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Cool flames in microgravity droplet combustion

29th American Society for Gravitational and Space Research
5th International Symposium for Physical Sciences in Space

November 3-8, 2013 – Orlando, Florida (USA)

Outline

1. Introduction
   - ✓ Cool flames
   - ✓ Low-temperature mechanism
2. Mathematical model
   - ✓ Governing equations and numerical methodology
   - ✓ Detailed kinetic mechanism
3. Auto-ignited n-decane ($C_{10}H_{22}$) droplets
   - ✓ Comparison with experiments
   - ✓ Structure of the cool flame
   - ✓ Numerical experiments on n-heptane and n-dodecane
4. Hot-wire ignited n-heptane (NC_7H_{16}) droplets
   - ✓ Comparison with experiments
   - ✓ Kinetic analysis
   - ✓ Comparison between different kinetic mechanisms
5. Conclusions and future works

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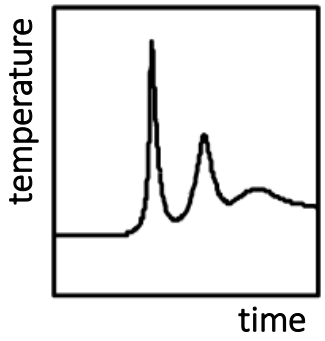
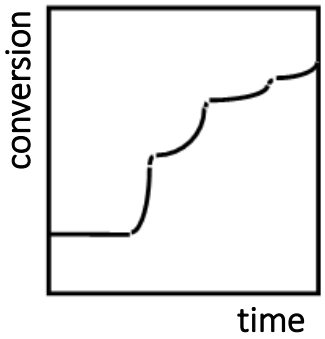
5. Conclusions and future works

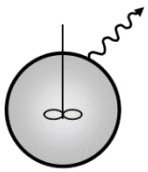
Cool flames

Closed, non-adiabatic systems

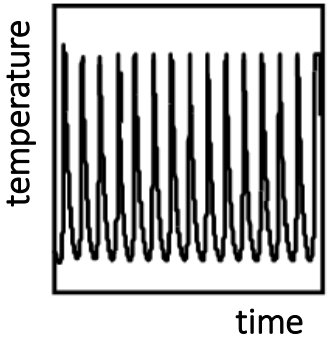


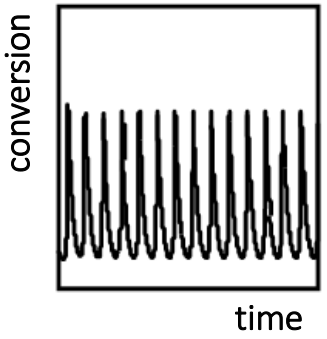


internal combustion engines, batch reactors, etc

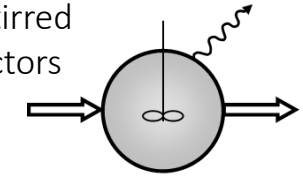


Open, non-adiabatic systems





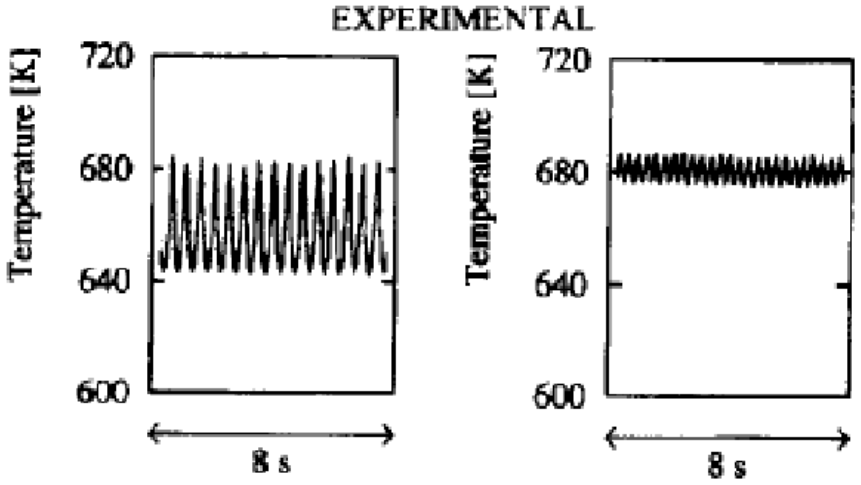
jet stirred reactors



Ordinary, visible flames burn at a high temperature between 1500K and 2000K.

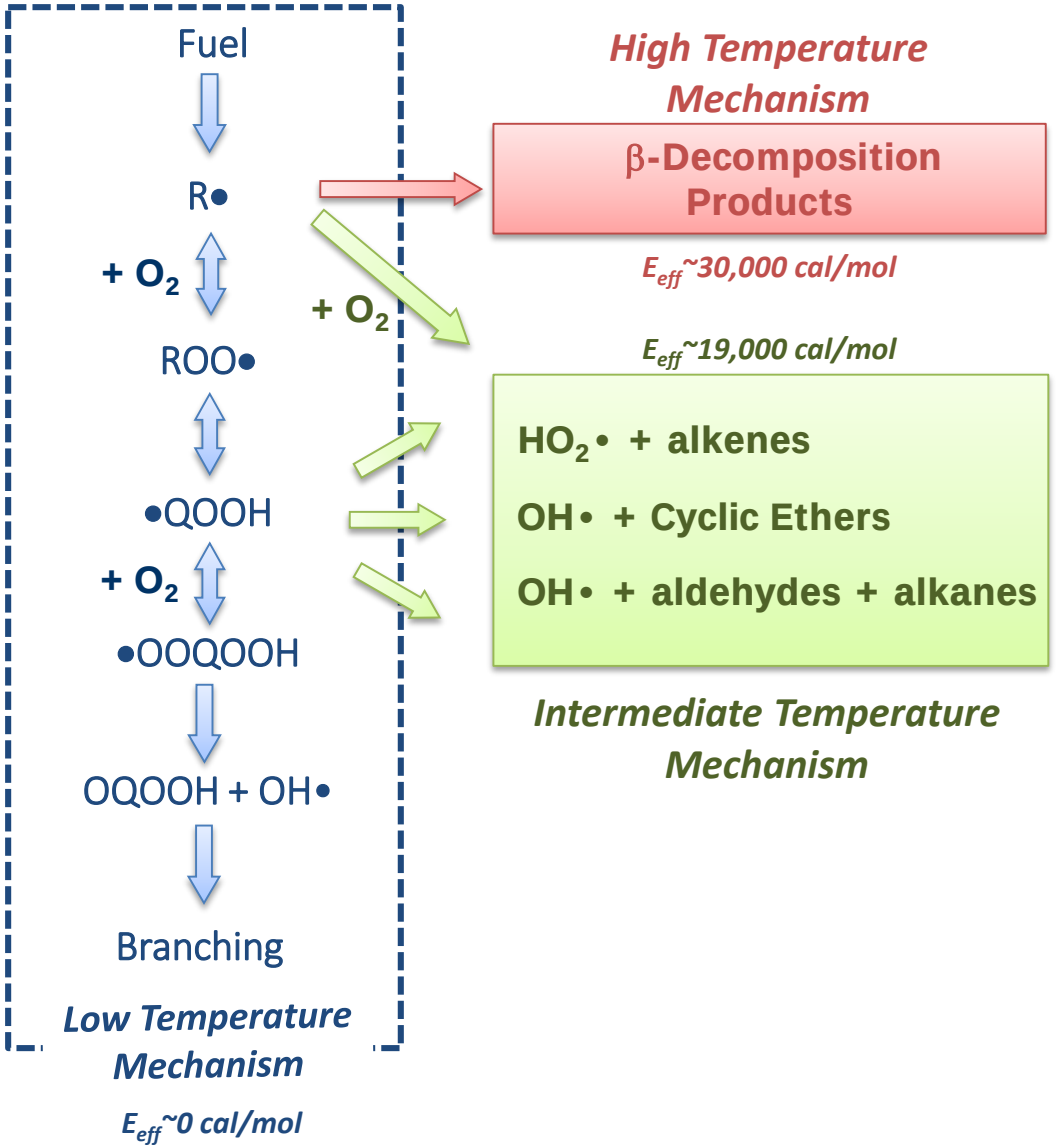
Cool flames burn at the relatively low temperature of 500K to 800K, and their chemistry is completely different. Normal flames produce soot, CO_2 and water. Cool flames produce CO and CH_2O.

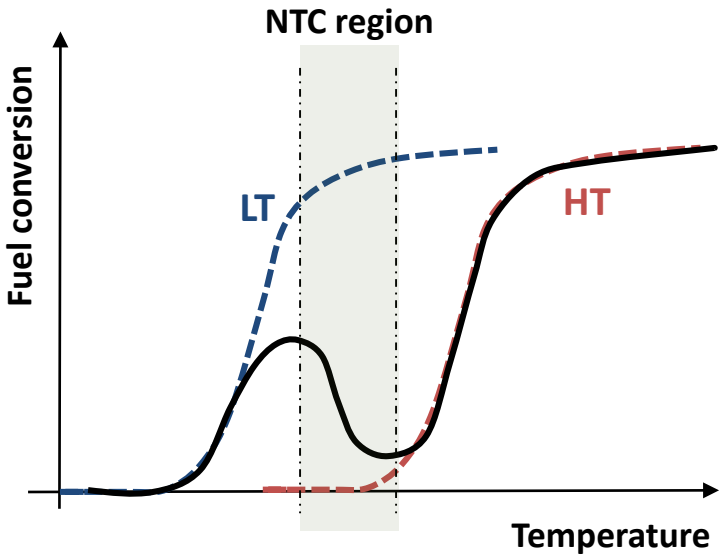
Jet Stirred Reactor: i-octane/air at 7 bar



Ranzi E., Faravelli T., Gaffuri P., Sogaro A., D'Anna A., Combustion and Flame 108, p. 24-42 (1997)

The low-temperature (LT) chemistry



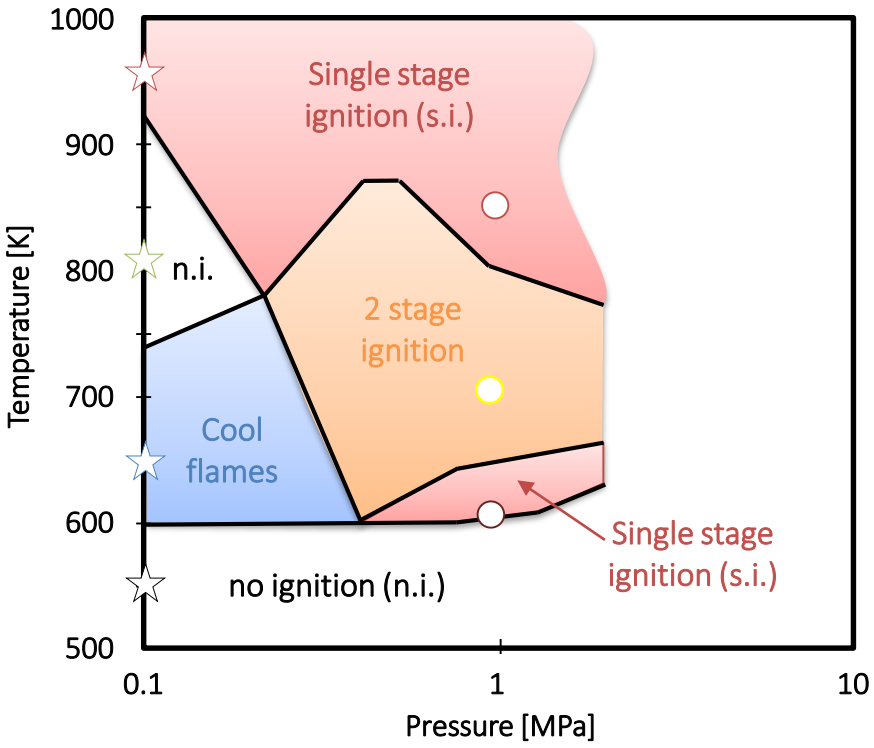


R• = alkyl-radical (e.g. C_7H_{15})
ROO• = peroxy radical
•QOOH = hydroperoxy-alkyl rad.
•OOQOOH = alkyl-hydroperoxy rad.
OQOOH = ketohydroperoxyde

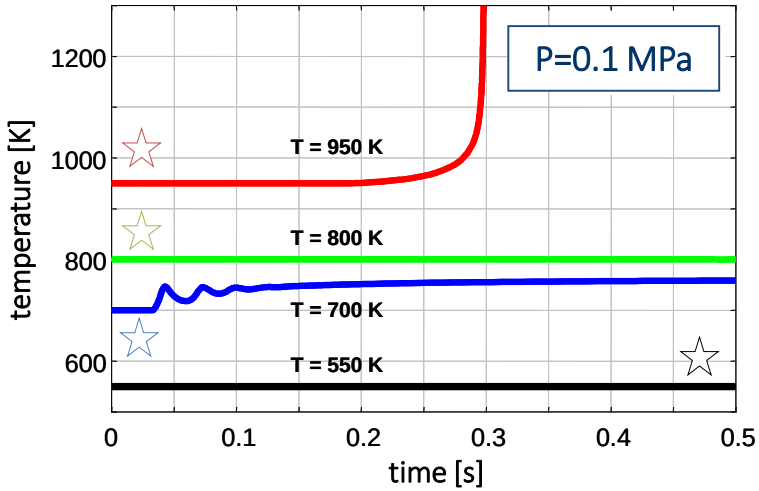
Cool flames in droplet combustion (I)

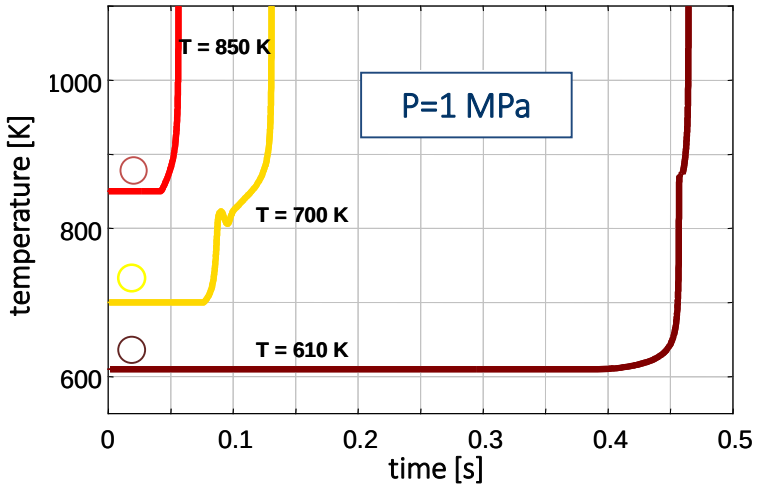
Auto-ignition experiments

n-heptane droplets in air (d_0=0.70 mm)



Adapted from: **Tanabe et al.**, 26th Symposium (International) on Combustion, p. 1637-1643 (1996)

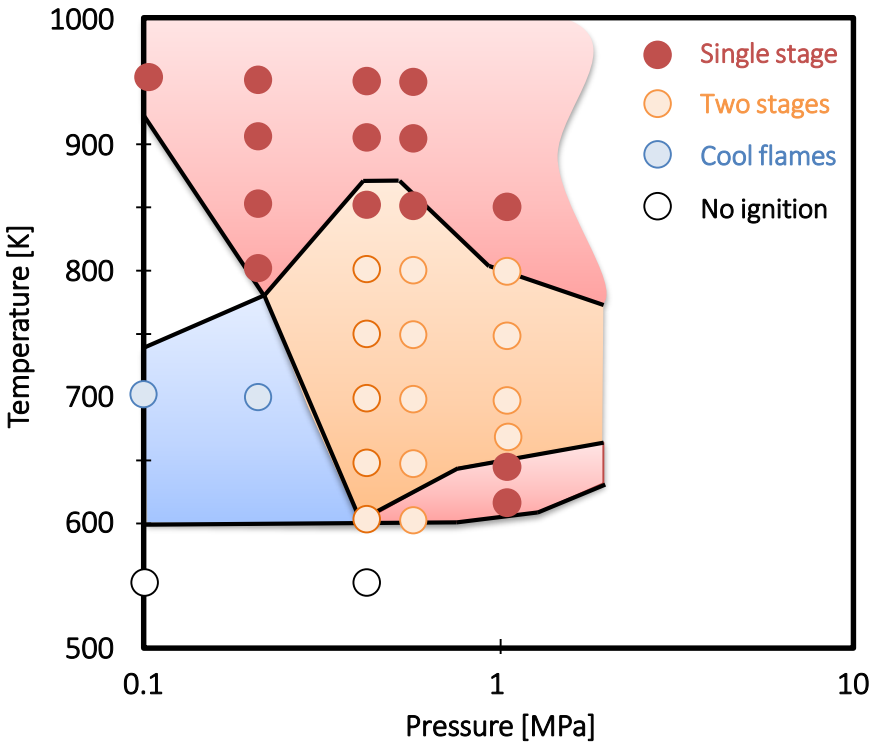




Cool flames in droplet combustion (II)

Numerical simulations

n-heptane droplets in air (d_0=0.70 mm)



Cuoci A., Mehl M., Buzzi-Ferraris G., Manca D., Faravelli T., Ranzi E., Autoignition and burning rates of fuel droplets under microgravity, Combustion and Flame 143, p. 211-226 (2005)

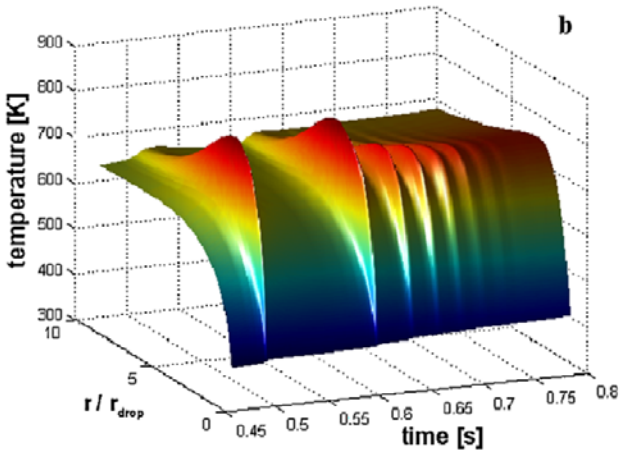


Fig. 4. Time evolution of the predicted maximum gas-phase temperature for different grid number of points in the gas phase (a); time and radial evolution of the predicted maximum gas-phase temperature (b) (autoignition simulation, *n*-decane droplet, $d_0 = 0.91$ mm, $P = 0.1$ MPa, $T_G = 633$ K).

1. Better understand the features of cool flames

2. Study the possible formation of cool flames in hot-wire ignitions

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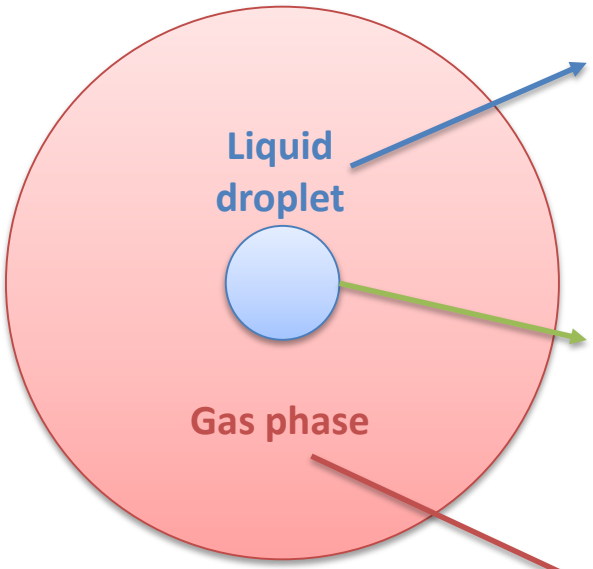
5. Conclusions and future works

Mathematical model



- ✓ Continuity equation
- ✓ Energy equation
- ✓ Species equations

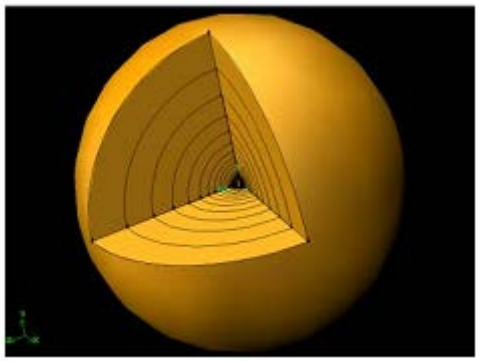
Interface (liquid/gas)

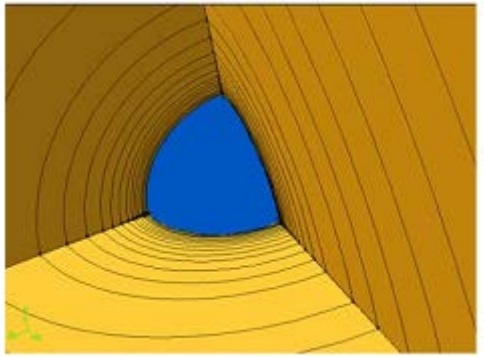
- ✓ Thermodynamic equilibrium
- ✓ Conservation of fluxes

- ✓ Continuity equation
- ✓ Energy equation
- ✓ Species equations

Cuoci et al., Combustion and Flame 143, p. 211-226 (2005)

- ✓ Spherical symmetry
- ✓ 1D equations
- ✓ Stretched grid





Kazakov A., Conley J., Dryer F.L., Combustion and Flame 134, p. 301-314 (2003)

Ratio between gas and liquid radii: ~120

Equation of state (gas phase): ideal gas

Radiative heat transfer (gas phase): from Kazakov et al. (2003)

Dufour effect: neglected

Soret effect: accounted for

Numerical methodology

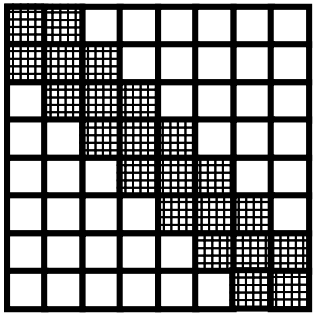
finite differences in space ⇒ Ordinary DAE system

large dimensions of the problem
non linearity of reaction rates and transport properties
⇒ Numerical difficulties in solving the resulting very stiff DAE system

The DAE system is structured as a (quasi) tridiagonal block matrix with square and dense submatrices whose dimensions depend on the number of chemical species included in the kinetic scheme

Example

200 points x 435 species ~ 90,000 equations ⇒ ~24 h of CPU time



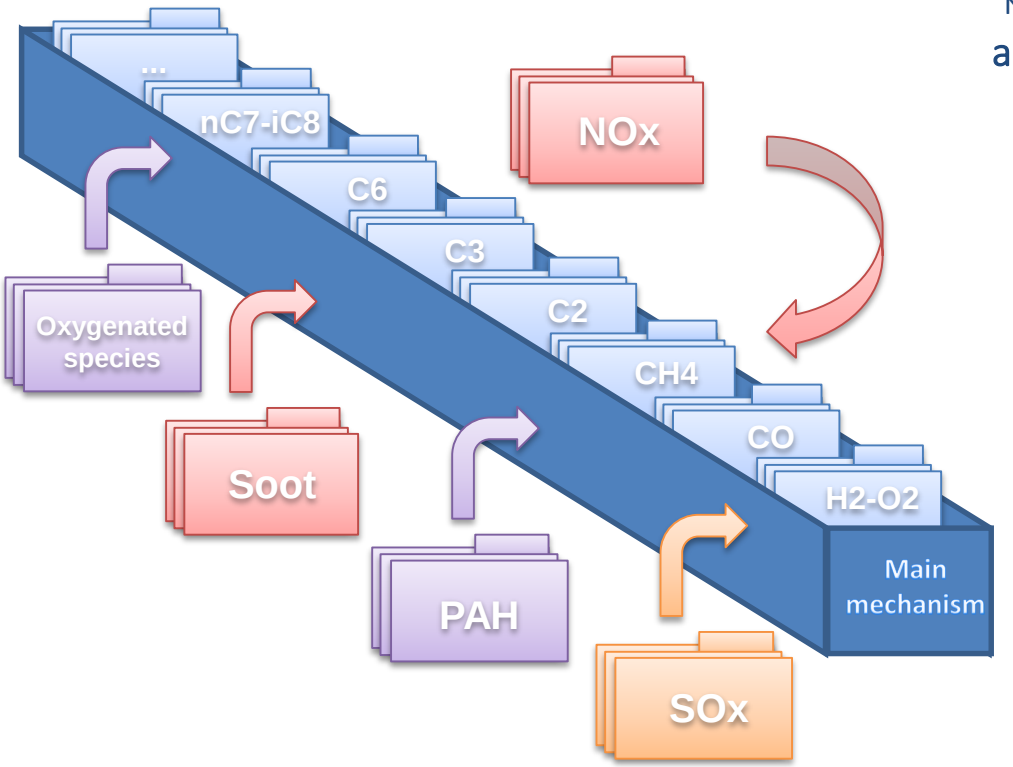
Jacobian matrix of the global system

BzzDAEBloTri, a specifically conceived numerical solver, allows to efficiently treat the structured sparsity of the Jacobian matrix as well as the stiffness of the DAE system.

http://www.chem.polimi.it/homes/gbuzzi

Buzzi-Ferraris G., Manca D., Computers and Chemical Engineering, 22(11), p. 1595-1621 (1998)

Detailed kinetic mechanism



Kinetic mechanism of **pyrolysis, oxidation and combustion** of small (C1-C3) and large hydrocarbons up to Diesel and jet fuels (C16) as well as several pollutants

Hierarchy

Modularity

Generality

~ 435 chemical species

~ 13,495 reactions

http://creckmodeling.chem.polimi.it

The kinetic mechanism is freely available in CHEMKIN format at this web address

Frassoldati, A. et al., Combustion and Flame 157(2010), pp. 2-16

Ranzi, E. at al., Progress in Energy and Combustion Science 38 (2012), pp. 468-501

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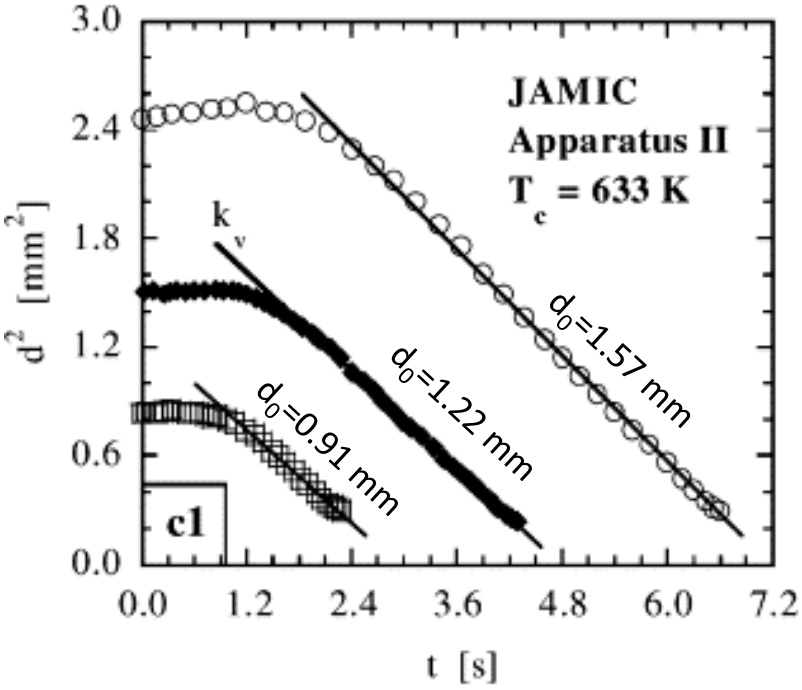
Description of the experiments

Autoignition experiments
Experiments performed in either the Japan Microgravity Center (JAMIC) or the NASA Glenn Research Center

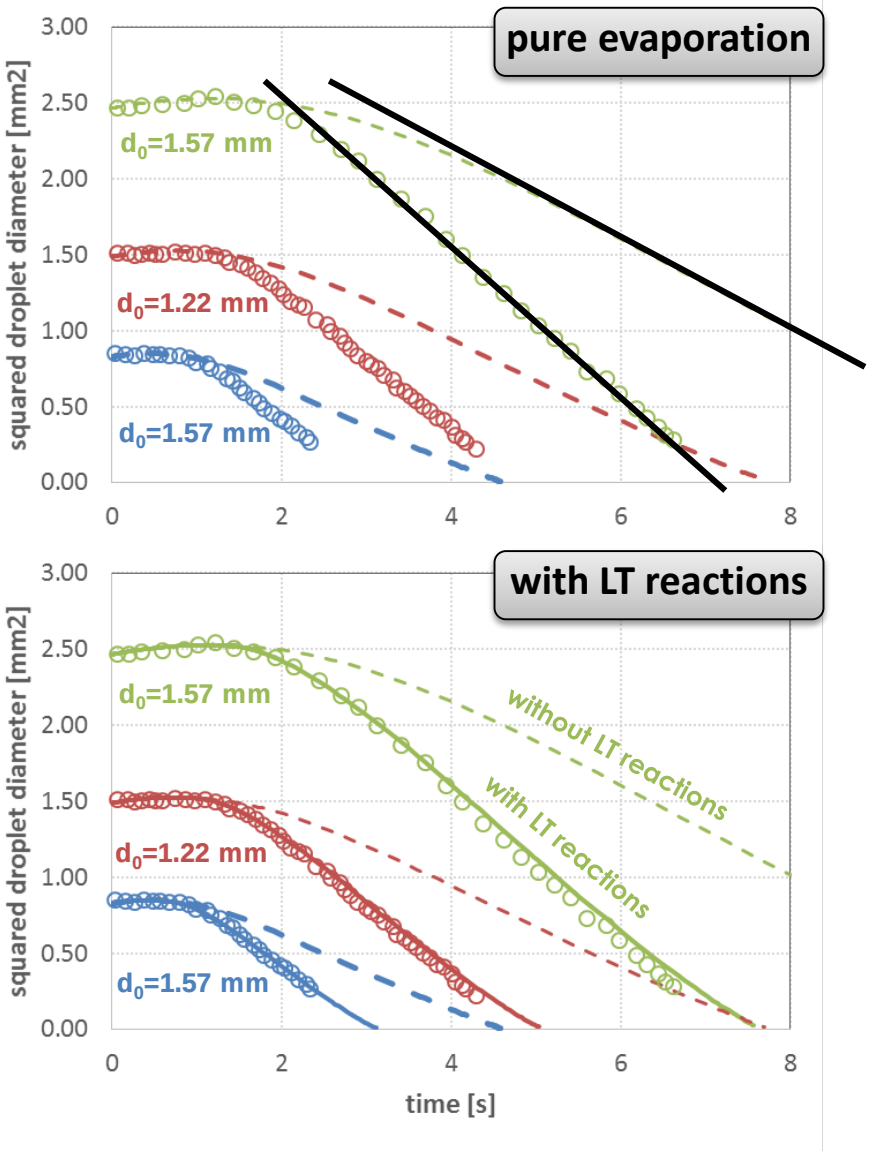
Fuel: **n-decane (NC10H22)**
Initial diameters: 0.91, 1.22 and 1.57 mm
Pressure: 1 atm
Droplet temperature: 300 K
Gas phase temperature: 633 K
Gas phase composition: air (21% O2, 79% N2)
Negligible soot formation
Droplet was suspended using a quartz fiber

Adapted from Xu et al. (2003)



Xu G., Ikegami M., Honma S., Ikeda K., Ma X., Nagaishi H., Dietrich D.L., Struk P.M., *Inverse influence of initial diameter on droplet burning rate in cold and hot ambiences: a thermal action of flame in balance with heat loss*, International Journal of heat and mass transfer, 46, p. 1155-1169 (2003)

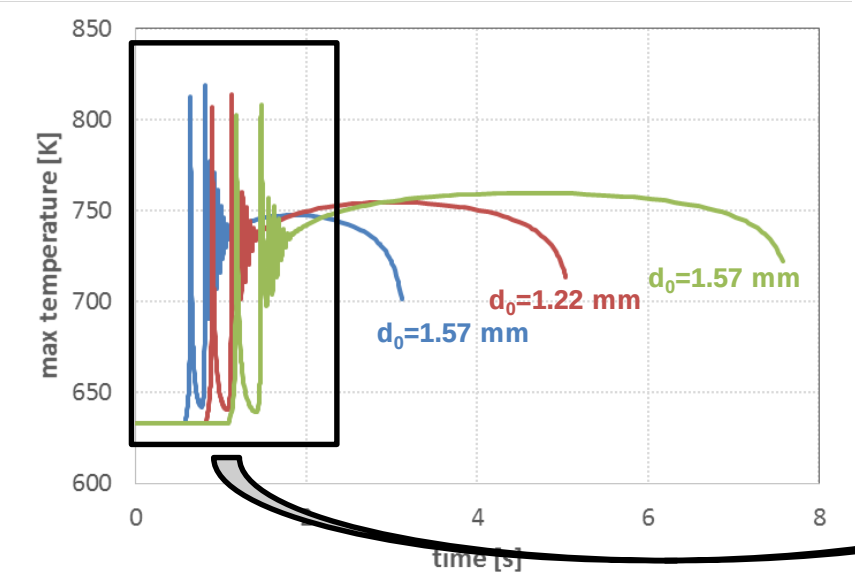
Numerical simulations

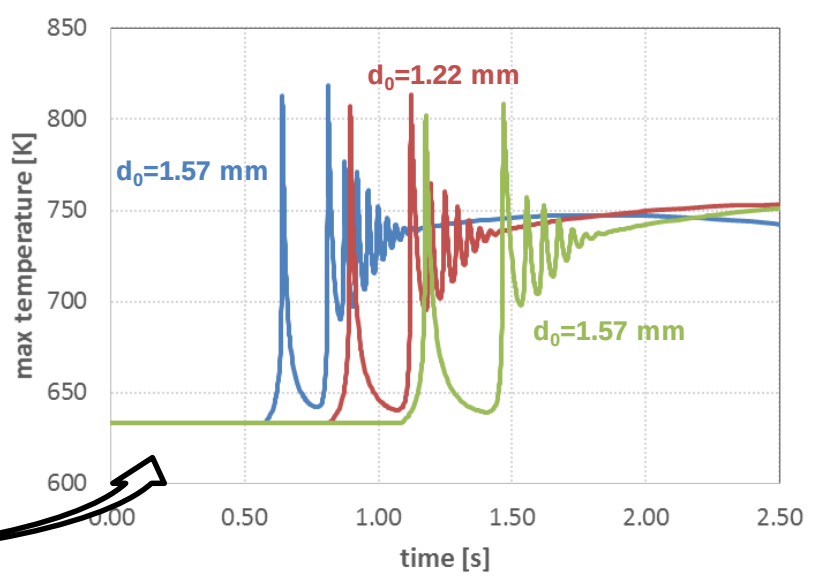


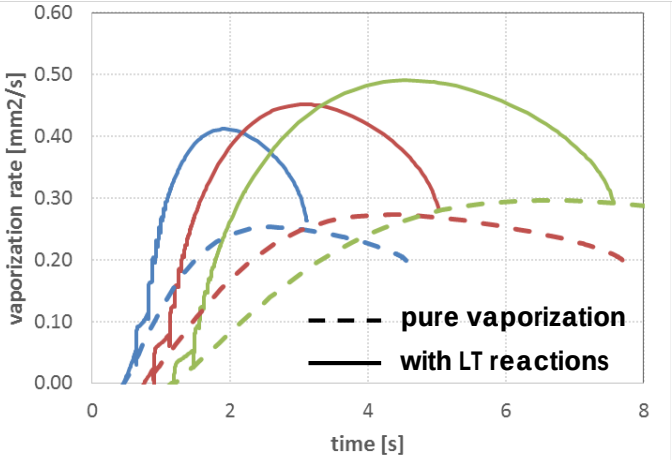
If the simulations are performed without considering any reactions in the gas phase, the calculated vaporization rate is smaller the experimental value

Only with the inclusion of low temperature (LT) reactions the numerical simulations are able to correctly reproduce the experimental data

Dumped cool flames







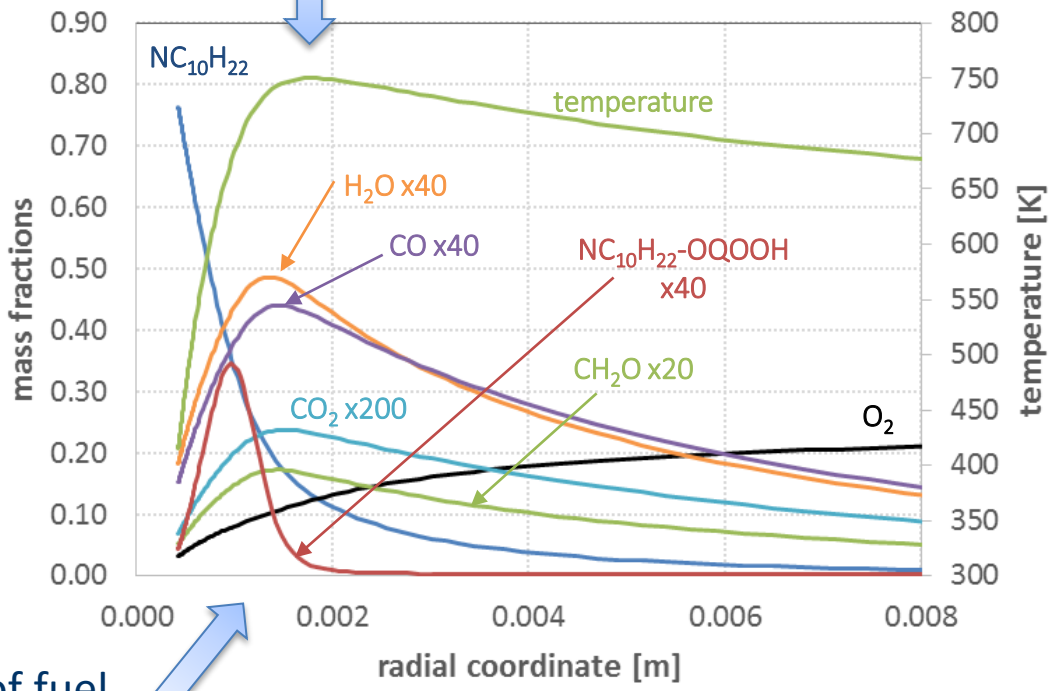
- ✓ initial dumped cool flame and a successive more stable temperature profile at ~750 K.
- ✓ once the first flame ignites, fuel is consumed and only partially replaced by the vaporization.
- ✓ the successive cool flames exihibit a higher frequency, produce less heat and gradually move the system from the cool flame to the slow combustion regime.

Cool flame structure

Small amounts of H_2O and CO_2 with respect to conventional flames
No OH radicals

Peak temperature ~750K

d_0=1.22 mm
Time = 3 s

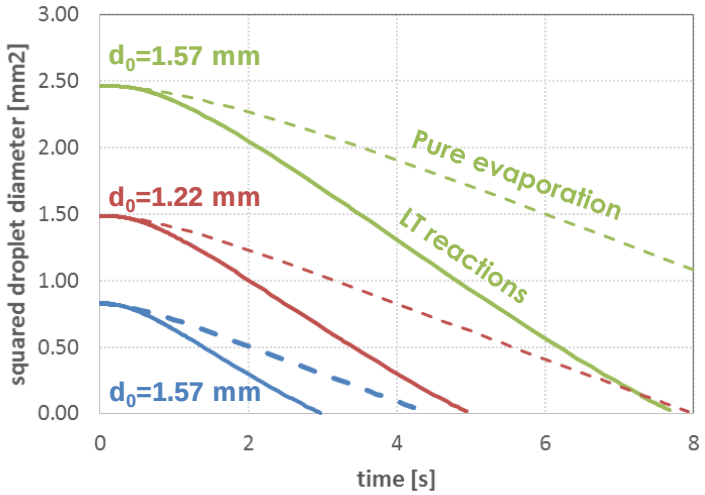


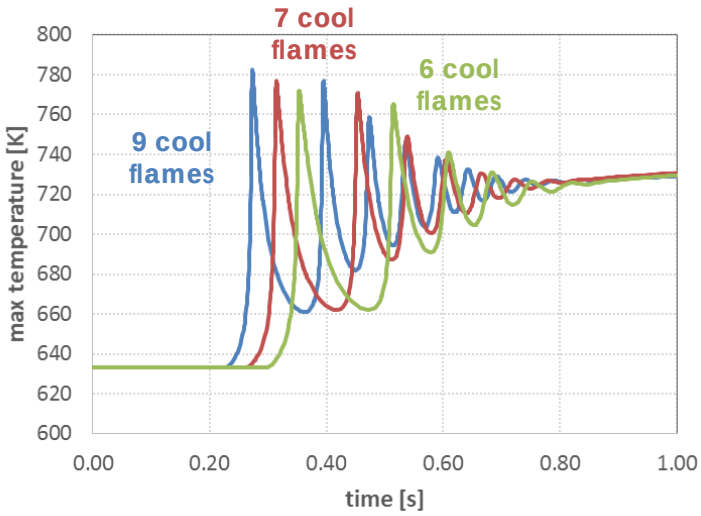
Co-existence of fuel ($C_{10}H_{22}$) and oxidizer (O_2)

Large amounts of ketohydroperoxides (e.g. $NC_{10}H_{22}$-OQOOH)

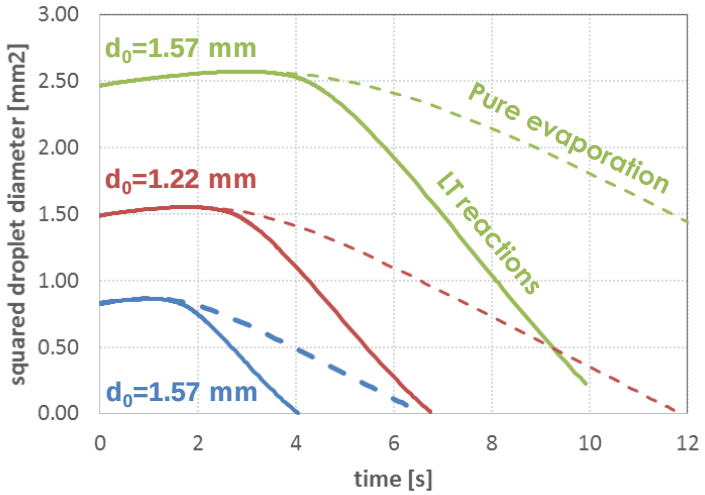
Extension to n-heptane and n-dodecane

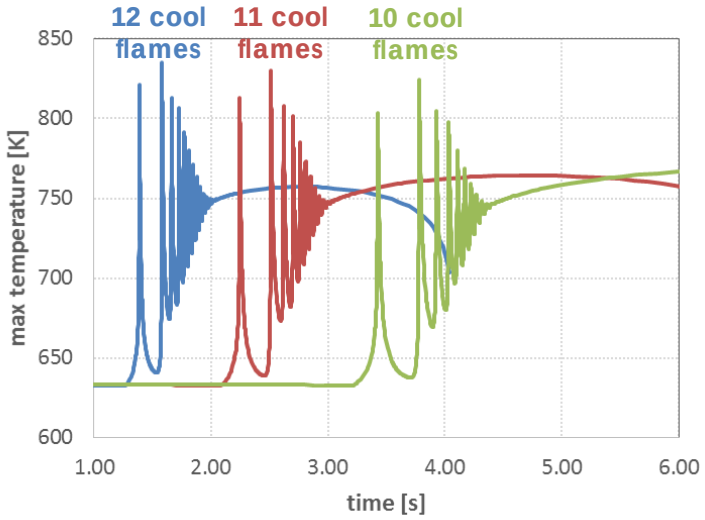
n-heptane





n-dodecane





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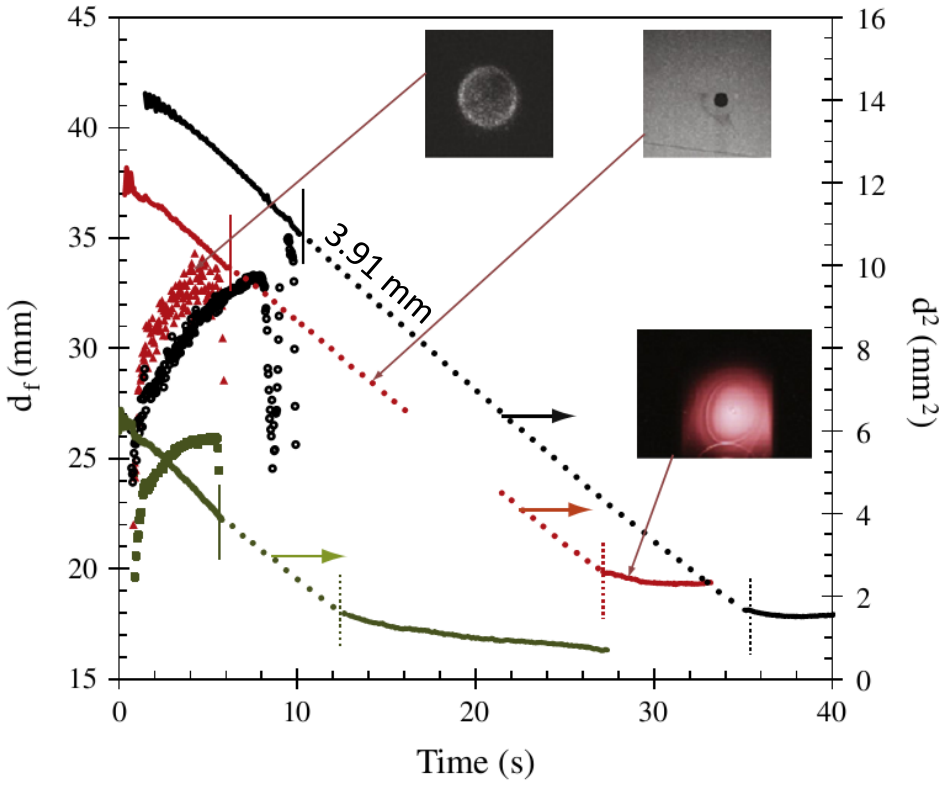
Description of the experiments

Hot-wire ignition experiments
Experiments performed on board the International Space Station (ISS) using the multi-User Droplet Combustion Apparatus (MDCA) installed in the Combustion Integrated Rack (CIR) facility as a part of the Flame Extinguishment Experiments (FLEXs)

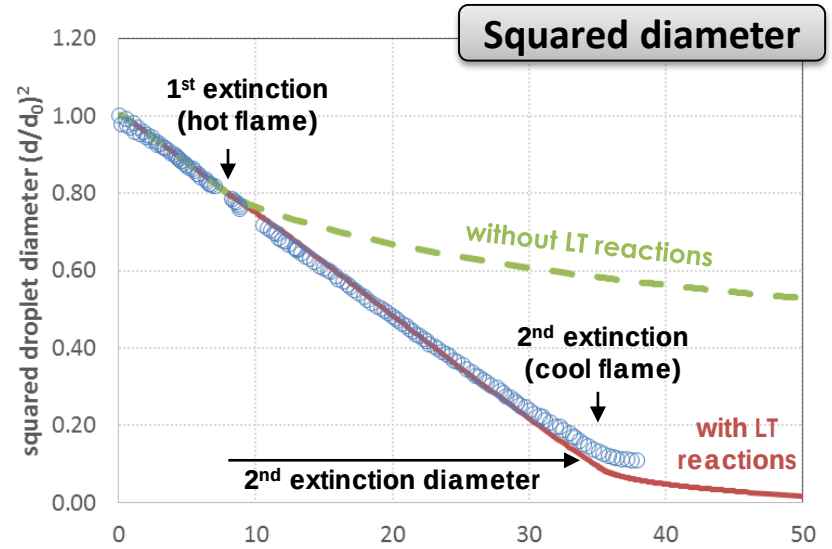
Fuel: n-heptane (NC7H16)
Initial diameter: 3.91 mm
Pressure: 1 atm
Initial temperature: 300 K
Gas phase composition: air
Negligible soot formation
Droplet tethered by a fine silicon carbide filament

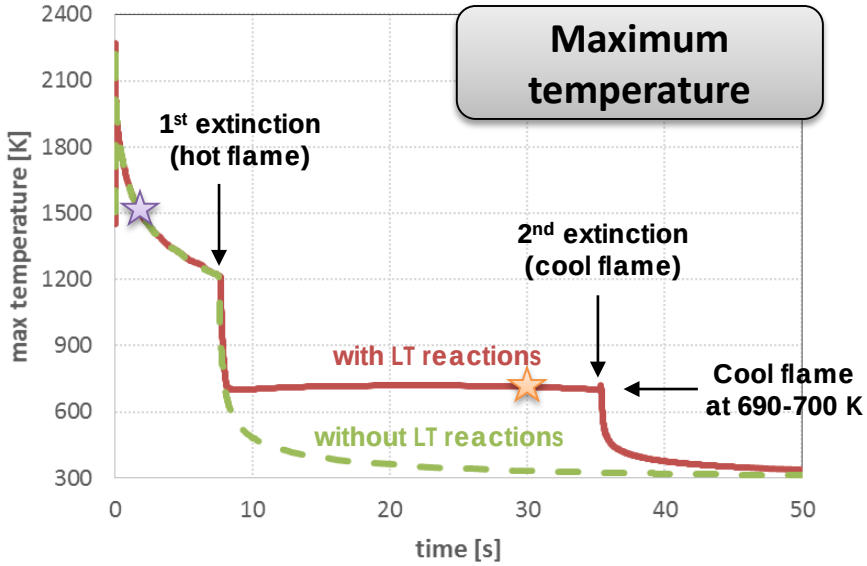
Adapted from Nayagam et al. (2012)



Nayagam V., Dietrich D.L., Ferkul P.V., Hicks M.C., Williams F.A., *Can cool flames support quasi-steady alkane droplet burning?*, Combustion and flame, 159, p. 3583-3588 (2012)

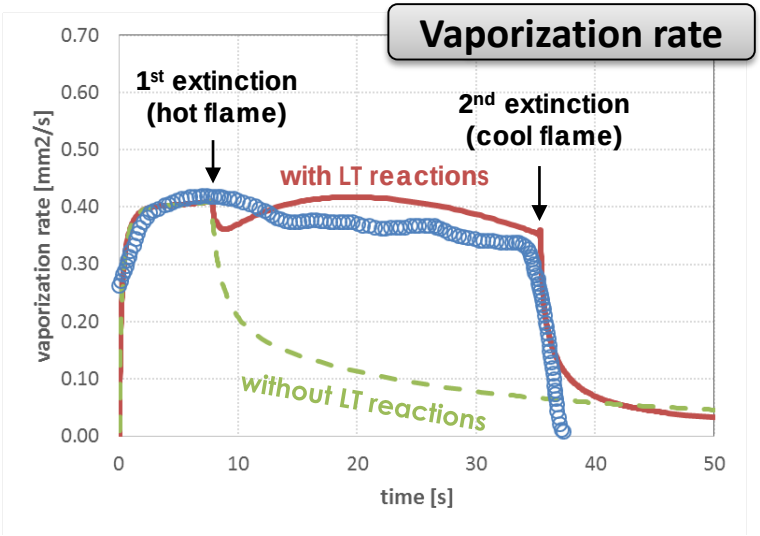
Numerical results





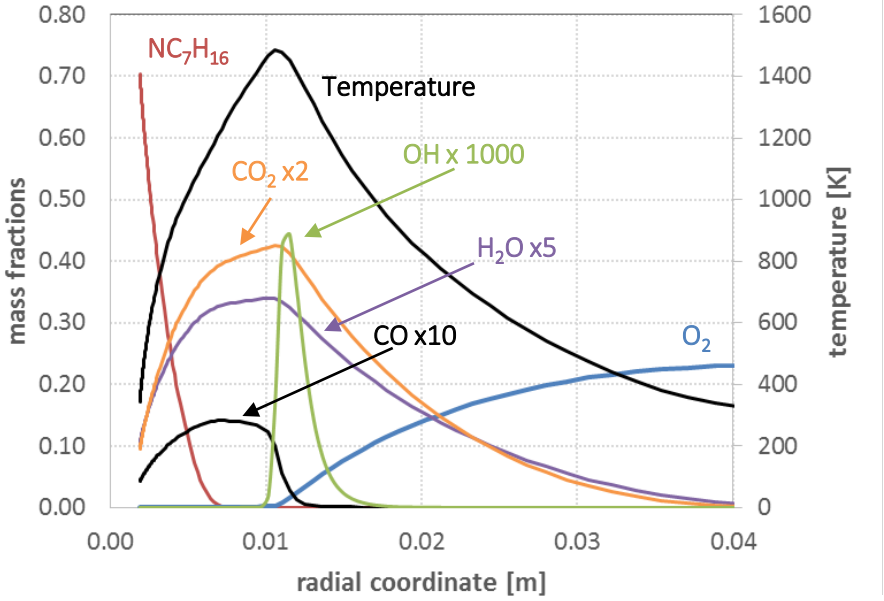
The agreement with the experiments is satisfactory if the LT mechanism is accounted for.

	Experiment	Simulation
1st extinction diameter [mm]	3.28	3.45
2nd extinction diameter [mm]	1.30	1.10
mean vaporization rate [mm2/s]	0.368	0.390

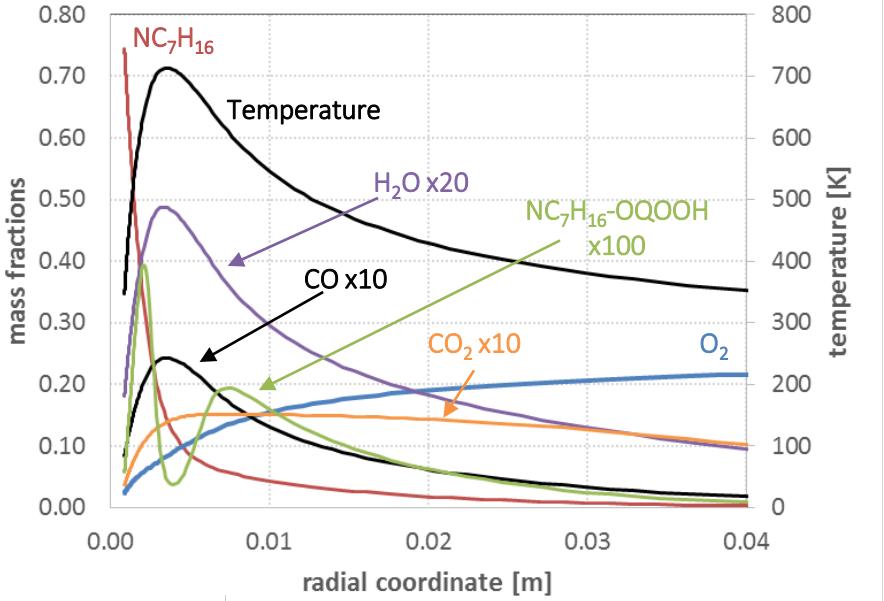


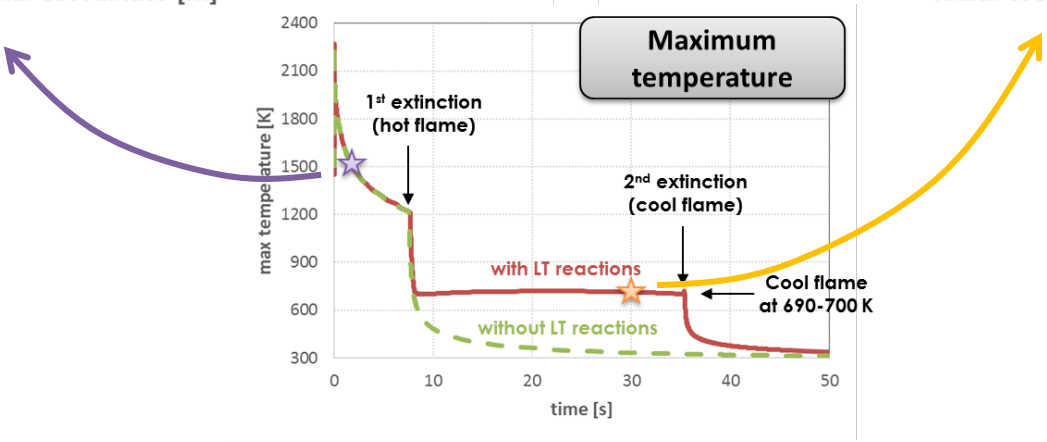
Flame structures

Hot flame @ 2 s



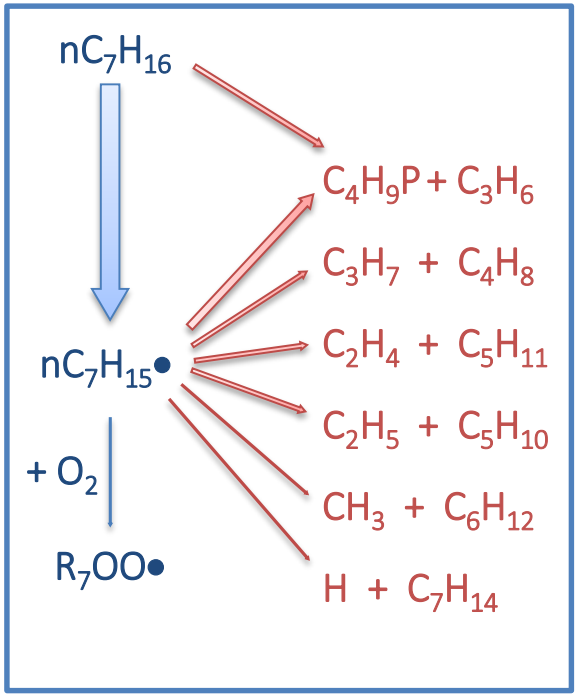
Cool flame @ 30 s





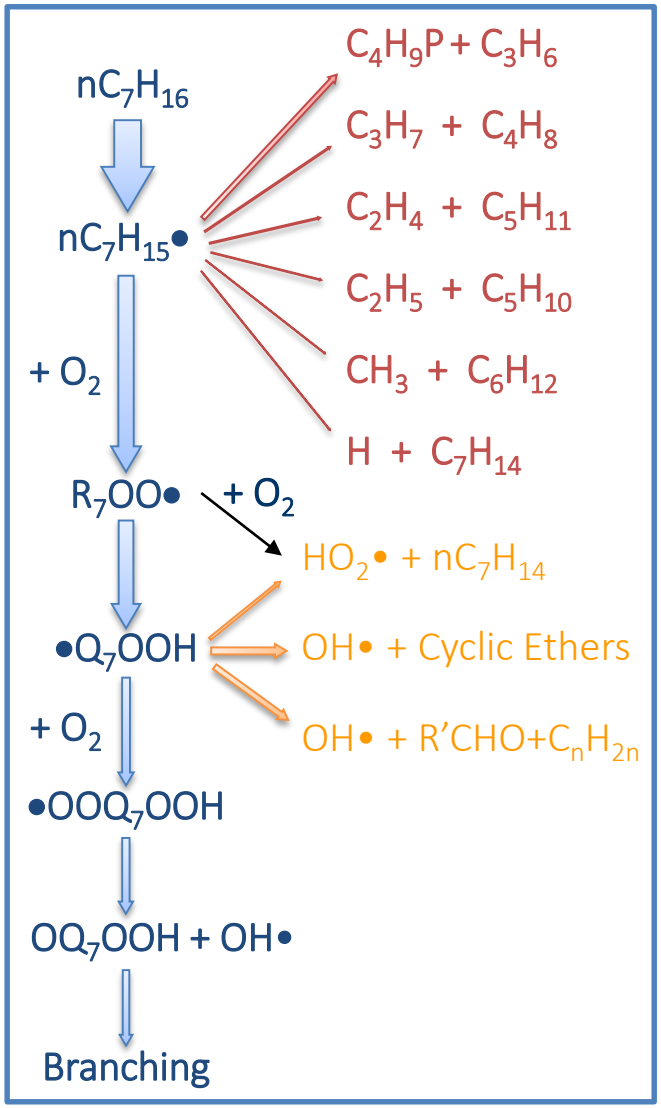
Path analysis

Hot flame @ 2 s

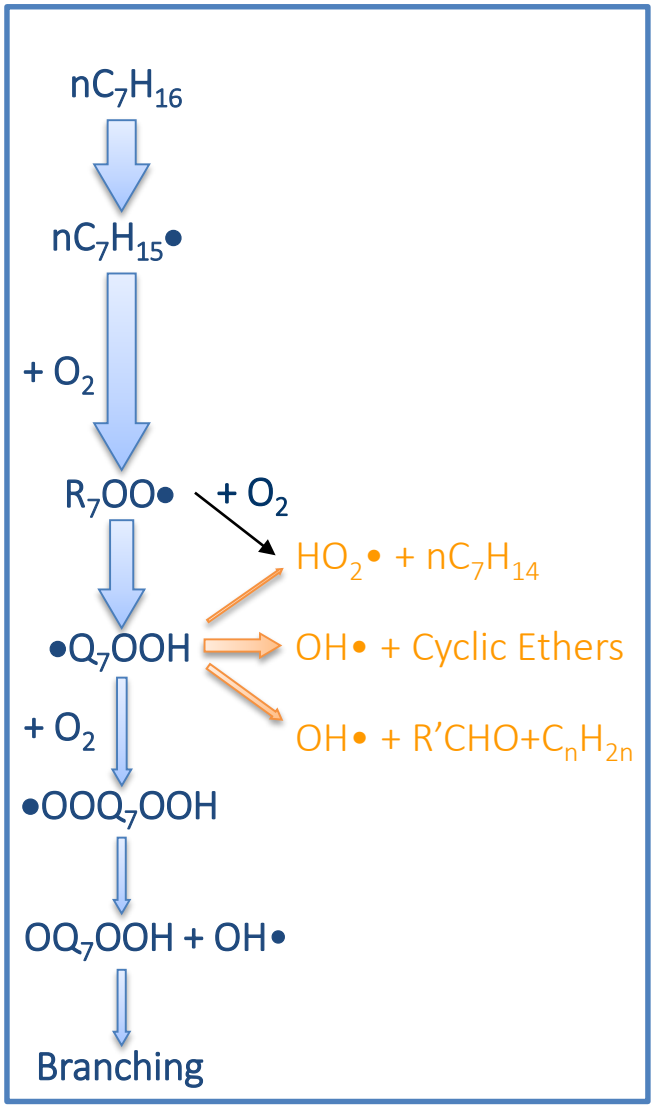


The thickness of the arrows is proportional to the importance of the corresponding flux

Transition @ 8 s

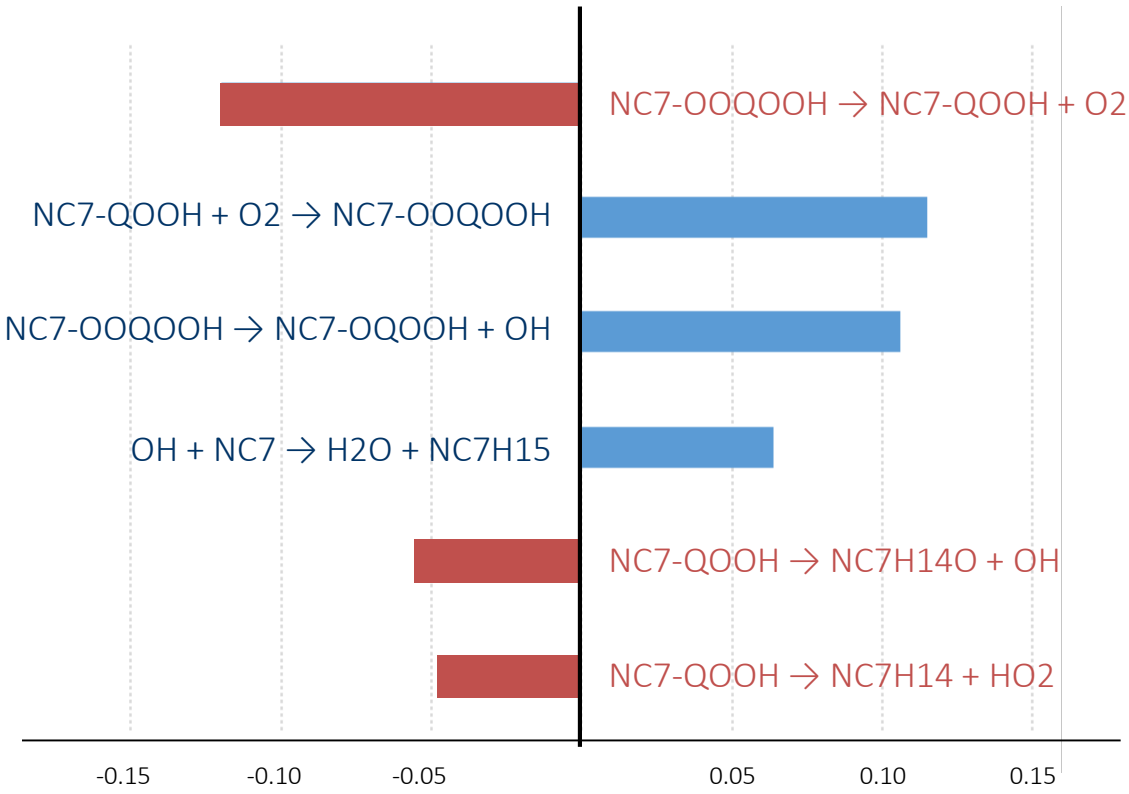


Cool flame @ 30 s

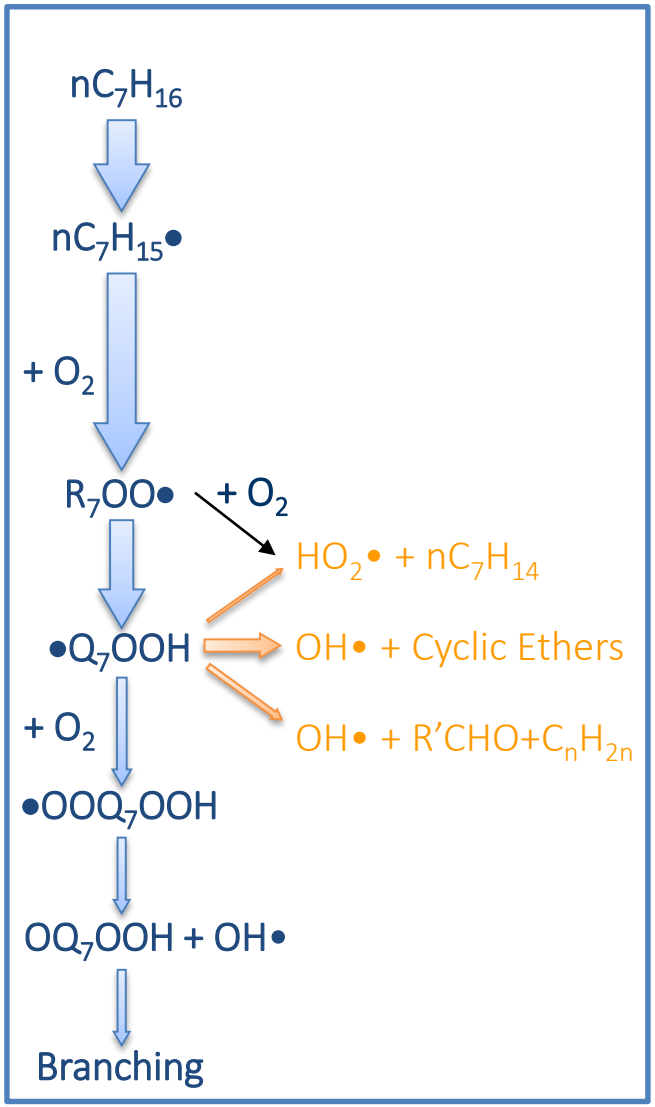


Sensitivity analysis

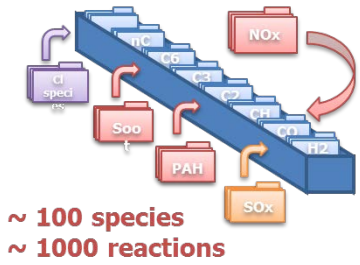
Global sensitivity coefficients of the vaporization rate during the LT combustion



Cool flame @ 30 s



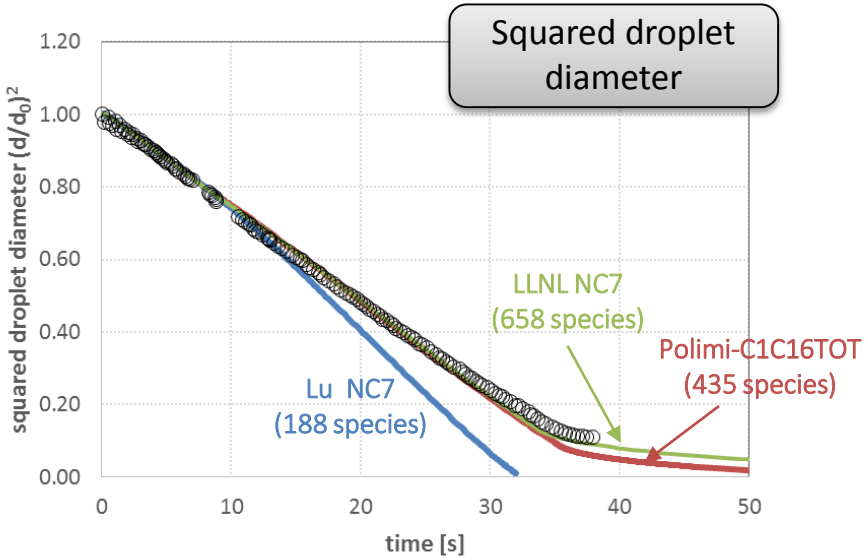
Comparison with other kinetic mechanisms (I)

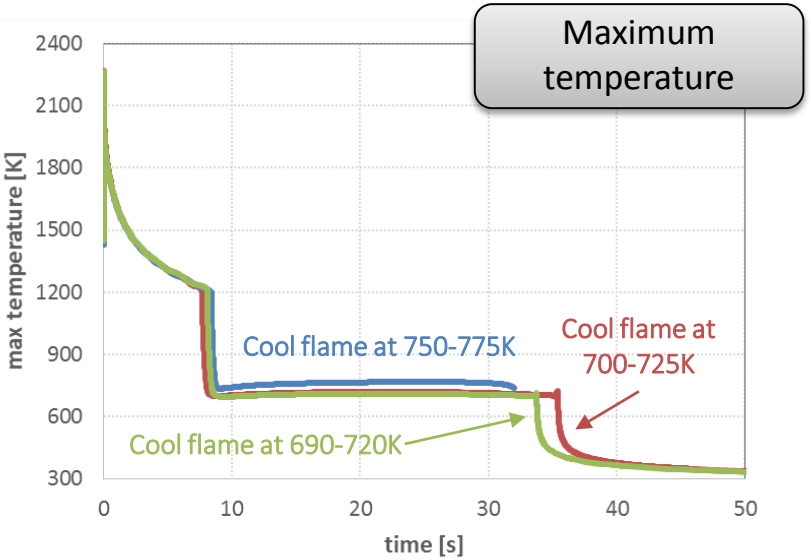


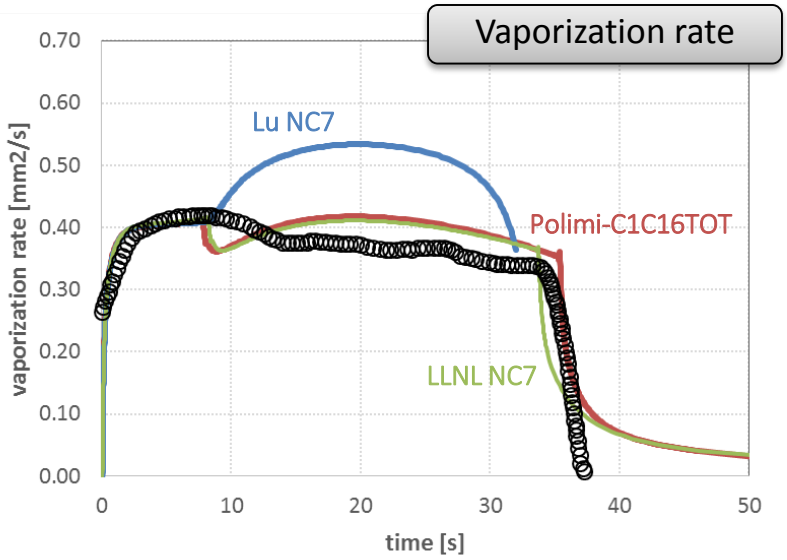
Several detailed kinetic mechanisms (with Low Temperature chemistry) were tested and compared

Polimi-C1C16TOT (version 1212)	**Species: 435 Reactions: 13,495**	**E. Ranzi, A. Frassoldati, R. Grana, A. Cuoci, T. Faravelli, A.P. Kelley, C.K. Law**, *Hierarchical and comparative kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels*, Progress in Energy and Combustion Science, 38 (4), pp. 468-501 (2012)
Lu-NC7	**Species: 188 Reactions: 939**	**C.S. Yoo, T.F. Lu, J.H. Chen, C.K. Law**, *Direct numerical simulations of ignition of a lean n-heptane/air mixture with temperature inhomogeneities at constant volume: Parametric study*, Combustion and Flame, 158(9), p.1727–1741 (2011)
LLNL-NC7	**Species: 658 Reactions: 2,827**	**Mehl M., W.J. Pitz, C.K. Westbrook, H.J. Curran,** *Kinetic Modeling of Gasoline Surrogate Components and Mixtures Under Engine Conditions*, Proceedings of the Combustion Institute33:193-200 (2011)

Comparison with other kinetic mechanisms (II)







The results are strongly affected by the ability of the **kinetic mechanism** to correctly capture the features of the cool flame (i.e. by the accuracy and the reliability of the low-temperature chemistry)

Outline

1. Introduction
   - ✓ Cool flames
   - ✓ Low-temperature mechanism
2. Mathematical model
   - ✓ Governing equations and numerical methodology
   - ✓ Detailed kinetic mechanism
3. Auto-ignited n-decane ($C_{10}H_{22}$) droplets
   - ✓ Comparison with experiments
   - ✓ Structure of the cool flame
   - ✓ Numerical experiments on n-heptane and n-dodecane
4. Hot-wire ignited n-heptane (NC_7H_{16}) droplets
   - ✓ Comparison with experiments
   - ✓ Kinetic analysis
   - ✓ Comparison between different kinetic mechanisms
5. **Conclusions and future works**

Conclusions

Numerical modeling of **auto-ignited** and **hot-wire ignited** isolated droplets in microgravity with **detailed kinetic mechanisms** were successfully performed

The formation of **cool flames**, both for **n-decane** and **n-heptane droplets**, was observed, explained and compared with experimental measurements

Auto-ignition of n-decane droplets (experiments performed by Xu et al.)

We demonstrated that the observed vaporization rates can be explained only by the presence of a cool flame around the droplet

Hot-wire ignited n-heptane droplets (experiments performed by Nayagam et al.)

We confirmed the hypothesis that after the first-stage extinction, the vaporization is sustained by a low-temperature, soot-free, ‘‘cool-flame’’ heat release.

Future work

Additional simulations of experiments of hot-wire ignition experiments on n-heptane droplets to check the formation of cool flames

Deeper investigations about the chemistry of cool flames

Improvements in the numerical model (radiative heat transfer, numerical methodology, etc.)

Modeling of soot formation through a detailed kinetic mechanism (based on the discrete sectional method)

Table 1
Experimental conditions, measured droplet initial diameter d_0, hot-flame extinction diameter d_{he}, and the second-stage extinction diameter d_{ce}.

Test #	P (atm)	O_2 (%)	CO_2 (%)	d_0 (mm)	d_{he} (mm)	d_{ce} (mm)	K (mm^2/s)	B
1	2	21	9	2.92	1.73	0.42	0.475	4.44
2	1	21	0	3.91	3.28	1.30	0.368	4.48
3	1	21	0	3.58	2.8	0.73	0.448	4.48
4	1	21	0	3.69	3.46	0.72	0.462	4.48
5	1	18	0	3.48	3.16	1.60	0.356	3.82
6	1	17.5	0	2.74	2.03	0.78	0.412	3.75
7	1	18	15	3.76	3.63	1.88	0.361	3.51
8	1	18	15	2.84	2.55	1.46	0.36	3.51
9	1	18	15	3.82	3.66	1.82	0.359	3.51
10	1	18	15	2.49	1.97	1.25	0.343	3.51
11	1	19	10	3.51	3.15	1.50	0.381	3.82
12	1	19	10	2.6	1.72	1.01	0.334	3.82
13	1	17	20	3.76	3.71	2.16	0.346	3.22
14	1	20	5	2.9	2.79	1.74	0.355	4.14
15	1	20	5	3.04	2.33	1.18	0.351	4.14
16	1	16	0	3.34	3.18	1.97	0.346	3.38
17	1	16	0	2.52	2.13	1.50	0.333	3.38
18	1	15	0	2.55	2.31	1.73	0.319	3.16
19	1	21	0	3.65	2.85	1.34	0.424	4.48
20	0.7	23.5	55.8	3.77	3.04	1.83	0.412	3.74
21	0.7	23	23	3.87	3.42	1.89	0.412	4.35
22	0.7	21	30	4.05	3.83	2.91	0.393	3.74
23	0.7	19.6	35	3.11	2.9	2.37	0.3649	3.43
24	0.7	18	40	2.68	2.49	2.16	0.3593	3.04
25	0.7	18	40	2.53	2.37	2.05	0.304	3.04
26	0.7	23	25	3.42	2.62	2.04	0.3542	4.21

Adapted from **Nayagam et al.,** Combustion and Flame, 159, p. 3583-3588 (2012)

Acknowledgments

The authors would like to acknowledge **Prof. Eliseo Ranzi** (Politecnico di Milano) for his interesting comments and **Dr. Daniel L. Dietrich** (NASA Glenn Research Center, Cleveland, USA) for the useful discussions and suggestions and the additional details about the hot-wire ignition experiments.

The work at Politecnico di Milano was partially supported by the **Italian Government MSE/CNR** (*Biofuel Project: Utilizzo di biocombustibili liquidi e gassosi per la generazione distribuita di energia elettrica*)

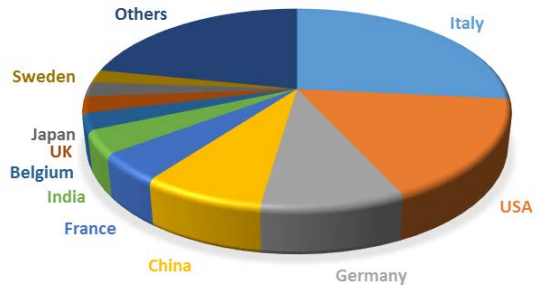
Additional slides

CRECKModeling on the web

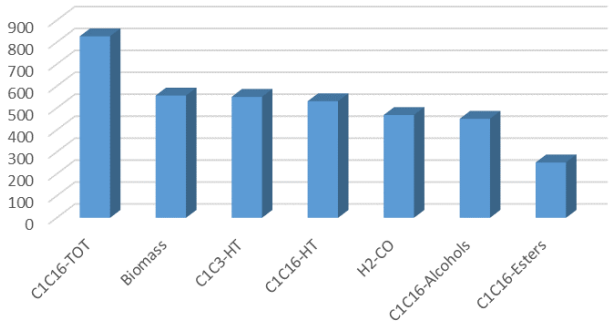
All our kinetic schemes can be freely downloaded in CHEMKIN format from our web site:

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

Statistics since January 2013
Unique visitors: 3,500
Visits: 6,700 (~25 per day)



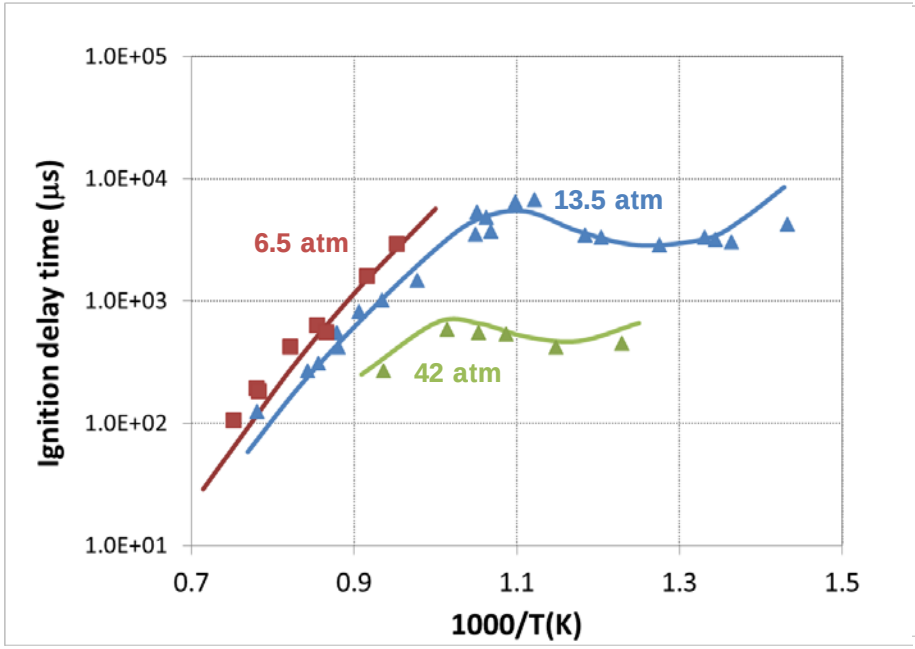
Our kinetic schemes were downloaded more than 3,600 times since Jan 2013



Validation of the kinetic mechanism: n-heptane

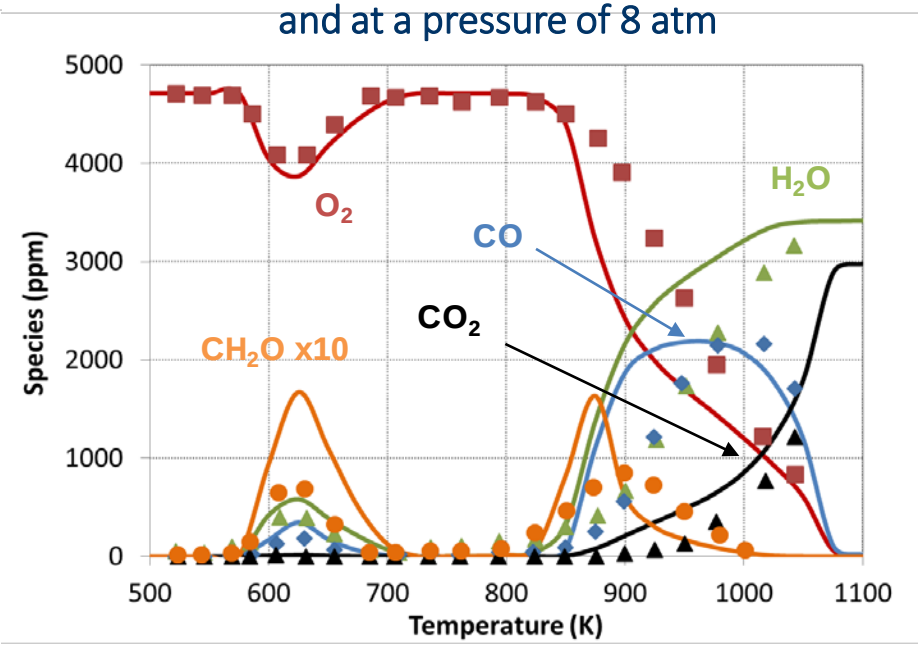
Polimi C1C16TOT (435 species)

Shock-tube experiments



Experimental data from:
Ciezki H.K. and Adomeit G., *Shock-tube investigation of self-ignition of n-heptane-air mixtures under engine relevant conitions*, Combustion and Flame 93 p. 421–433 (1993)

Princeton Variable Pressure Flow Reactor at temperatures of 500-1000 K and at a pressure of 8 atm

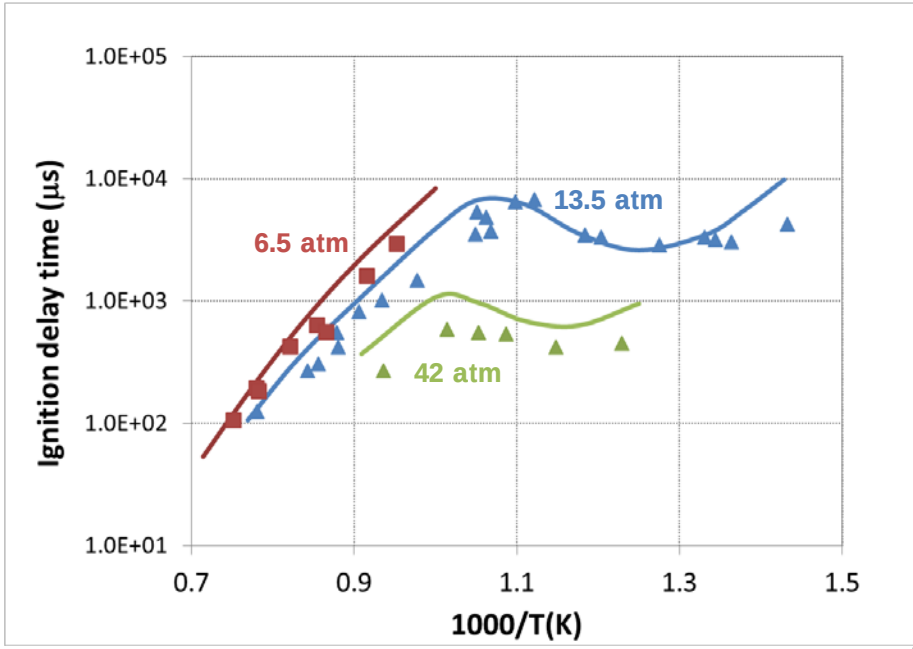


Experimental data from:
Veloo P.S., Jahangirian S., Dryer F.L., *An experimental and kinetic modeling study of the two stage auto-ignition kinetic behavior of C7, C10, C12, and C14 n-alkanes*, Spring Technical Meeting of the Central States Section of the Combustion Institute, Dayton, Ohio (2013)

Validation of the kinetic mechanism: n-heptane

Lu NC7 (188 species)

Shock-tube experiments



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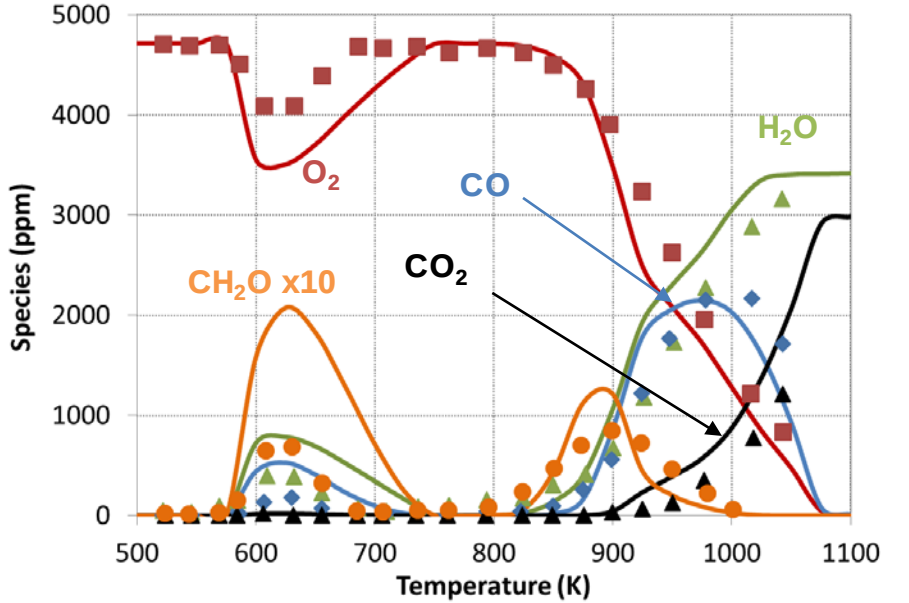
Princeton Variable Pressure Flow Reactor at temperatures of 500-1000 K and at a pressure of 8 atm



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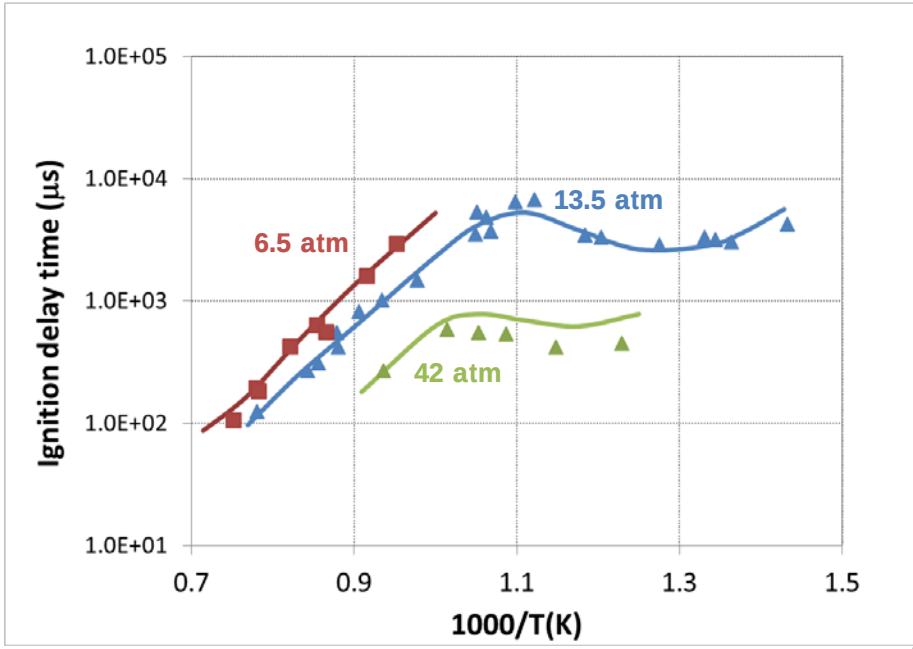
Veloo P.S., Jahangirian S., Dryer F.L., *An experimental and kinetic modeling study of the two stage auto-ignition kinetic behavior of C7, C10, C12, and C14 n-alkanes*, Spring Technical Meeting of the Central States Section of the Combustion Institute, Dayton, Ohio (2013)

Validation of the kinetic mechanism: n-heptane

LLNL NC7 (658 species)

Shock-tube experiments



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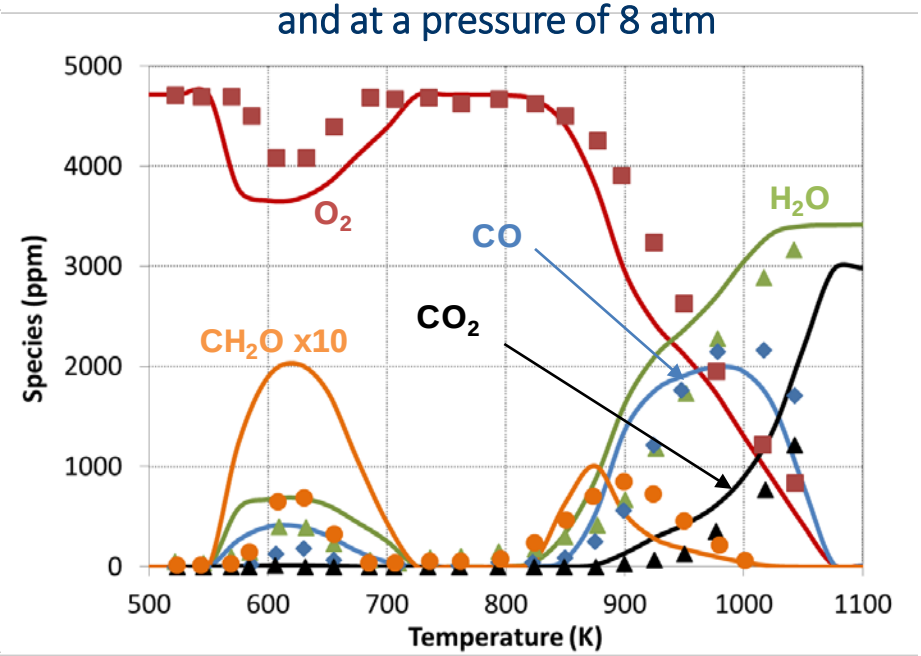
Princeton Variable Pressure Flow Reactor at temperatures of 500-1000 K and at a pressure of 8 atm



Experimental data from:
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Skeletal mechanisms

Polimi-C1C16TOT (version 1212)

Species: 435
Reactions: 13,495

E. Ranzi, et al., Progress in Energy and Combustion Science, 38 (4), pp. 468-501 (2012)

Species: 100
Reactions: 1,567

Reduction factor: 4.35

Stagni A., *Lumping and reduction of detailed kinetic schemes: an effective coupling*, Submitted to Industrial & Engineering Chemistry Research

Lu-NC7

Species: 188
Reactions: 939

C.S. Yoo et al., Combustion and Flame, 158(9), p.1727–1741 (2011)

Reduction performed by the authors

Species: 88
Reactions: 387

Reduction factor: 2.13

C.S. Yoo et al., Combustion and Flame, 158(9), p.1727–1741 (2011)

LLNL-NC7

Species: 658
Reactions: 2,827

Mehl M. et al., Proceedings of the Combustion Institute33:193-200 (2011)

Reduction performed by the authors

Species: 160
Reactions: 1,540

Reduction factor: 4.11

Seiser H. et al., Proceedings of the Combustion Institute28:2029-2037 (2000)

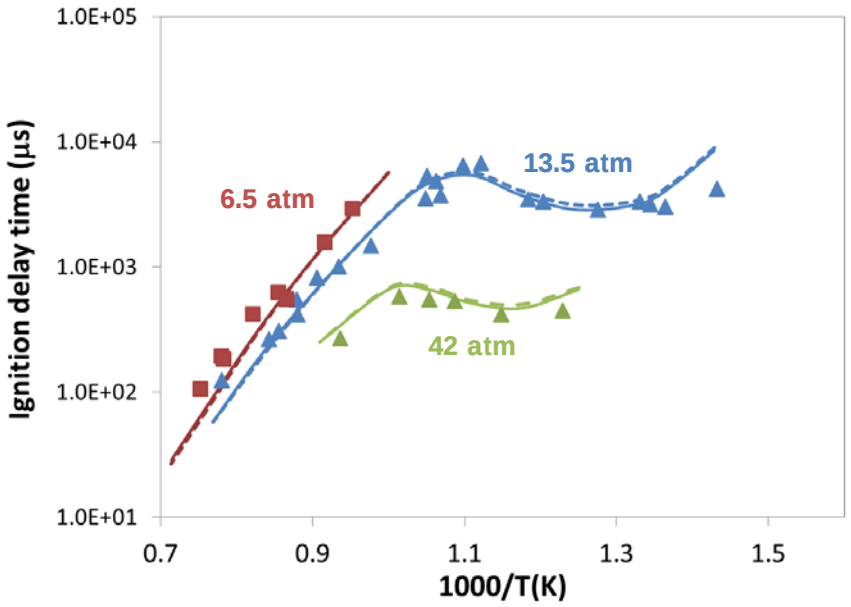
Validation of the kinetic mechanism: n-heptane

——— Original mechanism (435 species)

- - - - - Reduced mechanism (100 species)

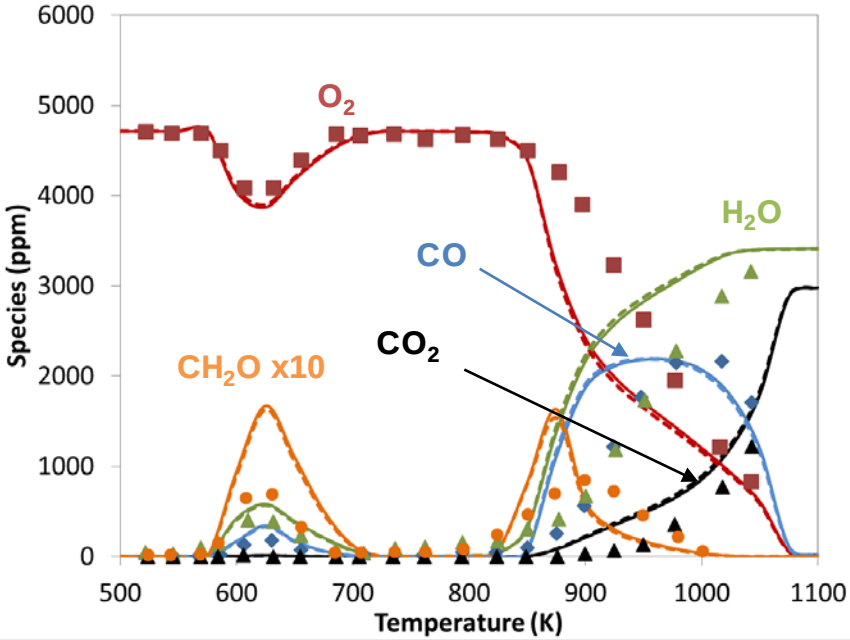
Polimi C1C16TOT

Shock-tube experiments



Experimental data from:
Ciezki H.K. and Adomeit G., Combustion and Flame 93 p. 421–433 (1993)

Princeton Variable Pressure Flow Reactor at temperatures of 500-1000 K and at a pressure of 8 atm



Experimental data from:
Veloo P.S., Jahangirian S., Dryer F.L., Spring Technical Meeting of the Central States Section of the Combustion Institute, Dayton, Ohio (2013)

Validation of the kinetic mechanism: n-heptane

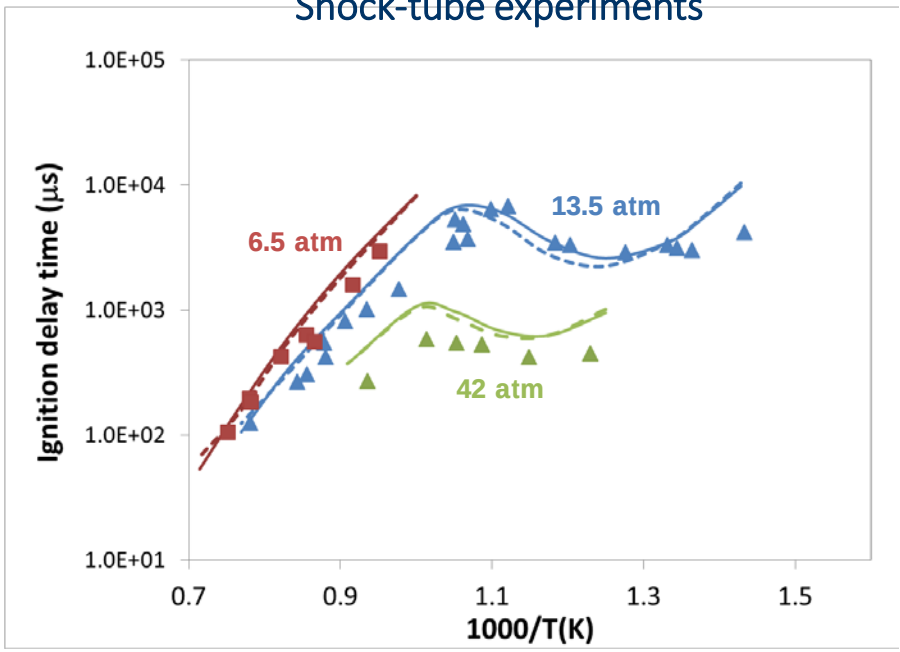
——— Original mechanism (188 species)

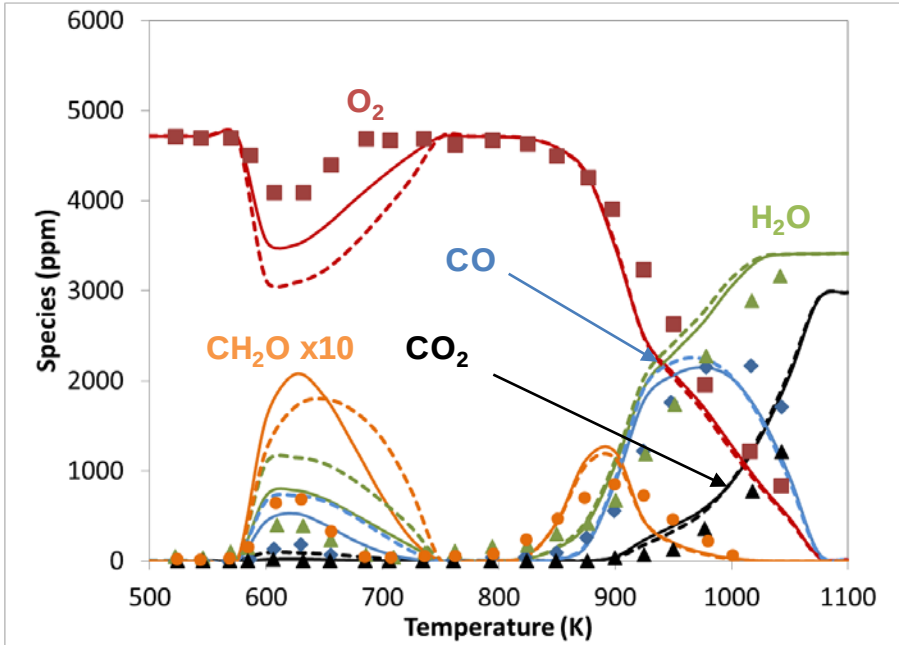
- - - - - Reduced mechanism (88 species)

Lu NC7

Princeton Variable Pressure Flow Reactor at temperatures of 500-1000 K and at a pressure of 8 atm

Shock-tube experiments





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Experimental data from:
Veloo P.S., Jahangirian S., Dryer F.L., Spring Technical Meeting of the Central States Section of the Combustion Institute, Dayton, Ohio (2013)

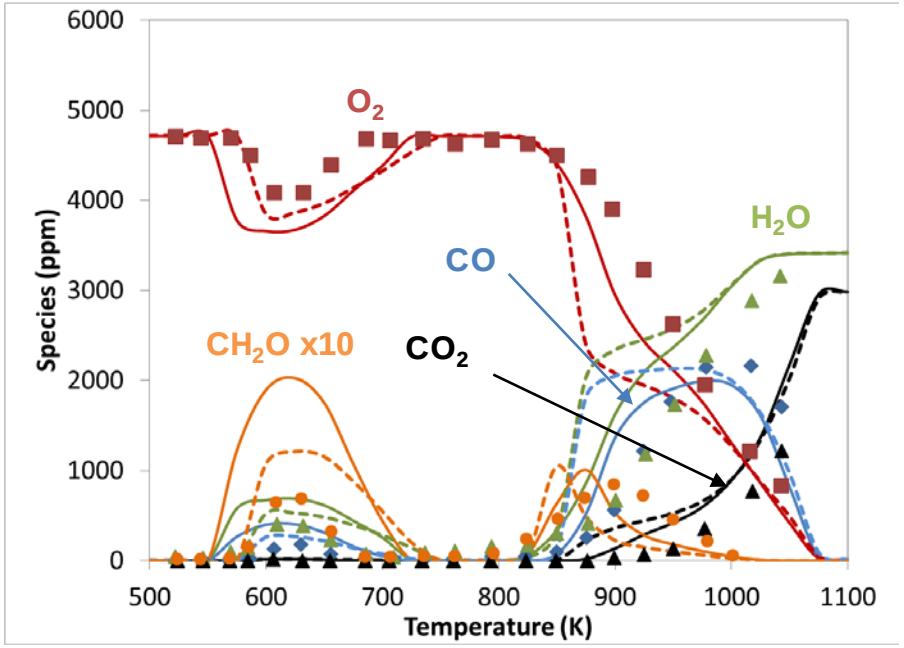
Validation of the kinetic mechanism: n-heptane

——— Original mechanism (658 species)

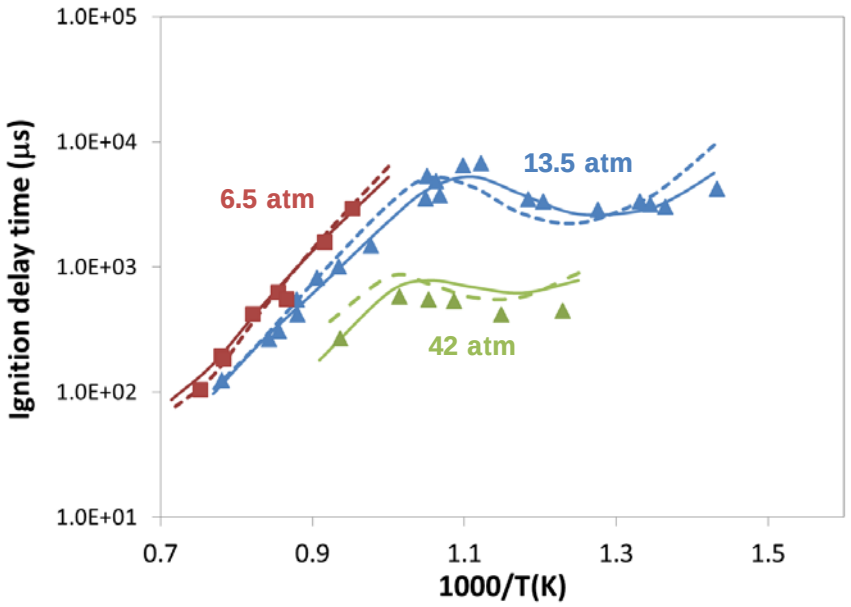
- - - - - Reduced mechanism (160 species)

LLNL NC7

Princeton Variable Pressure Flow Reactor at temperatures of 500-1000 K and at a pressure of 8 atm



Shock-tube experiments



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