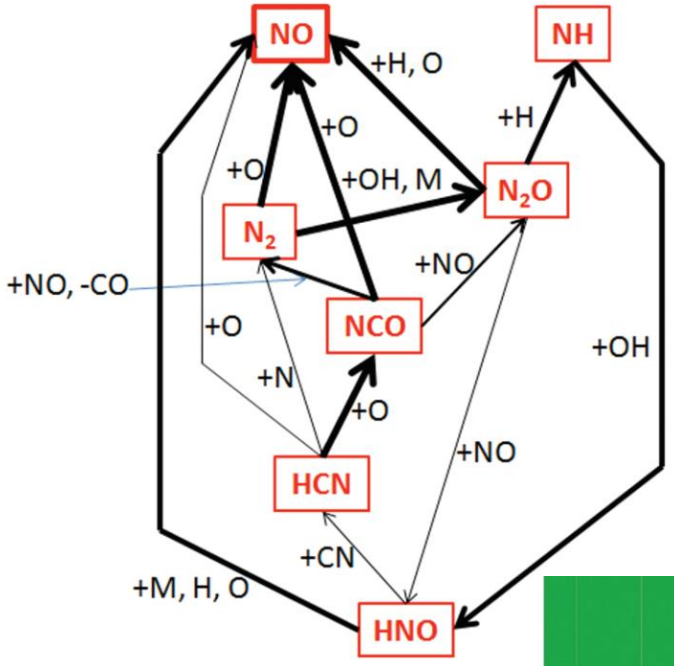


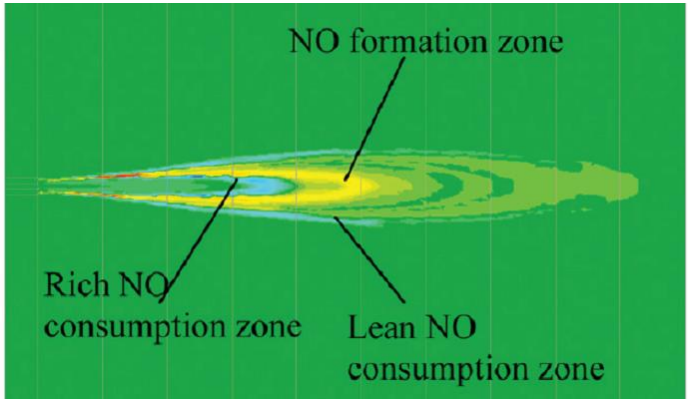


Of the total NOx produced by the Sandia D flame, 47% is due to the prompt pathway, 32% is due to the N2O pathway, and 21% is due to the thermal pathway.

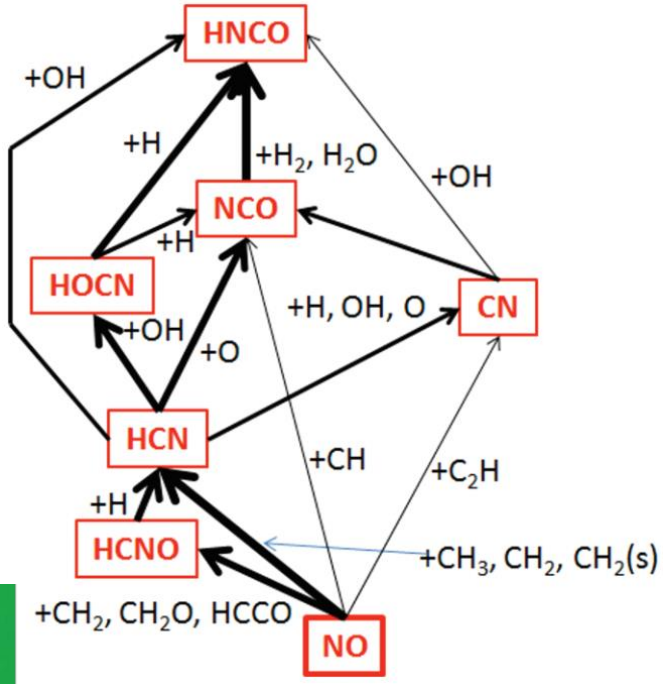
Reaction channels

Important reaction channels for NO production in the high-temperature flame brush.





Important reaction channels for NO consumption in the fuel-rich region.



Rates of production of NO

Validation: Sandia Syngas Flames

CO / H_2 / N_2 Jet Flames[1]

[1] Barlow, R.S., et al., *Sandia/ETH-Zurich CO/H2/N2 Flame Data - Release 1.1.* www.ca.sandia.gov/TNF, Sandia National Laboratories, 2002

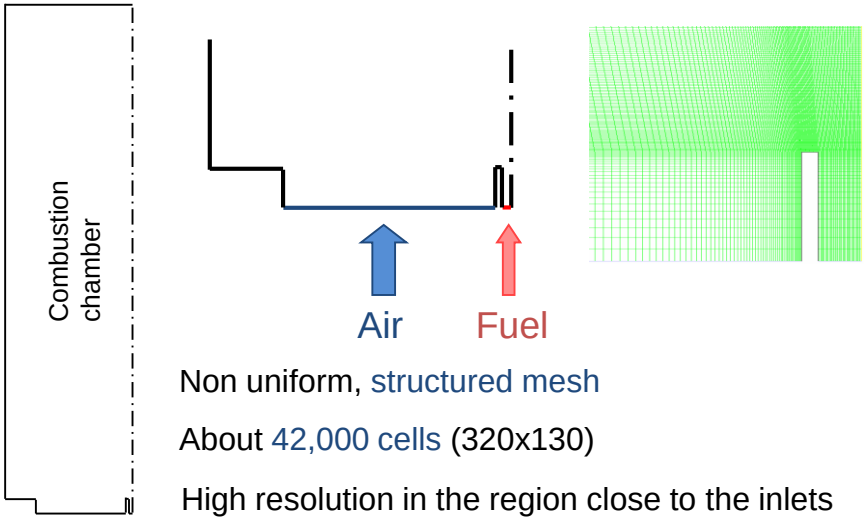
Unconfined turbulent jet flame in low-velocity coflow

Fuel composition:

40% CO, 30% H_2, 30% N_2

Fuel inlet velocity: ~ 45-76 m/s

Computational domain



Non uniform, structured mesh

About 42,000 cells (320x130)

High resolution in the region close to the inlets

CFD Simulation details

CFD Code	FLUENT 6.3.2
Space	2D Axial-Symmetric
Time	Steady
Turbulence modeling	Standard κ-ε turbulence model
Wall treatment	Standard wall functions
Radiation	Discrete Ordinate Model
Solver	Segregated implicit solver

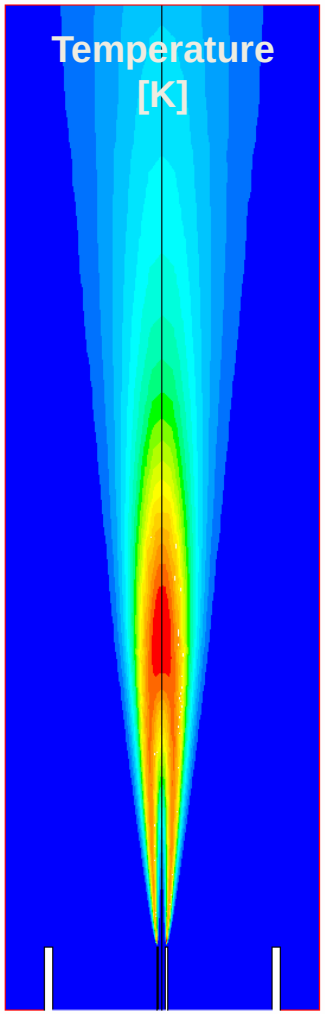
Spatial resolution	Second-Order Upwind scheme
Pressure Interpolation	PRESTO!
Combustion model	Eddy Dissipation Concept (EDC)

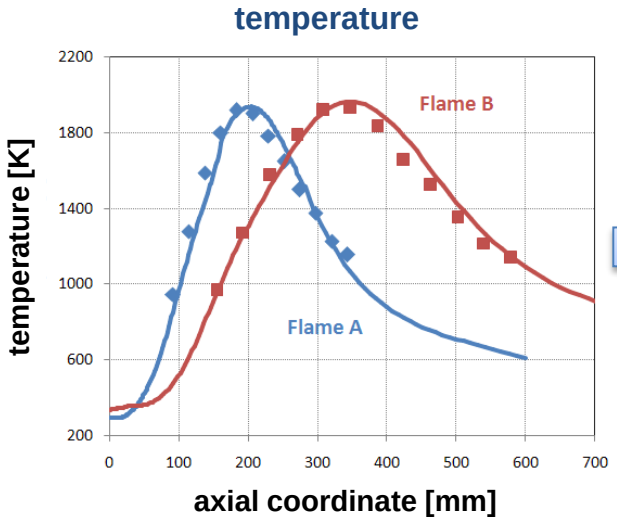
POLIMI_COH2 kinetic scheme

13 species

37 reactions

Validation: Sandia Syngas Flames

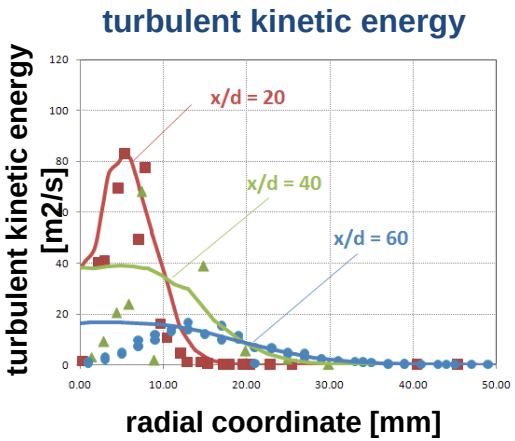


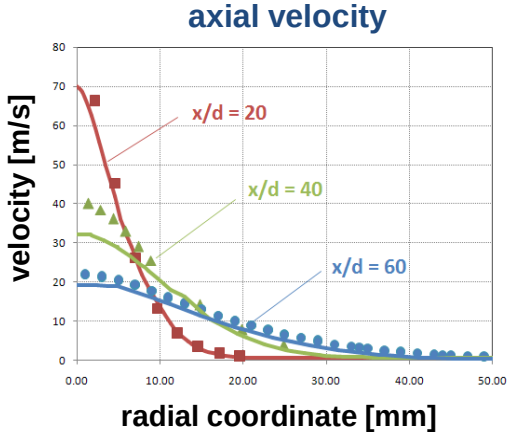


KPP

POLIMI_COH2NOX
32 species
178 reactions

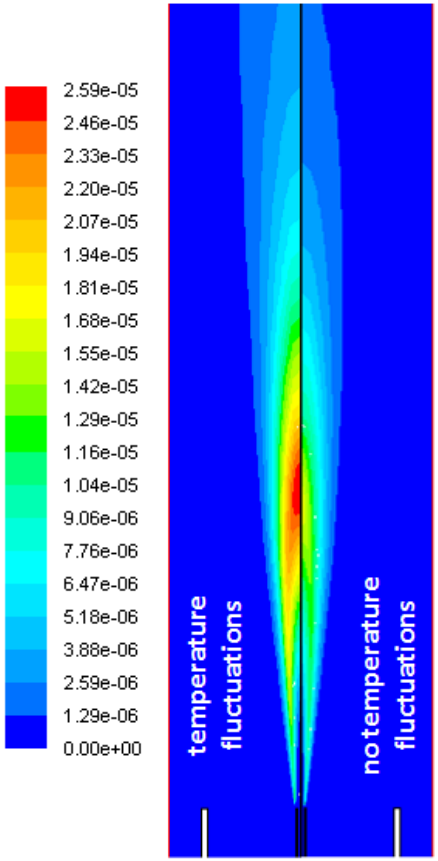
Number of Reactors:
2,500 (%5 of original number of cells)





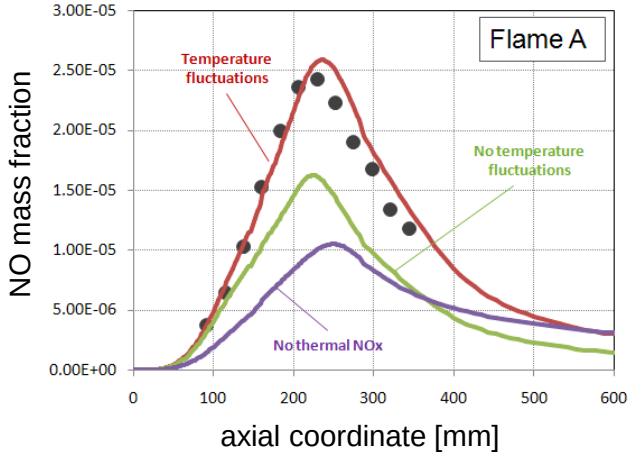
Validation: Sandia Syngas Flames

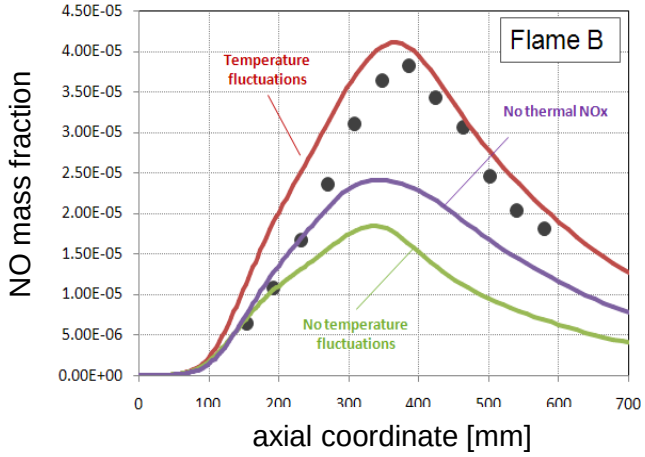
NO mass fraction



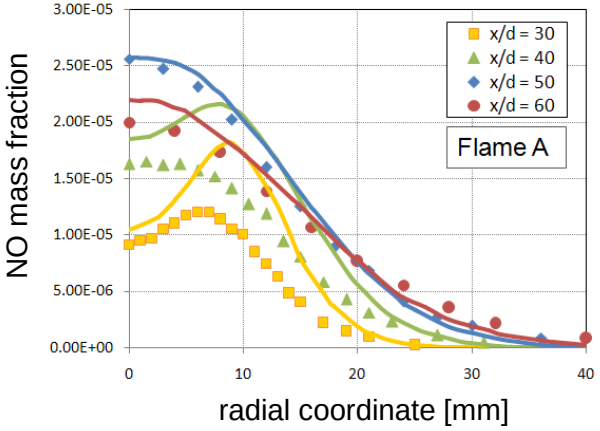
Barlow, R.S., et al., *Sandia/ETH-Zurich CO/H_2/N_2 Flame Data - Release 1.1.* www.ca.sandia.gov/TNF, Sandia National Laboratories, 2002

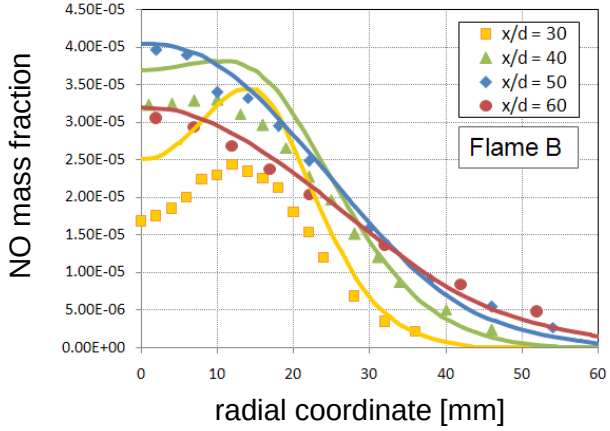
Axial profiles





Radial profiles

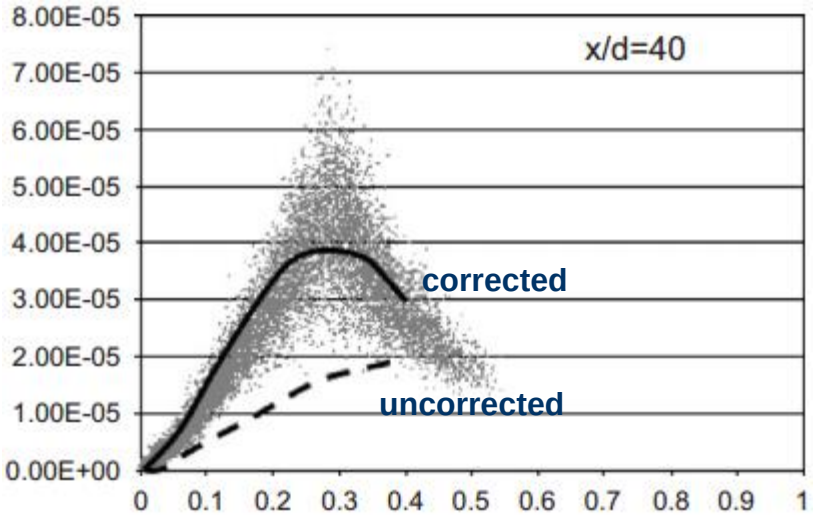




Validation: Sandia Syngas Flames

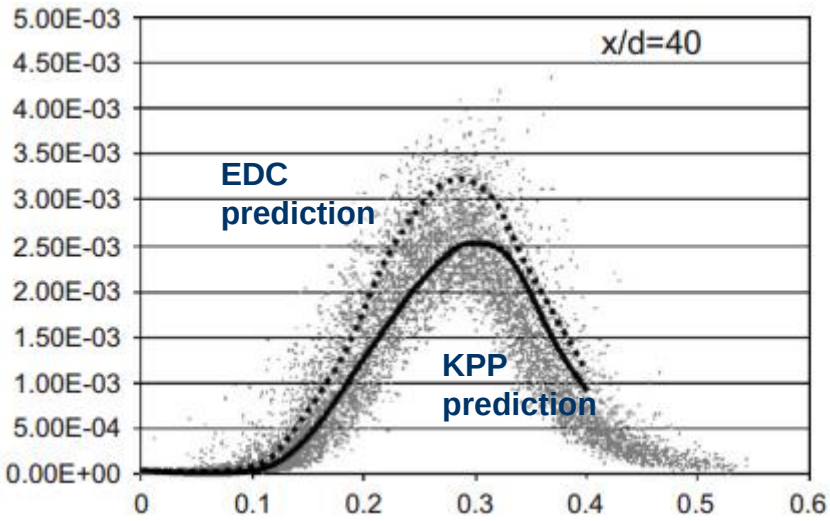
NO and OH mass fraction for Flame B
Comparison between single shot measurements (symbols) and numerical simulations (lines)

NO mass fraction



continuous line is the result of the KPP, dashed line shows the effect of neglecting temperature fluctuations on NO

OH mass fraction



OH radicals calculated using the EDC model in FLUENT (dotted line) and the KPP (continuous line).

Valiation: NH_3-Doped Jet Flame

CO / H_2 / N_2 Jet Flame

Drake, M.C., et al., *Nitric oxide formation from thermal and fuel-bound nitrogen sources in a turbulent nonpremixed syngas flame.* Twentieth Symposium (International) on Combustion - The Combustion Institute, 1984: p. 1983-1990.

Unconfined turbulent jet flame in low-velocity coflow

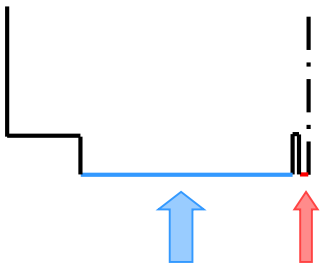
Fuel composition:

40% CO, 30% H_2, 30% N_2

Fuel inlet velocity: ~ 54 m/s

Small amounts of **ammonia** added to the fuel

Computational domain



Non uniform, unstructured mesh

Air Fuel + Ammonia (0-1.64% vol.)

About 36,000 cells

High resolution in the region close to the inlets

CFD Simulation details

CFD Code	FLUENT 6.2
Space	2D Axial-Symmetric
Time	Steady
Turbulence modeling	Standard κ-ε turbulence model
Wall treatment	Standard wall functions
Radiation	Discrete Ordinate Model
Solver	Segregated implicit solver

Spatial resolution	Second-Order Upwind scheme
Pressure Interpolation	PRESTO!
Combustion Model	Eddy Dissipation Concept

POLIMI_COH2 kinetic scheme

13 species

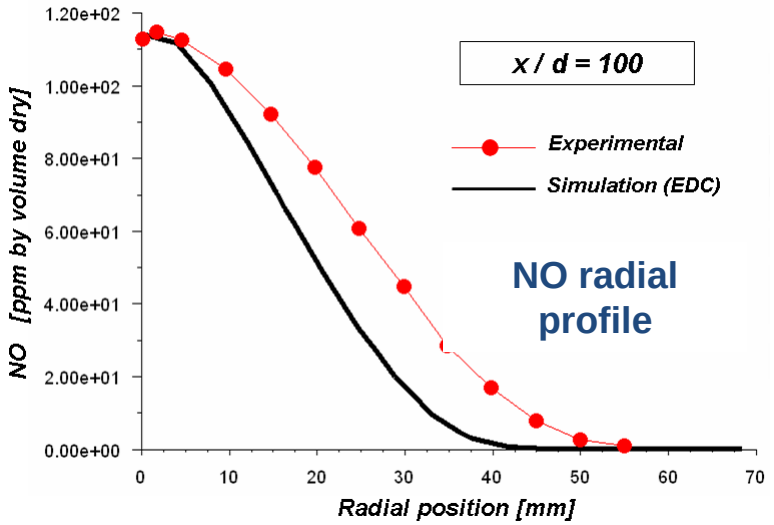
37 reactions

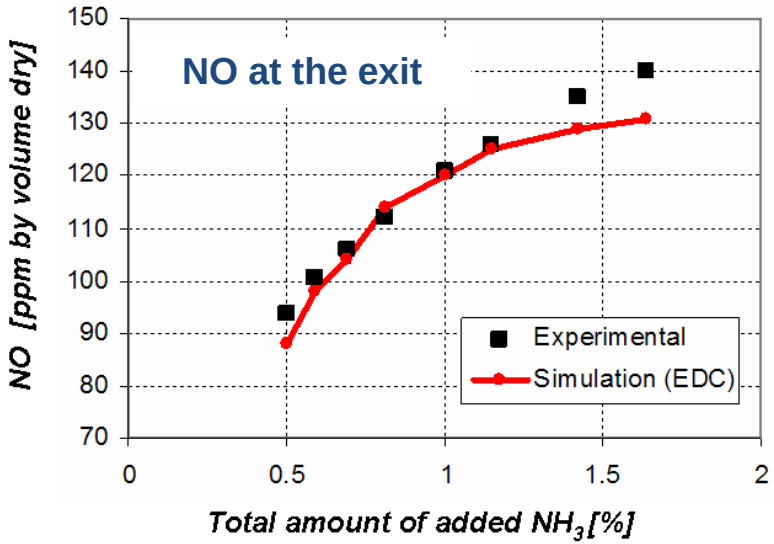
Valiation: NH_3-Doped Jet Flame

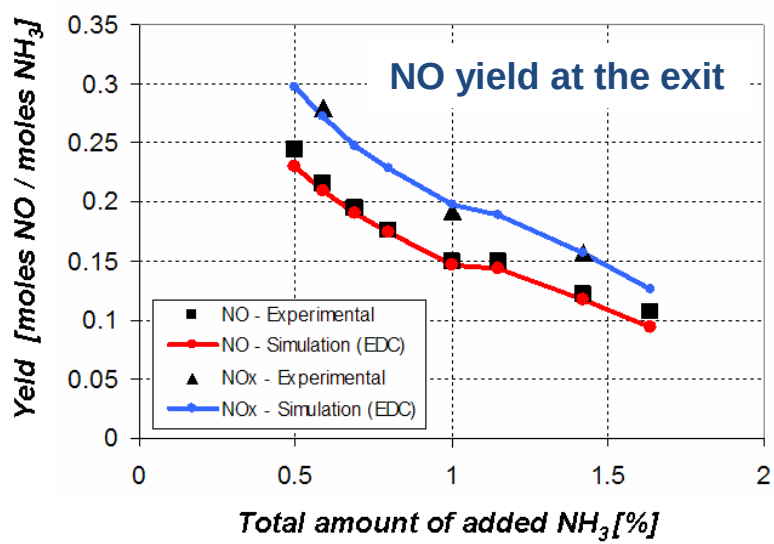
KPP

POLIMI_COH2NOX
32 species
178 reactions

Number of Reactors:
2,000 (%5 of original number of cells)

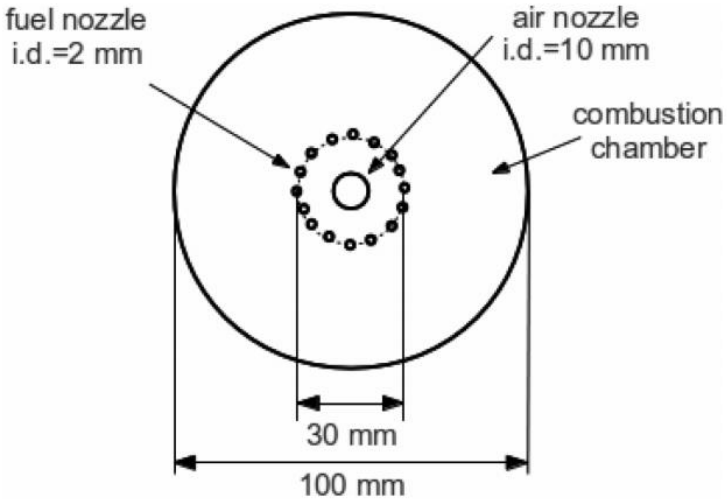






Small-scale MILD Combustor

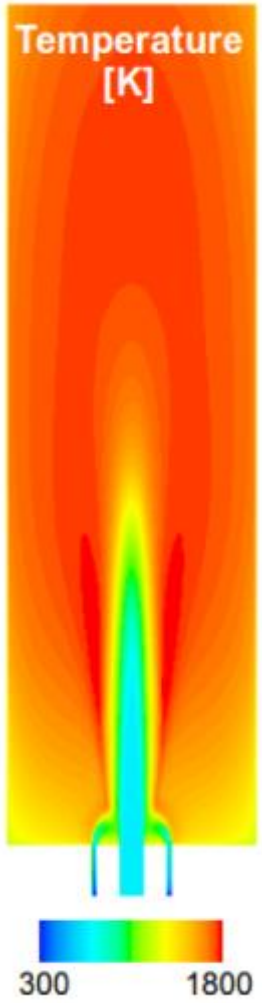
Verissimo, A.; Rocha, A.; Costa, M. *Operational, combustion, and emission characteristics of a small-scale combustor*, Energy Fuels 2011, 25(6), 2469–2480.



3D Computational Mesh
100,000 cells

RANS Simulation
K-e turbulent model
Eddy Dissipation Model

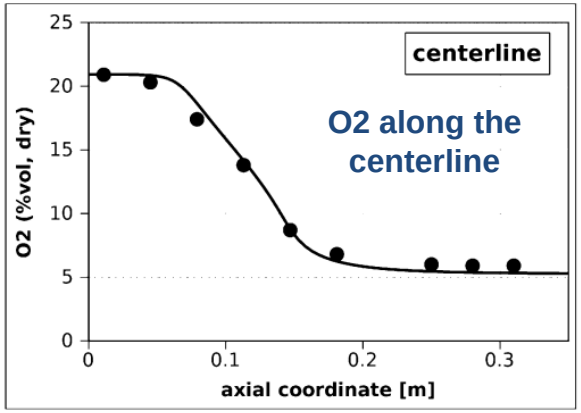
Kinetic Scheme
DRM22 (22 species, 111 reactions)

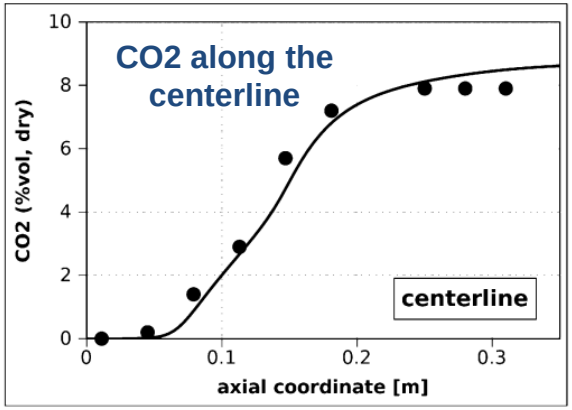


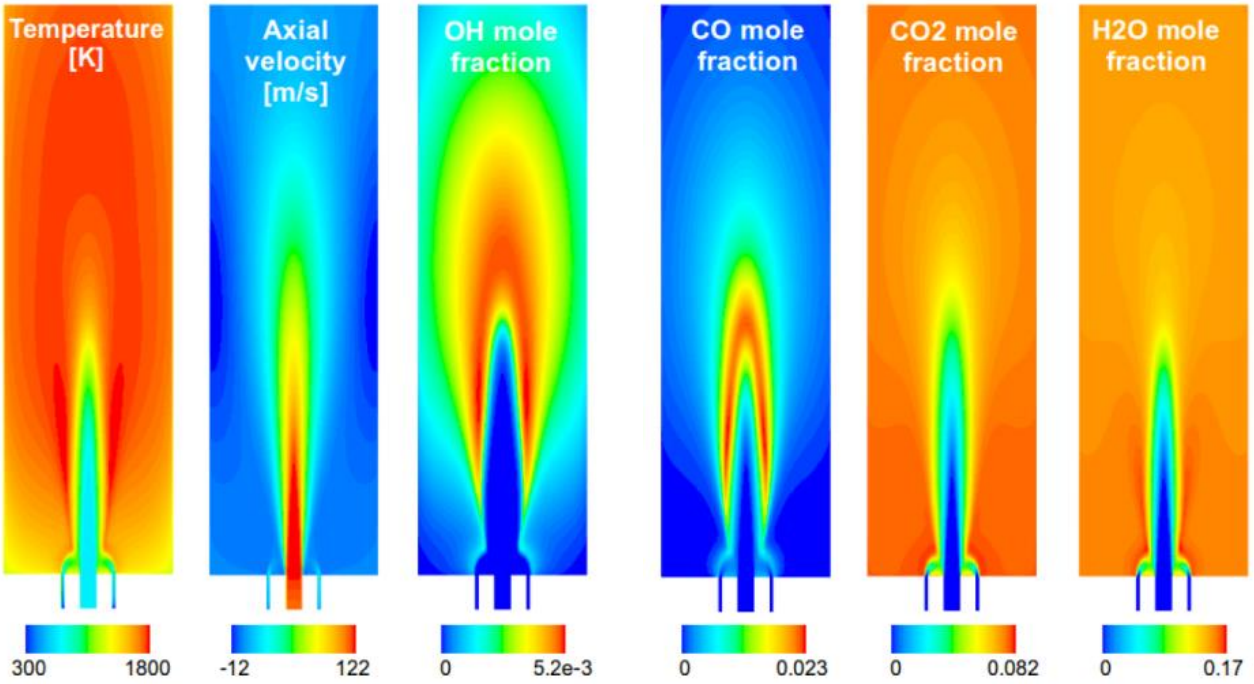
Combustion chamber
quartz glass cylinder
internal diameter of 100 mm and length of 340 mm.

Fuel: CH4 @ 300K supplied from 16 small orifices (Φ=2mm)
Oxidizer: air @ 673K supplied from a central nozzle (Φ=10mm)

Small-scale MILD Combustor



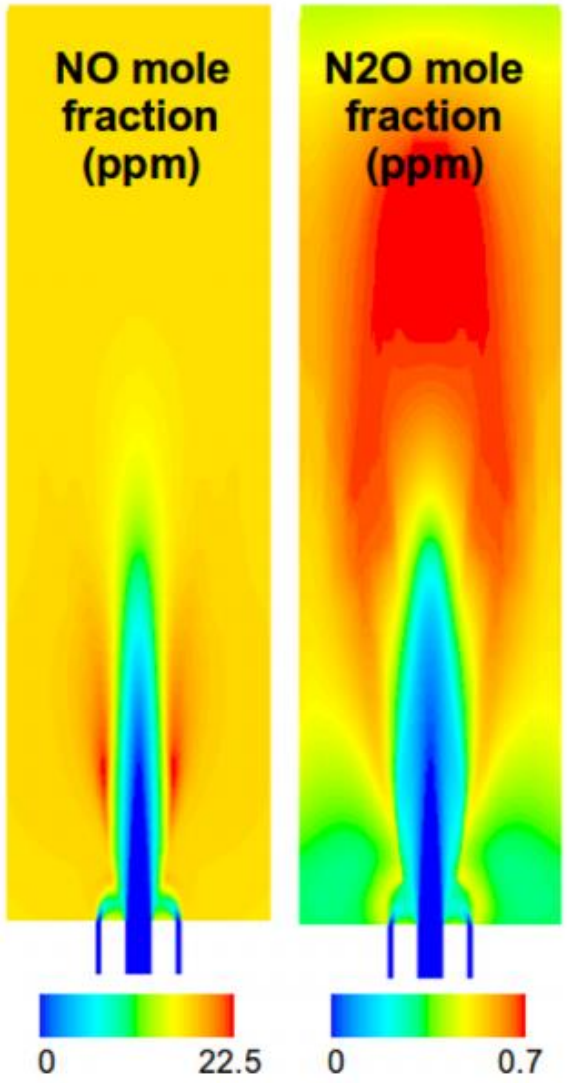




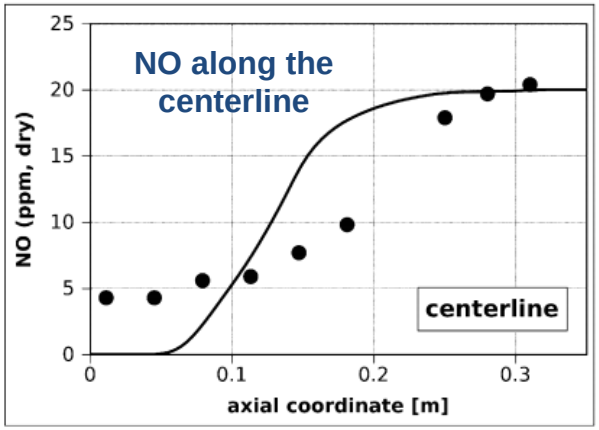
Kinetic Post Processing

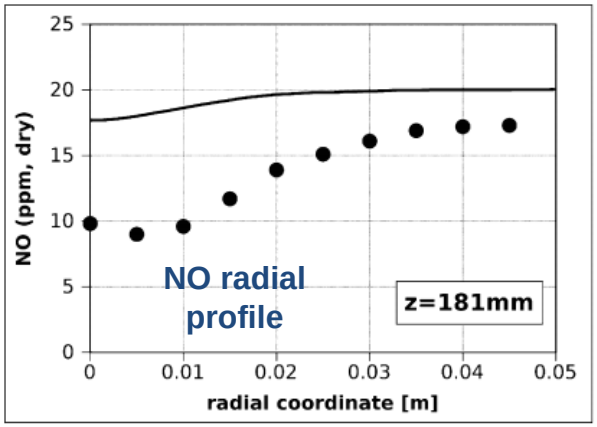
POLIMI_COH2NOX
114 species
2105 reactions

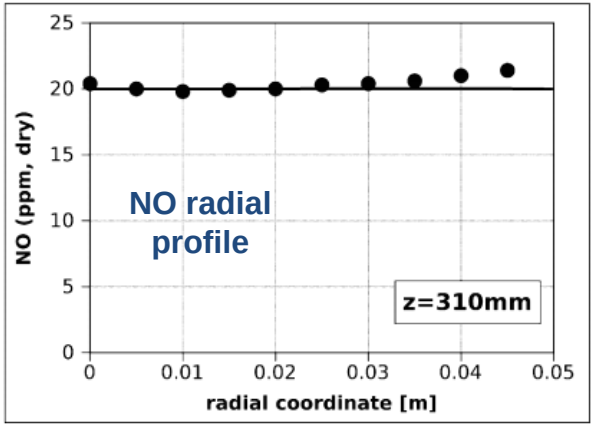
Small-scale MILD Combustor



Comparison between experiments and KPP predictions







Reactor Network:
5,000 reactors
(%5 of original number of cells)

Outline

1. The CRECK Modeling Group @ Politecnico di Milano
2. Introduction
3. The Kinetic Post Processing (KPP) Technique for NOx
   - ✓ Kinetic mechanisms for CFD applications
   - ✓ Reactor networks from CFD
   - ✓ Effects of temperature fluctuations on NOx formation
   - ✓ Solution of reactor networks
4. Applications to lab-scale and industrial flames
   - ✓ Lab-scale flames
   - ✓ **Industrial cases**
5. Extension to other pollutants
6. Conclusions

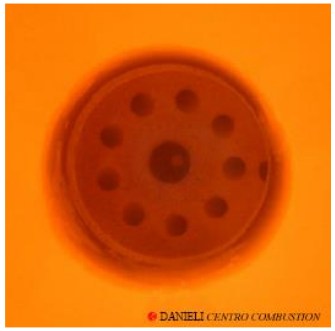
Corus I-70: NOx predictions

Danieli Centro Combustion

Curno, Italy

Test Furnace: up to 3 MW thermal power

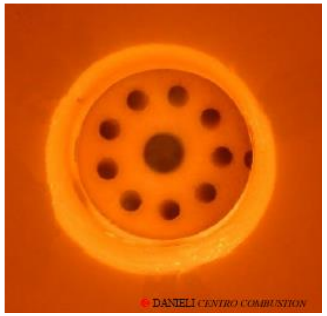
Fuel: gas mixtures with low calorific value or natural gas



Burner region

Gas mixture with low calorific value

30% H_2
15% CO
10% CH_4
45% N_2



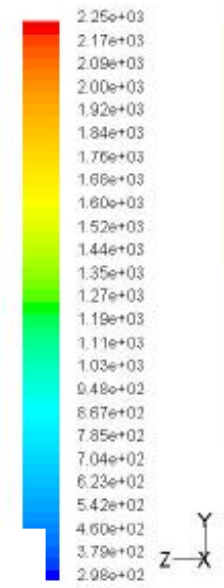
Burner region

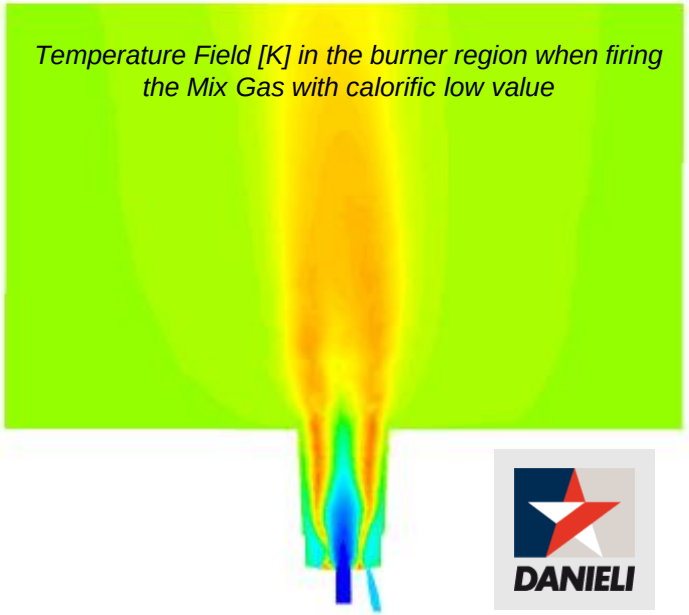
Natural Gas

95% CH_4
3% C_2H_6
1% N_2
1% other

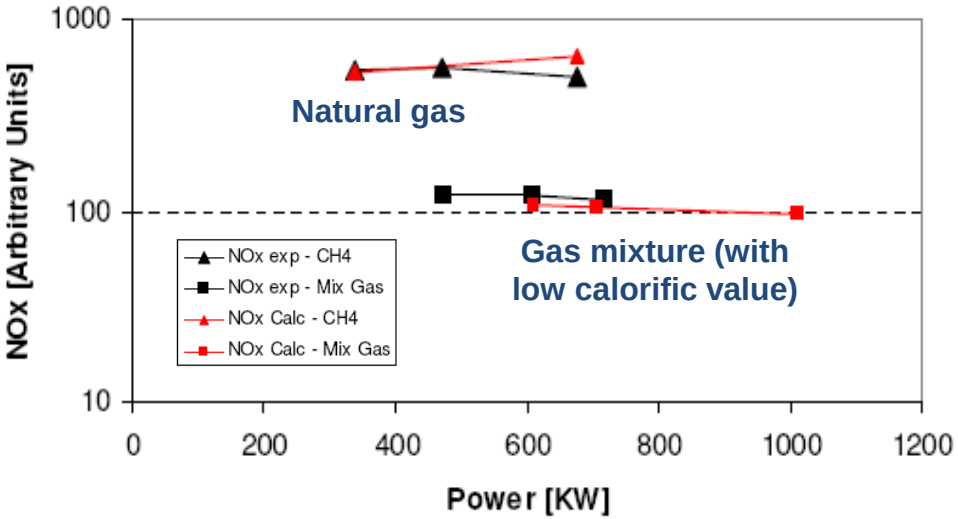
Corus I-70: NOx predictions

CFD Code	FLUENT 6.2
Space	3D
Grid	Structured (4,000,000 cells)
Time	Steady
Turbulence modeling	Standard κ-ε turbulence model
Wall treatment	Standard wall functions
Radiation	Discrete Ordinate Model
Spatial resolution	Second-order Upwind scheme
Pressure Interpolation	PRESTO!
Combustion model	EDC





Temperature Field [K] in the burner region when firing the Mix Gas with calorific low value



NOx emissions @3%O2 in waste gases – Air temperature: 490°C

Kinetic Schemes

CFD Simulation

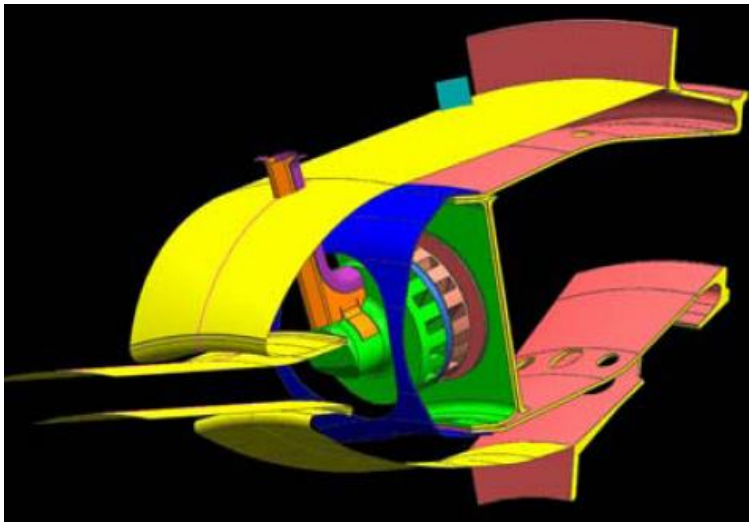
- 7 chemical species
- 3 reactions

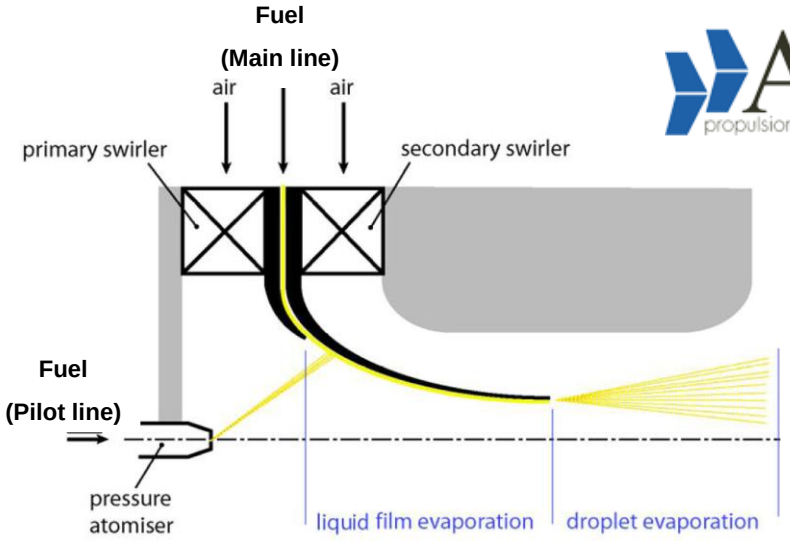
KPP

- 100 chemical species
- 1527 reactions

A. Frassoldati, T. Faravelli, E. Ranzi (2003)

PERM Injection System



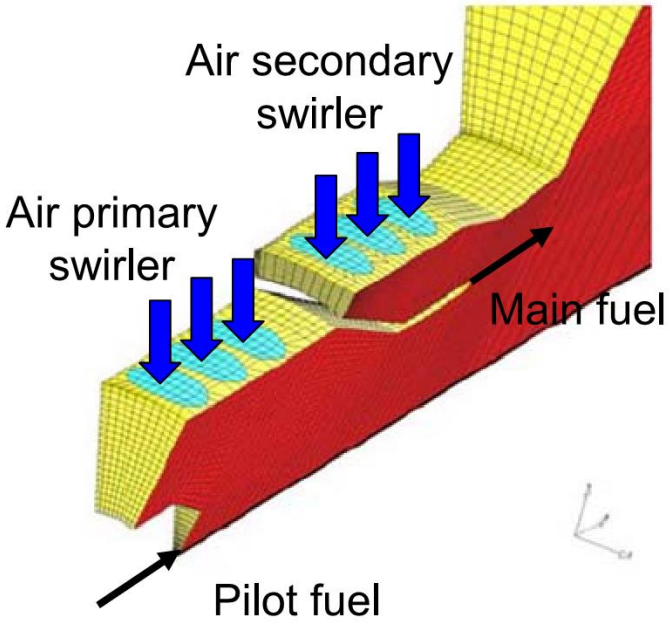


Avio propulsione aerospaziale

Studied the performance of the PERM (Partial Evaporation & Rapid Mixing) injection system in a **simple tubular combustor**

Experimental Data From	Karlsruhe University	ONERA
	Low P	High P
Inlet Pressure [bar]	8	22
Inlet Temperature [K]	506-522	811
Air/Fuel Ratio (AFR)	18-32	25.7-28.1
Pilot/Total Fuel Ratio	15%	15%

CFD Simulation (I)



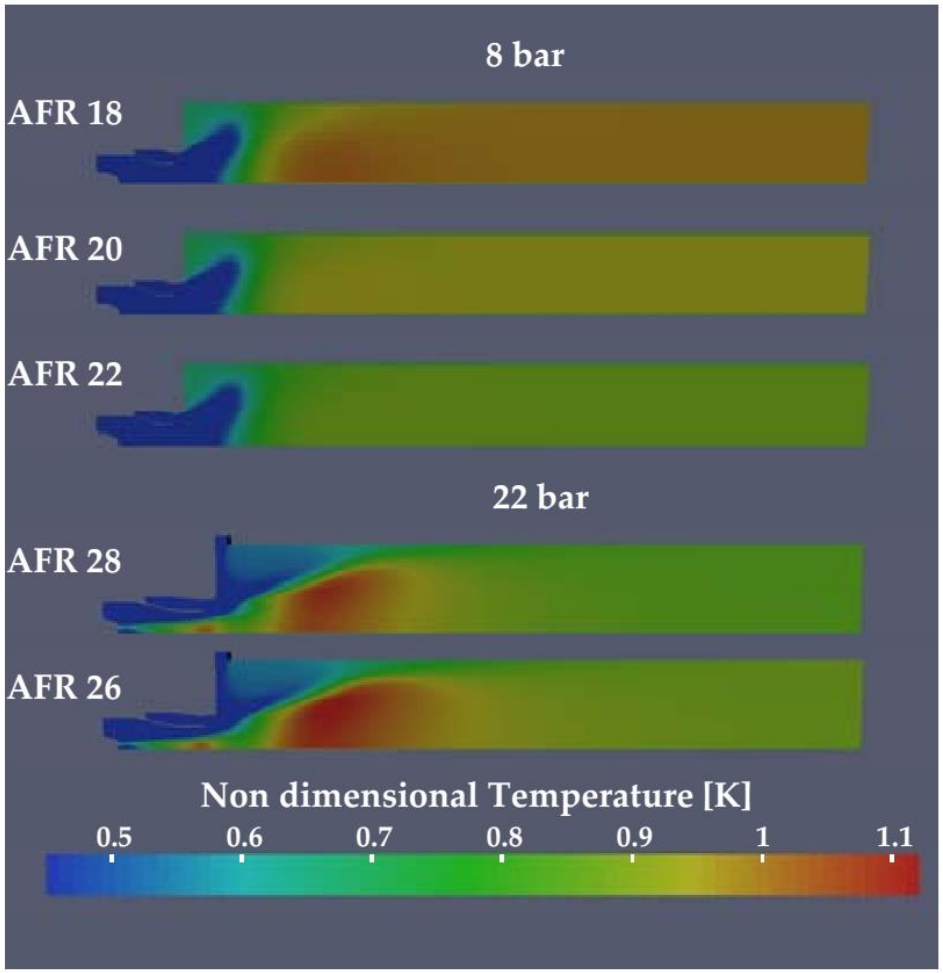
BODY3D CFD Code

K-e turbulence model

ED-FR Combustion model

Global 3-step kinetic mechanism

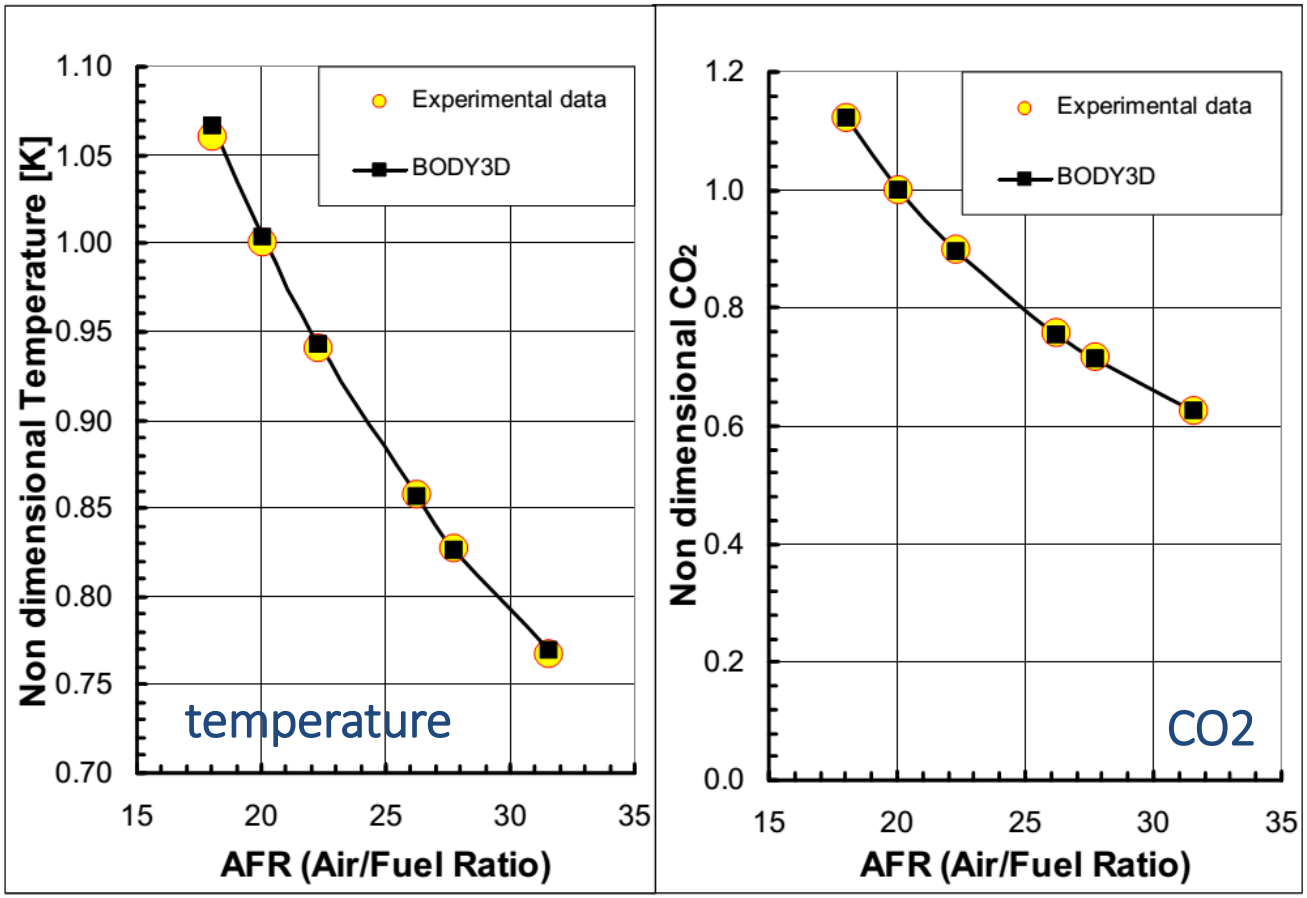
Mesh with 80,000 cells



AFR id the air/fuel ratio

CFD Simulation (II)

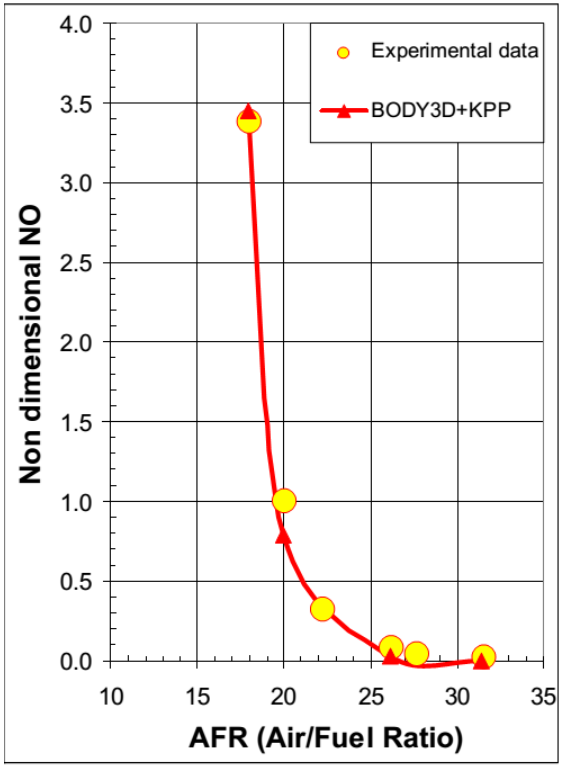
Comparison with measurements at the outlet

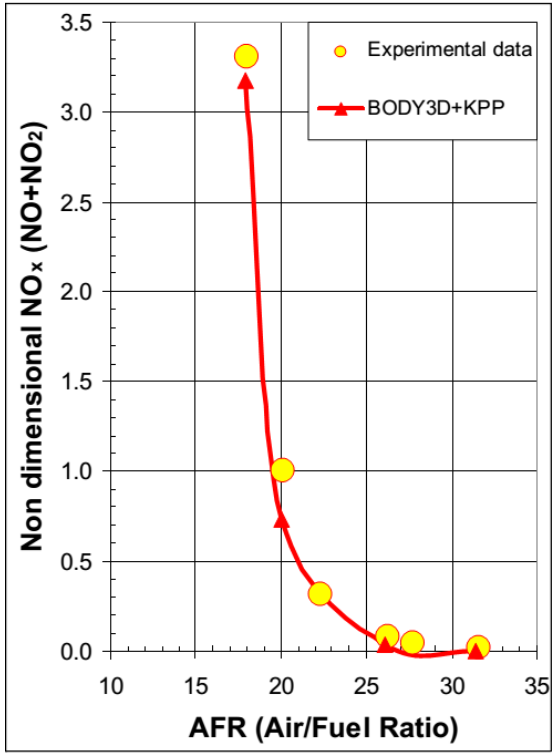


Low P (8 bar)

Kinetic post-processing (I)

Comparison with measurements at the outlet





Low P (8 bar)

Kinetic Post Processing

POLIMI_NC7
103 species
1500 reactions

Kinetic post-processing (II)

Low P (8 bar), AFR=18

Relative contribution to NO formation [%]

$N + NO = O + N_2$	*thermal mechanism*	70%
$CH + N_2 = HCN + N$	*prompt mechanism*	20%
$N_2O + [M] = N_2 + O + [M]$	*N_2O mechanism*	6%

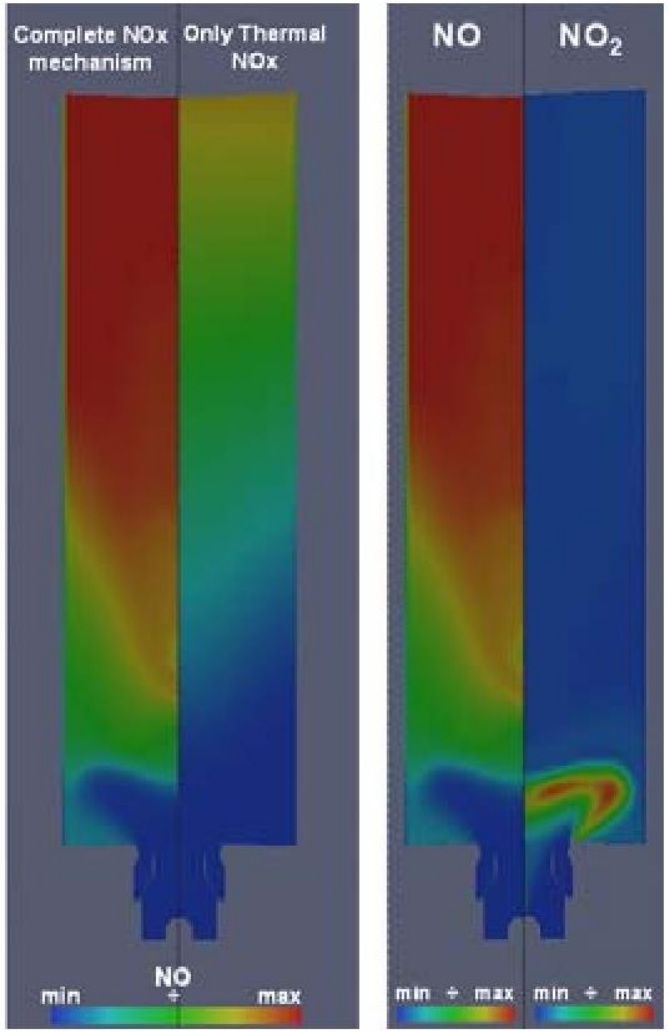
High temperature

Low P (8 bar), AFR=31

Relative contribution to NO formation [%]

$N_2O + [M] = N_2 + O + [M]$	*N_2O mechanism*	85%
$NNH + O_2 = N_2 + H + O_2$	*NNH mechanism*	10%
$NNH = N_2 + H$	*NNH mechanism*	2%

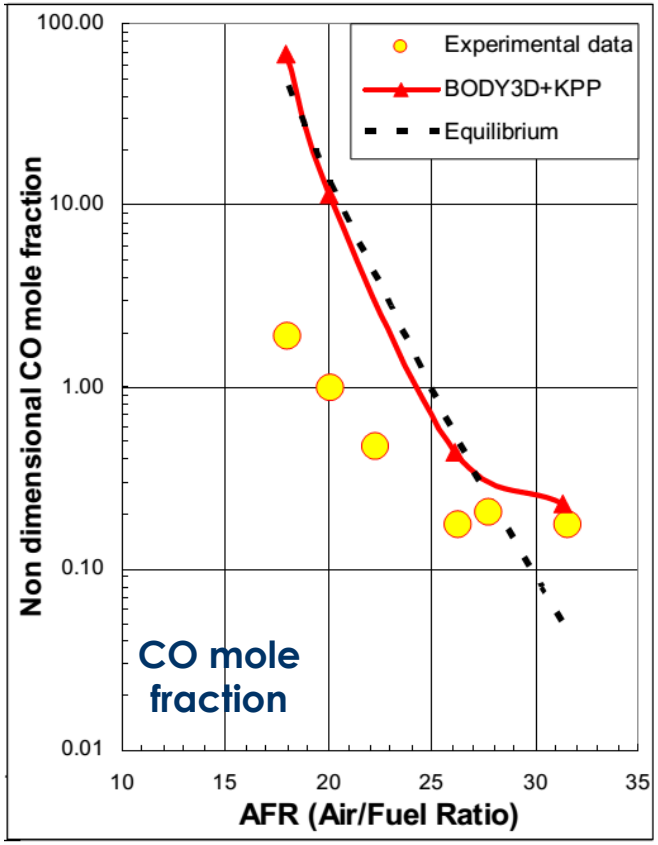
Low temperature

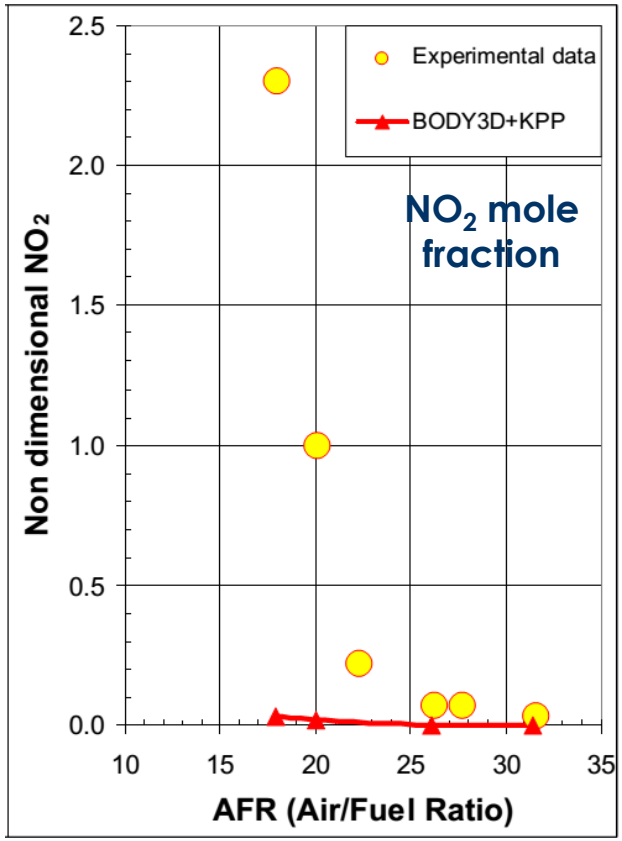


Low P (8 bar), AFR=21.16

The "probe effect" (I)

The model is able to capture the trends but tends to overestimate the CO emissions, especially at high temperatures. On the other hand, CO emissions predicted by the KPP are very close to the equilibrium value at high temperatures, while the effect of finite rate kinetics is evident at lower temperatures.



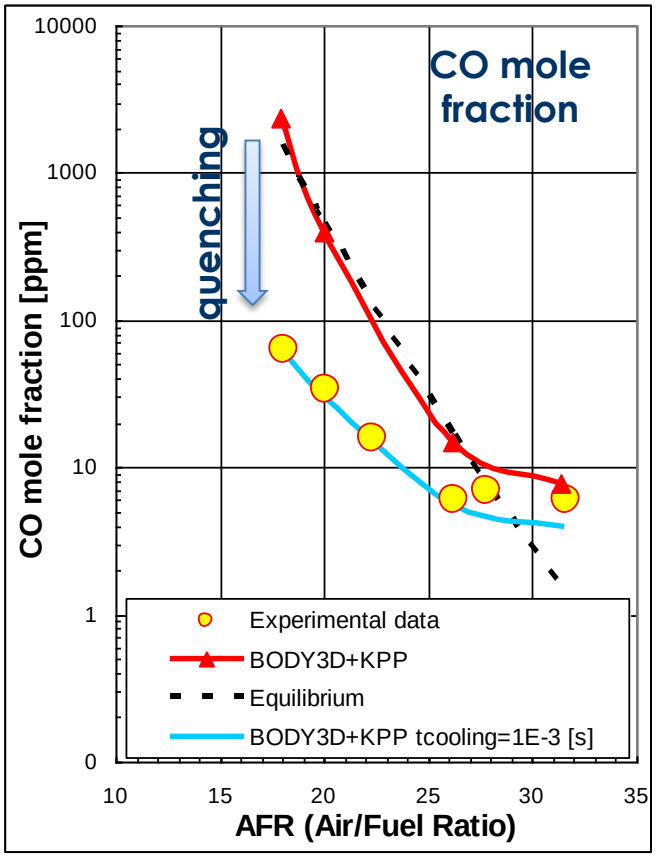


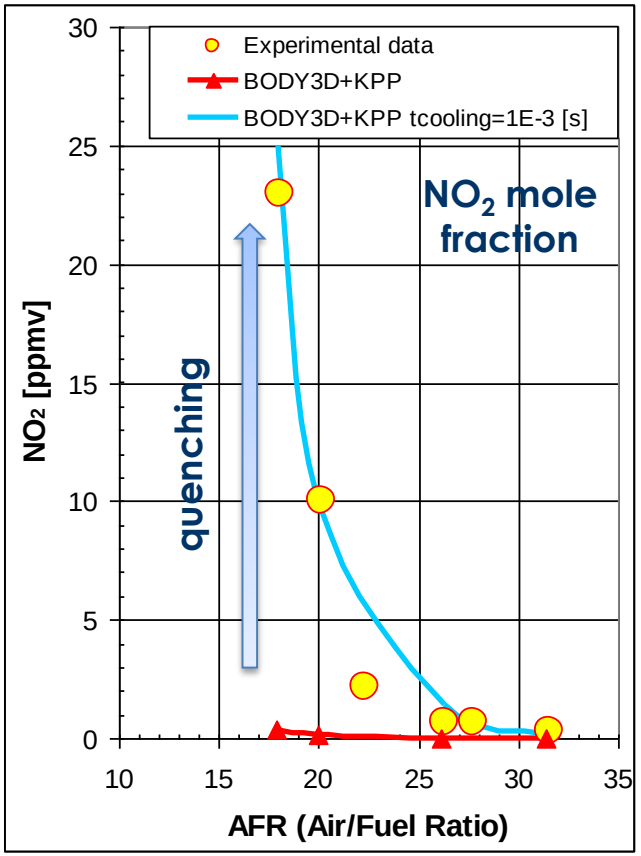
The "probe effect" (II)

Deviation on CO and NO_2 predictions can be explained as a possible effect of the measurement technique. This problem is known in the literature.

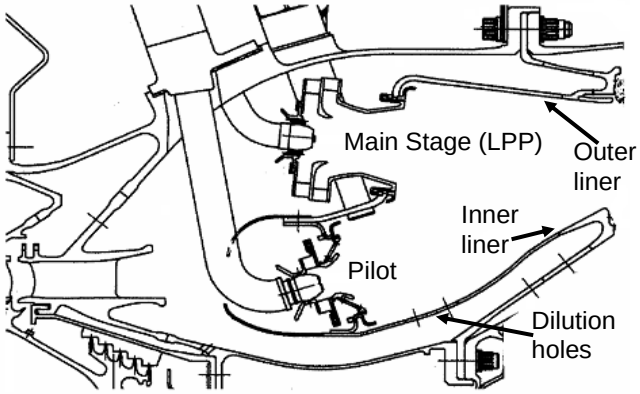
The cooling rate of the flue gases inside the sampling probe is not fast enough to "quench" the reactivity.

Conversion of CO to CO_2 and NO to NO_2 occurs in the probe.





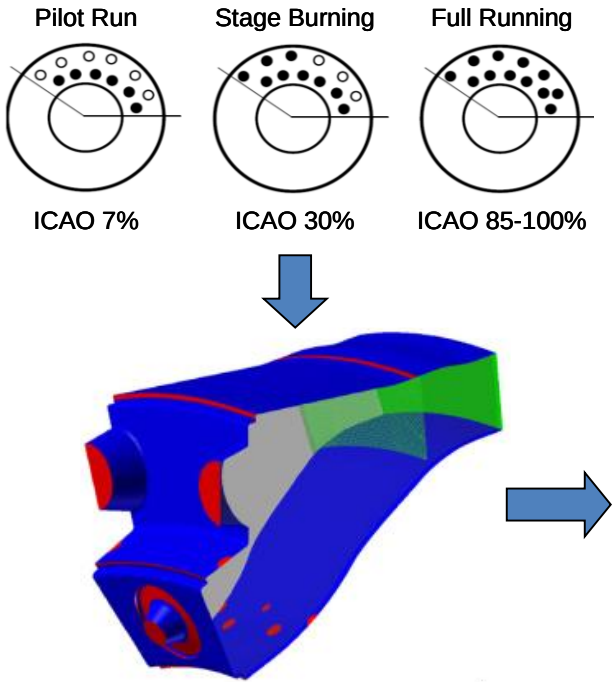
CLEAN Combustor



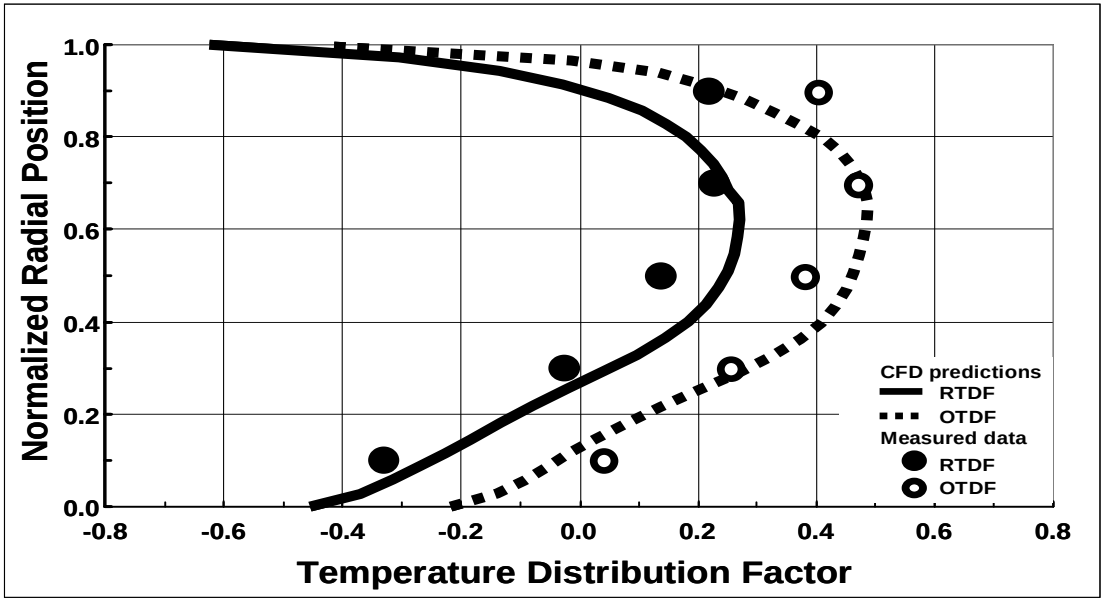
CLEAN is an axially staged combustor equipped with:

- 18 LPP injectors (Lean Premixed Prevaporized technology)
- 18 conventional pilot injectors

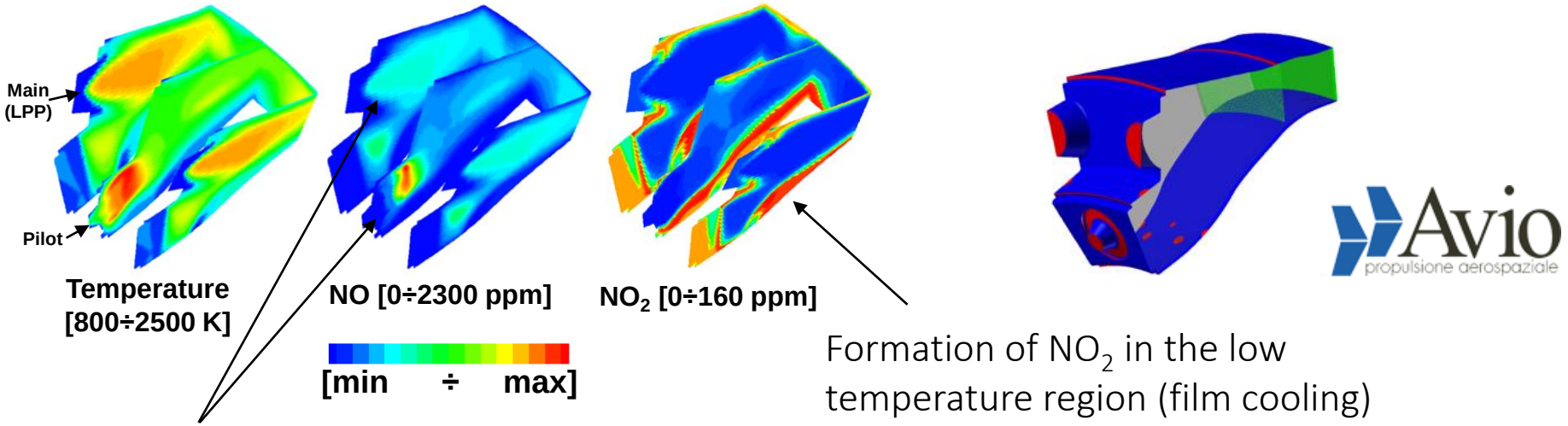
Avio propulsione aerospaziale



Good agreement with experimental measurements of Radial and Overall Temperature Distribution Factors at the outlet.



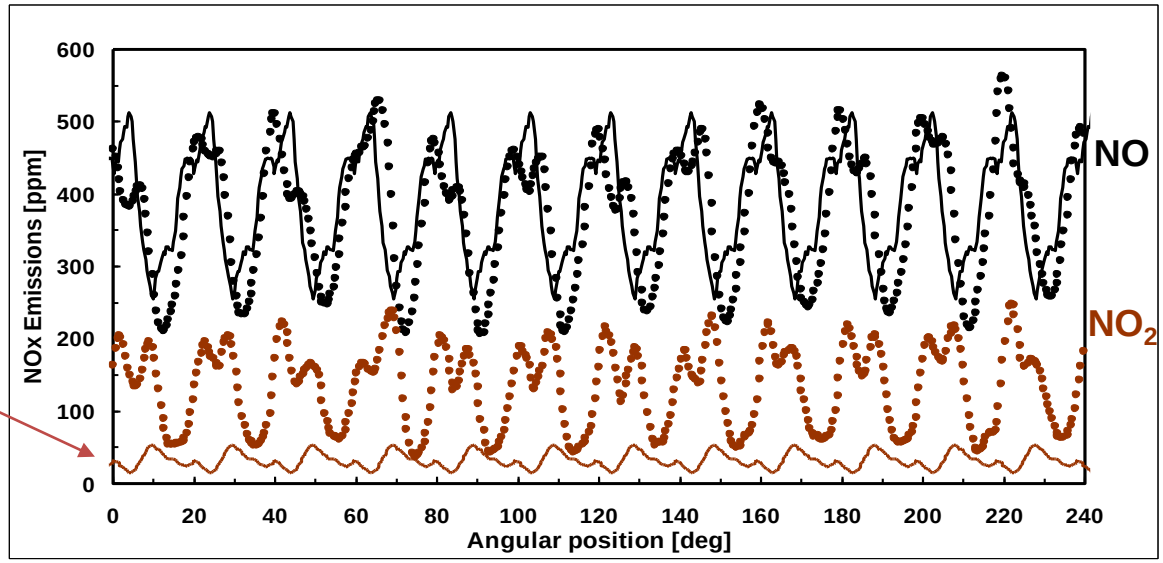
CLEAN Combustor



Formation of NO_2 in the low temperature region (film cooling)

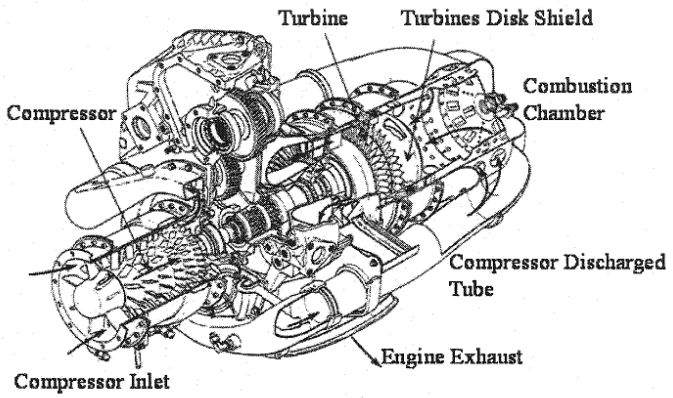
Different NOx formation in the conventional (pilot) and LPP injectors

Possible NO->NO2 conversion in the probe

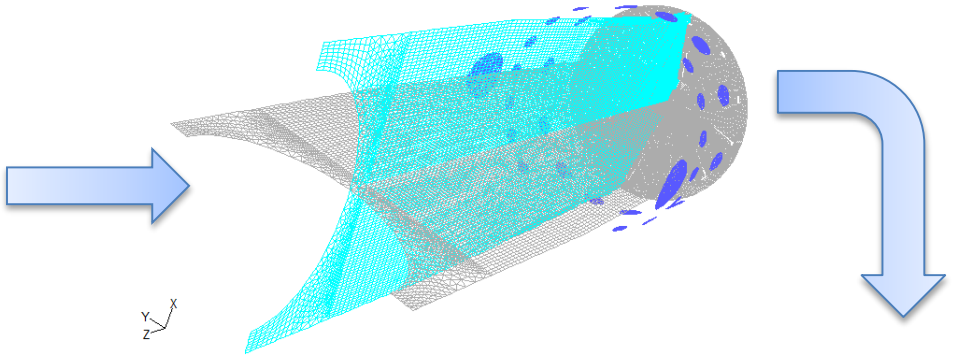


3-RR-Allison 250C engine

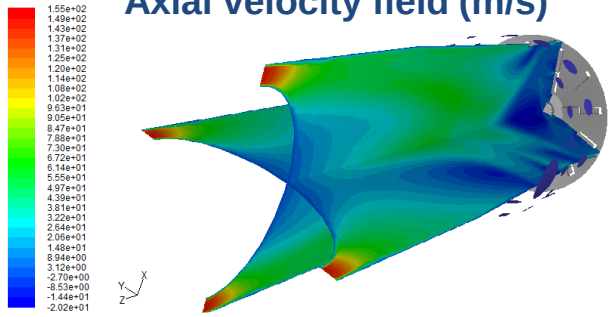
ROLL-ROYCE ALLISON 250 ENGINE



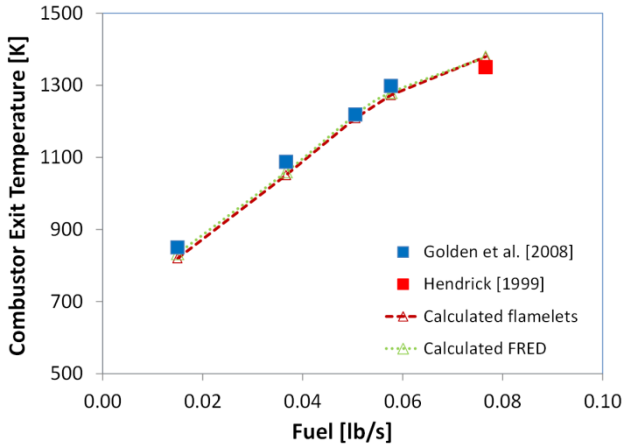
MESH (~1,000,000 cells)

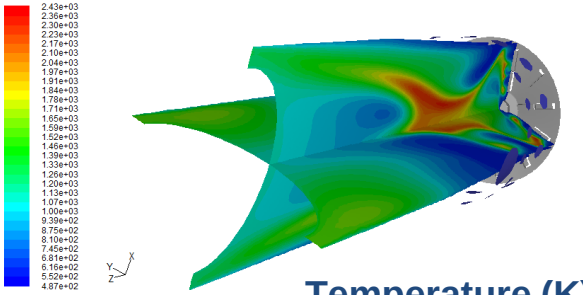


Axial velocity field (m/s)



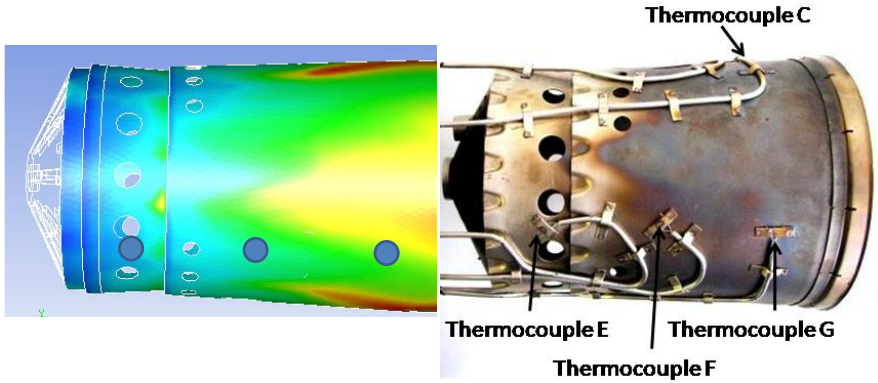
Comparison with experimental data



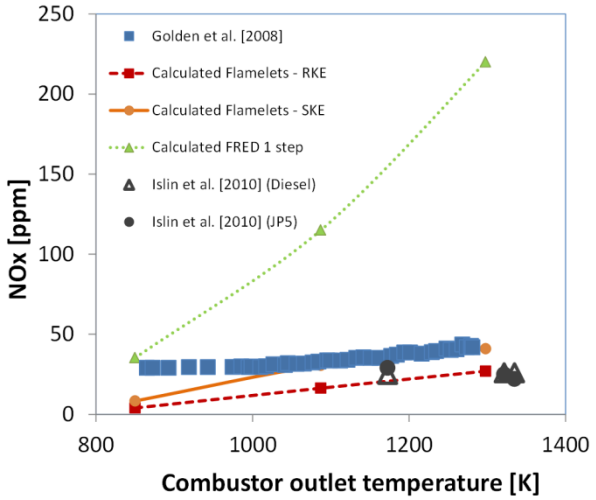


Temperature (K)

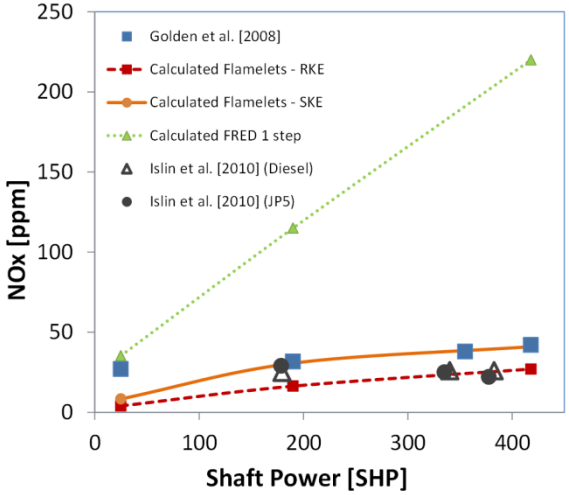
3-RR-Allison 250C engine

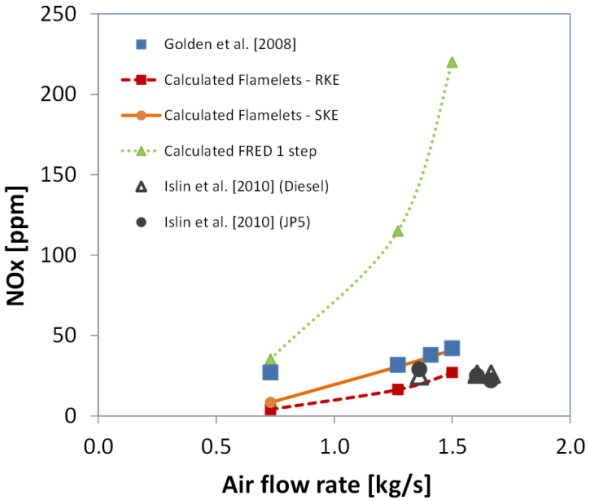


Bester et al., Proceedings of ASME Turbo Expo 2009: Power for Land, Sea and Air, GT2009-60333, June 8-12, 2009, Orlando, Florida, USA.



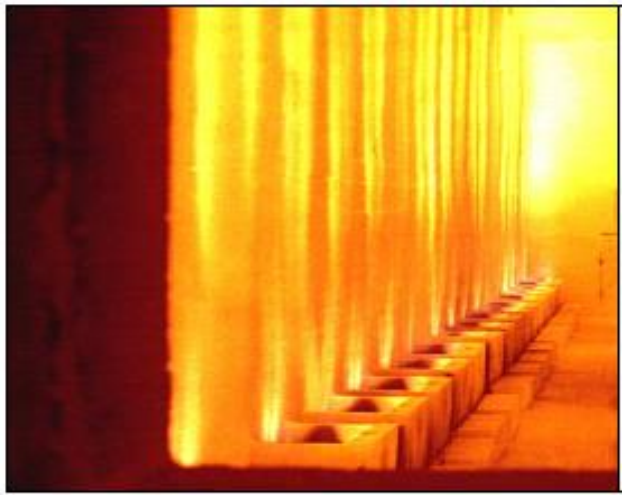
Golden et al., paper AIAA 2008-4902, 44th AIAA/ASME/SAE/ASEE Joint Propulsion Conference & Exhibit 21 - 23 July 2008, Hartford, CT.

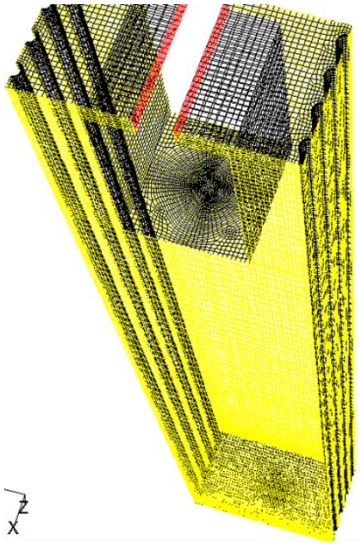


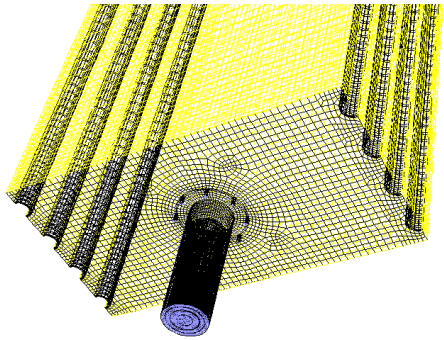


Islin et al., Proceedings of ASME Turbo Expo 2010: Power for Land, Sea and Air GT2010, paper 22436.

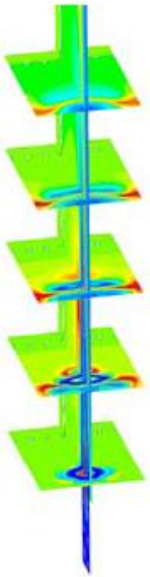
Technip GK6 Furnace





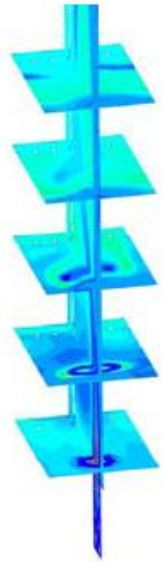


3D Computational mesh with 500,000 cells



KPP used to evaluate effect on NOx of **different burner design**, possible **burner-burner interaction** etc

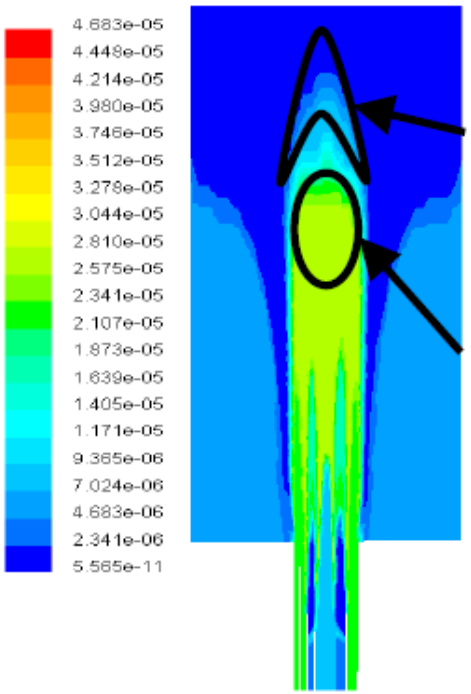
0 NOx Max



Technip developed a parallel version of the KPP code based on MPI

Technip GK6 Furnace

NO_2 mass fraction

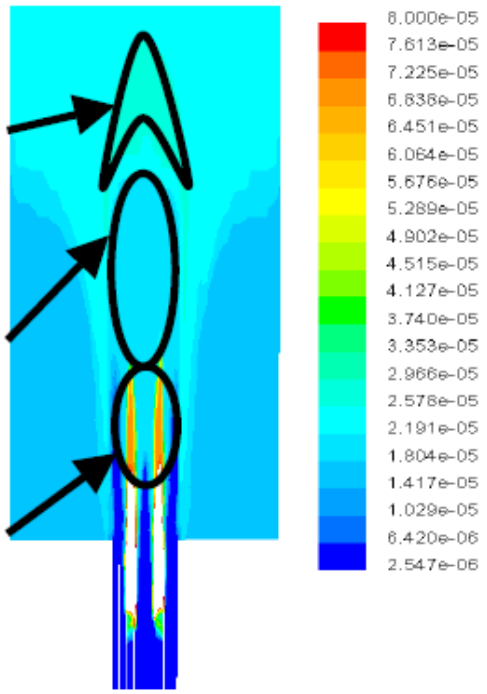


Zone 3, Reduction of NO2 to NO and N2

Zone 2, Mainly Thermal NO2, Low NO

Zone 1, Mainly Prompt NO, low NO2

NO mass fraction



CFD

Global Kinetic scheme
6 species
3 reactions

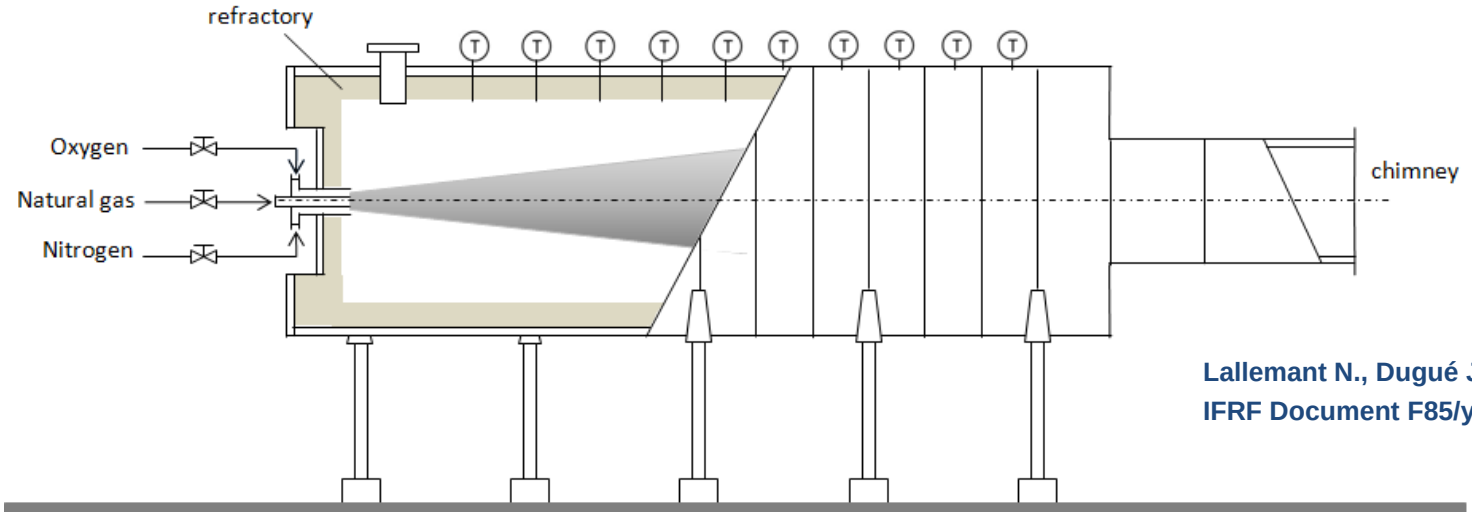
Eddy Dissipation Concept Model

POLIMI_C1C3HTNOX
100 species
1527 reactions

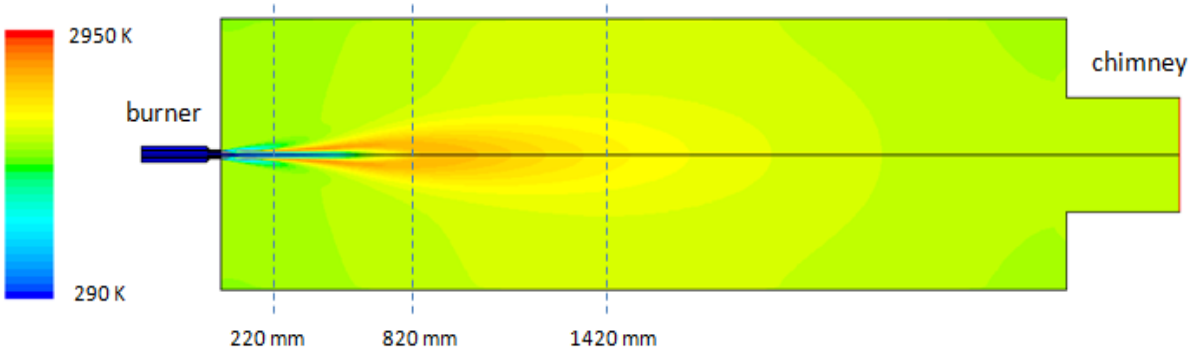
Number of Reactors:
500,000
(%100 of original number of cells)

KPP

IFRF Furnace (OxyFLAM2)



Lallemant N., Dugué J., Weber R.
IFRF Document F85/y/4 (1996)



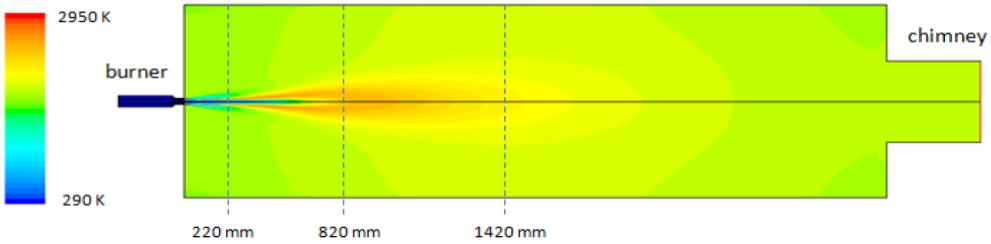
Experimental data

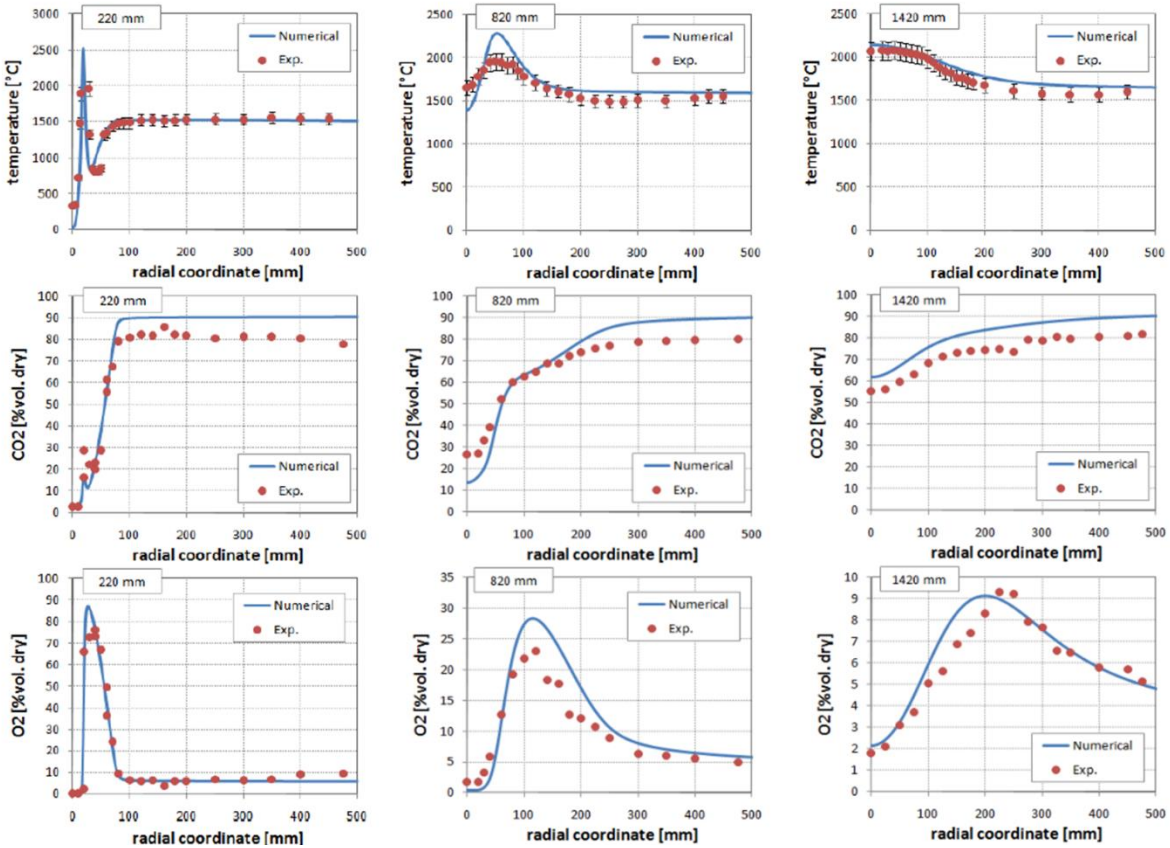
velocity, main species and temperature profiles inside the furnace at several axial locations

Furnace dimensions: 3750 x 1050 x 1050 mm

Thermal power: 0.78 MW

IFRF Furnace (OxyFLAM2)





CFD

Skeletal Kinetic Scheme
33 species
152 reactions

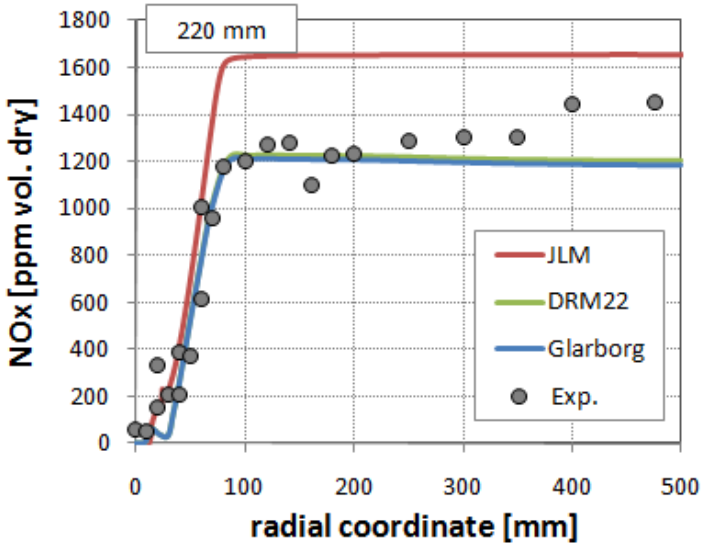
Eddy Dissipation Concept Model

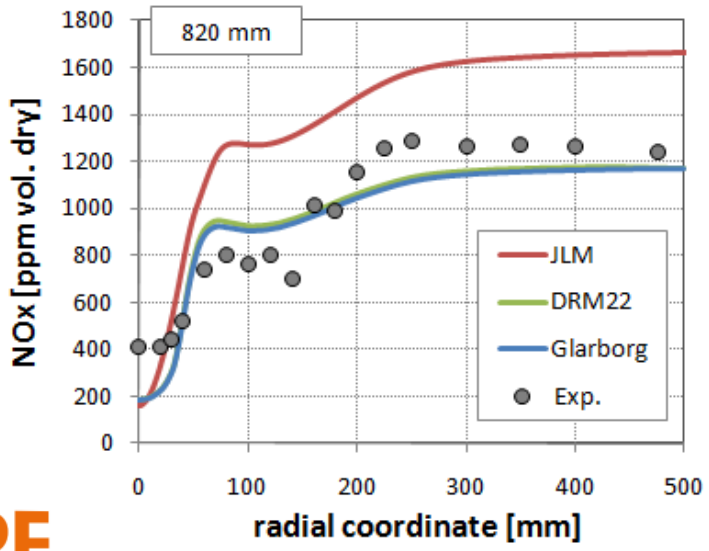
POLIMI_C1C3HTNOX
100 species
1527 reactions

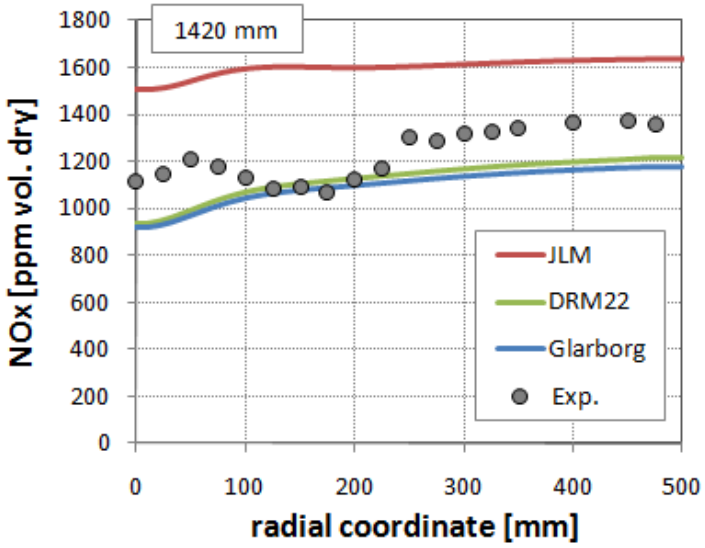
Number of Reactors:
5,000
(%10 of original number of cells)

KPP

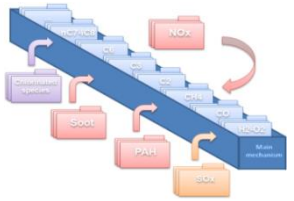
IFRF Furnace (OxyFLAM2)







MORE



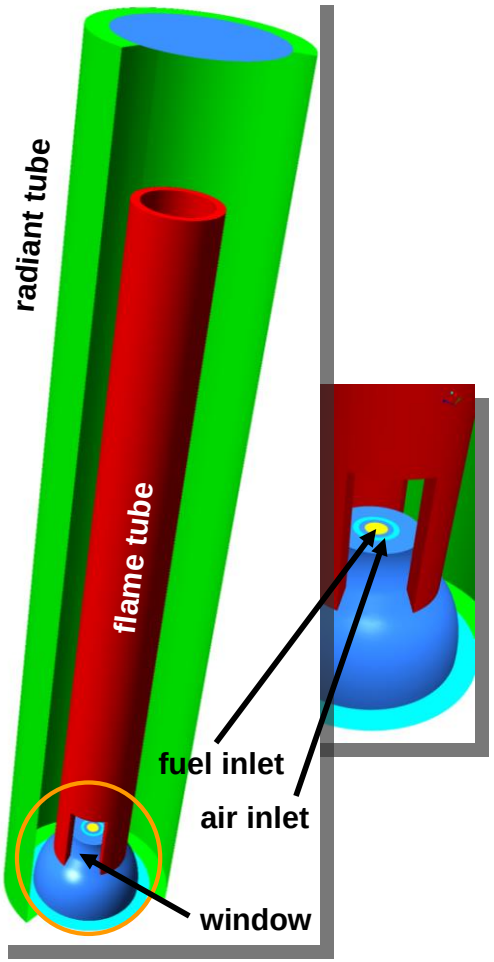
PolimiC1C3HT + NOX

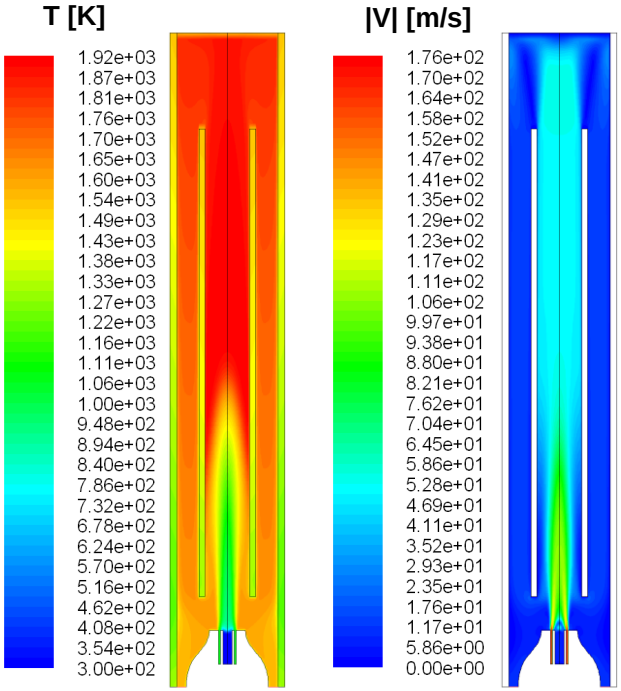
100 species, 1530 reactions

http://creckmodeling.chem.polimi.it

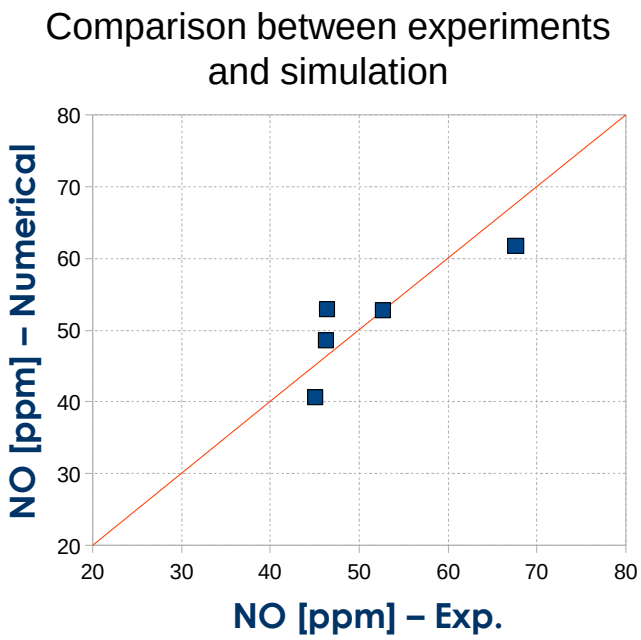
Ranzi E., Faravelli T.,Frassoldati A., Granata S., , Industrial and Engineering Chemistry Research, 44 (44), 5170-5183 (2005).

The FLOX® Burner





Mesh 9,500 cells

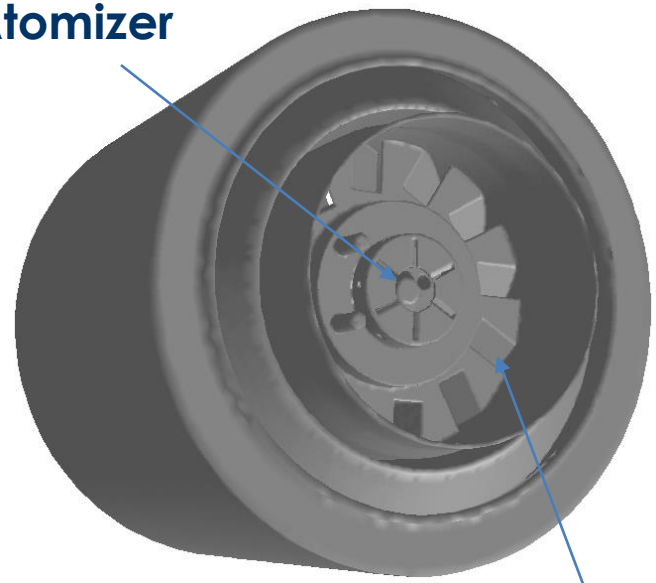


Case	Q [kW]	T exhaust [K]	T max [K]	NO exp [ppm]
1	8.23	1479	1815	5.8
2	9.13	1535	1920	18.9
3	9.31	1651	2034	40.7
4	9.90	1687	2065	52.9
5	10.53	1710	2066	52.8
6	10.70	1722	2096	61.8
7	10.42	1702	2049	48.6

A. Parente, A. Cuoci, C. Galletti, A. Frassoldati, T. Faravelli, L. Tognotti, *NO formation in flameless combustion: comparison of different modeling approaches,* European Combustion Meeting 2009 14-17 April 2009 - Vienna, Austria

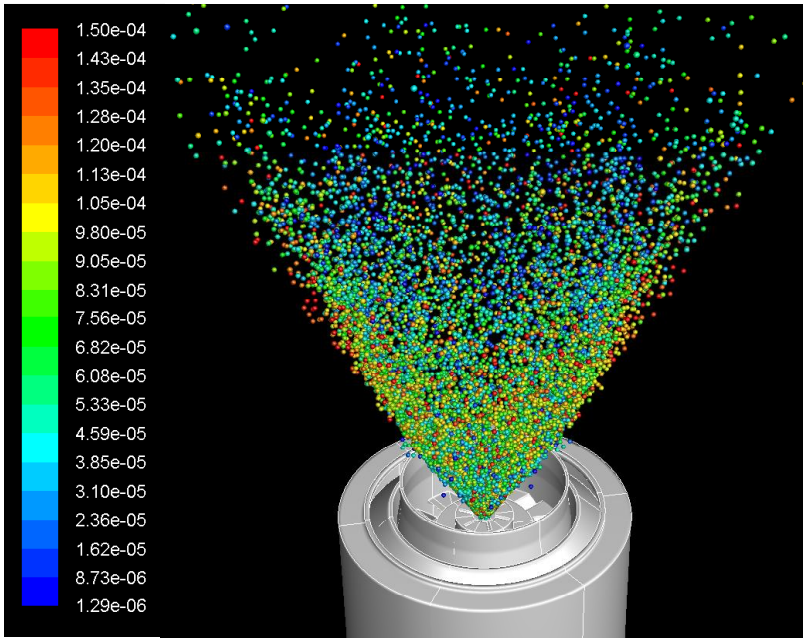
Riello Gasoil Burner

Atomizer

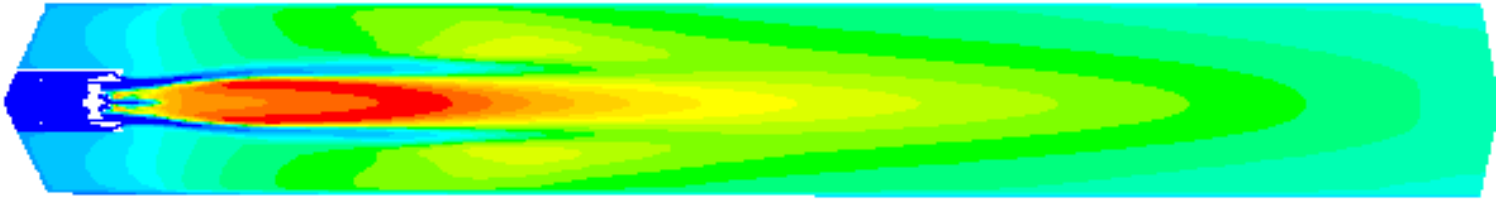


Swirler

Particle diameter [m]

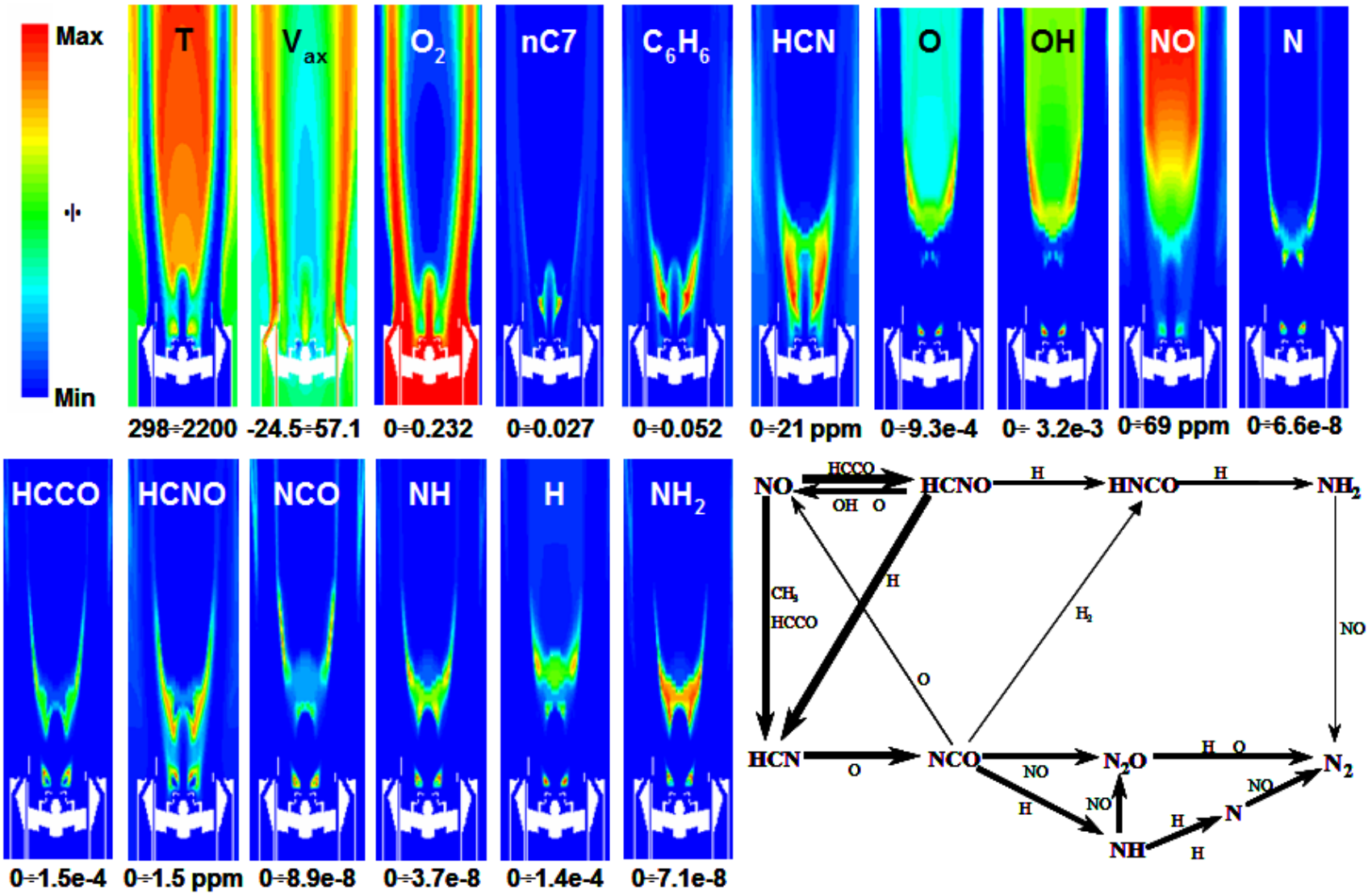


Typical hollow-cone structure obtained using a pressure-swirl atomizer

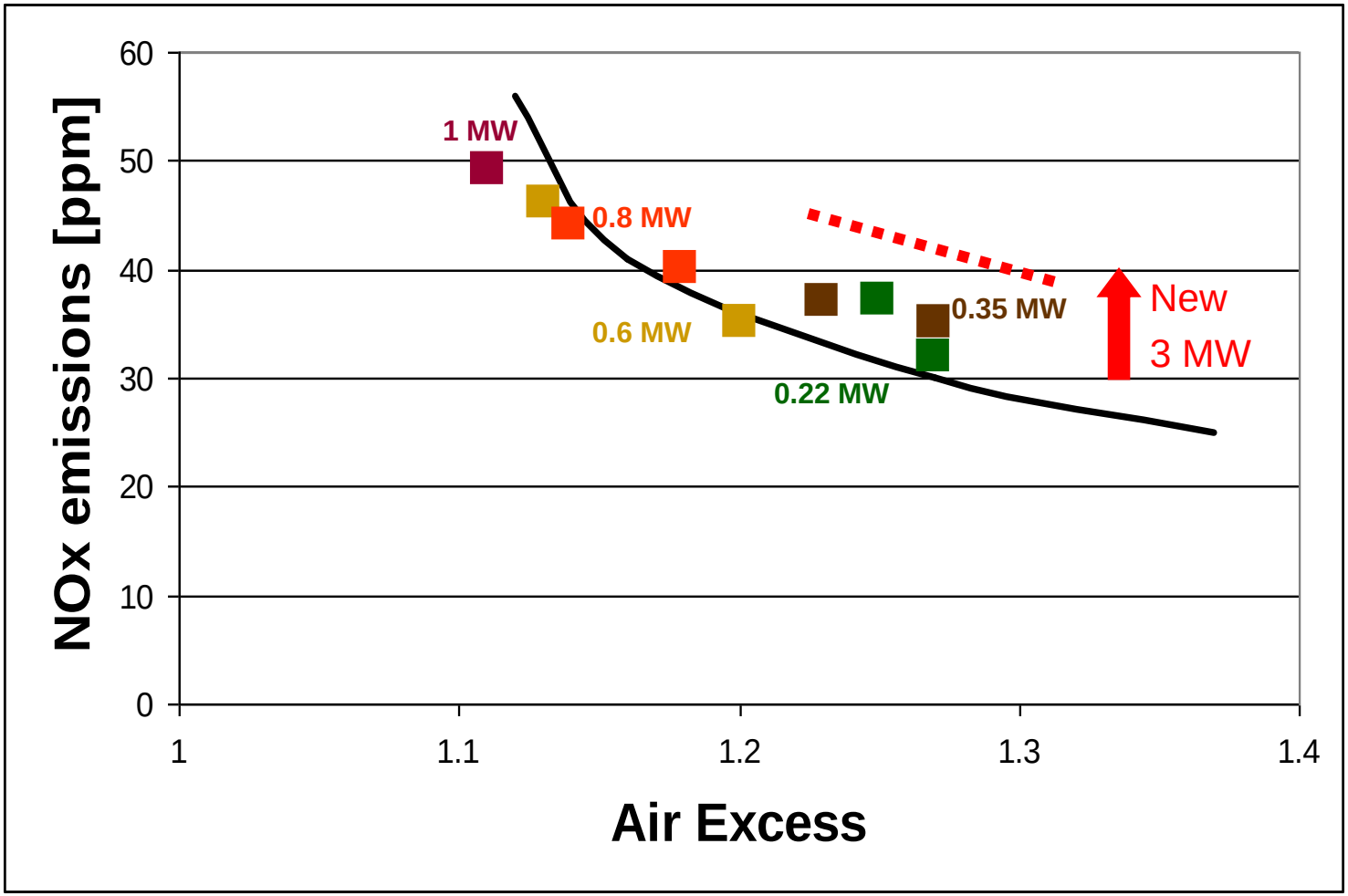


Temperature Field [K] 300 2270

Riello Gasoil Burner



Riello Gasoil Burner



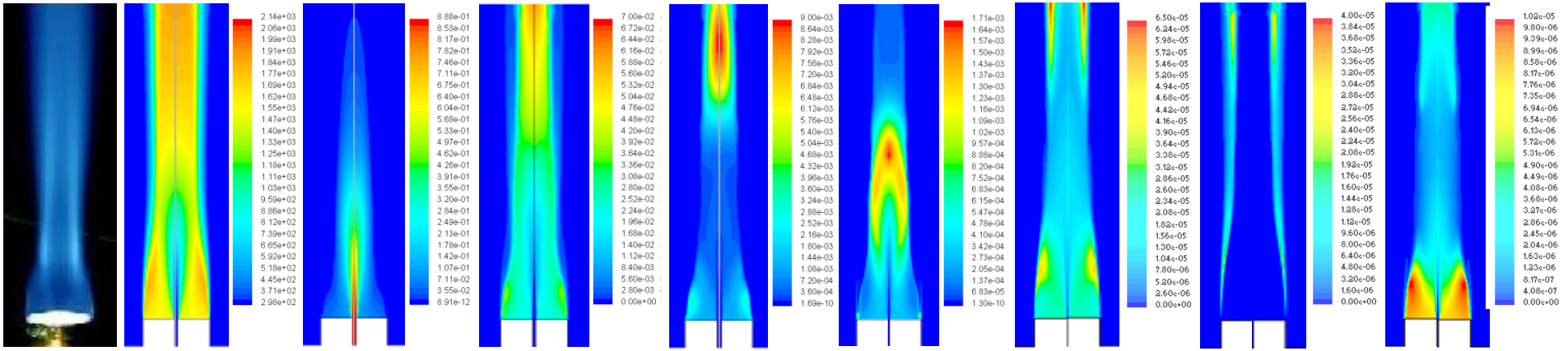
Comparison with measurements is satisfactory

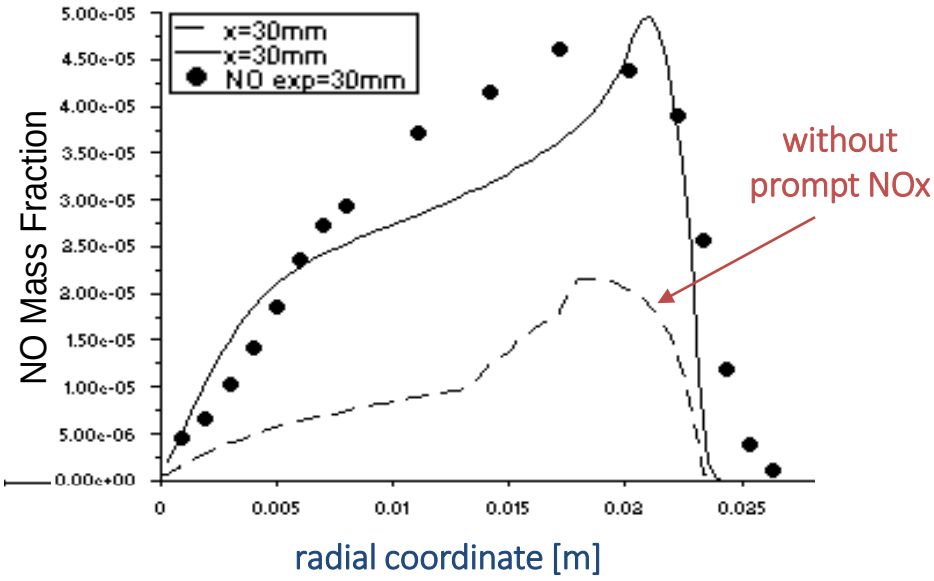
Only measurements at the outlet

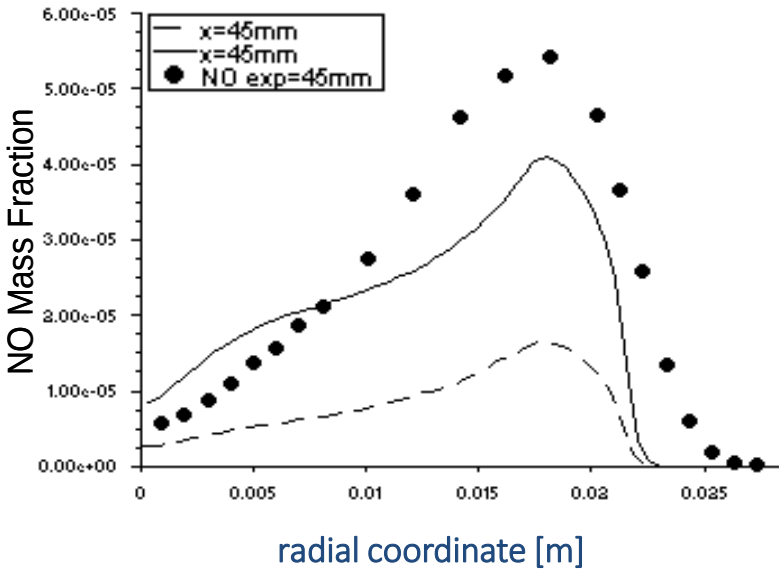
Outline

1. The CRECK Modeling Group @ Politecnico di Milano
2. Introduction
3. The Kinetic Post Processing (KPP) Technique for NOx
   - ✓ Kinetic mechanisms for CFD applications
   - ✓ Reactor networks from CFD
   - ✓ Effects of temperature fluctuations on NOx formation
   - ✓ Solution of reactor networks
4. Applications to lab-scale and industrial flames
   - ✓ Lab-scale flames
   - ✓ Industrial cases
5. **Extension to other pollutants**
6. Conclusions

Sandia Bluff-Body Flame







Local temperature unbalance

The **weak influence of the minor species on the temperature** fields was checked through an energy analysis of the reactor network. For each reactor, energy unbalances were calculated:

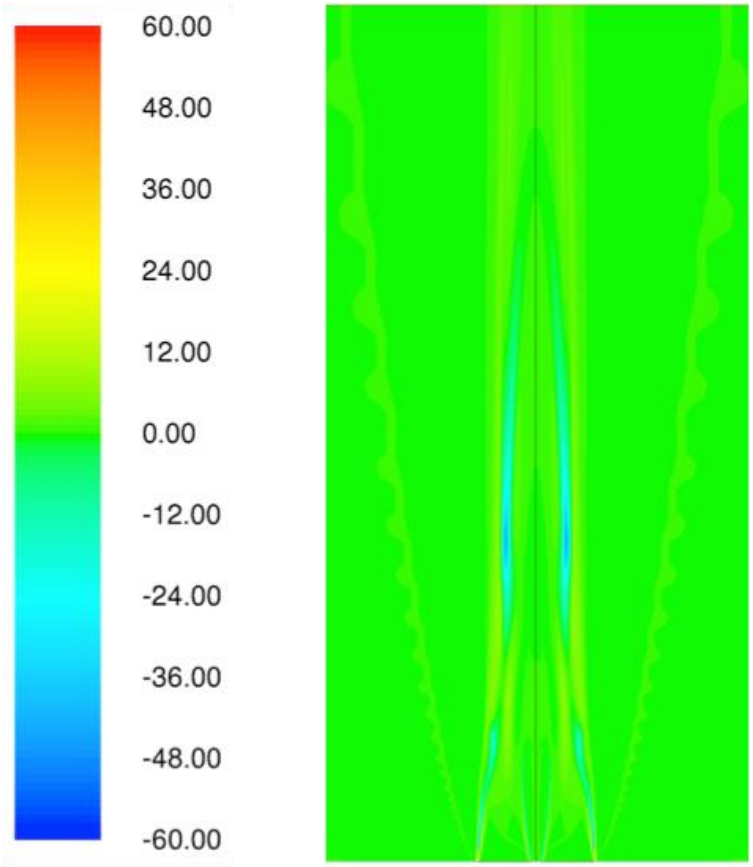
$$\Delta H_{CFD} = \left(H_{in} - H_{out}\right)_{CFD}$$

$$\Delta H_{KPP} = \left(H_{in} - H_{out}\right)_{KPP}$$

The overall energy unbalance due to the post-processing was evaluated as the difference. Then, the unbalance in terms of temperature was calculated as:

$$\Delta T = \frac{\Delta H_{KPP} - \Delta H_{CFD}}{C_P \dot{m}}$$

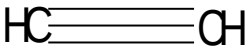
Local temperature unbalances in K

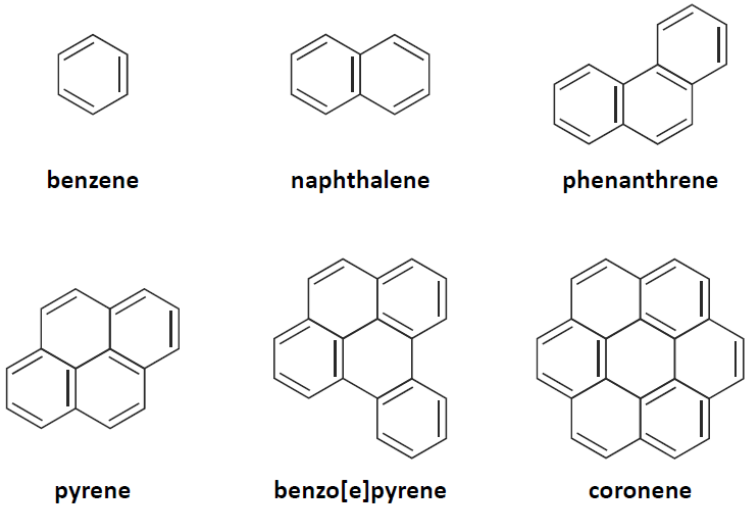


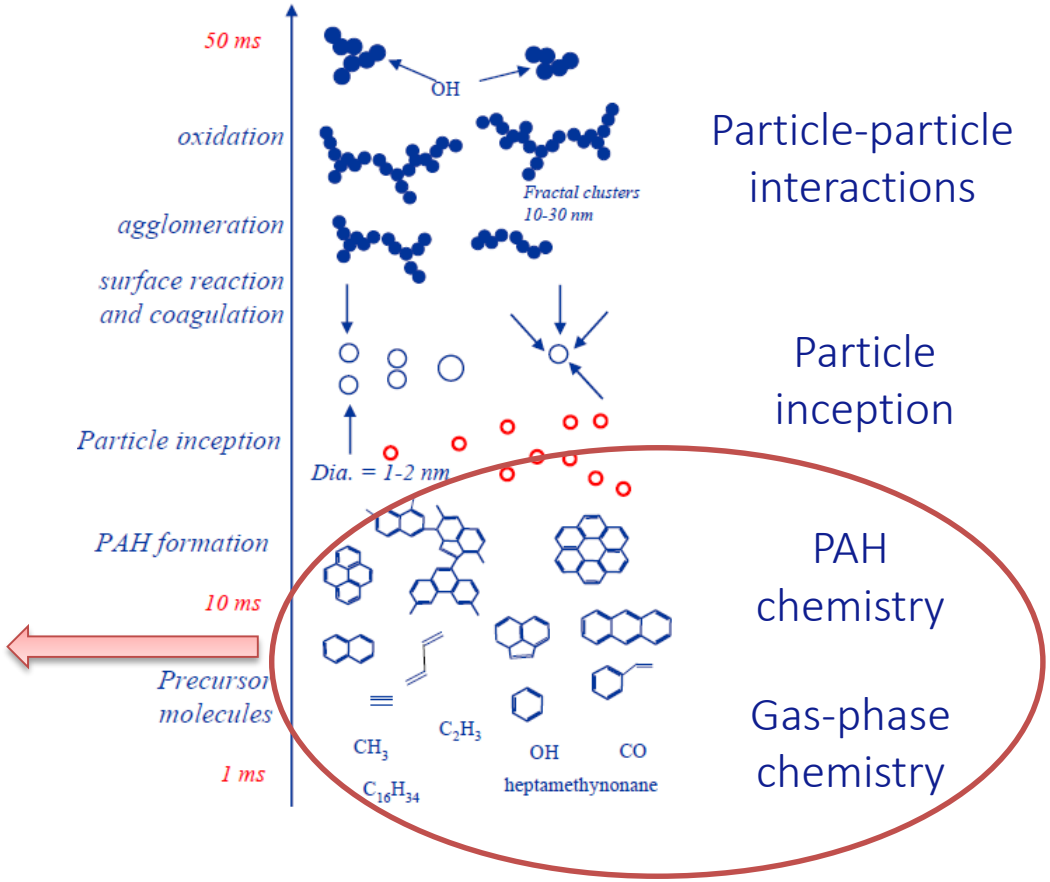
The average temperature unbalance is 0.27 K, with a standard deviation of 5.43 K

Soot formation mechanisms

Molecules as key precursor in soot formation

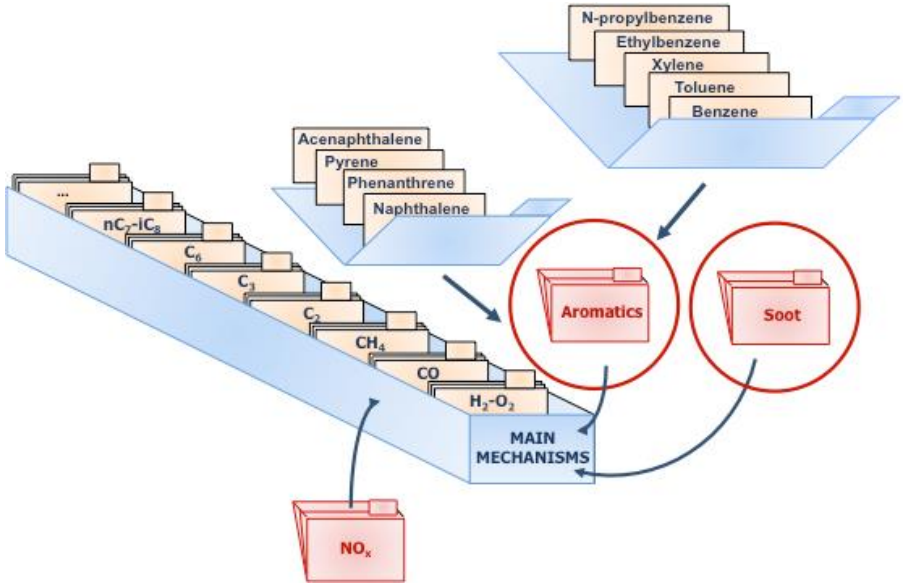






A. D'Anna et al., Combust. Flame 157 (2010) 2106–2115.

The Discrete Sectional Method



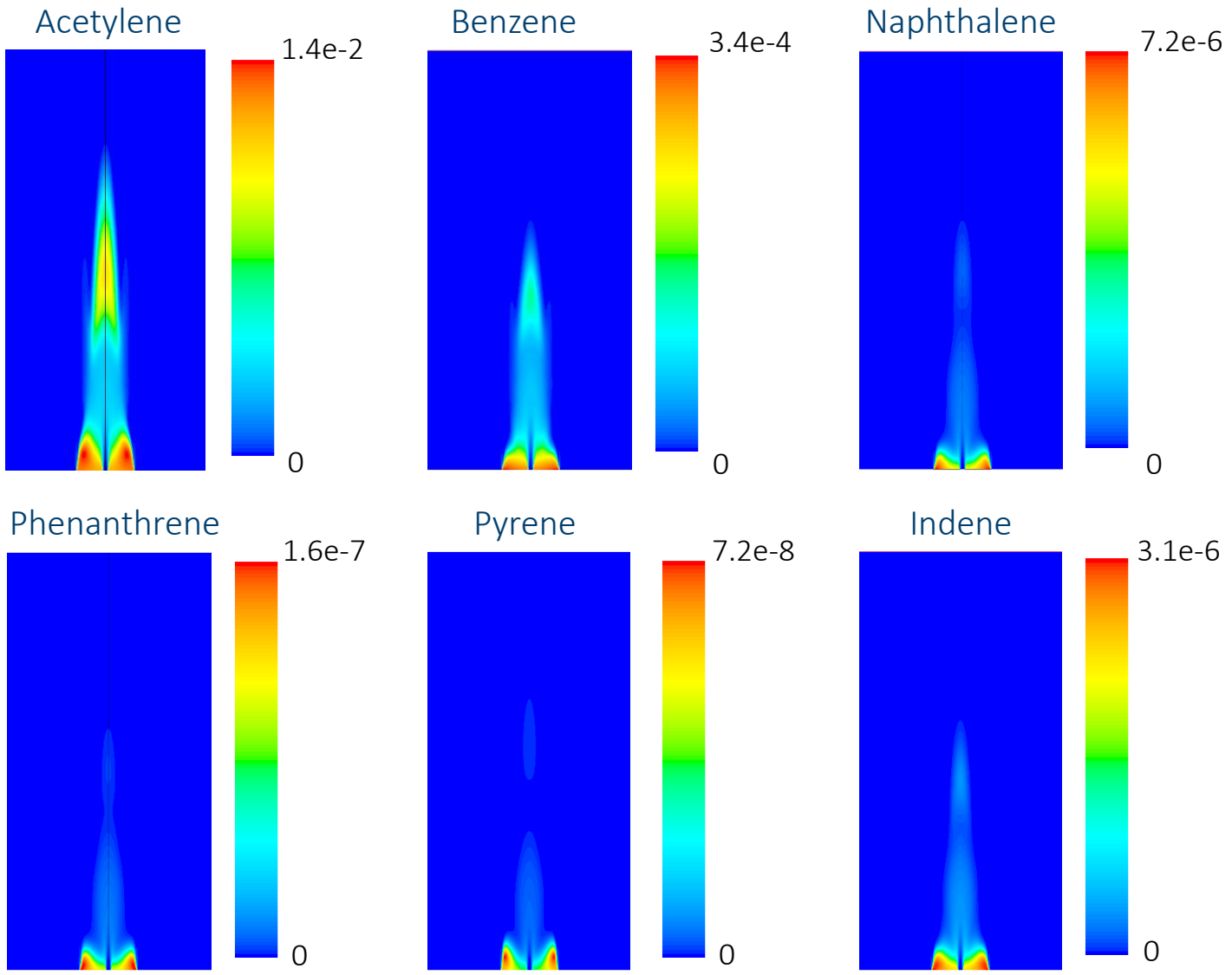
BIN	Mass [amu]	CxHy	Mean Diameter σ [nm]	H/C A	H/C B	H/C C
1	~ 250	$C_{20}H_{16}$-$C_{20}H_{10}$-$C_{20}H_{6}$	0.76	0.8	0.5	0.3
2	~ 500	$C_{40}H_{32}$-$C_{40}H_{20}$-$C_{40}H_{12}$	0.96	0.8	0.5	0.3
3	~ 1000	$C_{80}H_{60}$-$C_{80}H_{36}$-$C_{80}H_{24}$	1.21	0.75	0.45	0.3
4	~ 2000	$C_{160}H_{112}$-$C_{160}H_{64}$-$C_{160}H_{48}$	1.52	0.7	0.4	0.3
5	~ 4000	$C_{320}H_{208}$-$C_{320}H_{64}$-$C_{320}H_{64}$	1.91	0.65	0.35	0.20
6	~ 8000	$C_{640}H_{384}$-$C_{640}H_{224}$-$C_{640}H_{96}$	2.41	0.6	0.35	0.15
7	~ 15500	$C_{1250}H_{688}$-$C_{1250}H_{375}$-$C_{1250}H_{125}$	3.01	0.55	0.3	0.1
8	~ 30000	$C_{2500}H_{1250}$-$C_{2500}H_{625}$-$C_{2500}H_{250}$	3.78	0.5	0.25	0.1
9	~ 61000	$C_{5000}H_{2250}$-$C_{5000}H_{1000}$-$C_{5000}H_{500}$	4.76	0.45	0.2	0.1
10	~ 121000	$C_{10000}H_{4000}$-$C_{10000}H_{1500}$-$C_{10000}H_{1000}$	5.99	0.4	0.15	0.1

Discrete sectional method: Large PAHs and soot particles with diameters of up to ~60 nm are defined as classes with increasing molecular mass.

Each class is represented by a combination of lumped pseudo-species (BINs), each with an assigned H/C.

The first BIN is the species with **20** carbon atoms and mass of about 250 amu, which is the corannulene. The first particle of soot is considered of about 3000 amu, which is the **BIN5**.

Towards soot: from acetylene to PAHs



Formation of soot via KPP

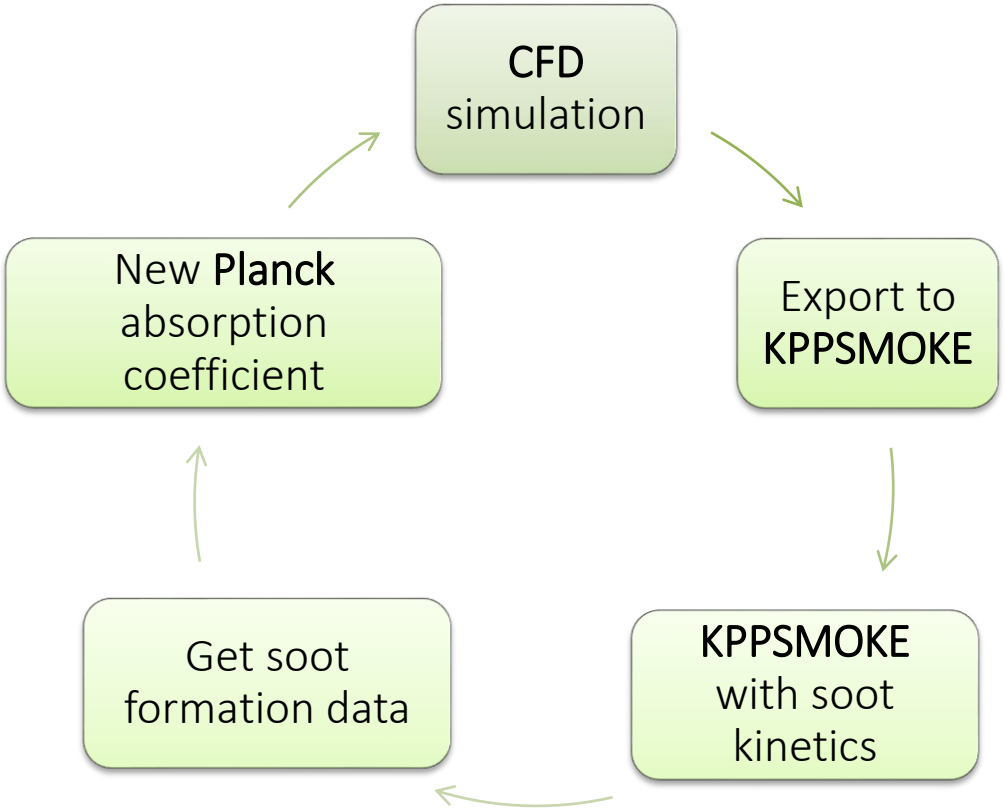
Soot particles **do** influence the temperature field through thermal radiation

KPPSMOKE **decoupling** between mass and energy balances is no longer valid

BUT

An iterative coupling between mass and energy balances is still possible

Planck absorption coefficient and loop closure



Outline

1. The CRECK Modeling Group @ Politecnico di Milano
2. Introduction
3. The Kinetic Post Processing (KPP) Technique for NOx
   - ✓ Kinetic mechanisms for CFD applications
   - ✓ Reactor networks from CFD
   - ✓ Effects of temperature fluctuations on NOx formation
   - ✓ Solution of reactor networks
4. Applications to lab-scale and industrial flames
   - ✓ Lab-scale flames
   - ✓ Industrial cases
5. Extension to other pollutants
6. **Conclusions**

Papers on Kinetic Post Processing of NOx (I)

Monaghan R., Tahir R., Bourque G., Gordon R., Cuoci A., Faravelli T., Frassoldati A., Curran H., "Detailed emissions prediction for a turbulent swirling non-premixed flame", (2014) Energy & Fuels, 28 (2), pp 1470-1488, DOI: 10.1021/ef402057w

Stagni A., Cuoci A., Frassoldati A., Faravelli T., Ranzi E., "A fully coupled, parallel approach for the post processing of CFD data through reactor network analysis", (2014) Computers & Chemical Engineering, 60, pp 197-212, DOI: http://dx.doi.org/10.1016/j.compchemeng.2013.09.002

Cuoci, A., Frassoldati, A., Stagni, A., Faravelli, T., Ranzi, E., Buzzi-Ferraris, G., Numerical modeling of NOx formation in turbulent flames using a kinetic post-processing technique (2013) Energy and Fuels, 27 (2), pp. 1104-1122, DOI: 10.1021/ef3016987

Shabanian, S.R., Medwell, P.R., Rahimi, M., Frassoldati, A., Cuoci, A., Kinetic and fluid dynamic modeling of ethylene jet flames in diluted and heated oxidant stream combustion conditions (2013) Applied Thermal Engineering, 52 (2), pp. 538-554 DOI: 10.1016/j.applthermaleng.2012.12.024

Monaghan, R.F.D., Tahir, R., Cuoci, A., Bourque, G., Furi, M., Gordon, R.L., Faravelli, T., Frassoldati, A., Curran, H.J., Detailed multi-dimensional study of pollutant formation in a methane diffusion flame (2012) Energy and Fuels, 26 (3), pp. 1598-1611, DOI: 10.1021/ef201853k

Papers on Kinetic Post Processing of NOx (II)

Frassoldati, A., Cuoci, A., Faravelli, T., Ranzi, E., Colantuoni, S., Di Martino, P., Cinque, G., Kern, M., Marinov, S., Zarzalis, N., Da Costa, I., Guin, C., Fluid dynamics and detailed kinetic modeling of pollutant emissions from lean combustion systems (2010) Proceedings of the ASME Turbo Expo, 2 (PARTS A AND B), pp. 451-459, DOI: 10.1115/GT2010-22551

Frassoldati, A., Sharma, P., Cuoci, A., Faravelli, T., Ranzi, E., Kinetic and fluid dynamics modeling of methane/hydrogen jet flames in diluted coflow (2010) Applied Thermal Engineering, 30 (4), pp. 376-383, DOI 10.1016/j.applthermaleng.2009.10.001

D. Manca, G. Buzzi-Ferraris, A. Cuoci, A. Frassoldati (2009). The solution of very large non-linear algebraic systems. COMPUTERS & CHEMICAL ENGINEERING, vol. 33, p. 1727-1734, ISSN: 0098-1354, doi: 10.1016/j.compchemeng.2009.04.010

A. CUOCI, A. FRASSOLDATI, BUZZI FERRARIS G, T. FARAVELLI, RANZI E.M. (2007). The ignition, combustion and flame structure of carbon monoxide/hydrogen mixtures. Note 2: Fluid dynamics and kinetic aspects of syngas combustion. INTERNATIONAL JOURNAL OF HYDROGEN ENERGY, vol. 32, p. 3486-3500, ISSN: 0360-3199, doi: 10.1016/j.ijhydene.2007.02.026

Other

Stagni A., Cuoci A., Frassoldati A., Faravelli T., Ranzi E., "Lumping and reduction of detailed kinetic schemes: an effective coupling", Industrial & Engineering Chemistry Research, Accepted, In press (2014), DOI: 10.1021/ie403272f

Ranzi, E., Frassoldati, A., Grana, R., Cuoci, A., Faravelli, T., Kelley, A.P., Law, C.K.. Hierarchical and comparative kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels (2012) Progress in Energy and Combustion Science, 38 (4), pp. 468-501, DOI: 10.1016/j.pecs.2012.03.004

Frassoldati, A., Cuoci, A., Faravelli, T., Niemann, U., Ranzi, E., Seiser, R., Seshadri, K., An experimental and kinetic modeling study of n-propanol and iso-propanol combustion (2010) Combustion and Flame, 157 (1), pp. 2-16, DOI: 10.1016/j.combustflame.2009.09.002