Curve Matching for mechanism validation and optimization

Prof. Alessandro Stagni

CRECK Modeling Lab.
DCMC, Politecnico di Milano.
alessandro.stagni@polimi.it

Outline

1. Introduction

2. Curve Matching

- → Functional estimation
- → Distance and similarity indices
- → Accounting for uncertainty through bootstrap
- → Overall framework

3. Creation of an integrated infrastructure

- → Data ecosystem and continuous validation
- → Experimental databases and simulations
- → The SciExpeM platform

4. Integration into the kinetic modeling framework

- → Coupling with chemical lumping
- → Enforcing physics into OME chemistry

5. Conclusions

What do I do?

- ✓ Chemical-kinetic analysis of reacting systems of renewable fuels at different levels:
  - → **Development** and **reduction** of chemical kinetic mechanisms
  - → **Application** in CFD computations
- ✓ Formation of **pollutant species** (NO_x, SO_x)
- ✓ **Energy carriers**
  - → **Ammonia**
  - → Oxymethylene ethers

BSc/MSc
Chem. Eng.
POLITECNICO MILANO 1863
2006

PhD
Chem. Eng.
POLITECNICO MILANO 1863 Stanford University
2011

Assistant Professor
POLITECNICO MILANO 1863 TECHNISCHE UNIVERSITÄT DARMSTADT
2016

Associate Professor
RECK POLITECNICO MILANO 1863
2024

The CRECK modeling lab

Permanent Staff


Tiziano Faravelli


Alessio Frassoldati


Alberto Cuoci


Marco Mehl

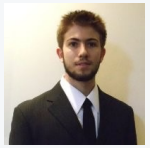

Alessandro Stagni


Matteo Pelucchi


Luna Pratali Maffei

External Collaborators


Carlo Cavallotti


Paulo De Biagi

Administrative Staff


Isabella Branca

PhD Students


M. Ahsan Amjed


Francesco Serse


Andrea Locaspi


Edoardo Ramalli

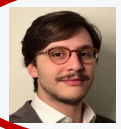

Andrea Nobili


Edoardo Cipriano


Clarissa Giudici


Alessandro Pegurri


Romina Papagni


Timoteo Dinelli

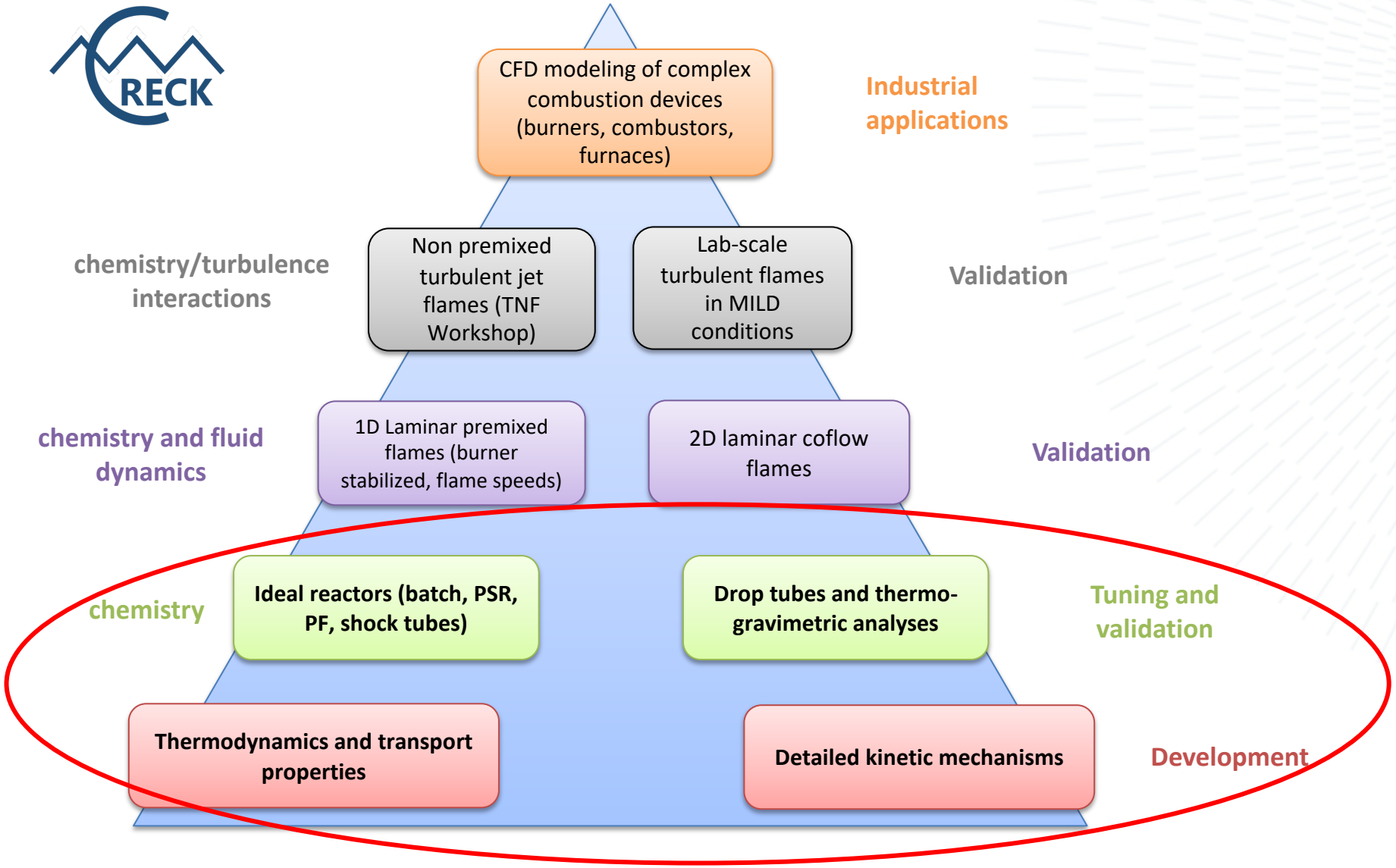

Riccardo Caraccio


Francesco Roman Artioli


Niccolò Fanari

Tomorrow afternoon (16:20-17:20)

CRECK modeling expertise

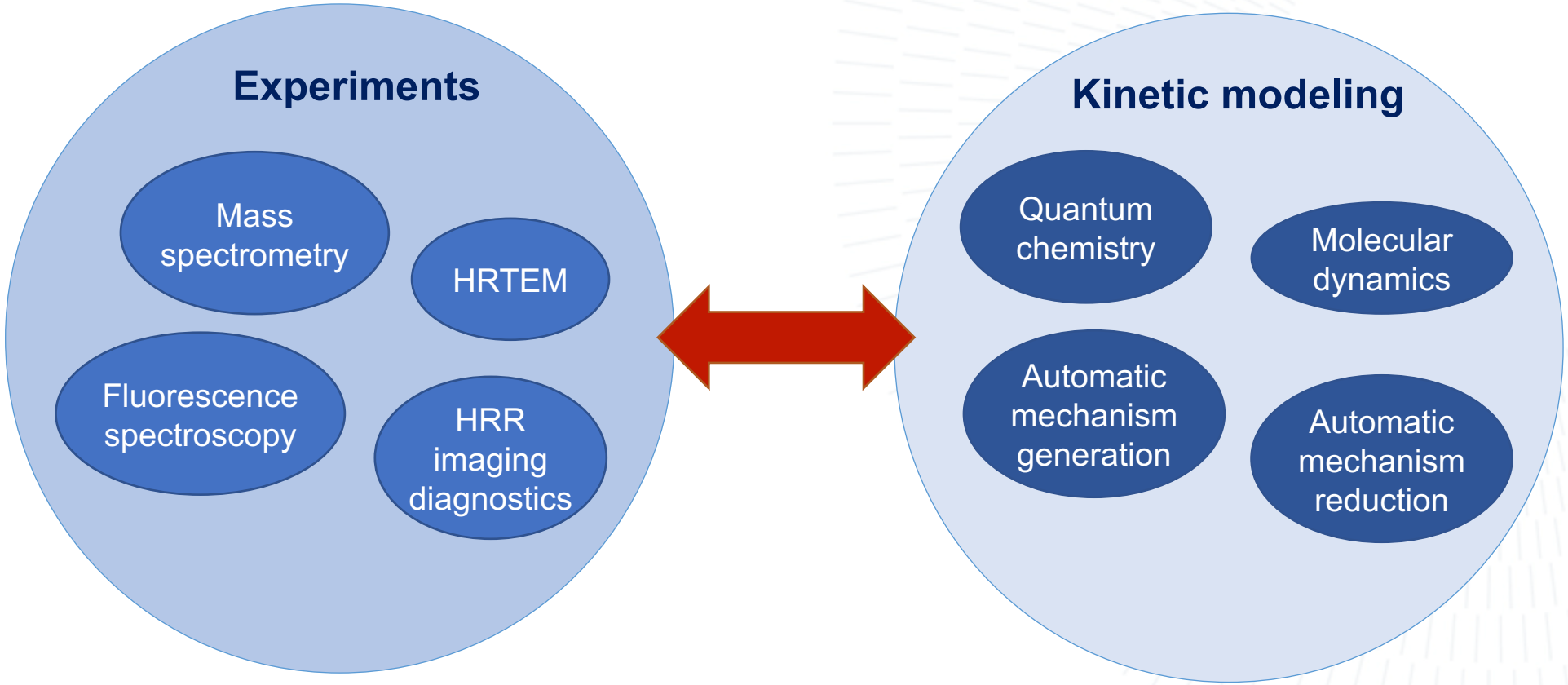


http://creckmodeling.chem.polimi.it

Introduction: Mechanism validation

POLITECNICO
MILANO 1863

Exploring combustion kinetics



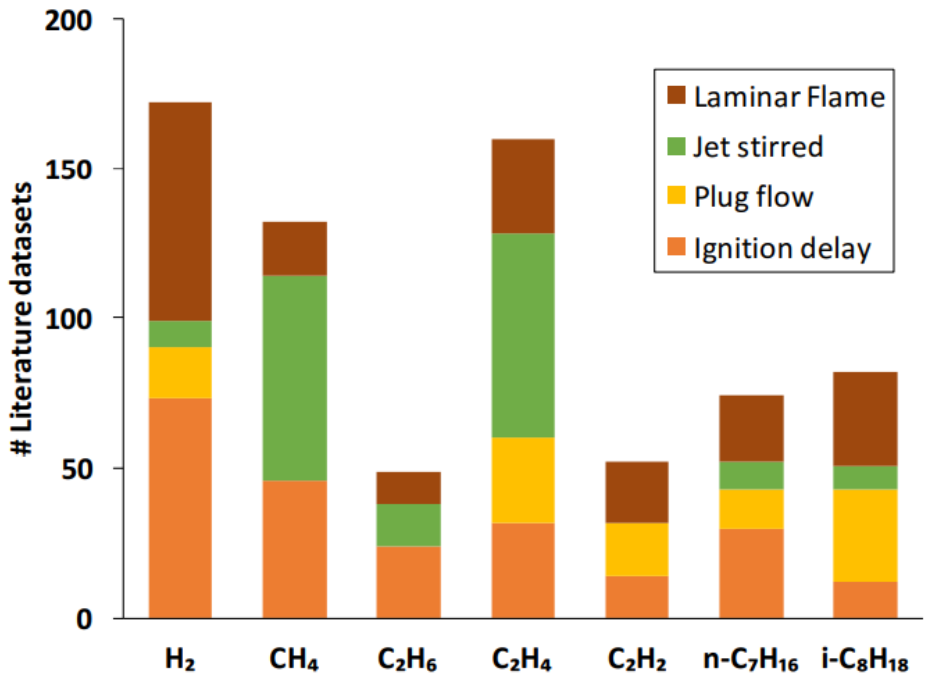
Higher **accuracy**
Wider **capabilities**
Faster sampling **frequency**

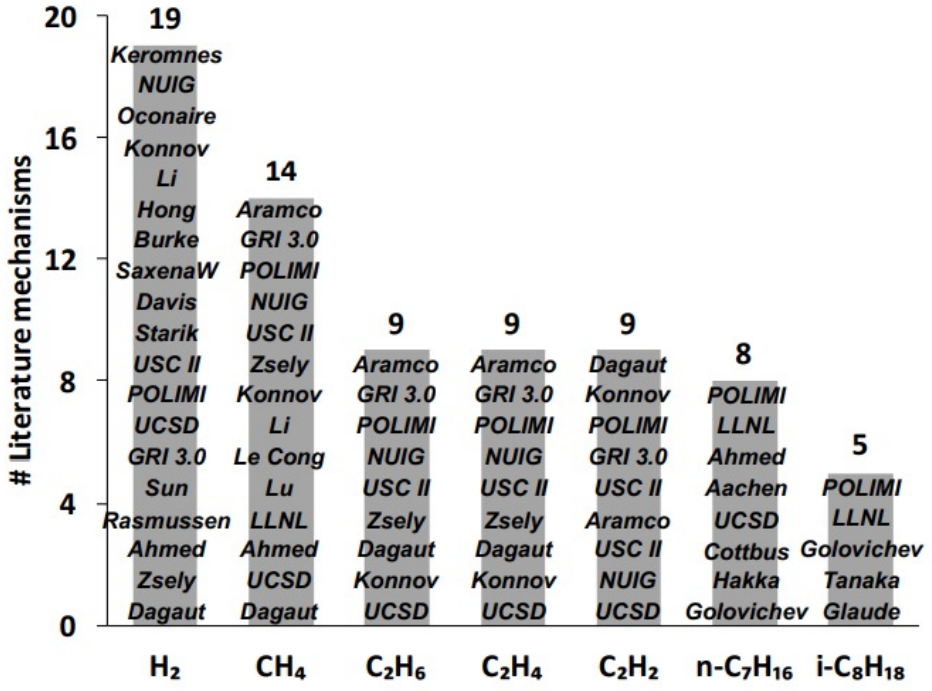
Higher computing **power**
Improved **numerical** techniques
Standardized **kinetics** formulation

A synergistic coupling?

Many data, many models

(updated in 2016…)





Literature datasets keep **increasing** over **time**

Mechanism validation is **time consuming**

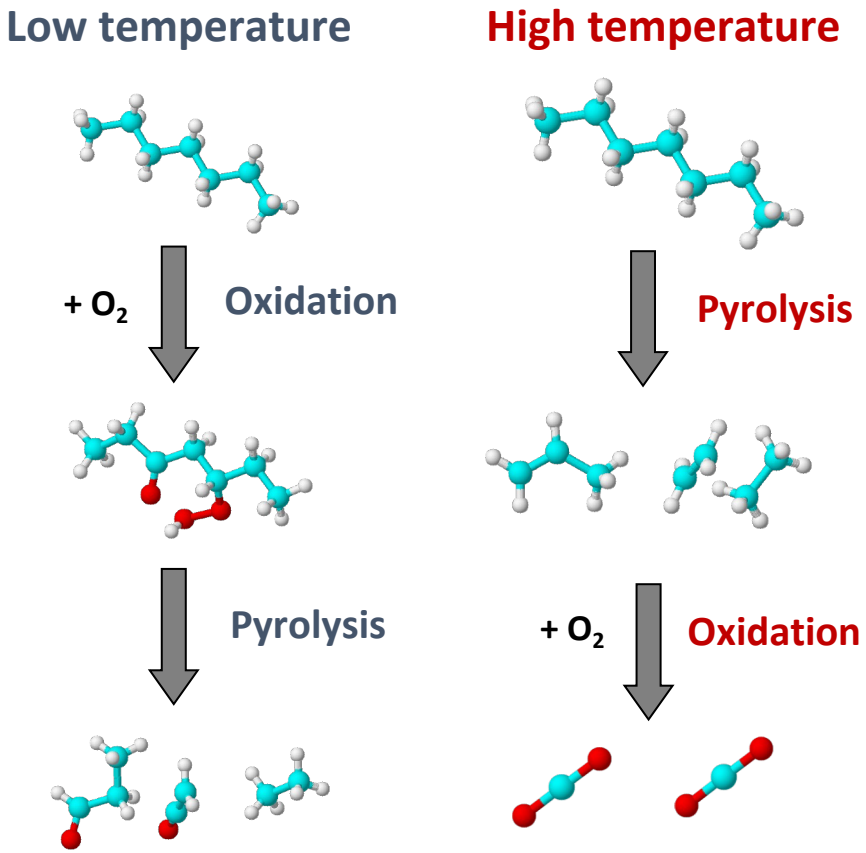
Several kinetic models representing the **same** fuel

Curran et al. Comb Flame, 114 (1998)
Curran et al. Comb Flame, 129 (2002)
Ranzi et al. Prog En Comb Sci, 38 (2012)

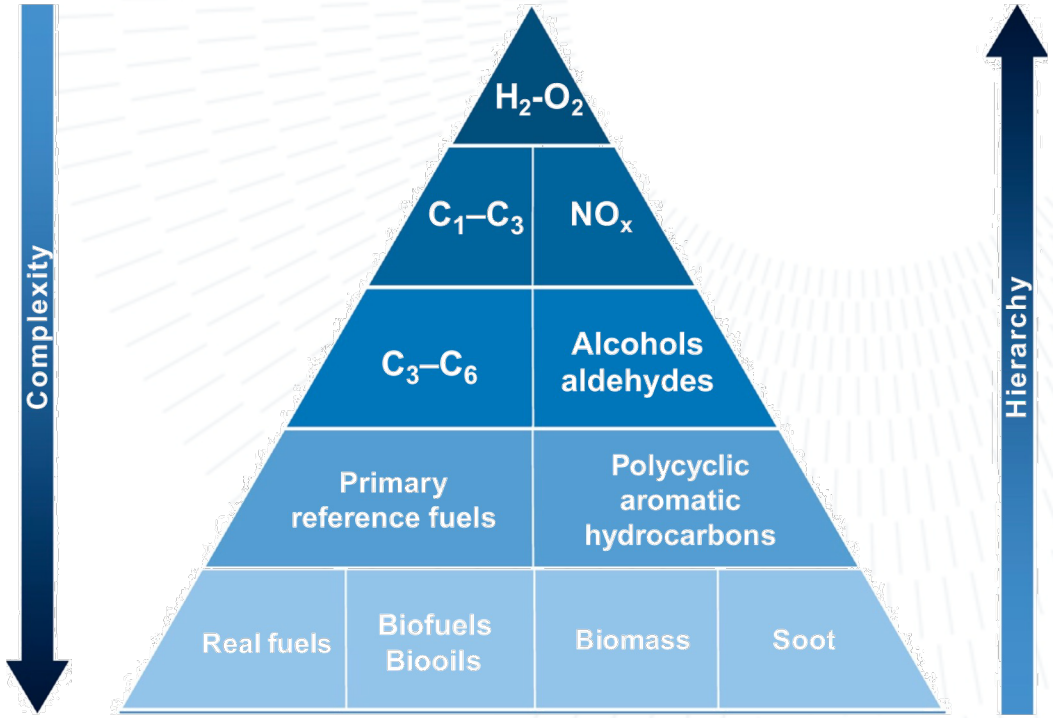
Metcalfe et al. Int J Chem Kin, 45 (2013)
Olm et al. Comb Flame, 161 (2014)
Stagni, Politecnico di Milano (2016)

Combustion is hierarchical

Fuel undergoes a sequential **breakup**



Lower-hierarchy levels depend on **higher** hierarchy ones



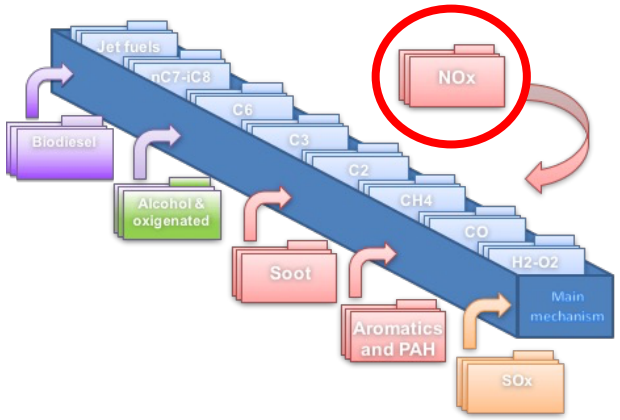
Mechanism validation
is a **continuous process**

Example: the NO_x case

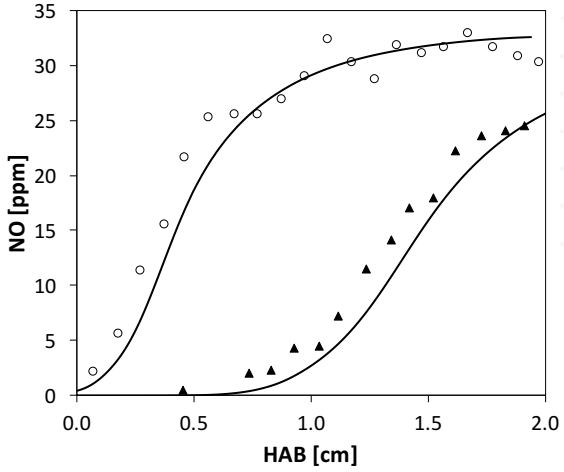
- **Hierarchical** dependencies strongly affect a kinetic mechanism
- E.g. **NO_x formation** depends on the core C_0-C_3 submechanism

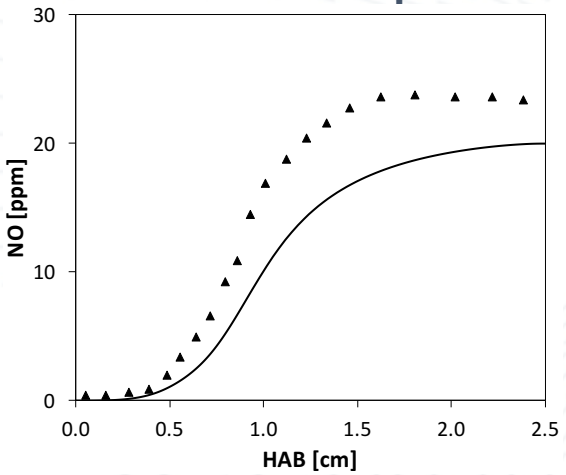
What can happen?

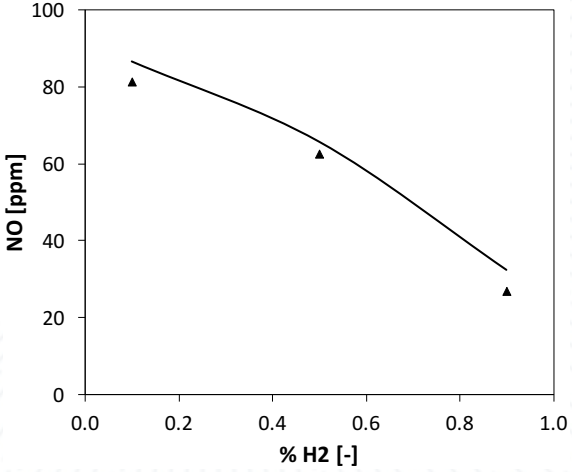
- January 2012:
  critical update to C_0-C_3



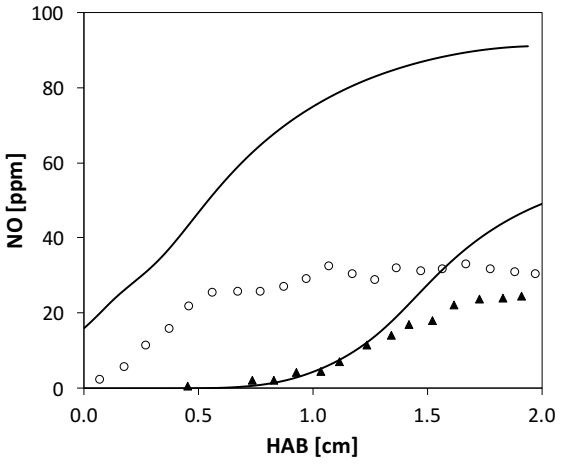
Before 2012 update

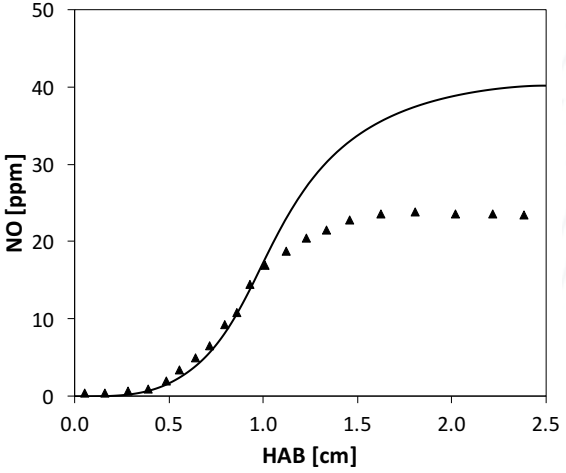


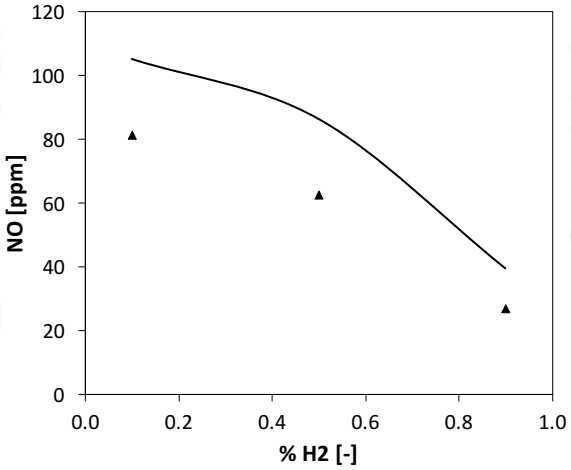




After 2012 update

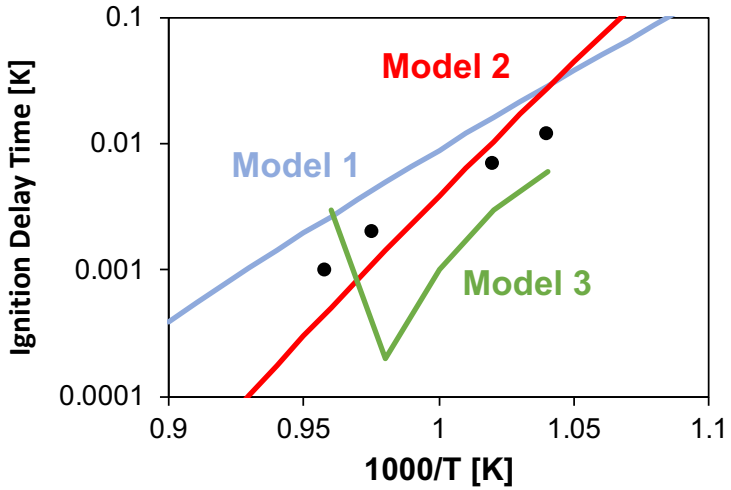


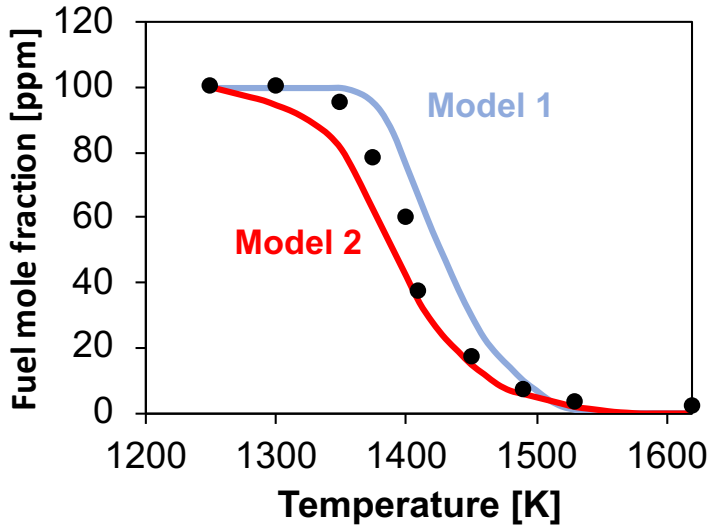




Pelucchi et al. Comp Aid Chem Eng (2019)

«Best» model?





Common practice:
Sum of Squares Error (SSE)

Model	SSE
1	213
2	203
3	168

- Model 1 is slower than experiments
- Model 2 has a different **activation energy** (slope)
- Model 3 output likely suffers from a **post-processing error**

Model	SSE
1	8400
2	7400

- Model 1 correctly predicts the reactivity through the temperature, but has a **shift**
- Model 2 predicts an earlier onset of consumption

A single indicator does not always represent models' predictive features

→ **Curve Matching**

Automating the validation of kinetic mechanisms

4 **questions** to be addressed:

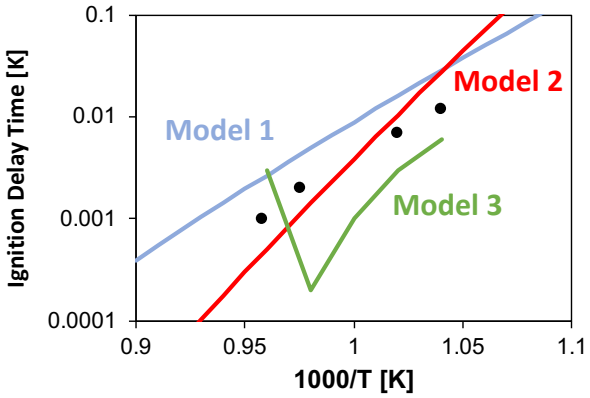
→ How to set up an **intelligent** data ecosystem?

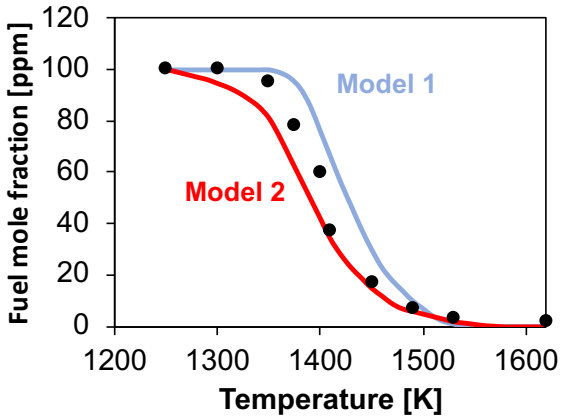
→ How to include **data knowledge** to develop detailed kinetics?

→ How to **automatically quantify** the predictive degree of a model?

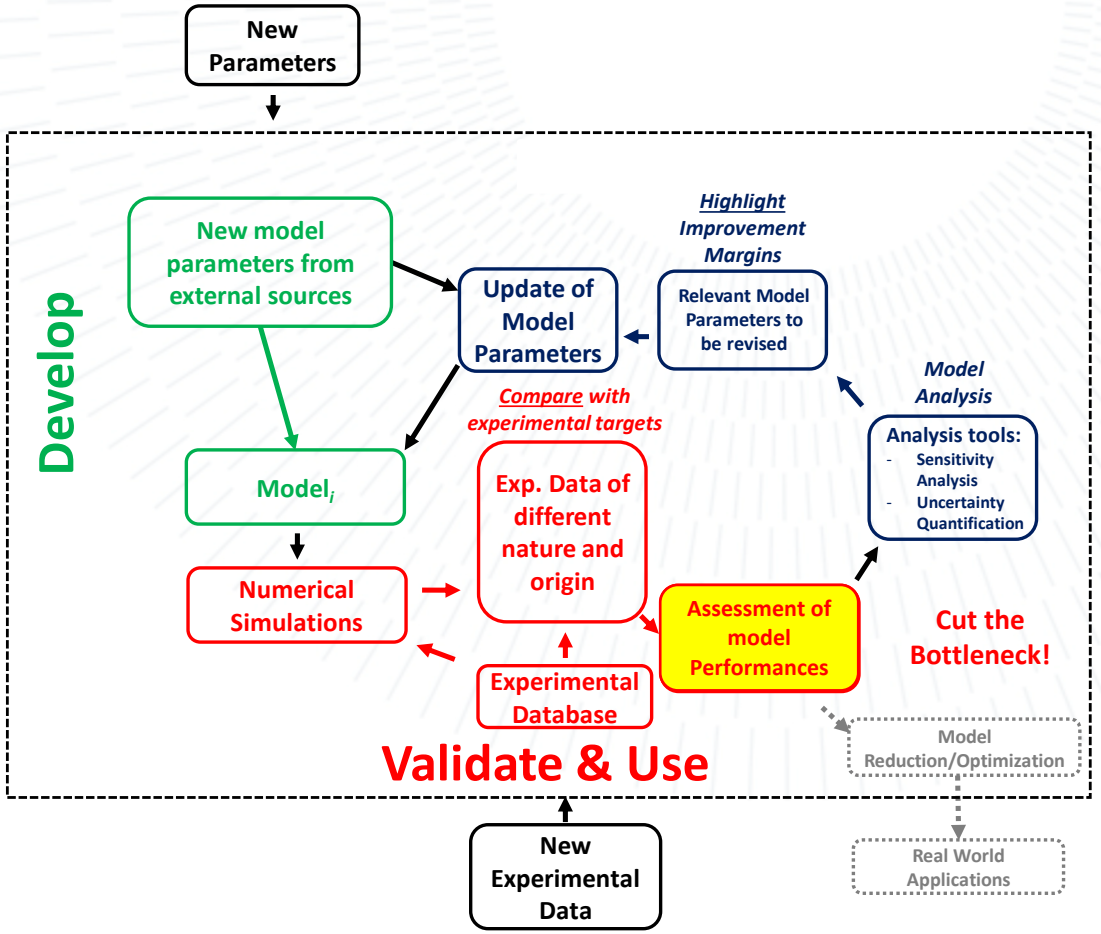
→ How to create **physics-informed reduced** models?

Curve Matching

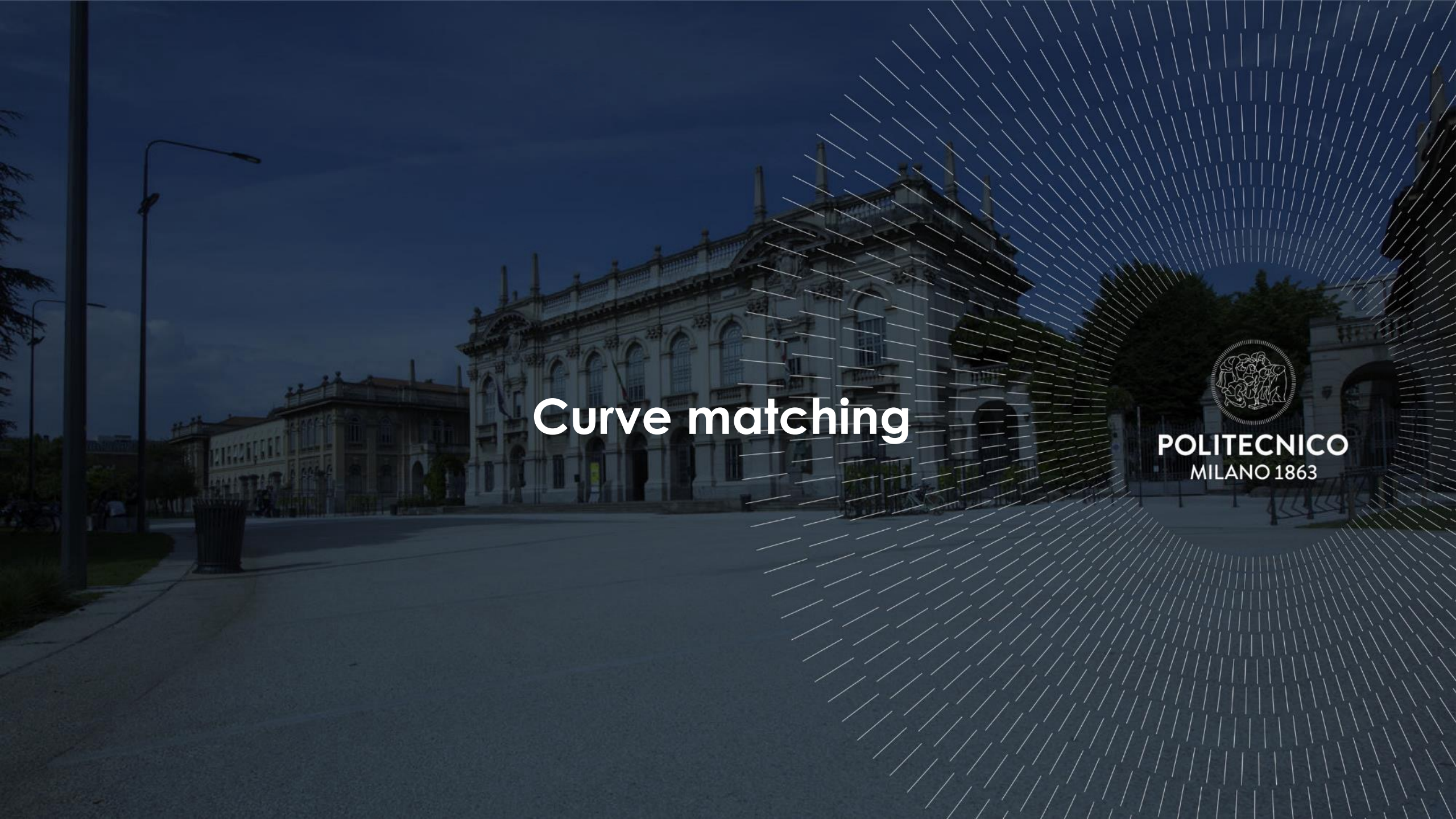




IMPROVE & LEARN



Curve matching



Functional estimation

B. Silverman & J. Ramsay, Functional Data Analysis, Springer, 2005
Bernardi et al. Combust Flame 168 (2016)

- **Experimental data** are "*noisy measurements of an underlying regular process*"
- **Spline functions** (5th degree) are used to fit the **experimental** points and **modeling** predictions

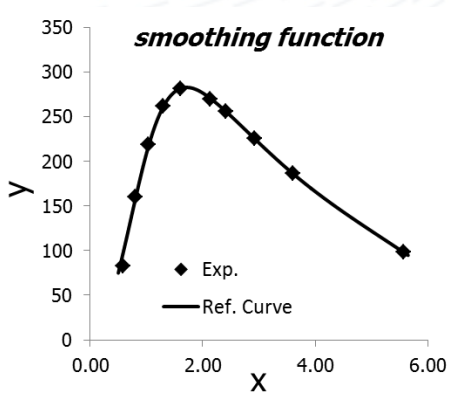
$$\hat{f} = argmin_{f \in F}\left[\underbrace{\sum_{i=1}^{n}\left(y_i - f(x_i)\right)^2}_{\text{SSE}} + \lambda \underbrace{\int \left(f''(x)\right)^2 dx}_{\text{Smoothing}}\right]$$

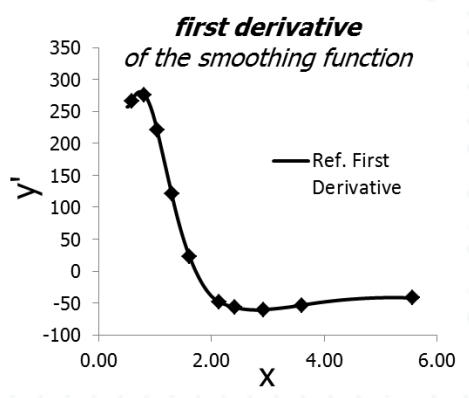
Spline smoothing

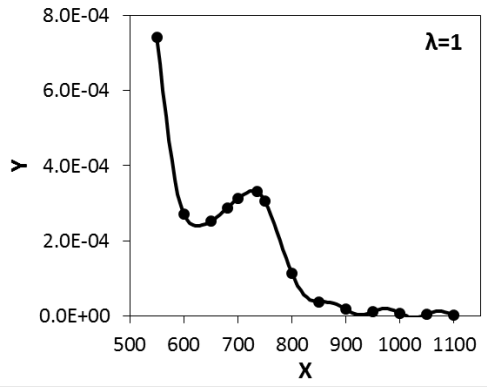
- **λ** value**: smoothing parameter** weighing a **roughness penalty**
- Generalized Cross Validation **(GCV)** criterion on **zero** and **first derivatives** of experimental data

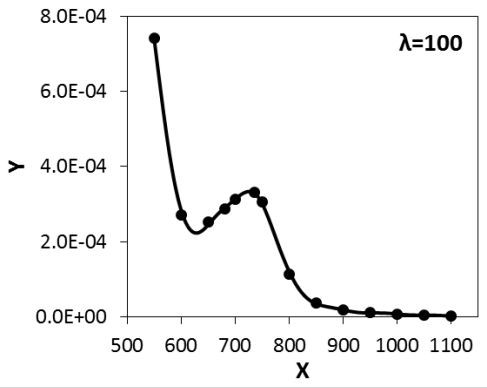
$$GCV_0(\lambda) = \frac{n\sum_{i=1}^{n-1}\left(y_i - \hat{f}(x_i)\right)^2}{\left(n - df(\lambda)\right)^2}$$

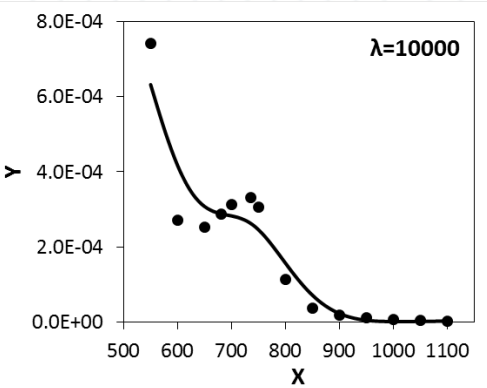
$$GCV_1(\lambda) = \frac{n\sum_{i=1}^{n-1}\left(y'_i - \hat{f}'(x_i)\right)^2}{\left(n - df(\lambda)\right)^2}$$











Optimal penalty factor (λ)

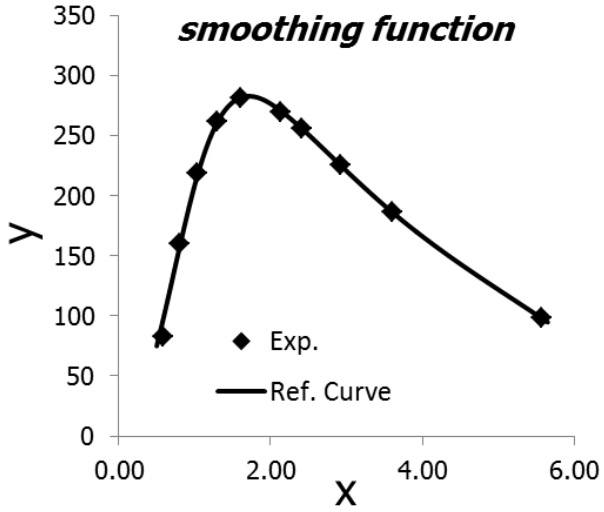
Classical approach

$$GCV_0 = \frac{nSSE_0}{(n - df(\lambda))^2}$$

$$\lambda \to -\infty \; (under - fitting)$$
$$\lambda \to +\infty \; (over - fitting)$$

$$\lambda_{opt} = argmin_{\lambda \in \mathbb{R}^+} GCV_0(\lambda)$$

Roughness is penalized directly on the main function

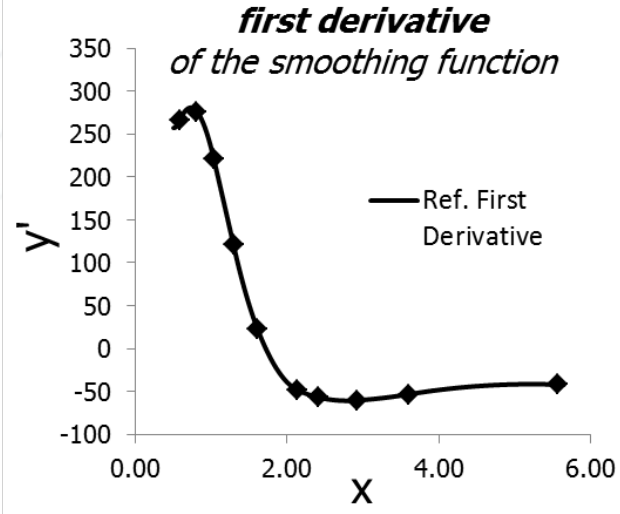


Modified approach

$$GCV_1 = \frac{nSSE_1}{(n - df(\lambda))^2}$$

$$\lambda_{opt} = argmin_{\lambda \in \mathbb{R}^+} GCV_0(\lambda)$$

Roughness is penalized directly on the derivative of the main function



Trade-off

$$f_{opt}(\lambda) = \log(GCV_0) + \log(GCV_1)$$

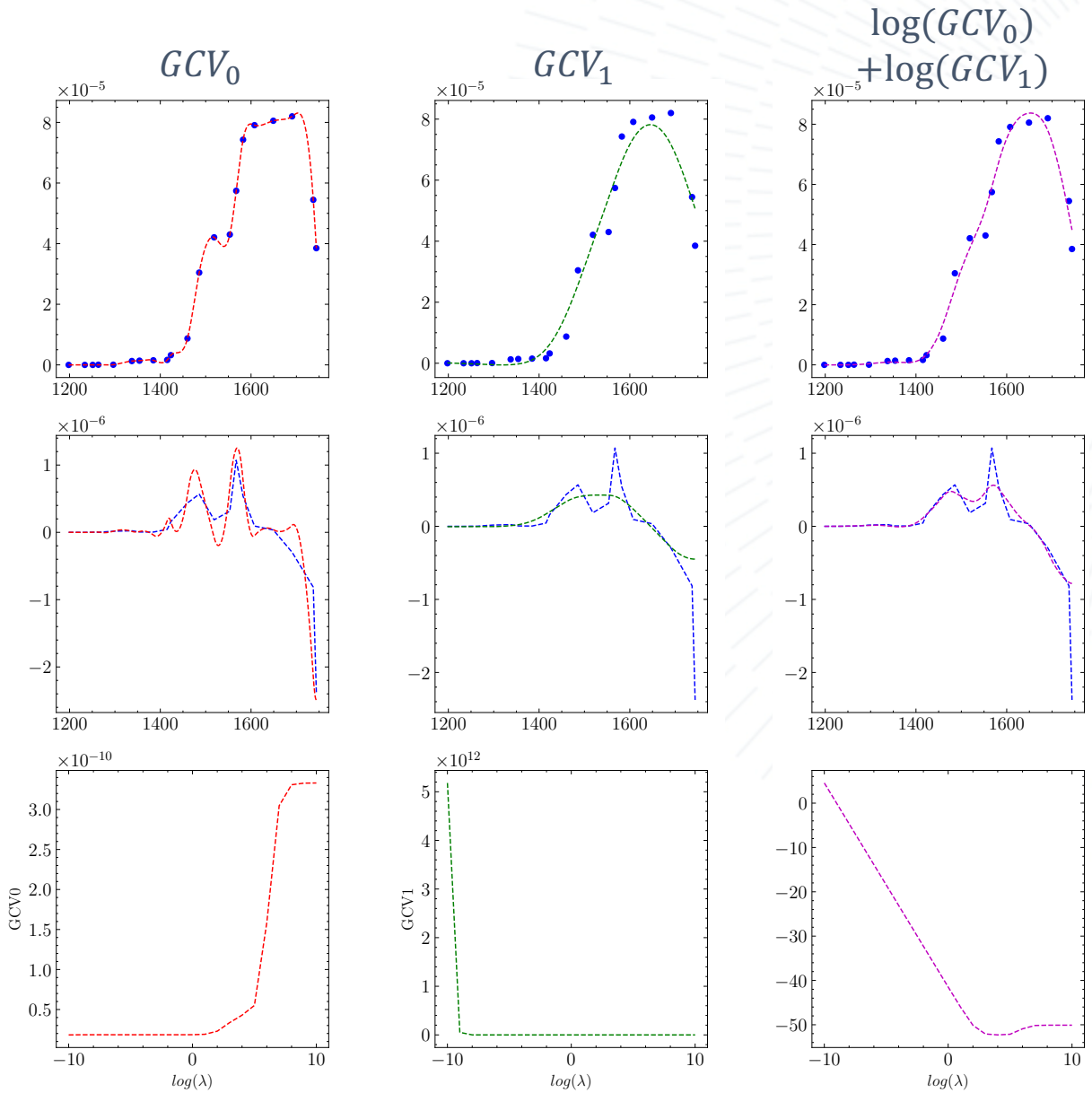
$$\lambda_{opt} = argmin_{\lambda \in \mathbb{R}^+} f_{opt}(\lambda)$$

GCV (λ)

Data VS Curve

(First derivative) Data VS Curve

Loss, Cost, Objective



Distance and similarity indices

Distance	Similarity
$d^0_{L_2}(f,g) = \frac{1}{1+\frac{\|f-g\|}{\|D\|}} \in (0,1)$	$d^0_P(f,g) = 1 - \frac{1}{2}\left\|\frac{f}{\|f\|} - \frac{g}{\|g\|}\right\| \in (0,1)$
$d^1_{L_2}(f,g) = \frac{1}{1+\frac{\|f'-g'\|}{\|D\|}} \in (0,1)$	$d^1_P(f,g) = 1 - \frac{1}{2}\left\|\frac{f'}{\|f'\|} - \frac{g'}{\|g'\|}\right\| \in (0,1)$

If $f \to g$ all the indices tend to 1

1 = very **good**. **0** = very **bad**

with $\|f\| = \sqrt{\int_D f(x)^2 dx}$

D = domains **intersection**
(0) = **functions**
(1) = first **derivatives**

$$CM_{score} = \frac{d^0_{L^2} + d^1_{L^2} + d^0_p + d^1_p}{4}$$

Different indices see different things

Example

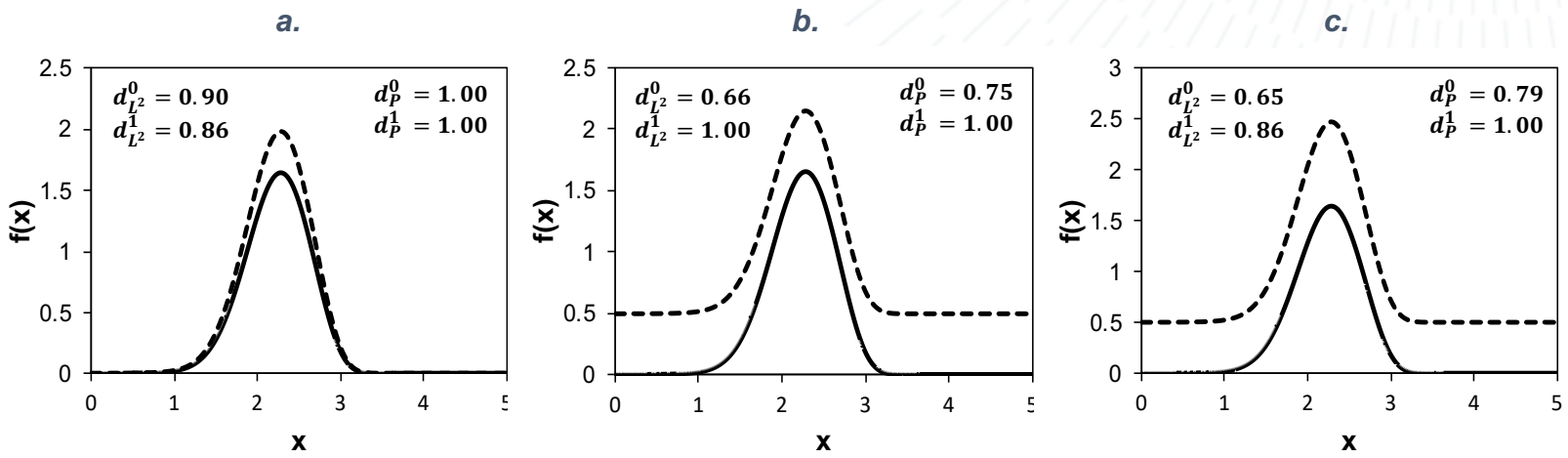
$a.\quad g(x) = a * f(x)$

$b.\quad g(x) = f(x) + b$

$c.\quad g(x) = a * f(x) + b$

with

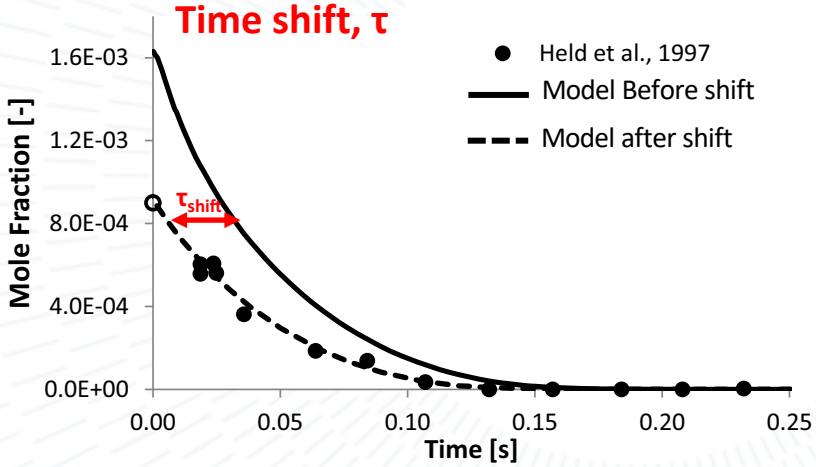
$a = 1.2 \qquad b = 0.5$



Bernardi et al. *Combust Flame 168, 2016*

Shift index and model performance

- The difference between model and experiment can be (also) due to horizontal shift
- The **flow reactor** case: **mixing effects** at the reactor inlet cause an early reaction. This is typically considered via a 'manual' shift of the time coordinate



Shift index

$$S = \max\left(1 - \frac{|\delta|}{D}, 0\right) \in (0,1)$$

1 = already **aligned**

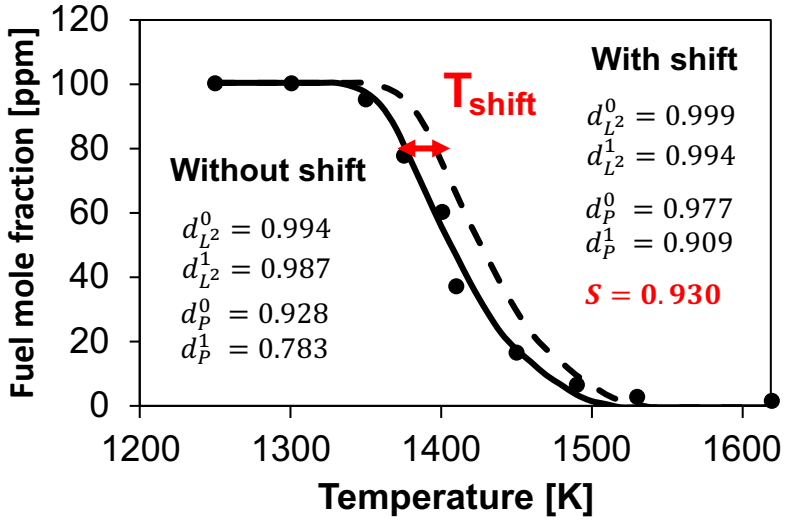
$$\delta = argmax_{\delta}\left(d^0_{L_2} + d^1_{L_2} + d^0_P + d^1_P\right)$$

δ: domain **shift** optimizing the alignment

Model performance

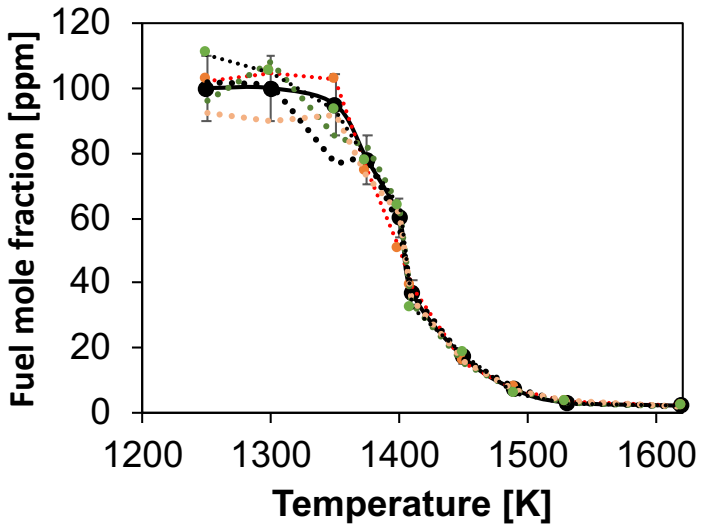
$$M = \frac{d^0_{L_2,shift} + d^1_{L_2,shift} + d^0_{P,shift} + d^1_{P,shift} + 2S}{6} \in (0,1)$$

Example



Bootstrapping: accounting for experimental error

- Experimental points are affected by **uncertainty**
- The higher experimental **uncertainty**, the higher the **variability** of the performance indices
- Need to keep it into account to identify the **confidence interval** of the performance indices



Bootstrap

Random generation of exp datasets with a normal distribution

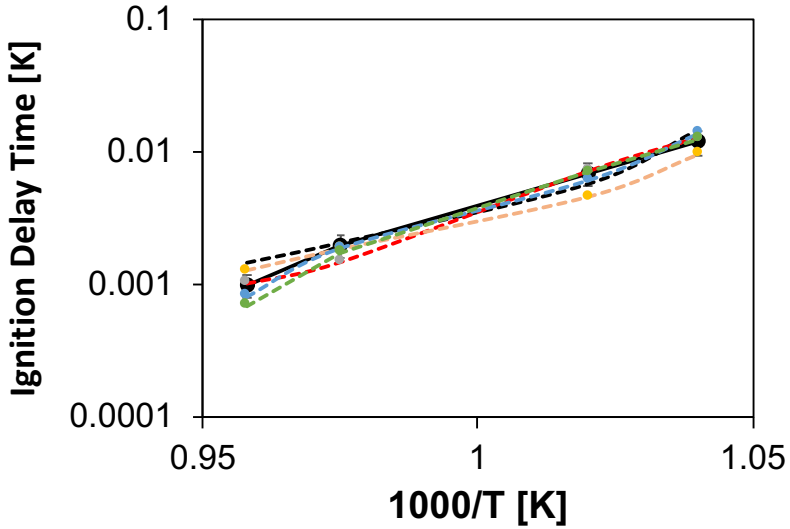
- Data point as the mean value
- Uncertainty as the standard deviation

Curve matching is performed with **each** generated dataset as **reference** curve

Performance index

$$M = \frac{\sum_{i=1}^{N} M_i}{N} \quad \pm \quad s = \sqrt{\sum_{i=1}^{N} \frac{(M_i - M)^2}{N-1}}$$

Confidence interval

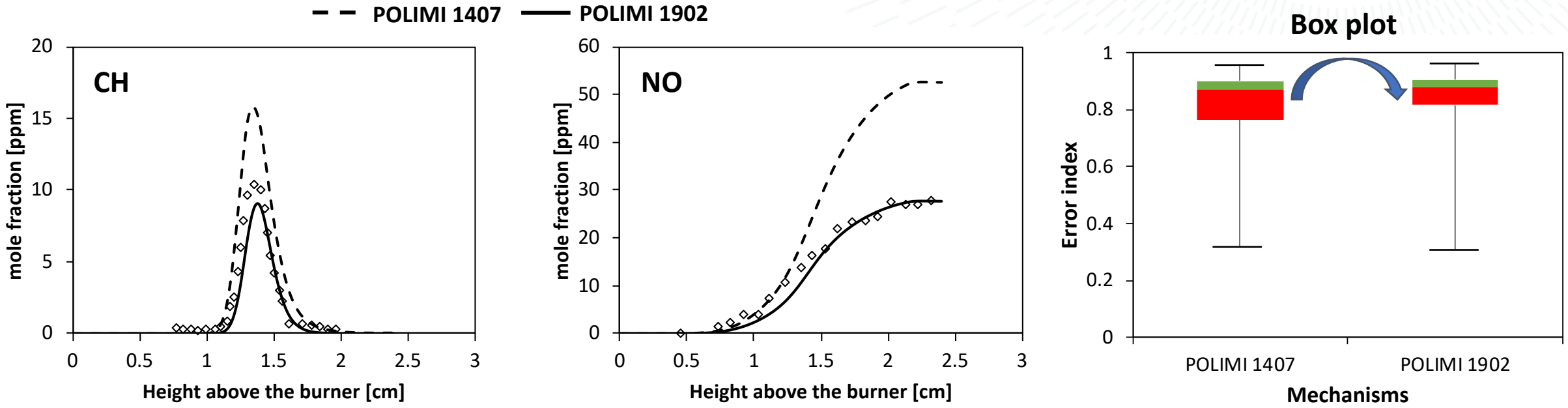


Hjorth, J. U. Computer intensive statistical methods: Validation, model selection, and bootstrap. Routledge (2017).

What happened to the 'bugged' NO_x mechanism?

	Model	$d^0_{L_2}$	$d^1_{L_2}$	d^0_P	d^1_P	S	M	s
CH	POLIMI 1407	0.813	0.842	0.940	0.878	0.997	**0.911**	**0.009**
	POLIMI 1902	0.931	0.917	0.955	0.895	0.975	**0.941**	**0.014**
NO	POLIMI 1407	0.703	0.718	0.966	0.705	0.942	**0.829**	**0.014**
	POLIMI 1902	0.962	0.826	0.967	0.706	0.947	**0.892**	**0.018**

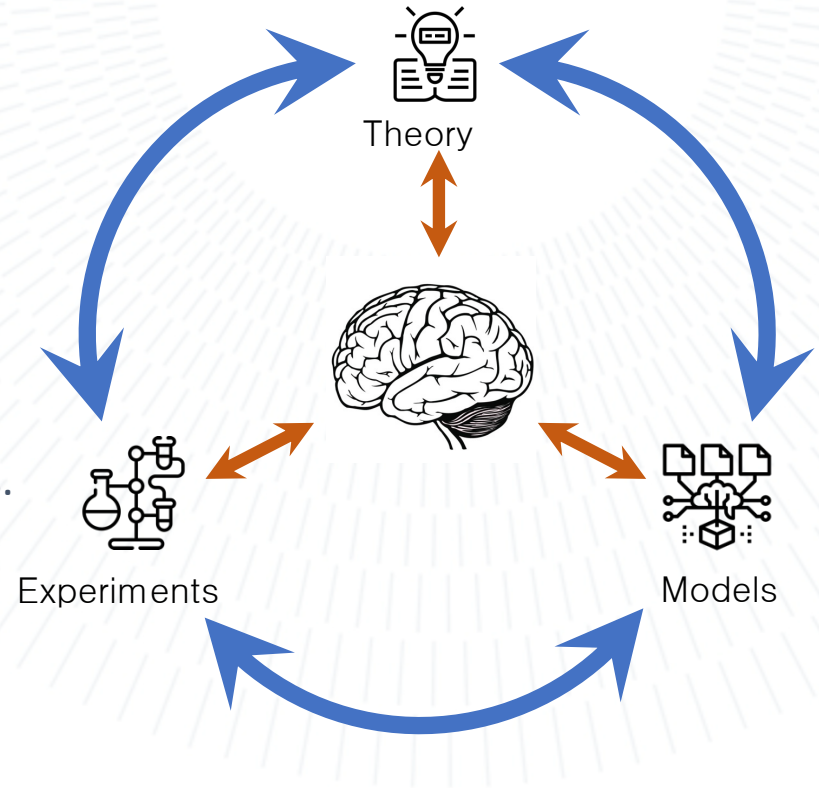
- Improved predictions in prompt & reburning **submechanisms**
- Box plot shows the overall improvements, as well as the **outliers** to be further **investigated**

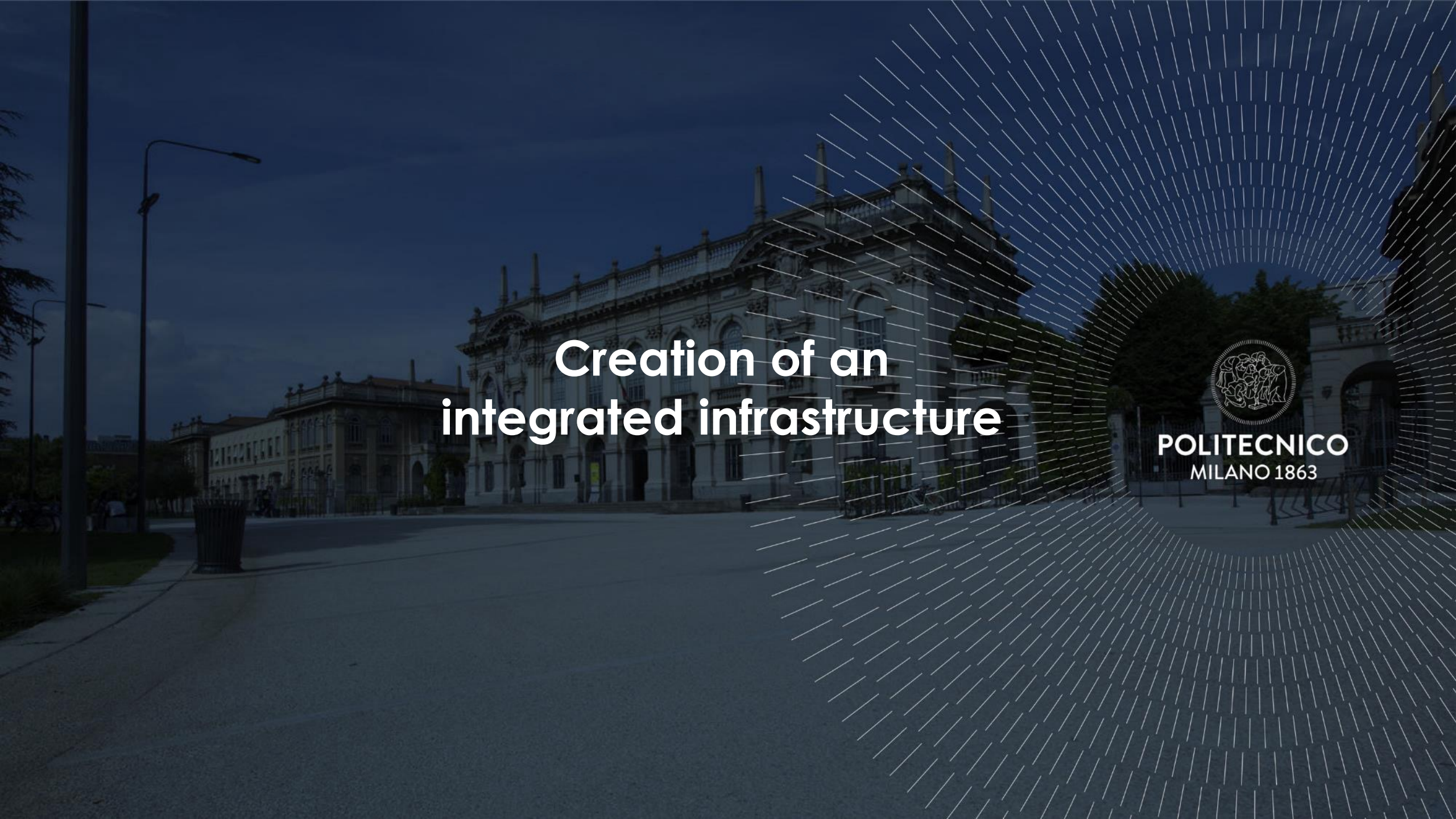


Van Essen et al. Combust Flame 153 (2008)

Take-home messages

- ✓ **Mechanism validation** is often the major bottleneck in model development
- ✓ **Setting up data ecosystems** is a necessary step to leverage large amounts of data to develop predictive kinetic mechanisms
  - Physical behavior is **complex,** quantifying predictability **is, too.**
  - **Uncertainty** matters
  - **Knowledge** can be extracted from data behavior
- ✓ **Experiments/theory/modeling**: the cross and delight of chemical kinetics
  - The technology boost increases knowledge
  - Increasing knowledge creates some traffic…
- ✓ **Multi-faceted** analysis of functional data obtained from models and experiments.
  - ✓ Distance and similarity **norms**, and horizontal **shift**
  - ✓ Functions and first derivatives
  - ✓ **Bootstrapping** to estimate the index confidence interval




Creation of an
integrated infrastructure
POLITECNICO
MILANO 1863

Beyond Curve Matching: an integrated infrastructure

Need to effectively **manage** a huge amount of data:

→ **Continuous**, multi-source integration

→ **Dynamic** acquisition of new data

→ **Continuous** validation

→ Data **exploration**

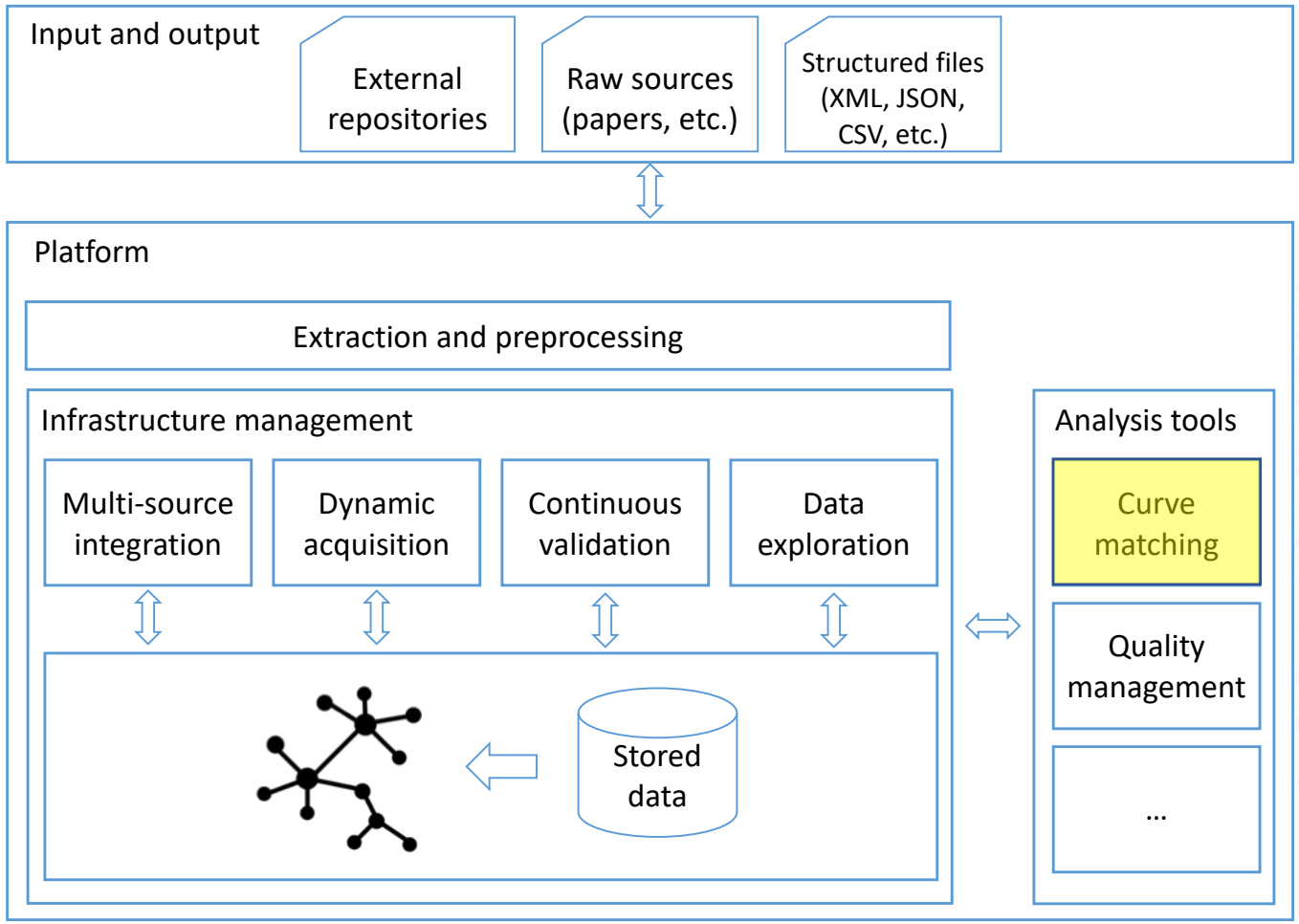
Creation of a **common** database, interfaced with

→ **Simulations** platform (e.g. OpenSMOKE++)

→ **Validation** platform (Curve Matching)

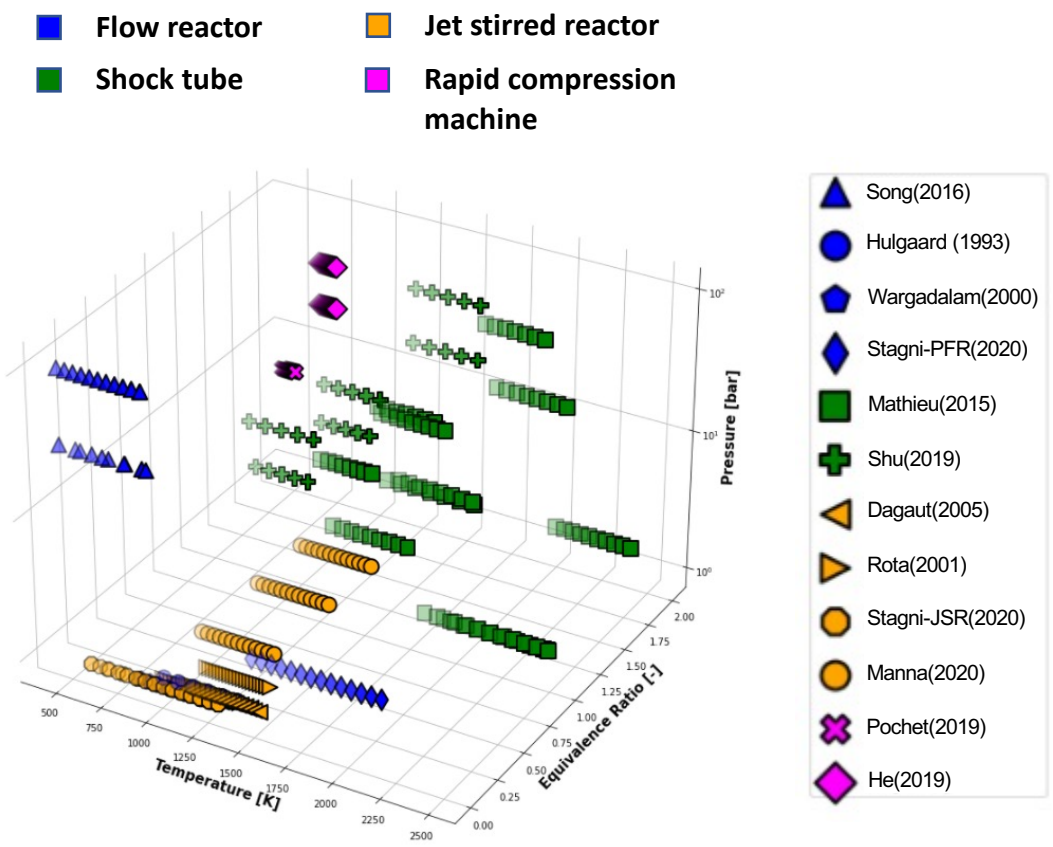
SCIEXPEM

https://sciexpem.polimi.it/

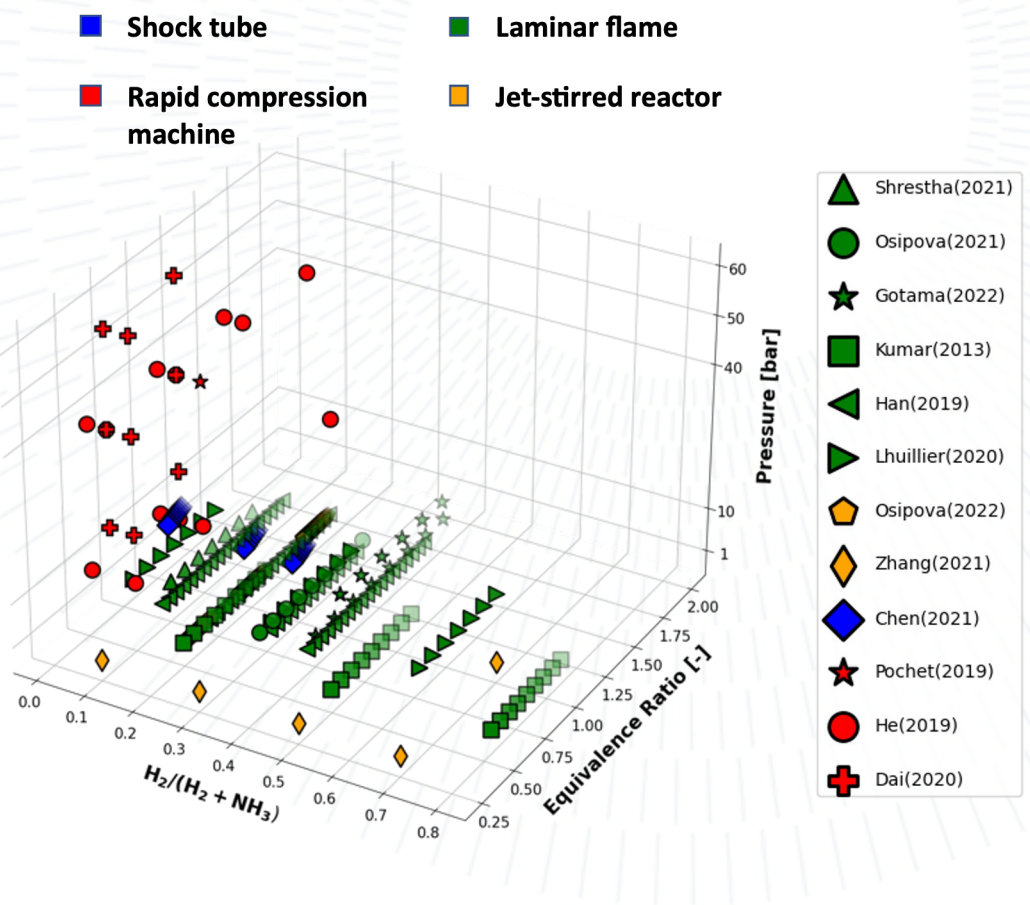


Scalia, G., et al. In Semantics, Analytics, Visualization. Springer, Cham. (2018)

Experimental datasets

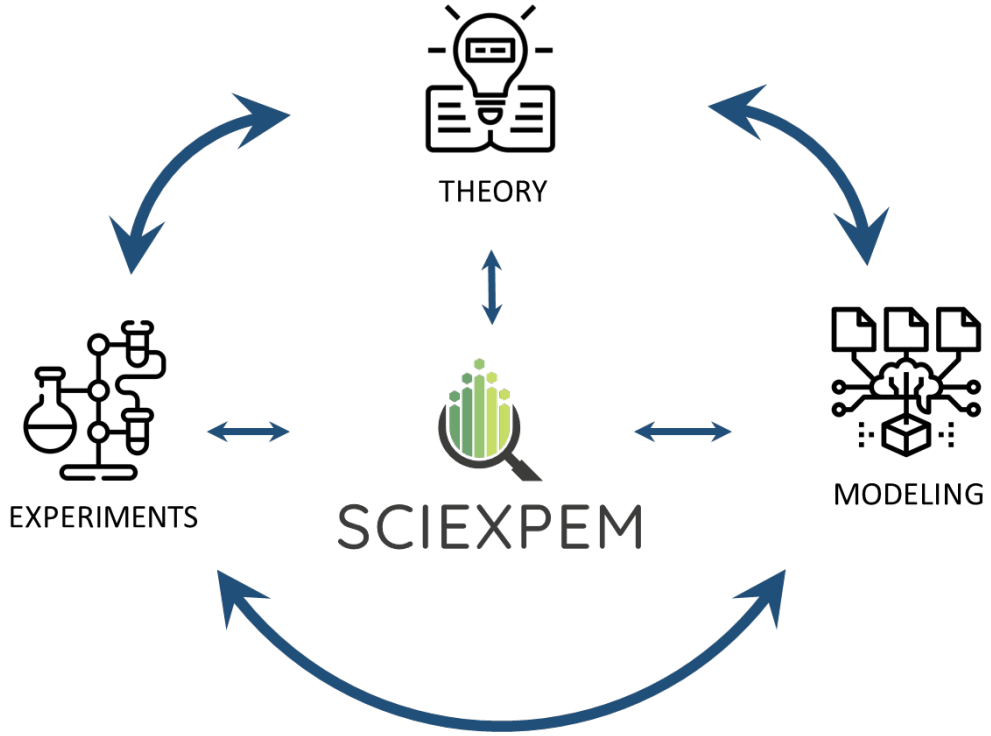


NH_3



NH_3/H_2

A threefold approach



Ramalli et al. Chem Eng J 454 (2023)
Ramalli et al. Front Big Data 4 (2021)

Methodology:

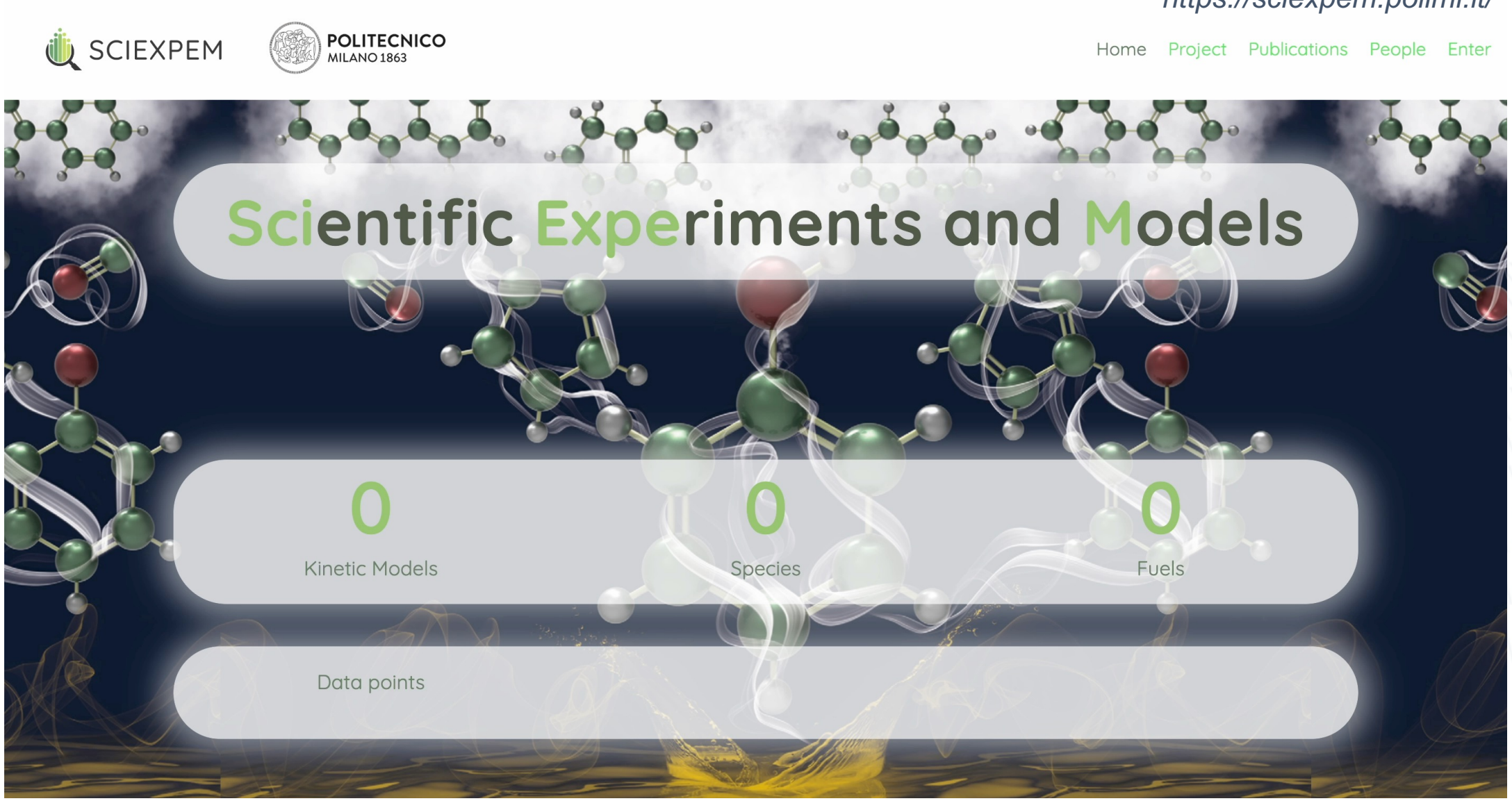
- **Synergistic integration** of i) experimental data, ii) theoretical calculations, iii) kinetic modeling
- **Automated kinetic simulations**
- Model **performance analysis**

Continuous-improvement workflow

Perform **experiments** and **theoretical** studies in the most **critical** operating conditions

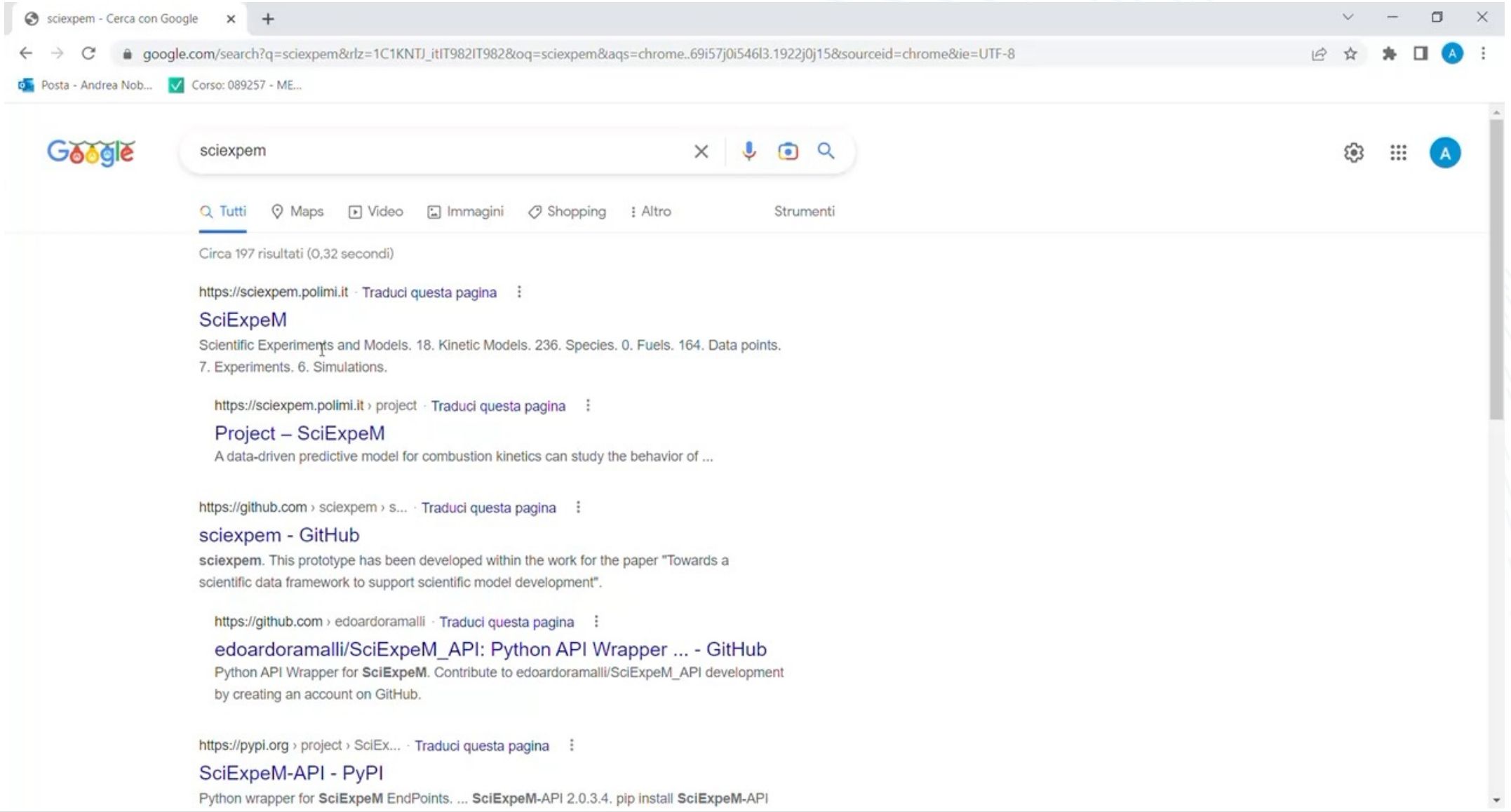
Sciexpem

https://sciexpem.polimi.it/



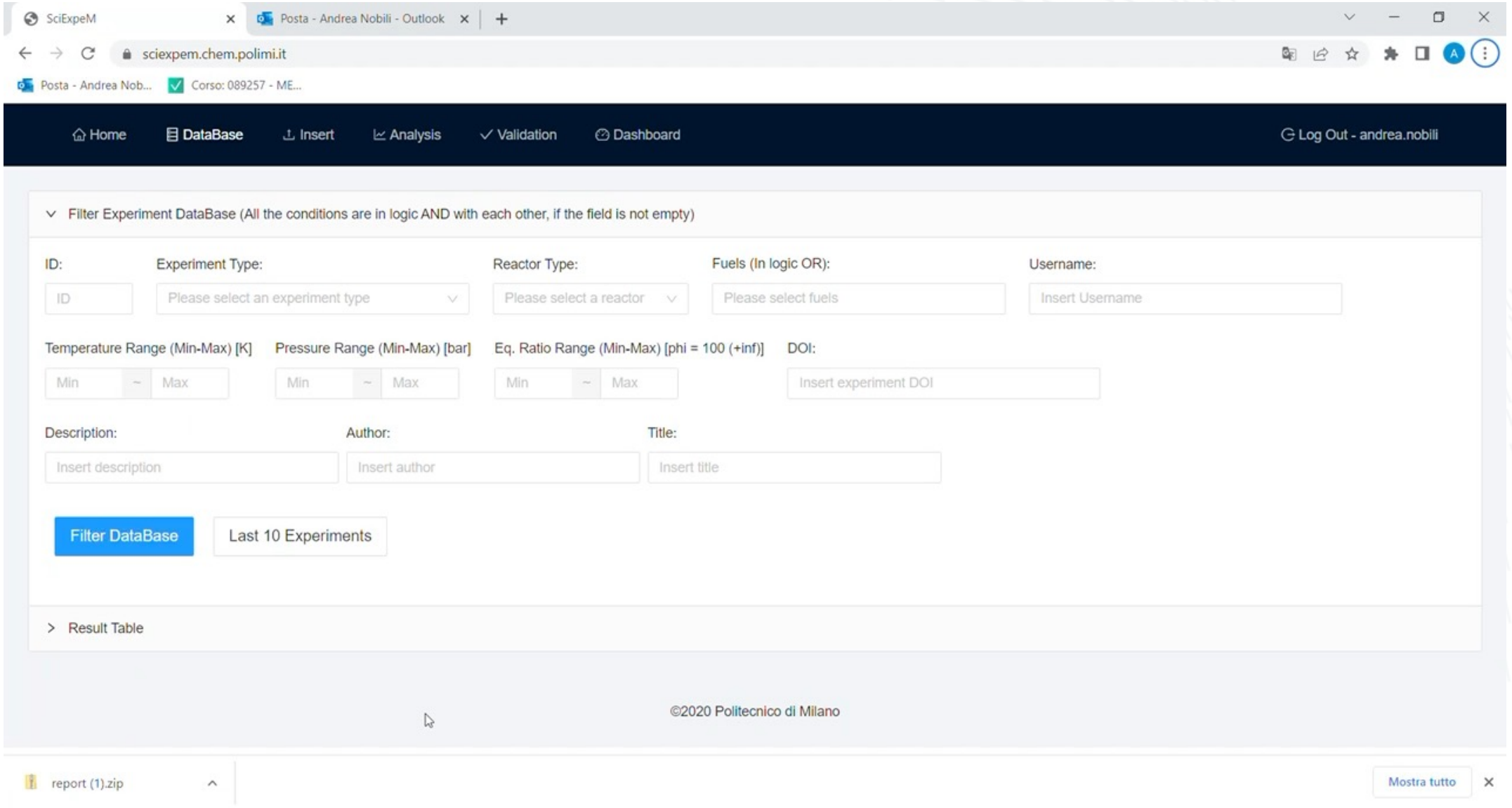
Sciexpem: the ‘experiment’

https://sciexpem.polimi.it/



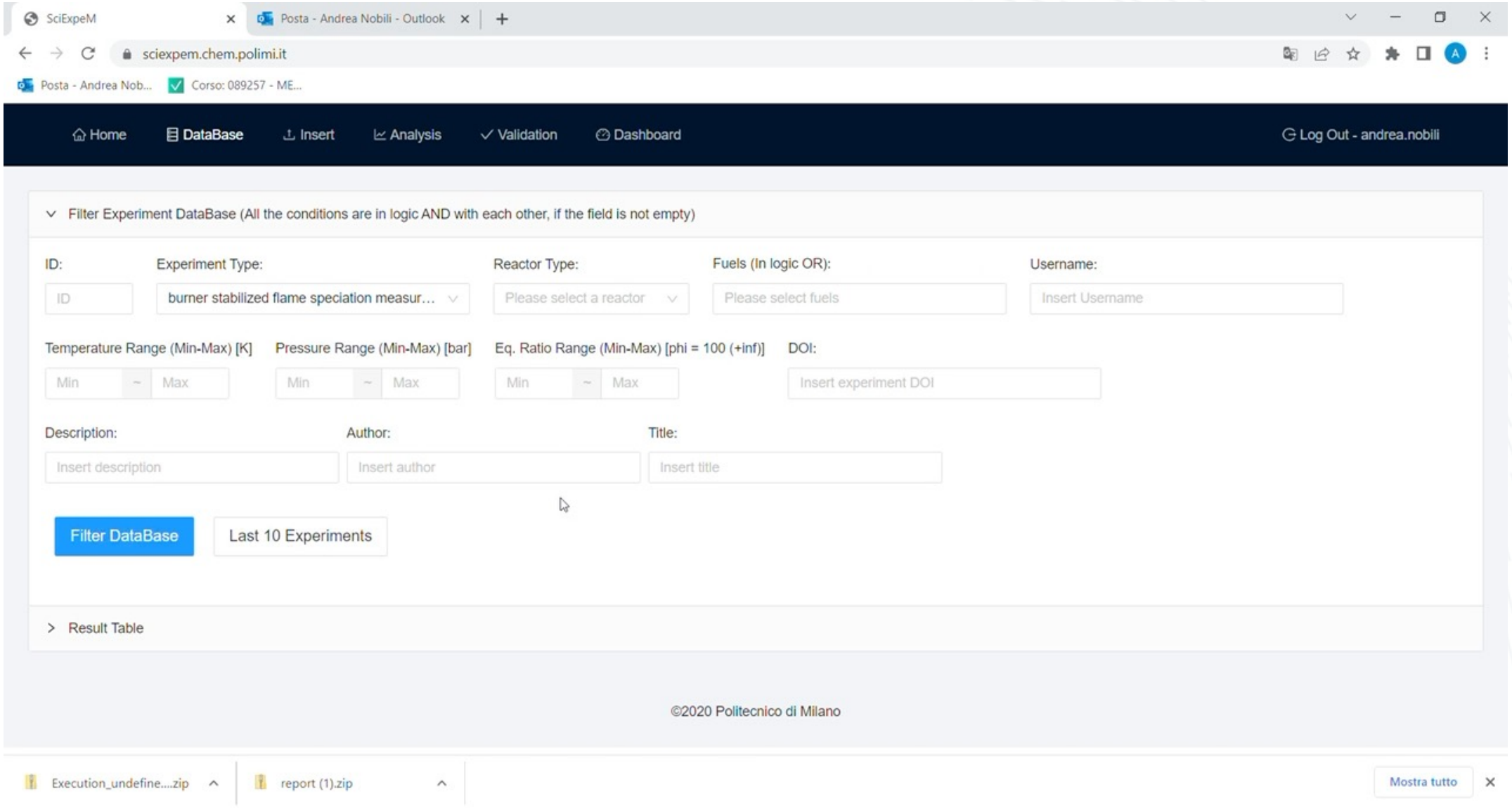
Sciexpem: the ‘database’

https://sciexpem.polimi.it/



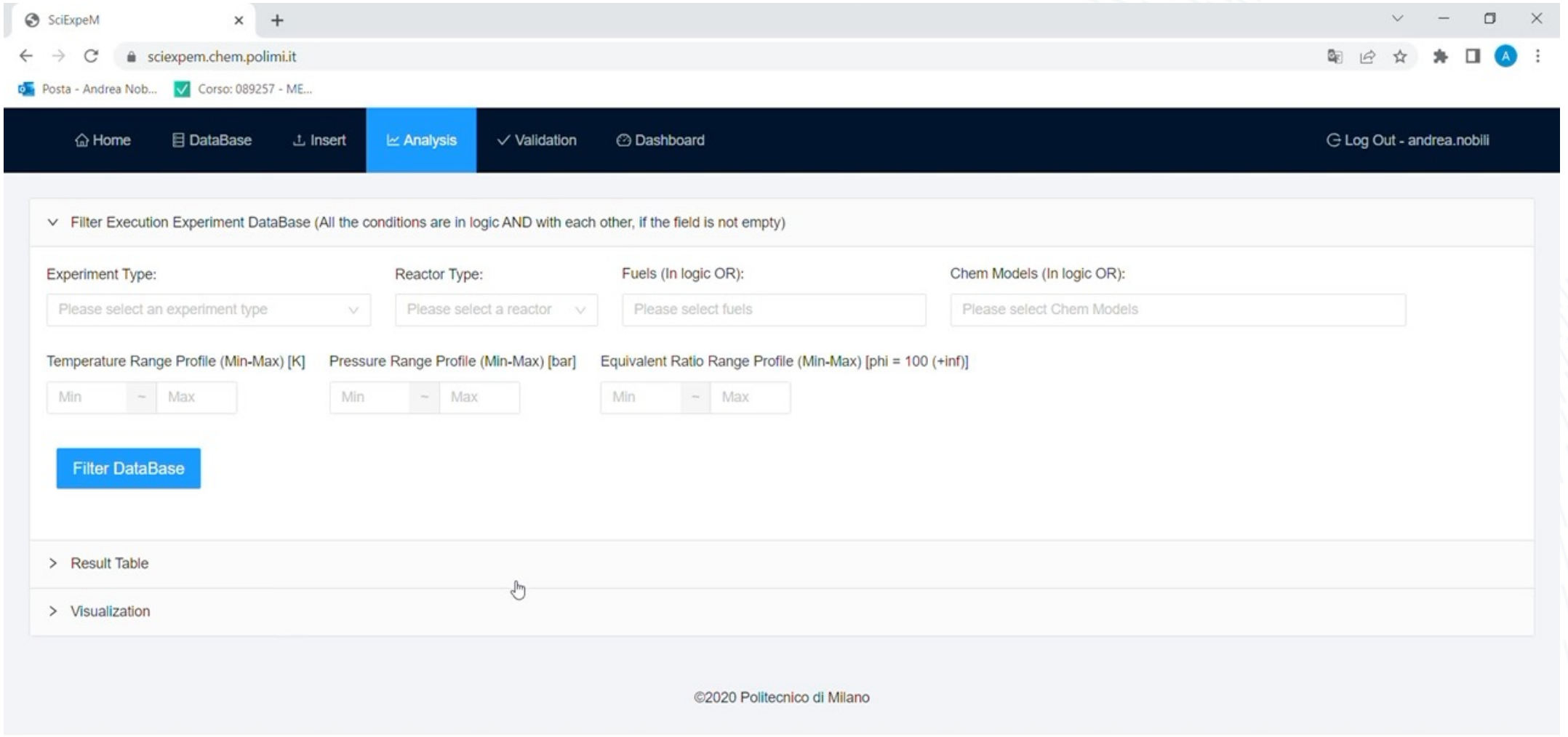
Sciexpem: the ‘simulation’

https://sciexpem.polimi.it/



Sciexpem: model validation and analysis

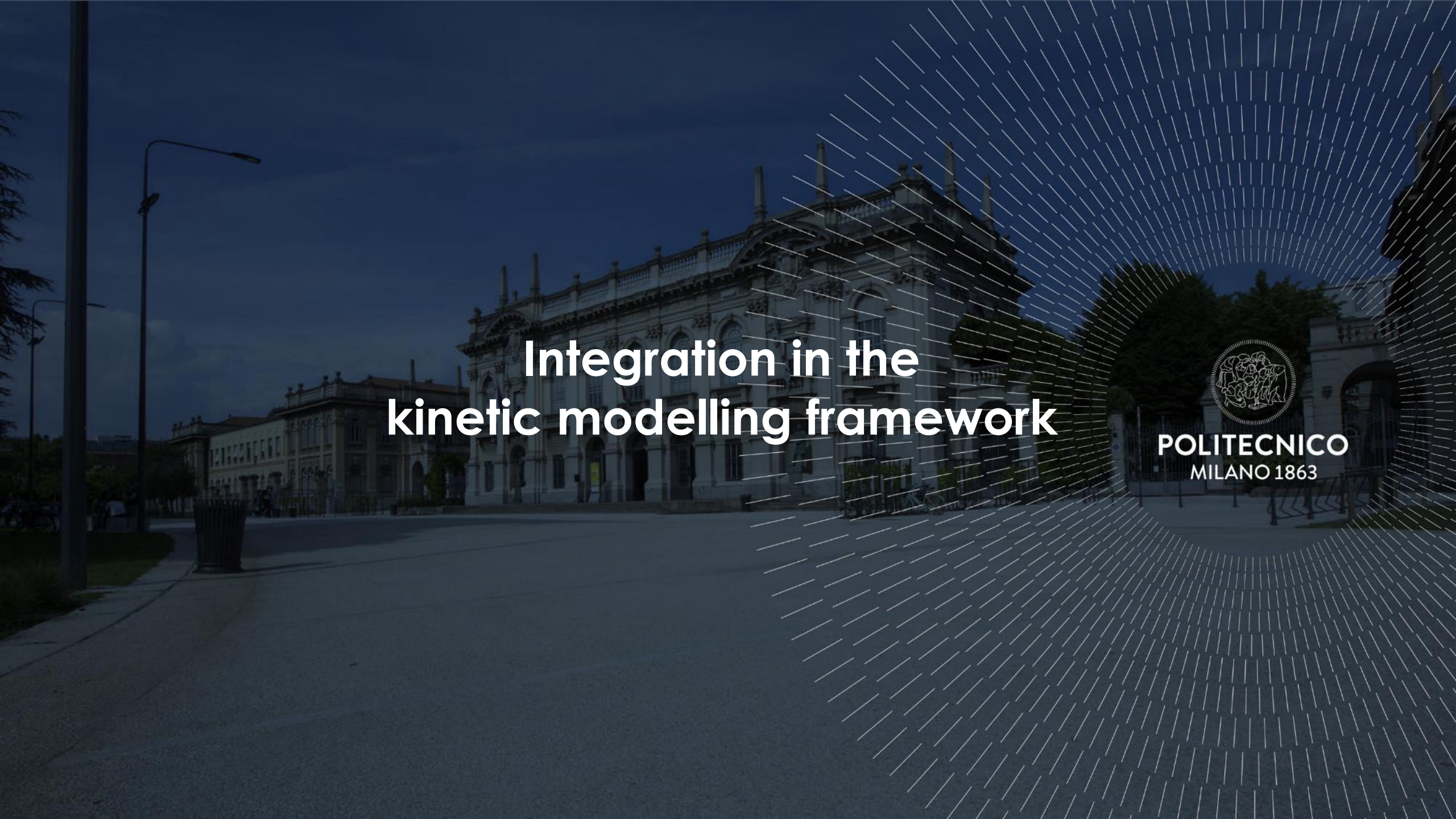
https://sciexpem.polimi.it/



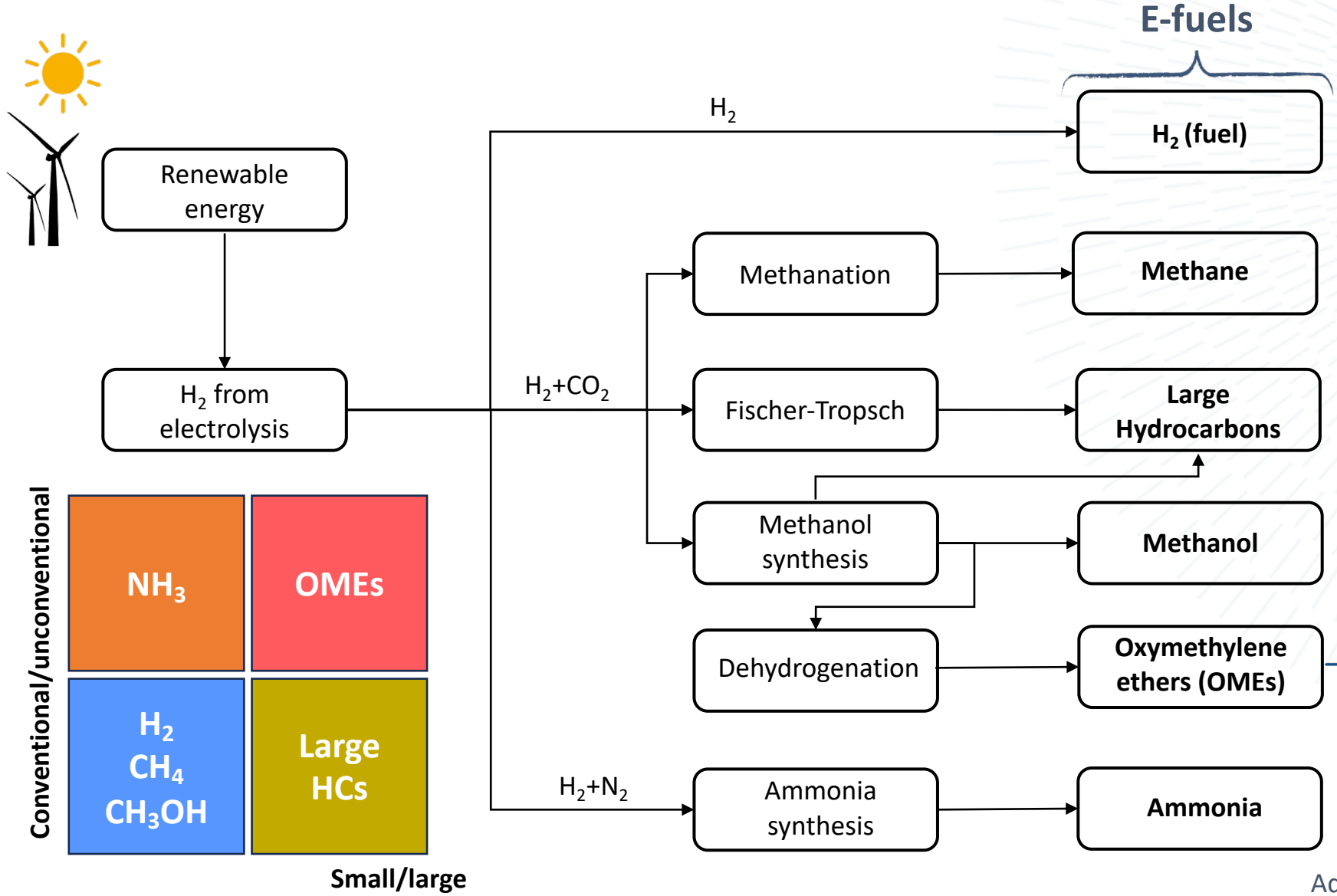
Take-home messages

- **SciExpeM** and **Data Ecosystems:** effective tools that can foster the development of chemical kinetic mechanisms.
- SciExpeM specifically as a tool is still under development (**JOIN US IN THIS JOURNEY**).
- Data sharing, and definition of standard benchmarks needs to be established to develop new and consistent methodologies to reduce optimize mechs…

→ Further exploitation of this huge amount of experimental data collected, towards **model discovery** and **generation**.


Integration in the
kinetic modelling framework
POLITECNICO
MILANO 1863

Kinetic modeling in the energy transition scenario



Current bottlenecks:

→ **Theoretical knowledge** (e.g. NH_3, OMEs)

→ **Chemistry-physics interactions** (e.g. H_2)

→ **Mechanism size** (Large HCs, OMEs)

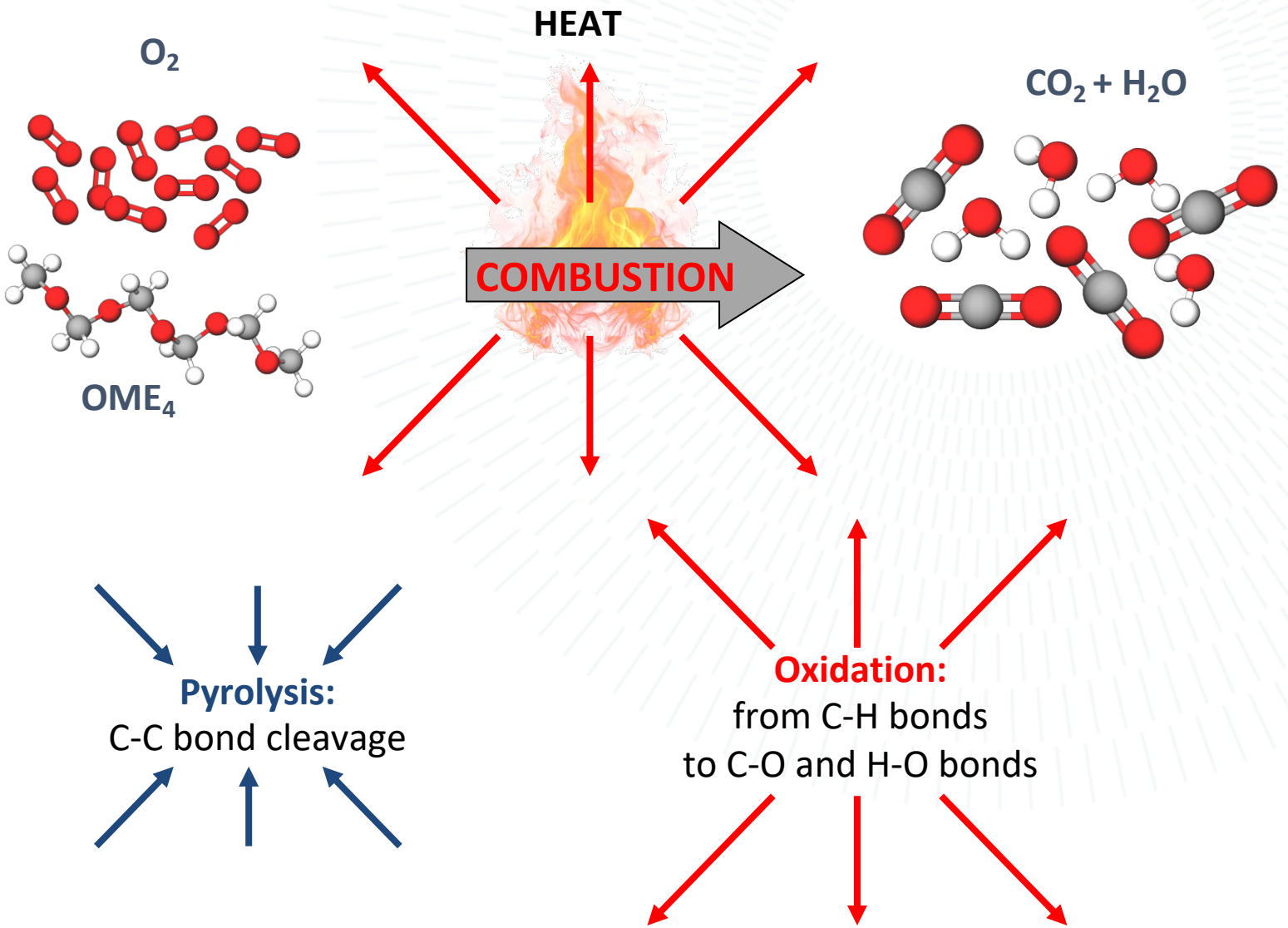
Alkane-like chemistry
LT vs HT

Adapted from Masri, *Proc Combust Inst* 38 (2021)

A step back: modeling combustion kinetics

- ✓ Regardless of the fuels, **combustion kinetics** is:
  - → **Hierarchical**
  - → **One-way**
  - → Based on i) the **pyrolysis** and ii) **oxidation** concepts
- ✓ The **energy transition** can **leverage** the longstanding and established kinetic modelling tools and knowledge obtained with conventional fuels
- ✓ From **larger to smaller** molecules: pyrolysis and oxidation **break bonds**

Which comes first?

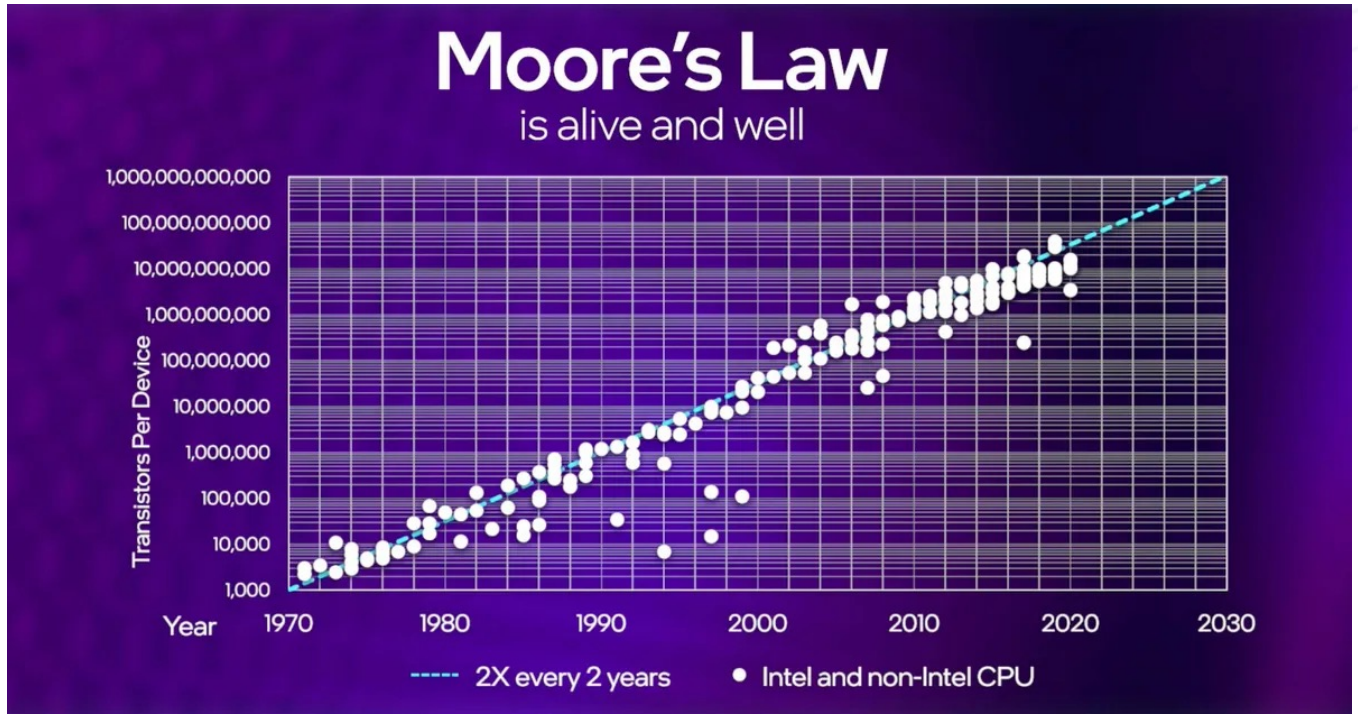


Limitations of detailed chemistry

✓ Computational availability increases exponentially over time (**Moore's** law)

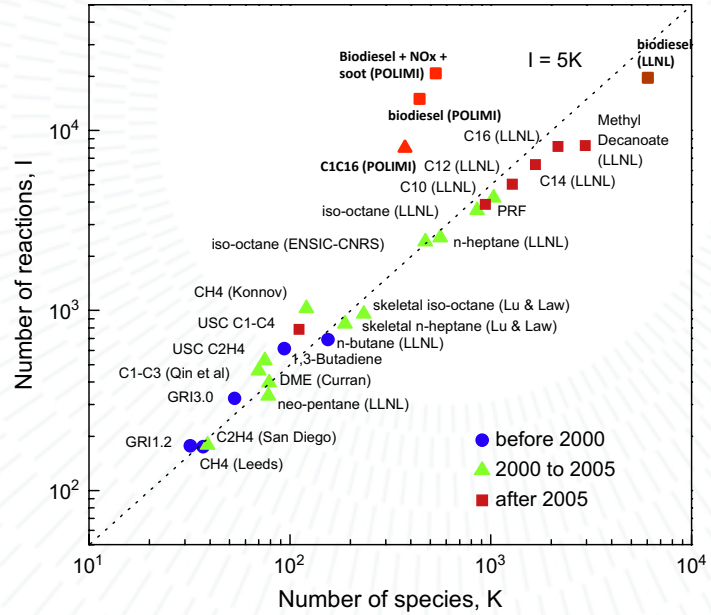
😐 Computational cost scales with power law (Jacobian matrix **construction/factorization**)

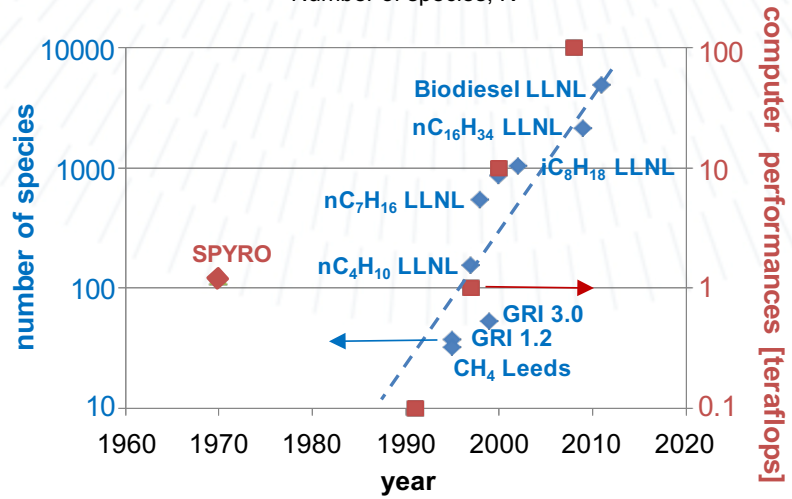
✗ Detailed mechanisms of real fuels are **not** applicable for most computationally demanding **applications**



https://www.linkedin.com/pulse/what-moores-law-ritik-kumar-singh-wr4zc/

Lu & Law, Prog Energy Comb Sci 35 (2009)





Chemistry complexity

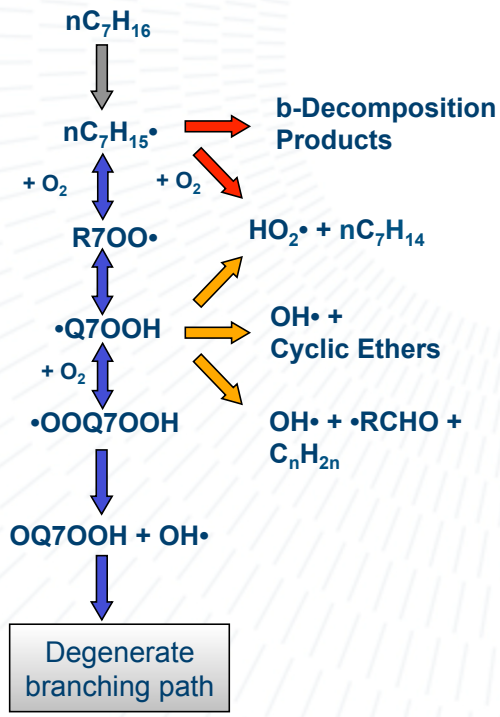
Complexity of liquid feedstocks

#C	Paraffin isomers	Petroleum fraction
8	18	Gasoline and naphthas
10	75	Kerosene
12	355	Jet Fuels
15	4347	Diesel Fuels
20	$3.66 \cdot 10^5$	Light Gasoil
25	$3.67 \cdot 10^7$	Gasoil
30	$4.11 \cdot 10^9$	Heavy Gasoil
35	$4.93 \cdot 10^{11}$	Atmospheric Residue

Altgelt and Boduszynski (1994)

Use of representative molecules
Surrogate fuels

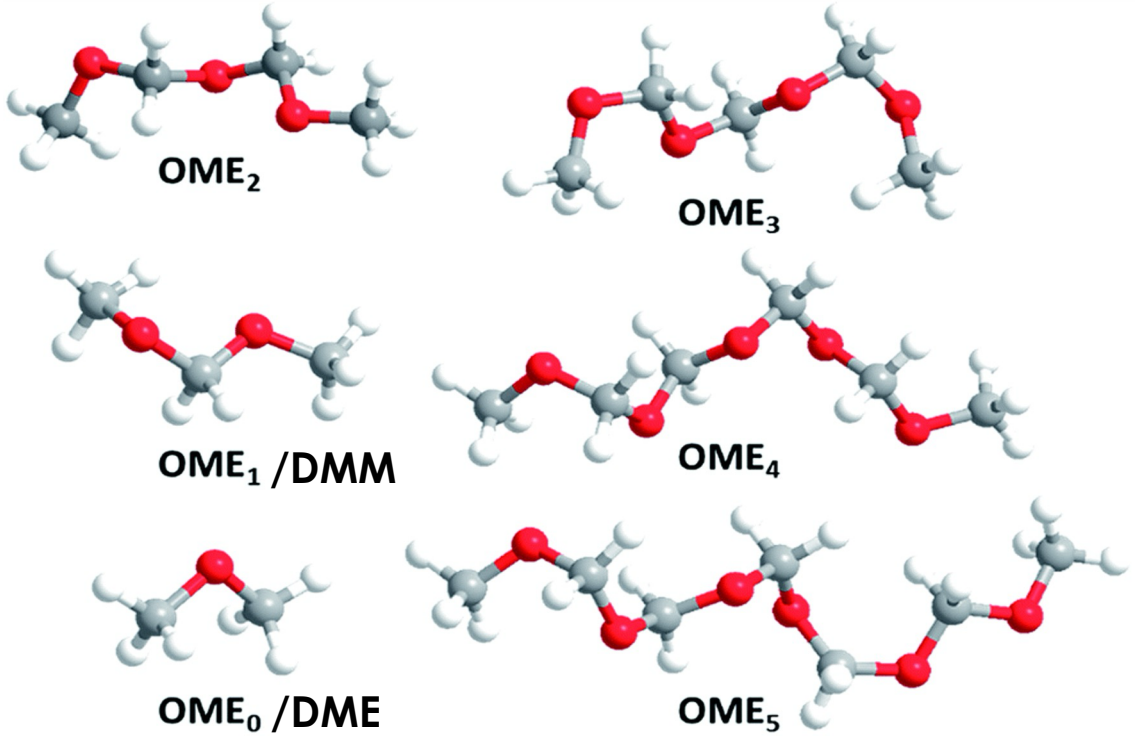
Complexity of reaction mechanisms



Reduction techniques
Species Lumping
Skeletal Reduction

Case study: Oxymethylene ethers (OMEs)

$CH_3O[CH_2O]_nCH_3$



	OME_{3-5}*	Fossil diesel
Density at 15°C [g/cm^3]	1.057	0.835
Oxygen content [wt%]	48	~ 0
Cetane number [-]	80	54
Flash point [°C]	62	55
Boiling point [°C]	140–318	200-360
Melting point [°C]	−18	~ −9

* 0.1 wt% OME_1, 0.2 wt% OME_2, 45 wt% OME_3, 25 wt% OME_4, 17 wt% OME_5, 7 wt% OME_6, 3 wt% OME_7, 1 wt% OME_8

Great potential as **drop-in fuels**

Physico-chemical properties **similar** to those of **diesel** fuels

Established **synthesis** processes

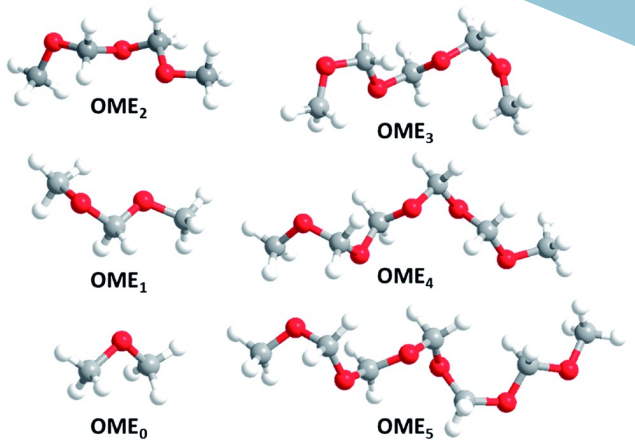
Reduction in **NO_x** and **particulate** formation

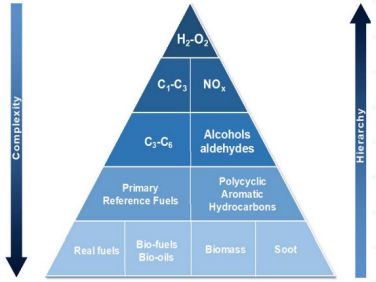
Omari et al. *Applied energy*, 239:1242–1249, 2019.

Himmel et al. *Sustainable Energy Fuels*, 1:1177–1183, 2017.

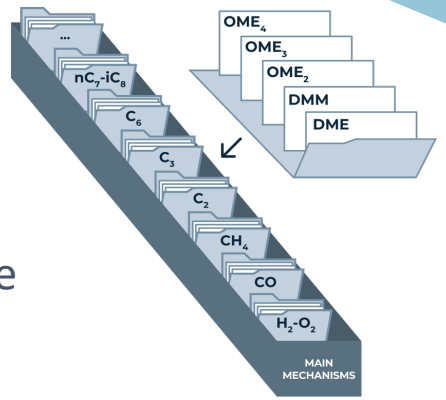
Setting up OME chemistry

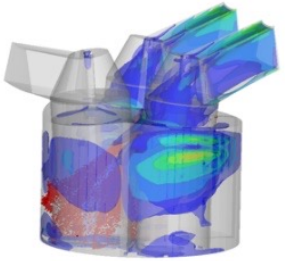
OME mixtures





Kinetic modeling





CFD applications

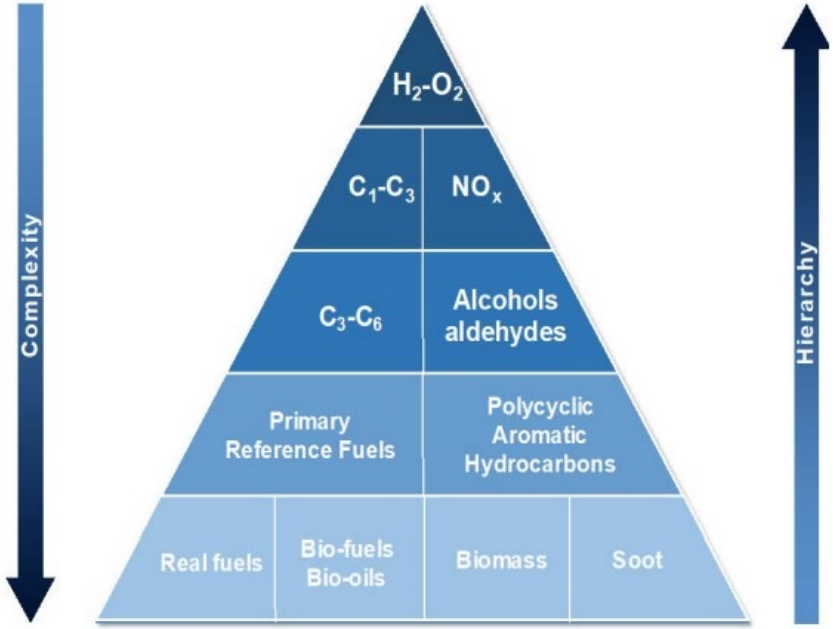
→ Set up a **workflow** to accommodate the chemistry of longer-chain fuels into a semidetailed model

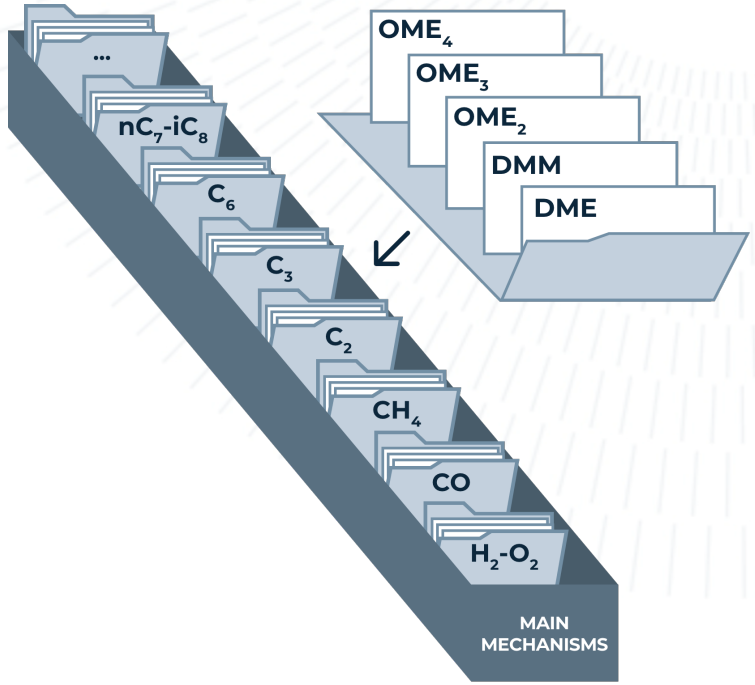
→ Apply to OME_{2-5} as a **case study**

Kinetic modeling is modular

Set up of a **core** C_0-C_3 chemistry → Define **archetypal** lumped chemistry (OME_1) → Set up OME_{2-5} model: reaction classes, rate rules → Data-driven, **physics-enforced** optimization

Hierarchy, **modularity**, and **generality** principles





Pelucchi et al. *Comp Aided Chem Eng*, 45, 2019.

Pegurri , Master Thesis, Poitecnico di Milano (2022)

Chemical lumping

→ With an increasing molecule size, the number of species and structural isomers increases exponentially

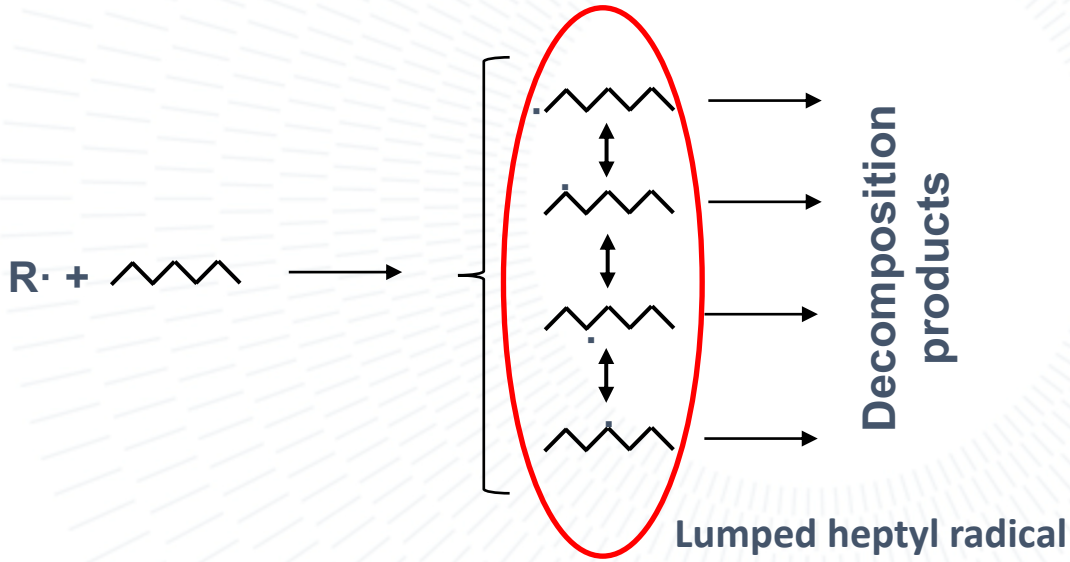
→ Yet, the reaction classes are **always the same**…

→ **Chemical lumping**: structural isomers can be grouped into **pseudo-species**, thus limiting the increase in the number of species (Ranzi, 2001)

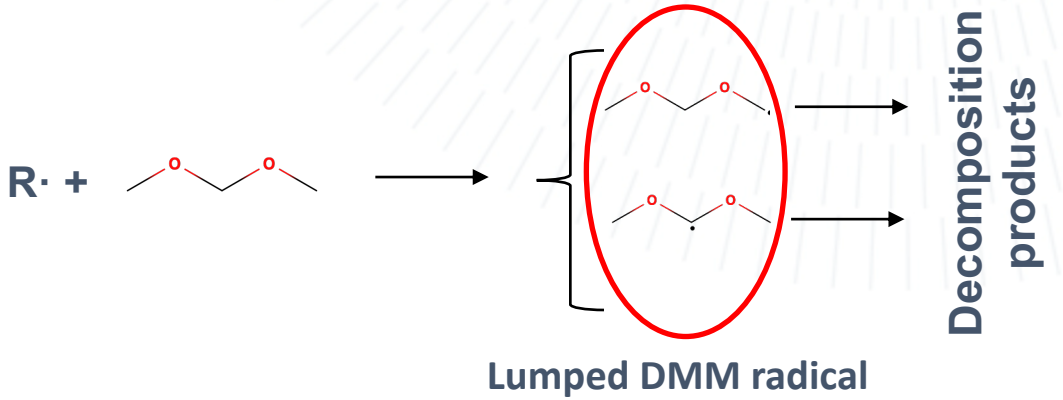
#C	Paraffin isomers	Petroleum fraction
8	18	Gasoline and naphthas
10	75	Kerosene
12	355	Jet Fuels
15	4347	Diesel Fuels
20	$3.66 \cdot 10^5$	Light Gasoil
25	$3.67 \cdot 10^7$	Gasoil
30	$4.11 \cdot 10^9$	Heavy Gasoil
35	$4.93 \cdot 10^{11}$	Atmospheric Residue

Altgelt and Boduszynski (1994)

This was developed for fossil-based fuels…



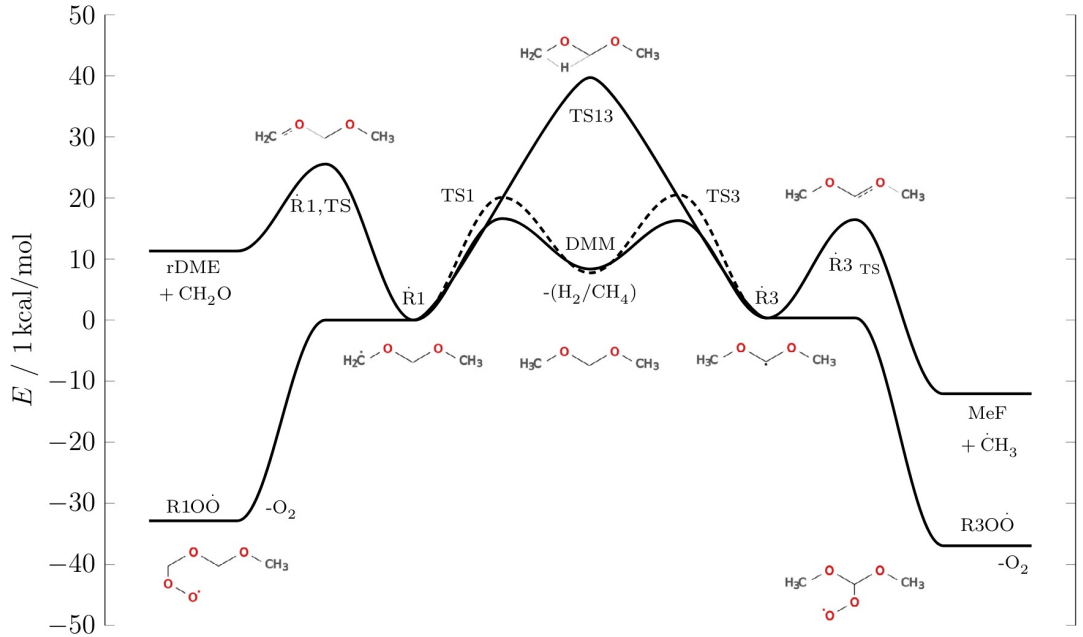
But it holds equally for next-generation ones!



Ranzi et al. *Progr Energy Combust Sci*, *27*, 2001

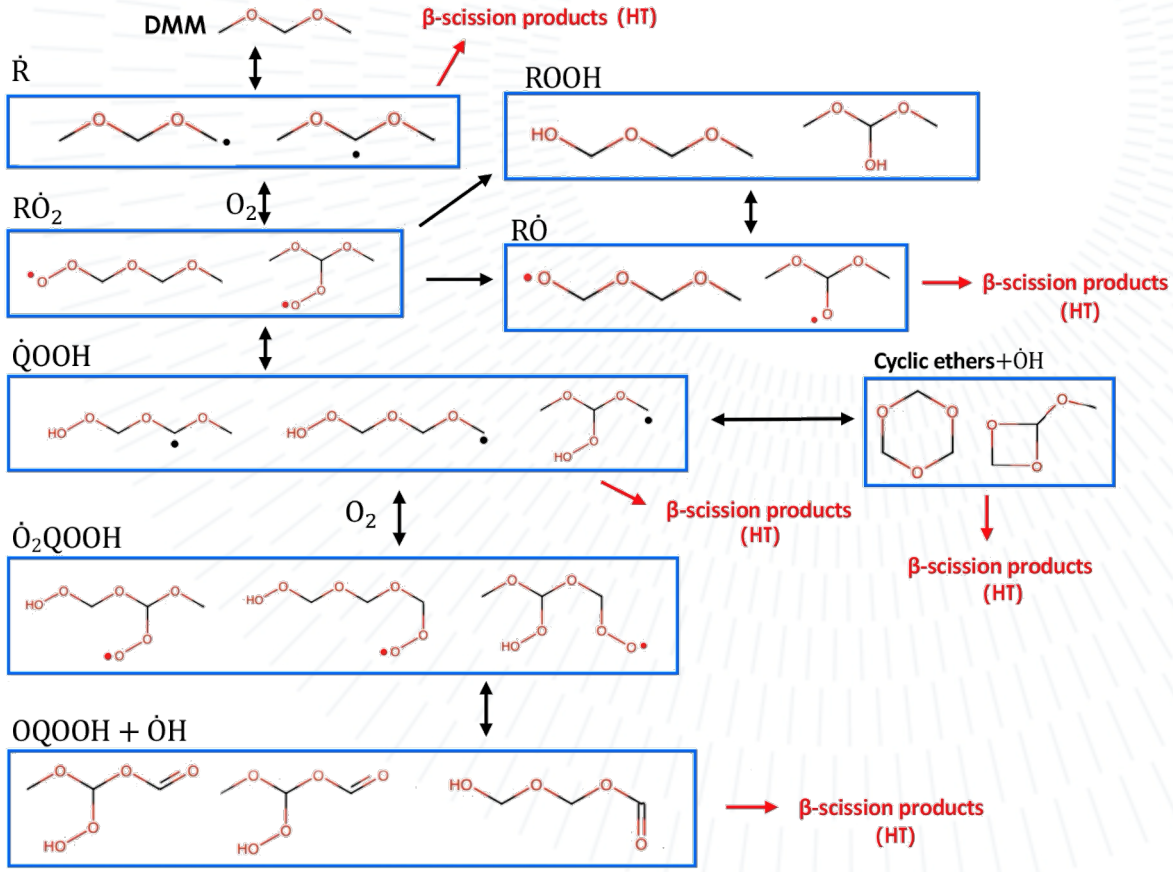
DMM (OME_1) kinetic model as an archetypal

For small molecules like DMM, the key steps can be often evaluated **ab-initio**



Reaction classes and rate rules can be implemented

High- and low-temperature pathways



Jacobs et al. *Combust Flame*, *189,* 2018

Pegurri et al. *Combust Flame*, *260,* 2024

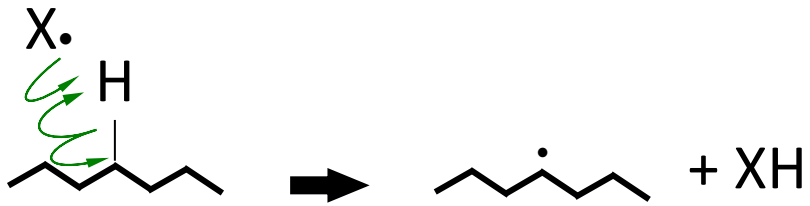
Lumping OMEs

Reaction classes and rate rules

→ Reaction rate constants mostly depend on the **reacting moiety**, and the **related short-range interactions** (Benson, 1976)

→ "Similar" reactions have similar reaction rates on all fuels: rate rules can be defined

Example: H-abstractions

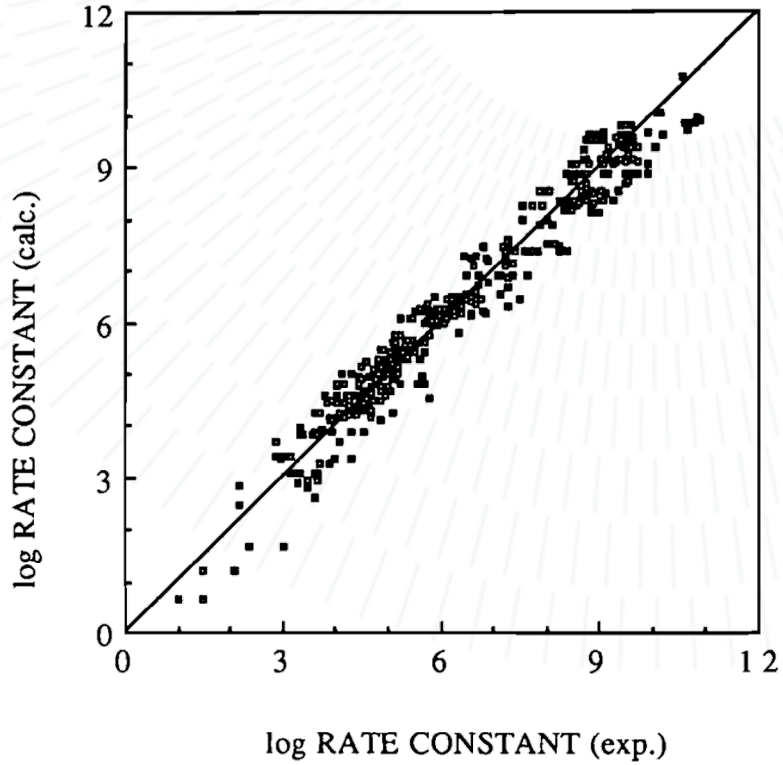


The reaction rate depends on:

→ The **abstracting** radical

→ The hydrogen **location**

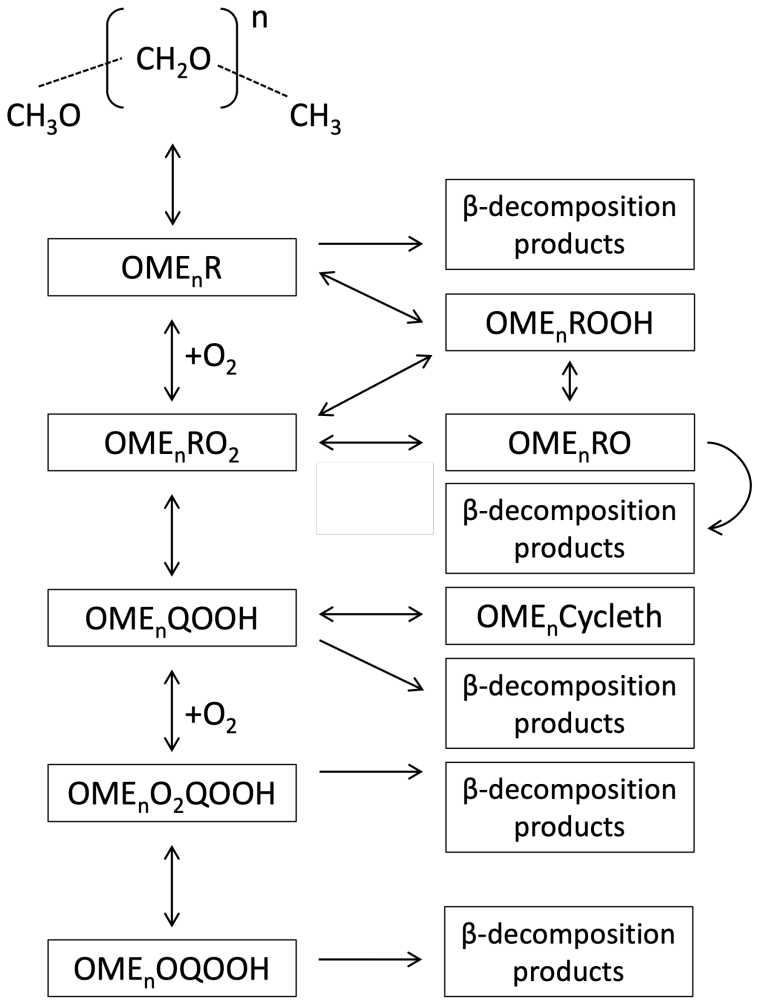
$$k = \underbrace{A^0_{ref,R} \exp\left(-E^0_{ref,R}/RT\right)}_{\text{Parameters of the abstracting radical}} \times \underbrace{A^0_{CR'H} \exp\left(-E^0_{R'H}/RT\right)}_{\text{Parameters of the hydrogen bond}}$$



Benson, "Thermochemical kinetics", 2nd edition, New York (1976)

Ranzi et al. *Comb Sci Technol 95 (1993)*

From OME_1 to higher OMEs



Reaction-class systematic methodology

1. Unimolecular decomposition
2. $OME_n + \dot{R}' \leftrightarrow OME_n\dot{R} + R'H$ → From Ranzi's methodology
3. $OME_n\dot{R} \leftrightarrow \beta$-decomposition products
4. $O_2 + OME_n\dot{R} \leftrightarrow OME_nR\dot{O}_2$
5. $\dot{R}O_2 + OME_n\dot{R} \leftrightarrow R\dot{O} + OME_nR\dot{O}$
6. $OME_nR\dot{O}_2 \leftrightarrow OME_n\dot{Q}OOH$
7. $\dot{R} + OME_nROOH \leftrightarrow RH + OME_nR\dot{O}_2$
8. $OME_nROOH \leftrightarrow OME_nR\dot{O} + \dot{O}H$
9. $OME_nR\dot{O} \leftrightarrow \beta-$decomposition products
10. $OME_n\dot{Q}OOH \leftrightarrow OME_n$ cyclic ether
11. $OME_n\dot{Q}OOH \leftrightarrow \beta-$decomposition products
12. $OME_n\dot{Q}OOH + O_2 \leftrightarrow OME_n\dot{O}_2QOOH$
13. $OME_nOQOOH + \dot{O}H \leftrightarrow OME_n\dot{O}_2QOOH$
14. $OME_nOQOOH \leftrightarrow \beta-$decomposition products

Scaled From DMM model

Ranzi et al. *Progr Energy Combust Sci*, *27,* 2001

Shrestha et al. *Combust Flame* 246 (2022)

Pegurri et al. *Combust Flame*, *260,* 2024

Optimization

$$k = A\,T^{\beta}\,e^{-\frac{Eact}{RT}}$$

→ Non-linear constraint, factor 2 adopted.

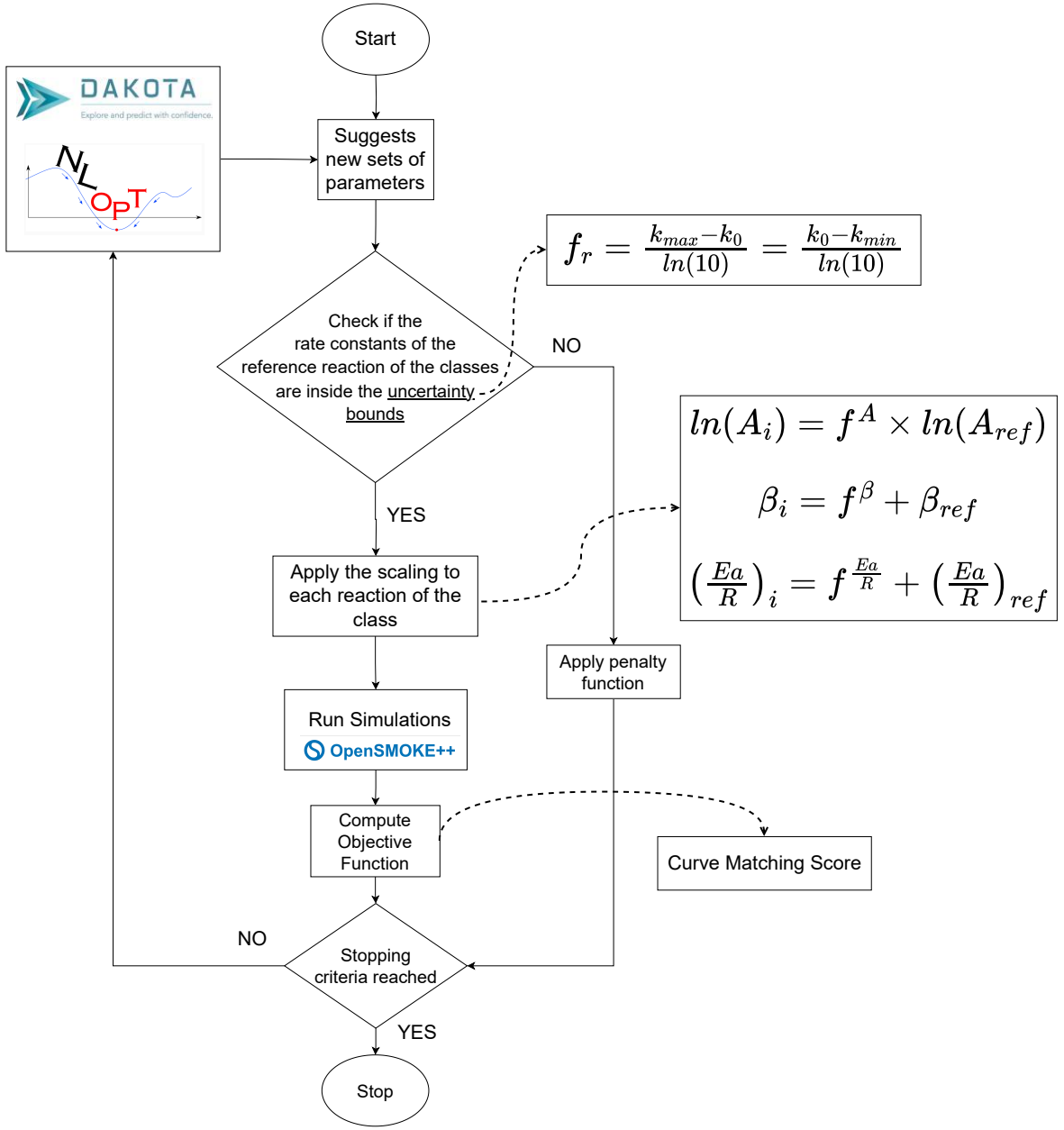
$$f_r = \frac{\mathcal{K}_{max} - \mathcal{K}_0}{ln(10)} = \frac{\mathcal{K}_0 - \mathcal{K}_{min}}{ln(10)}$$

→ Objective function based on Curve Matching index

$$\mathcal{L} = \frac{1}{N}\sum_{i}^{N}\left(1 - \frac{1}{N_b}\sum_{j}^{N_b} CM_{i,j}\right)$$

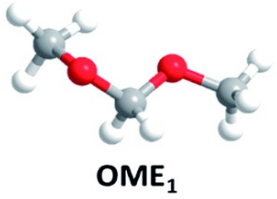
→ Reaction Class scaling

$$ln(A) = f^{A}_{scaling} \times ln(A_{ref})$$
$$\beta = f^{\beta}_{scaling} + \beta_{ref}$$
$$\frac{E_a}{R} = f^{\frac{E_a}{R}}_{scaling} + \left(\frac{E_a}{R}\right)_{ref}$$

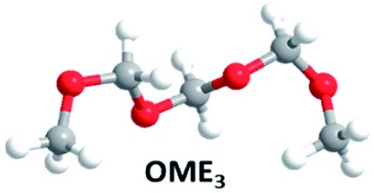


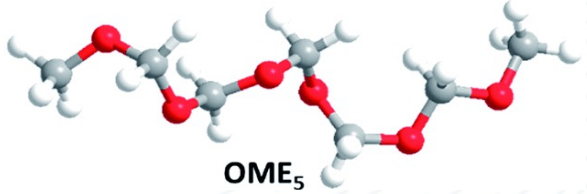
Scaling rates, retaining chemistry

Reference species



Larger species





- → **Reference parameters** are taken from DMM chemistry
- → An **uncertainty factor** f_r is assigned to each reaction class:

$$f_r = \frac{K_{max} - K_0}{\ln(10)} = \frac{K_0 - K_{min}}{\ln(10)}$$

Generic **rate**:

$$k_1 = A_1 \cdot T^{\beta_1} \cdot exp\left(-\frac{E_{a,1}}{RT}\right)$$

$$\ln(k_1) = \ln(A_1) + \beta_1 \ln(T) - \left(\frac{E_a}{R}\right)_1 \frac{1}{T}$$

Scaling factors

$$f_i^A = \frac{\ln(A_i)}{\ln(A_1)} \qquad f_i^\beta = \beta_i - \beta_1 \qquad f_i^{\frac{E_a}{R}} = \left(\frac{E_a}{R}\right)_i - \left(\frac{E_a}{R}\right)_1$$

→ Kept constant during optimization

Detailed mechanism → **Lumped mechanism** → **Optimized mechanism**

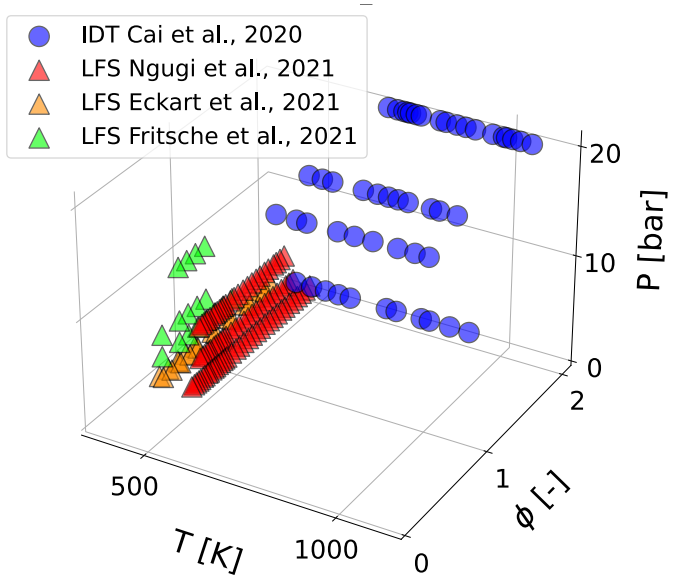
$f_i^A, f_i^\beta, f_i^{\frac{E_a}{R}}$

Fürst et al. *Comp Phys Comm 264, 2021*

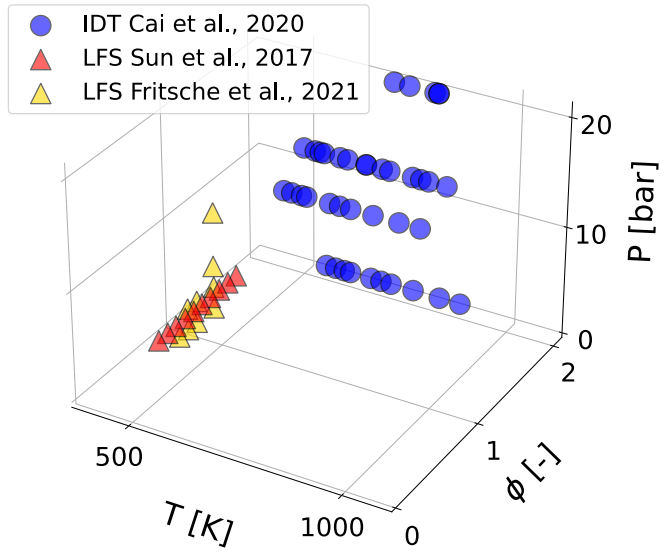
Bertolino et al. *Combust Flame 229, 2021*

Experimental database & optimization targets

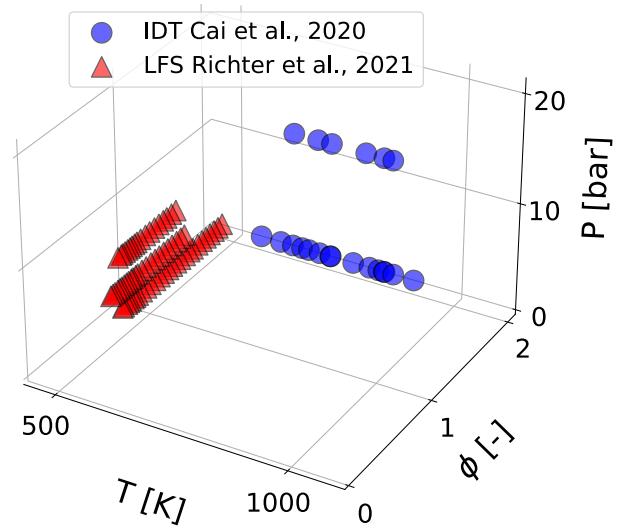
OME_2



OME_3



OME_4



→ Ignition delay time & Jet Stirred Reactor selected from the Sciexpem database

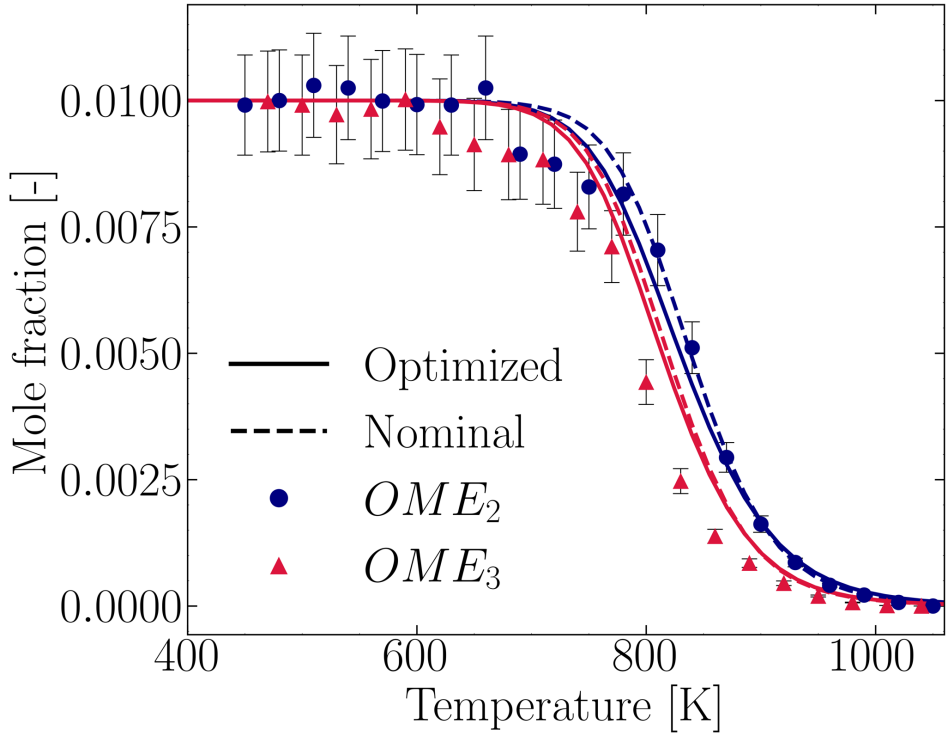
→ Most data on $OME_{2\text{-}4}$ (only 1 dataset available for OME_5)

→ Plug flow reactor used for validation

→ Laminar flame speed used for validation

Model validation

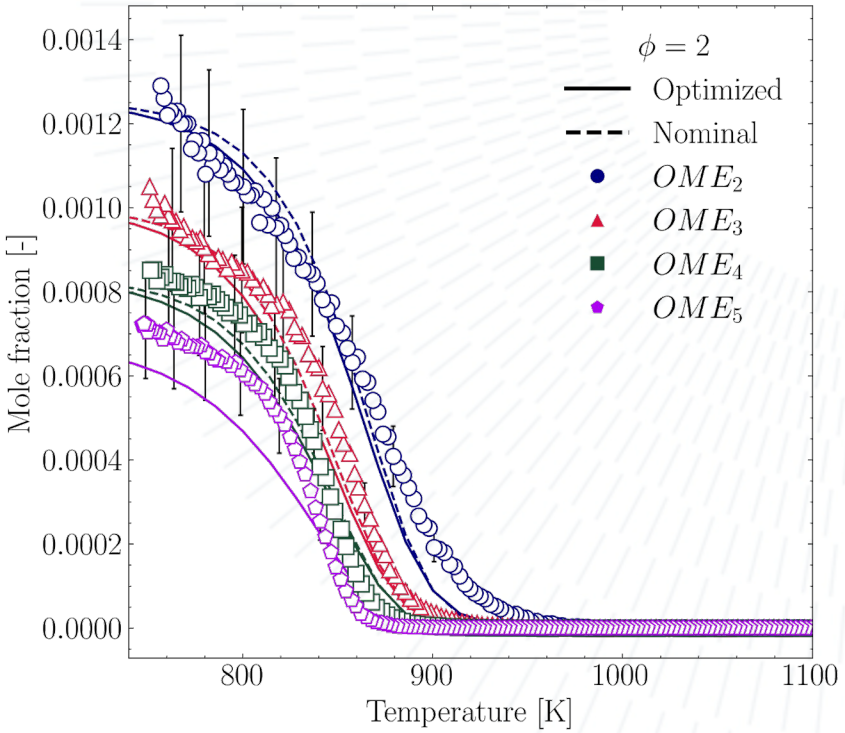
Pyrolysis



Scaled OME reactivity caught reasonably well

Zhong et al. *J Anal Appl Pyr*, *159*, 2021

Oxidation

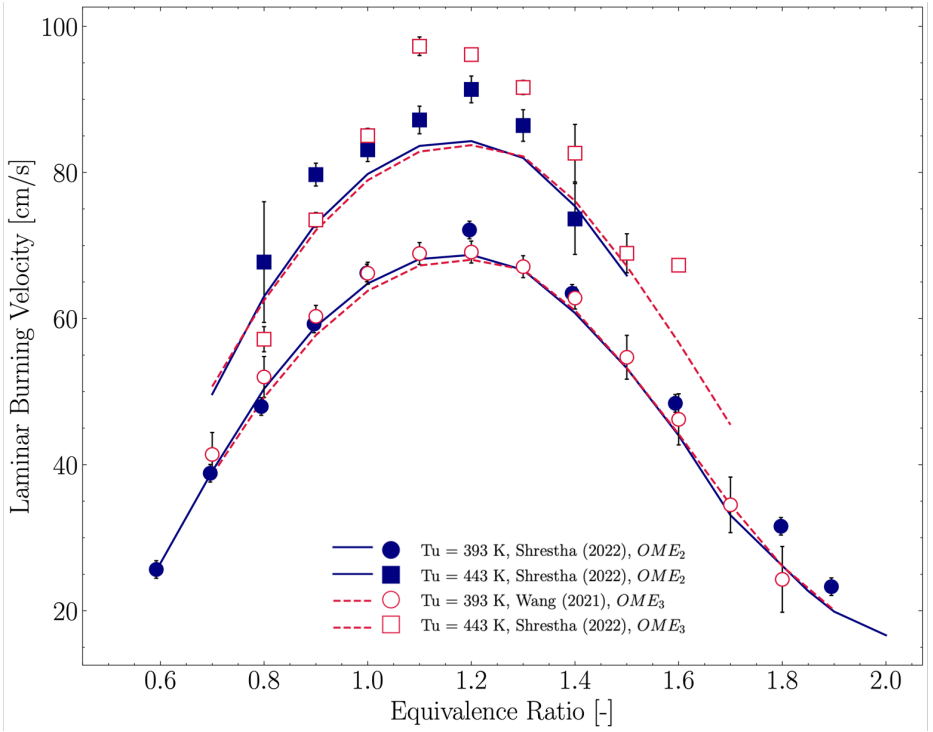


OME_5 well caught (although not used as optimization target)

Gaiser et al. *Fuel*, *313*, 2022

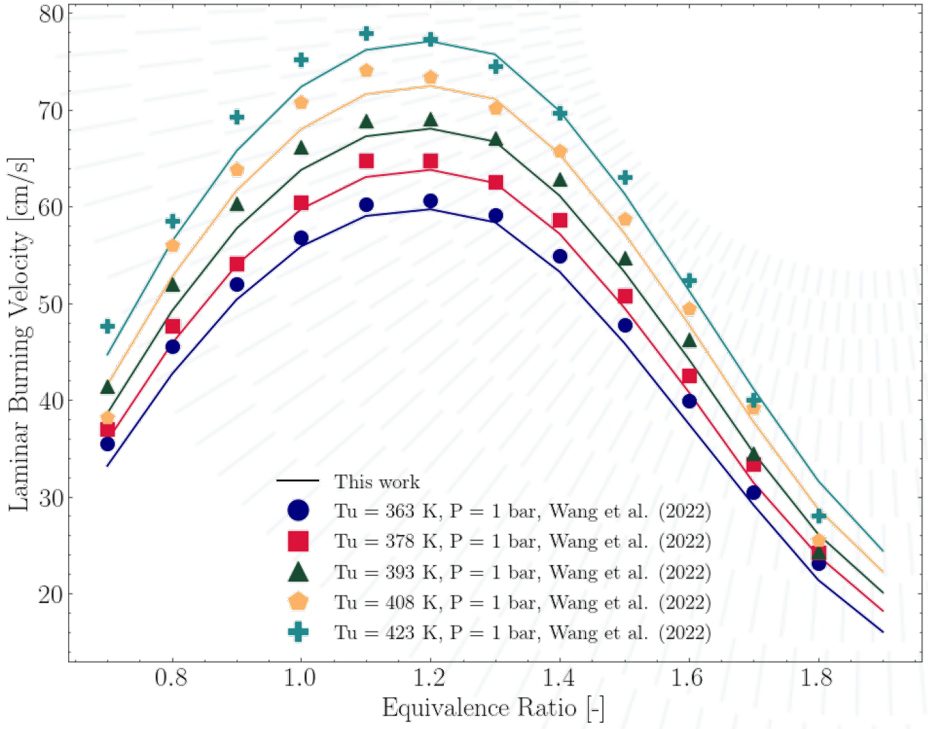
Model validation: laminar flame speed

OME_2 vs OME_3



Laminar flame speed is independent of OME chain length (C_0-C_3 controlling)

Temperature scaling (OME_3)



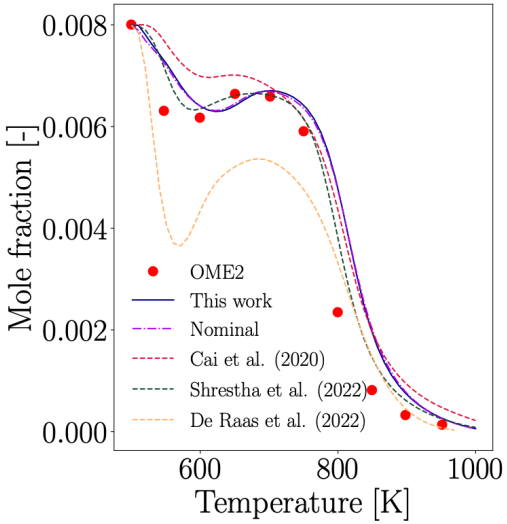
Reasonable prediction of LFS scaling with the temperature

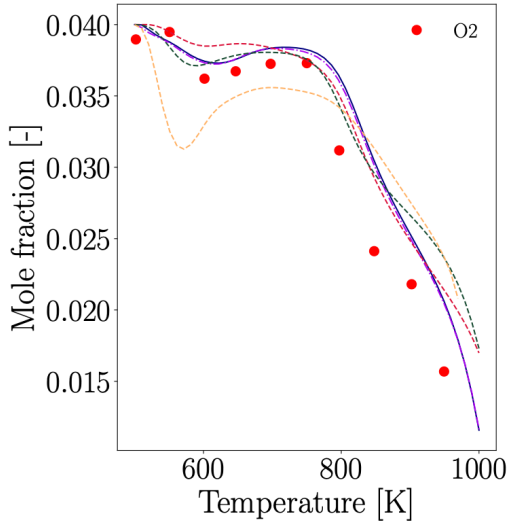
Shrestha et al. *Combust Flame* 246 (2022)

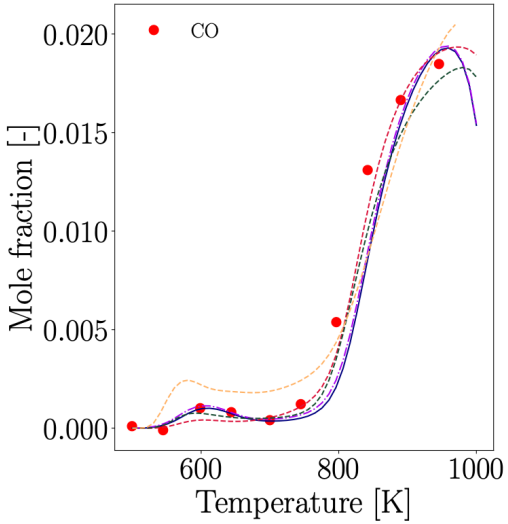
Wang et al. *Fuel, 297, 120754* (2022)

Mechanism validation

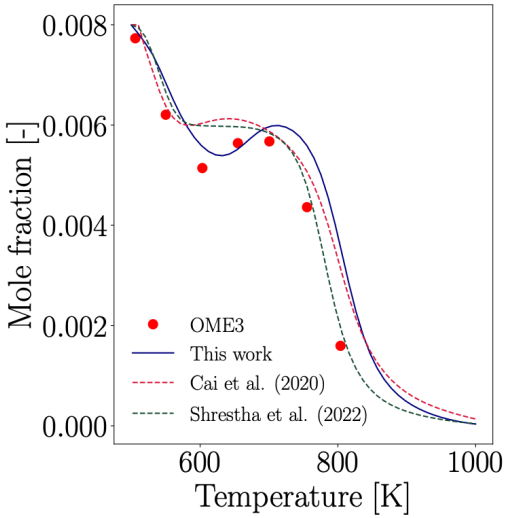
OME_2

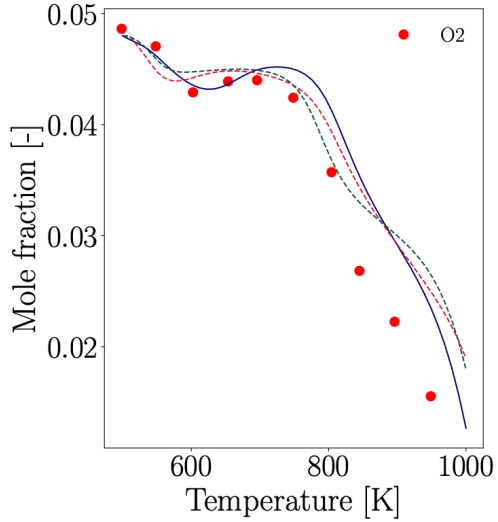


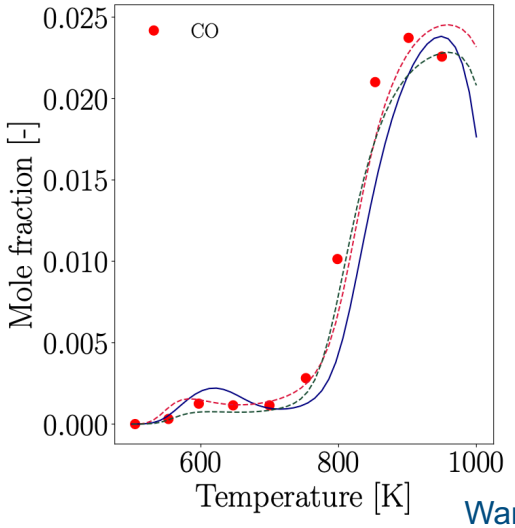




OME_3

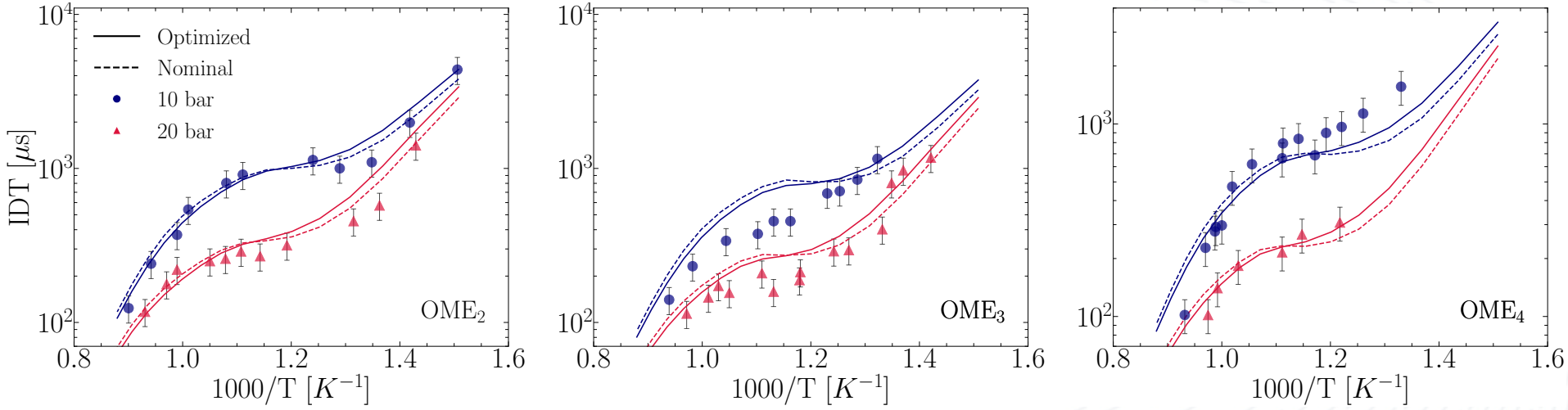


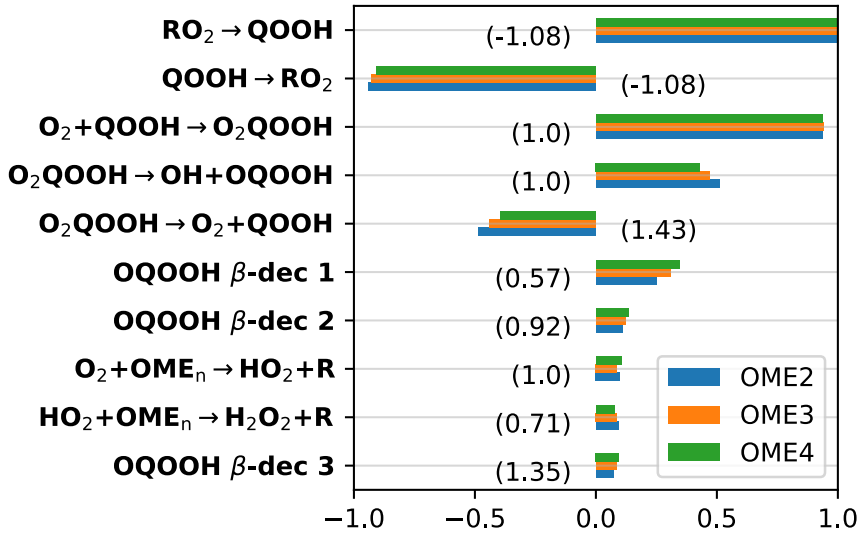




Wang et al. *Combust Flame* 245 (2022)

Ignition delay times and kinetic analysis





→ Consistent **scaling** of OME_{2-4} ignition delay times

→ β-decompositions are **slowed down** to decrease low T reactivity

→ Reverse QOOH oxidation to O2QOOH was increased to decrease low T reactivity

→ The **constraints on the scaling factors** prevent further improvements on the final mechanism (the 'short-blanket problem')

Take-home messages

→ Combustion is **hierarchical**, regardless of the kind of fuel

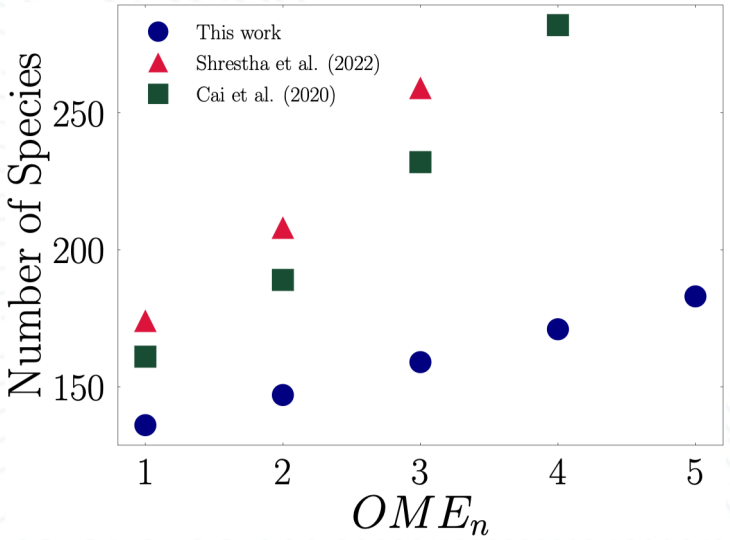
→ Modeling the next-generation, CO_2-neutral fuels can rely on the same kinetic modeling tools and methodologies once developed for fossil fuels

→ For longer-chain fuels (OMEs), the same size issues once met for fossil fuels must be faced: mechanism size and complexity

→ The combination of i) **chemical lumping** and ii) **mechanism optimization** can deliver **compact mechanisms**, with a linear increase in the number of species

→ Reaction classes and rate rules are able to enforce physics in kinetic mechanisms, easing their development

Cai et al. *Fuel 264* (2020)
Shrestha et al. *Combust Flame* 246 (2022)



Is it enough to actually use these mechanisms?

Not always! We might need to couple the workflow to **reduction techniques** to provide ***ad hoc***, **compact** kinetic mechanisms

Stay Tuned

Conclusions

→ The energy transition introduces **novel challenges** in modeling combustion kinetics

- ✓ **New fuels**: NH_3, OME…
- ✓ **Heteroatoms chemistry** (N, O, S…)
- ✓ **New formation pathways** of old pollutants (soot, NO_x)

→ Compared to the times of fossil fuels chemistry (90s-2000s):

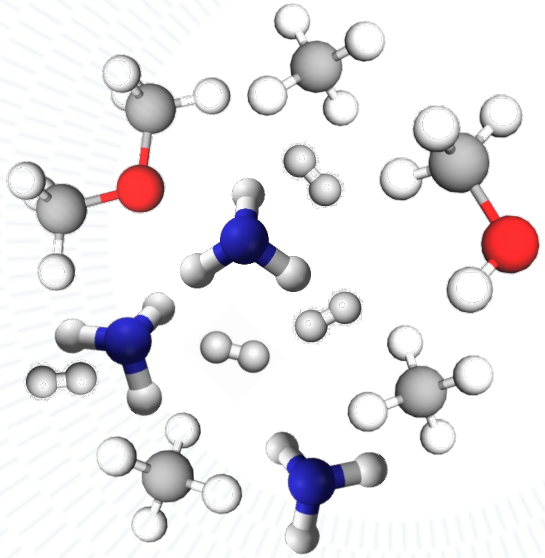
- ✓ **Huge amount** of experimental data
- ✓ Kinetic modeling and analysis capabilities are **much stronger**

→ We can leverage the **same tools** once developed for fossil fuels. Combustion principles are unchanged, too. Thus:

- ✓ **Hierarchical** and **modular** formulation
- ✓ **Reaction classes** and **rate rules**
- ✓ **Reduction techniques**: lumping and skeletal reduction

→ The **validation bottleneck** must be cut, though

- ✓ We must develop and improve **automated methodologies** for model validation and analysis



Acknowledgements

Timoteo Dinelli

Edoardo Ramalli

Tiziano Faravelli

Laura Sangalli

Piercesare Secchi

Funded by the European Union

Thank you for your attention