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Exercise 4
Flame Inhibitors

Combustion Fundamentals and New Technologies

Conservatorio delle Orfane a Terra Murata
Isola di Procida, Napoli, Italy
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Introduction

Reactor models

Solver for 1D laminar flames from the OpenSMOKE++ Suite

`OpenSMOKE_PremixedLaminarFlame1D`

Reaction mechanism

GRI-Mech 3.0 (without NOx) with addition of Fe(CO)5 or CF3Br chemistry

Purpose

Familiarize the student with numerical evaluation of laminar flame speeds. Introduce a practical example on the importance of chain terminating reactions.

Background (I)

The action of chemical inhibitors on combustion has been a subject of continuing interest. Research in this area has received a major impetus from the need to seek replacements for currently used fire inhibitors in view of their effects on the ozone layer and resulting international conventions

In particular, the compound CF3Br (Halon 1301) was the commonly used retardant, whose production is currently prohibited in most nations by international convention.
Thus, halogenated compounds such as CF3Br or C2F4Br2 need to be replaced. However, it has proven difficult to find environmentally acceptable replacements. Current efforts aim to understand the inhibition mechanisms of known, effective flame inhibitors to help direct the search.

Background (II)

Additive Quantity Required for 10% Reduction of Burning Velocity of Stoichiometric Methane-Air Mixture (Based on Data Presented in [2, 5, 6])

Additive	Molecules of inhibitor required per 100 molecules of CH_4 for 10% reduction of S_u	Coefficient of efficiency relative to CF_3Br
CO_2	10	0.12
CH_3Cl	4.9	0.24
Cl_2	3.8	0.32
CHF_3	3	0.4
HBr	1.8	0.67
CH_3I	1.7	0.71
CH_3Br	1.6	0.75
CF_3Br	1.2	1
Br_2	0.83	1.4
$(CH_3)_3PO_4$	0.3	4
$TiCl_3$	0.22	5.5
PCl_3	0.175	6.9
$NaHCO_3$	0.1	12
$Pb(C_2H_5)_4$	0.022	55
$Fe(CO)_5$	0.02	60

Decreases in burning velocities of premixed flames in the presence of inhibitors are generally considered a measure of the effectiveness of a flame retardant.

Depending on the additive, the amount necessary for a constant reduction in the velocity of a CH4/air flame shows enormous variations.

The effect of carbon CO2 is entirely due to physical effects.

For the commonly used halogenated compounds, the difference in the efficiency from CO2 is about 1 order of magnitude.

Thus, on a mole basis, the ratio of concentrations of CO2, CF3Br, and Fe(CO)5 required for equal decreases in flame velocities at the levels given in 8.3:1:0.017.

For “super” inhibitors, the extreme effectiveness can only arise from chemical effects.

Background (III)

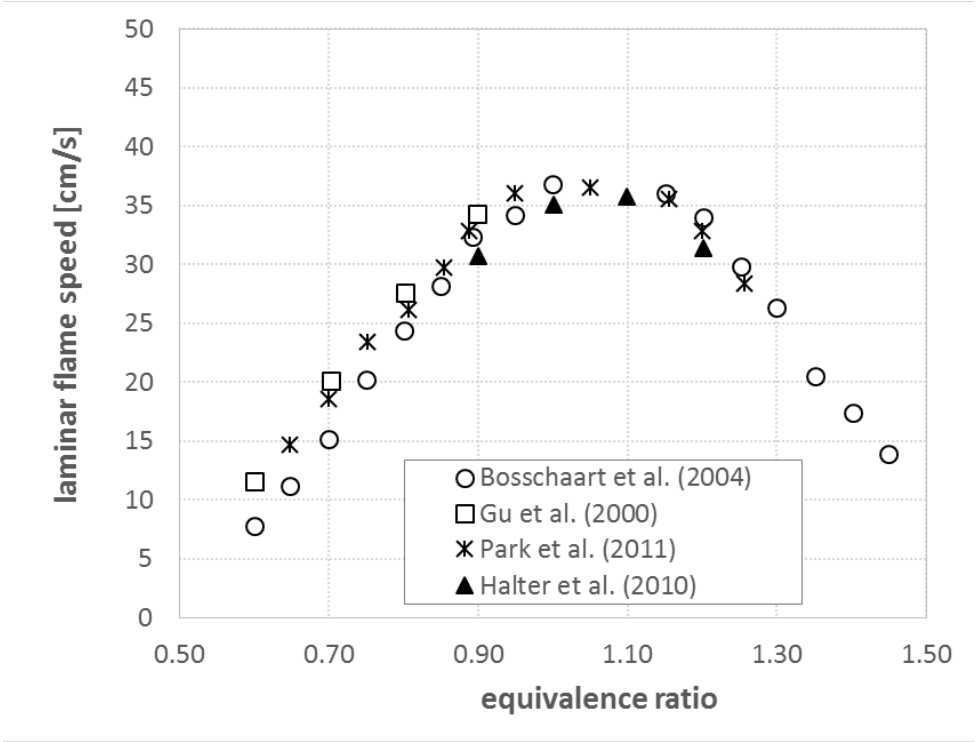
The purpose of this exercise is to investigate the effect of an inert (CO2) and a chemically active agent (iron pentacarbonyl, Fe(CO)5) on the flame speed of an atmospheric, stoichiometric methane/air flame.

Employ the code to determine the flame speed, using GRI-Mech 3.0:

a) with a subset for Fe(CO)5 (iron pentacarbonyl) chemistry (Rumminger, 1999)
b) with and without a subset added for C F 3 Br chemistry (Babushok, 2012)

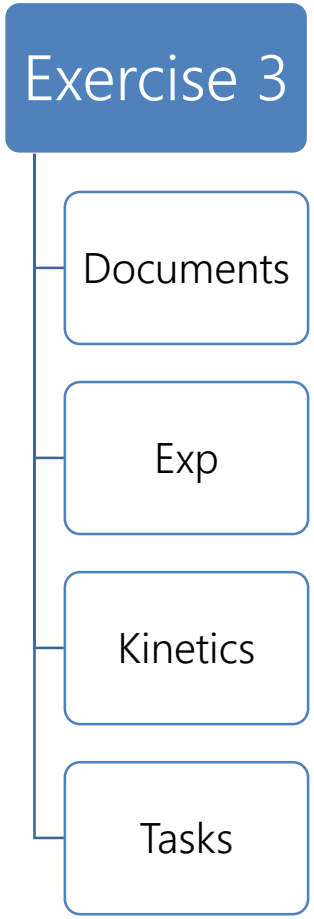
Tasks

1. Check the ability of GRI-Mech 3.0 to correctly describe the laminar flame speed of methane in air at atmospheric pressure. For this purpose, compare the numerical calculations with experimental data available.
2. Determine the amount of CO2 addition required to obtain a 10% decrease in the flame speed of an atmospheric, stoichiometric methane/air flame.
3. Add to GRI-Mech 3.0 the subset of reactions describing the chemistry of Fe(CO)5. Determine the amount of Fe(CO)5 addition required to obtain a 10% decrease in the flame speed of an atmospheric, stoichiometric methane/air flame. Hint: iron pentacarbonyl is much more efficient than CO2.
4. Add to GRI-Mech 3.0 the subset of reactions describing the chemistry of CF3Br. Compare the efficiency of CF3Br as fire supressant with respect to Fe(CO)5. Consider that 1-2 molecules of CF3Br per 100 molecules of CH4 are sufficient to obtain a 10% decrease in the flame speed of an atmospheric, stoichiometric methane/air flame.



Laminar flame speeds of methane/air mixtures at atmospheric pressure (T=298K)

Organization



Folder containing the text of this practical session, this presentation, and additional papers which may be useful to better comment the numerical results

Folder containing the experimental data (in text format) to be used for comparison with the numerical results

Folder containing the thermodynamic data and kinetic mechanism files in CHEMKIN format

The kinetic mechanisms

GRI-30 Mech (without NOX)

For the purposes of the present calculations, the subset of reactions describing the chemistry of NOX was removed in order to have a small number of species, leading to a reduction of computational times

Number of species: 53 → 36
Number of reactions: 325 → 219

M. Frenklach, H. Wang, M. Goldenberg, G.P. Smith, D.M. Golden, C.T. Bowman, R.K. Hanson, W.C. Gardiner, and V. Lissianski. Gri-mech: an optimized detailed chemical reaction mechanism for methane combustion. Report No. GRI-95/0058, 1995.

Fe(CO)5 subset

Subset of reactions describing the chemistry of Fe(CO)5. This subset has to be added to GRI-30 mechanism.

Number of additional species: 9
Number of additional reactions: 48

M.D. Rumminger, D. Reinelt, V. Babushok, and G.T. Linteris. Numerical study of the inhibition of premixed and diffusion flames by iron pentacarbonyl. Combustion and Flame, 116(1-2):207-219, 1999

CF3Br (Halon 1301)

Subset of reactions describing the chemistry of Halon 1301. This subset has to be added to GRI-30 mechanism.

Number of additional species: 72
Number of additional reactions: 767

V.I. Babushok, G.T. Linteris, and O.C. Meier. Combustion properties of halogenated re suppressants. Combustion and Flame, 159(12):3569-3575, 2012

Task 0: preprocessing of kinetic mechanisms (I)

Before application in **OpenSMOKE++ Suite**, the kinetic schemes have to be pre-processed. The pre-processing must be performed only once, using **OpenSMOKE_CHEMKIN_PreProcessor** utility. As an example, for the GRI-30 mechanism:

1. Thermodynamic data (**thermo30_without_NOX.dat**), kinetic mechanism (**grimech30_without_NOX.dat**) and transport data (**transport_without_NOX.dat**) files are available in the **Kinetics** folder

2. Open the **Task0** folder and create a new input file (**input.gri30_without_NOX.dic** in the following) in which you specify the thermodynamic and kinetic files and the destination folder:

```
Dictionary CHEMKIN_PreProcessor
{
  @Kinetics          ../../Kinetics/GRI30_without_NOX/grimech30_without_NOX.dat;
  @Thermodynamics    ../../Kinetics/GRI30_without_NOX/thermo_without_NOX30.dat;
  @Transport         ../../Kinetics/GRI30_without_NOX/transport_without_NOX.dat;
  @Output            GRI30_without_NOX;
}
```

Remember the transport properties! We want to model a flame!

input.gri30_without_NOX.dic

Task 0: preprocessing of kinetic mechanisms (II)

3. Run the kinetic pre-processor using the following command (in Microsoft Windows):

```
%OPENSMOKEPP_EXE_FOLDER%\OpenSMOKE_CHEMKIN_PreProcessor.exe –input input.gri30_without_NOX.dic
```

4. If everything works properly, you will find the result of this pre-processing operation in the folder you specified through the `@Output` keyword in the `input.gri30_without_NOX.dic` file

5. Open the `log` file to make sure no errors were encountered in the reaction mechanism.

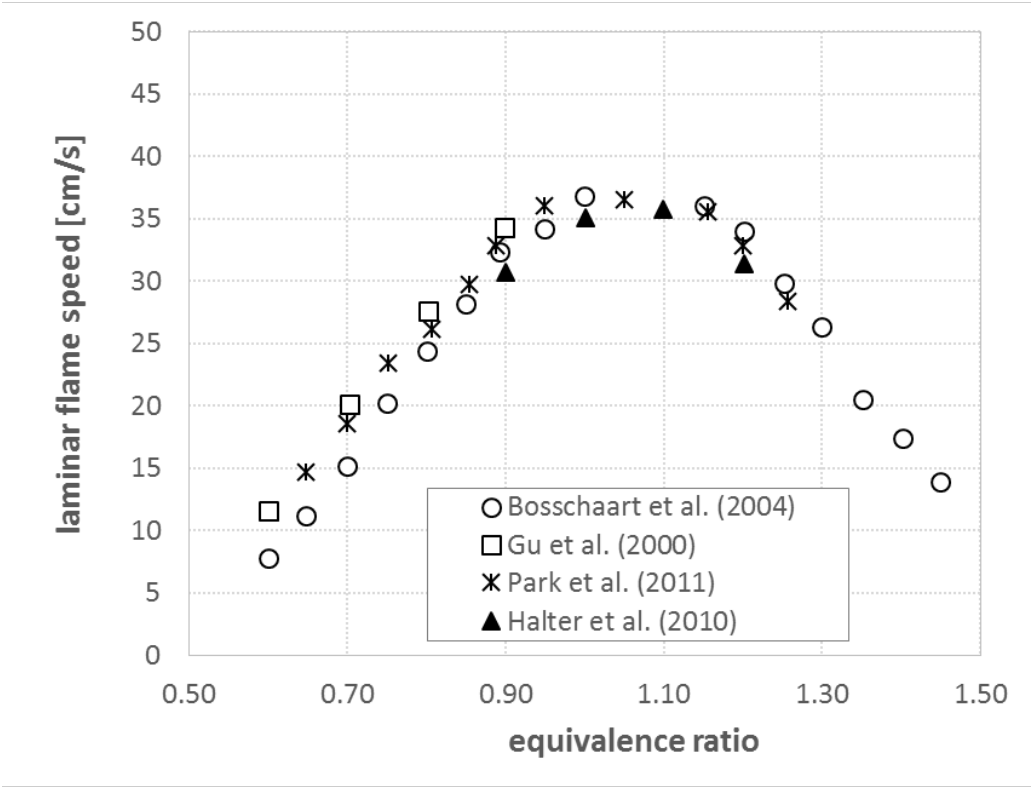
Task 1: flame speed of CH_4/air flames without inhibitors

Simulation conditions

Laminar flame speed

Temperature = 298 K
Pressure = 1 atm

Mixture: CH4 + air (21%O2/79%N2)
Equivalence ratios: 0.70-1.30



K.J. Bosschaart and L.P.H. De Goey. The laminar burning velocity of flames propagating in mixtures of hydrocarbons and air measured with the heat flux method. Combustion and Flame, 136(3):261-269, 2004

X.J. Gu, M.Z. Haq, M. Lawes, and R. Woolley. Laminar burning velocity and Markstein lengths of methane-air mixtures. Combustion and Flame, 121(1-2):41-58, 2000

O. Park, P.S. Veloo, N. Liu, and F.N. Egolfopoulos. Combustion characteristics of alternative gaseous fuels. Proceedings of the Combustion Institute, 33(1):887-894, 2011

F. Halter, T. Tahtouh, and C. Mounaim-Rousselle. Nonlinear effects of stretch onthe flame front propagation. Combustion and Flame, 157(10):1825-1832, 2010

Task 1: flame speed of CH4/air flames without inhibitors

1. Open the `Task1` folder and for each kinetic mechanism to be investigated, create new input files (`input.inp`) specifying the conditions under investigation

```
Dictionary PremixedLaminarFlame1D
{
   @KineticsFolder ..\..\Task0\kineticsGRI30_without_NOX;

   @InletStream           inlet-stream;
   @OutletStream          outlet-stream;

   @InletVelocity         38 cm/s;

   @Grid                  grid;

   @Output                Output;

   @UseDaeSolver          false;
}
```

Folder containing the pre-processed kinetic mechanism (Task0)

Dictionaries defining the inlet stream (composition, temperature and pressure) and first-guess outlet stream

Laminar flame speed: first guess

Dictionary defining the initial grid and the rules to add new points (i.e. to refine the grid to have more accurate solutions)

Name of folder where to write the results

For very simple kinetic mechanisms you may avoid the solution of intermediate DAE systems in order to speed-up the calculations. In general, it is safer to turn on this option, to have a more robust simulation

Task 1: flame speed of CH4/air flames without inhibitors

```
Dictionary inlet-stream
{
   @FuelMoles              CH4 1;
   @OxidizerMoles          O2 0.21 N2 0.79;
   @EquivalenceRatio       1 1.05 1.1 1.15 1.20 1.25 1.3
                           0.95 0.90 0.85 0.80;

   @Temperature            298 K;
   @Pressure               1 atm;
}
```

We can define the list of equivalence ratios we want to simulate. In most cases, if possible, it is more convenient for numerical reasons start the calculations at the equivalence ratio equal to 1

```
Dictionary outlet-stream
{
        @Moles             CO2 1.5 H2O 1.5 N2 7.52;
        @Temperature       2300 K;
        @Pressure          1 atm;
}
```

This is only a first guess, needed to start the calculations
In this example, only the main combustion products (H2O and CO2) were specified. It is important to specify a sufficiently large temperature, in order to give the inlet mixture the possibility to ignite

Task 1: flame speed of CH4/air flames without inhibitors

```
Dictionary grid
{
   @Length                 3 cm;



   @InitialPoints          12;


   @Type                   database;



   @MaxPoints              1000;

   @MaxAdaptivePoints      15;

   @GradientCoefficient    0.075;
   @CurvatureCoefficient   0.25;

   @Threshold              1e-5;
}
```

Length of computational domain
The computational domain must be sufficiently long, to ensure flat species and temperature profiles both on the inlet and outlet boundaries (i.e. no diffusion, no conduction). This can be verified only a posteriori, but usually, for conventional conditions and fuels, 3-4 cm are enough

Initial number of points
It is better to start with a small number of points (7-15) and then progressively refine the grid

Distribution of initial points (better to avoid equispaced grids)

Maximum number of points allowed

Maximum number of points which can be added in each refinement operation

Coefficients governing the addition of new points. Smaller values cause more grid points to be used

Only species with mass fraction larger than this value are accounted for to choose the new points during the refinement operations

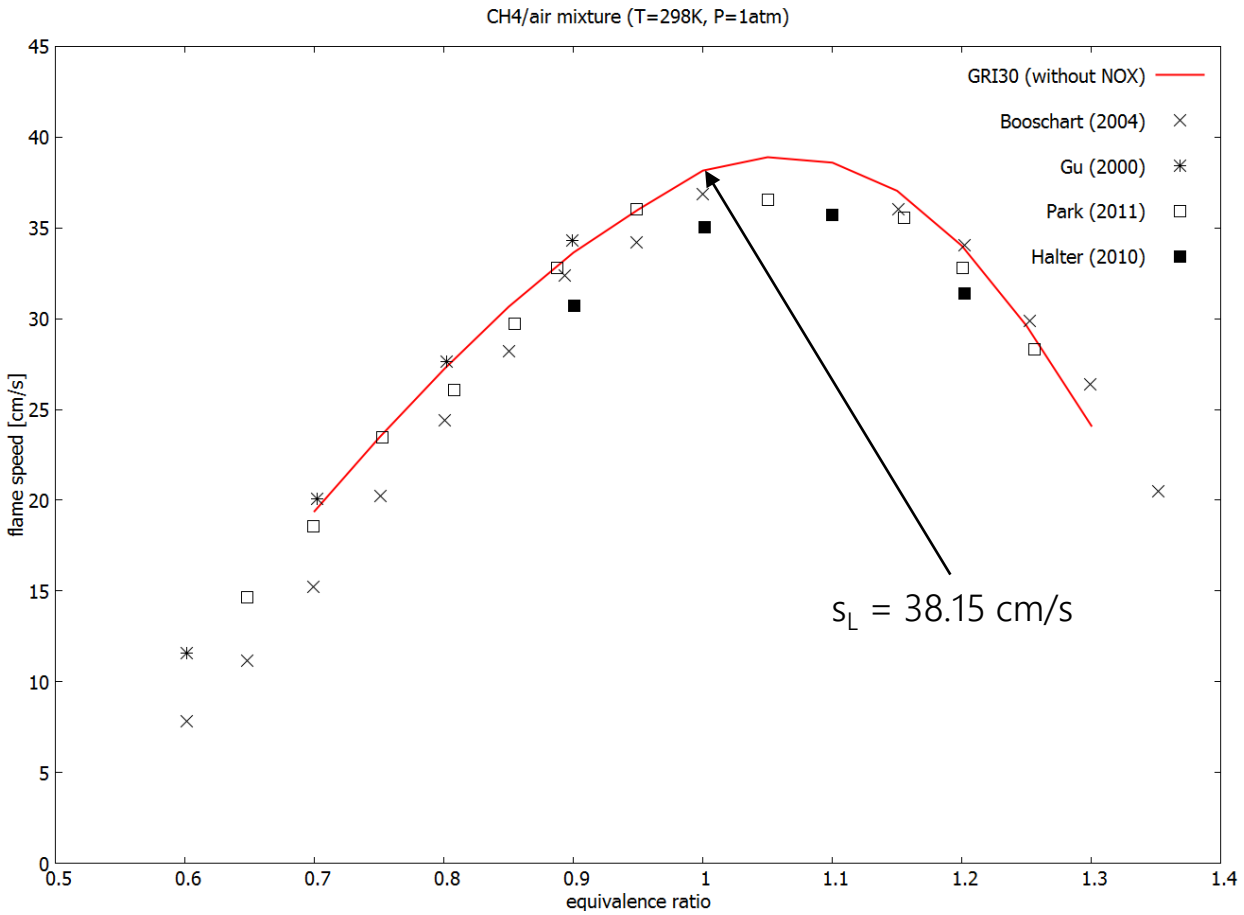
Task 1: flame speed of CH4/air flames without inhibitors

5. Results are available in the `Output` folder.

   In particular, for each equivalence ratio you specified in the dictionary defining the inlet stream, a dedicated folder with name `CaseYY` is available. The `Solution.Final.out` file reports the final solution for each case. As usual, this file is organized in columns: mass fractions of species have the `_w` suffix, while mole fractions have the `_x` suffix.

   The `FlameSpeeds.out` file contains the calculated flame speeds (column 2) for each equivalence ratio (column 3) you specified in the dictionary defining the inlet stream.

Task 1: flame speed of CH4/air flames without inhibitors



As expected, the GRI-30 mechanism is able to correctly describe the laminar flame speed for a mixture of methane and air at atmospheric pressure for equivalence ratios close to 1

In particular, the calculated laminar flame speed at stoichiometric conditions, is equal to 38.15 cm/s

We can now focus the attention only on the flame with equivalence ratio equal to 1

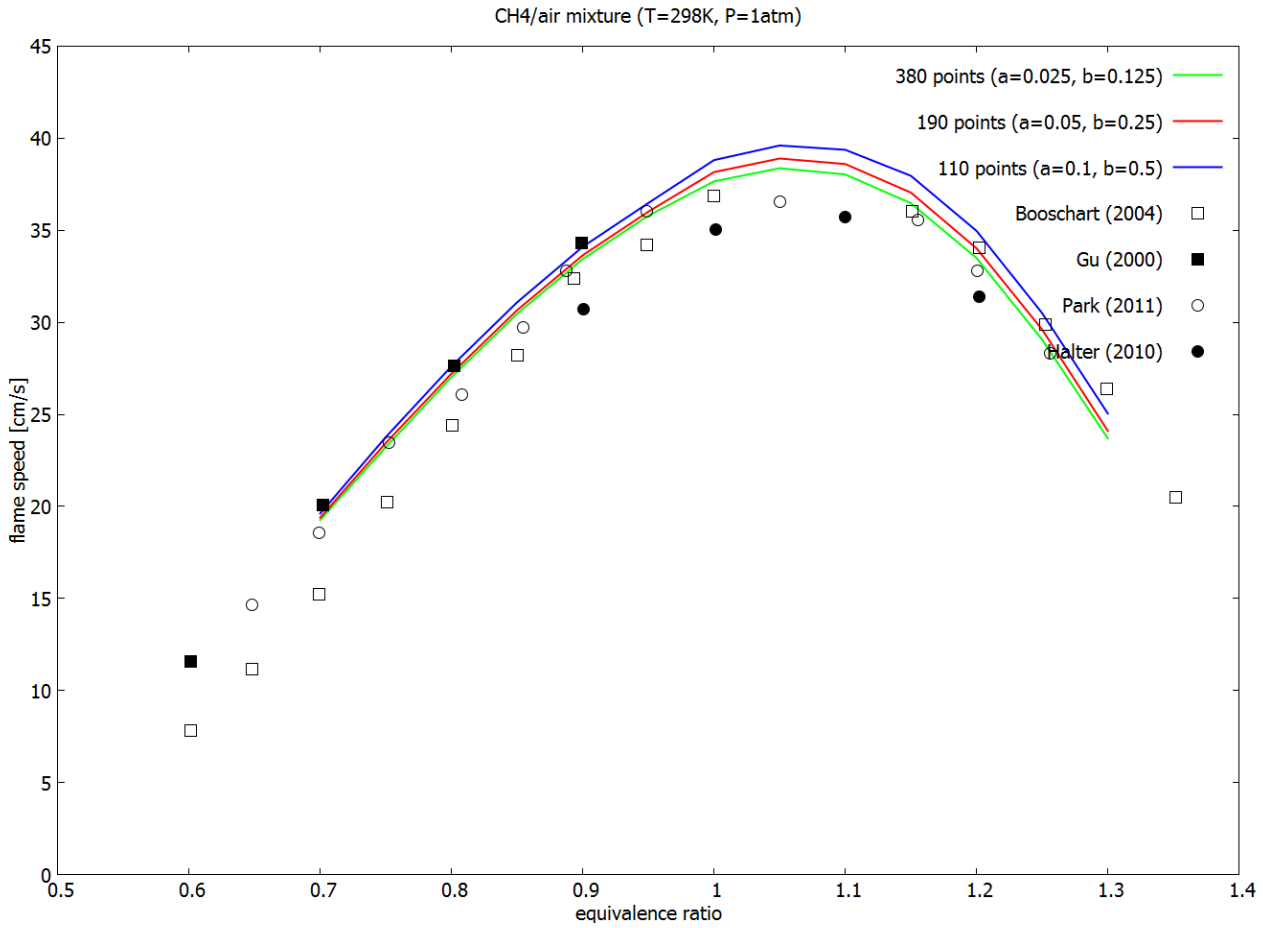
```
Dictionary inlet-stream
{
   @FuelMoles              CH4 1;
   @OxidizerMoles          O2 0.21 N2 0.79;
   @EquivalenceRatio       1;

   @Temperature            298 K;
   @Pressure               1 atm;
}
```

Importance of computational grid

The calculation of laminar flame speeds looks like a very simple problem: we have to solve only species and energy transport equations over a 1D computational domain!

However, the problem is not so trivial, because the solution is strongly dependent on the quality of the computational grid. If the number of points is not sufficiently high and/or they are not correctly distributed, the calculated laminar flame speed can be affected by relative errors larger than 5%

The coefficients governing the grid refinement (`@GradientCoefficient` and `@CurvatureCoefficient)` must be sufficiently small in order to ensure a sufficiently number of grid points. In this practical sessions, in order to reduce the computational time, we are considering grids with 180-200 points, However, if you want to perform very accurate calculations, usually a larger number of points is needed and a sensitivity analysis to the grid is strongly suggested.



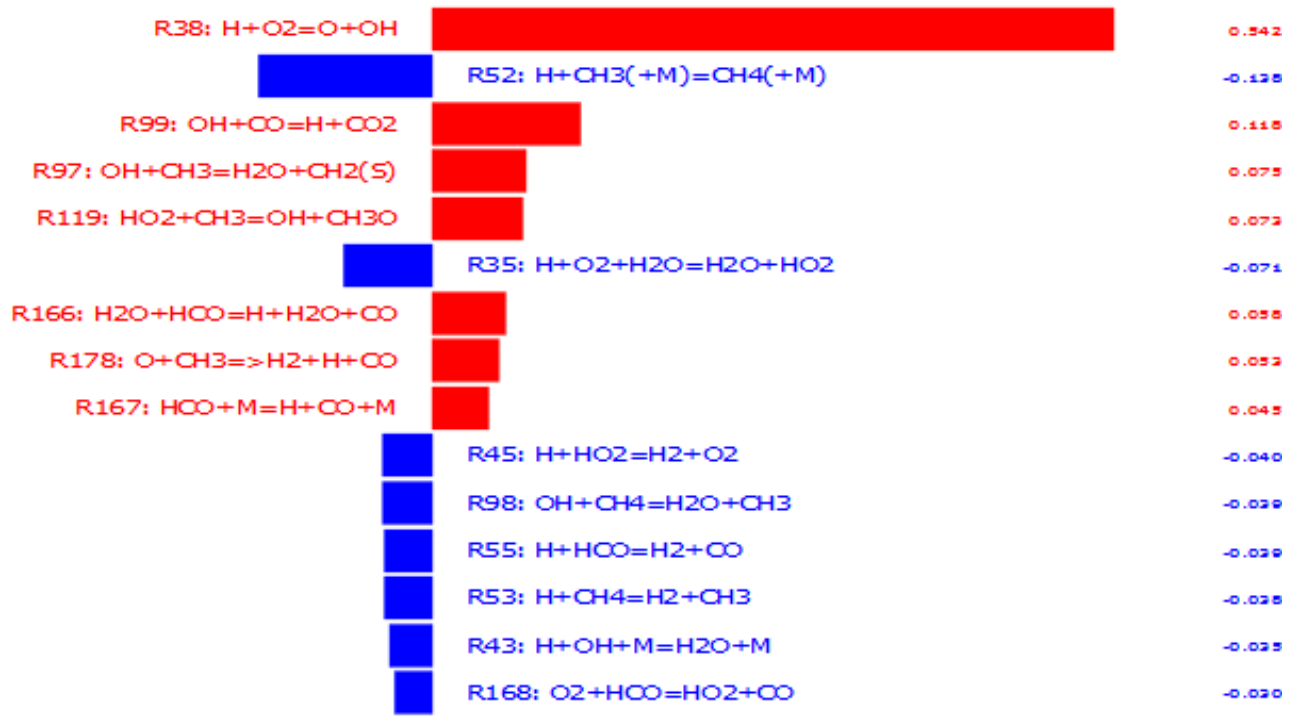
Sensitivity Analysis

You may also consider the possibility to perform a sensitivity analysis, in order to locate the most important reactions for determining the laminar flame speed

You need to add the `@SensitivityAnalysis` keyword to the main dictionary and the corresponding sub-dictionary, in which additional options are specified

```
Dictionary PremixedLaminarFlame1D
{
  …
  @SensitivityAnalysis  sensitivity;
  …
}

Dictionary sensitivity
{
  @Species                CH4 H2O OH;
}
```

Sensitivity Analysis: laminar flame speed



Please, remember to ask sensitivity coefficients for a limited number of species. The output files associated to sensitivity analysis have a lot of data and are usually huge

Task 2: flame speed of CH_4/air flames with CO_2

The objective is to find the amount of CO2 to be added to the stoichiometric CH4/air mixture to decrease the laminar flame speed by 10%.

Laminar flame speed without additives: 38.15 cm/s
Target laminar flame speed: 34.33 cm/s

Stoichiometric composition

CH4	0.095
O2	0.19
N2	0.715

First guess composition

CH4	0.09410
O2	0.18821
N2	0.70827
CO2	0.00941

Basically, we have to proceed by trial & error.

Hint: to have a reasonable first-guess value, you can have a look at the table reported at page 4, in which the experimentally measured amount of CO2 to be added is reported:

CO2 ~ 10% CH4

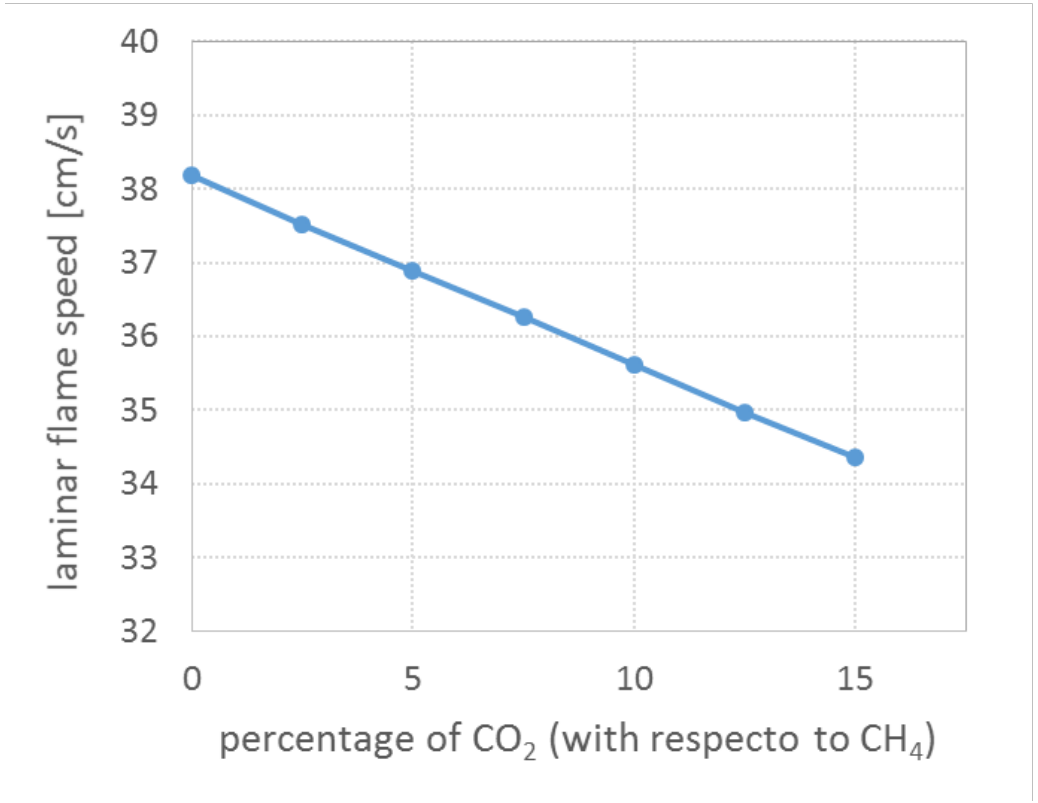
Task 2: flame speed of CH_4/air flames with CO_2

First guess composition

CH4	0.09366
O2	0.18733
N2	0.70495
CO2	0.01405

At the end of the trial & error procedure, the following quantity of CO2 must be added in order to have a reduction of 10% for the flame speed:

CO2 ~ 15% CH4



The reduction of flame speed is linear with respect to the amount of CO2

Task 3: flame speed of CH4/air flames with $Fe(CO)_5$

1. Extend the GRI-30 mechanism with the chemistry describing Fe(CO)5, reported in the `Kinetics/FeC5O5-submechanism.txt` file. Consider that the extension requires the introduction of 9 additional species, together with the corresponding thermodynamic and transport properties

```
Fe                J 3/78FE  1    0    0    0G   200.000  6000.000 1000.       1
3.26197970E+00-1.05582533E-03 5.92906998E-07-1.07189455E-10 7.48064402E-15    2
4.90969873E+04 3.52443894E+00 1.70744428E+00 1.06339224E-02-2.76118171E-05    3
2.80917854E-08-1.01219824E-11 4.91843725E+04 9.80811099E+00 4.99728787E+04    4
FeCO              J 3/78FE 1.C  1.O  1.   0.G   200.000  6000.000 995.043     1
5.62462735E+00 1.94037201E-03-7.75413065E-07 1.34363796E-10-8.45965975E-15    2
3.08266656E+04 -1.81310144E+00 3.40858296E+00 1.31011812E-02-2.09955691E-05   3
1.59565948E-08 -4.55529964E-12 3.11561677E+04 8.30669275E+00                  4
...
```

thermodynamics properties

```
Fe(CO)5=>Fe(CO)4+CO 2.00E+15  0         40000
Fe(CO)4+CO=>Fe(CO)5 3.50E+10  0         0
Fe(CO)4=>Fe(CO)3+CO 3.00E+15  0         4999
Fe(CO)3+CO=>Fe(CO)4 1.30E+13  0         0
Fe(CO)3=>Fe(CO)2+CO 3.00E+15  0         32000
...
```

Fe(CO)5 kinetic sub-mechansim

```
FeC5O5    2         530       6.0       0  0  0
FeO       1         3000      4.3       0  0  0
FeO2      2         400       4.4       0  0  0
...
```

transport properties

Task 3: flame speed of CH4/air flames with $Fe(CO)_5$

2. Run the kinetic pre-processor on the extended GRI-30 mechanism

3. If everything works properly, you will find the result of this pre-processing operation in the folder you specified through the `@Output` keyword

4. Open the `log` file to make sure no errors were encountered in the reaction mechanism.

Task 3: flame speed of CH4/air flames with $Fe(CO)_5$

The objective is to find the amount of Fe(CO)5 to be added to the stoichiometric CH4/air mixture to decrease the laminar flame speed by 10%.

Laminar flame speed without additives: 38.15 cm/s
Target laminar flame speed: 34.33 cm/s

Stoichiometric composition

CH4	0.095
O2	0.19
N2	0.715

First guess composition

CH4	9.502082E-02
O2	1.900416E-01
N2	7.149185E-01
Fe(CO)5	1.900452E-05

Basically, we have to proceed by trial & error.

Hint: to have a reasonable first-guess value, you can have a look at the table reported at page 4, in which the experimentally measured amount of Fe(CO)5 to be added is reported:

Fe(CO)5 ~ 0.02% CH4

Task 3: flame speed of CH4/air flames with $Fe(CO)_5$

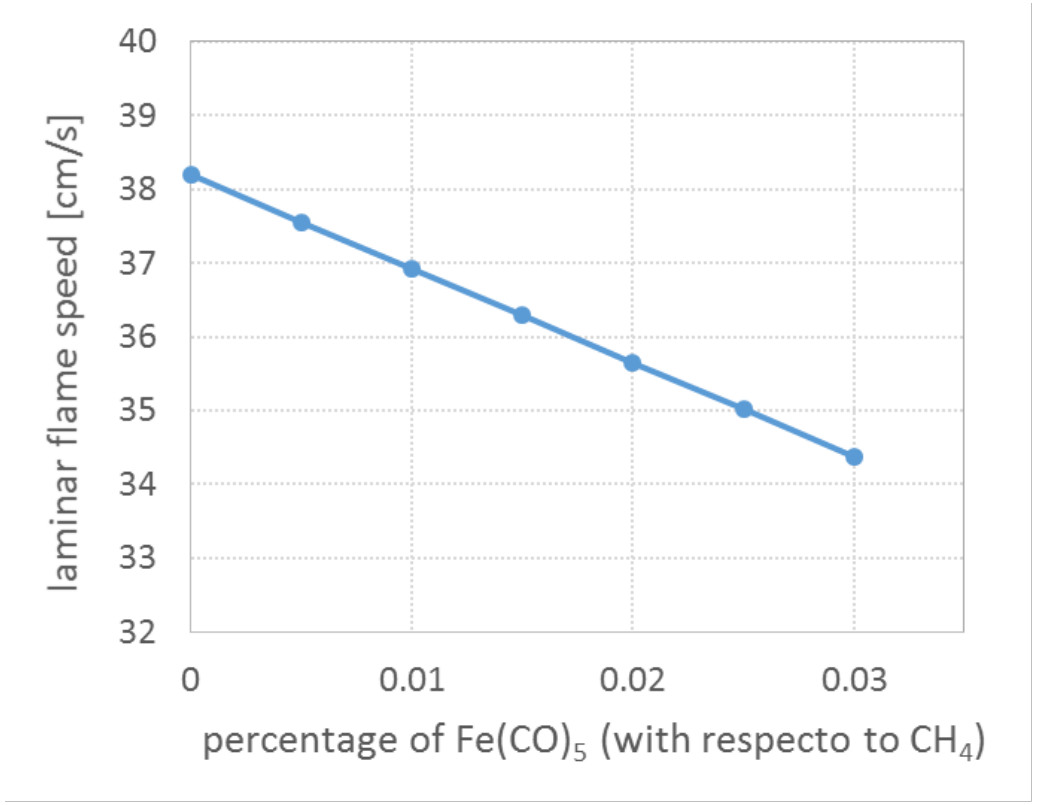
Final composition

CH4	0.094997293
O2	0.189994585
N2	0.714979623
Fe(CO)5	2.84992E-05

This is the amount of Fe(CO)5 to be added to observe the requested decrease of 10% in laminar flame speed:

Fe(CO)5 ~ 0.030% CH4

This number is in satisfactory agreement with the experimental measurements (0.020%)



Task 4: flame speed of CH_4/air flames with CF_3Br

1. Extend the GRI-30 mechanism with the chemistry describing CF3Br, reported in the `Kinetics/CF3Br-submechanism.txt` file. Consider that the extension requires the introduction of 72 additional species, together with the corresponding thermodynamic and transport properties

```
F         71STPR        F   1    0    0    0G   300.00   3000.00  1400.00      1
 0.26511661E+01-0.14012971E-03 0.51923643E-07-0.88495445E-11 0.59028014E-15    2
 0.87582901E+04 0.40785743E+01 0.29037076E+01-0.63529632E-03 0.26473487E-06    3
 0.76906306E-10-0.54525355E-13 0.86722692E+04 0.27082800E+01                   4
HF        71STPR        H   1F   1    0    0    0G   300.00   3000.00  1250.00      1
 0.27812981E+01 0.10395908E-02-0.24173550E-06 0.26841590E-10-0.10976637E-14    2
-0.33504174E+05 0.50197012E+01 0.34365739E+01 0.48602072E-03-0.12523971E-05    3
 0.13647500E-08-0.40957404E-12-0.33800089E+05 0.12068184E+01                   4
...
```

thermodynamics properties

```
H+HBr=H2+Br                1.26E10    1.05     160.
H+Br2=HBr+Br               2.28E11    1.       440.
Br+Br+M=Br2+M              1.92E14    0.     -1700.
Br2+CH3=Br+CH3Br           1.21E13    0.      -390.
...
```

CF3Br kinetic sub-mechanism

```
F          0    80.0      2.750      0.00    0.00    0.0
F2         1    125.7      3.301     0.00    1.60    3.8
HF         1    330.0      3.148     1.92    2.46    1.0
...
```

transport properties

Task 4: flame speed of CH_4/air flames with CF_3Br

2. Run the kinetic pre-processor on the extended GRI-30 mechanism

3. If everything works properly, you will find the result of this pre-processing operation in the folder you specified through the `@Output` keyword

4. Open the `log` file to make sure no errors were encountered in the reaction mechanism.

Task 4: flame speed of CH_4/air flames with CF_3Br

The objective is to find the amount of CF3Br to be added to the stoichiometric CH4/air mixture to decrease the laminar flame speed by 10%.

Laminar flame speed without additives: 37.11 cm/s
Target laminar flame speed: 33.39 cm/s

Stoichiometric composition

CH4	0.095
O2	0.19
N2	0.715

First guess composition

CH4	9.489621E-02
O2	1.897924E-01
N2	7.139810E-01
CF3Br	1.330317E-03

Basically, we have to proceed by trial & error.

Hint: to have a reasonable first-guess value, you can have a look at the table reported at page 4, in which the experimentally measured amount of CF3Br to be added is reported:

CF3Br ~ 1.2% CH4

Task 4: flame speed of CH_4/air flames with CF_3Br

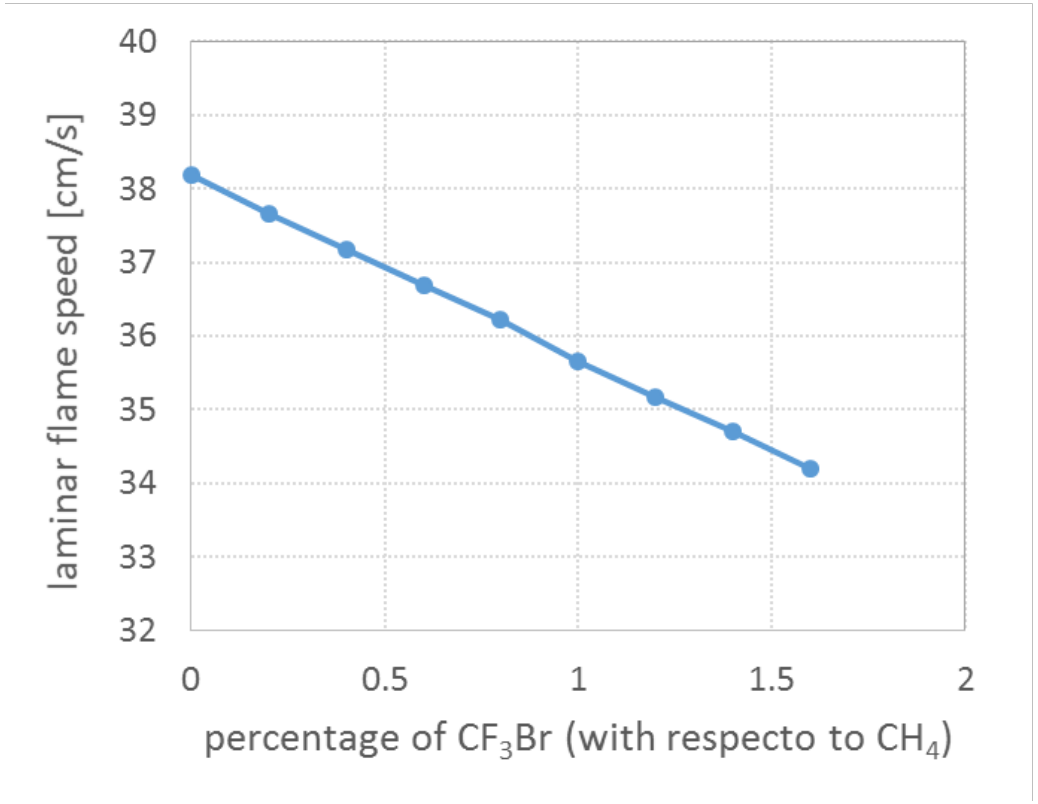
Final composition

CH4	9.489621E-02
O2	1.897924E-01
N2	7.139810E-01
CF3Br	1.330317E-03

This is the amount of CF3Br to be added to observe the requested decrease of 10% in laminar flame speed:

CF3Br ~ 1.5% CH4

This number is in good agreement with experimental measurements (1.2%)



References (I)

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