Exploring the reactivity of *n*-C_4-C_6 alcohols: from JSR and RCM experiments to operating regimes in a HCCI engine

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IMPROOF Project

cost EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

CM1404 SMARTCATs

Objectives

1. **New Ignition Delay Time data for C_2-C_5 linear alcohols**
NUIG Rapid Compression Machine (T=700-925 K, p=10-30 bar)

2. **New JSR data for C_4-C_6 linear alcohols**
CNRS Jet Stirred Reactor (T=500-1100 K, p=1.06 bar)

3. **Update and extension of the POLIMI kinetic model for alcohols LT combustion**

4. **Evaluation of operability maps in HCCI engine**
n-butanol, *n*-pentanol

5. **Relevant pathways underlying the auto-ignition phenomena**

IMPROOF Project

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Introduction and Motivations

New Fuel Requirements

- **Compatible** with existing infrastructures

  (engines, distribution etc.): **ignition**, miscibility, **flame speed**, viscosity, boiling point, corrosive potential etc.
- **Cleaner**
- **Sustainable** production

Fuel	LHV (MJ/L)	RON	MON	CN
Gasoline	~30-33	88-98	80-88	n.d.
Diesel	~35	n.d.	n.d.	40-55
Ethanol	21.4	109	90	n.d.
n-butanol	26.9	98	85	12
n-pentanol	28.5	80	74	20
n-hexanol	29.3	56	46	24

Sarathy et al. (*Prog. Ener. Combust. Sci.*, 2014) and Kalghatgi (*Int. J. Engine Res.*, 2014)

New Fuels

Today (% v/v)

Ethanol: 5-85% in Gasoline

Tested

n-butanol: 13-26% in Gasoline
up to 24% in Diesel

n-pentanol: 10-30% in Diesel

Trends

Increasing Biofuel content

Co-Design of Fuels and Engines

Alcohols show promising physical and chemical properties!

Ignition Delay Time Measurements in RCM: *n*-butanol and *n*-pentanol

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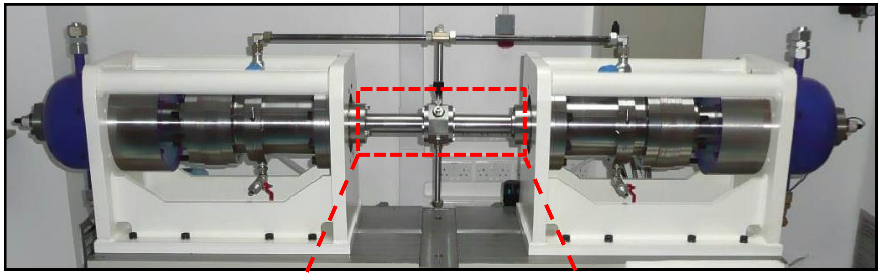
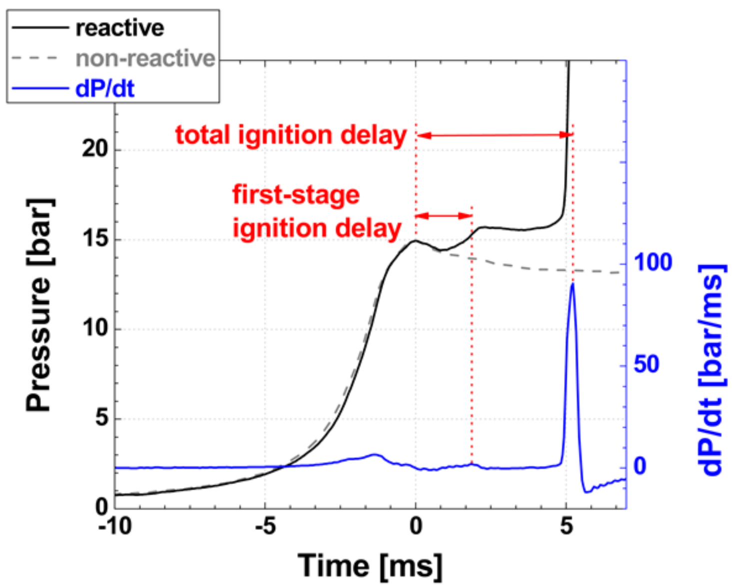
Rapid Compression Machine



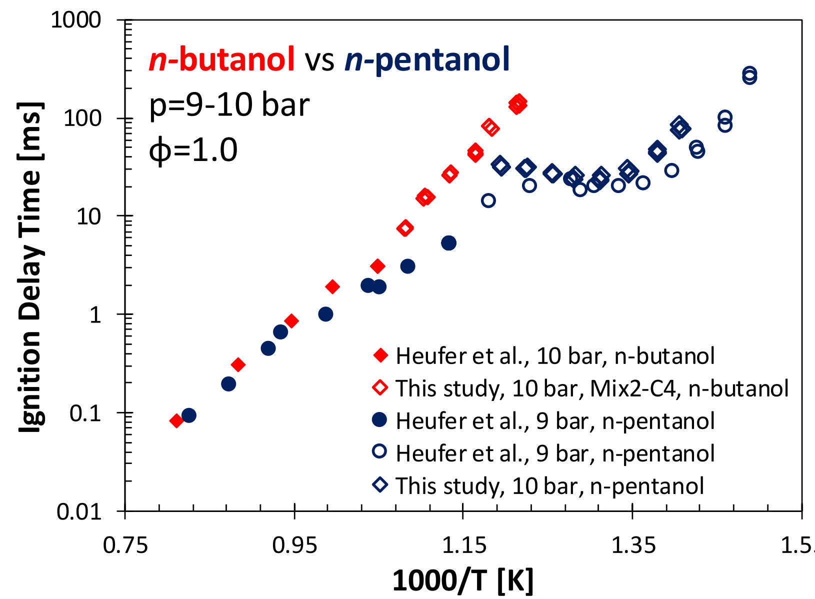
piston motion



Fuel/air, Φ=1.0, mole %

n-butanol						
Mixture	**Fuel**	**O_2**	**N_2**	**Ar**	**CO_2**	**P[bar]**
1-C_4	3.38	20.29	68.70	7.63	0.00	30
2-C_4	3.38	20.28	15.26	61.09	0.00	10
3-C_4	3.39	20.36	53.61	0.00	22.63	30
***n*-pentanol**						
1-C_5	2.72	20.43	76.85	0.00	0.00	10
2-C_4	2.72	20.43	38.42	38.42	0.00	10

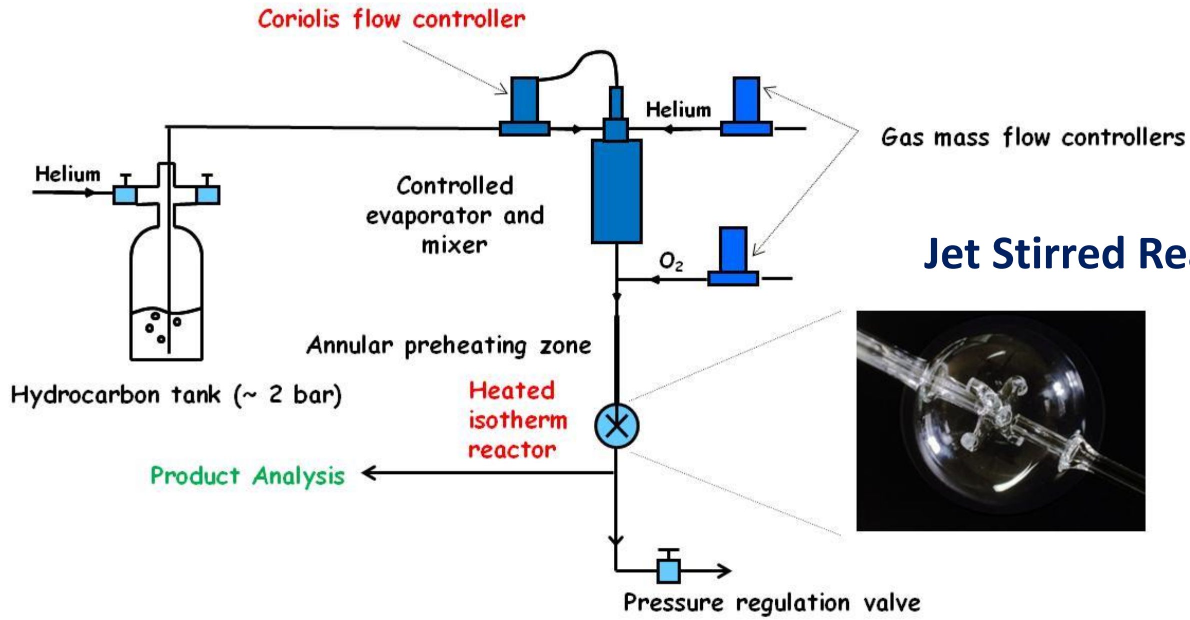
Pelucchi et al. *SAE Int. J. Engine*, 2017

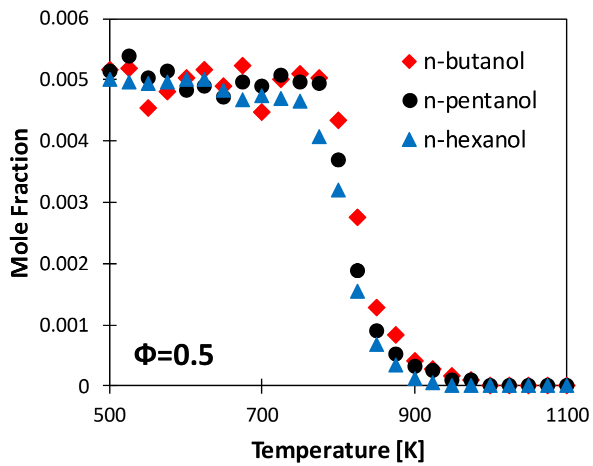


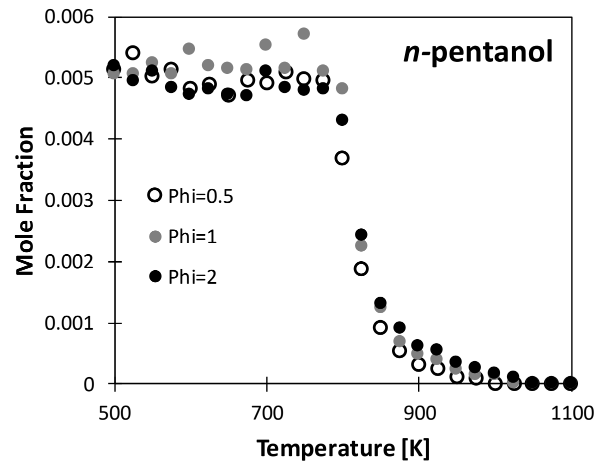
Heufer et al. *Proc Combust Inst*, 2013

Species Measurements in JSR: *n*-butanol and *n*-pentanol

0.5% fuel/O_2/He mixtures (*n*-butanol, *n*-pentanol); Φ=0.5, 1.0, 2.0; p=1.06 bar; τ=2 s.

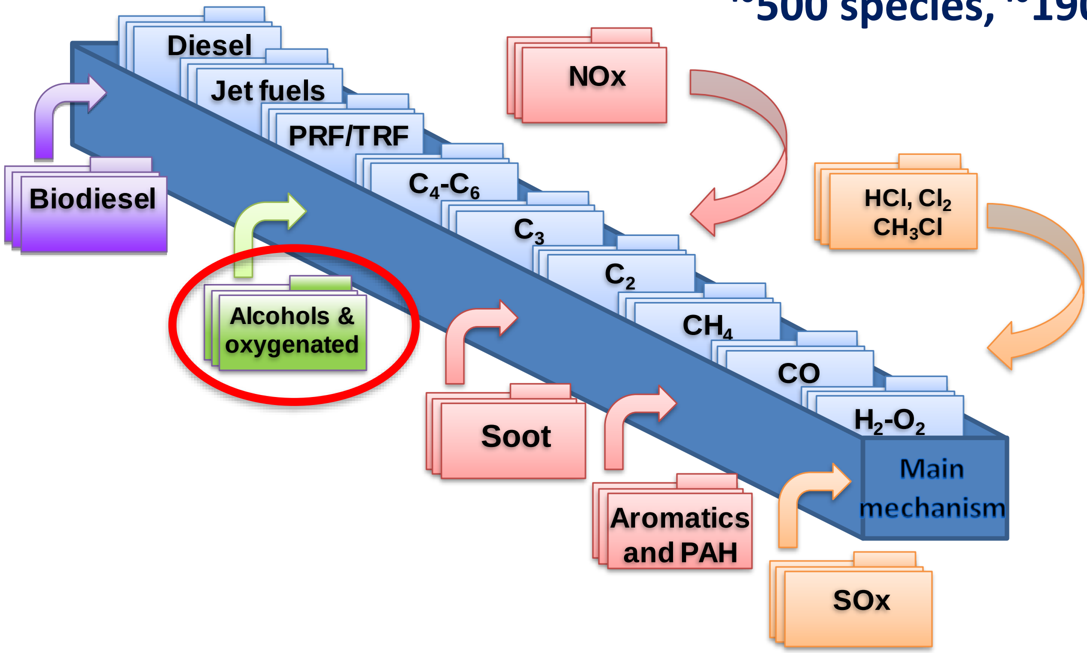






POLIMI Kinetic Mechanism: alcohols module and recent updates

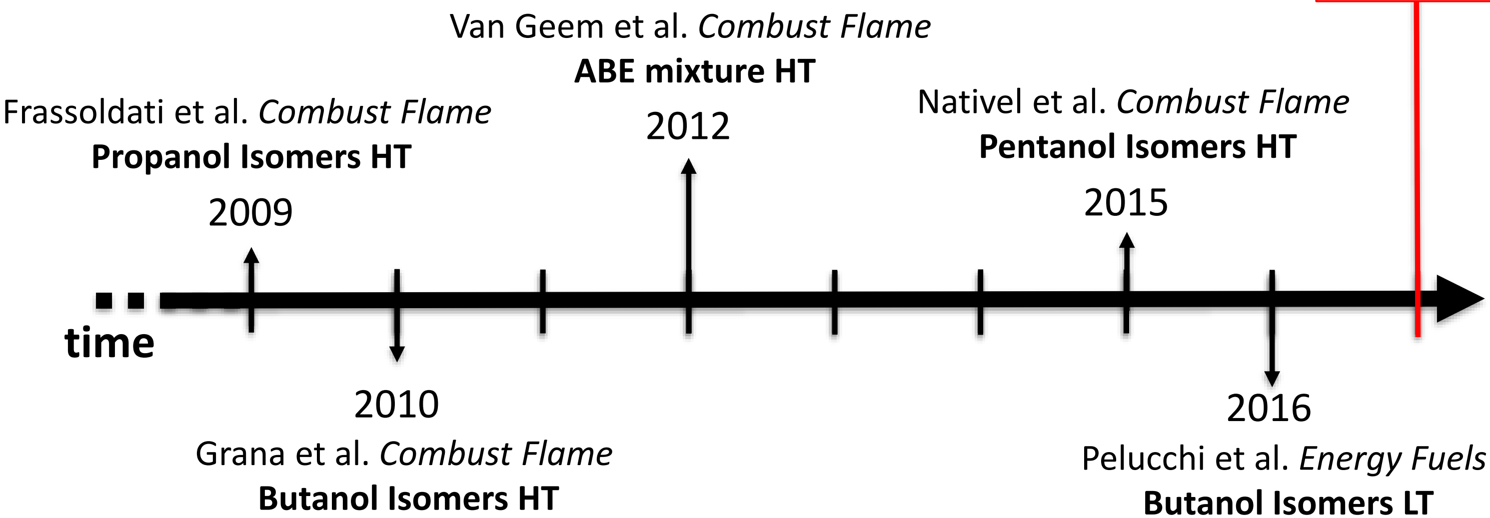
~500 species, ~19000 reactions



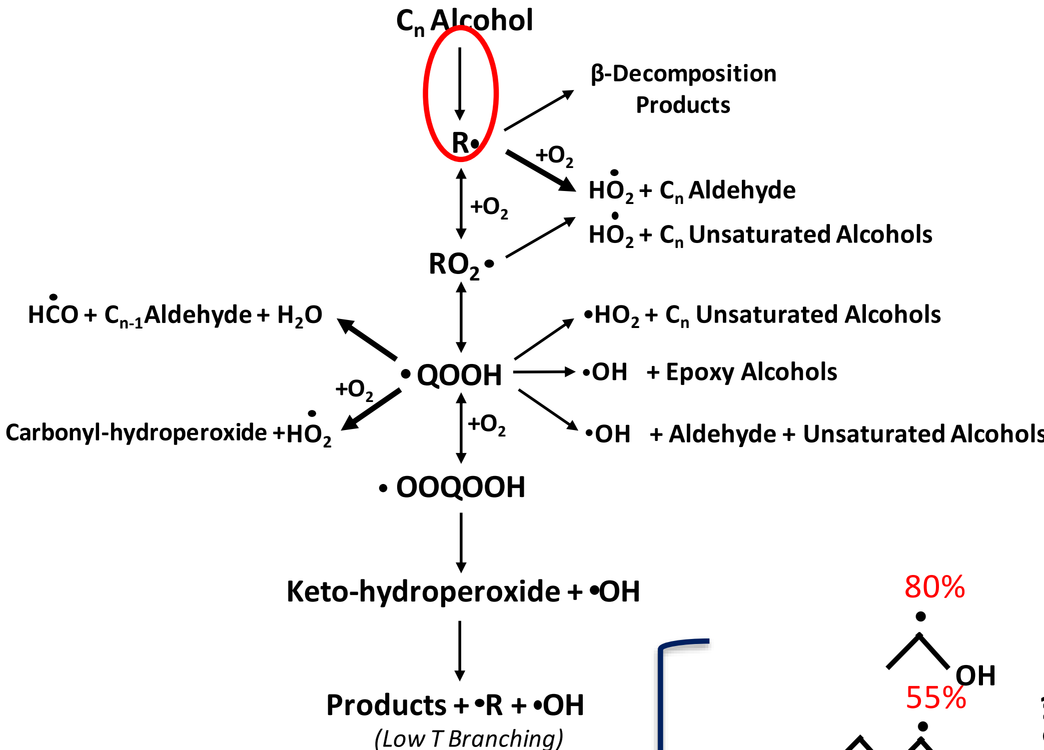
2017

- Implementation of NUIG C_0-C_2 mech*
- **C_2-C_6 alcohols LT extension and revision**

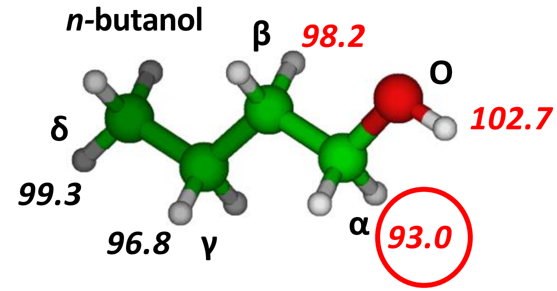
*Keromnes et al. Combust Flame 2013
Metcalfe et al. *Int. J. Chem. Kin. 2013*
Burke et al. *Combust Flame 2014*



Low Temperature Oxidation Pathways



G4 BDE @ 298 K

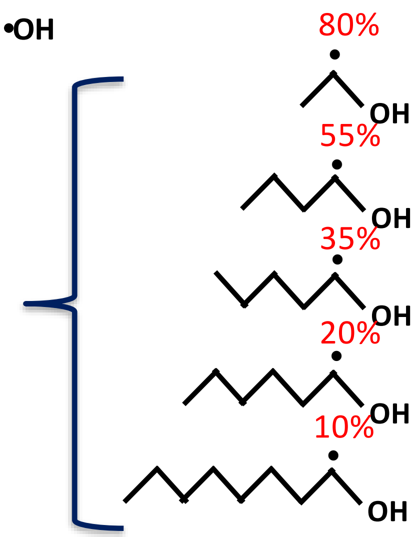


Cδ--Cγ--Cβ--Cα--OH

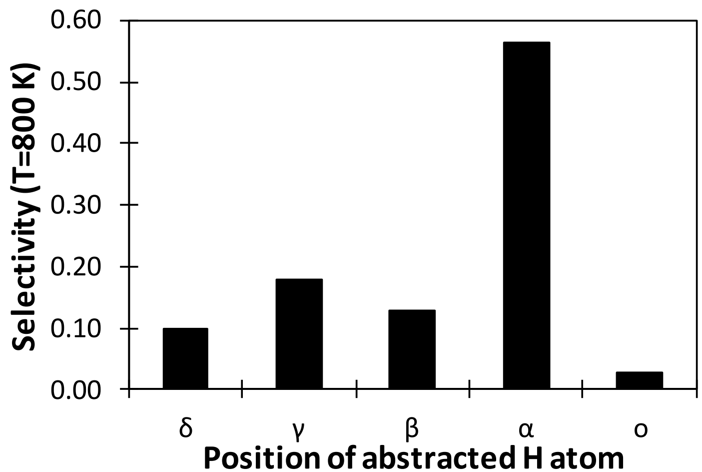
Alkane-like Alcohol-specific

C_n alcohol → C_n alkane

for increasing n

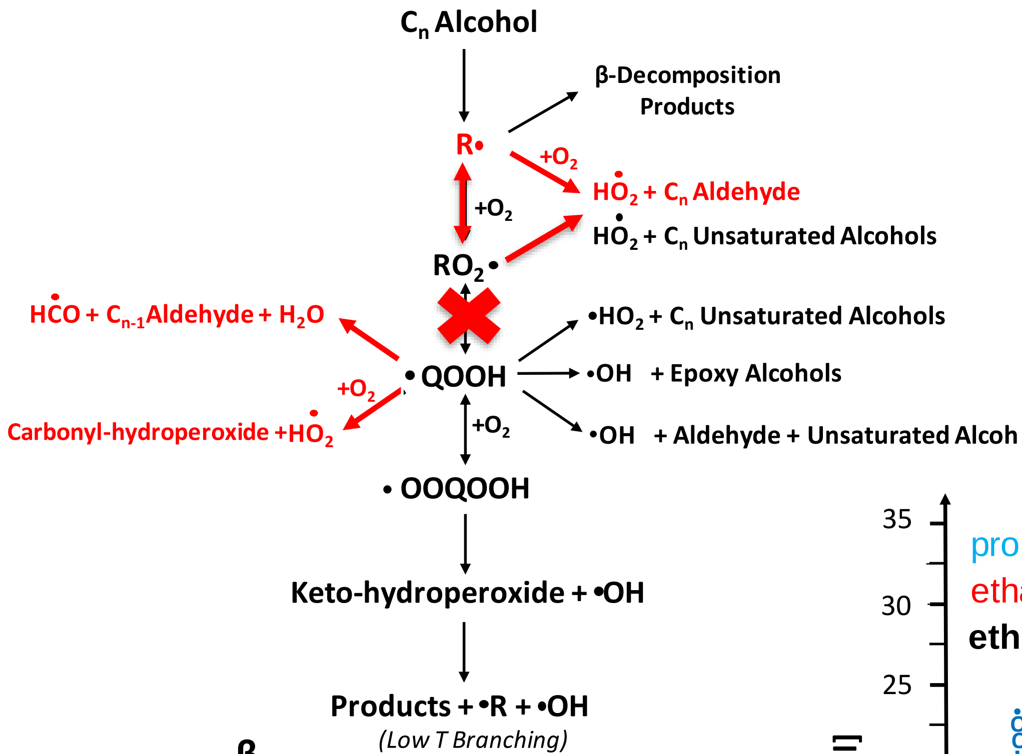


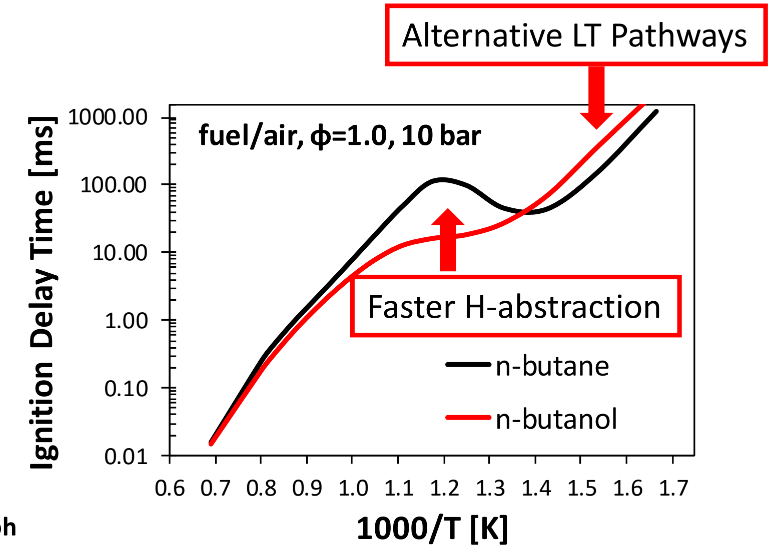
OH + n-butanol = H_2O + R

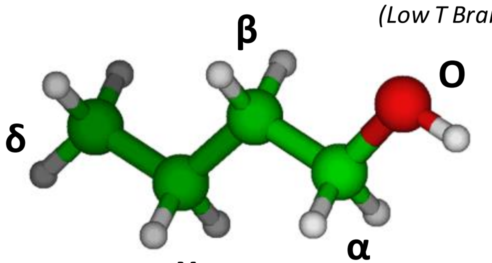


Kinetic model of *n*-butanol and *n*-pentanol LT combustion

Low Temperature Oxidation Pathways

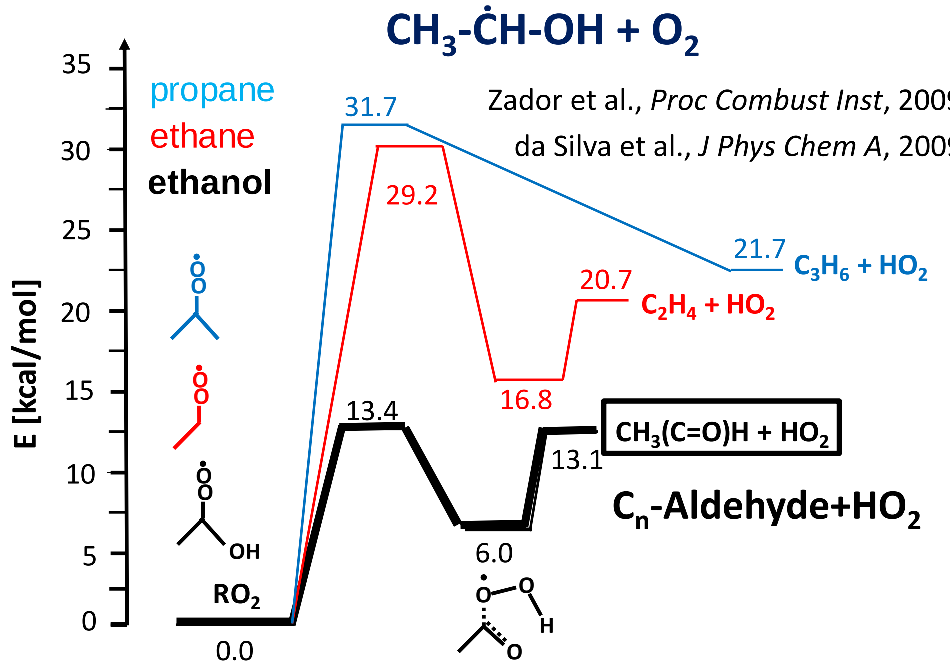




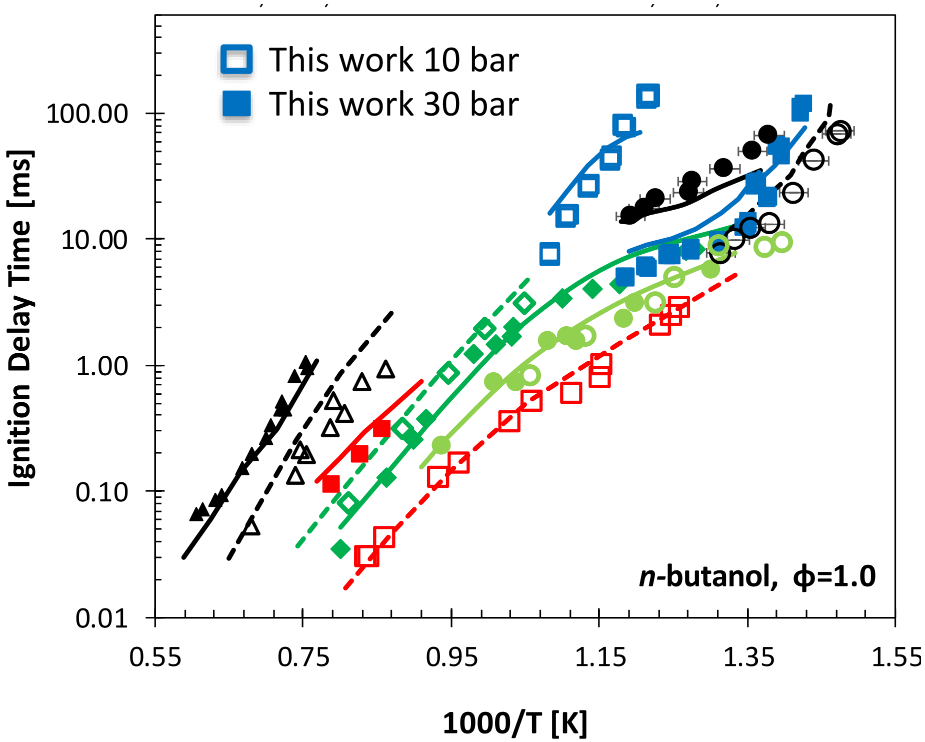


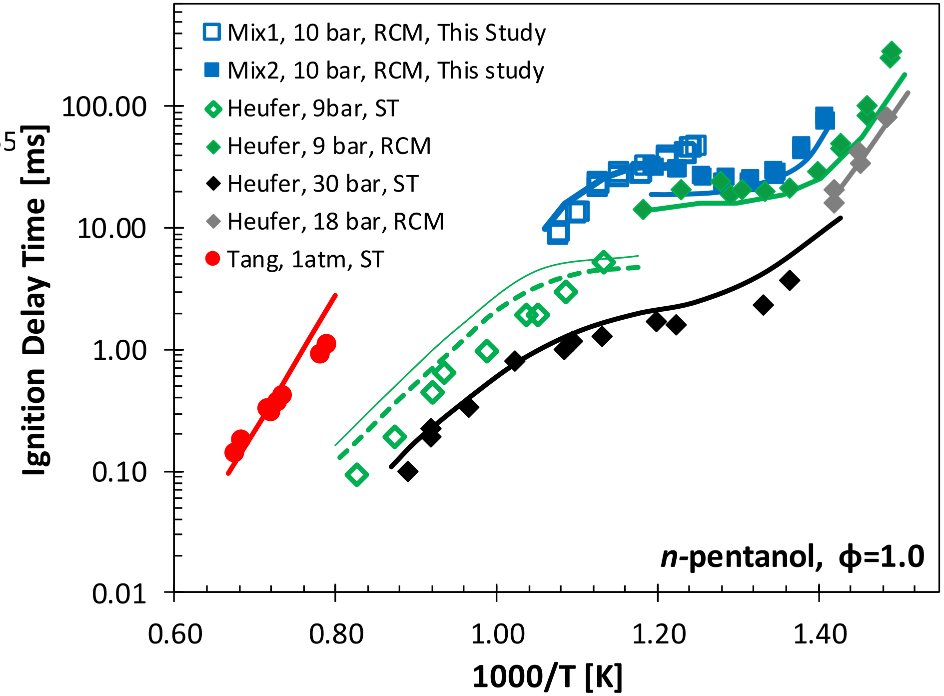
Cδ--Cγ--Cβ--Cα--OH

Alkane-like Alcohol-specific

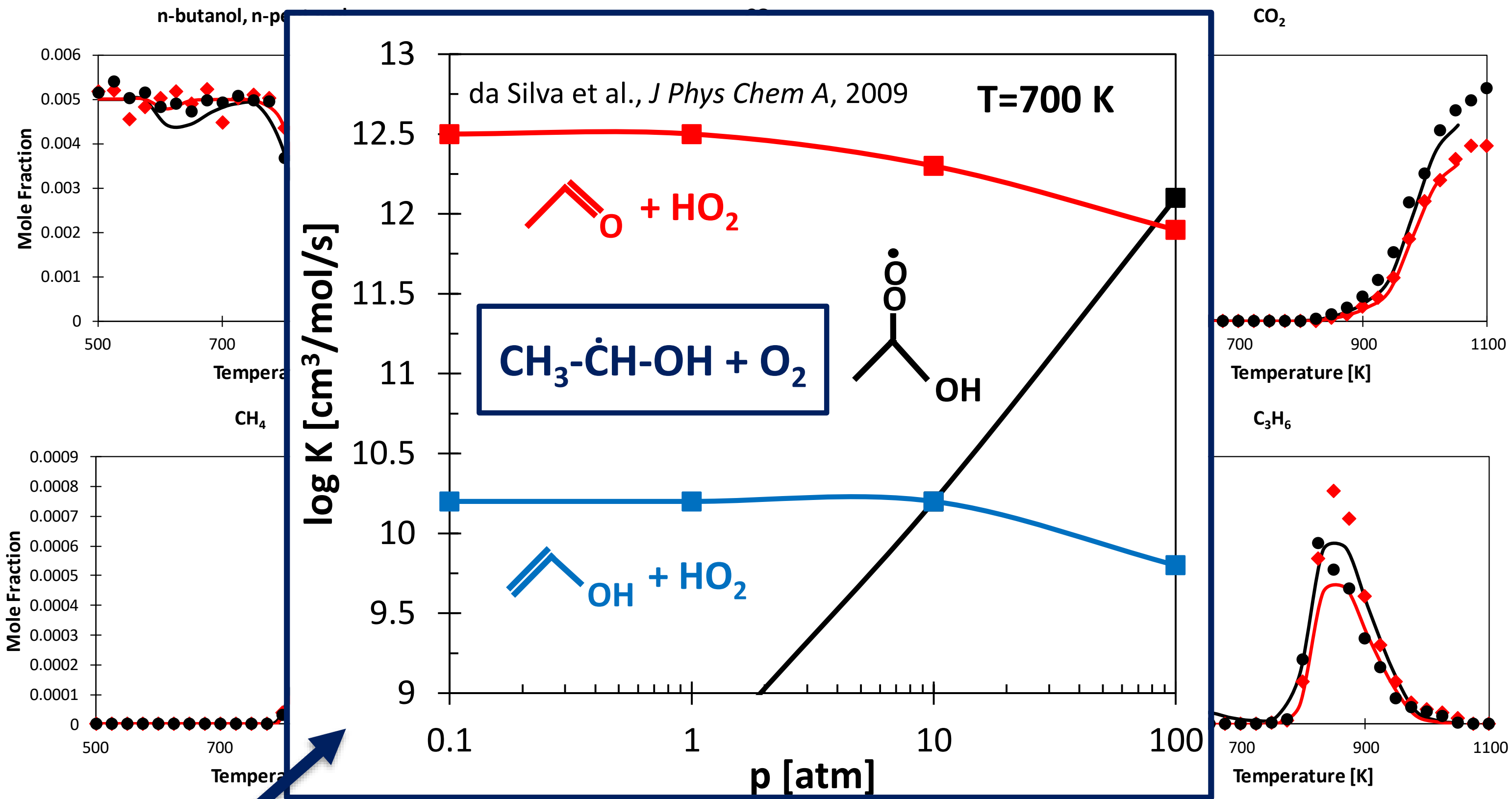


Kinetic model of *n*-butanol and *n*-pentanol: validation, ST / RCM data

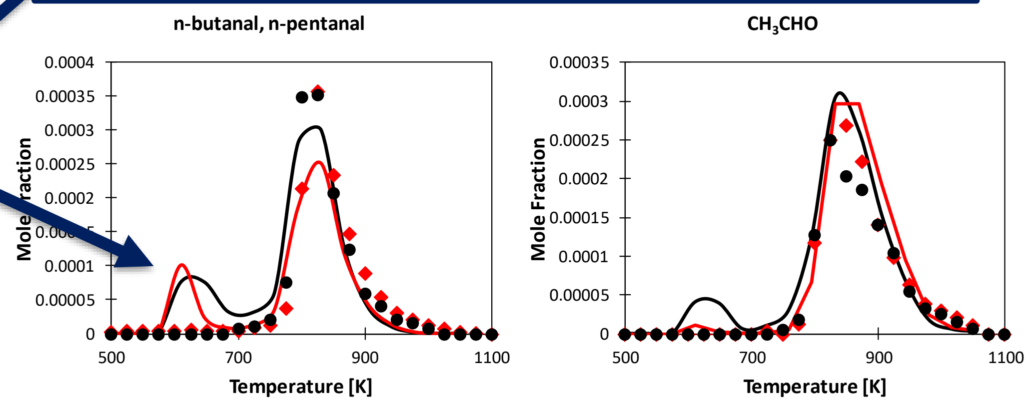




Kinetic model of *n*-butanol and *n*-pentanol: validation, JSR data



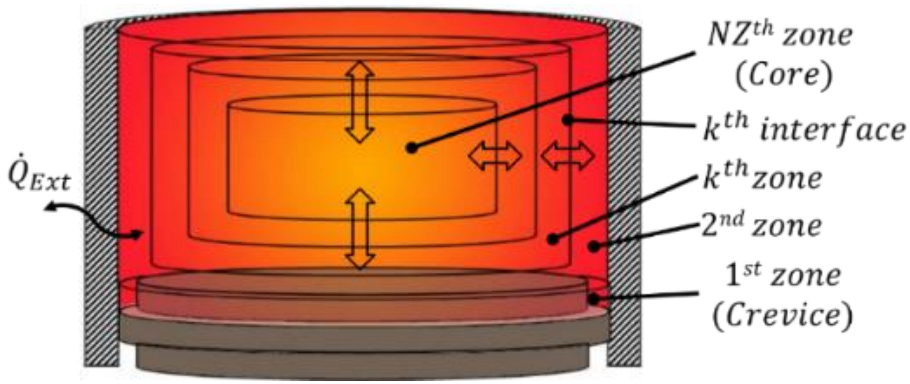
Pressure dependence of **Rα+O$_2$** pathway?



- **HCCI:** Homogeneous Charge Compression Ignition
- **RCCI:** Reactivity Controlled Compression Ignition
- **PCI:** Premixed Compression Ignition
- **GCI:** Gasoline Compression Ignition

POLIMI multi-zone model (ICE)

Bissoli et al. *SAE Int. J. Engines*, 2013; *Appl. Energ.*, 2016; *Energ. Fuel.*, 2017



✓ **Conceived to handle detailed/semi-detailed chemistry**

OpenSMOKE++ framework

Cuoci et al. *Comp. Phys. Comm.*, 2015

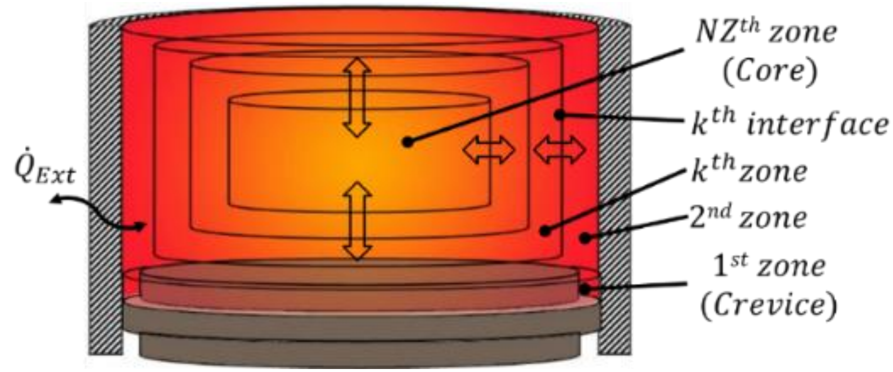
- Ideal reactors
- RCM
- Laminar Flames
- Droplets
- Surface Reactor
- …

http://www.opensmoke.polimi.it/

Multi-zone model of HCCI Engine: OpenSMOKE++ ICE Model

✓ **General structure**

- Multi-Zone **“onion-like”** structure
- Mixture threated as an **ideal gas**
- **Velocity field not solved**
- **From IVC to EVO**



✓ **Zone structure**

- Well-mixed reactors, V(t), uniform P
- **Transport among zones** (laminar and turbulent)
- **Crevices**: fixed-volume variable-mass zone

✓ **Sub-models**

- **Wall heat transfer**
- **Turbulence**

Non-reactive CFD used to define
3 engine-specific parameters (Cu_z, C_x, Cu_w)

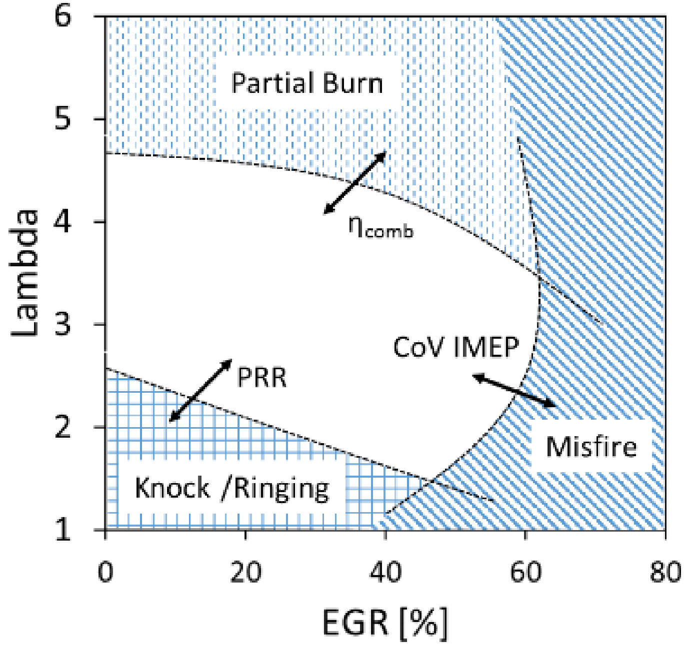
- Residual Burned Gases (RBG): cycle-to-cycle predictions
- **Tools for kinetic analyses**

Validation and further model details

Bissoli et al. *SAE Int. J. Engines*, 2013; *Appl. Energ.*, 2016; *Energy Fuels*, 2017

Multi-zone model of HCCI Engine: Operability Maps

2-D operative maps identify stable operability regions
i.e. set of different **λ-EGR** conditions satisfying the constraints below:



Limits

- Partial Burn: $\eta_{COMB} \geq 80\%$
- Knock/Ringing: **PRR ≤ 6 [bar/deg]**
- Misfire: **CoV Indicated Mean Effective Pressure ≤ 60%**

$$\eta_{comb} = \frac{\int HRR}{\Delta H_{comb}}$$

$$IMEP = \frac{\int pdV}{V_{disp}} \qquad CoV\ IMEP = \frac{\sigma_{IMEP}}{IMEP}$$

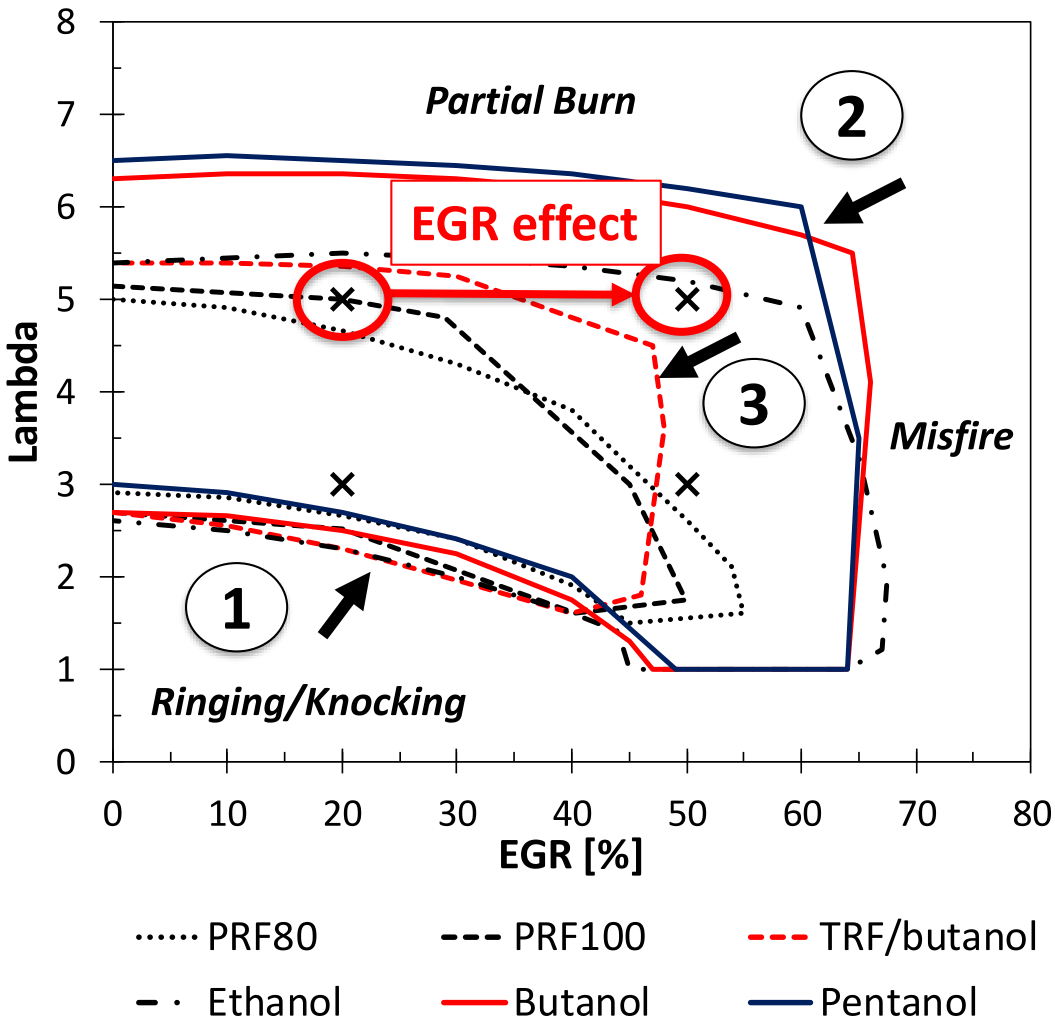
Ricardo E6 engine Brunel University[2]

Displacement	**504 cm^3**	**CR**	**11.5**
Bore	76.2 mm	**Speed**	1500 rpm
Stroke	111.1 mm	**IVC**	137 °ATDC
Rod Length	241.3 mm	**EVO**	144 °BTDC

Model configuration
15 zones (14+crevice)
50 cycles (EGR effects)
>150 λ-EGR combinations for each map

[1] Bissoli et al. *Energy Fuels,* 2017; [2] Oakley, PhD Thesis, 2001

Multi-zone model of HCCI Engine: Operability Maps



General Trends

1. **Ethanol** and **TRF/butanol** extend the operability maps towards **ringing region**
   (highly anti-knocking components: toluene, butanol)

2. **n-butanol** and **n-pentanol** show the highest flexibility to load and EGR

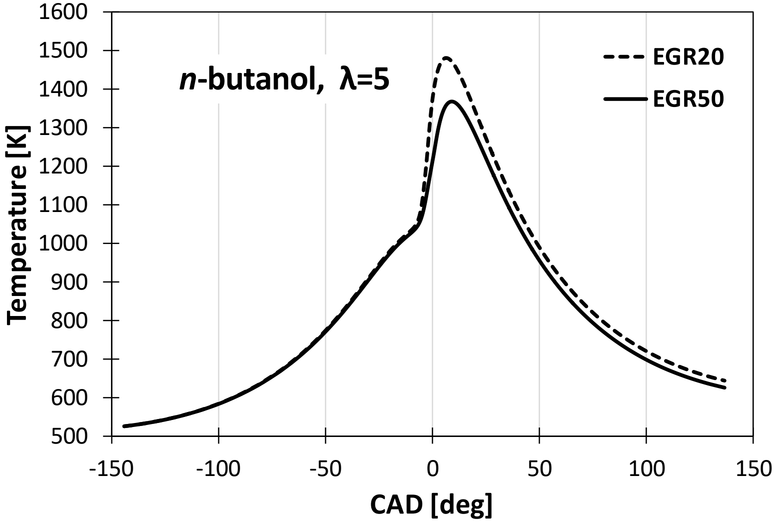
3. **TRF/butanol extends partial burn limits** compared to ethanol and PRFs

TRF/butanol (RON=95, MON=87): *iso*-octane/*n*-heptane/toluene/***n*-butanol** (41.2/8.1/22.4/**28.3** mole%)

Agbro et al. *Fuel*, 2017

Multi-zone model of HCCI Engine: Operability Maps

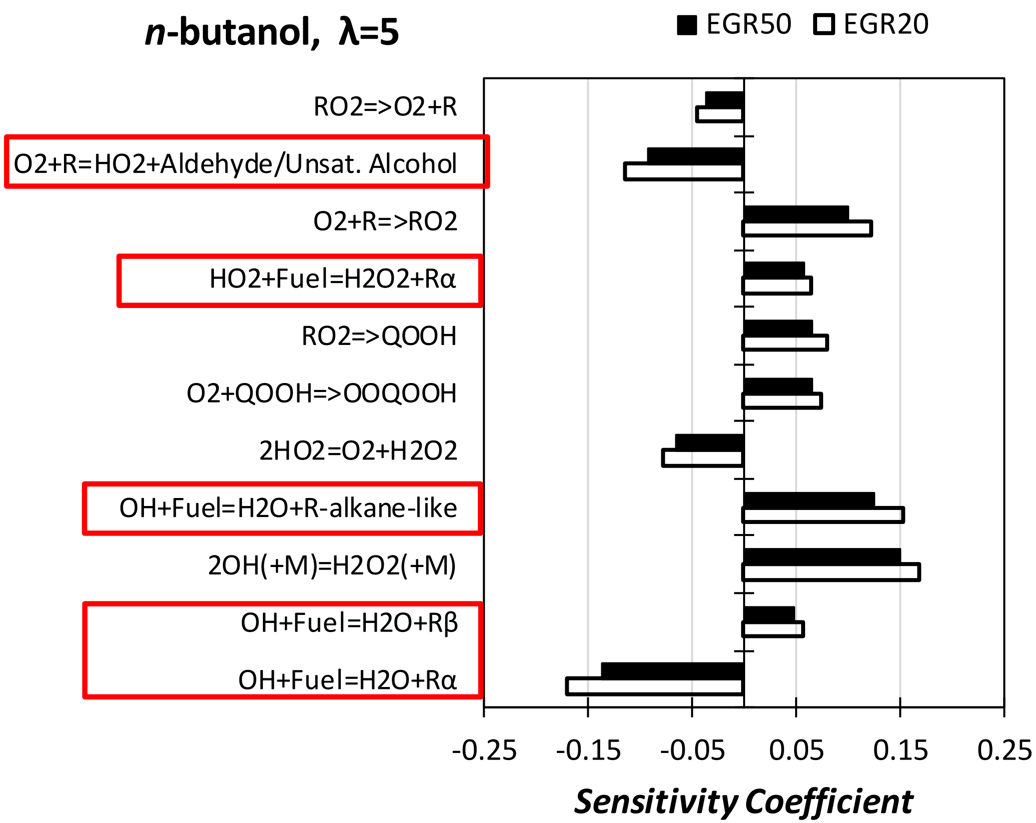
Sensitivity Analysis to T, Inner Zone



- **O_2+radicals=HO_2+aldehyde/enol**

  Only available for ethanol

  ✓ Da Silva et al. and Zador et al. provide basis: rate rule is needed!



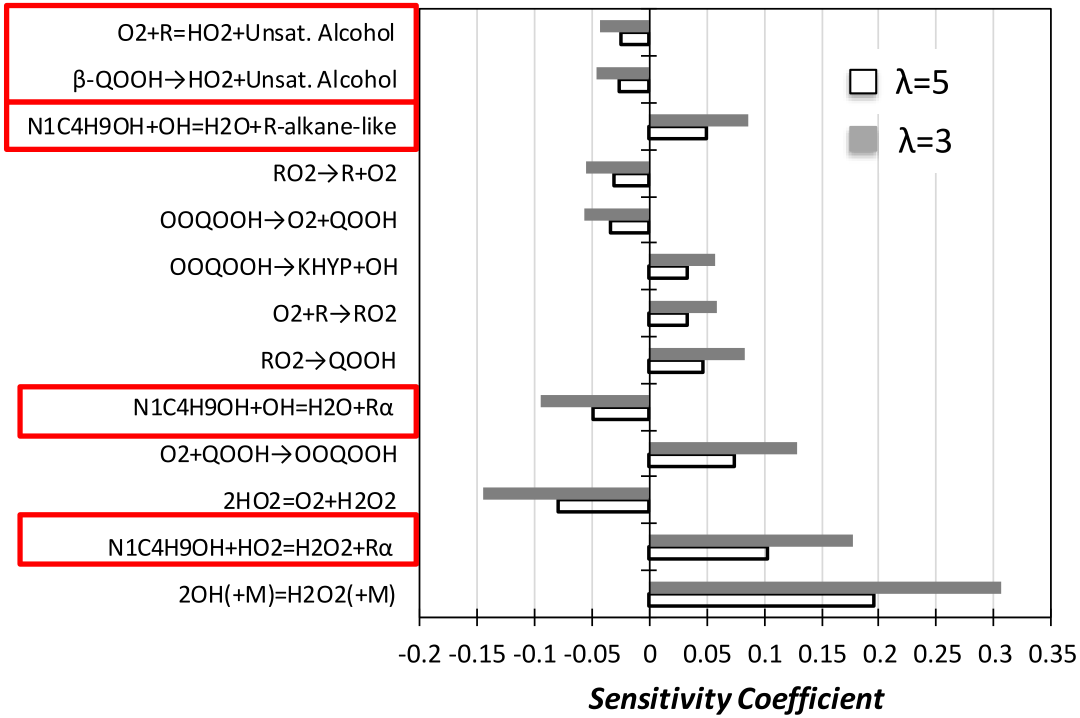
- **Relative Branching of H-abstraction** (OH, **HO_2**)
  - Alkane moiety

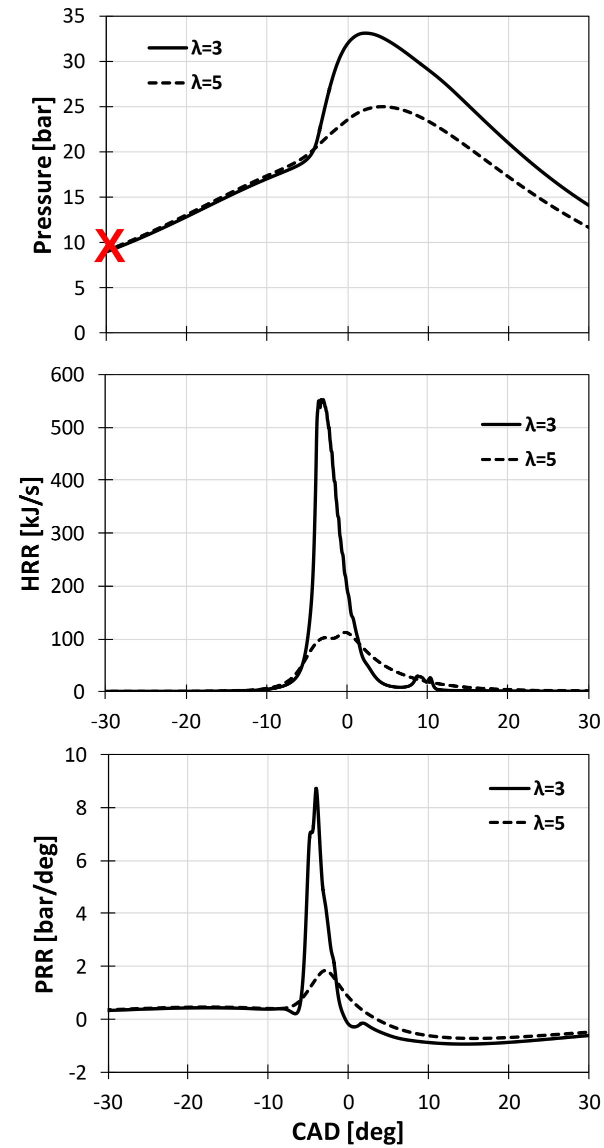
    enhances ignition at LT
  - Alcohol moiety

    inhibits ignition at LT

Multi-zone model of HCCI Engine: OpenSMOKE++ ICE Model

CAD ~ -30, p=9.1 atm T=904K

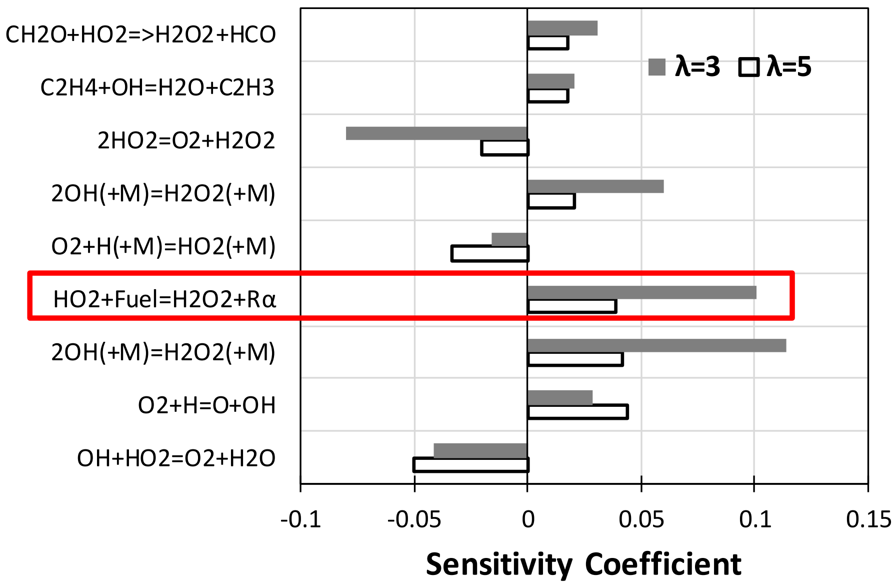


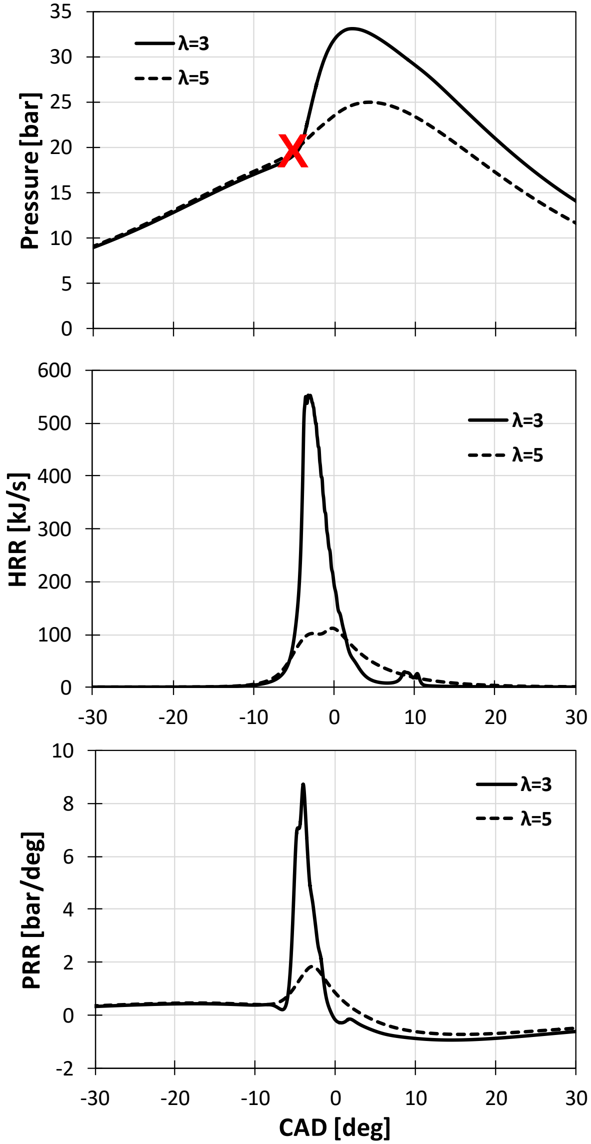


Mostly Fuel specific chemistry

Multi-zone model of HCCI Engine: OpenSMOKE++ ICE Model

CAD ~ -5, p=18.9 atm, T=1034 K





Mostly C_0-C_2 and HO_2 chemistry

Conclusions

- **New Experimental Measurements in RCM and JSR** extend the scarce experimental data on alcohols oxidation at conditions relevant for real systems

- **POLIMI Kinetic Mechanism** has been **extended** to describe **the low temperature oxidation of alcohols (C_4-C_6) (with a new core mechanism!)**

- Coupling of the **POLIMI HCCI (ICE) Model** allows to **qualitatively explore the potential of alcohols as fuels or additives in HCCI Engine**, by means of **detailed kinetics**

- **Butanol and pentanol extend the operability region** allowing lower loads (i.e. reduce the partial burn region) compared to TRF/PRF mixtures and ethanol

- **Relevant kinetic pathways still deserve an accurate revision,** due to their strong impact on auto-ignition in real systems

Thank you!