Rapid Compression Machine Assessment of Anti-knocking Properties of Oxygenated Aromatic Hydrocarbons from the Fast Pyrolysis of Biomass: Experimental, Theoretical and Kinetic Modelling Study

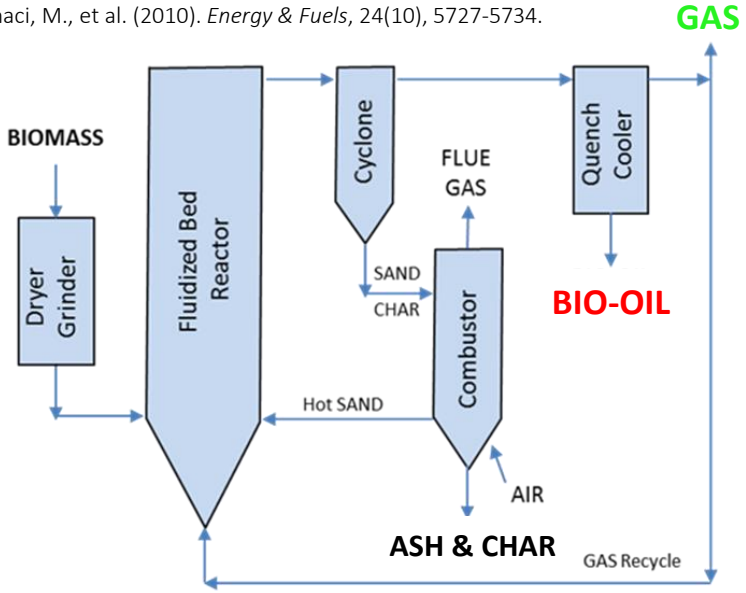
Matteo Pelucchi, Luna Pratali Maffei, René Daniel Buttgen, Marco Mehl, Alessio Frassoldati, Alexander Heufer, Carlo Cavallotti, Tiziano Faravelli

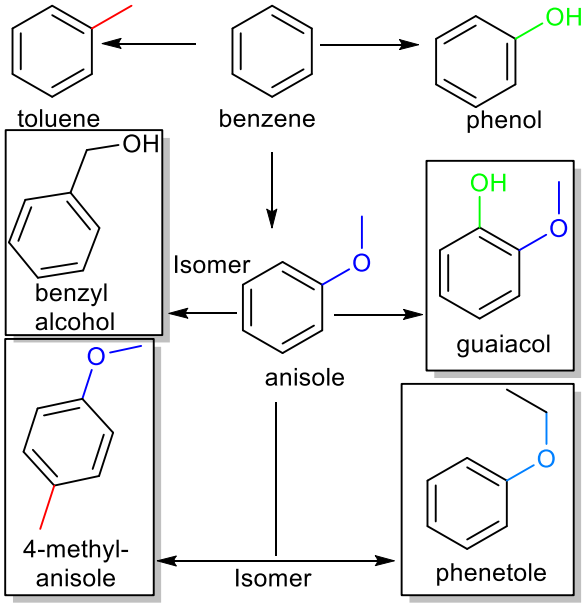
RECK Chemical Reaction Engineering and Chemical Kinetics Lab

PCFC Physico-Chemical Fundamentals of Combustion | RWTH AACHEN UNIVERSITY

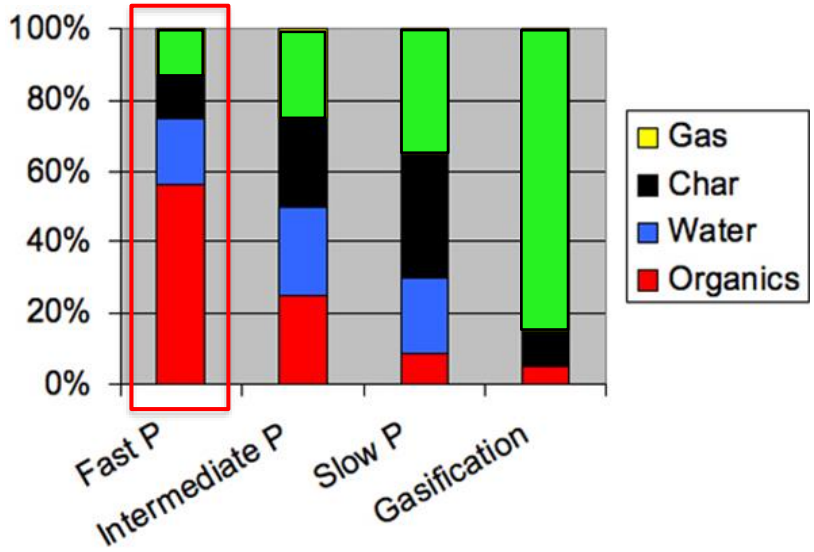
Fuels from Biomass Fast Pyrolysis

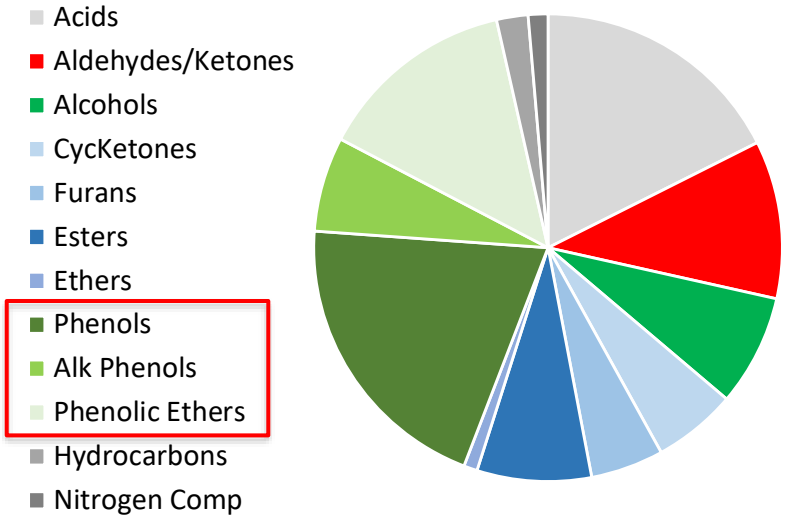
Calonaci, M., et al. (2010). *Energy & Fuels*, 24(10), 5727-5734.





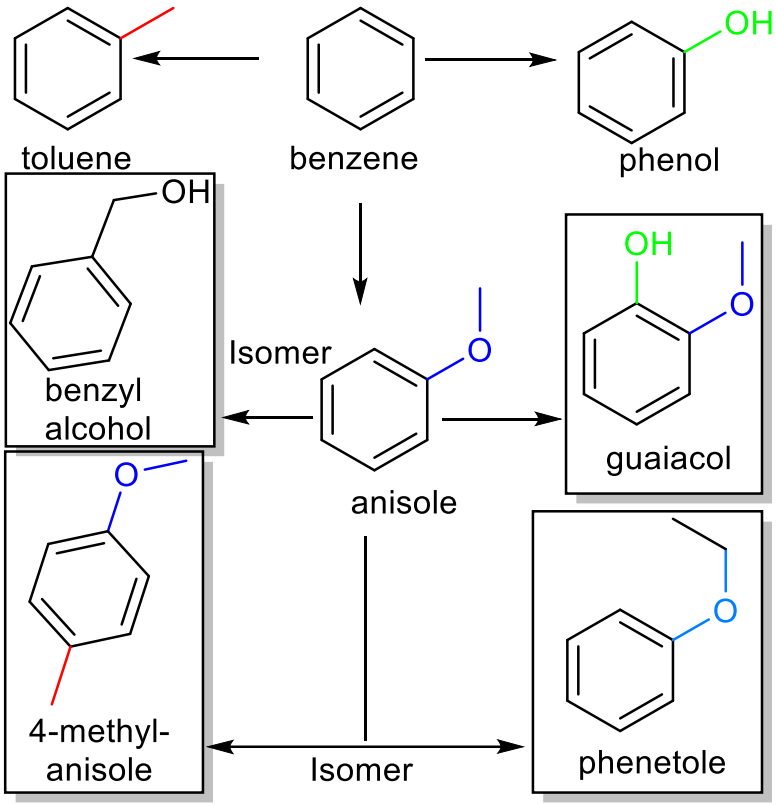
Bridgwater, A. V. (2012). *Biomass and bioenergy*, 38, 68-94.





Bertero, M. (2012). *Fuel*, 95, 263-271.

Antiknocking Properties of Oxygenated Aromatic Hydrocarbons (OAHCs)

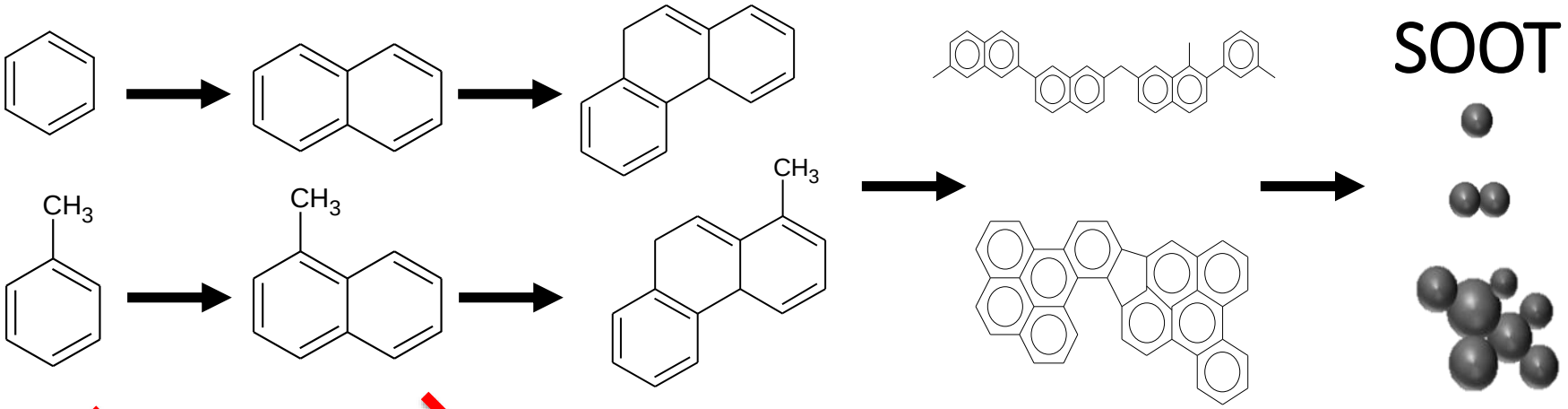


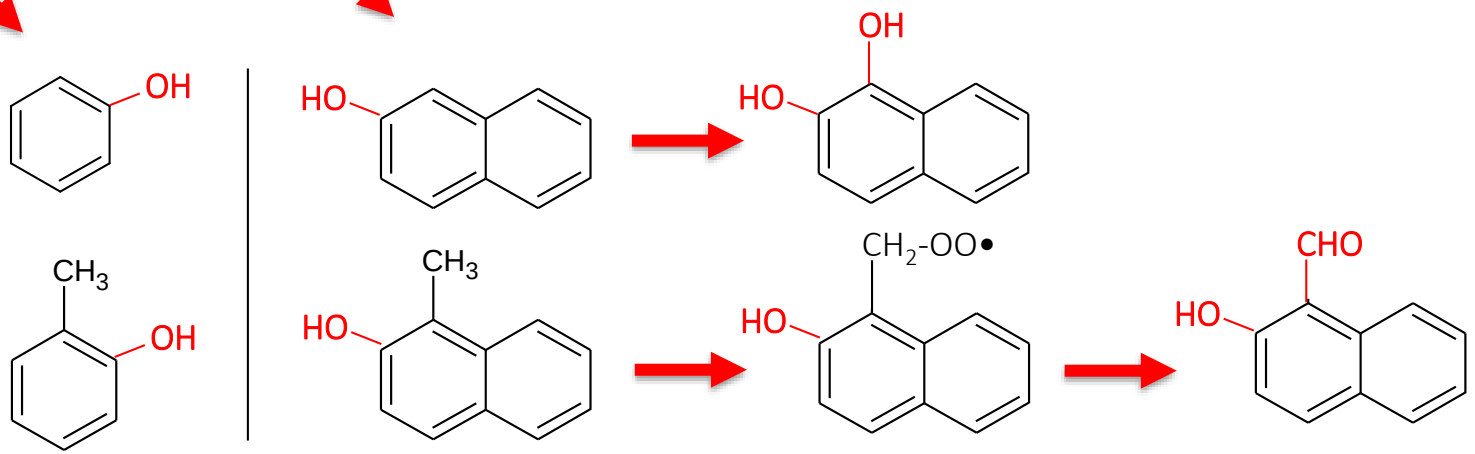
Compound		RON	MON	DCN
Ethanol	*EtOH*	109	90	
Toluene	*TOL*	121	107	
Anisole	AN	120	98	6
Benzyl-alcohol	BA	111	92	8
Guaiacol	GA			19
4-methyl-anisole	MA	166	148	7
Phenetol	PHT	<120	<98	

Buttgen, R.D. et al. (2020). Submitted to *Proceedings of the Combustion Institute*

Additional Motivations: PAHs Growth and Oxidation Kinetics

Growth





Oxidation

Kinetic Model Development: Recent Efforts @ CRECK-POLIMI

Goals:

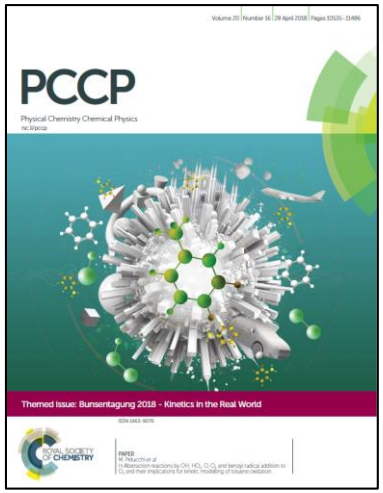
- Characterize the reactivity of OAHs by investigating the **influence of single and multiple substitutions**

  (-OCH_3, OH, CH_3, -CH_2OH, -CHO, …)

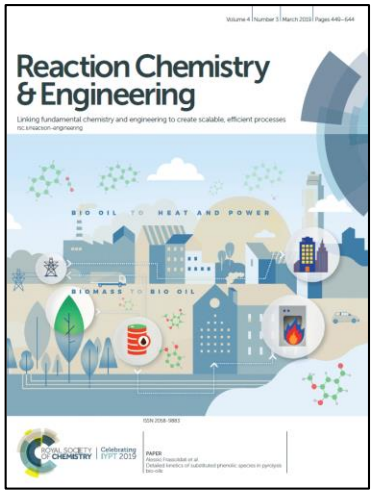
- **Define Reaction Classes** applicable to MAHs (benzene, toluene, …), OAHs (phenol, anisole, guaiacol, methyl-anisole, methyl-phenol, …) and PAHs – *same approach as for linear/branched fuels*
- **Compute rate constants** of the above reactions classes with high accuracy ***ab initio* methods**
- **Derive Rate Rules** from the above calculations
- **Test and validate** a detailed kinetic model for OAHCs anticknocking additives (**Guaiacol** and **Phenetol**)

Recent efforts:

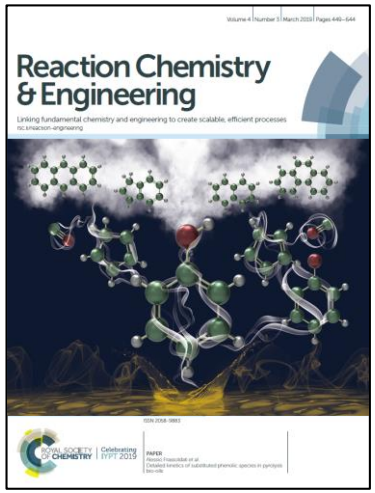
Phys. Chem. Chem. Phys (2018), 20.16



Reac. Chem. Eng. (2019), 4.3



Reac. Chem. Eng. (2020), in press.



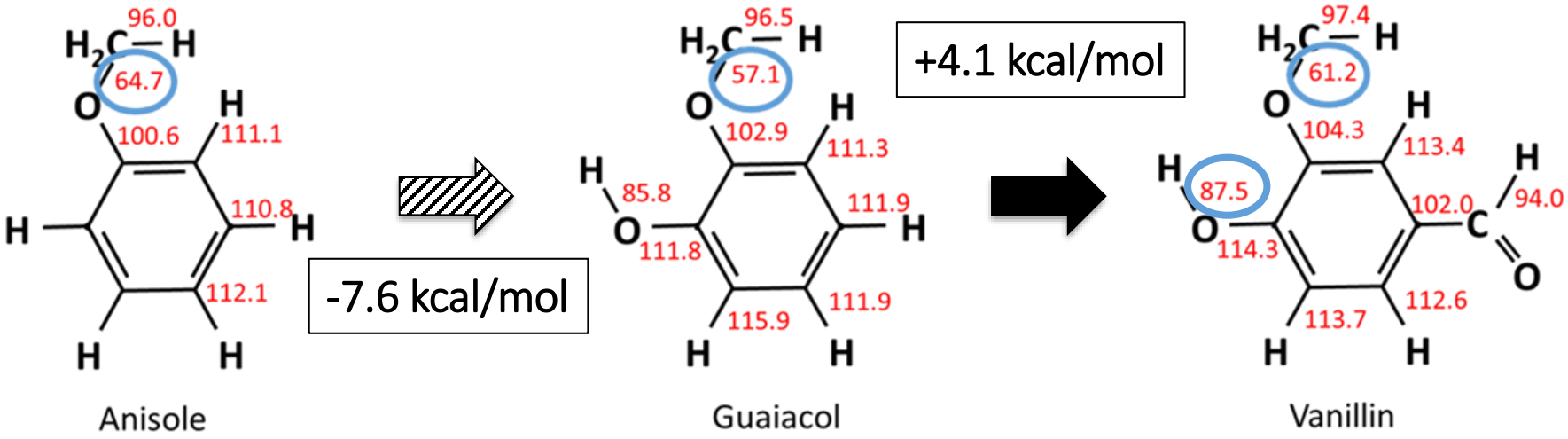
<u>+ 3 Symposium Submissions</u>

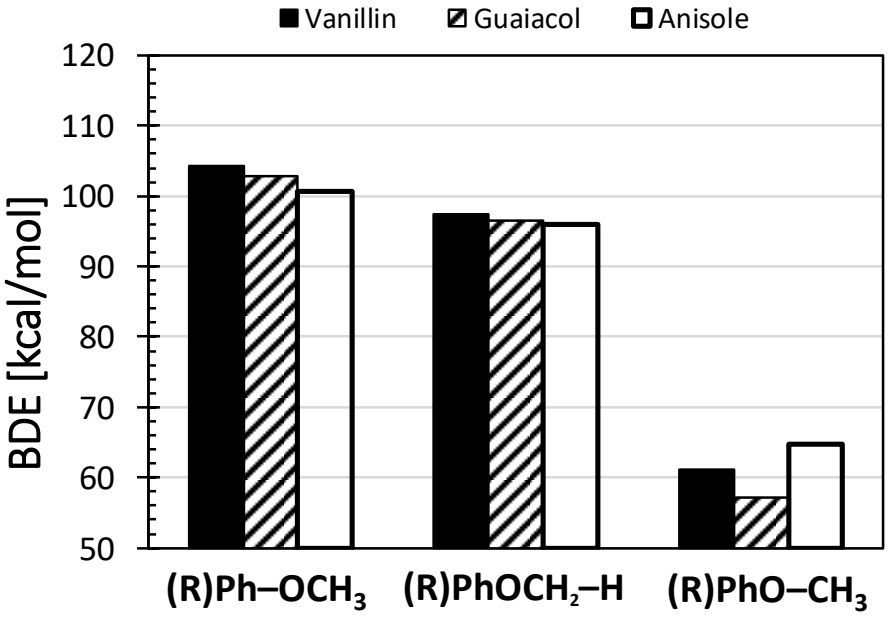
(POLIMI/RWTH)

- 1 Experimental study in RCM
- 2 Theoretical studies

Proximity Effects on BDE in Oxygenated Mono-Aromatic Hydrocarbons

Ortho–OH substitution strongly reduces O — CH_3 BDE

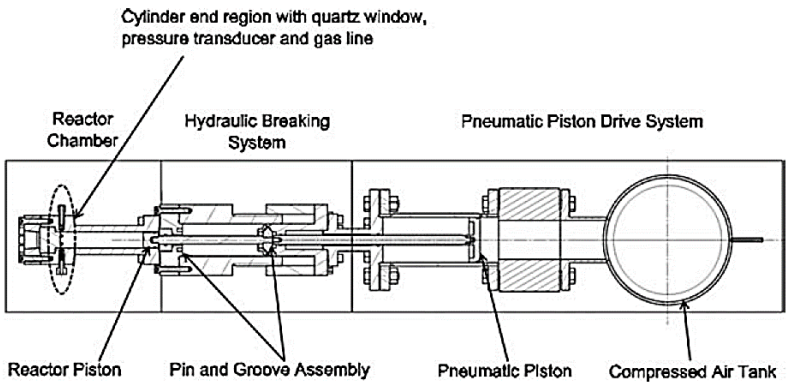


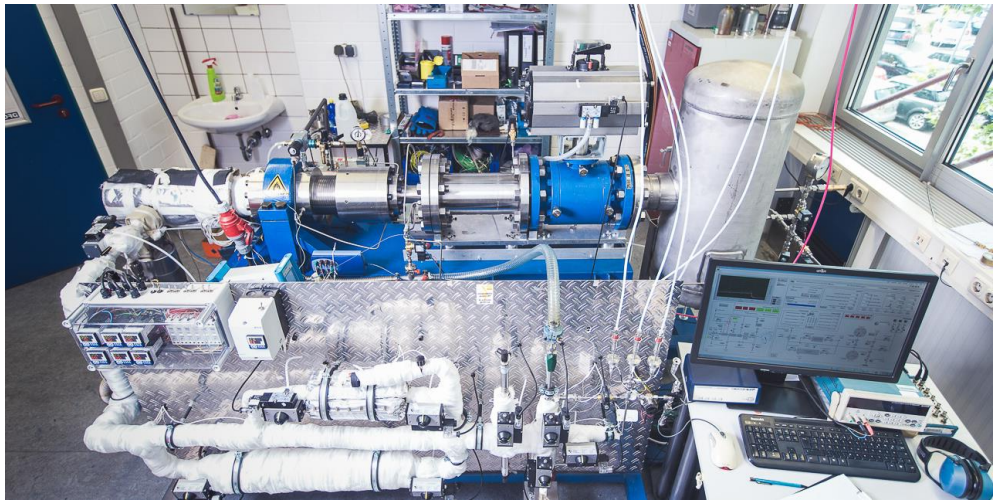


Substitution of a —(C=O)H group increases CH_3—O and O—H BDEs

Pelucchi et al. *Reac. Chem. Eng.* (2019), 4.3

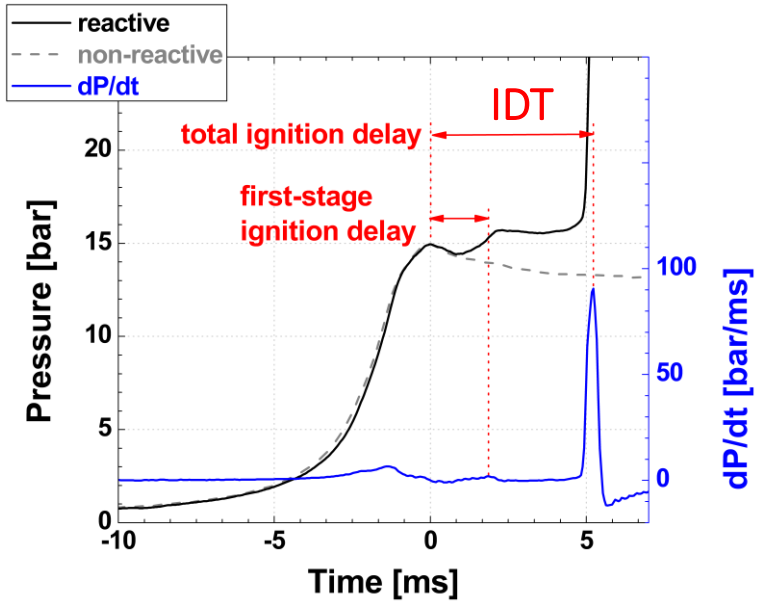
Rapid Compression Machine Experiments @ PCFC-RWTH





p=10-80 bar, IDT=5-300 ms, T=650-1100 K

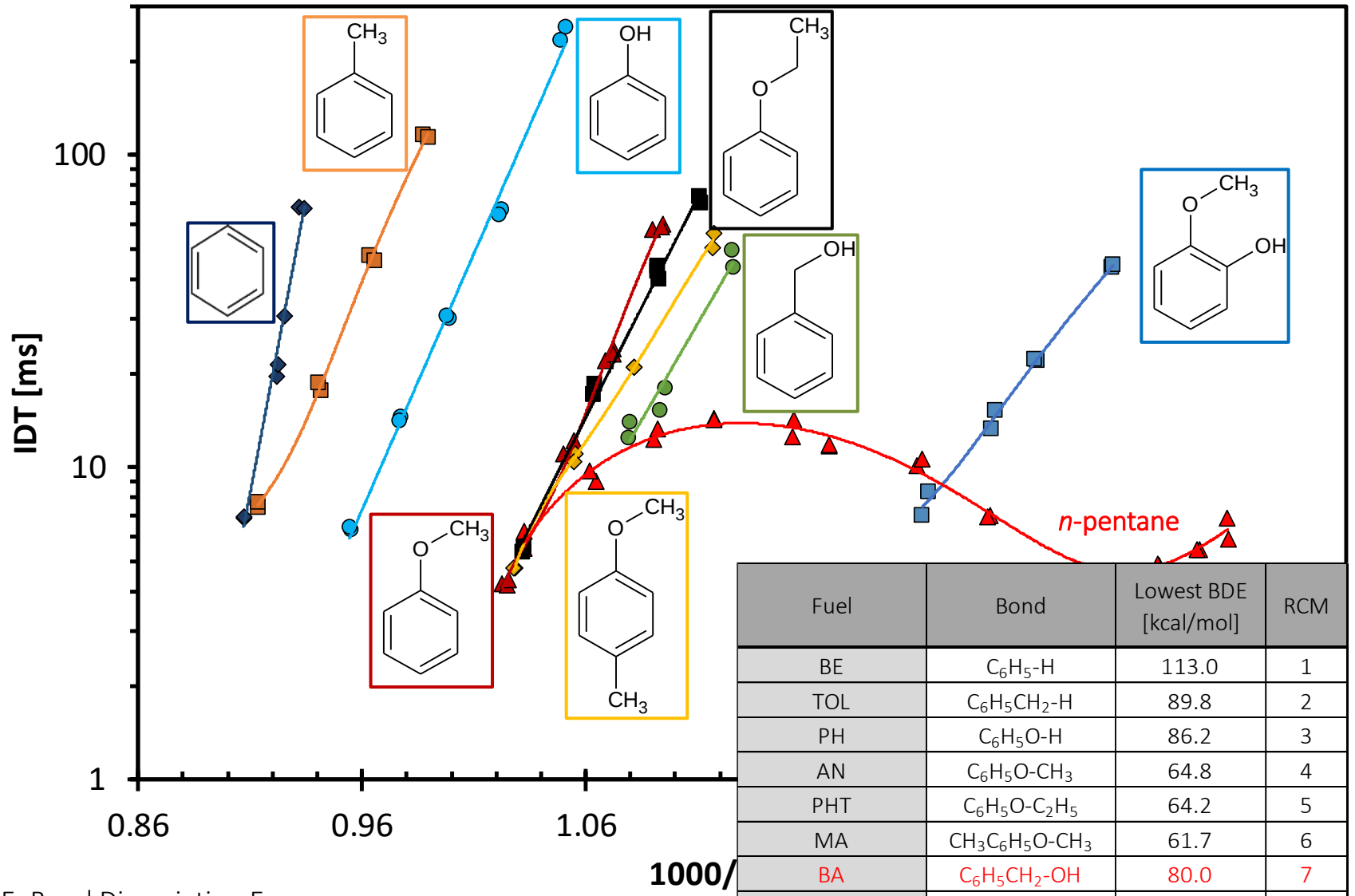
Fuel	p_c	Fuel	O_2	Ar	N_2
	bar	*mol%*			
Phenetol (PHT)	10, 20	2.1	20.6	31.0	46.3
4-Methylanisole (MA)	10, 20	2.0	20.6	31.0	46.4
Guaiacol (GA)	10	2.6	20.5	53.9	23.0
	20	2.6	20.5	3.9	73.0
Benzyl alcohol (BA)	10, 20	2.4	20.5	3.9	73.2



- ✓ 8 datasets for **pure additives** in «air», ϕ=1.0
- ✓ 4 datasets for ***n*-pentane/additive mixtures** (80/20 mol%) in «air» ($RON_{n\text{-}C5}$=62, RON_{mix}=72-83), ϕ=1.0, p=10 bar

Rapid Compression Machine Experiments @ PCFC-RWTH

p=10 bar, ϕ=1.0



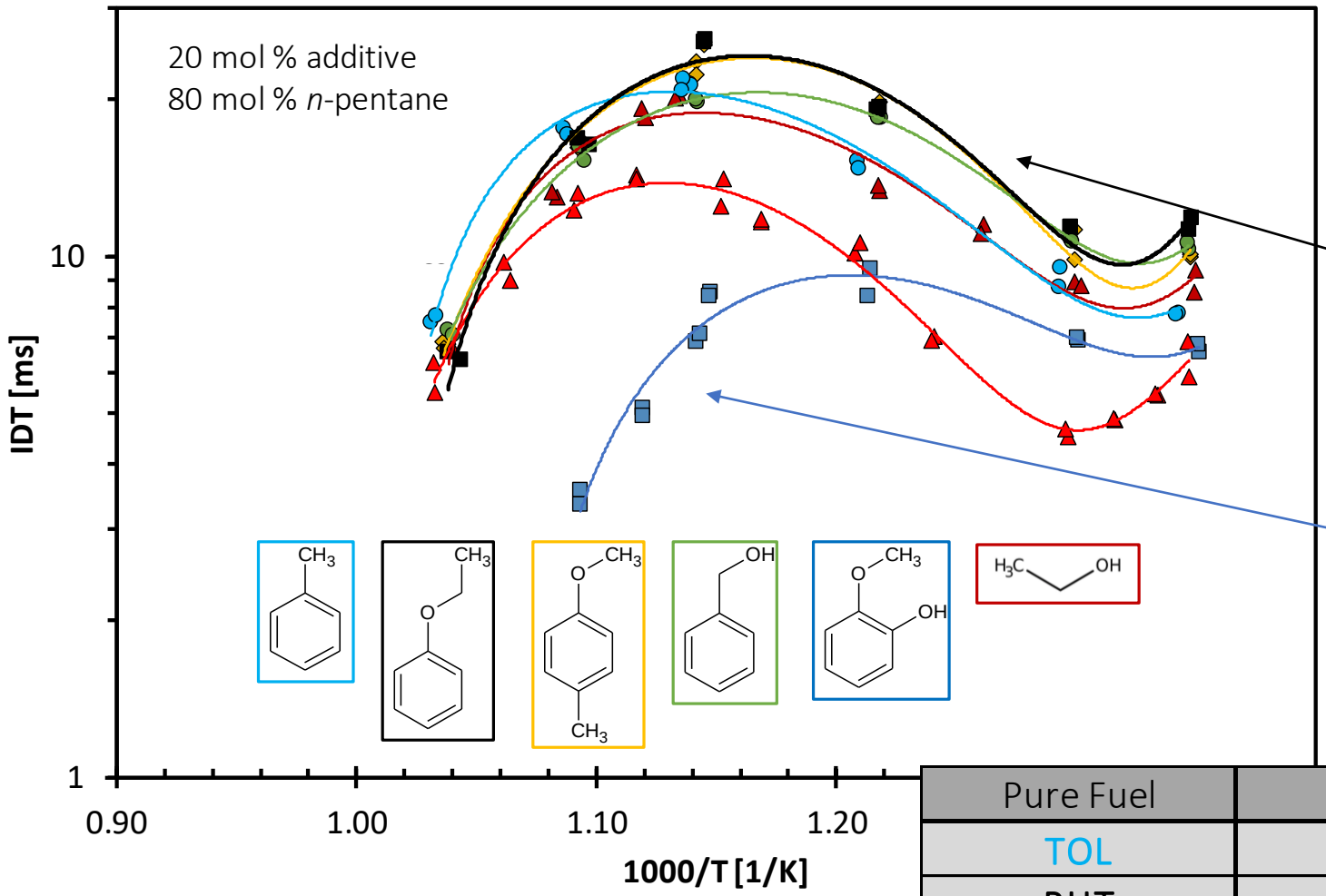
Fuel	Bond	Lowest BDE [kcal/mol]	RCM
BE	C_6H_5-H	113.0	1
TOL	$C_6H_5CH_2$-H	89.8	2
PH	C_6H_5O-H	86.2	3
AN	C_6H_5O-CH_3	64.8	4
PHT	C_6H_5O-C_2H_5	64.2	5
MA	$CH_3C_6H_5O$-CH_3	61.7	6
BA	$C_6H_5CH_2$-OH	80.0	7
GA	HOC_6H_5O-CH_3	57.2	8

Slowest

Fastest

BDE=Bond Dissociation Energy

Rapid Compression Machine Experiments @ PCFC-RWTH



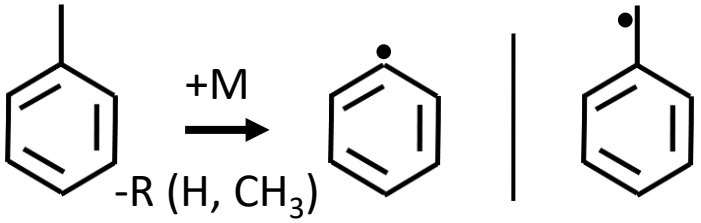
Pure Fuel	Mixture
TOL	PHT
PHT	MA
MA	TOL
BA	BA
GA	GA

Slowest

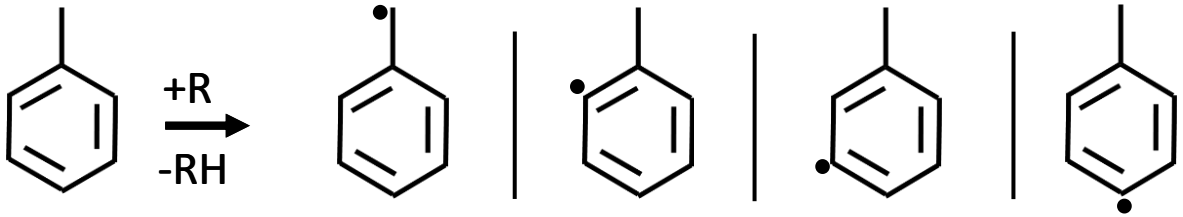
Fastest

Thus we started to develop detailed kinetic models for the best (PHT-Phenetol) and the worst (GA-Guaiacol) candidates!

Kinetic model development: Reaction Classes (example: toluene)

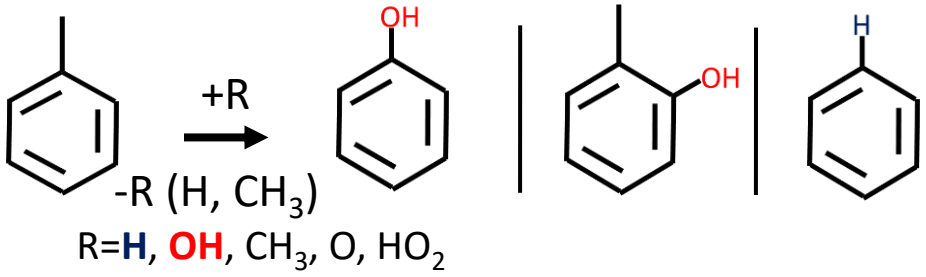


Initiation reactions



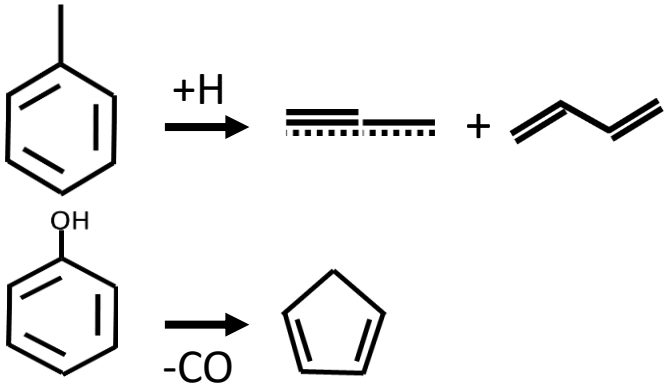
H-abstraction reactions

Pratali Maffei et al.
Submitted to *Proc. Comb. Inst.* (2020)



(Ipso-)Addition reactions

Pratali Maffei et al.
Submitted to *Proc. Comb. Inst.* (2020)



Radical addition and **decomposition** to smaller molecules (or smaller rings) *via* **ring opening**

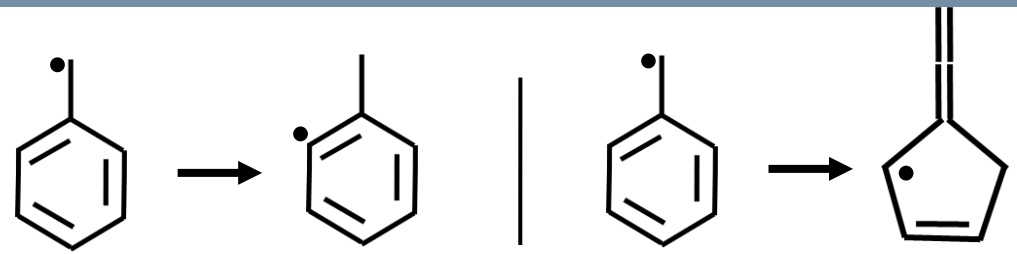
Molecular reactions

Pelucchi et al. *Phys. Chem. Chem. Phys* (2018), 20.16

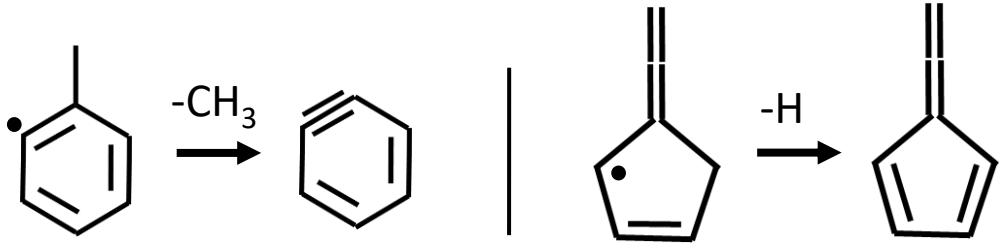
Pelucchi et al. *Reac. Chem. Eng.* (2019), 4.3

Pratali Maffei et al. *Reac. Chem. Eng.* (2020), in press

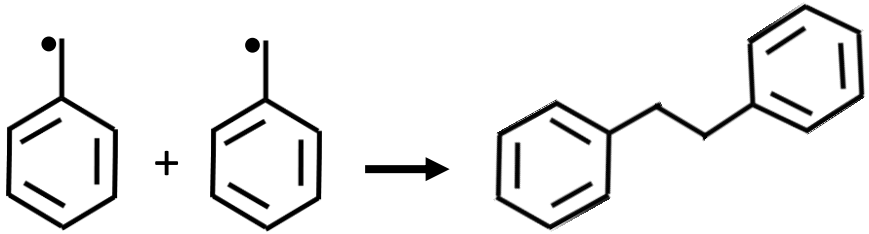
Kinetic model development: Reaction Classes (example: toluene)



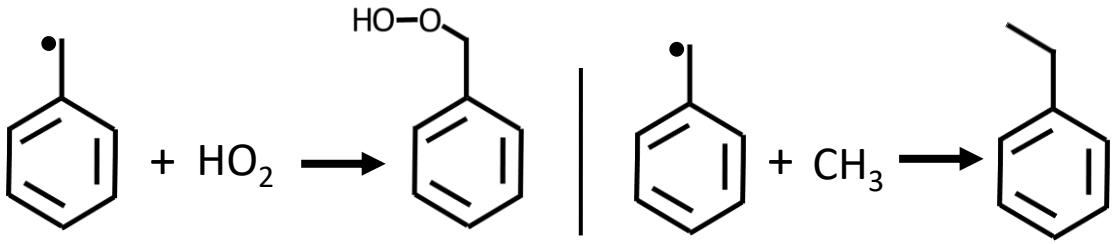
Radical isomerizations



Radical decomposition



Resonance Stabilized Radicals recombination



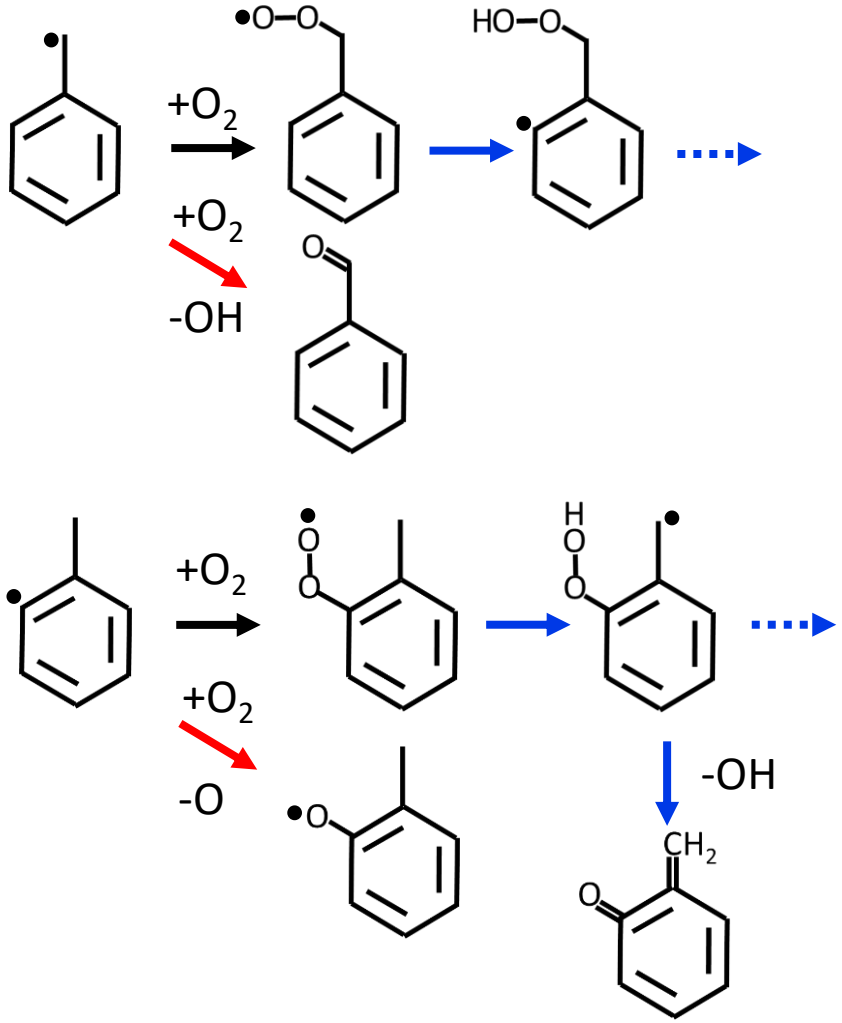
Radical recombination

Pelucchi et al. *Phys. Chem. Chem. Phys* (2018), 20.16

Pelucchi et al. *Reac. Chem. Eng.* (2019), 4.3

Pratali Maffei et al. *Reac. Chem. Eng.* (2020), in press

Kinetic model development: Reaction Classes (example: toluene)



Radical oxidation reactions

Radical addition to O_2

Radical addition and elimination (can be well skipping, and give "branching")

Peroxy radical isomerization to phenylhydroperoxy or benzylhydroperoxy radicals

Hydroperoxy radical decomposition to quinone species

Ring opening, extra addition to O_2, cyclization reactions,
da Silva et al., *J. Phys. Chem. A*, (2007)

Pelucchi et al. *Phys. Chem. Chem. Phys* (2018), 20.16

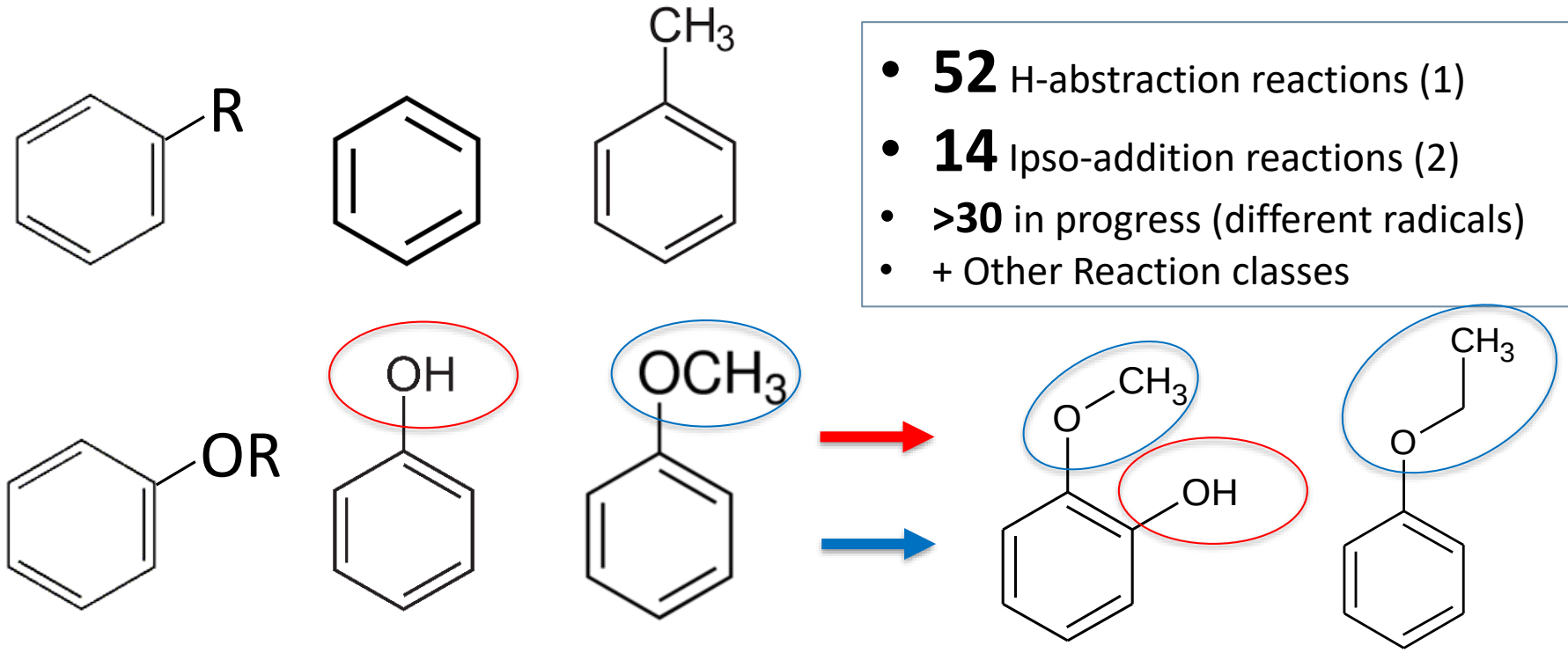
Kinetic Model Development: Rate Rules from Theoretical Calculations

1) "Rate constants for the H-abstraction reactions from mono-aromatic hydrocarbons by $\dot{H}$, $\dot{C}H_3$, $\dot{O}H$ and $^3O_2$: a systematic theoretical investigation."

*Luna Pratali Maffei, *Matteo Pelucchi, Rene Daniel Büttgen, Karl Alexander Heufer, Tiziano Faravelli, Carlo Cavallotti*

2) "Rate constants for the $\dot{H}$ ipso-addition reactions on mono-aromatic hydrocarbons with single and double OH/CH_3 substitutions: a systematic theoretical investigation."

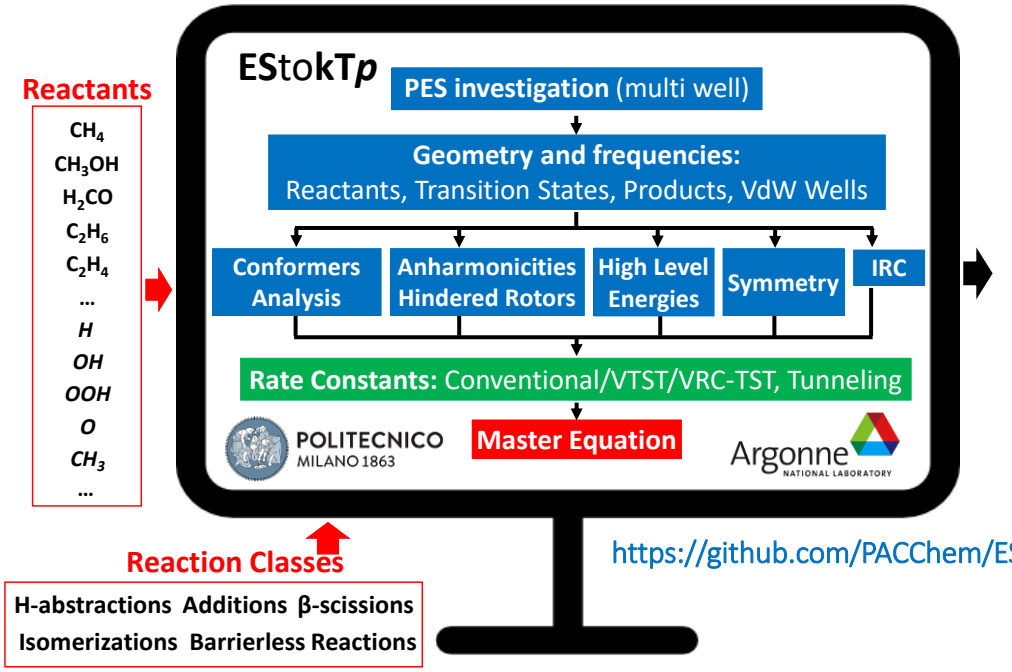
*Luna Pratali Maffei,*Matteo Pelucchi, Tiziano Faravelli, Carlo Cavallotti*



- **52** H-abstraction reactions (1)
- **14** Ipso-addition reactions (2)
- **>30** in progress (different radicals)
- + Other Reaction classes

Kinetic Model Development: Rate Rules from Theoretical Calculations

Rate constant calculation according to EStokTP protocol[1]

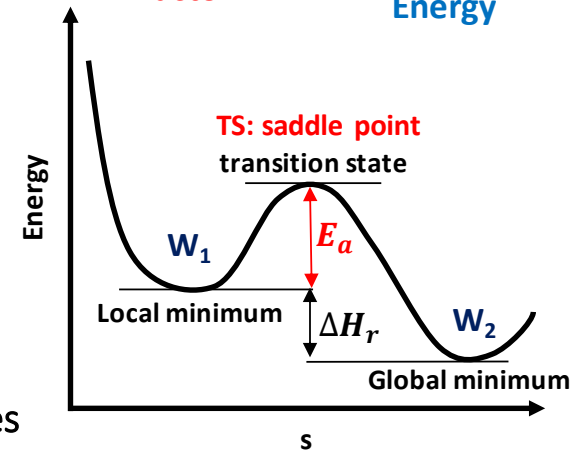


Theoretical Gas Phase Kinetics

Transition State Theory

$$k_{TST} = \kappa\left(\frac{k_B T}{h}\right)\left(\frac{Q^{\neq}}{Q^{w}}\right)\exp\left(-\frac{E_a}{RT}\right)$$

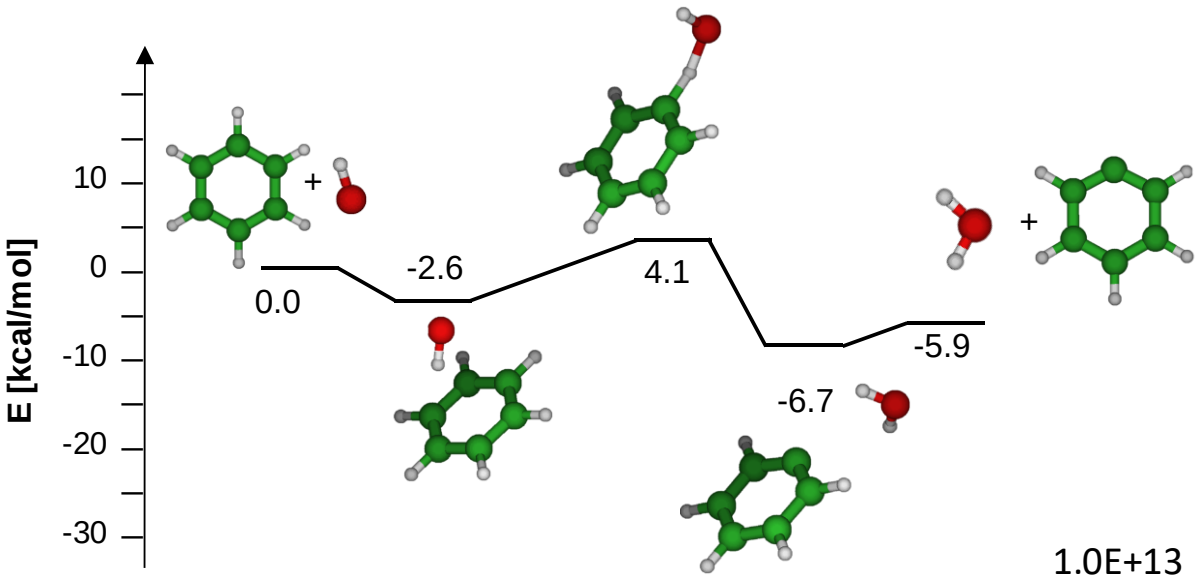
A-factor — Activation Energy

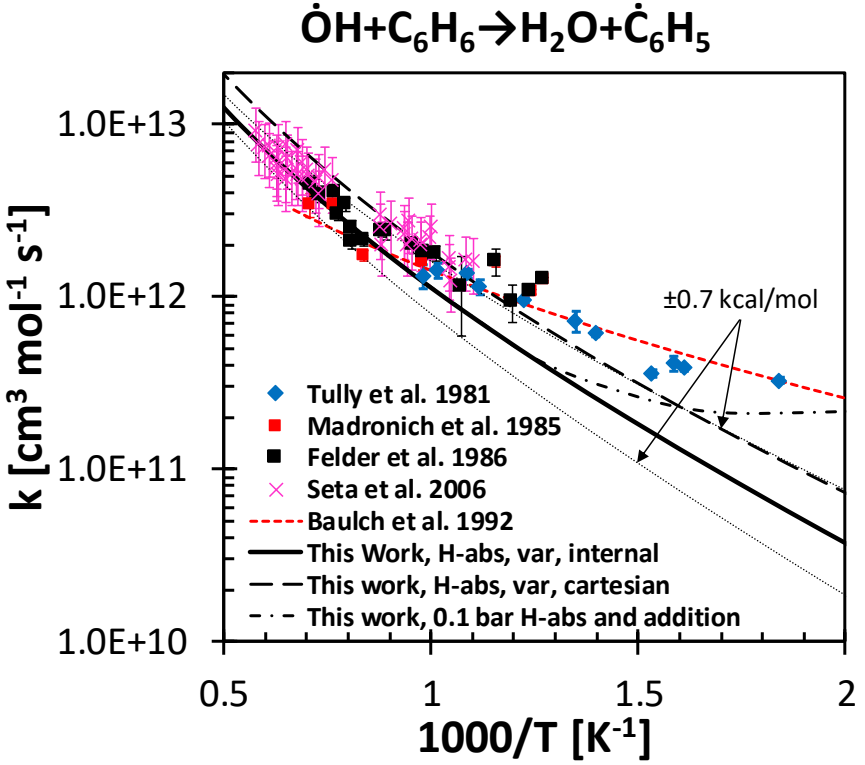


- Allows to **automatically compute rate constants** with a factor of ~2 accuracy (±0.7 kcal/mol, «chemical accuracy»)
- **Optimized routines developed and tested for different Reaction Classes**
- Different parallel jobs allow to:
  - **Investigate chemistry by Reaction Classes** (i.e. changing reactants)
  - **Assess the accuracy** of the methods for a given Reaction Class (by comparison with experimental *ks*)
  - **Derive fundamentally based Rate Rules, by analogy**

Cavallotti et al., *J. Chem. Theory Comput.*, 15.2 (2018): 1122-1145.

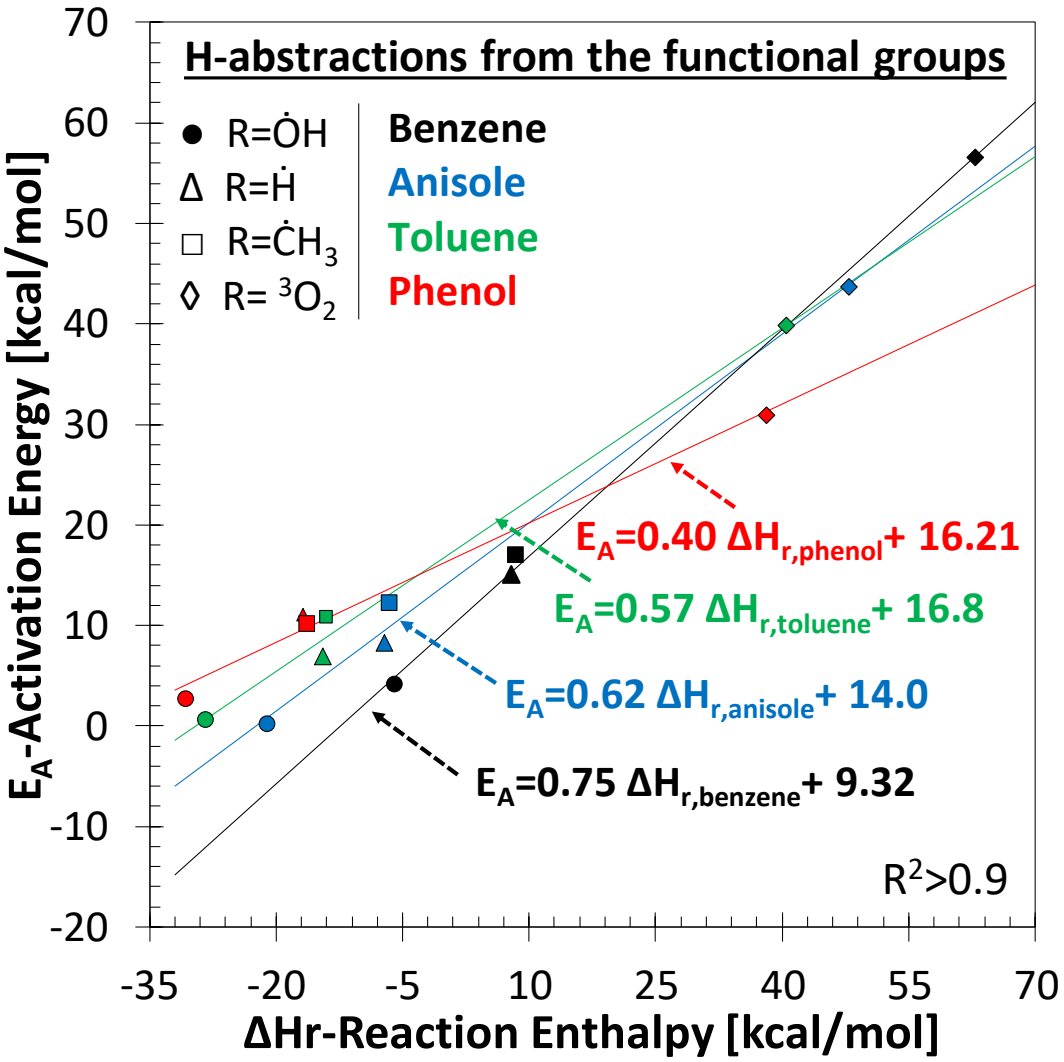
Kinetic Model Development: Rate Rules from Theoretical Calculations

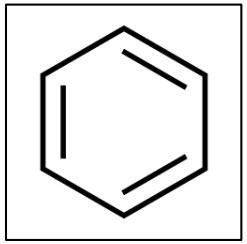


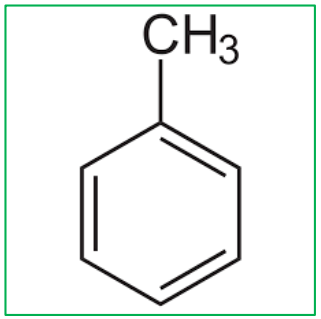


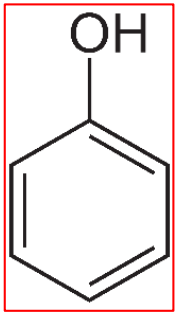
Pratali Maffei et al., Submitted to *Proc. Comb. Inst.* (2020)

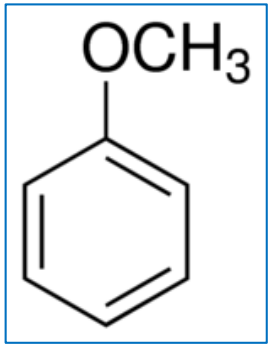
Kinetic Model Development: Rate Rules from Theoretical Calculations





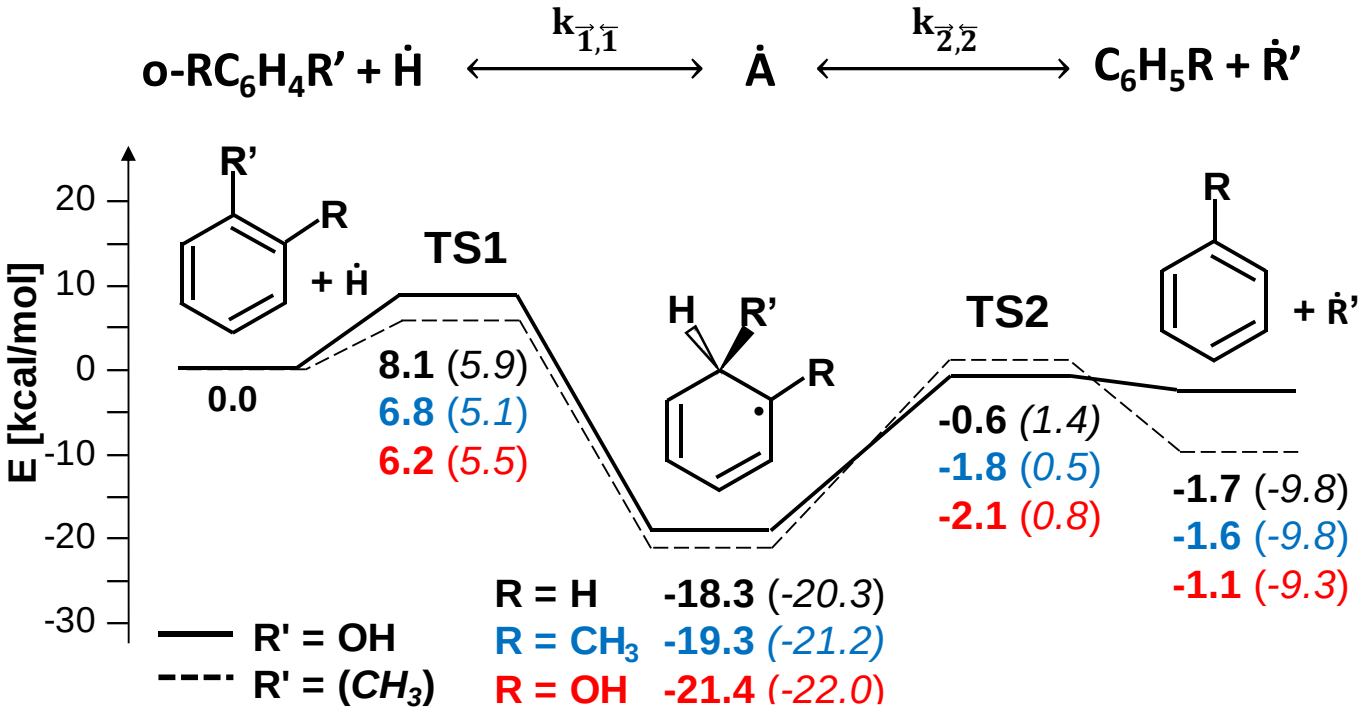




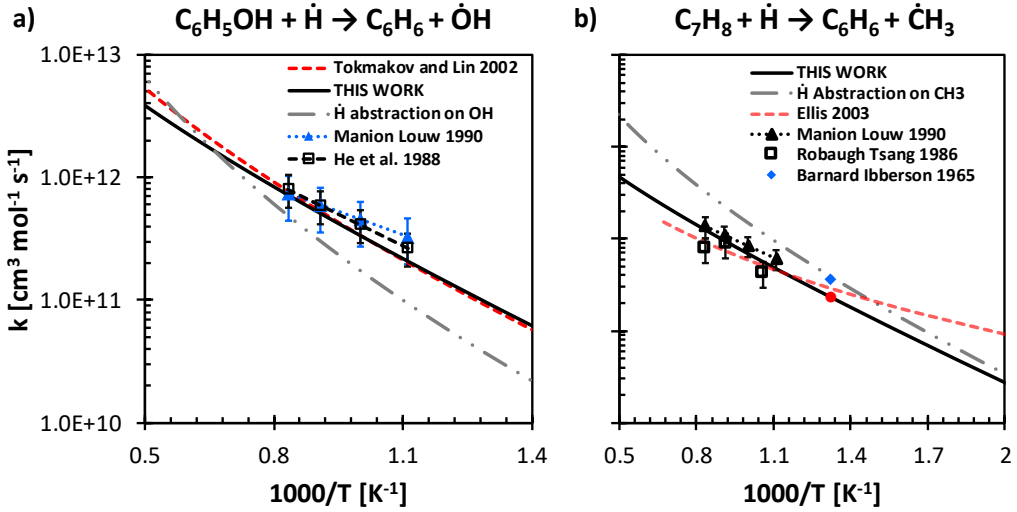


Pratali Maffei et al., Submitted to *Proc. Comb. Inst.* (2020), 1

Kinetic Model Development: Rate Rules from Theoretical Calculations



Ipso-Addition Reactions, by H

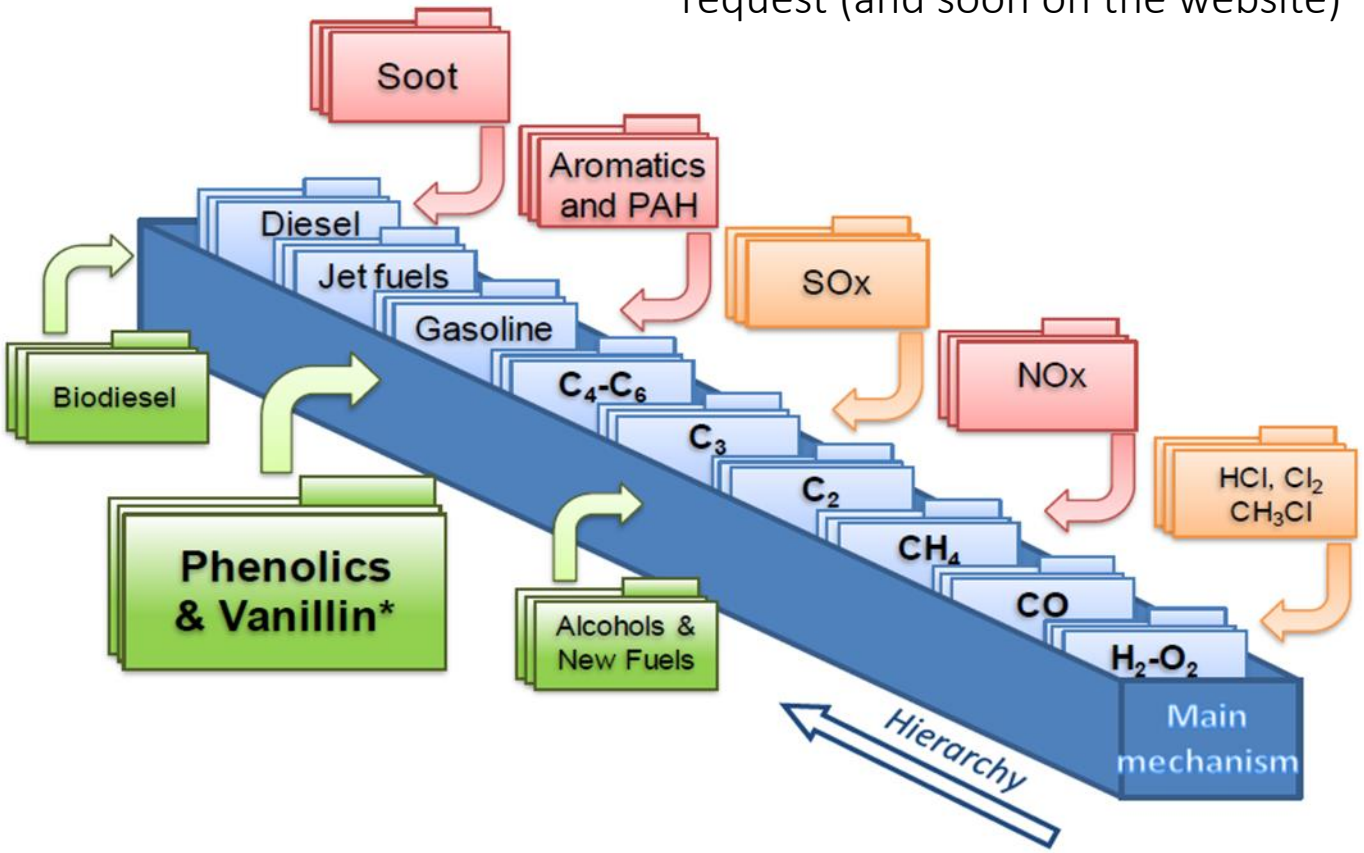


Pratali Maffei et al., Submitted to *Proc. Comb. Inst.* (2020), 2

CRECK Model Update

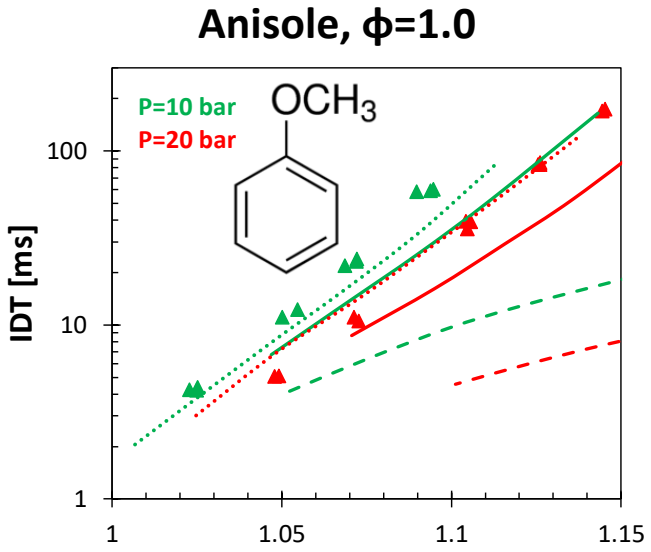
- ❑ ~600 species, ~20000 reactions
- ❑ Modularity
- ❑ Hierarchy

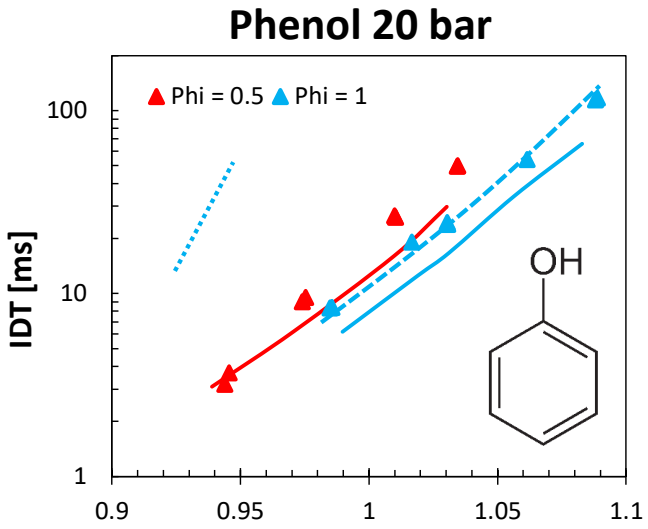
- H_2 to Heavy Fuel Oils (HT and LT) + NOx + SOOT
- Smaller subsets, obtained from the same global model, available on the website
- *Ad Hoc* **Reduced Mechanisms** available upon request (and soon on the website)

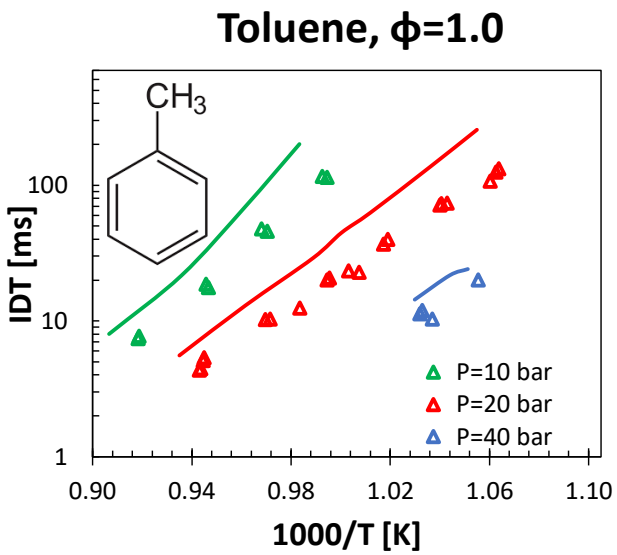


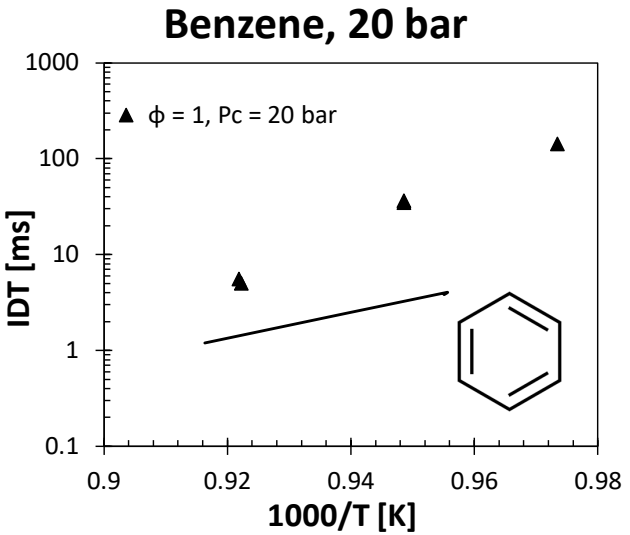
NEW! Version 1911 Available @ creckmodeling.chem.polimi.it

Model Validation, criticisms of interconnected pathways









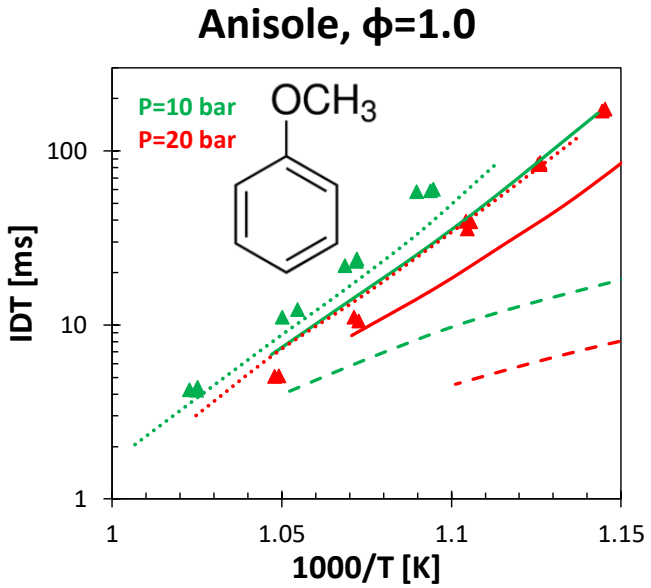
CRECK-POLIMI[1]

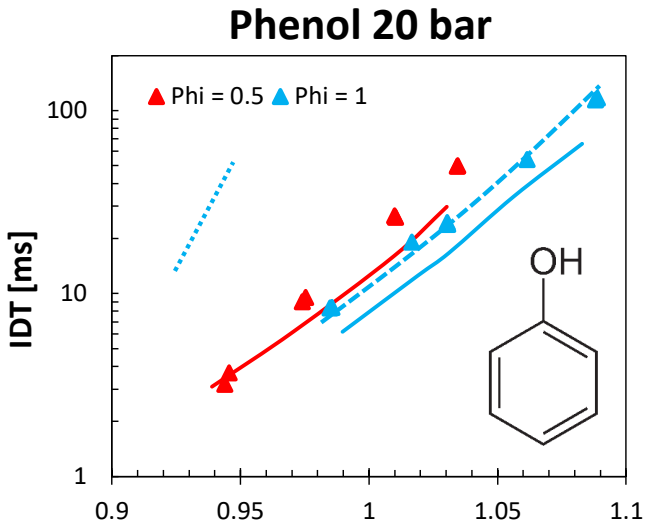
CNRS Nancy[3]

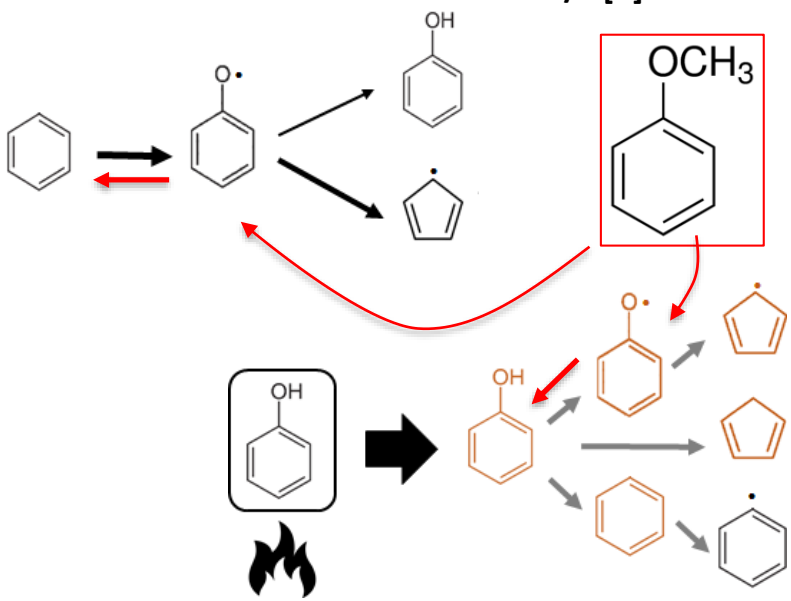
LLNL-LUND[2]

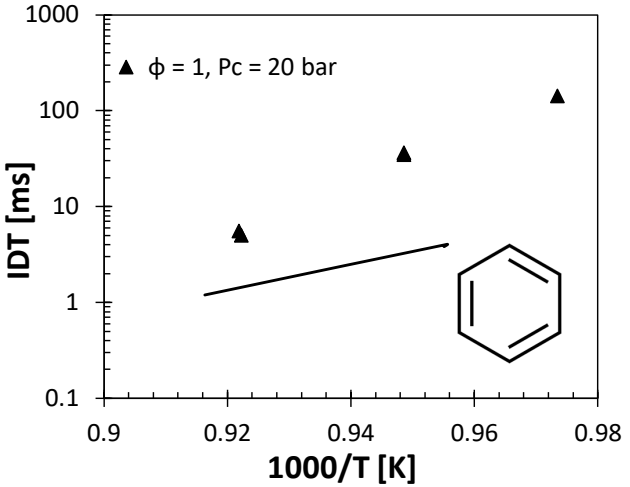
1) Pelucchi et al., *Reac. Chem. Eng. 4.3 (2019)* | 2) Wagnon et al., *Combust. Flame 189 (2018)* |3) Nowakowska et al., *Combust. Flame 161.6 (2014)*

Model Validation, criticisms of interconnected pathways









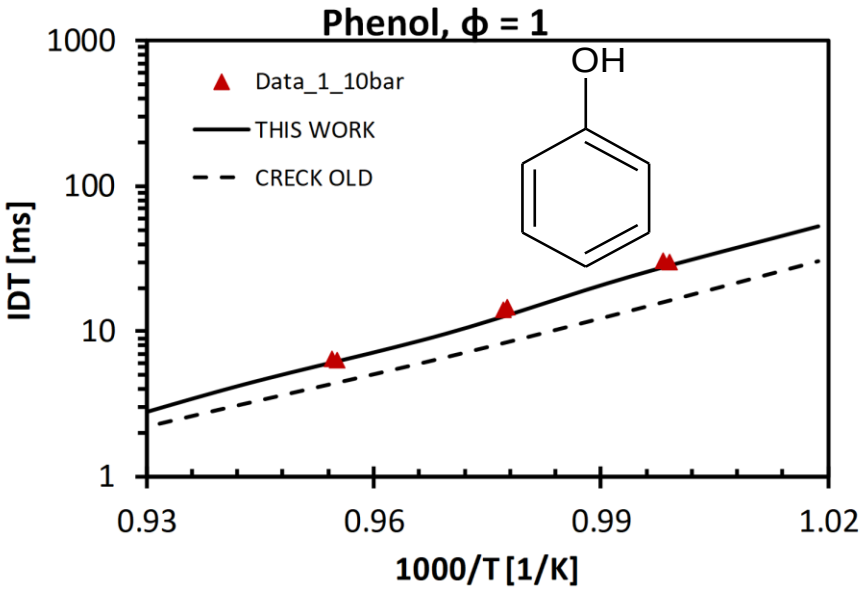
CRECK-POLIMI[1]

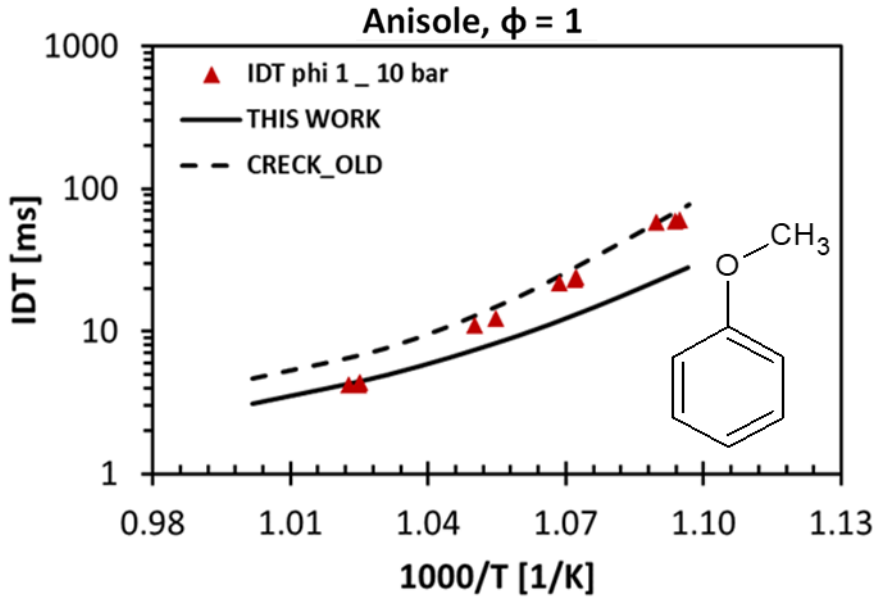
LLNL-LUND[2]

CNRS Nancy[3]

1) Pelucchi et al., *Reac. Chem. Eng. 4.3 (2019)* | 2) Wagnon et al., *Combust. Flame 189 (2018)* |3) Nowakowska et al., *Combust. Flame 161.6 (2014)*

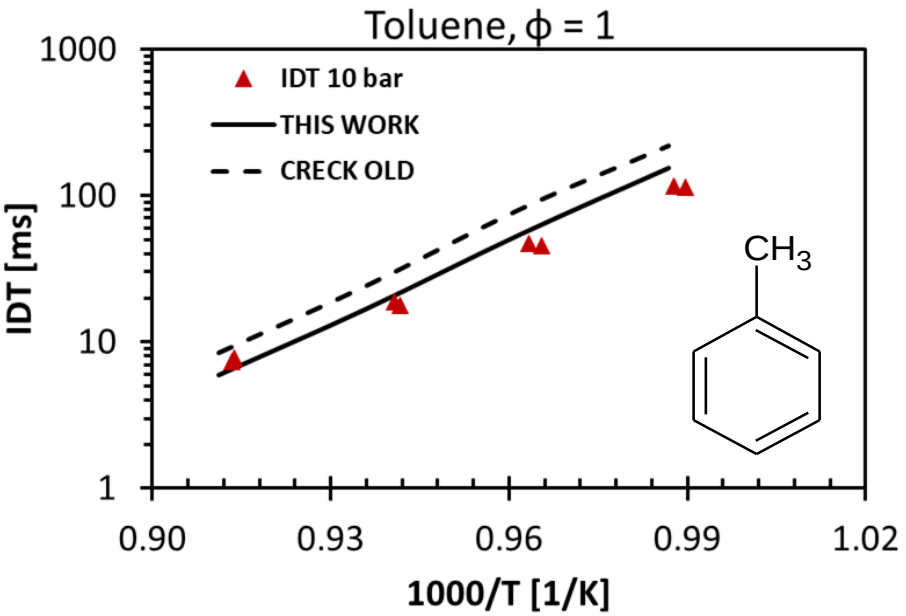
Model Validation: Toluene, Phenol and Anisole



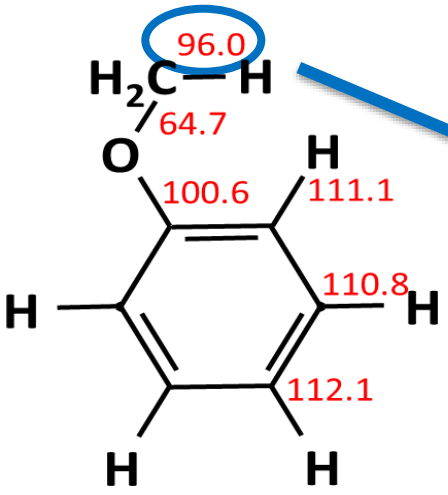


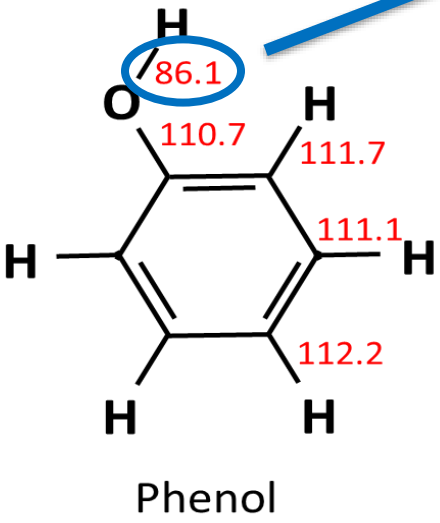
- **Good model performances** after update with new sets of rate constants from theory
- **IDT targets** include Shock Tubes and RCM (p=10-40 bar, T=800-1400 K)
- Other targets include **speciation measurements** in ideal reactors, and flame speeds

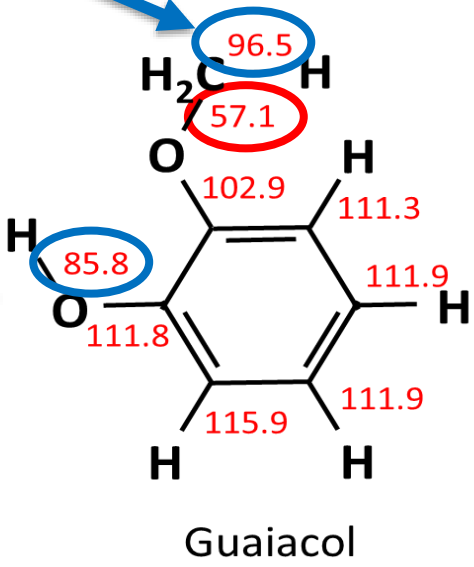
→Solid basis to develop a model for Guaiacol and Phenetol



Kinetic Model Development: Analogy



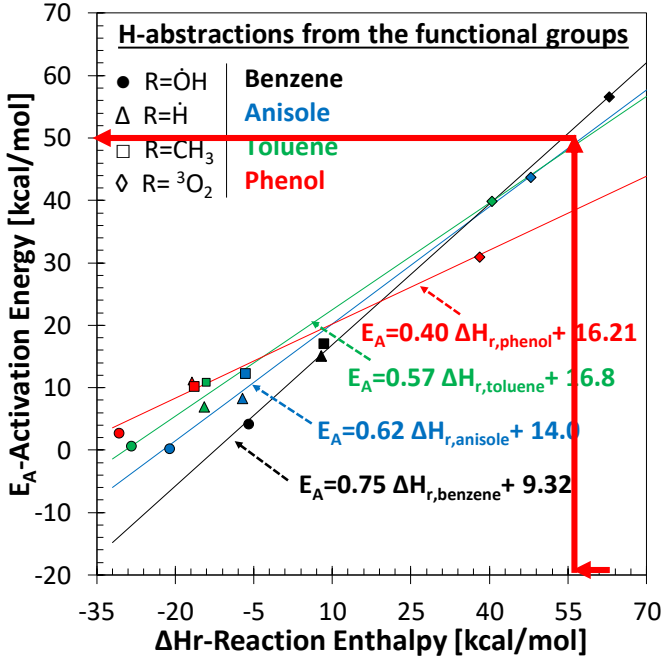




Difference in BDE (+0.5 kcal/mol) within the expected accuracy (±0.7 kcal/mol) of theory,

→reasonable to assume that the rate constants involving this bond will be similar to that of anisole

If Δ > than expected accuracy rate parameters can be derived to account for a different reactivity



Kinetic Model Development: Guaiacol from Anisole and Phenol!

1) GUAIACOL = RCATEC + CH3

Unimolecular Initiation

2) GUAIACOL + H = RGUAIACOL + H2
3) GUAIACOL + OH = RGUAIACOL + H2O
4) GUAIACOL + CH3 = RGUAIACOL + CH4
5) GUAIACOL + O2 = RGUAIACOL + HO2 (dup)
6) GUAIACOL + H = RGUAIACOLC + H2
7) GUAIACOL + OH = RGUAIACOLC + H2O
8) GUAIACOL + CH3 = RGUAIACOLC + CH4
9) GUAIACOL + O2 = RGUAIACOLC + HO2

H-abstraction reactions

10) H + GUAIACOL = CATECHOL + CH3
11) H + GUAIACOL = OH + CRESOL
12) H + GUAIACOL = OH + C6H5OCH3
13) H + GUAIACOL=C6H5OH + CH3O
14) OH + GUAIACOL=CATECHOL + CH3O
15) CH3 + GUAIACOL = CRESOL + CH3O

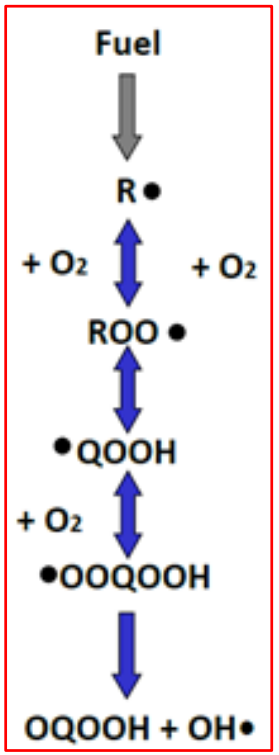
Ipso-additions

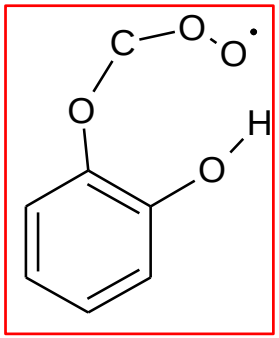
16) GUAIACOL => CO + CH2CO + C4H6
17) RGUAIACOL => RGUAIACOLC
18) RGUAIACOLC => CH2O + C6H4OH
19) RGUAIACOL => CO + CH2O + C5H5

Radical decomposition and isomerizations

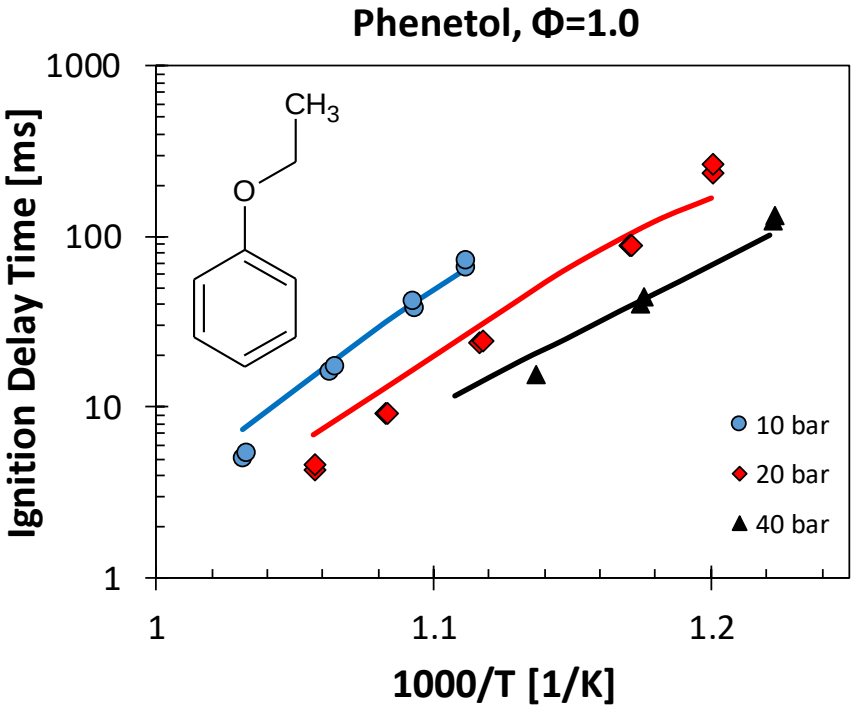
20) RGUAIACOLC + O2 = RGUAIACOLC-OO
21) RGUAIACOLC-OO = RGUAIACOLC-QOOH
22) RGUAIACOLC-QOOH => C4H4 + CH2O + 2CO + OH

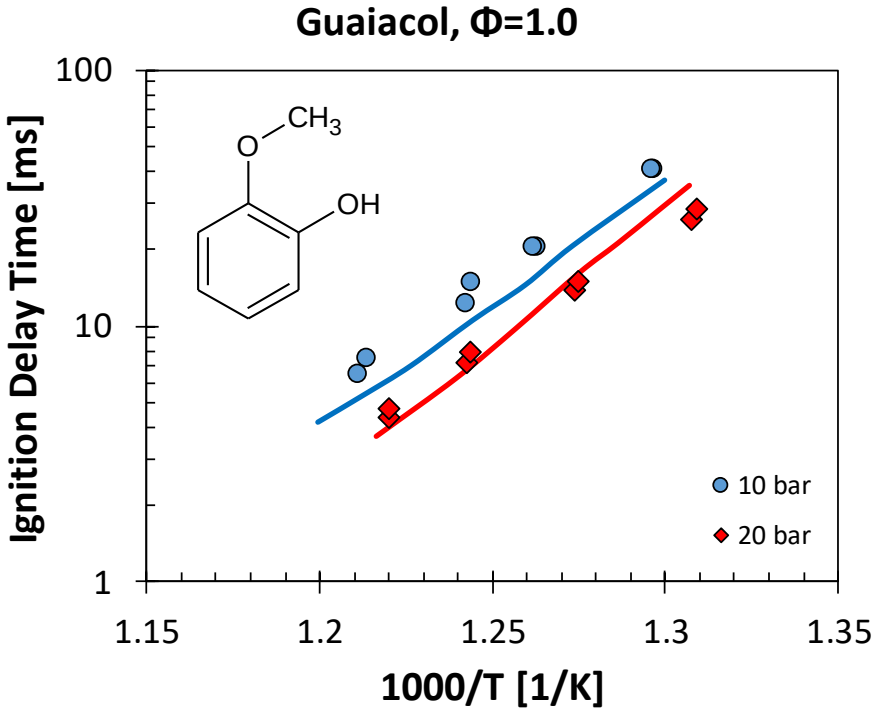
Radical oxidation reactions (LT-like)



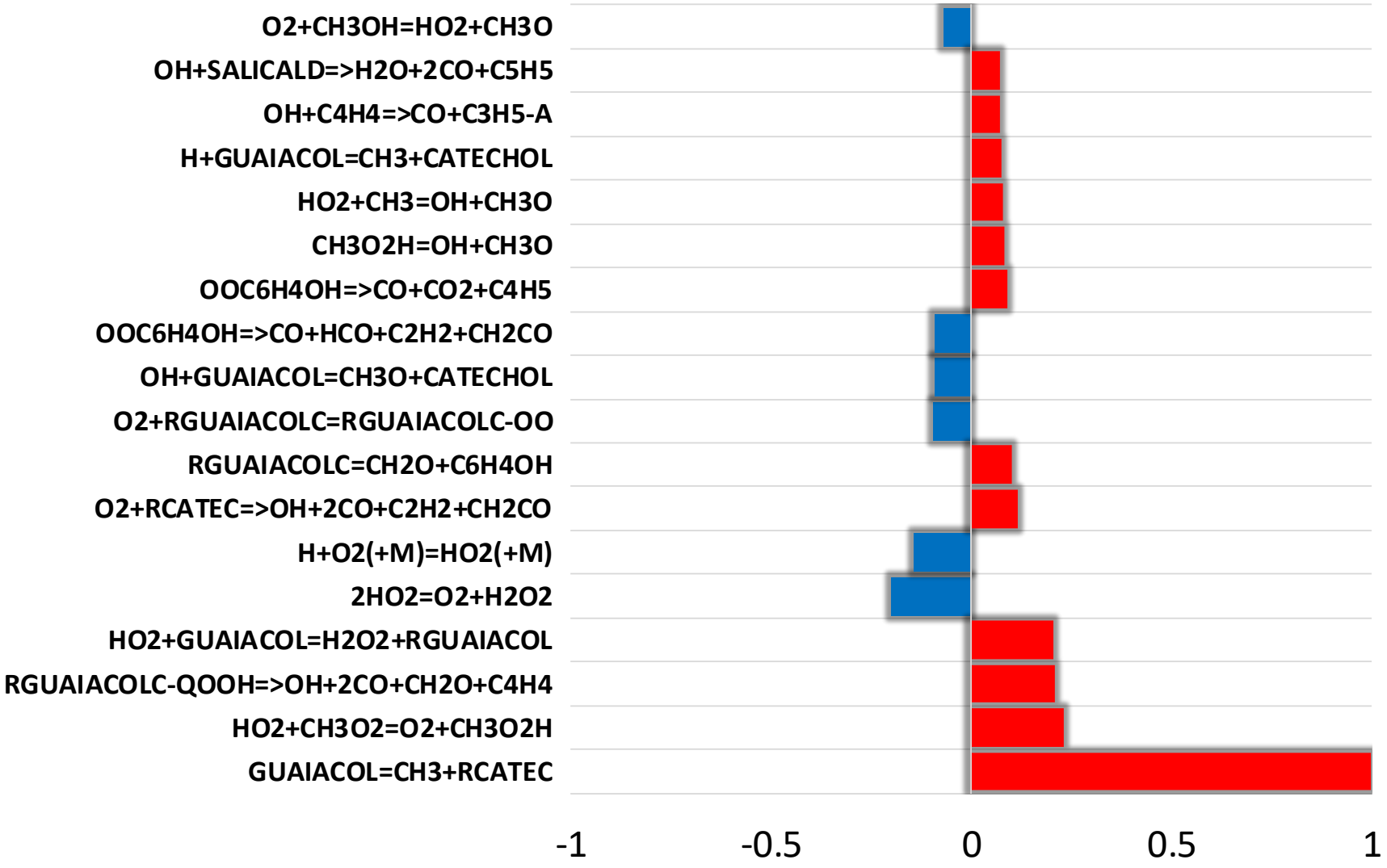


Model Validation: Guaiacol and Phenetol

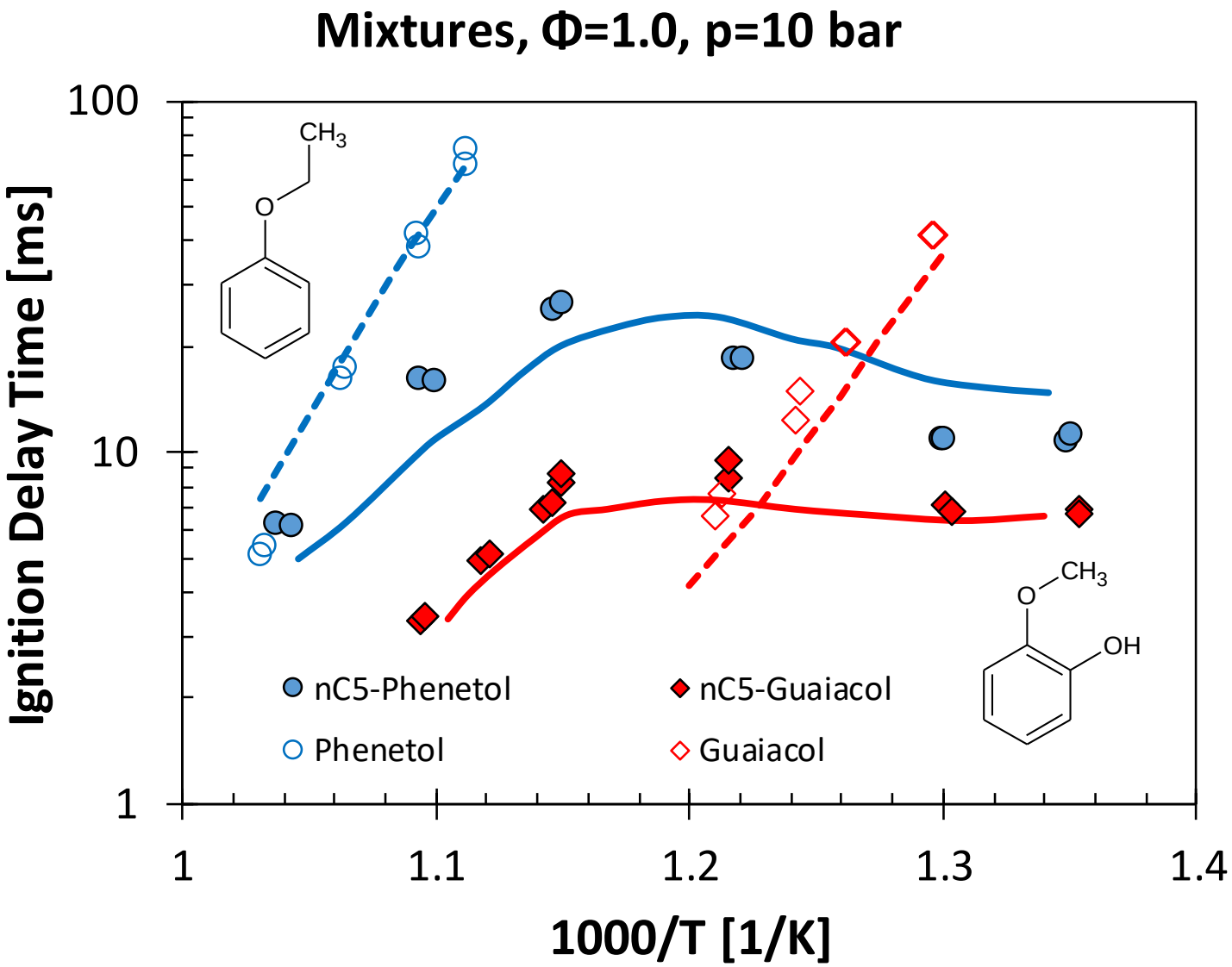




Kinetic analysis



Model Validation: OAHs/*n*-pentane



Conclusions and future work

- Why mono-aromatic and oxygenated mono-aromatic hydrocarbons combustion chemistry?
  - Promising anti-knocking additives (impact on PAH/SOOT to be investigated) from biomass conversion
  - Reference fuels (e.g. toluene, xylene…)
  - Key building blocks in PAHs and Soot Growth/Oxidation
  - Systematic definition of Reaction Classes and Rate Rules is missing from the literature
- Ignition Delay Time Measurements in Rapid Compression Machine (and Shock Tube) confirm the anti-knock potential of oxygenated aromatics and serve as a first target for kinetic models
- A first working model developed by better defining Reaction Classes and Rate Rules from theory and by analogy from an ongoing thorough revision of MAH/PAHs kinetics
- Systematic theoretical calculations are useful to define accurate rate rules,

  in particular when only limited experimental targets exist (IDT, LFS, …, ks), and no comprehensive theoretical investigations exist
- A fully theory-based approach to fuel design is achievable, but some limitations still exist
  - Model has to be working anyway (very interconnected pathways might be an issue)
  - It is a critical iterative process (develop => implement new parameters => re-validate and fix!), but it is starting to be faster (and automated)

Acknowledgements

POLITECNICO
MILANO 1863

Residue2Heat

The authors from **Politecnico di Milano** gratefully acknowledge the financial support for this research provided by the **European Union** under the **Horizon 2020** research and innovation programme (**Residue2Heat** project, G.A. No 654650).

Master students: Ing. Stefano Caruso and Ing. Gianmarco Cislaghi

RWTH AACHEN UNIVERSITY

DFG Deutsche Forschungsgemeinschaft

The authors from **PCFC RWTH Aachen** University gratefully acknowledge the **German Research Foundation (DFG)** for financial support for this research provided (HE 7599/1-1).

Contacts: matteo.pelucchi@polimi.it, creckmodeling.chem.polimi.it

The CRECK Modeling Lab

Permanent Staff


Tiziano Faravelli


Alessio Frassoldati


Alberto Cuoci


Marco Mehl


Carlo Cavallotti


Alessandro Stagni


Matteo Pelucchi

PhD Students


Andrea Bertolino
POLIMI/ULB


Giuseppe D'Alessio
POLIMI/ULB


Andrea Locaspi


Andrea Nobili


Luna Pratali Maffei


Abd Essamade Saufi

Available numerical codes and infrastructure

Linux High Performance Computing Cluster with **~700 proprietary processors located in POLIMI**

Availability of **in-house and commercial codes** for CFD and combustion kinetic calculation (ideal reactors, kinetic mechanism reduction, flames, droplet combustion, solid particle pyrolysis-gasification-combustion etc.)