

Curve Matching for mechanism validation and optimization

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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.



2006



2011

PhD
Chem. Eng.



2016



Assistant Professor



2024

Associate Professor



The CRECK modeling lab

Permanent Staff



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Alessio Frassoldati



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Marco Mehl



Alessandro Stagni



Matteo Pelucchi



Luna Pratali Maffei

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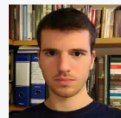
Francesco Serse



Andrea Locaspi



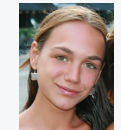
Edoardo Ramalli



Andrea Nobili



Edoardo Cipriano



Clarissa Giudici



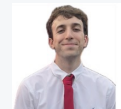
Alessandro Pegurri



Romina Papagni



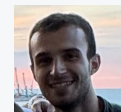
Timoteo Dinelli



Riccardo Caraccio



Francesco Roman Artioli



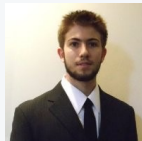
Niccolò Fanari



Administrative Staff
External Collaborators



Carlo Cavallotti



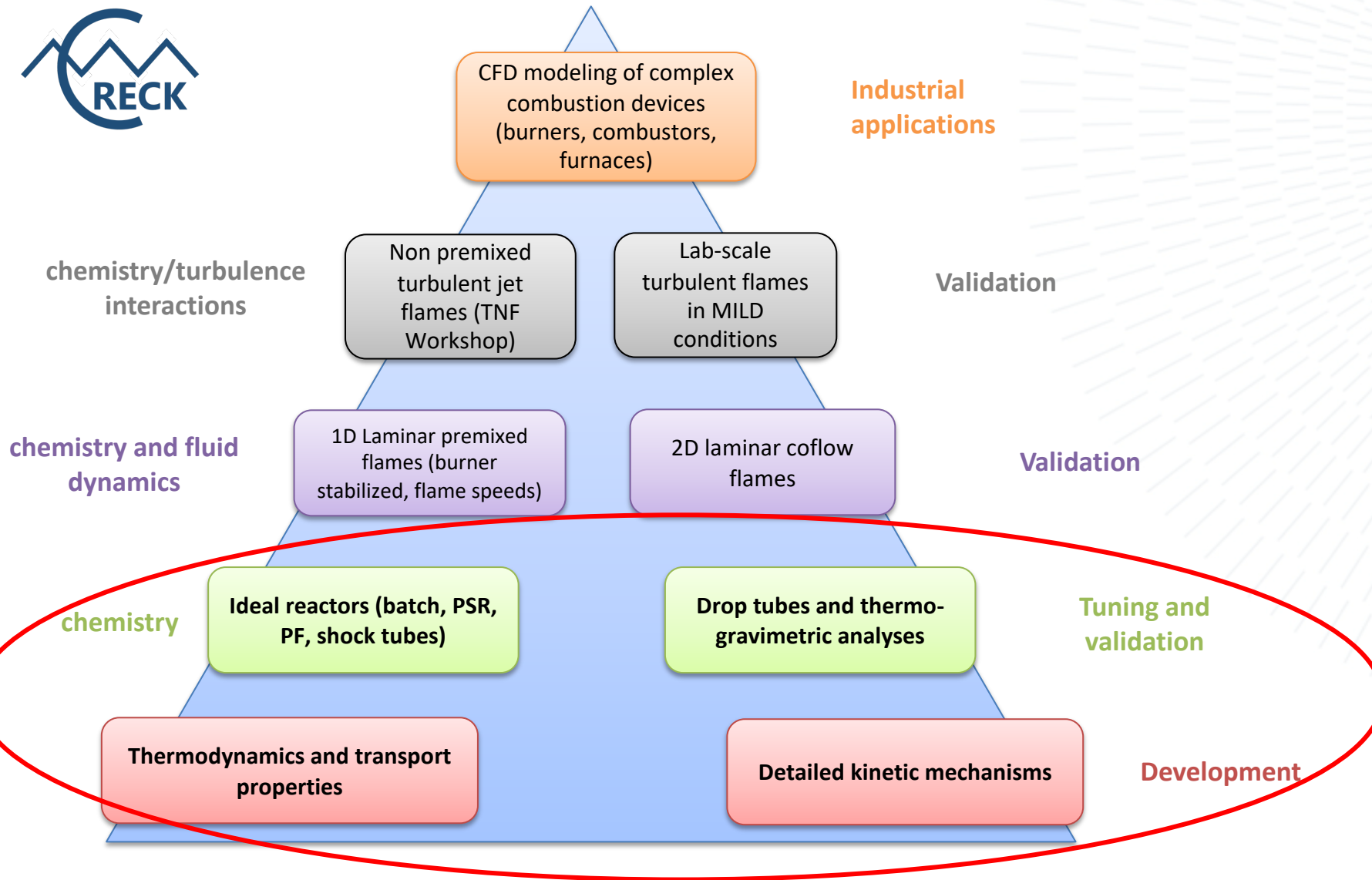
Paulo De Biagi



Isabella Branca

**Tomorrow afternoon
(16:20-17:20)**

CRECK modeling expertise



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

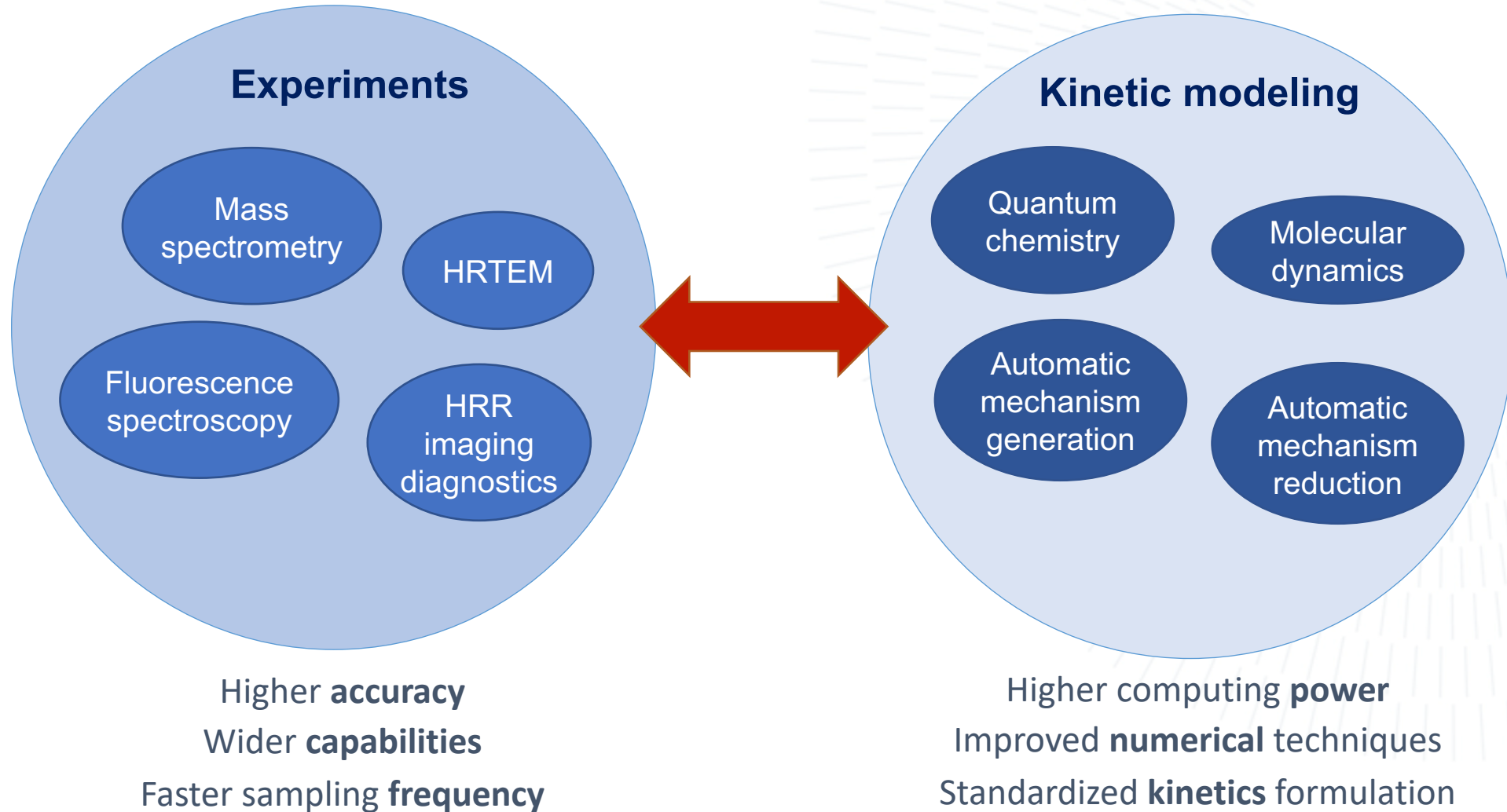


Introduction: Mechanism validation



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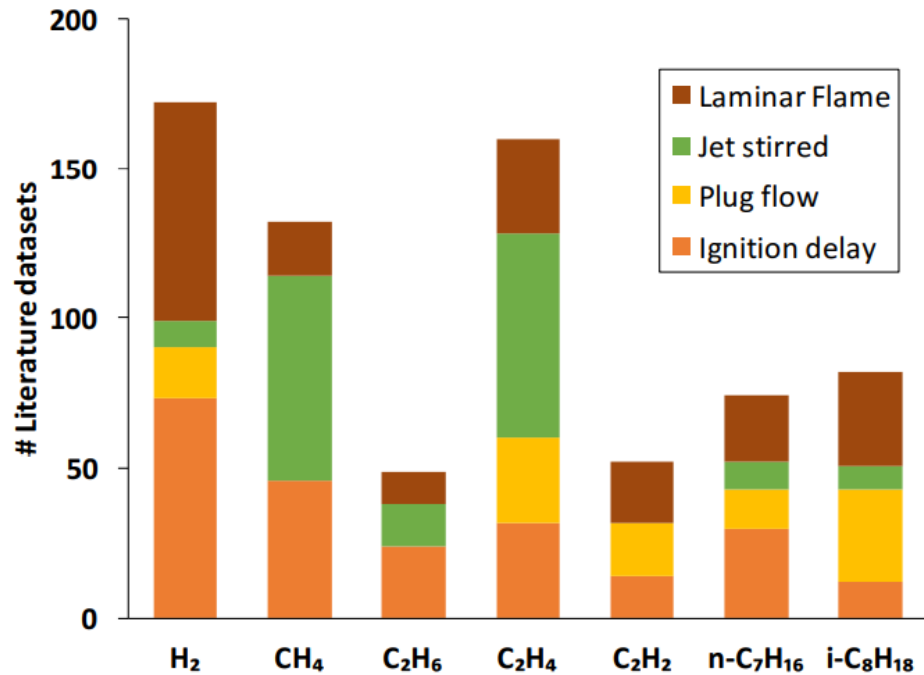
Exploring combustion kinetics



A synergistic coupling?

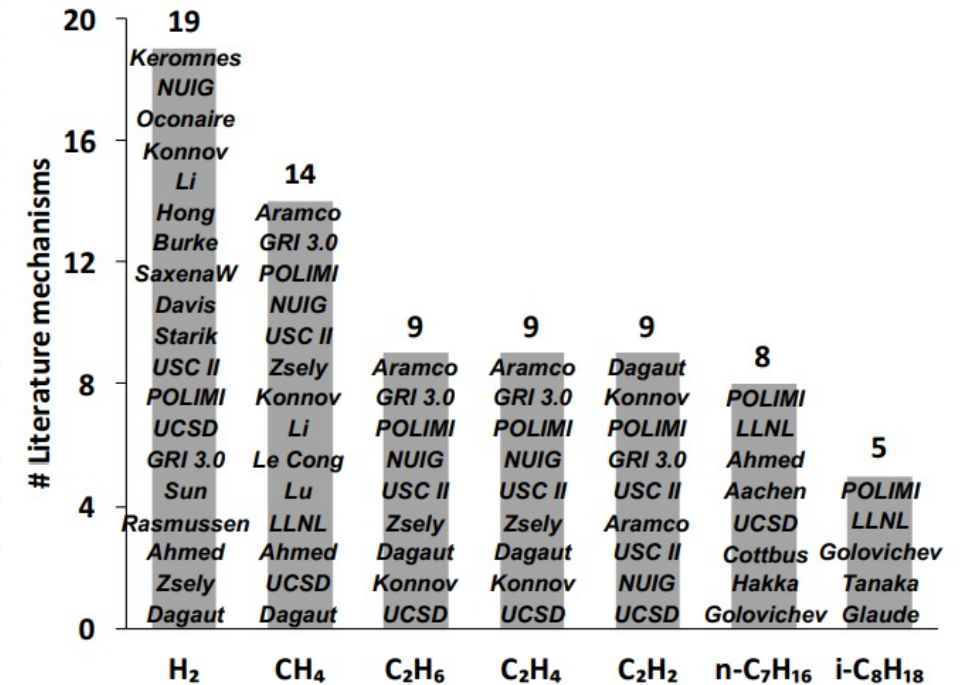
Many data, many models

(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)

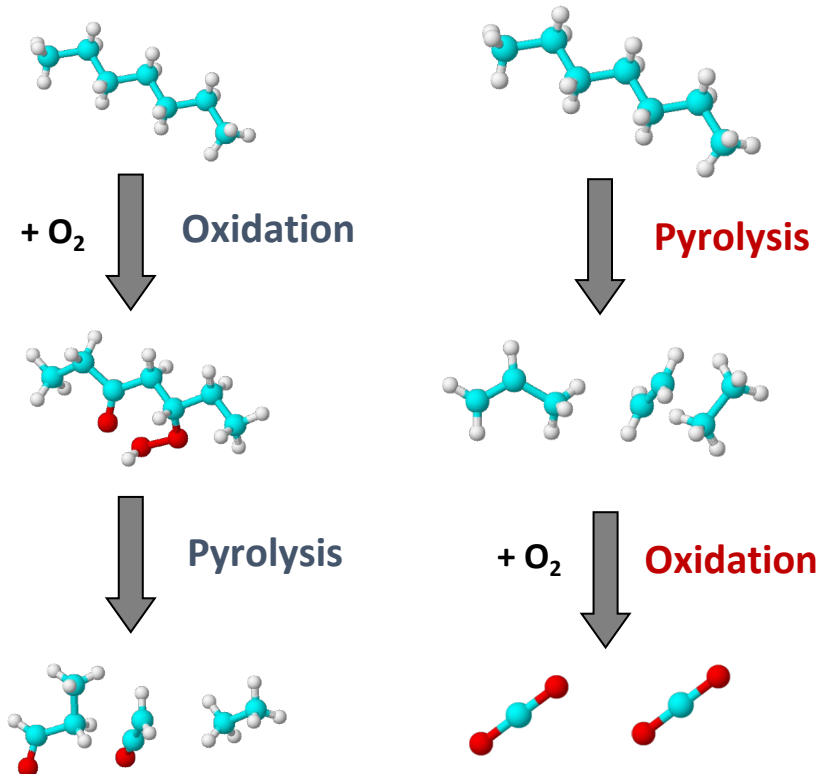
Metcalfe et al. Int J Chem Kin, 45 (2013)
Olm et al. Comb Flame, 161 (2014)
Stagni, Politecnico di Milano (2016)

Combustion is hierarchical

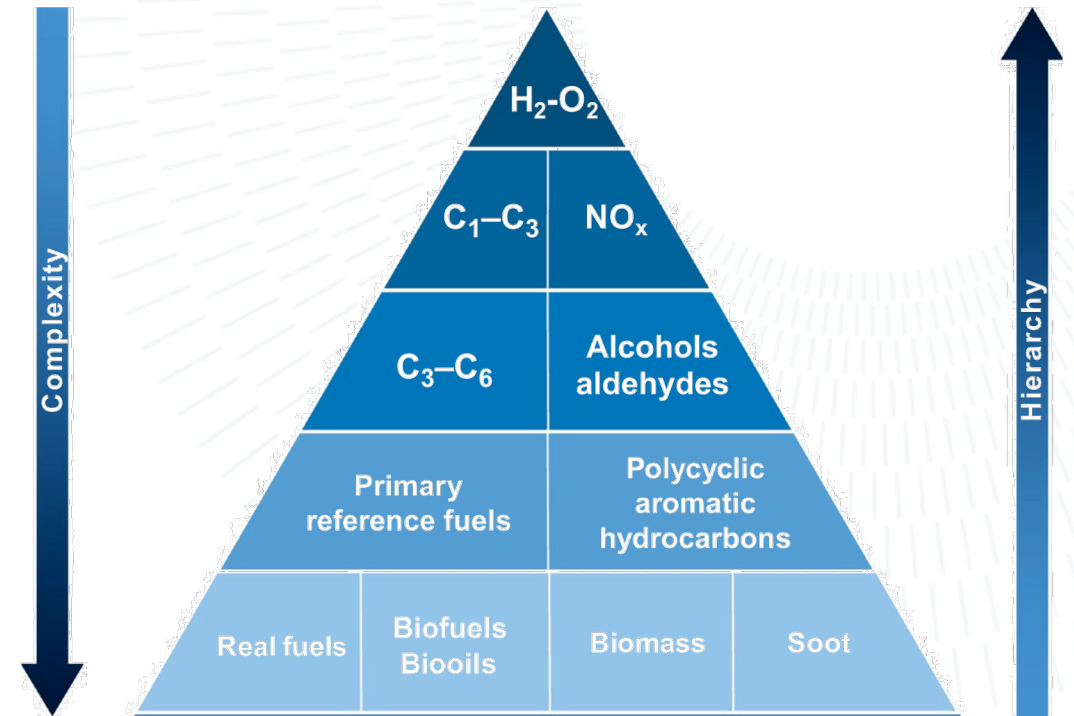
Fuel undergoes a sequential **breakup**

Low temperature

High temperature



Lower-hierarchy levels depend on higher hierarchy ones



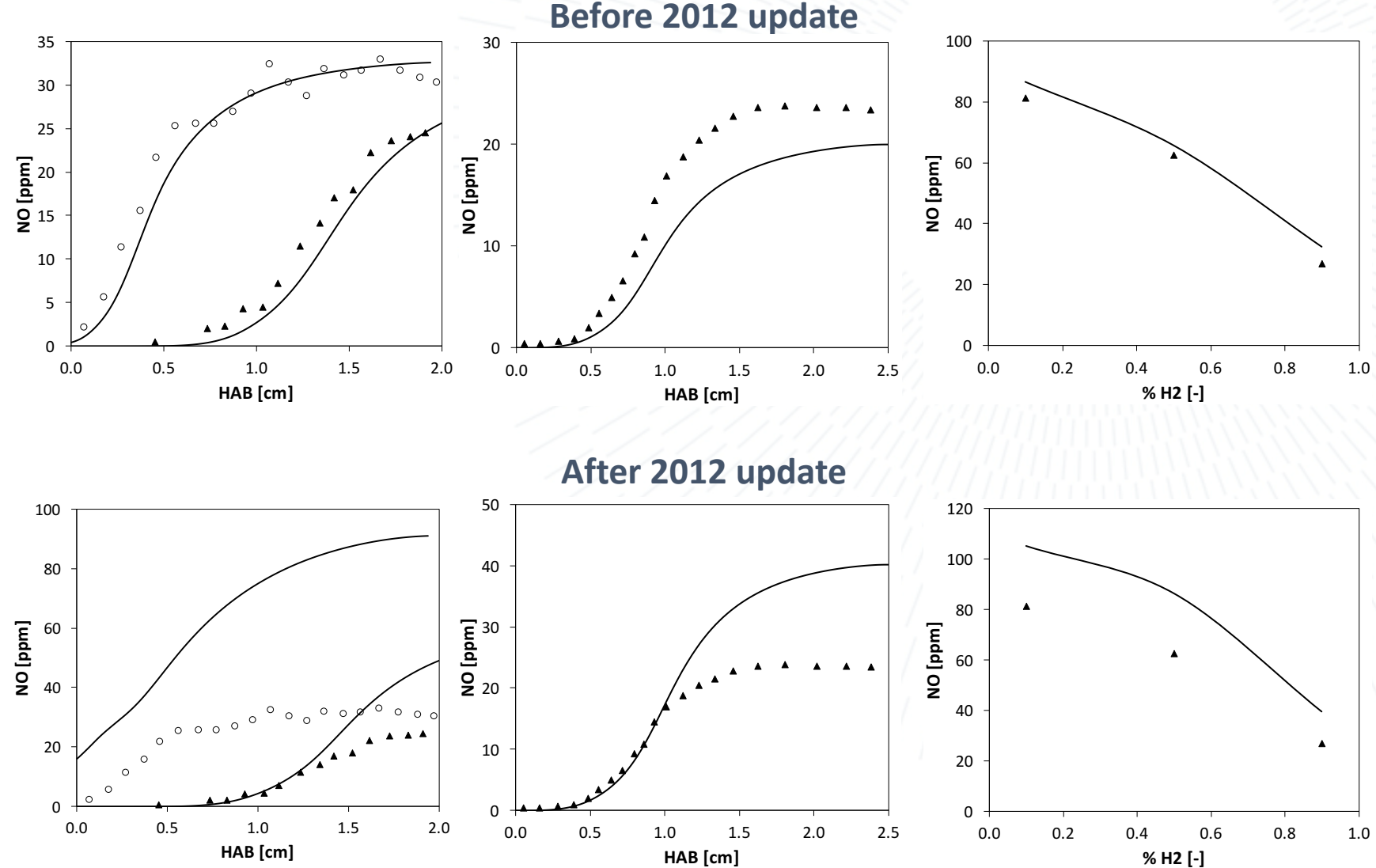
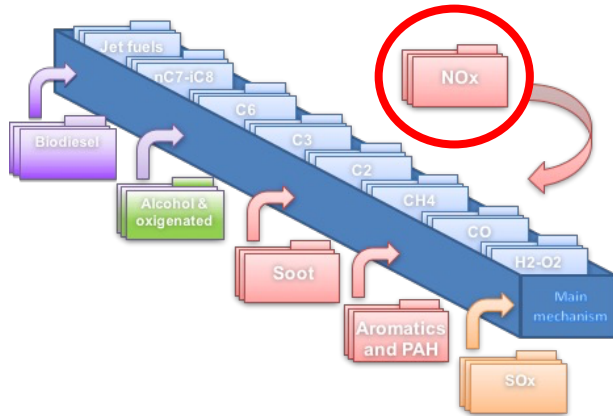
Mechanism validation is a **continuous process**

Example: the NO_x case

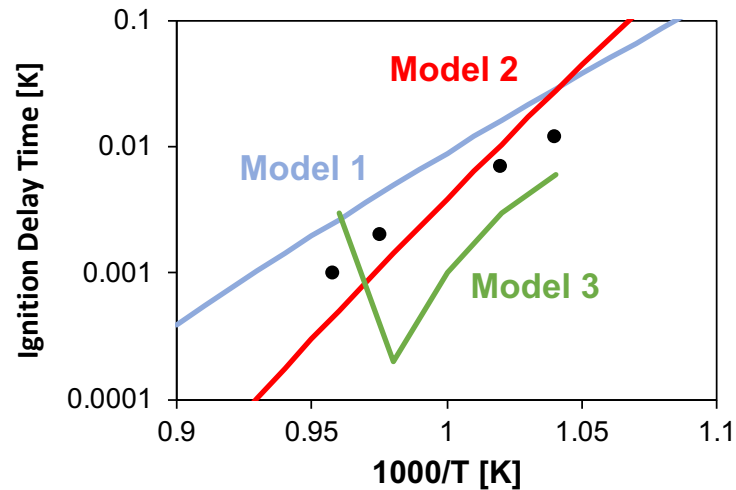
- **Hierarchical** dependencies strongly affect a kinetic mechanism
- E.g. **NO_x formation** depends on the core C₀-C₃ submechanism

What can happen?

- January 2012:
critical update to C₀-C₃

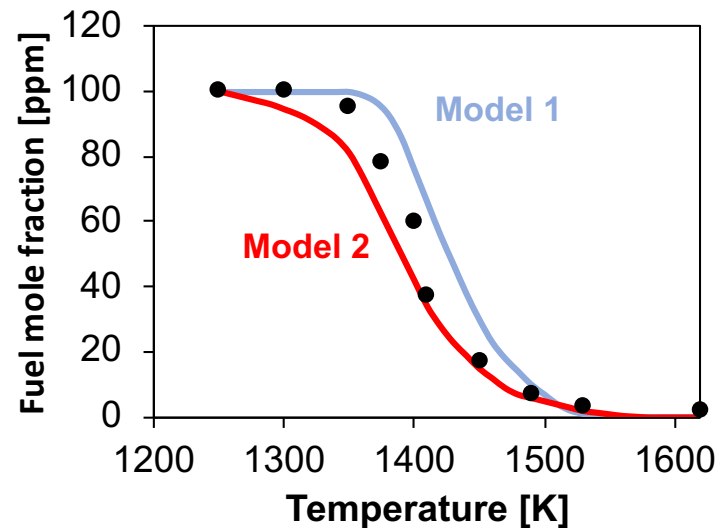


«Best» model?



Common practice:
Sum of Squares Error (SSE)

Model	SSE
1	213
2	203
3	168



Model	SSE
1	8400
2	7400

**A single indicator does not
always represent models'
predictive features**

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



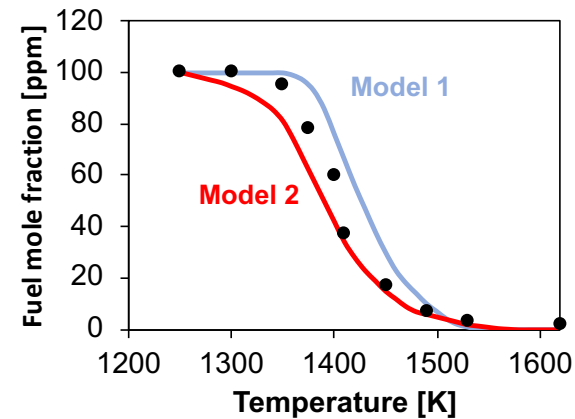
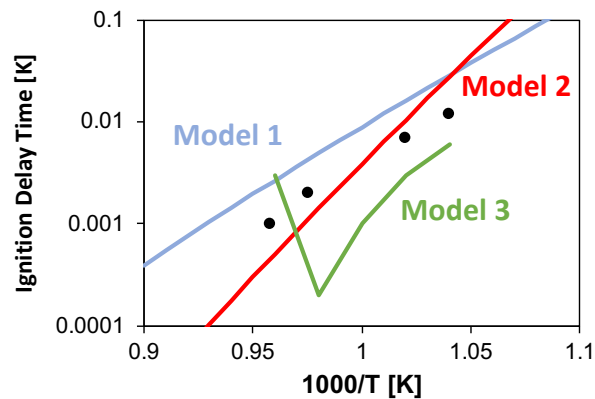
Curve Matching

Automating the validation of kinetic mechanisms

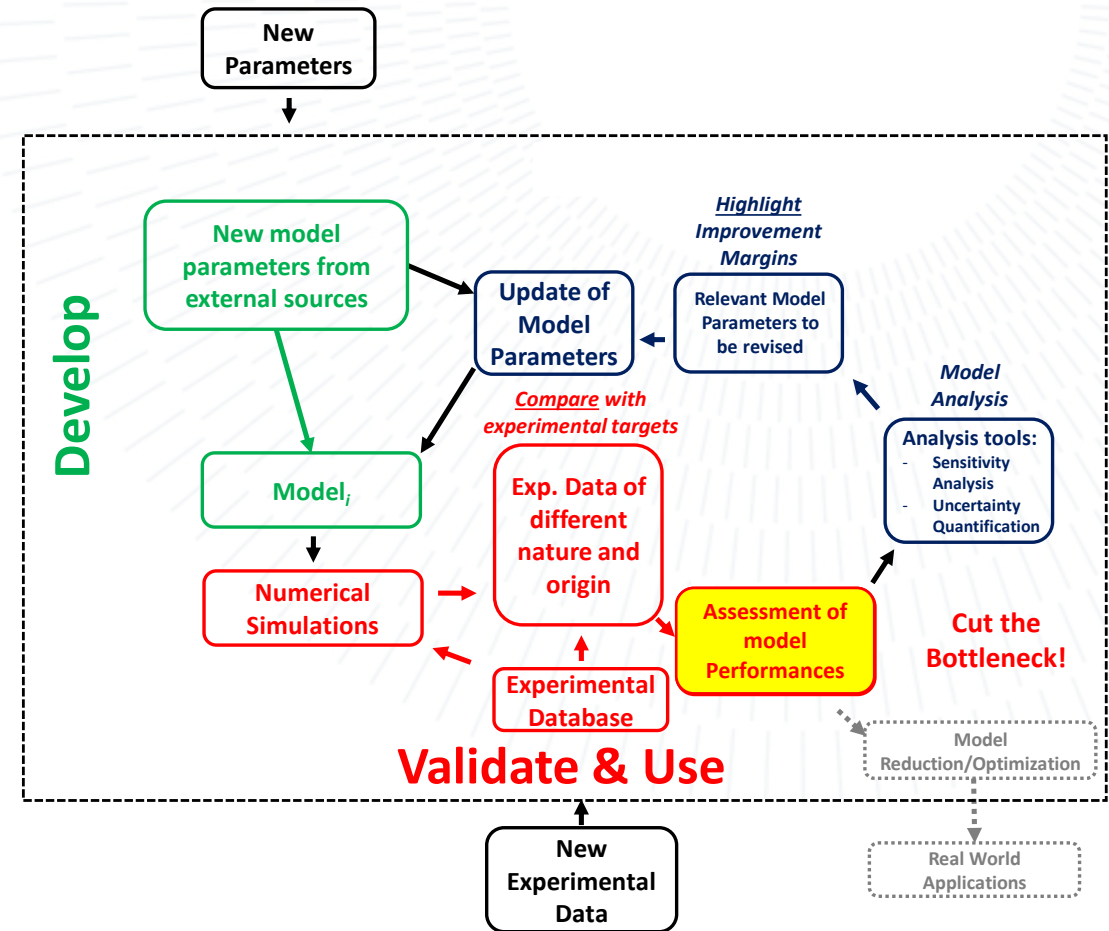
4 questions to be addressed:

- 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



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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

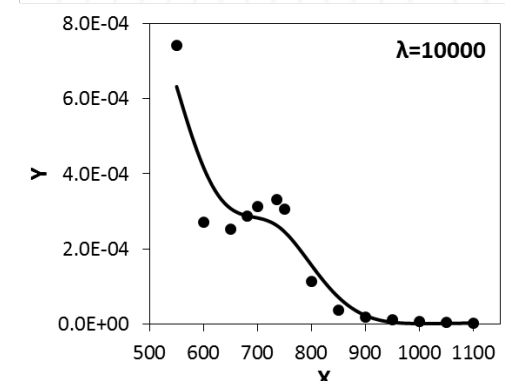
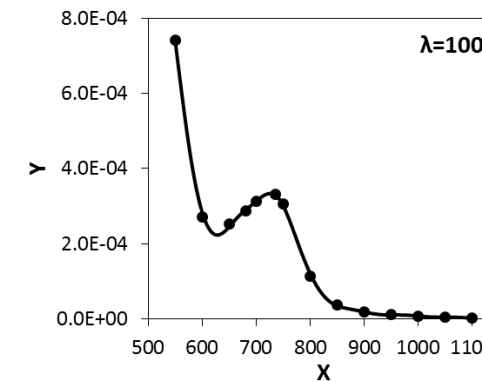
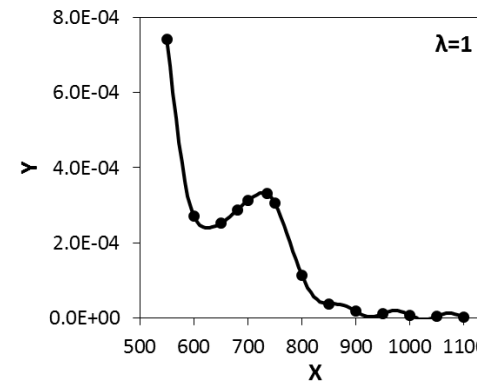
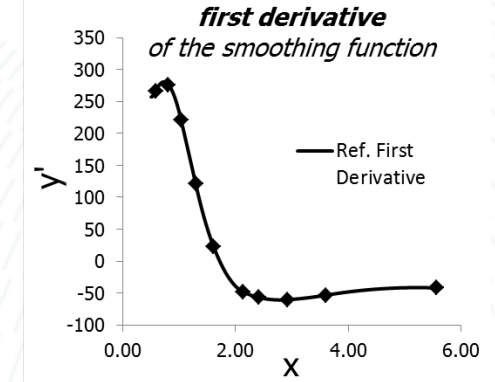
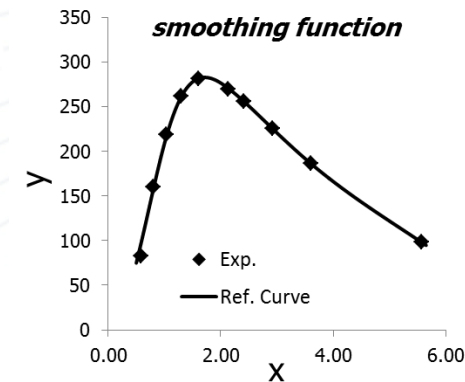
Spline smoothing

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

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

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

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



Optimal penalty factor (λ)

Classical approach

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

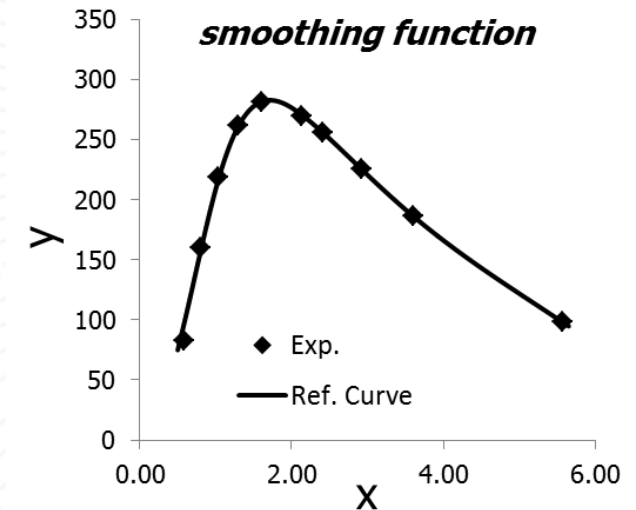


$\lambda \rightarrow -\infty$ (*under-fitting*)

$\lambda \rightarrow +\infty$ (*over-fitting*)

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

Roughness is penalized directly on the main function

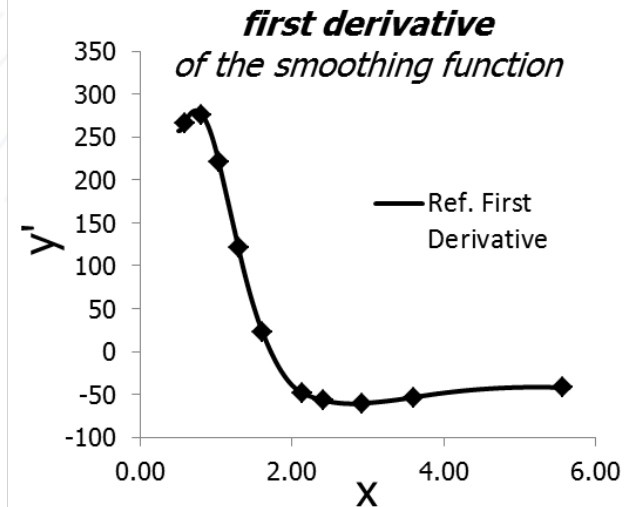


Modified approach

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

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

Roughness is penalized directly on the derivative of the main function



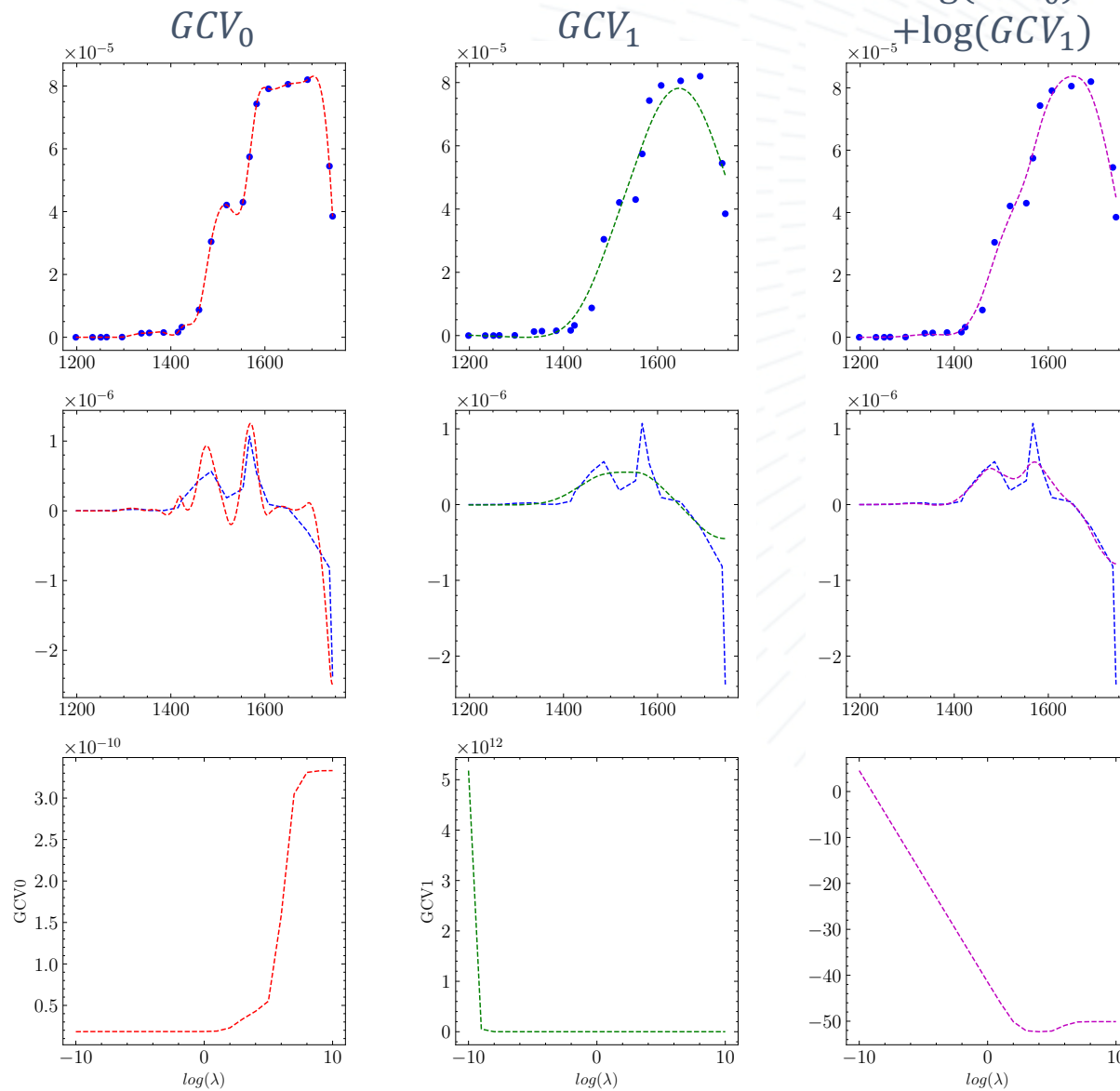
Trade-off

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

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

GCV (λ)

Data VS Curve



(First derivative)
Data VS Curve

Loss, Cost,
Objective

Distance and similarity indices

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

If $f \rightarrow g$ 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**

$$CM_{score} = \frac{d_{L_2}^0 + d_{L_2}^1 + d_p^0 + d_p^1}{4}$$

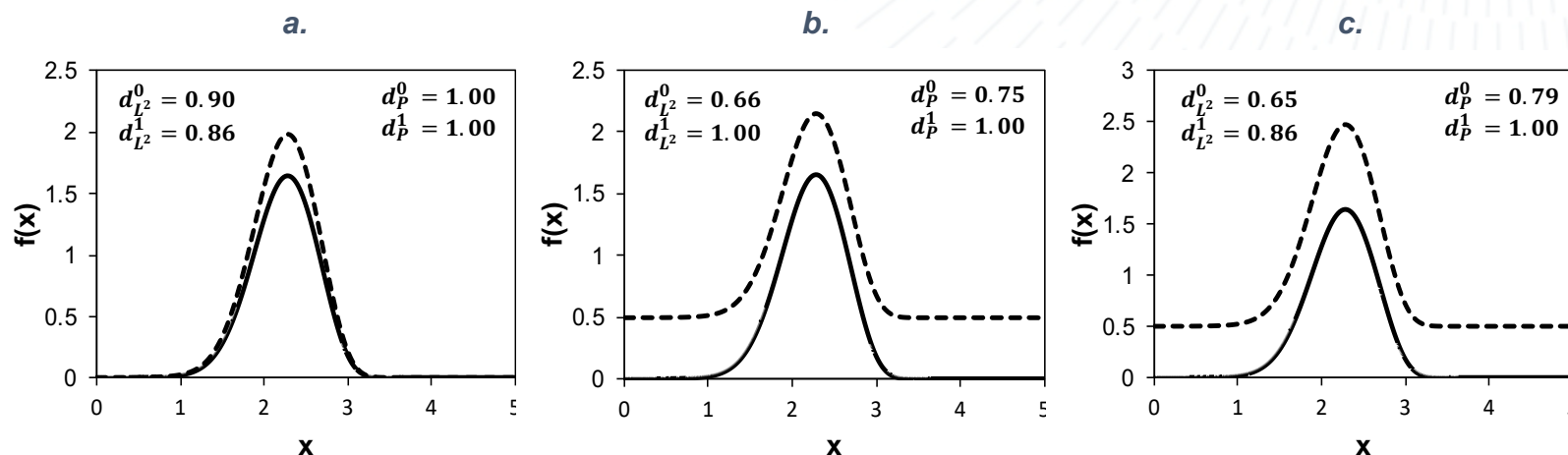
Different indices see different things

Example

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

with

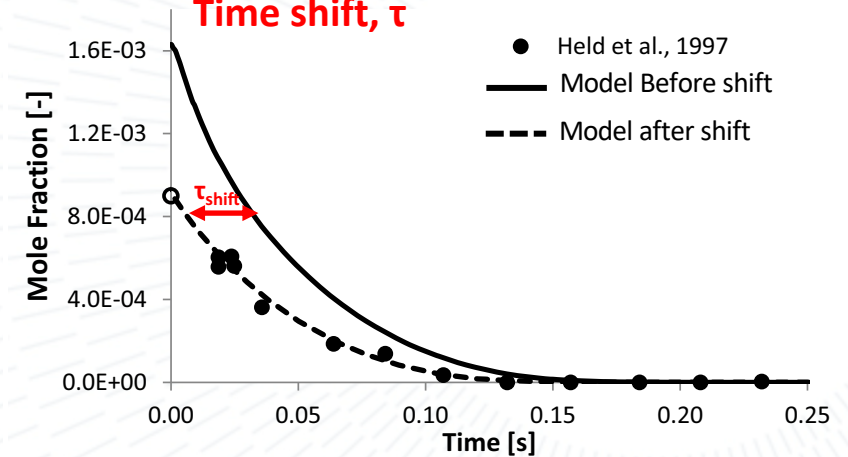
$$a = 1.2 \quad b = 0.5$$



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

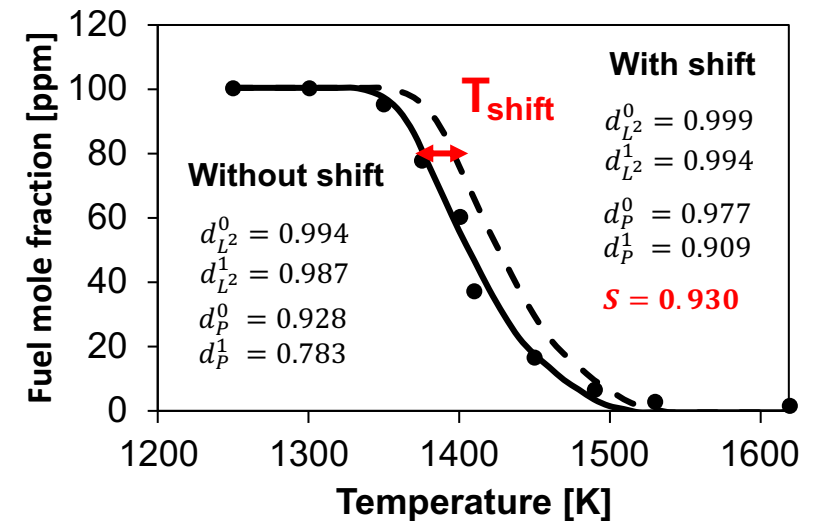
$$S = \max\left(1 - \frac{|\delta|}{D}, 0\right) \in (0,1) \quad 1 = \text{already aligned}$$

$$\delta = \operatorname{argmax}_{\delta}(d_{L_2}^0 + d_{L_2}^1 + d_P^0 + d_P^1) \quad \delta: \text{domain shift optimizing the alignment}$$

Model performance

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

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

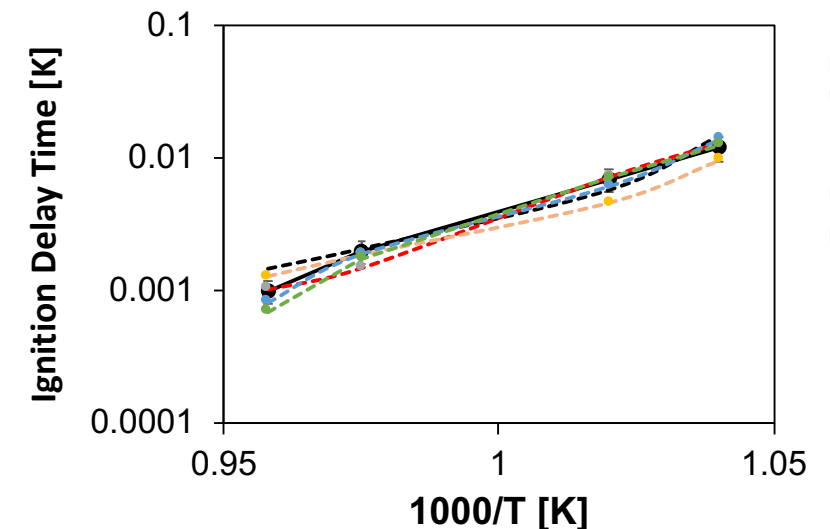
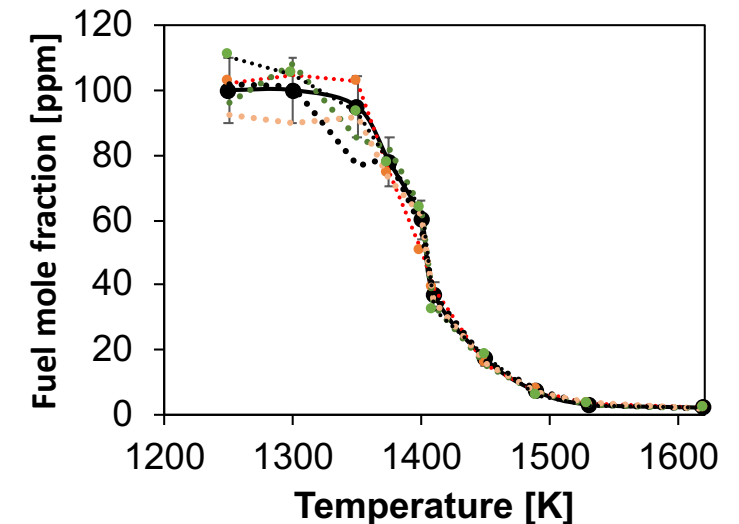
- Data point as the mean value
- Uncertainty as the standard deviation

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

Performance index

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

Confidence interval

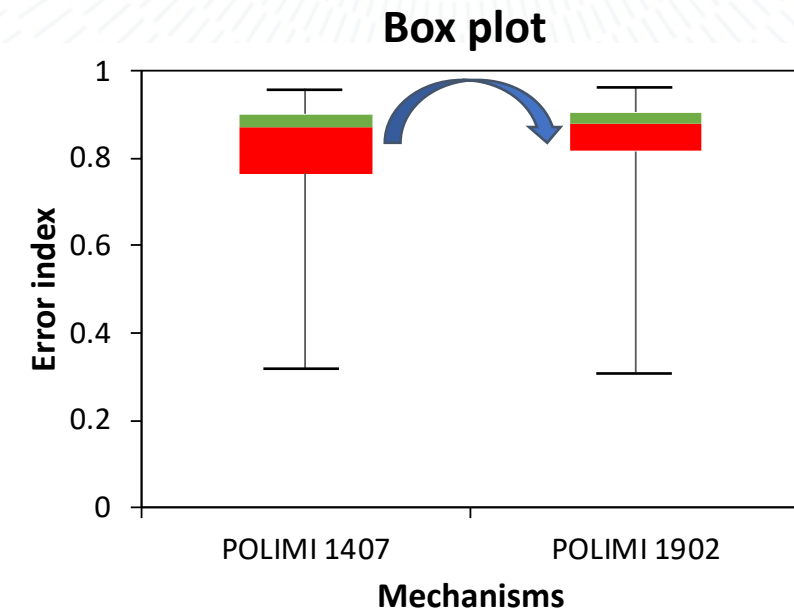
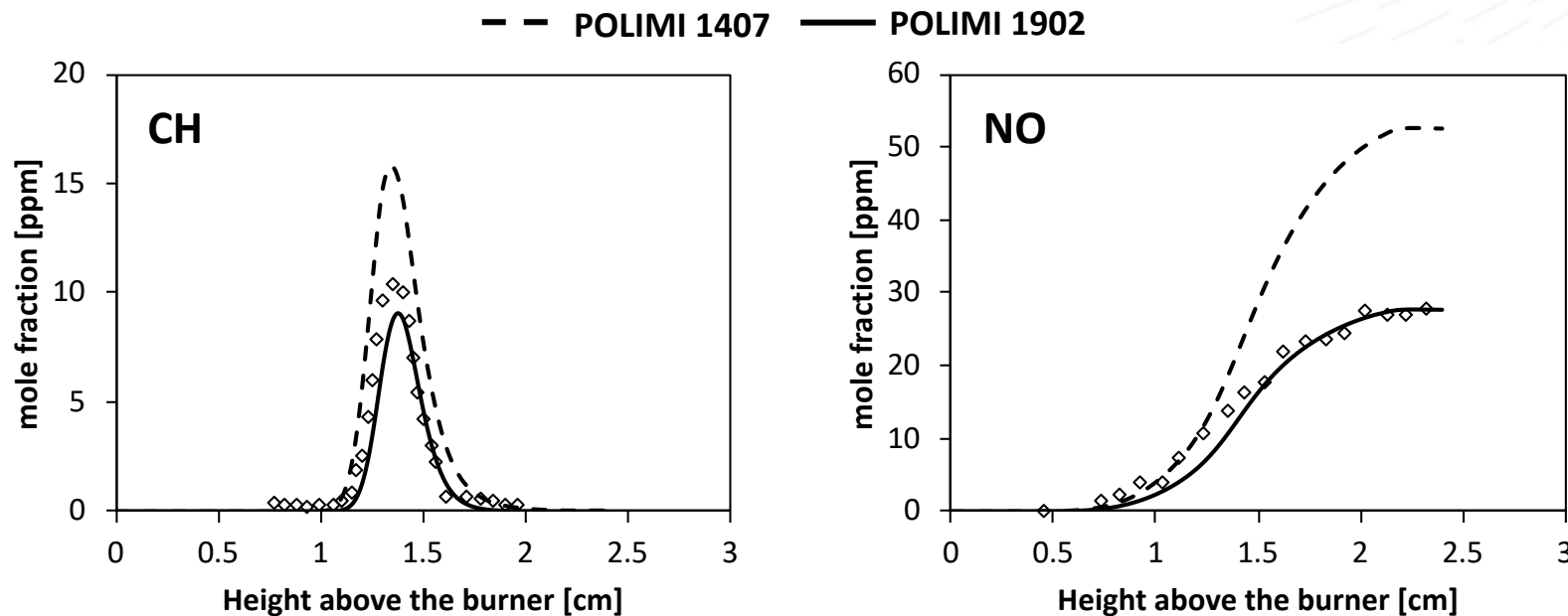


Hjorth, J. U. *Computer intensive statistical methods: Validation, model selection, and bootstrap*. Routledge (2017).

What happened to the ‘bugged’ NO_x mechanism?

	Model	$d_{L_2}^0$	$d_{L_2}^1$	d_P^0	d_P^1	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

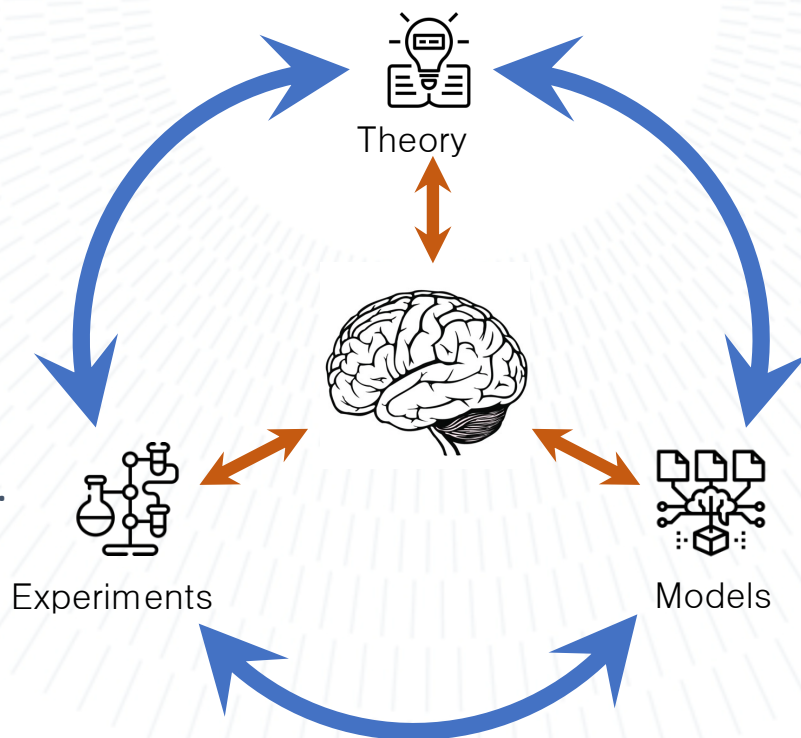
- Improved predictions in prompt & reburning **submechanisms**
- Box plot shows the overall improvements, as well as the **outliers** to be further **investigated**



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



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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**

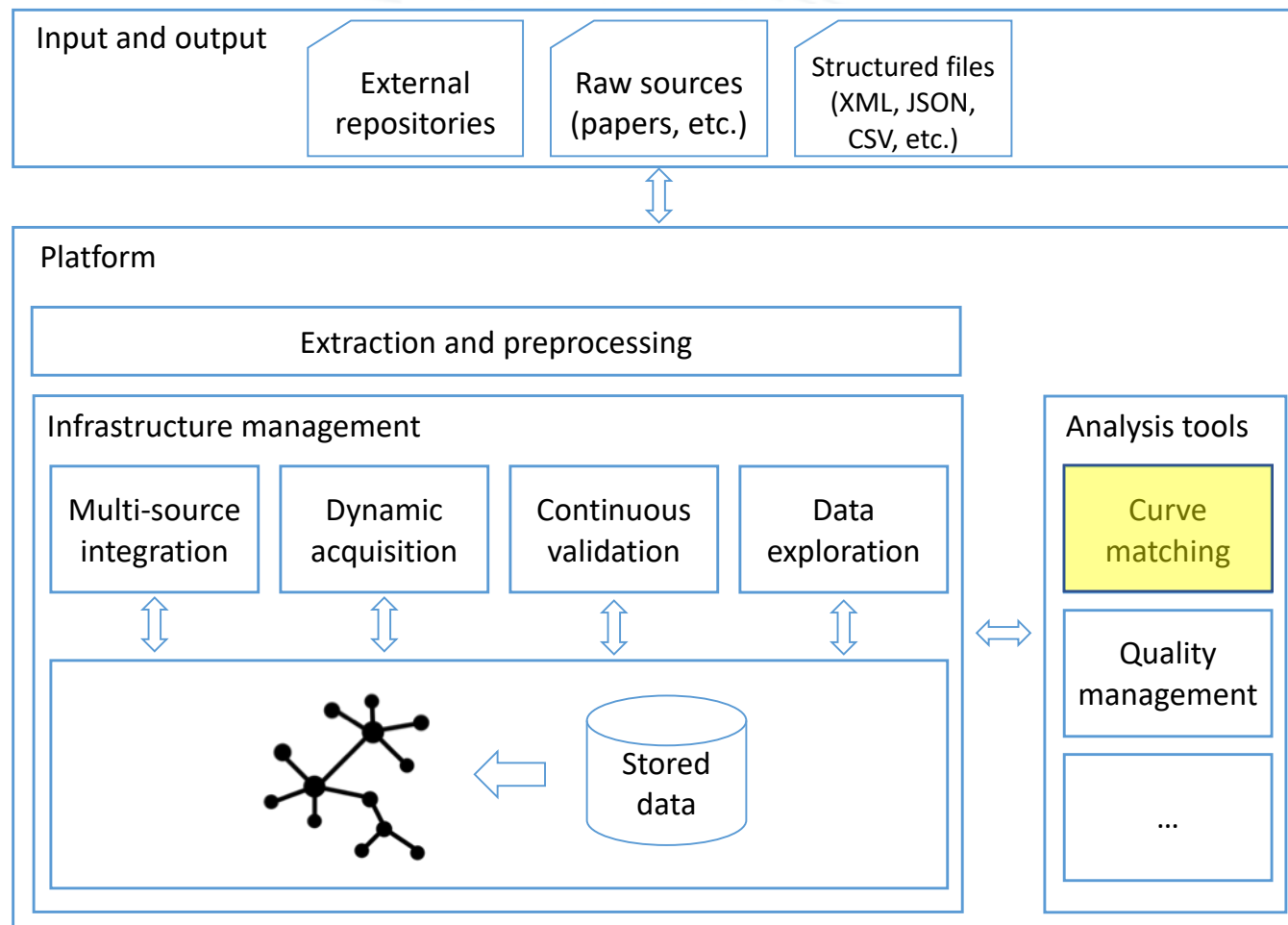
Creation of a **common** database, interfaced with

- **Simulations** platform (e.g. OpenSMOKE++)
- **Validation** platform (Curve Matching)



SCIEXPEN

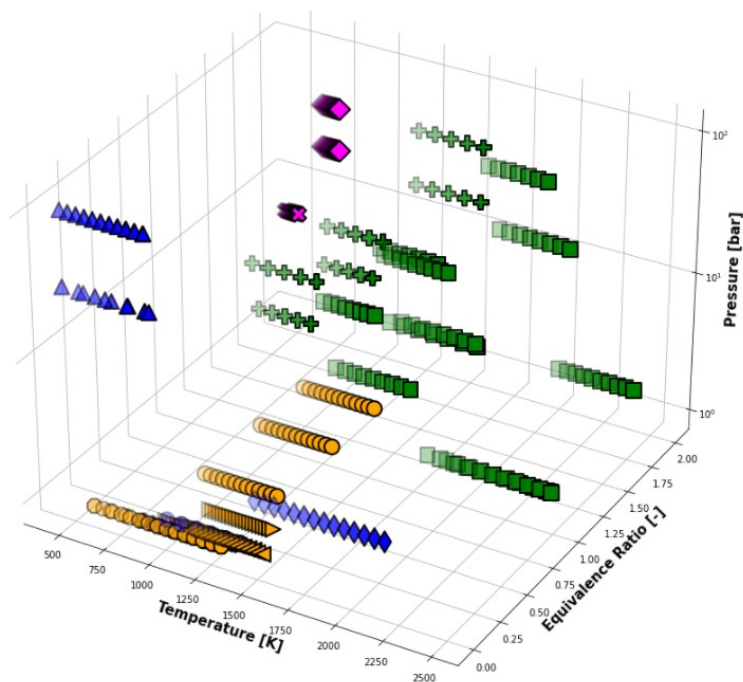
<https://sciexpem.polimi.it/>



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

Experimental datasets

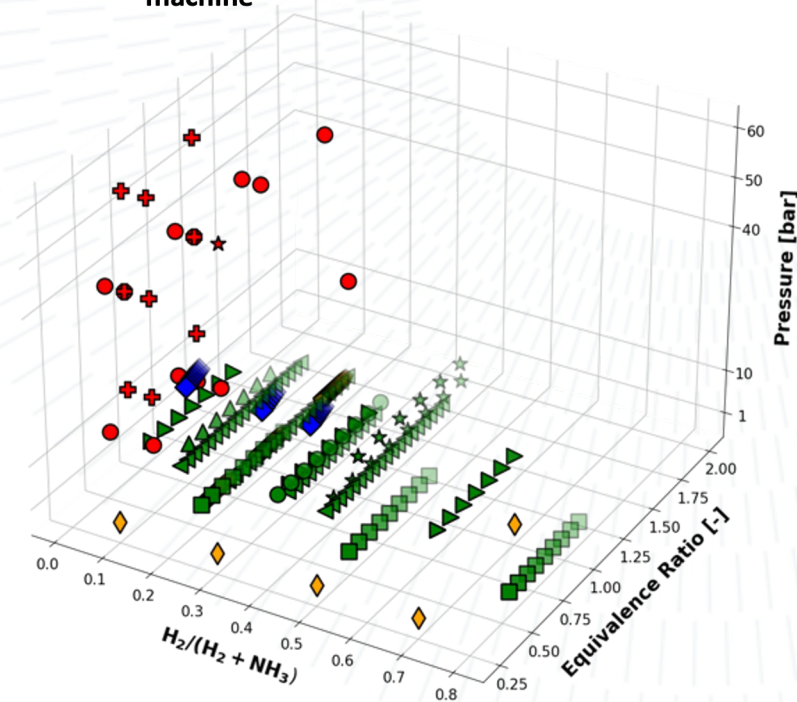
- Flow reactor
- Shock tube
- Jet stirred reactor
- Rapid compression machine



NH_3

- Song(2016)
- Hulgaard (1993)
- Wargadalam(2000)
- Stagni-PFR(2020)
- Mathieu(2015)
- Shu(2019)
- Dagaut(2005)
- Rota(2001)
- Stagni-JSR(2020)
- Manna(2020)
- Pochet(2019)
- He(2019)

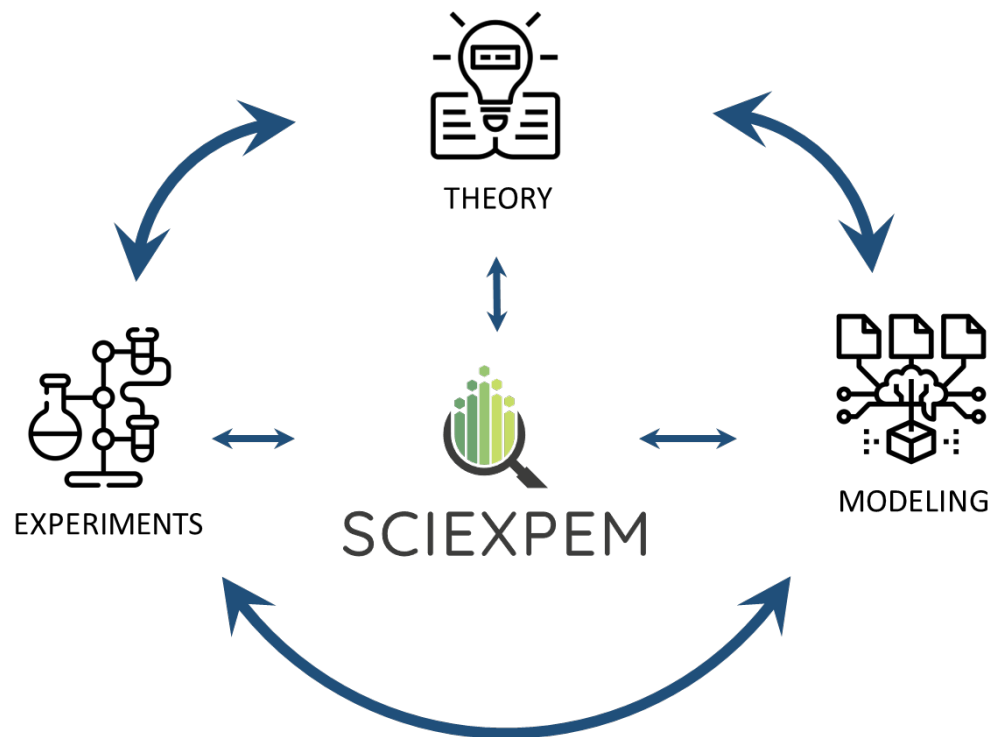
- Shock tube
- Rapid compression machine
- Laminar flame
- Jet-stirred reactor



NH_3/H_2

- Shrestha(2021)
- Osipova(2021)
- Gotama(2022)
- Kumar(2013)
- Han(2019)
- Lhuillier(2020)
- Osipova(2022)
- Zhang(2021)
- Chen(2021)
- Pochet(2019)
- He(2019)
- Dai(2020)

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

Scientific Experiments and Models

0

Kinetic Models

0

Species

0

Fuels

Data points

Sciexpem: the 'experiment'

<https://sciexpem.polimi.it/>

The screenshot shows a Google search for 'sciexpem'. The search bar at the top contains the text 'sciexpem'. Below the search bar, the results are displayed. The first result is for 'https://sciexpem.polimi.it' with the title 'SciExpem' and a description: 'Scientific Experiments and Models. 18. Kinetic Models. 236. Species. 0. Fuels. 164. Data points. 7. Experiments. 6. Simulations.' The second result is for 'https://sciexpem.polimi.it > project' with the title 'Project – SciExpem' and a description: 'A data-driven predictive model for combustion kinetics can study the behavior of ...'. The third result is for 'https://github.com > sciexpem > s...' with the title 'sciexpem - GitHub' and a description: 'sciexpem. This prototype has been developed within the work for the paper "Towards a scientific data framework to support scientific model development".' The fourth result is for 'https://github.com > edoardoramalli' with the title 'edoardoramalli/SciExpem_API: Python API Wrapper ... - GitHub' and a description: 'Python API Wrapper for SciExpem. Contribute to edoardoramalli/SciExpem_API development by creating an account on GitHub.' The fifth result is for 'https://pypi.org > project > SciEx...' with the title 'SciExpem-API - PyPI' and a description: 'Python wrapper for SciExpem EndPoints. ... SciExpem-API 2.0.3.4. pip install SciExpem-API'.

sciexpem - Cerca con Google

google.com/search?q=sciexpem&rlz=1C1KNTJ_itIT982IT982&oq=sciexpem&aqs=chrome..69i57j0i546l3.1922j0j15&sourceid=chrome&ie=UTF-8

Posta - Andrea Nob... Corso: 089257 - ME...

Google

sciexpem

Tutti Maps Video Immagini Shopping Altro Strumenti

Circa 197 risultati (0,32 secondi)

<https://sciexpem.polimi.it> · Traduci questa pagina

SciExpem

Scientific Experiments and Models. 18. Kinetic Models. 236. Species. 0. Fuels. 164. Data points. 7. Experiments. 6. Simulations.

<https://sciexpem.polimi.it > project> · Traduci questa pagina

Project – SciExpem

A data-driven predictive model for combustion kinetics can study the behavior of ...

<https://github.com > sciexpem > s...> · Traduci questa pagina

sciexpem - GitHub

sciexpem. This prototype has been developed within the work for the paper "Towards a scientific data framework to support scientific model development".

<https://github.com > edoardoramalli> · Traduci questa pagina

edoardoramalli/SciExpem_API: Python API Wrapper ... - GitHub

Python API Wrapper for SciExpem. Contribute to edoardoramalli/SciExpem_API development by creating an account on GitHub.

<https://pypi.org > project > SciEx...> · Traduci questa pagina

SciExpem-API - PyPI

Python wrapper for SciExpem EndPoints. ... SciExpem-API 2.0.3.4. pip install SciExpem-API

Sciexpem: the 'database'

<https://sciexpem.polimi.it/>

The screenshot shows the SciExpem web application interface. The browser address bar displays `sciexpem.chem.polimi.it`. The application has a dark blue navigation bar with links: Home, DataBase, Insert, Analysis, Validation, and Dashboard. A user is logged in as 'Log Out - andrea.nobili'. The main content area is titled 'Filter Experiment DataBase (All the conditions are in logic AND with each other, if the field is not empty)'. It contains several input fields for filtering experiments: ID, Experiment Type, Reactor Type, Fuels (In logic OR), Username, Temperature Range (Min-Max) [K], Pressure Range (Min-Max) [bar], Eq. Ratio Range (Min-Max) [phi = 100 (+Inf)], DOI, Description, Author, and Title. Below these fields are two buttons: 'Filter DataBase' and 'Last 10 Experiments'. At the bottom of the main content area is a link '> Result Table'. The footer of the application shows '©2020 Politecnico di Milano'. A file upload bar at the very bottom shows 'report (1).zip' and a 'Mostra tutto' button.

SciExpem

Posta - Andrea Nobili - Outlook

sciexpem.chem.polimi.it

Posta - Andrea Nob... Corso: 089257 - ME...

Home DataBase Insert Analysis Validation Dashboard Log Out - andrea.nobili

Filter Experiment DataBase (All the conditions are in logic AND with each other, if the field is not empty)

ID: Experiment Type: Reactor Type: Fuels (In logic OR): Username:

ID Please select an experiment type Please select a reactor Please select fuels Insert Username

Temperature Range (Min-Max) [K] Pressure Range (Min-Max) [bar] Eq. Ratio Range (Min-Max) [phi = 100 (+Inf)] DOI:

Min ~ Max Min ~ Max Min ~ Max Insert experiment DOI

Description: Author: Title:

Insert description Insert author Insert title

Filter DataBase Last 10 Experiments

> Result Table

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report (1).zip

Mostra tutto

Sciexpem: the 'simulation'

<https://sciexpem.polimi.it/>

The screenshot displays the SciExpem web application interface. At the top, a dark navigation bar contains links for Home, DataBase, Insert, Analysis, Validation, and Dashboard, along with a user profile icon and the text "Log Out - andrea.nobili". Below this, a light gray filter section titled "Filter Experiment DataBase (All the conditions are in logic AND with each other, if the field is not empty)" contains several input fields: "ID:" with a text box containing "ID"; "Experiment Type:" with a dropdown menu showing "burner stabilized flame speciation measur..."; "Reactor Type:" with a dropdown menu showing "Please select a reactor"; "Fuels (In logic OR):" with a text box showing "Please select fuels"; "Username:" with a text box showing "Insert Username"; "Temperature Range (Min-Max) [K]" with three input boxes for Min, ~, and Max; "Pressure Range (Min-Max) [bar]" with three input boxes for Min, ~, and Max; "Eq. Ratio Range (Min-Max) [phi = 100 (+inf)]" with three input boxes for Min, ~, and Max; and "DOI:" with a text box showing "Insert experiment DOI". Below these fields are three text boxes for "Description:" (containing "Insert description"), "Author:" (containing "Insert author"), and "Title:" (containing "Insert title"). At the bottom of the filter section are two buttons: "Filter DataBase" (blue) and "Last 10 Experiments" (white). Below the filter section is a "Result Table" section with a collapse icon and the text "> Result Table". At the bottom of the page, there is a footer with the text "©2020 Politecnico di Milano". The browser's taskbar at the bottom shows two open files: "Execution_undefine....zip" and "report (1).zip", and a "Mostra tutto" button.

SciExpem

Posta - Andrea Nobili - Outlook

sciexpem.chem.polimi.it

Posta - Andrea Nob... Corso: 089257 - ME...

Home DataBase Insert Analysis Validation Dashboard Log Out - andrea.nobili

Filter Experiment DataBase (All the conditions are in logic AND with each other, if the field is not empty)

ID: Experiment Type: Reactor Type: Fuels (In logic OR): Username:

ID burner stabilized flame speciation measur... Please select a reactor Please select fuels Insert Username

Temperature Range (Min-Max) [K] Pressure Range (Min-Max) [bar] Eq. Ratio Range (Min-Max) [phi = 100 (+inf)] DOI:

Min ~ Max Min ~ Max Min ~ Max Insert experiment DOI

Description: Author: Title:

Insert description Insert author Insert title

Filter DataBase Last 10 Experiments

> Result Table

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Execution_undefine....zip report (1).zip Mostra tutto

Sciexpem: model validation and analysis

<https://sciexpem.polimi.it/>

The screenshot shows the SciExpem web application interface. The browser address bar displays `sciexpem.chem.polimi.it`. The application has a dark blue navigation bar with the following menu items: Home, DataBase, Insert, Analysis (highlighted), Validation, and Dashboard. A user login status "Log Out - andrea.nobili" is visible on the right.

Below the navigation bar, a section titled "Filter Execution Experiment DataBase (All the conditions are in logic AND with each other, if the field is not empty)" contains several filter options:

- Experiment Type:** A dropdown menu with the placeholder text "Please select an experiment type".
- Reactor Type:** A dropdown menu with the placeholder text "Please select a reactor".
- Fuels (In logic OR):** A text input field with the placeholder text "Please select fuels".
- Chem Models (In logic OR):** A text input field with the placeholder text "Please select Chem Models".

Below these, there are three range profile filters, each with a "Min", a range selector (represented by a minus sign in a box), and a "Max" input:

- Temperature Range Profile (Min-Max) [K]**
- Pressure Range Profile (Min-Max) [bar]**
- Equivalent Ratio Range Profile (Min-Max) [ϕ = 100 (+Inf)]**

A blue button labeled "Filter DataBase" is positioned below the range filters.

At the bottom of the filter section, there are two expandable options:

- > Result Table
- > Visualization

The footer of the application displays the copyright notice: ©2020 Politecnico di Milano.

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...



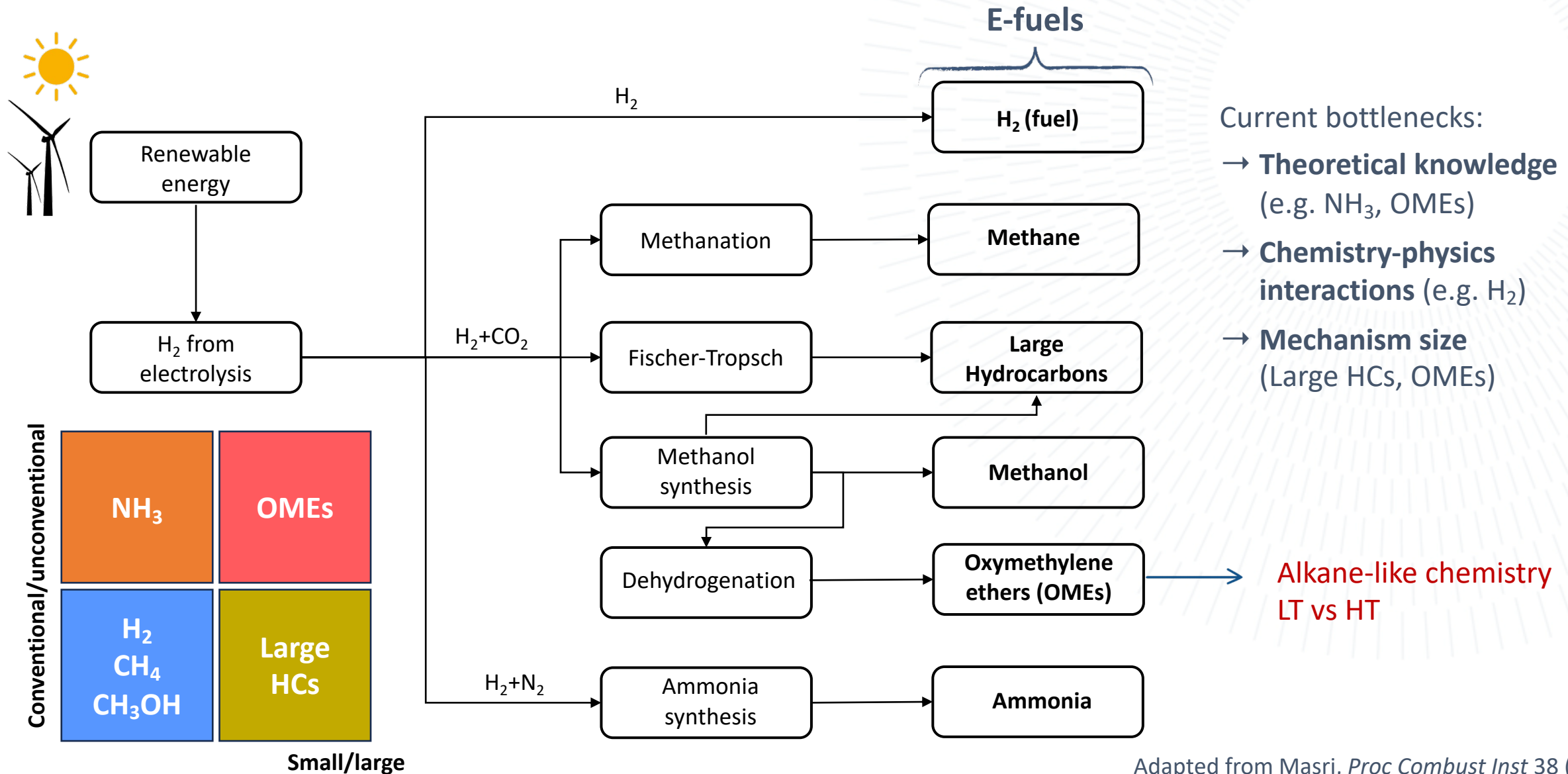
→ Further exploitation of this huge amount of experimental data collected, towards **model discovery** and **generation**.

Integration in the kinetic modelling framework



POLITECNICO
MILANO 1863

Kinetic modeling in the energy transition scenario



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

A step back: modeling combustion kinetics

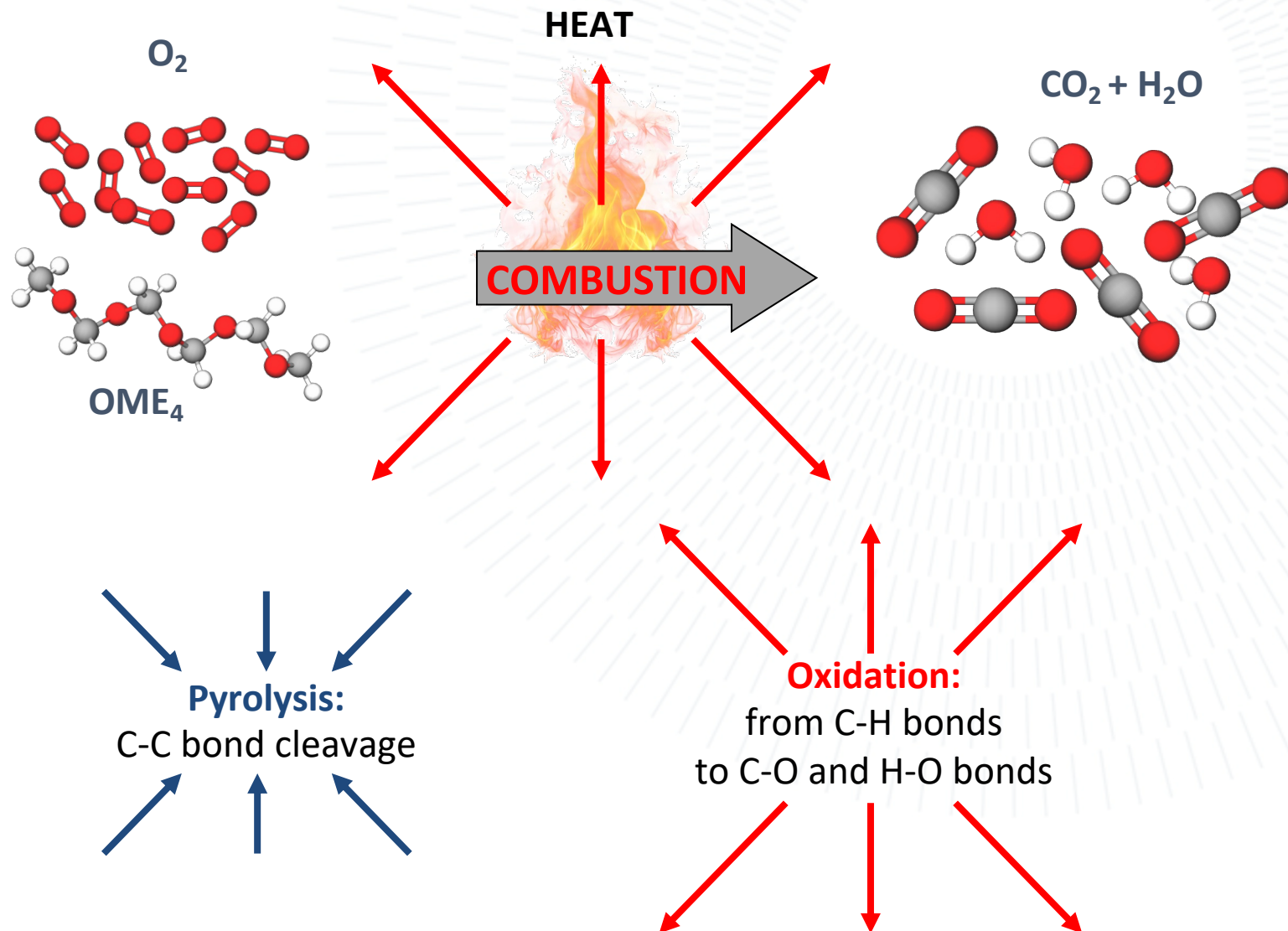
✓ Regardless of the fuels, **combustion kinetics** is:

- **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

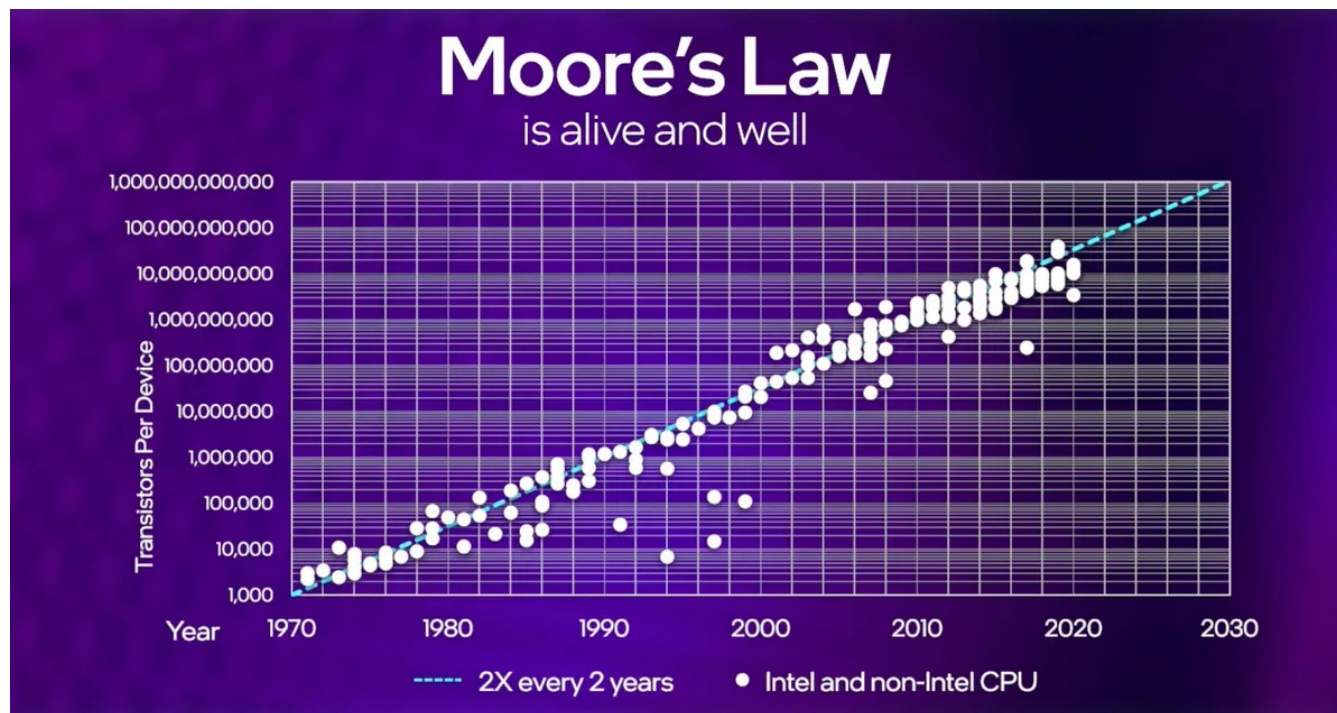
✓ From **larger to smaller** molecules: pyrolysis and oxidation **break bonds**

Which comes first?



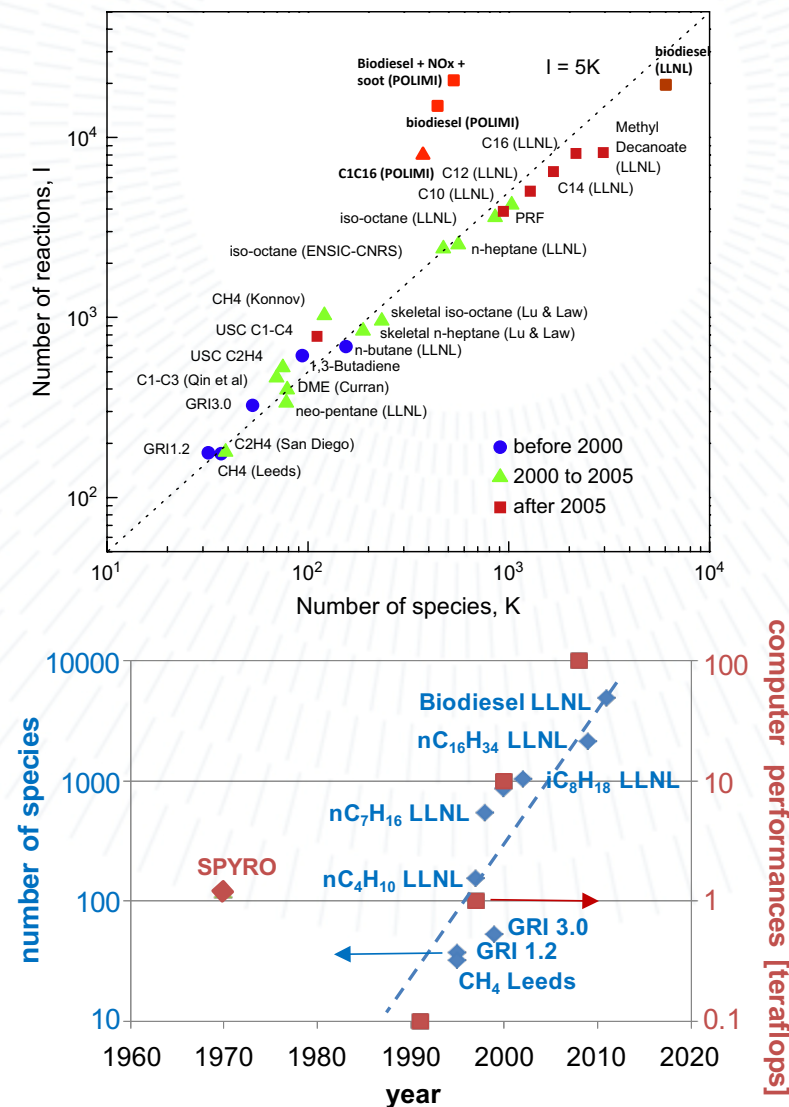
Limitations of detailed chemistry

- ✓ 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

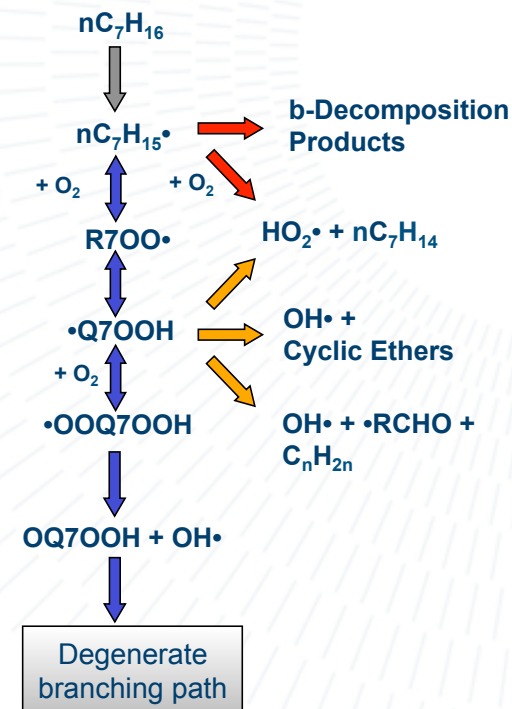
Complexity of liquid feedstocks

#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)

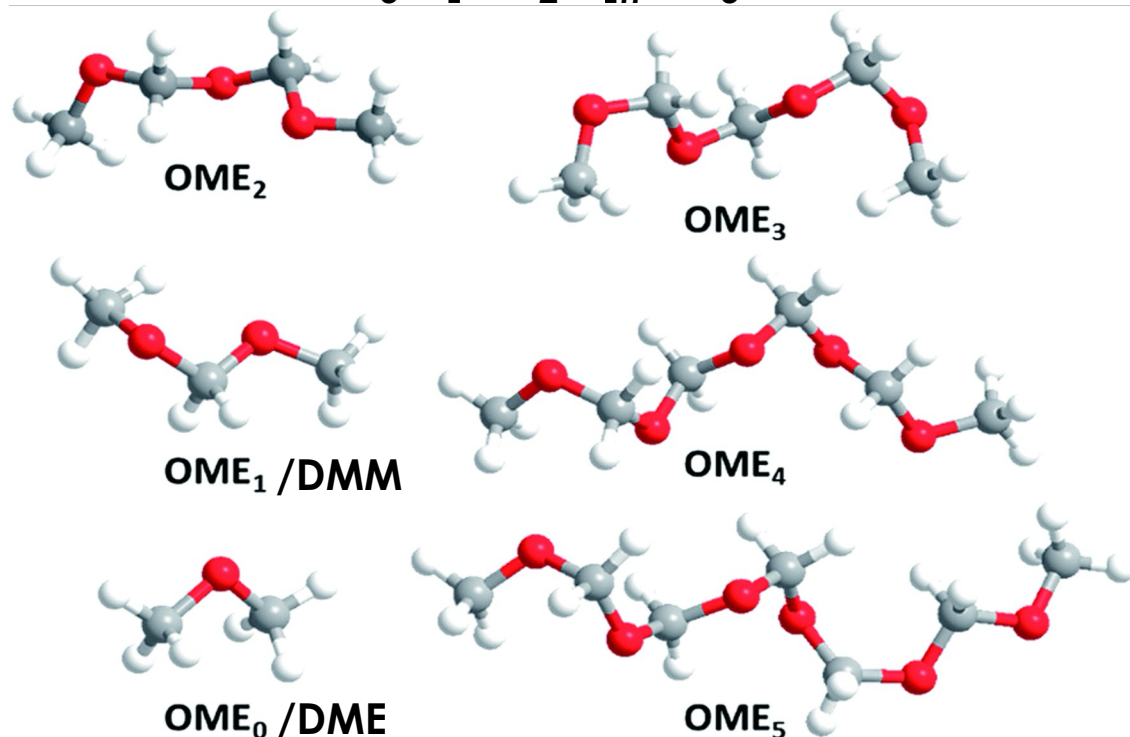
Use of representative molecules
Surrogate fuels

Complexity of reaction mechanisms



Reduction techniques
Species Lumping
Skeletal Reduction

Case study: Oxymethylene ethers (OMEs)



	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% OME₁, 0.2 wt% OME₂, 45 wt% OME₃, 25 wt% OME₄, 17 wt% OME₅, 7 wt% OME₆, 3 wt% OME₇, 1 wt% OME₈

Great potential as
drop-in fuels



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

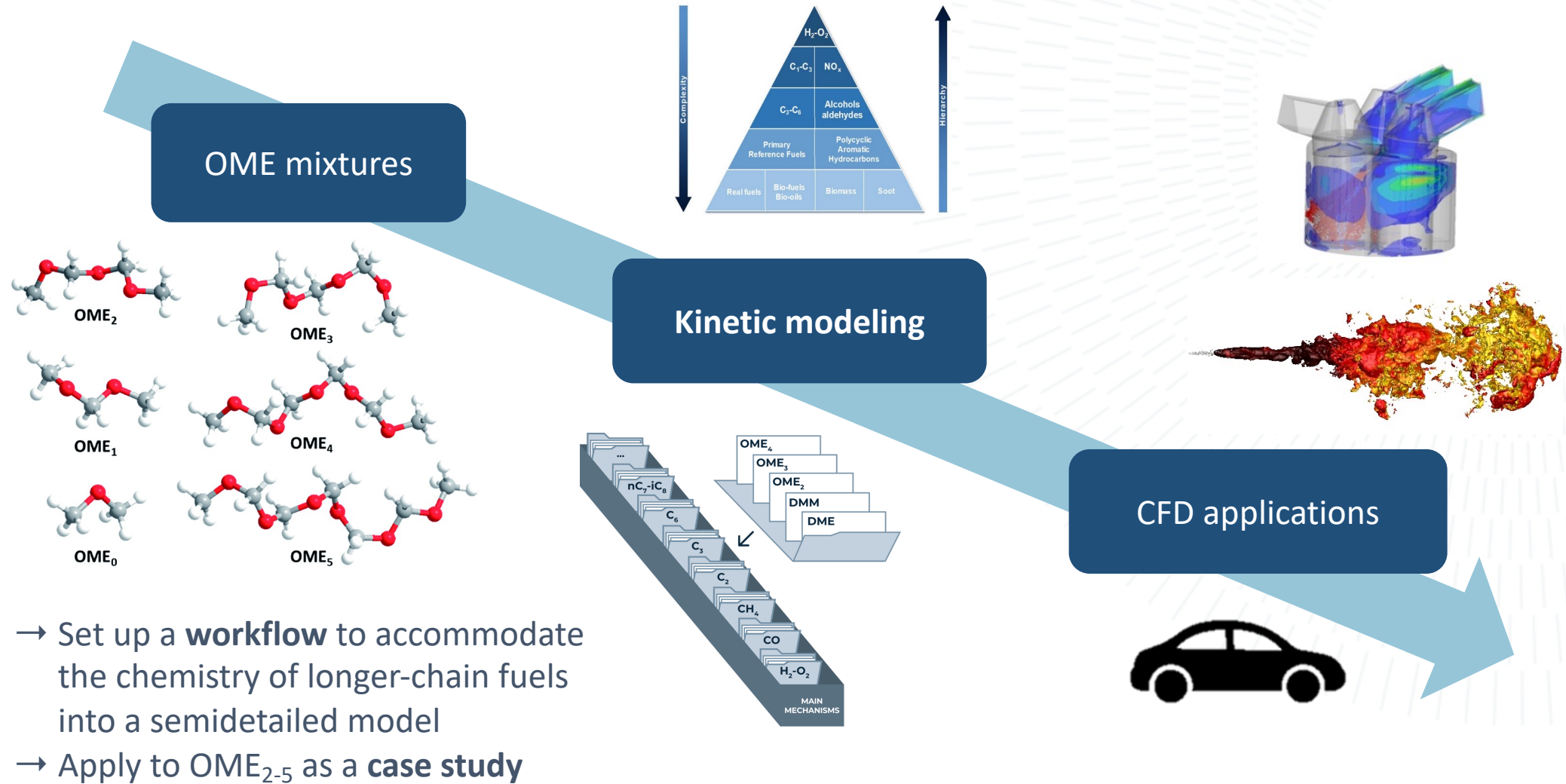
Established **synthesis** processes

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.

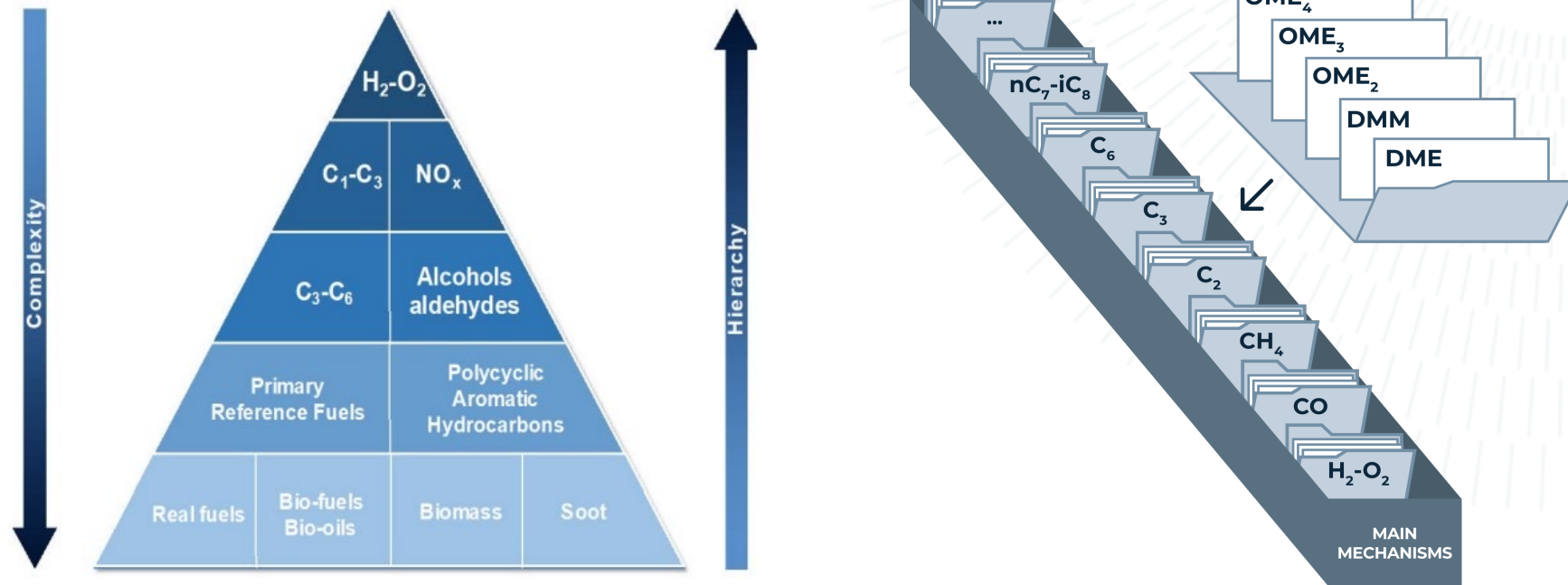
Setting up OME chemistry



Kinetic modeling is modular



Hierarchy, modularity, and **generality** principles



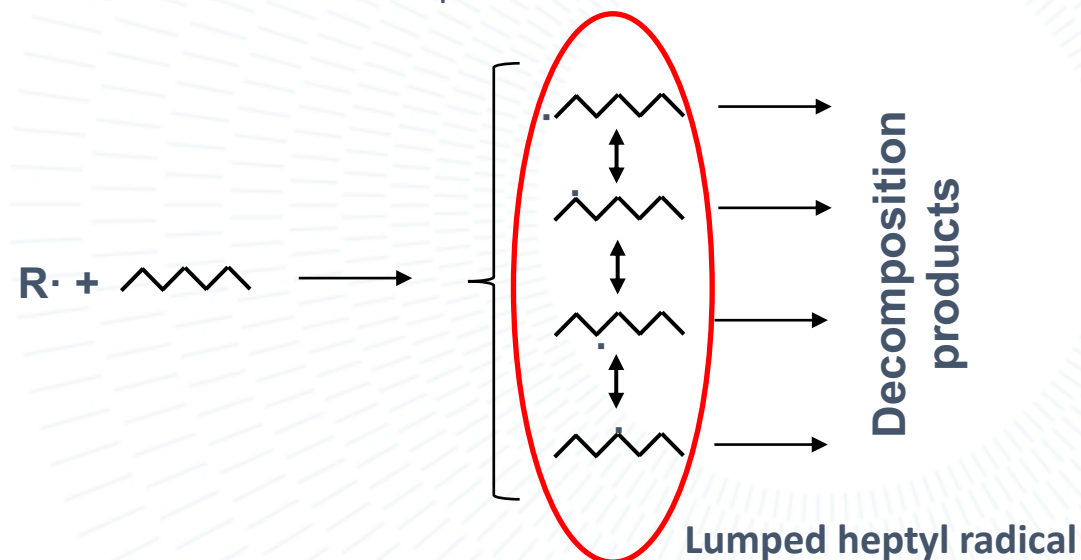
Chemical lumping

- 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)

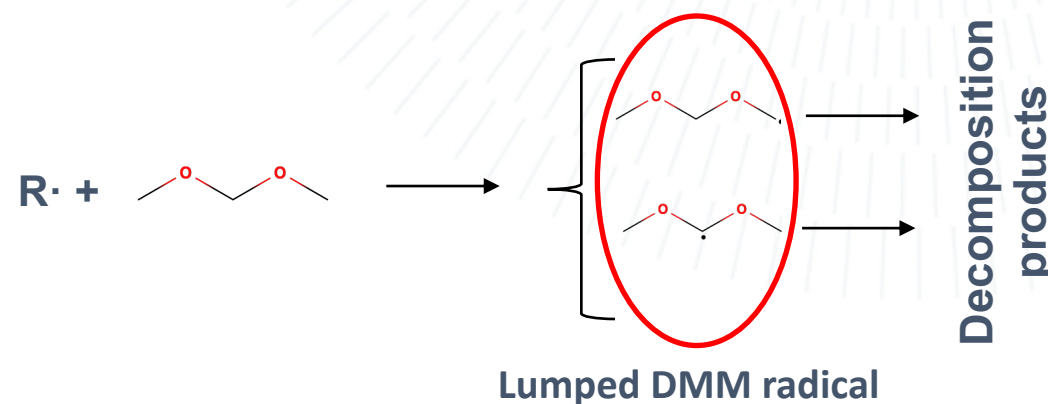
#C	Paraffin isomers	Petroleum fraction
8	18	Gasoline and naphthas
10	75	Kerosene
12	355	Jet Fuels
15	4347	Diesel Fuels
20	$3.66 \cdot 10^5$	Light Gasoil
25	$3.67 \cdot 10^7$	Gasoil
30	$4.11 \cdot 10^9$	Heavy Gasoil
35	$4.93 \cdot 10^{11}$	Atmospheric Residue

Altgelt and Boduszynski (1994)

This was developed for fossil-based fuels...



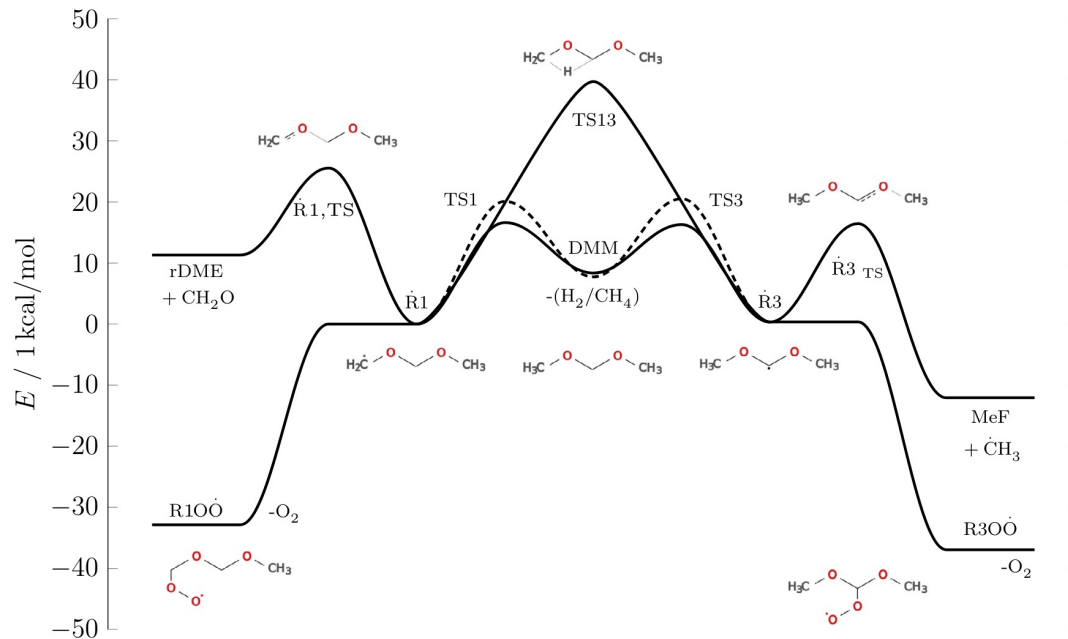
But it holds equally for next-generation ones!



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

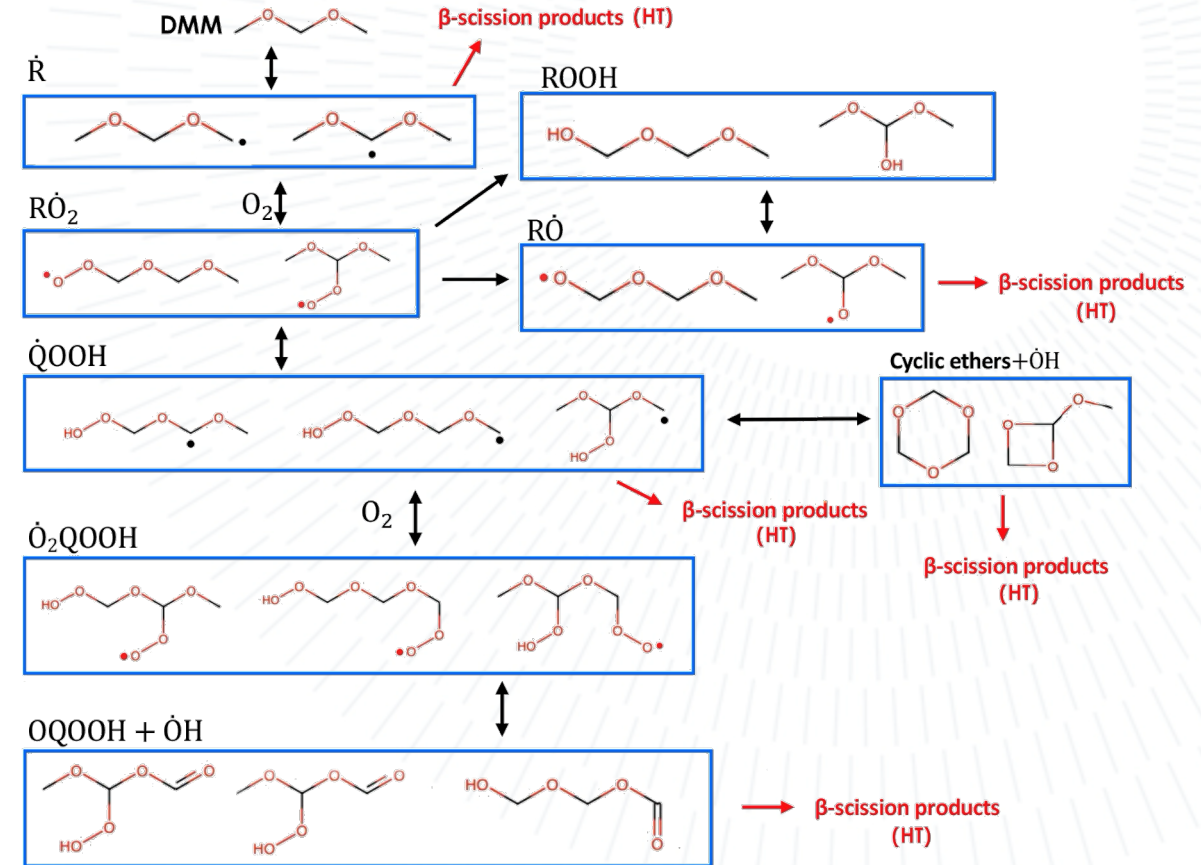
DMM (OME₁) kinetic model as an archetypal

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



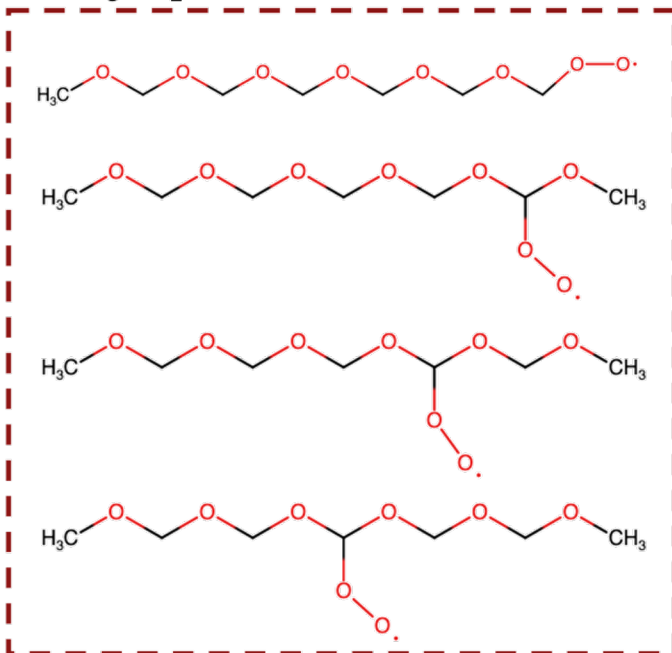
Reaction classes and rate rules can be implemented

High- and low-temperature pathways

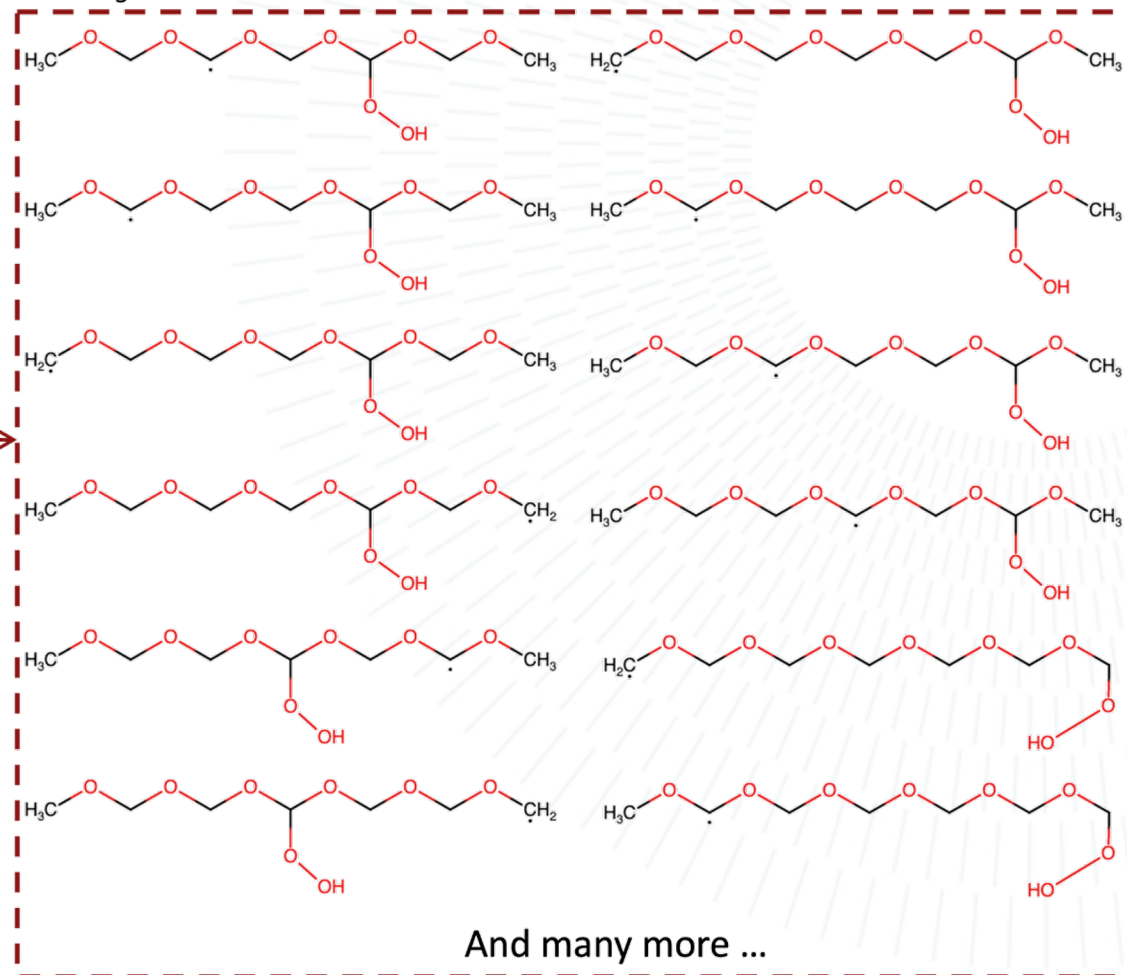


Lumping OMEs

OME₅RO₂



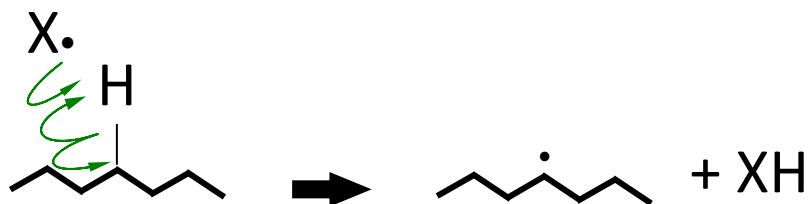
OME₅QOOH



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



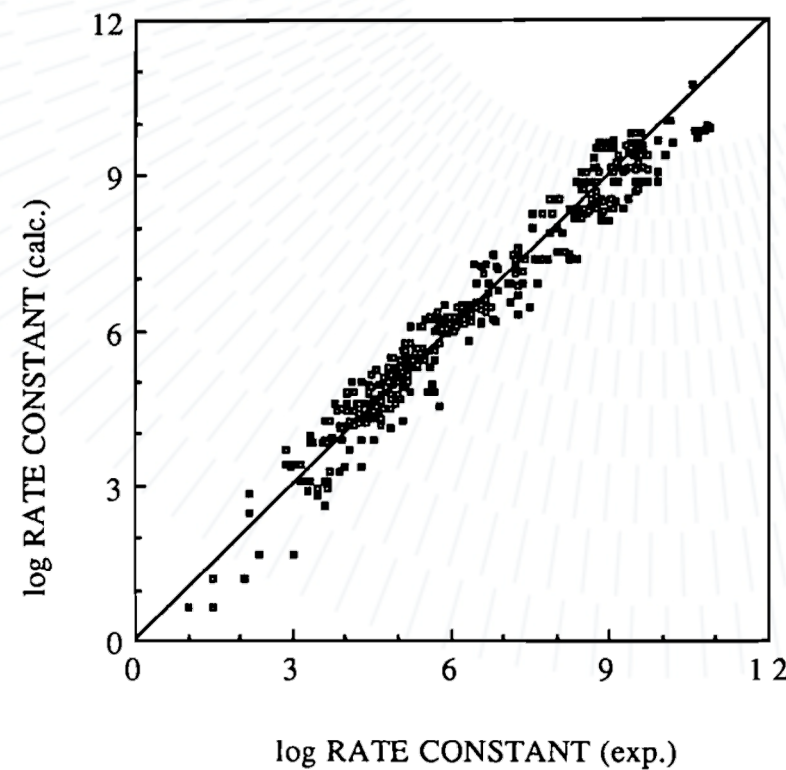
The reaction rate depends on:

- The **abstracting radical**
- The hydrogen **location**

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

Parameters of the
abstracting radical

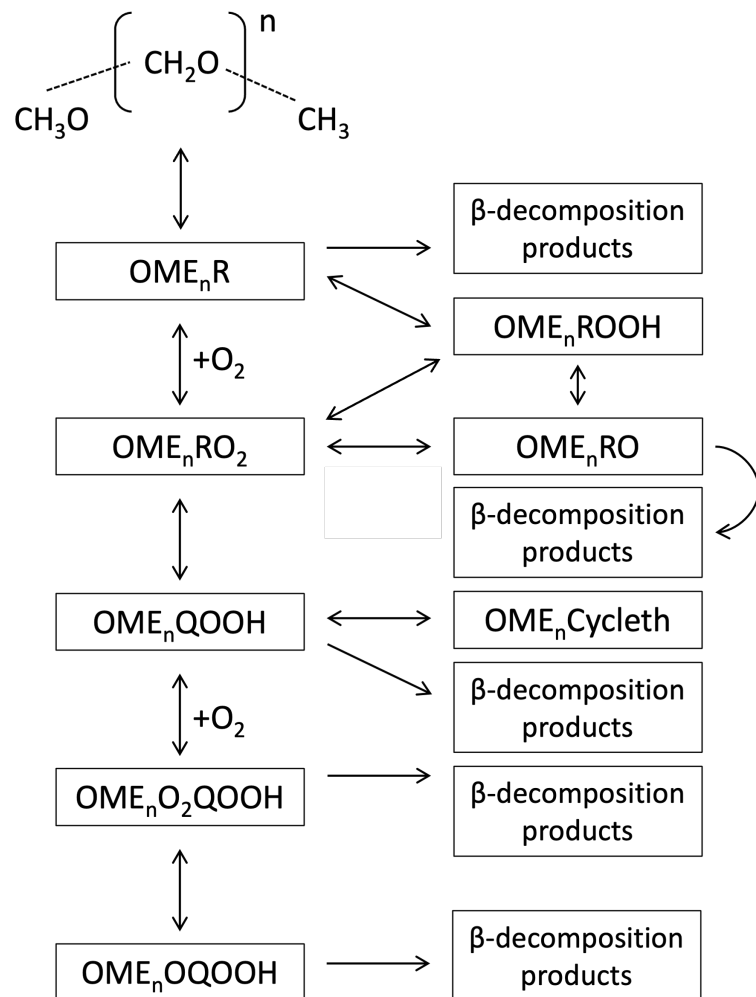
Parameters of the
hydrogen bond



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

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

From OME₁ to higher OMEs



Reaction-class systematic methodology

1. Unimolecular decomposition
2. $\text{OME}_n + \dot{\text{R}}' \leftrightarrow \text{OME}_n \dot{\text{R}} + \text{R}'\text{H}$ → From Ranzi's methodology
3. $\text{OME}_n \dot{\text{R}} \leftrightarrow \beta\text{-decomposition products}$
4. $\text{O}_2 + \text{OME}_n \dot{\text{R}} \leftrightarrow \text{OME}_n \dot{\text{R}}\text{O}_2$
5. $\dot{\text{R}}\text{O}_2 + \text{OME}_n \dot{\text{R}} \leftrightarrow \text{R}\dot{\text{O}} + \text{OME}_n \dot{\text{R}}\text{O}$
6. $\text{OME}_n \dot{\text{R}}\text{O}_2 \leftrightarrow \text{OME}_n \dot{\text{Q}}\text{OOH}$
7. $\dot{\text{R}} + \text{OME}_n \text{ROOH} \leftrightarrow \text{RH} + \text{OME}_n \dot{\text{R}}\text{O}_2$
8. $\text{OME}_n \text{ROOH} \leftrightarrow \text{OME}_n \dot{\text{R}}\text{O} + \dot{\text{O}}\text{H}$
9. $\text{OME}_n \dot{\text{R}}\text{O} \leftrightarrow \beta\text{-decomposition products}$
10. $\text{OME}_n \dot{\text{Q}}\text{OOH} \leftrightarrow \text{OME}_n \text{cyclic ether}$
11. $\text{OME}_n \dot{\text{Q}}\text{OOH} \leftrightarrow \beta\text{-decomposition products}$
12. $\text{OME}_n \dot{\text{Q}}\text{OOH} + \text{O}_2 \leftrightarrow \text{OME}_n \dot{\text{O}}_2 \text{QOOH}$
13. $\text{OME}_n \text{OQOOH} + \dot{\text{O}}\text{H} \leftrightarrow \text{OME}_n \dot{\text{O}}_2 \text{QOOH}$
14. $\text{OME}_n \text{OQOOH} \leftrightarrow \beta\text{-decomposition products}$

Scaled
From DMM model

Optimization

$$k = A T^{\beta} e^{-\frac{E_{act}}{RT}}$$

→ 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

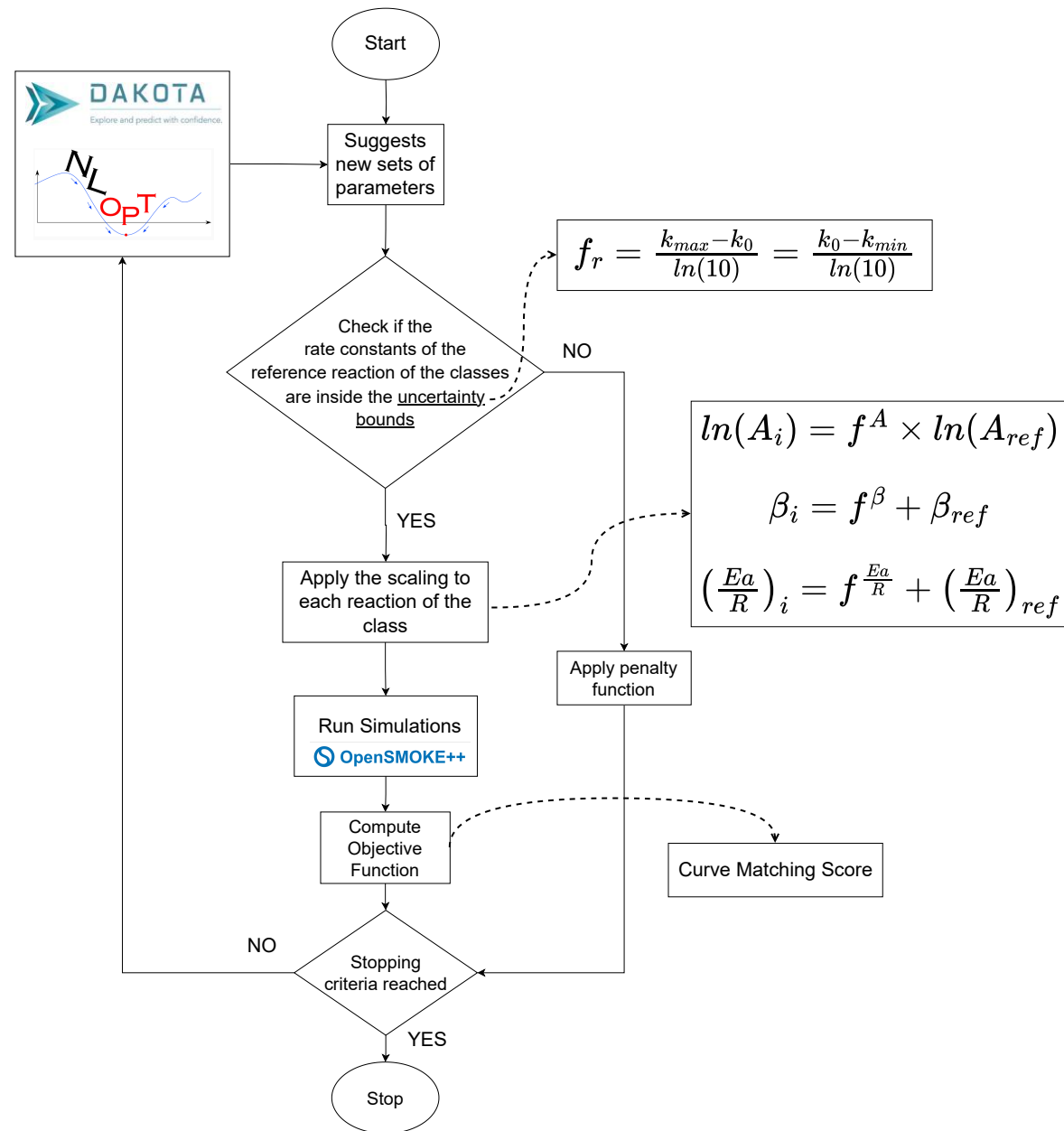
$$\mathcal{L} = \frac{1}{N} \sum_i^N \left(1 - \frac{1}{N_b} \sum_j^{N_b} CM_{i,j} \right)$$

→ Reaction Class scaling

$$\ln(A) = f_{scaling}^A \times \ln(A_{ref})$$

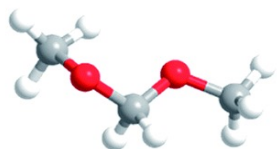
$$\beta = f_{scaling}^{\beta} + \beta_{ref}$$

$$\frac{E_a}{R} = f_{scaling}^{\frac{E_a}{R}} + \left(\frac{E_a}{R} \right)_{ref}$$



Scaling rates, retaining chemistry

Reference species



OME₁

Generic rate:

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



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



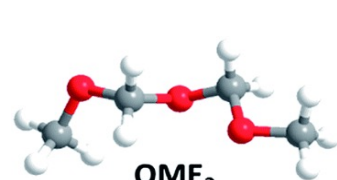
$$f_i^A = \frac{\ln(A_i)}{\ln(A_1)}$$

$$f_i^\beta = \beta_i - \beta_1$$

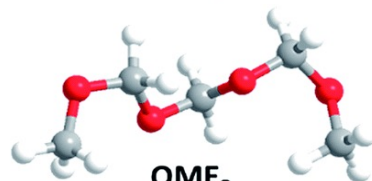
$$f_i^{\frac{E_a}{R}} = \left(\frac{E_a}{R}\right)_i - \left(\frac{E_a}{R}\right)_1$$

Kept constant during optimization

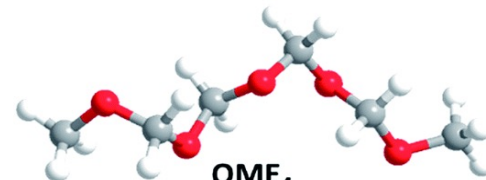
Larger species



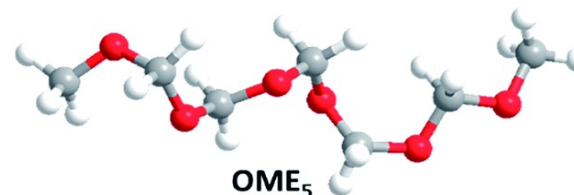
OME₂



OME₃



OME₄



OME₅

Scaling factors

→ Reference parameters are taken from DMM chemistry

→ An **uncertainty factor** f_r is assigned to each reaction class:

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

Detailed
mechanism



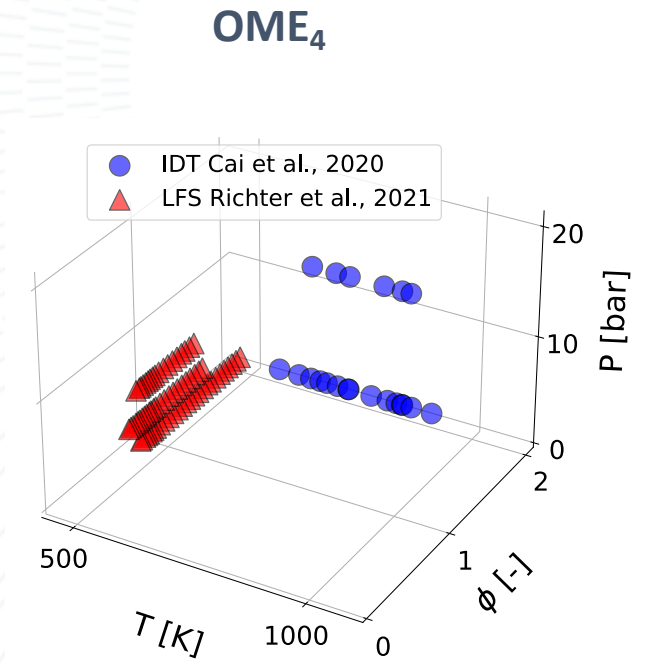
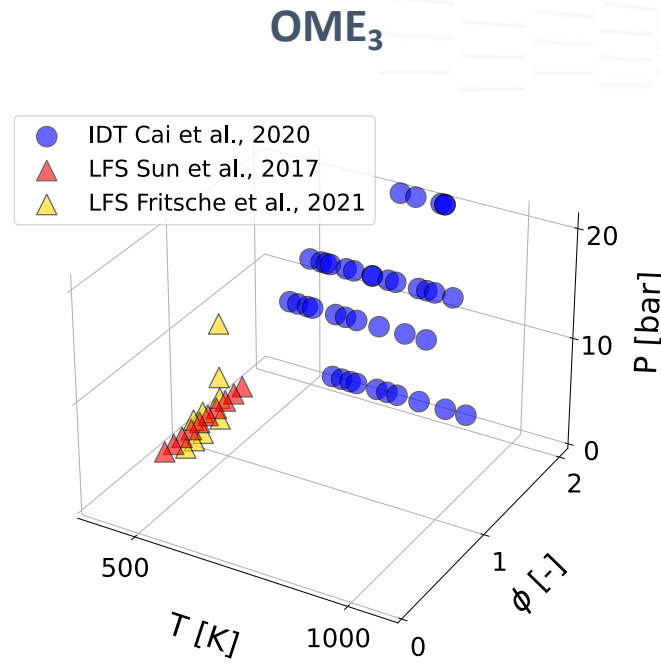
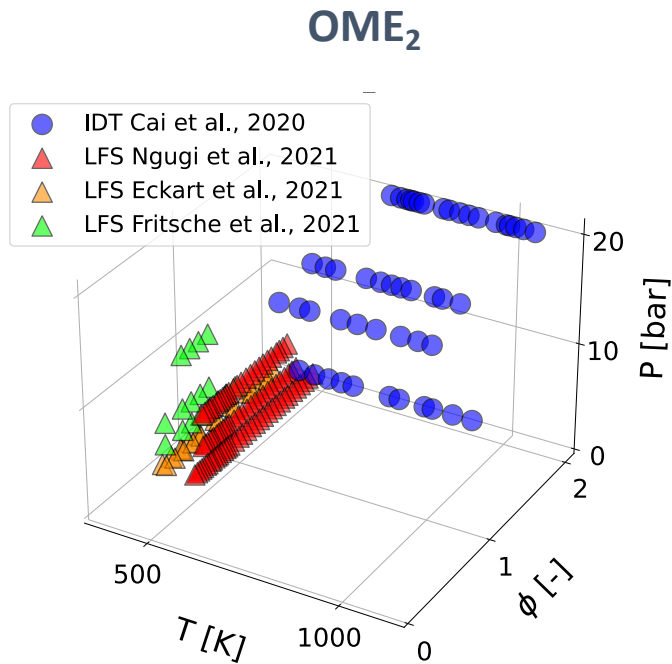
Lumped
mechanism



Optimized
mechanism

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

Experimental database & optimization targets

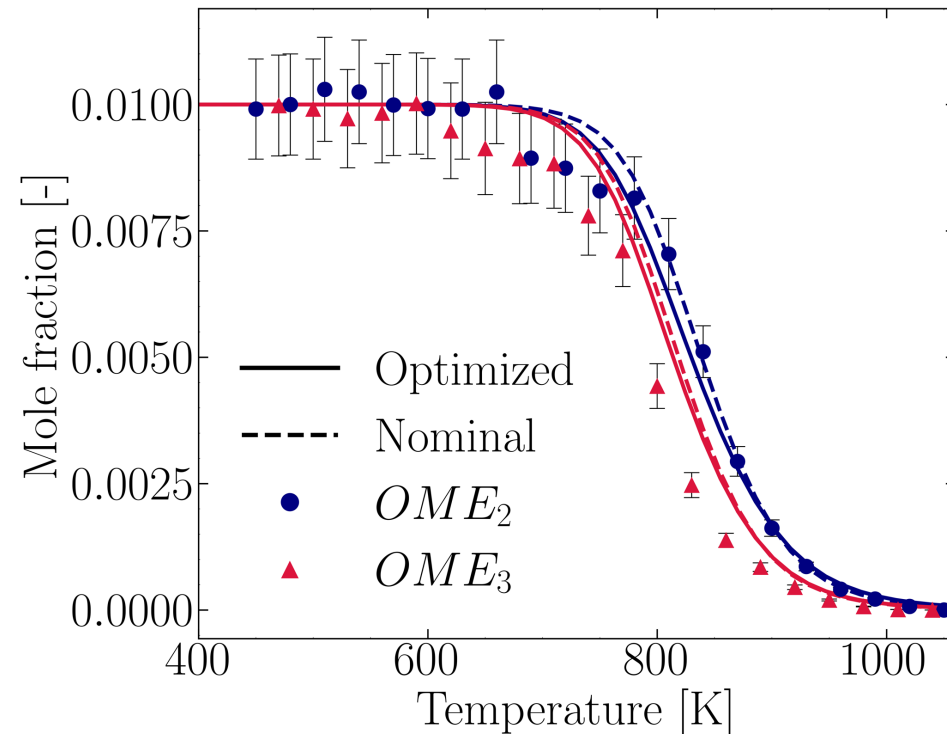


- Ignition delay time & Jet Stirred Reactor selected from the Sciexpem database
- Most data on OME₂₋₄ (only 1 dataset available for OME₅)

- Plug flow reactor used for validation
- Laminar flame speed used for validation

Model validation

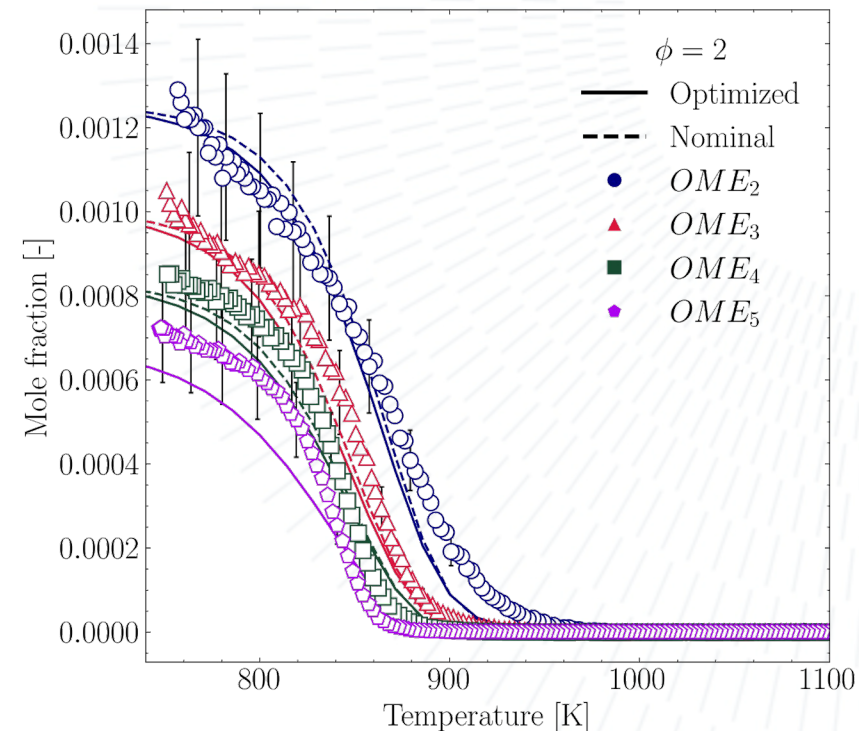
Pyrolysis



Scaled OME reactivity caught reasonably well

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

Oxidation

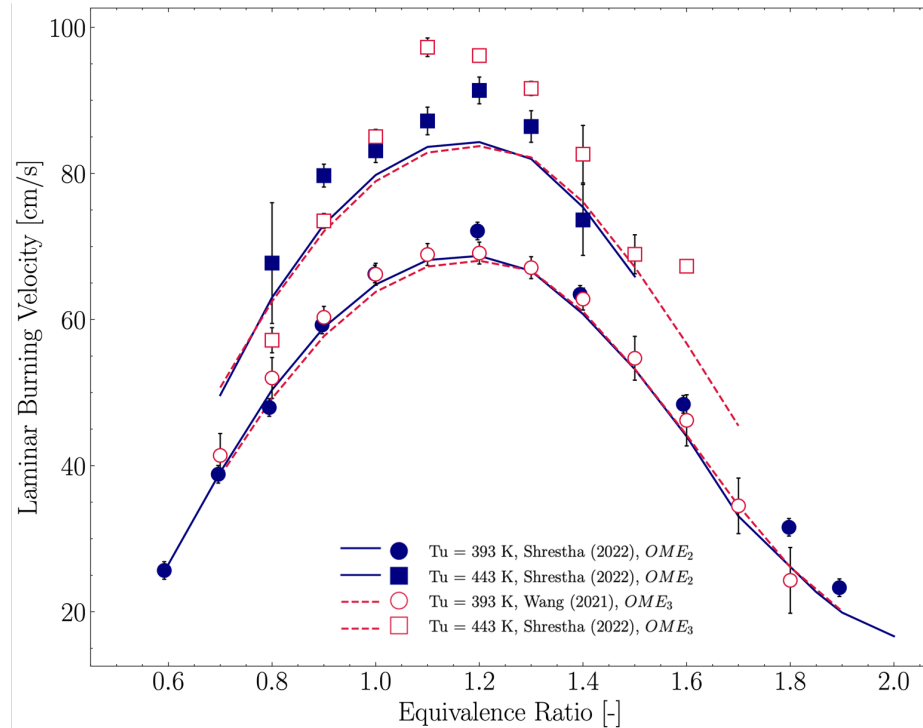


OME_5 well caught (although not used as optimization target)

Gaiser et al. *Fuel*, 313, 2022

Model validation: laminar flame speed

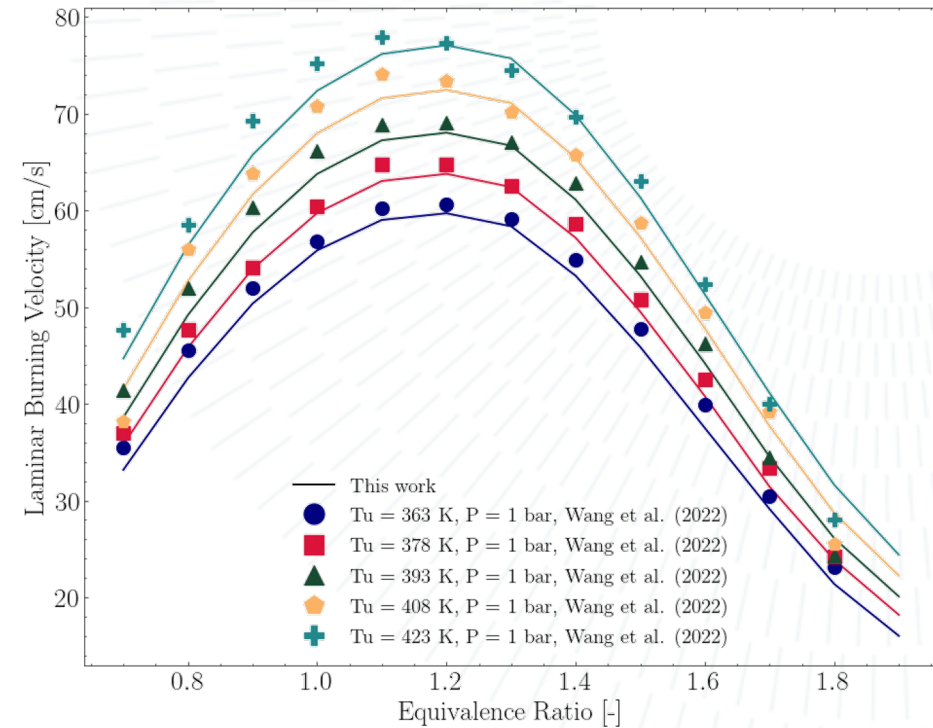
OME₂ vs OME₃



Laminar flame speed is independent of
OME chain length (C₀-C₃ controlling)

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

Temperature scaling (OME₃)

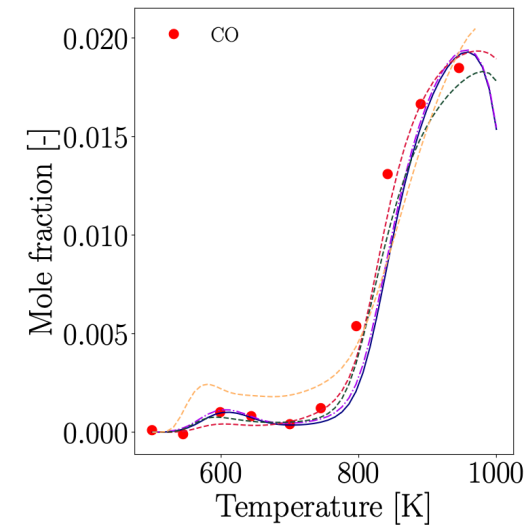
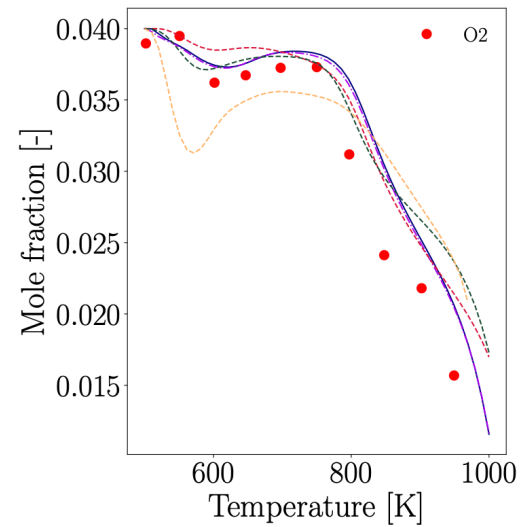
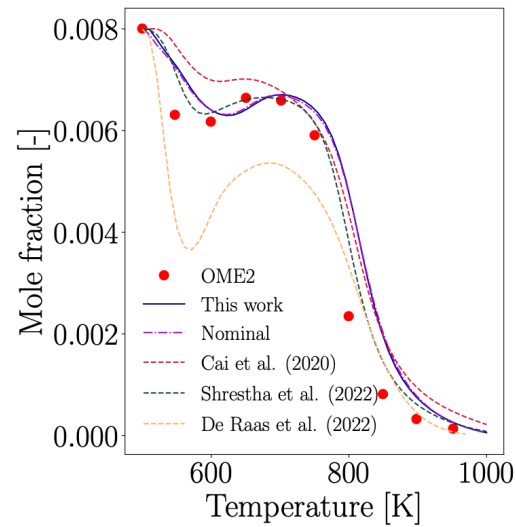


Reasonable prediction of LFS scaling
with the temperature

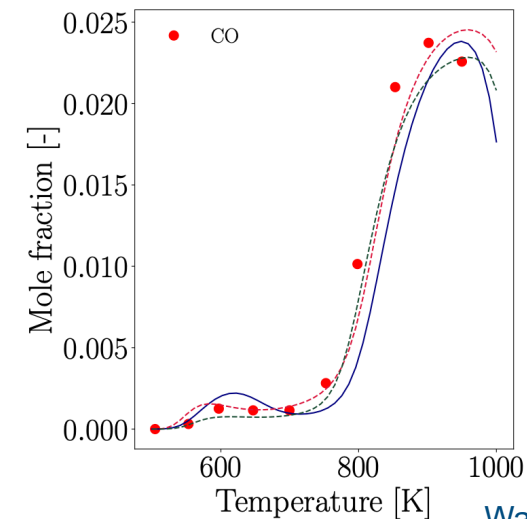
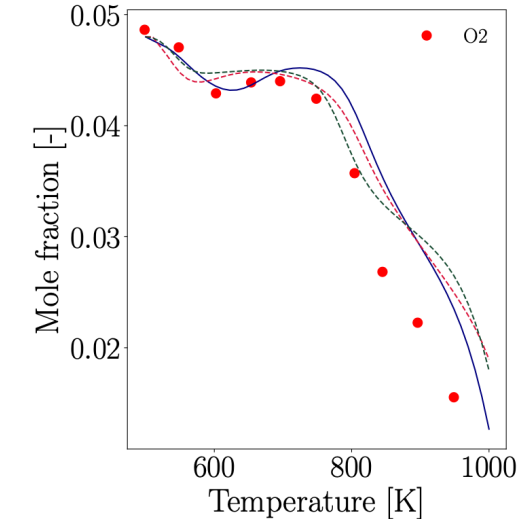
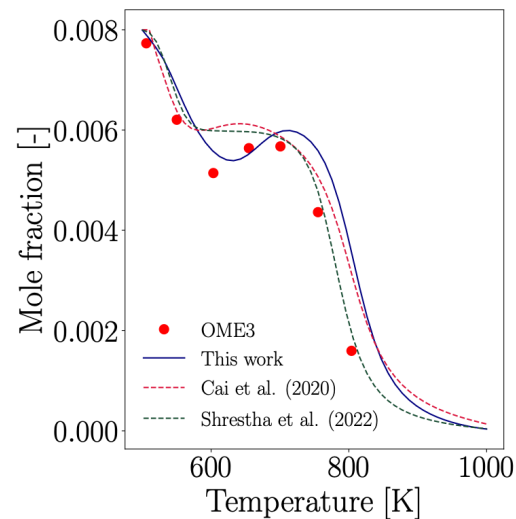
Wang et al. *Fuel*, 297, 120754 (2022)

Mechanism validation

OME₂

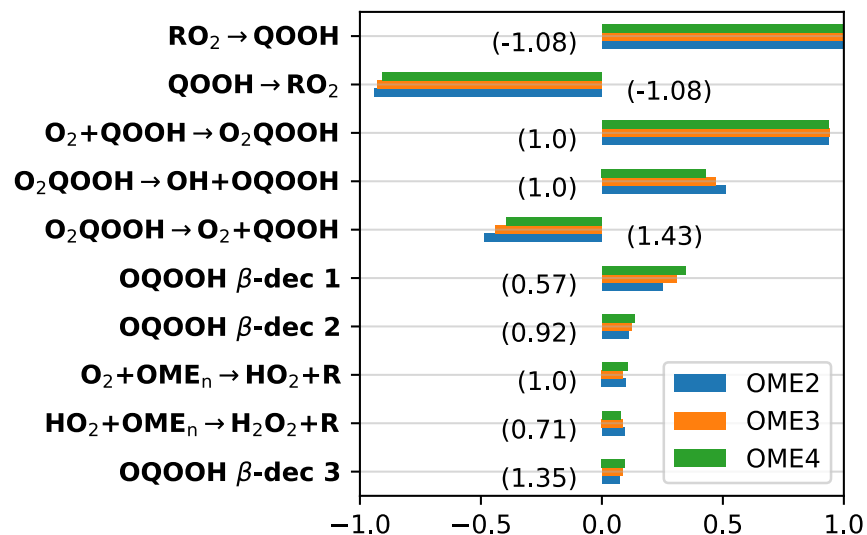
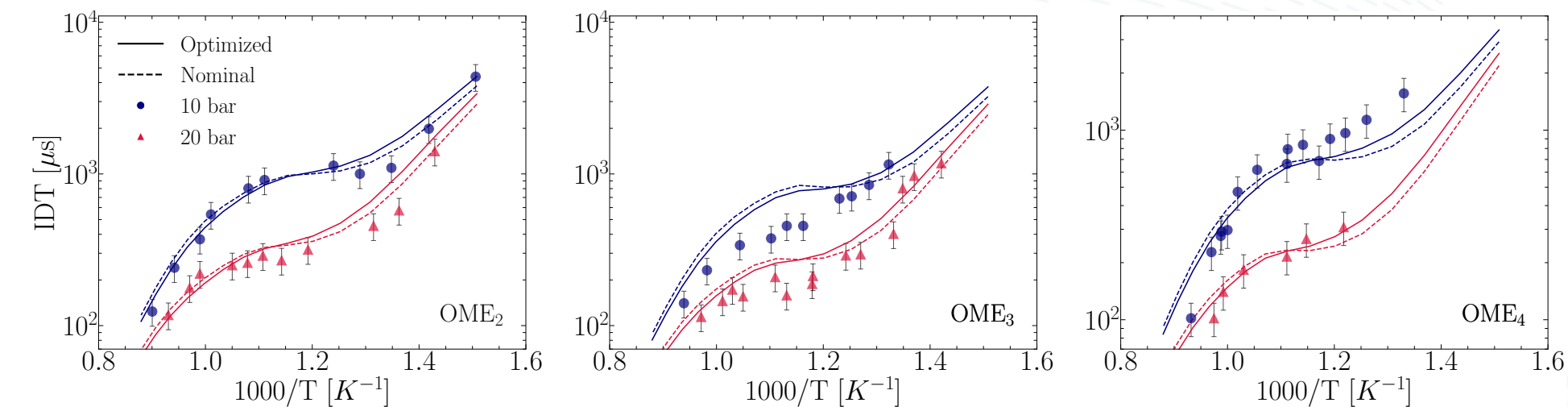


OME₃



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 O_2QOOH 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

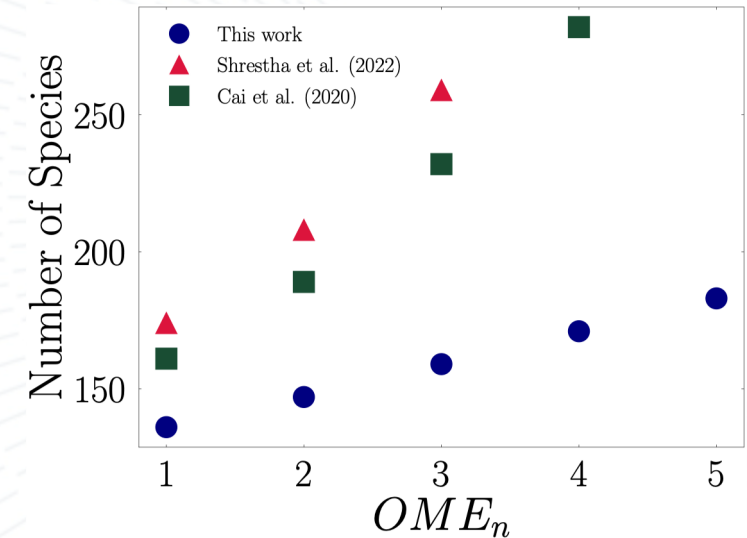
- Combustion is **hierarchical**, regardless of the kind of fuel
- Modeling the next-generation, CO₂-neutral fuels can rely on the same kinetic modeling tools and methodologies once developed for fossil fuels
- For longer-chain fuels (OMEs), the same size issues once met for fossil fuels must be faced: 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

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

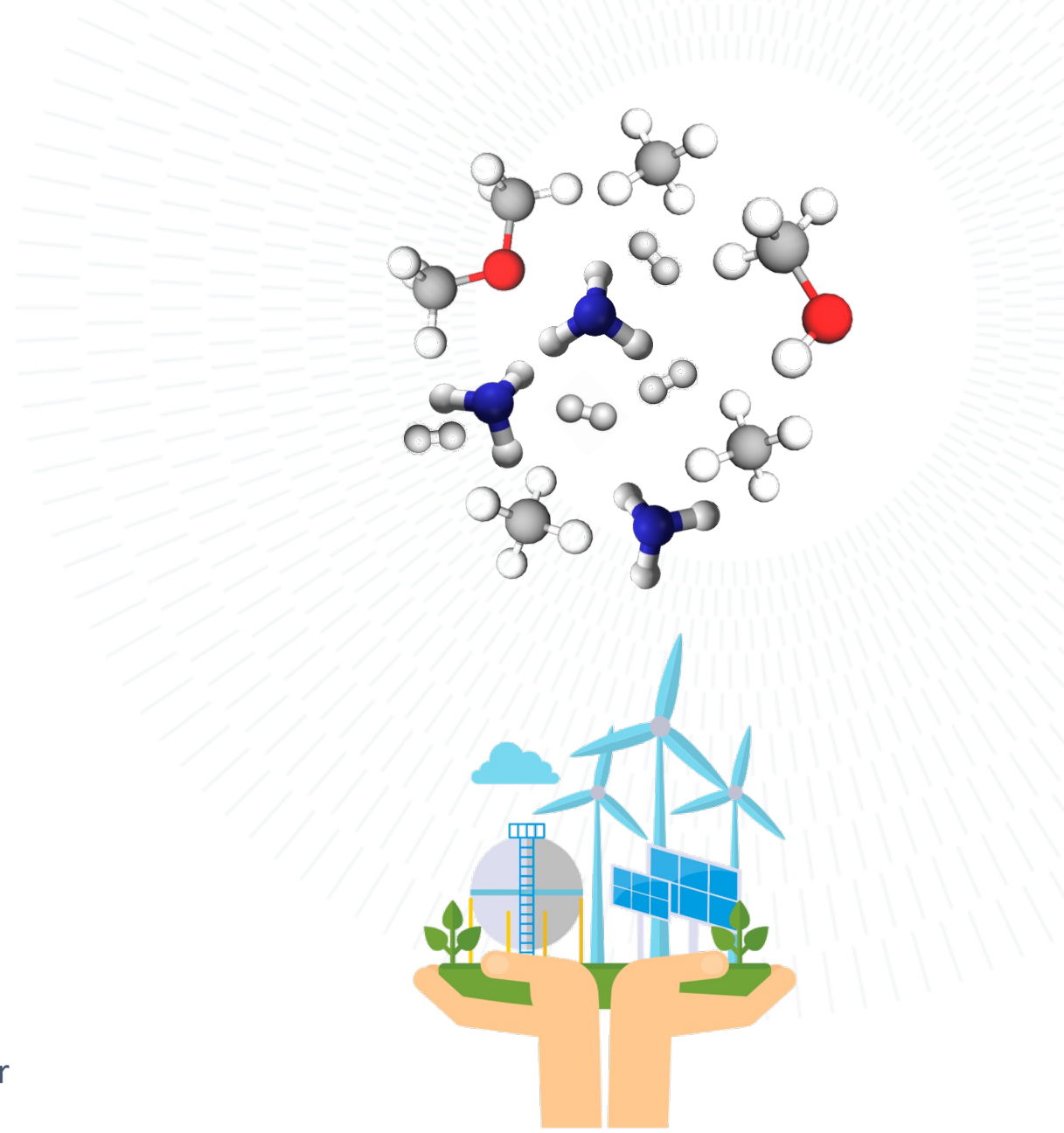
Stay Tuned

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



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



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Laura Sangalli



Piercesare Secchi



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the European Union**



Thank you for your attention

