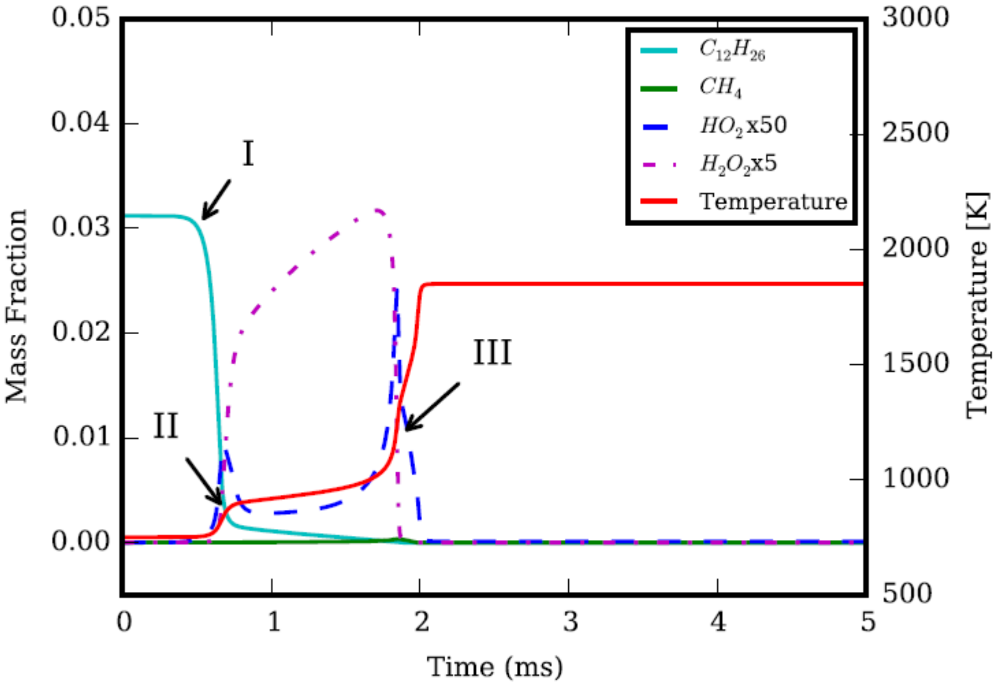
Investigating the ignition mechanism in ultra-lean gas engines using detailed chemistry simulations

Anders Brink and Paulo Santochi Pereira de Silva
Åbo Akademi University

Background

- Ignition of hydrocarbons can be divided into low temperature and high temperature chemistry
- Cross over temperature when simultaneous



M. Ghaderi Masouleh et al. / Fuel 191 (2017) 62–76

Background

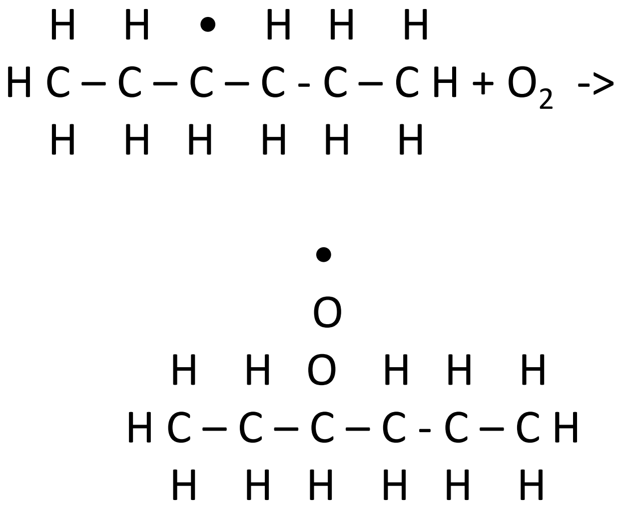
- Low temperature chemistry (LTC) region important for correct prediction of ignition events
- Negative temperature coefficient (NTC) refers that the oxidation rate of a hydrocarbon decrease with increasing temperature

Low temperature oxidation

- Key reaction 1: Alkyl (C_nH_{2n+1}) oxidation

$R + O_2 = RO_2$

- Reaction important at low temperature. Rising temperature leads to dissociation and ends low temperature oxidation
- Rate and stability of this RO_2 depends on the type of site where the O_2 attaches

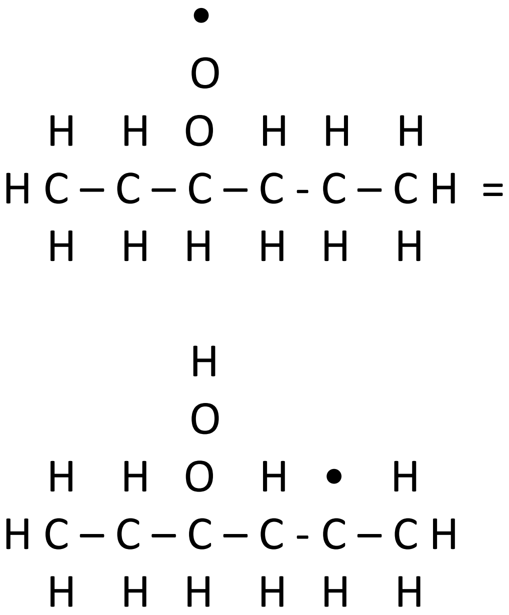


$$\begin{matrix} H & H & \bullet & H & H & H & \\ HC - & C - & C - & C - & C - & CH & + O_2 \; -> \\ H & H & H & H & H & H & \end{matrix}$$

$$\begin{matrix} & & \bullet & & & \\ & & O & & & \\ H & H & O & H & H & H \\ HC - & C - & C - & C - & C - & CH \\ H & H & H & H & H & H \end{matrix}$$

Negative temperature coefficient

- Key reaction 2: Alkyl peroxyradical isomerization **RO_2 =QOOH**
- Important for branching and propagation reactions
- Balance between pathways
  - decomposition
  - cyclic ether formation
  - second O_2 addition
  - HO_2 elimination
  - N-heptane RON=0, iso-octane RON=100!

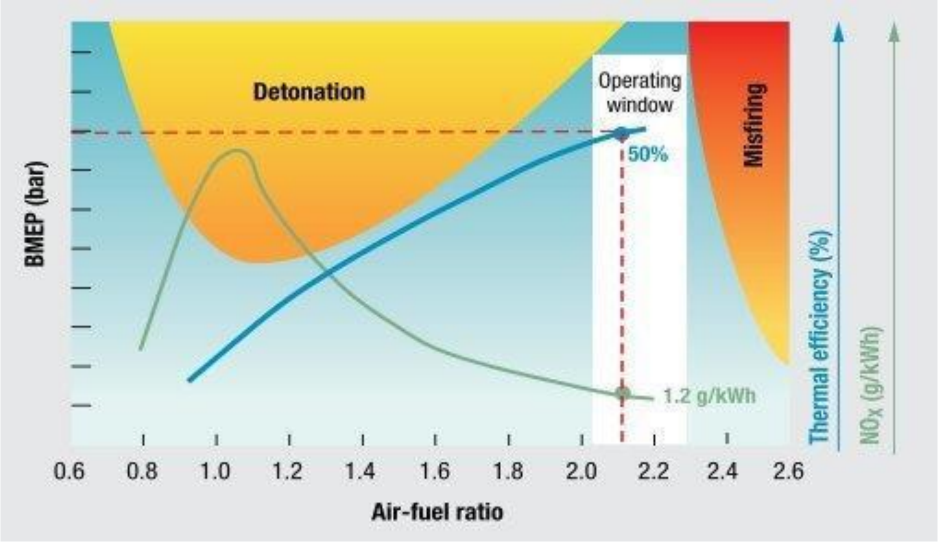


$$\begin{array}{cccccc} & & \bullet & & & \\ & & O & & & \\ H & H & O & H & H & H \\ HC- & C- & C- & C- & C- & CH \\ H & H & H & H & H & H \end{array} =$$

$$\begin{array}{cccccc} & & H & & & \\ & & O & & & \\ H & H & O & H & \bullet & H \\ HC- & C- & C- & C- & C- & CH \\ H & H & H & H & H & H \end{array}$$

Background

- Lean gas mixtures desirable to reduce NOx and increase efficiency
- Ignition a limiting factor
  - Pre-chamber of dual-fuel



Background

- In dual-fuel ultra lean gas engines injection of a high reactivity fuel is used to ignite the premixed gas-air mixture
- Ignition timing and control of the heat release a key factor for high efficiency engines

Aim of this study

- Ignition behavior of methane (natural gas) using a n-dodecane as pilot
    - Influence of primary stoichiometry
    - Influence of temperature
    - Influence of pressure

Simulation tools

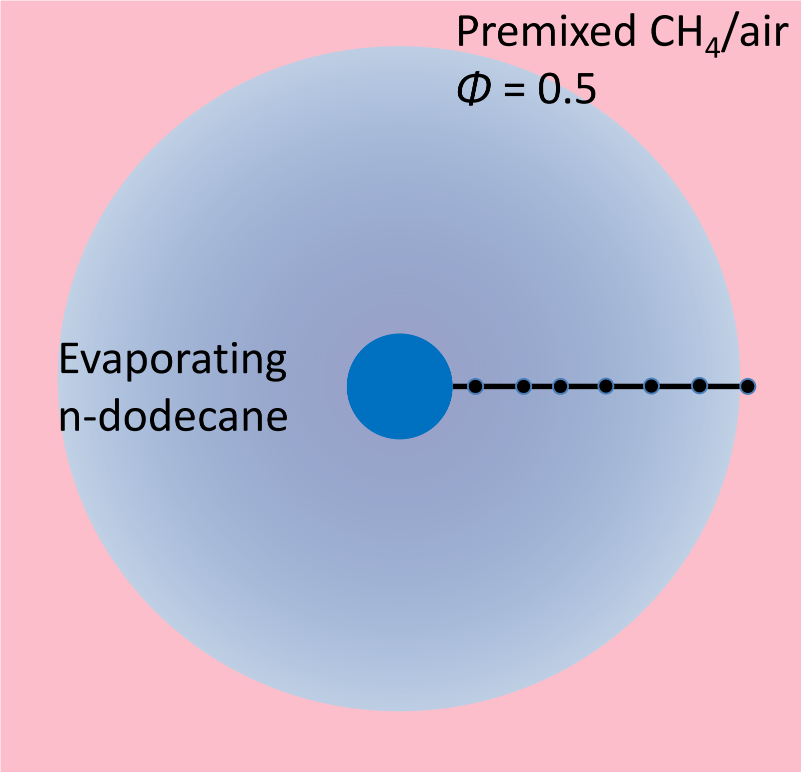
- Chemkin
  - Originally developed as a non-commercial tool for (simple) simulations at Sandia National Laboratory
  - Now own and further developed by Reaction Design as a commercial product
- Cantera
  - A non-commercial open-source alternative to Chemkin

Reaction mechanism

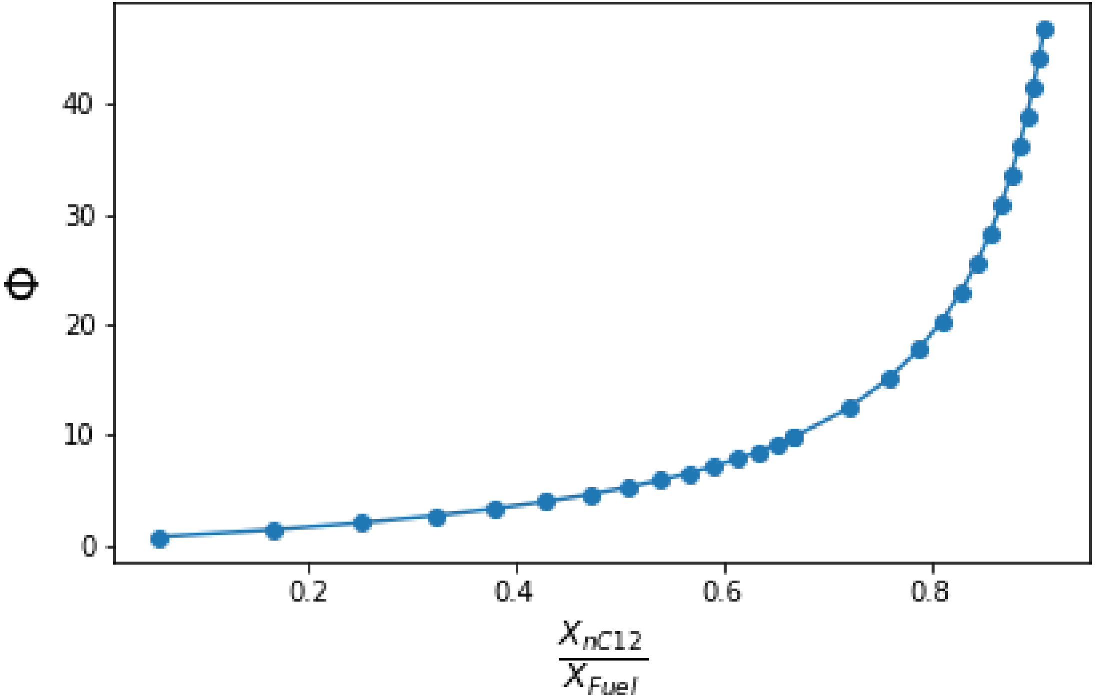
- Massive reaction mechanism for ”simple” fuels available (rule based, machine generated)
- Even more massive reactions for bio-oils available
- In this study the Polimi-mechanism is used (E. Ranzi et al., Progress in Energy and Combustion Science, 2012
    - 451 species 17848 reactions
    - semi-detailed oxidation

Case setup

- Time dependent
- Adiabatic 0D
  - Initial T=700K
- Constant pressure
  - 5MPa

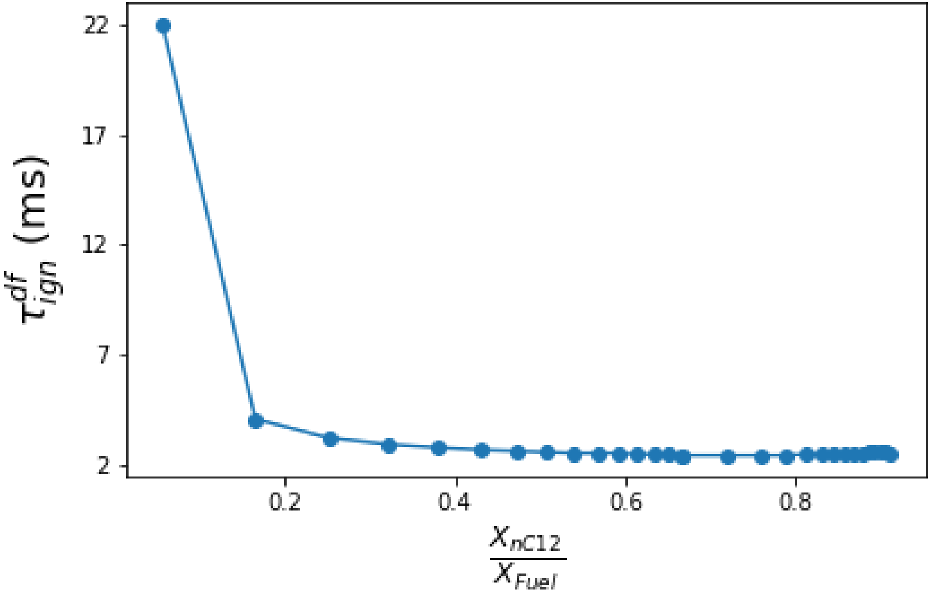


Case setup

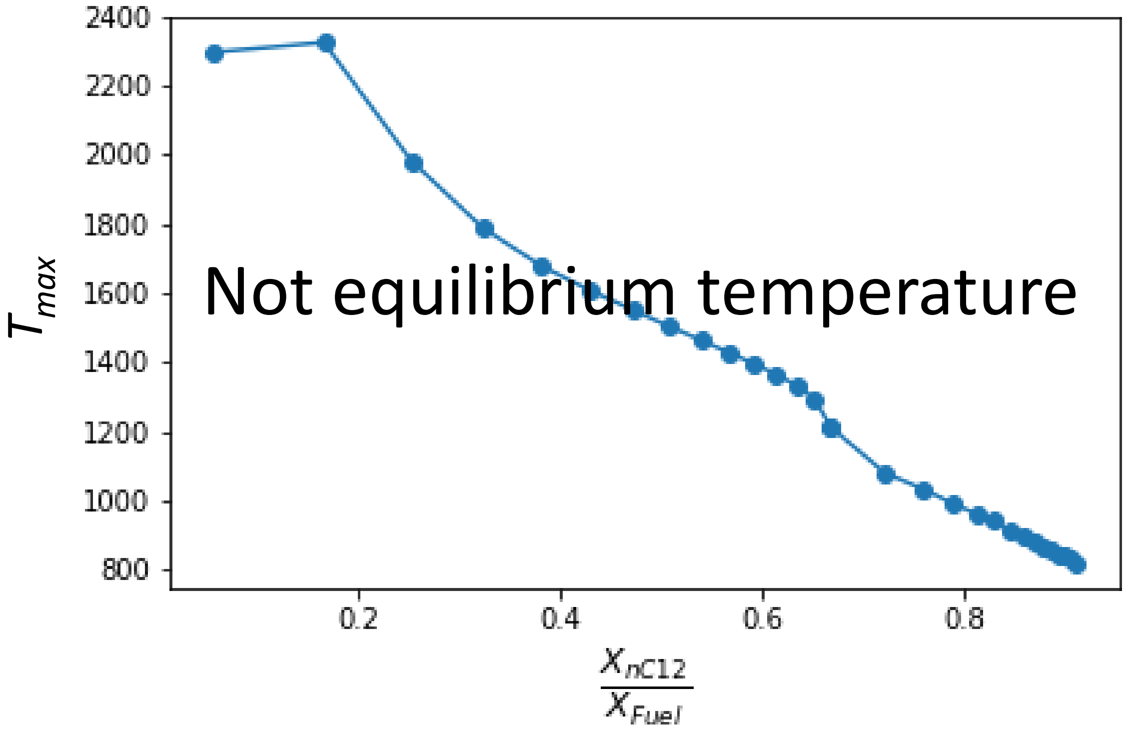


Ignition delay

- Defined as time to reach 95% of maximum temperature

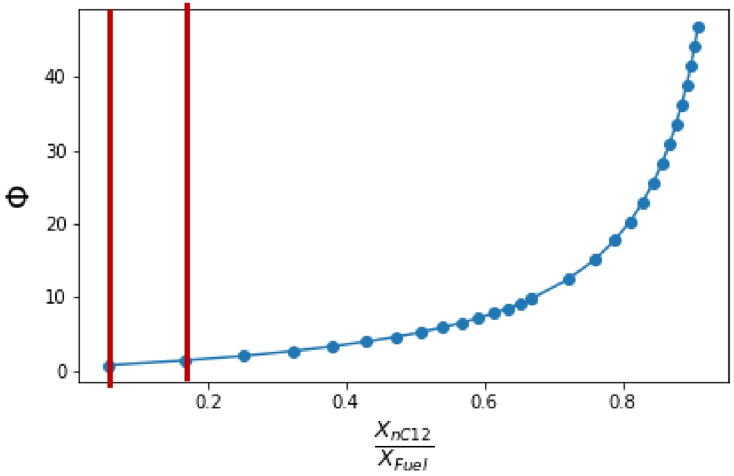


Maximum temperature

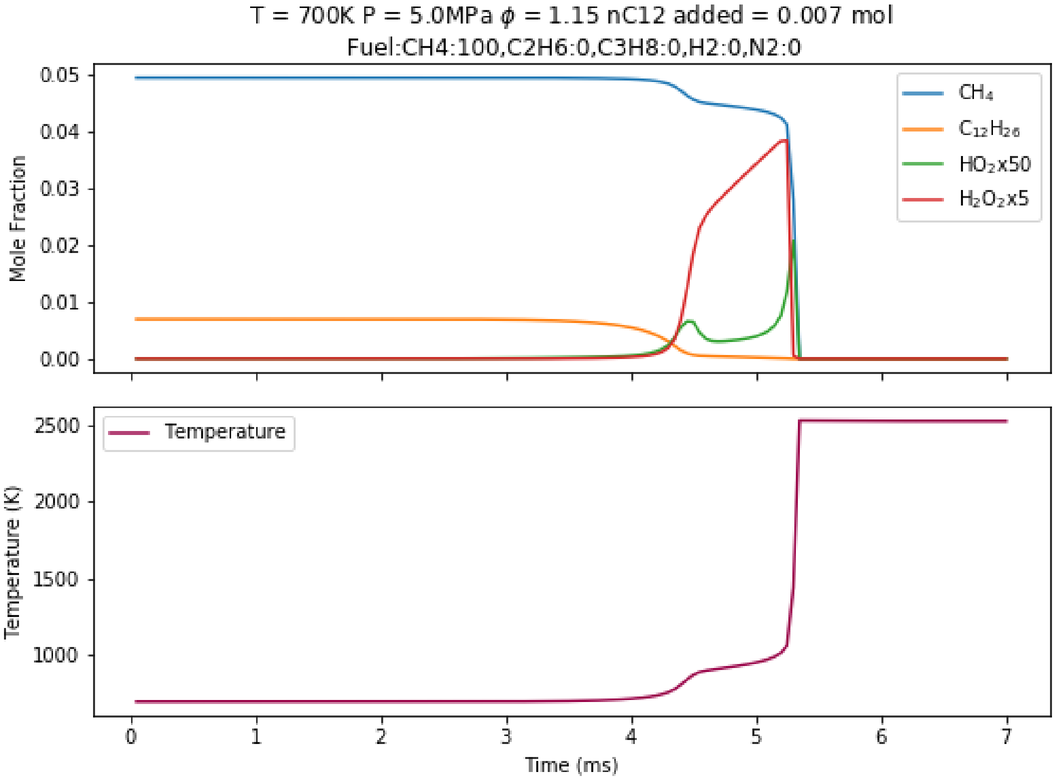


Not equilibrium temperature

Results

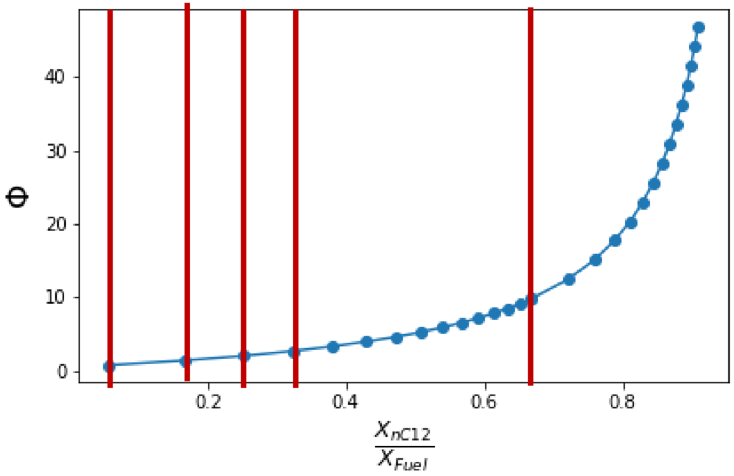


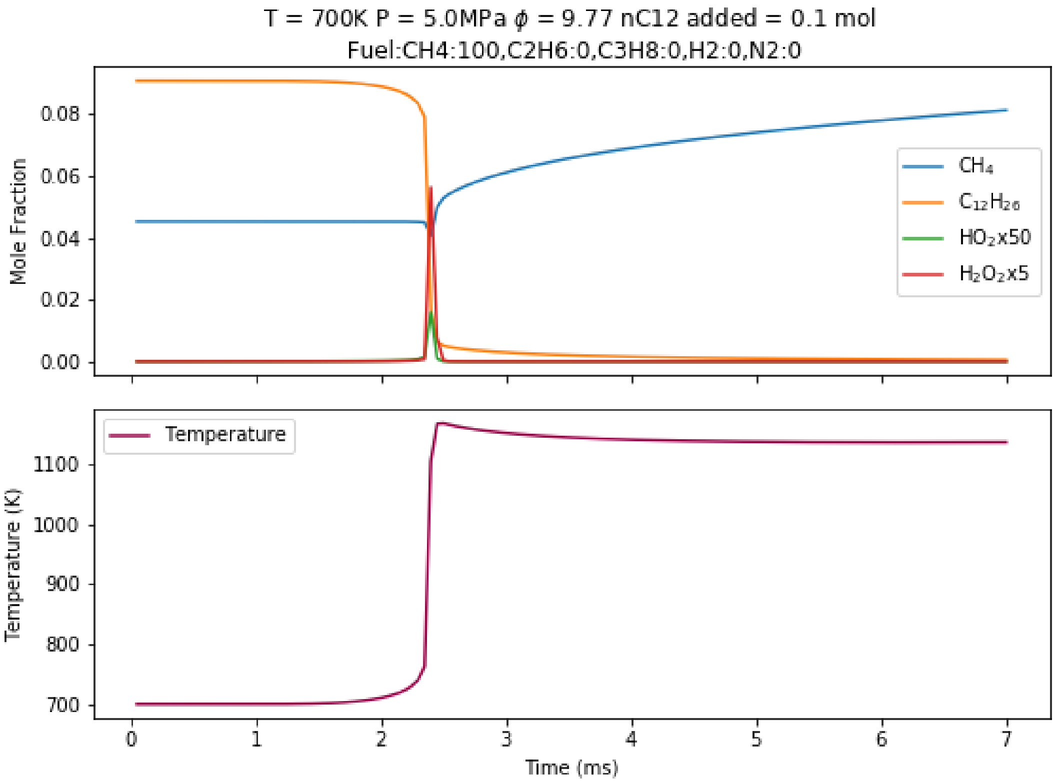
40
30
20
10
0
Φ
0.2
0.4
0.6
0.8
$\frac{X_{nC12}}{X_{Fuel}}$



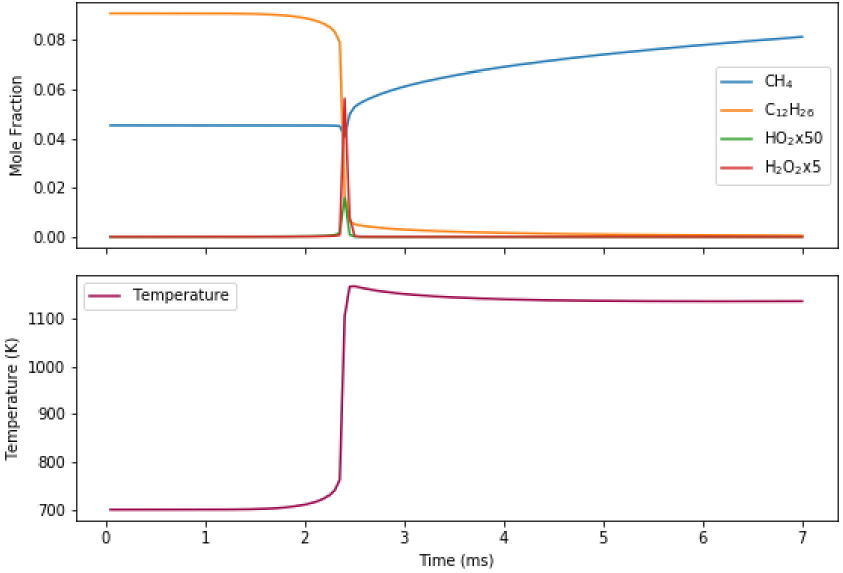
T = 700K P = 5.0MPa ϕ = 1.15 nC12 added = 0.007 mol
Fuel:CH4:100,C2H6:0,C3H8:0,H2:0,N2:0
Mole Fraction
0.05
0.04
0.03
0.02
0.01
0.00
CH_4
$C_{12}H_{26}$
HO_2x50
H_2O_2x5
Temperature
Temperature (K)
2500
2000
1500
1000
0
1
2
3
4
5
6
7
Time (ms)

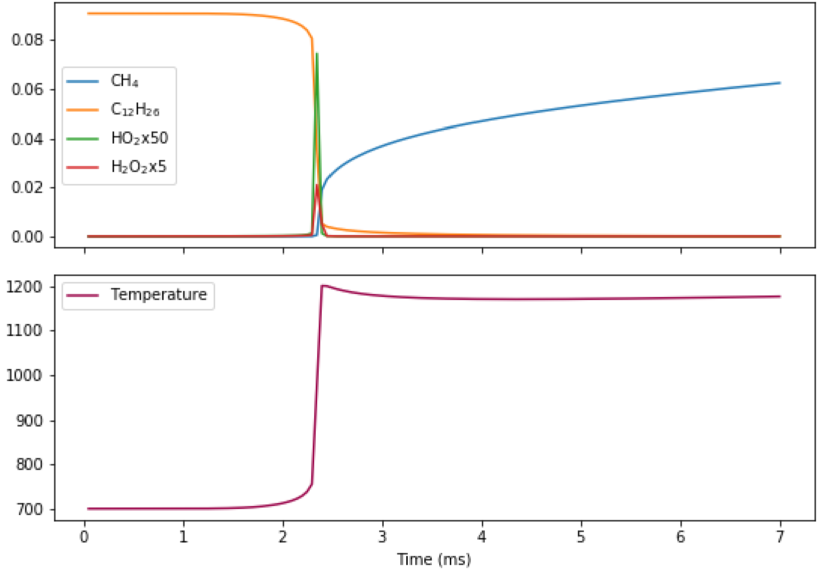
Results


Φ
0
10
20
30
40
0.2
0.4
0.6
0.8
$\frac{X_{nC12}}{X_{Fuel}}$

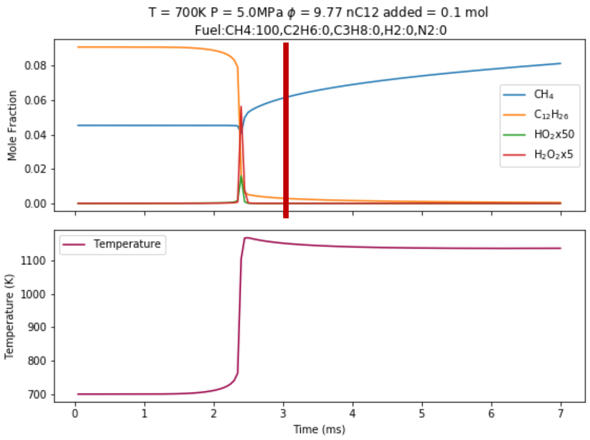

T = 700K P = 5.0MPa ϕ = 9.77 nC12 added = 0.1 mol
Fuel:CH4:100,C2H6:0,C3H8:0,H2:0,N2:0
Mole Fraction
0.00
0.02
0.04
0.06
0.08
CH_4
$C_{12}H_{26}$
HO_2x50
H_2O_2x5
Temperature
Temperature (K)
700
800
900
1000
1100
0
1
2
3
4
5
6
7
Time (ms)

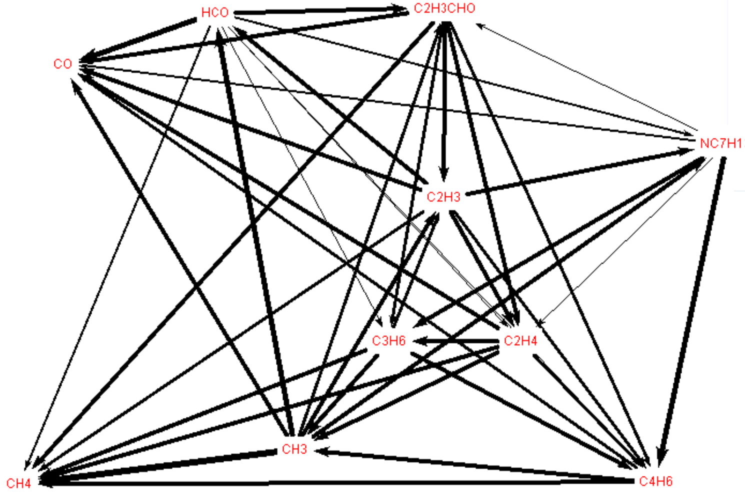
Species evolution in rich mixtures

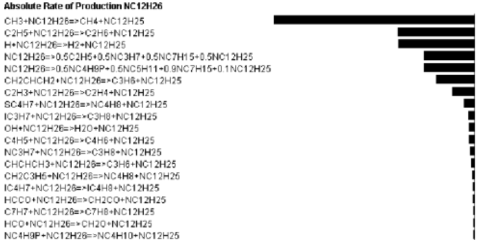

T = 700K P = 5.0MPa ϕ = 9.77 nC12 added = 0.1 mol
Fuel:CH4:100,C2H6:0,C3H8:0,H2:0,N2:0


T = 700K P = 5.0MPa ϕ = 8.81 nC12 added = 0.1 mol
Fuel:CH4:0,C2H6:0,C3H8:0,H2:0,N2:100

Reaction path analysis







Conclusions

- N-dodecane behaves as a reactive ignition fuel at fuel lean to slightly fuel rich conditions
- Cross over stoichiometry!
- Methane behaves as a bath gas at rich conditions
- Pyrolysis reactions of n-dodecane at very rich conditions
- Ignition if methane partly consumed?

Acknowledgement

- This work is financed by the Academy of Finland within the project ”New insight into the ignition in ultra-lean gas combustion”

Aalto University

Åbo Akademi

SUOMEN AKATEMIA