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Exercise 2
Oxidation of Aromatic Compounds

Combustion Fundamentals and New Technologies

Conservatorio delle Orfane a Terra Murata
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Introduction

Reactor models

Plug Flow reactor (PFR) and Perfectly Stirred reactor (PSR) from the OpenSMOKE++ Suite

Reaction mechanism

Oxidation of benzene (C_6H_6/O_2)

Purpose

Familiarize the student with the numerical simulation of plug flow reactors (PFR) and perfectly stirred reactors (PSR). Make the student aware of current limitations in predictive capabilities for aromatics oxidation.

Background

Aromatic compounds are formed to some extent in most combustion processes. In addition they are added in considerable quantities to unleaded gasolines in order to increase the octane number and prevent knock in engines.

Aromatic species are of environmental concern, both because they are harmful to the environment and because they are important precursors to dioxins and to soot formation.

Despite significant efforts over the past many years, details of the oxidation chemistry of even the simplest aromatic species, benzene and toluene, remain uncertain. The purpose of this exercise is to assess the ability of a recent reaction mechanism from for benzene oxidation to describe the overall oxidation behavior and furthermore to evaluate current regulations, applying to municipal waste incinerators, that aim to ensure complete oxidation of aromatic species.

Tasks

Evaluate the capabilities of the proposed kinetic mechanism for describing the overall oxidation behavior of benzene by comparing predictions with experimental results obtained in a turbulent flow reactor and well-stirred reactors.

1. Compare modeling predictions in a near-adiabatic plug flow reactor with the experimental results for benzene and phenol of Lovell et al.

2. Compare modeling predictions in well-stirred reactors with the experimental results of Da Costa et al. for benzene and phenol (low-temperature partial oxidation of benzene conditions)

3. Compare modeling predictions in well-stirred reactors with the experimental results of Chai and Pfefferle for benzene and phenol.

4. Comment on the ability of the model to predict benzene and phenol under the conditions investigated.

5. Current regulations that apply to municipal waste incinerators require post-flame conditions with 800°C and 6% O2 for at least 2 seconds to ensure oxidation of combustible species, in particular organic compounds like dioxins. Taking benzene as a characteristic compound, evaluate whether these conditions ensure complete oxidation of aromatic species.

Organization

Exercise1

Documents

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

Exp

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

Kinetics

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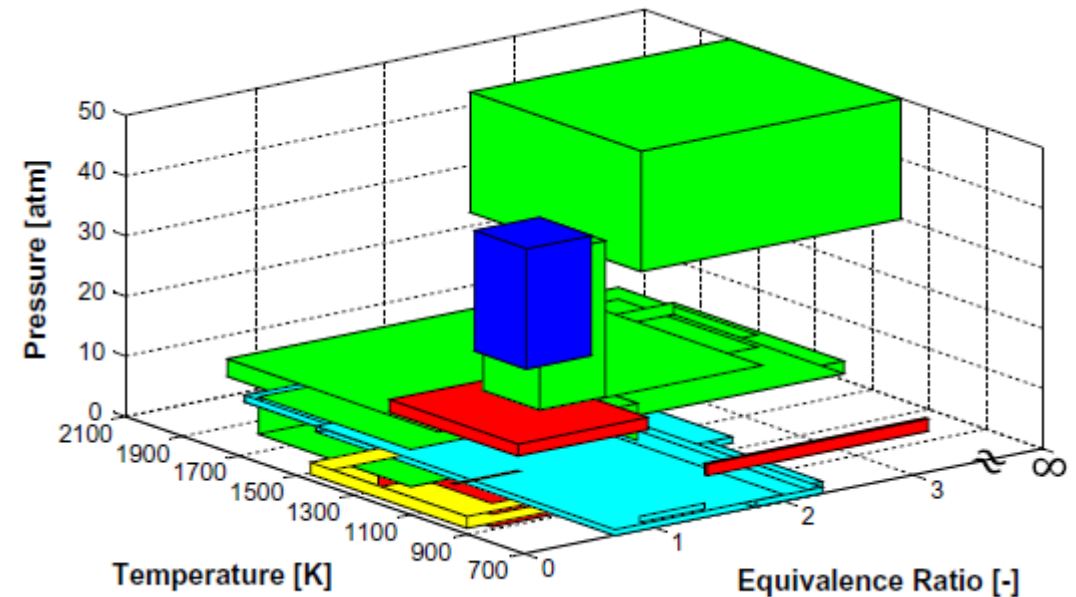
Task

The kinetic mechanism

POLIMI_PRF_PAH_LT_1412

Detailed and semi-detailed (lumped) mechanism of the pyrolysis, partial oxidation and combustion Primary Reference Fuels, including PAH (Polycyclic Aromatic Hydrocarbons) formation up to C20.

Number of species: 300
Number of reactions: 11790

The mechanism was validate in a wide range of operating conditions:

1. Shock tube experiments of benzene pyrolysis.
2. Benzene pyrolysis and oxidation in flow-reactors.
3. Ignition delay time of benzene oxidation.
4. Partial oxidation and combustion in jet stirred reactors.
5. Premixed laminar flames.

Saggese C., Frassoldati, Cuoci A., Faravelli T., Ranzi, *A wide range kinetic modeling study of pyrolysis and oxidation of benzene*, Combustion and Flame, 160, p. 1168-1190 (2013)
DOI: 10.1016/j.combustflame.2013.02.013

Task 0: preprocessing of kinetic mechanism (I)

Before application in `OpenSMOKE++ Suite`, the kinetic scheme has to be pre-processed. The pre-processing of a kinetic mechanism must be performed only once, using **OpenSMOKE_CHEMKIN_PreProcessor** utility.

1. Thermodynamic data (`POLIMI_TOT_NOX_1412.CKT`) and kinetic mechanism (`POLIMI_PRF_PAH_LT_1412.CKI`) files are available in the Kinetics folder

2. Open the `Task0` folder and create a new input file (`input.dic` in the following, but in principle you are free to choose the name you prefer) in which you specify the thermodynamic and kinetic files and the destination folder:

```
Dictionary CHEMKIN_PreProcessor
{
    @Kinetics            ../../Kinetics/POLIMI_PRF_PAH_LT_1412.CKI;
    @Thermodynamics      ../../Kinetics/POLIMI_TOT_NOX_1412.CKT;
    @Output              kinetics-POLIMI_PRF_PAH_LT_1412;
}
```

You can choose to use local or absolute paths

input.dic

Task 0: preprocessing of kinetic mechanism (II)

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

```
%OPENSMOKEPP_EXE_FOLDER%\OpenSMOKE_CHEMKIN_PreProcessor.exe -input input.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.dic` file

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

Task 1: plug flow reactor

Experimental investigations

Near-adiabatic plug flow reactor

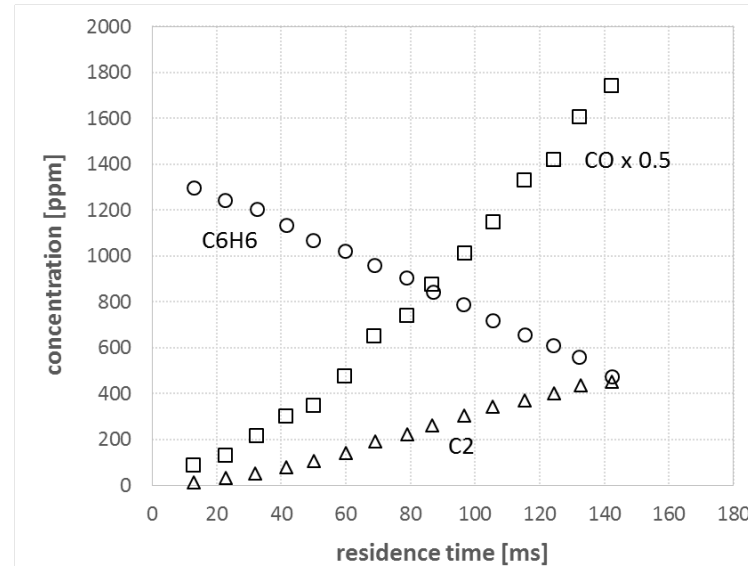Inlet temperature: 1098 K

Inlet composition:
    C6H6=1571 ppm
    O2=15900 ppm
    balance N2

Pressure: atmospheric

A.B. Lovell, K. Brezinsky, and I. Glassman. *Benzene oxidation perturbed by NO2 addition*, Symposium (International) on Combustion, 22(1):1063-1074, 1989 DOI: 10.1016/S0082-0784(89)80116-X.
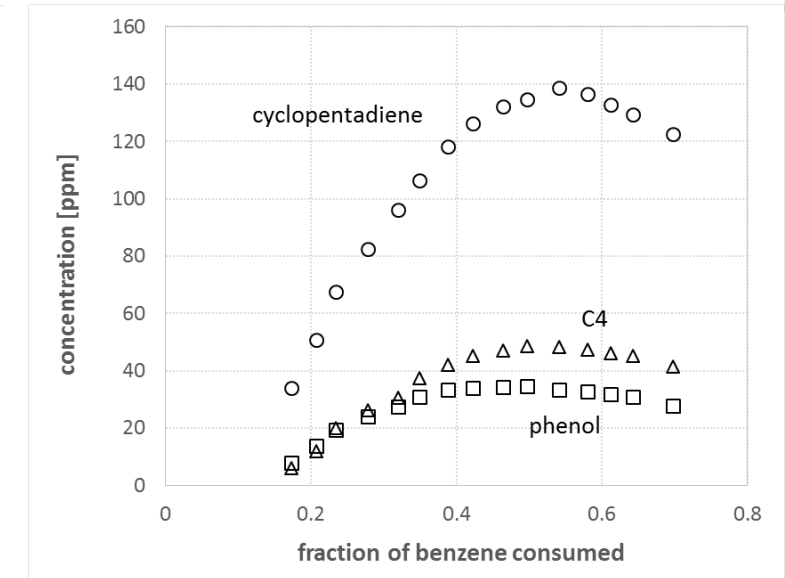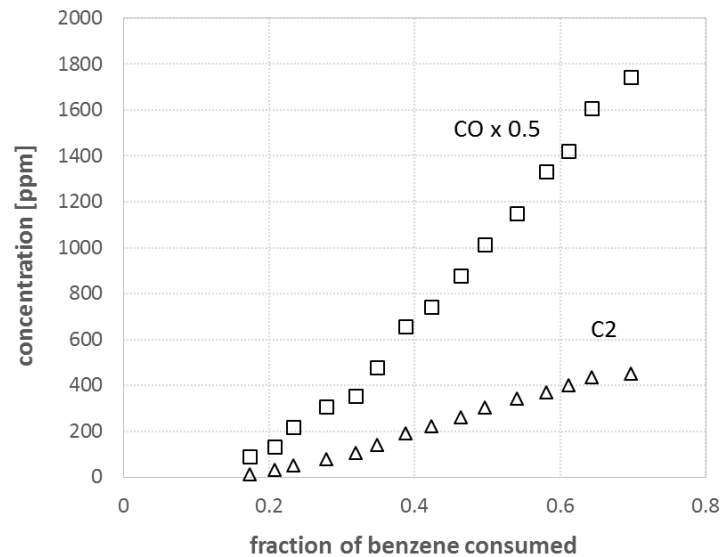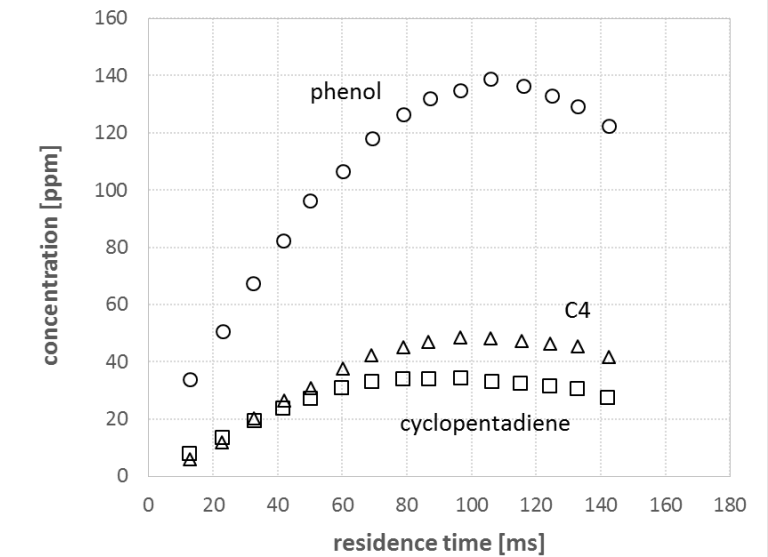
Task 1: plug flow reactor

1. Open the `Task1` folder and create a new input file (`input.dic` in the following) specifying the reaction conditions corresponding to those of experiments of Lovell et al.:

```
Dictionary PlugFlowReactor
{
  @KineticsFolder        ../Task0/kinetics-POLIMI_PRF_PAH_LT_1412;
  @Type                  NonIsothermal;
  @InletStatus           inlet-mixture;
  @ResidenceTime         300 ms;
  @ConstantPressure      true;
  @Velocity              1 m/s;
}


Dictionary inlet-mixture
{
  @Temperature   1098.  K;
  @Pressure      101325 Pa;
  @Moles         C6H6 1571  O2 15900  N2 982529;
}
```

pre-processed kinetic mechanism (Task 0)

adiabatic reactor

it is important only if you are interested in plotting the results vs the reactor length

be careful, normalization is done automatically!

Task 1: plug flow reactor

2. Run the solver for plug flow reactors using the following command (in Microsoft Windows):

```
%OPENSMOKEPP_EXE_FOLDER%\OpenSMOKE_PlugFlowReactor.exe –input input.dic
```

3. If everything works properly, you will find the results in the `Output` folder:

   o <u>FinalSummary.out</u>: this file reports the initial and final status of the reacting mixture (temperature, pressure, density, composition, etc.)

   o <u>Output.out</u>: it is organized in columns and the first row reports the meaning of each column, together with a number which refers to the column number. Both the mole (x suffix) and mass fractions (w suffix) of species are reported. You can easily import this file in Microsoft Excel, Matlab, etc. or you can use Gnuplot to directly plot the results (also on the fly)

   o <u>Output.xml</u>: XML output file to be used by the OpenSMOKE++ graphical post-processor
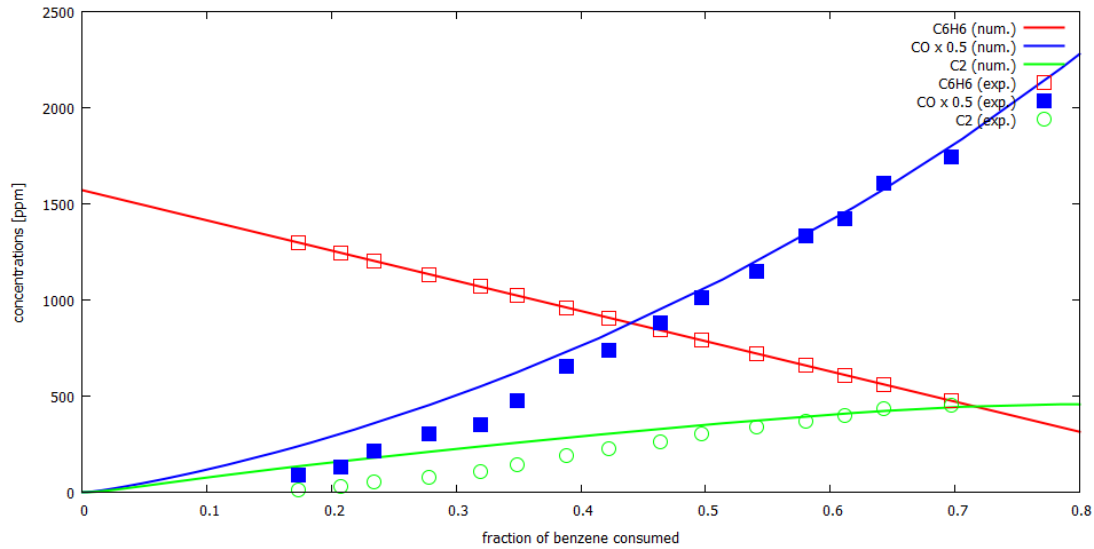
Task 1: plug flow reactor
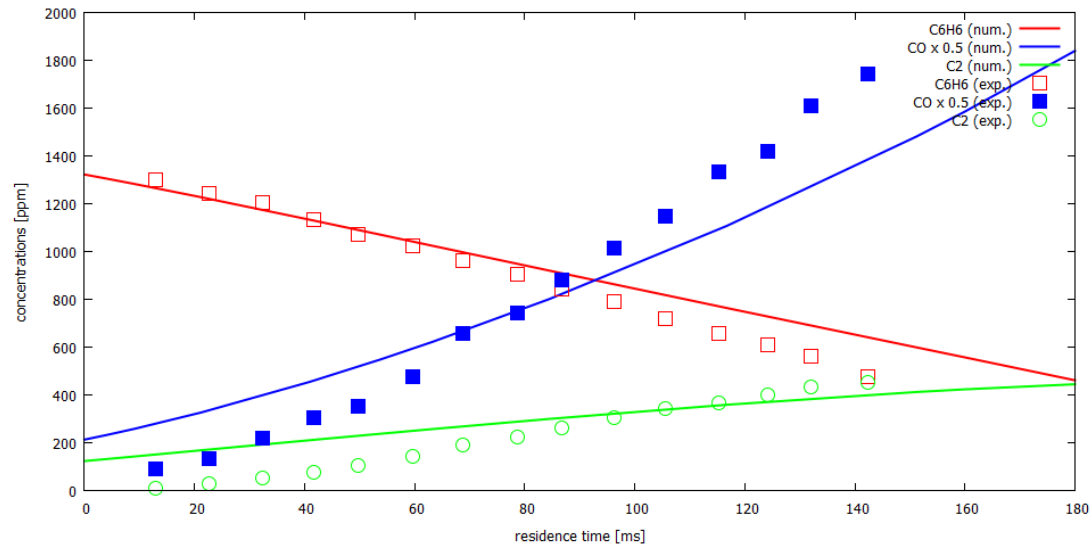
The numerical results have been shifted of 70 ms in order to take into account the initial mixing of reactants
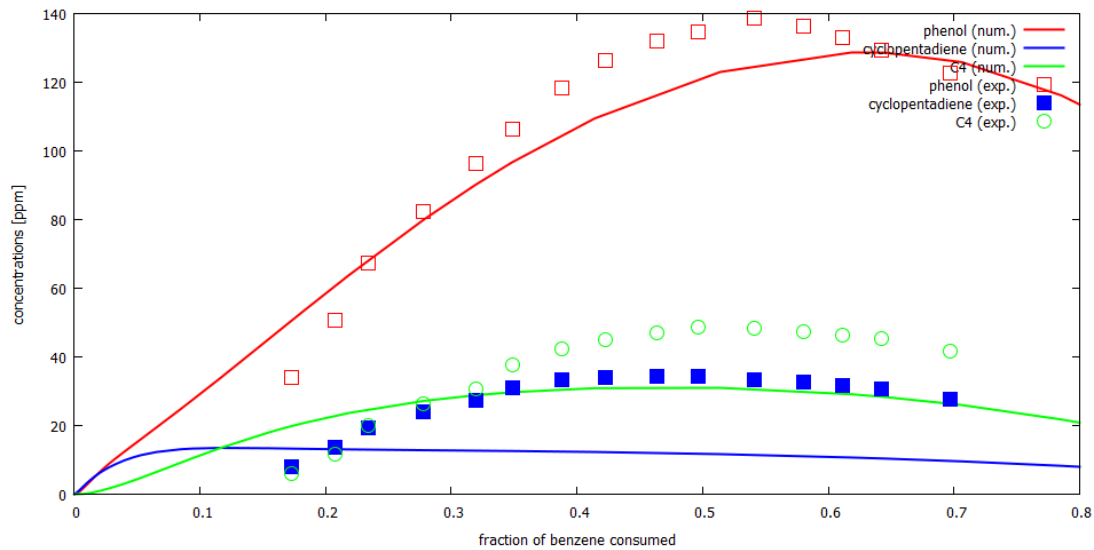
A systematic under prediction of overall benzene reactivity is observed.
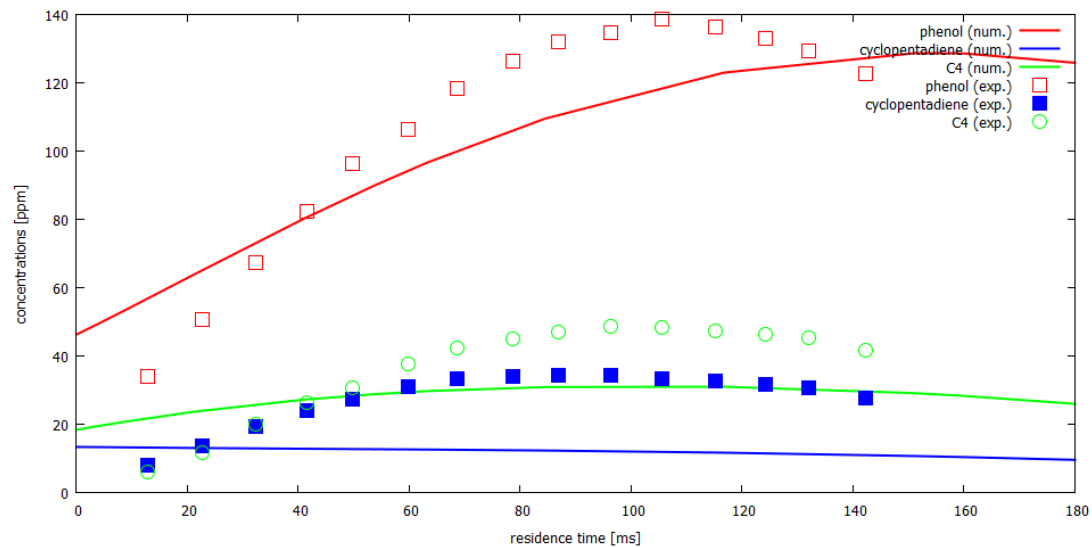
The model properly reflects the relative amount of main products

Task 2: perfectly stirred reactor (low-T)

Experimental investigations

Isothermal perfectly stirred reactor

Temperature: 923 K
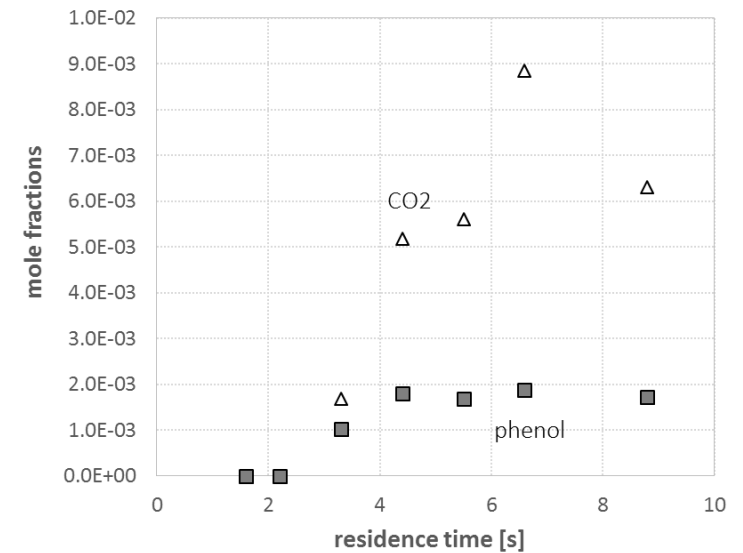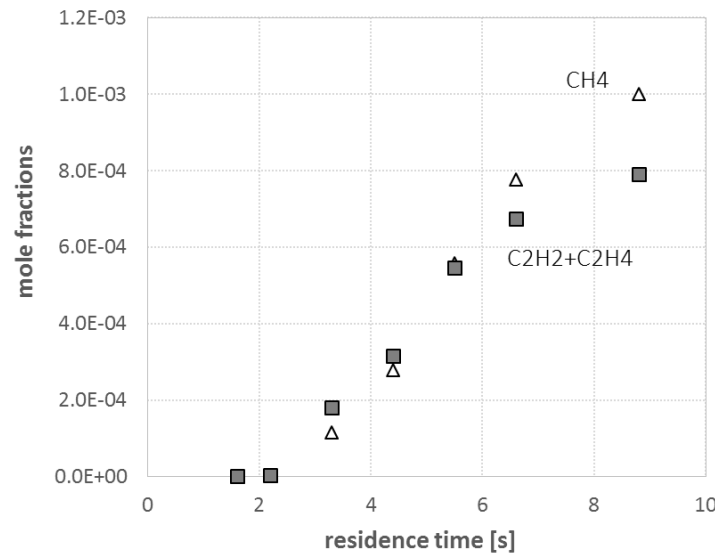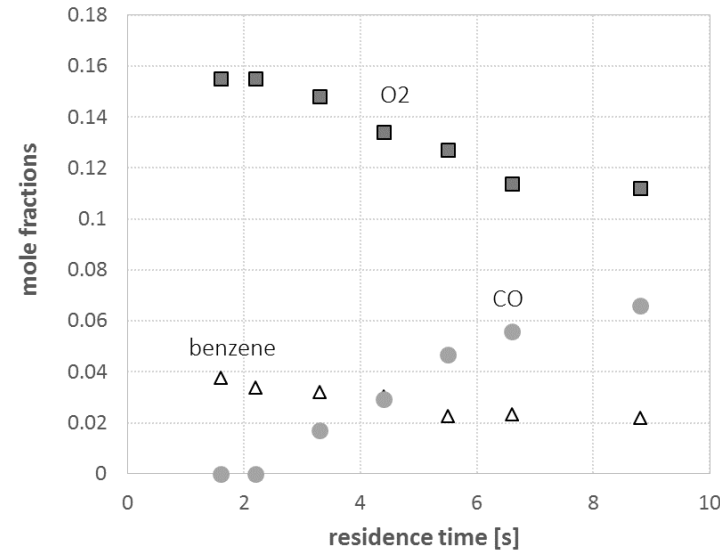Volume: 88 cm3
Residence time: 1-10 s

Inlet composition (%vol.):
    He=80.5%
    O2=15.5%
    C6H6=4%

Pressure: atmospheric

I. Da Costa, R. Fournet, F. Billaud, and F. Battin-Leclerc, *Experimental and modeling study of the oxidation of benzene* International Journal of Chemical Kinetics, 35(10):503-524, 2003
DOI: 10.1002/kin.10148.

Task 2: perfectly stirred reactor (low-T)

1. Open the `Task2` folder and create a new input file (`input.dic` in the following) specifying the reaction conditions corresponding to those of experiments of Da Costa et al.:

```
Dictionary PerfectlyStirredReactor
{
  @KineticsFolder        ../Task0/kinetics-POLIMI_PRF_PAH_LT_1412;
  @Type                  Isothermal-ConstantPressure;
  @InletStatus           inlet-mixture;
  @ResidenceTime         1 s;
  @Volume                88 cm3;
  @ParametricAnalysis  parametric-analysis;
}

Dictionary inlet-mixture
{
  @Temperature 923.    K ;
  @Pressure    1       atm ;
  @Moles       C6H6 4  O2 15.5  HE 80.5;
}
```

pre-processed kinetic mechanism (Task 0)

adiabatic reactor

Since different reactor temperature have to be investigated (i.e. several simulations have to be performed), it is more convenient to ask for a parametric analysis

be careful, normalization is done automatically!

Task 2: perfectly stirred reactor (low-T)

```
Dictionary parametric-analysis
{
        @Type                   residence-time;

        @NumberOfPoints         40;
        @MinimumValue           1  s;
        @MaximumValue           10 s;

        @NumberOfThreads        1;

}
```

The parametric analysis is done by varying the residence time

Interval of residence time for parametric analysis (min, max, and number of intervals)

On multi-core machines the calculations can be distributed on more than one core

2. Run the solver for perfectly stirred reactors using the following command (in Microsoft Windows):

```
%OPENSMOKEPP_EXE_FOLDER%\OpenSMOKE_PerfectlyStirredwReactor.exe –input input.dic
```

Task 2: perfectly stirred reactor (low-T)

3. If everything works properly, you will find the results in the `ParametricAnalysis.out` file, contained in the `Output` folder. Each row in this file corresponds to a specific reactor simulated during the parametric analysis. It is organized in columns and the first row reports the meaning of each column, together with a number which refers to the column number. Both the mole (x suffix) and mass fractions (w suffix) of species are reported.

4. In addition, for each reactor simulated during the parametric analysis (40 in this examples), you will find a dedicated folder, with names `Case0`, `Case1`, `Case2`, and so on. For each case the following files are available

    o FinalSummary.out: this file reports the initial and final status of the reacting mixture (temperature, pressure, density, composition, etc.)

    o Output.history: this file reports the output of ODE integration performed to reach the steady state conditions

    o Output.xml: XML output file to be used by the OpenSMOKE++ graphical post-processor

Task 2: perfectly stirred reactor (low-T)
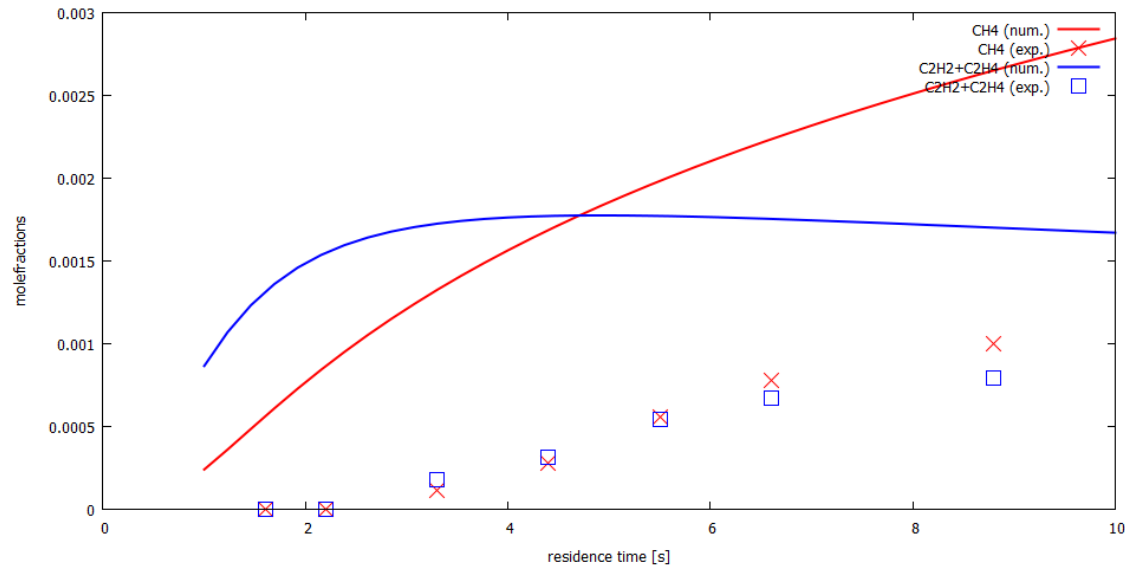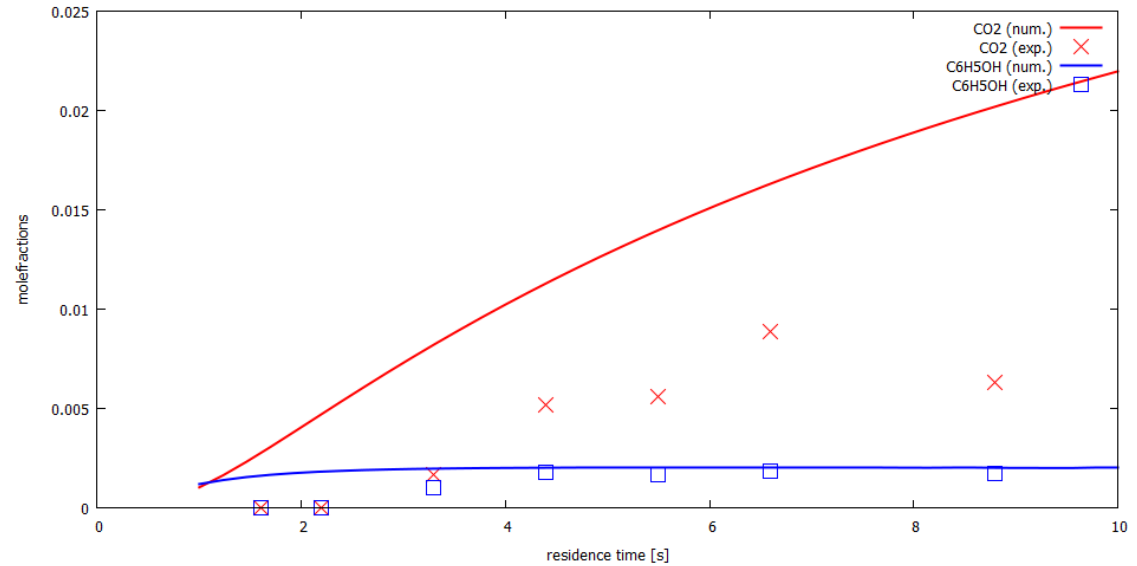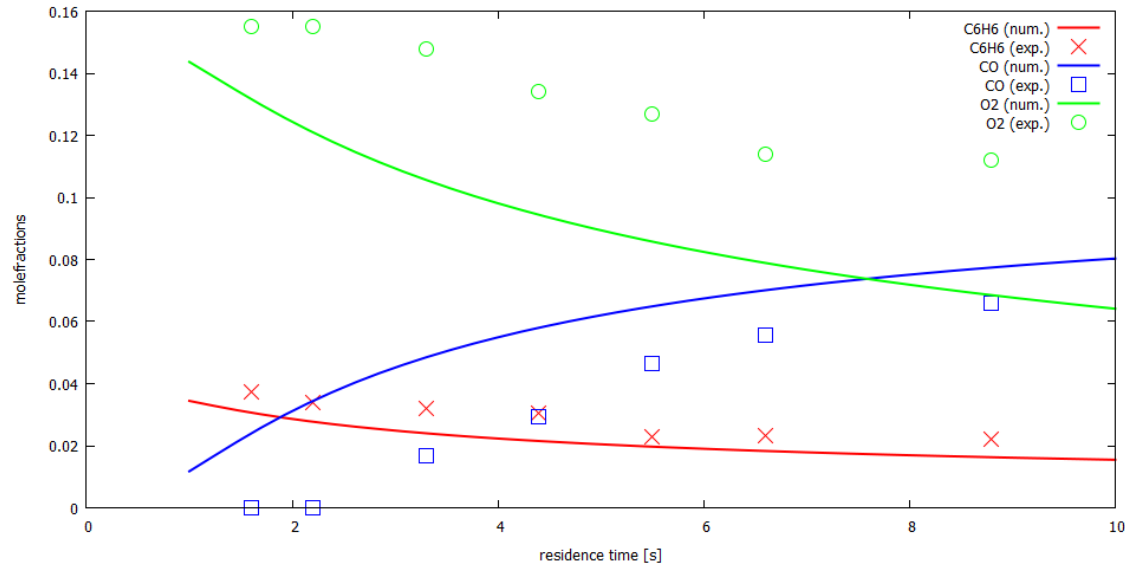
Phenol yields are properly predicted but the model systematically overestimates benzene conversion and C2 species, which come mainly from successive decomposition reactions of benzoquinone and the cyclo-pentadienyl radical. Similar reactivity deviations were also observed by others in low temperature toluene oxidation, where the same chemistry of phenoxy radical plays a crucial role.

Experimental investigations

Isothermal perfectly stirred reactors

Pressure: 350 torr
Residence time: 50 ms

Inlet composition (Φ=0.19):
C_6H_6=5100 ppm
O_2=20.13%
Ar=balance

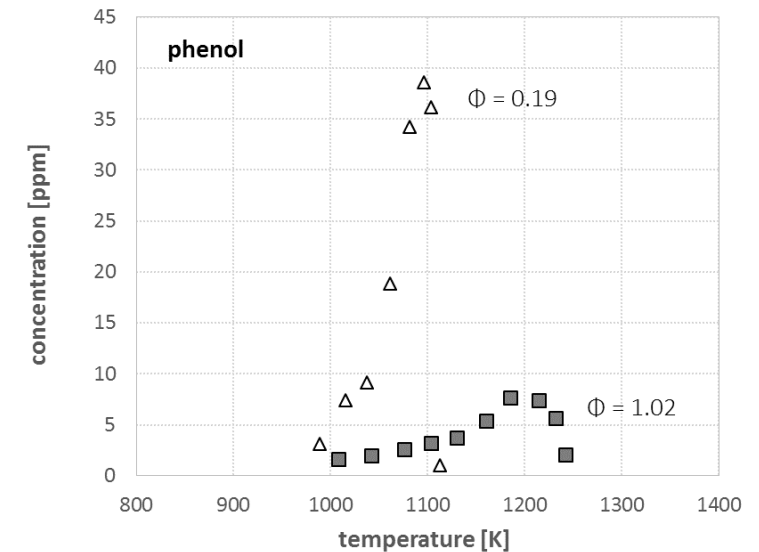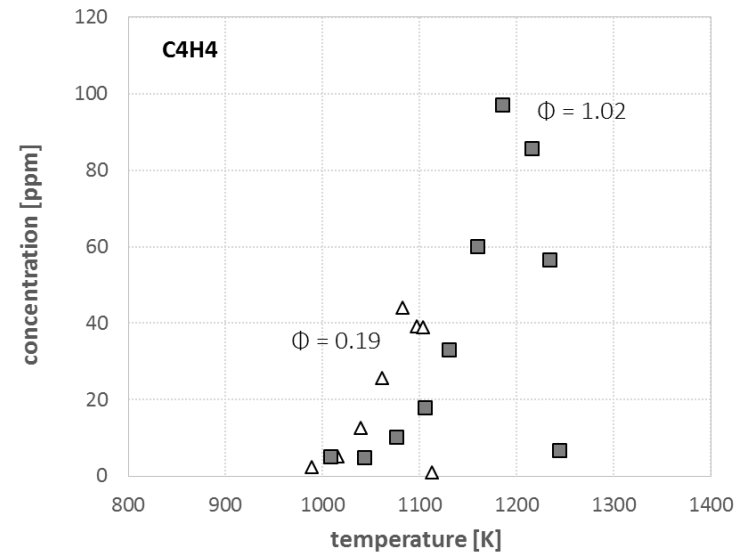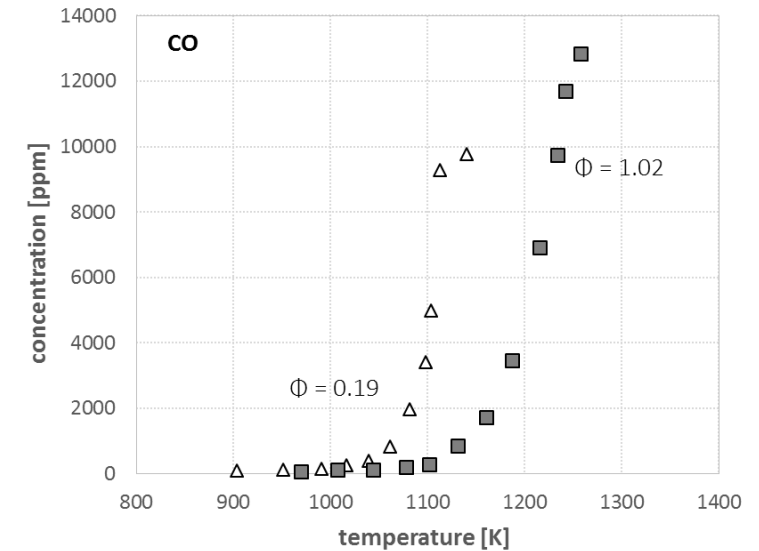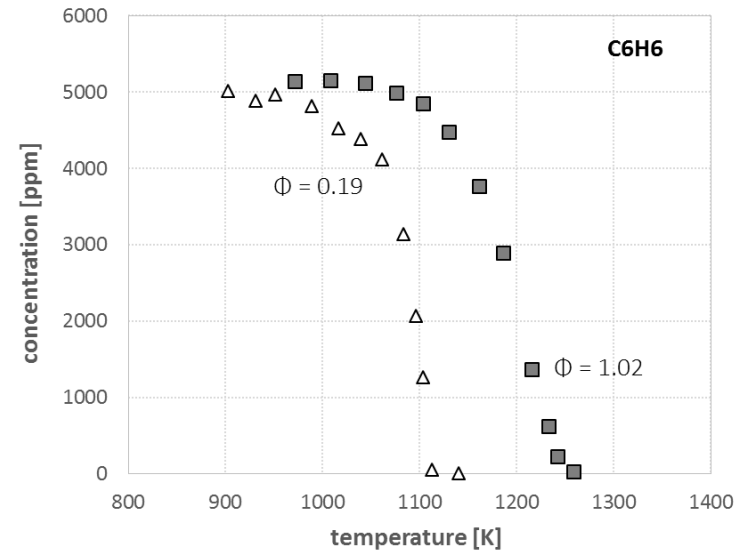Inlet composition (Φ=1.02):
C_6H_6=5100 ppm
O_2=3.75%
Ar=balance

Y. Chai and L.D. Pfefferle. *An experimental study of benzene oxidation at fuel-lean and stoichiometric equivalence ratio conditions*, Fuel, 77(4):313-320, 1998.

Task 3: perfectly stirred reactor

1. Open the `Task3` folder and create a new input file (`input.phi019.dic` in the following) specifying the reaction conditions corresponding to those of experiment of Chai and Pfefferle at Φ=0.19:

```
Dictionary PerfectlyStirredReactor
{
  @KineticsFolder        ../Task0/kinetics-POLIMI_PRF_PAH_LT_1412;
  @Type                  Isothermal-ConstantPressure;
  @InletStatus           inlet-mixture;
  @ResidenceTime         50 ms;
  @Volume                1 cm3;
  @Options               output-options;
  @ParametricAnalysis    parametric-analysis;
}

Dictionary inlet-mixture
{
  @Temperature 750.    K ;
  @Pressure      0.46    atm ;
  @Moles         C6H6 0.0051  O2 0.201315789 AR 0.793584211;
}
```

pre-processed kinetic mechanism (Task 0)

Isothermal reactor

the results are independent of volume

you may consider the possibility to change the options governing the output operations

since different reactor temperature have to be investigated (i.e. several simulations have to be performed), it is more convenient to ask for a parametric analysis

Task 3: perfectly stirred reactor

```
Dictionary parametric-analysis
{

  @Type                 temperature;


  @NumberOfPoints       40;
  @MinimumValue         850 K;
  @MaximumValue         1350 K;


  @NumberOfThreads      1;
}
```

The parametric analysis is done by varying the reactor temperature

Interval of residence time for parametric analysis (min, max, and number of intervals)

On multi-core machines the calculations can be distributed on more than one core

```
Dictionary output-options
{

  @OutputFolder Output-phi019;
  @StepsFile    1000;
  @StepsVideo   50;
}
```

Name of output folder

Number of integration time steps to write the results on files

Number of integration time steps to write the results on the screen

2. Run the solver for perfectly stirred reactors using the following command (in Microsoft Windows):

```
%OPENSMOKEPP_EXE_FOLDER%\OpenSMOKE_PerfectlyStirredwReactor.exe -input input.019.dic
```
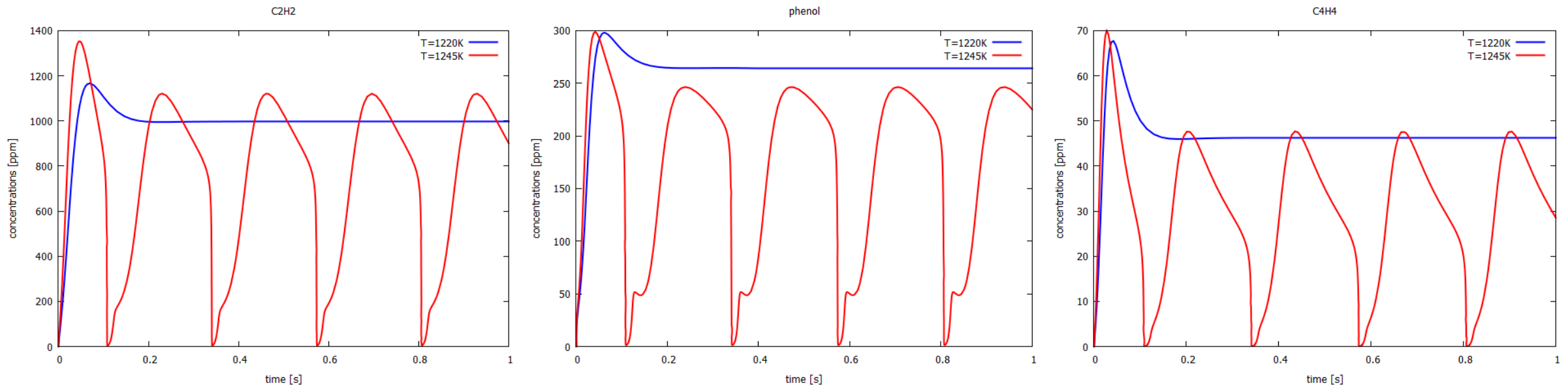
Task 3: perfectly stirred reactor

Simulations of reactors at Φ=1.02 in the interval between 1200K and 1300K are numerically challenging, because in those conditions no steady-state solution is available for the PSR, since the concentrations of species oscillate around a mean value
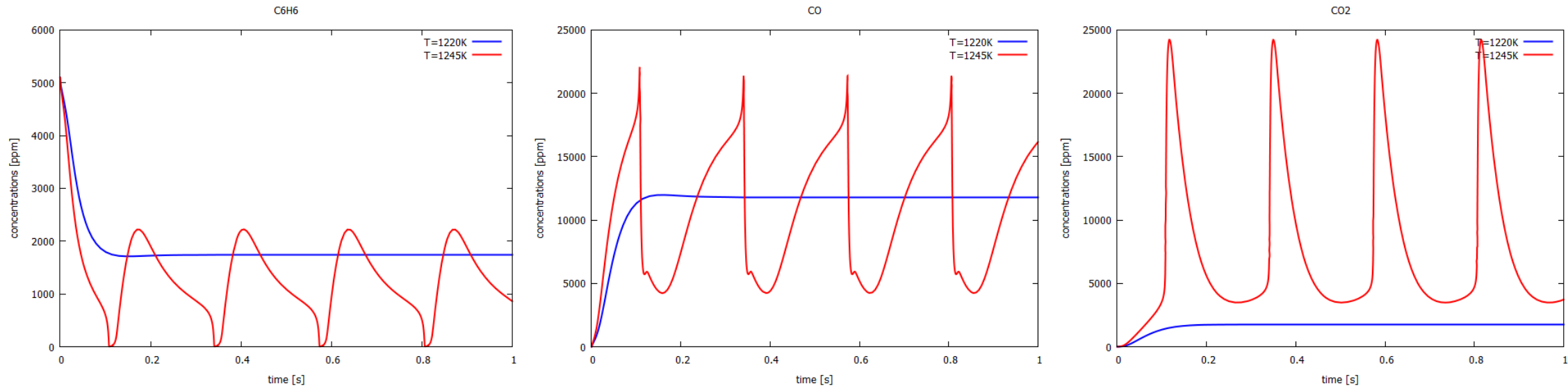
The difference between the two simulations is only the reactor temperature (ΔT=25K only), but the behavior is completely different.

Task 3: perfectly stirred reactor

In particular, for conditions corresponding to Φ=1.02, the region characterized by the oscillations is in the range 1240-1280 K. Results in this region must be carefully analyzed and interpreted.

Numerical problem

Since no steady state solution exists is oscillations occurs, the ODE solver `OpenSMOKE++` uses to solve the perfectly stirred reactor never will stop to integrate the governing equations. In order to avoid this, we have to fix a maximum integration time using the `@EndTime` keyword

Task 3: perfectly stirred reactor

1. Open the `Task3` folder and create a new input file (`input.phi102.dic` in the following) specifying the reaction conditions corresponding to those of experiment of Chai and Pfefferle at Φ=1.02:

```
Dictionary PerfectlyStirredReactor
{
   @KineticsFolder          ../Task0/kinetics-POLIMI_PRF_PAH_LT_1412;
   @Type                    Isothermal-ConstantPressure;
   @InletStatus             inlet-mixture;
   @ResidenceTime           50 ms;
   @Volume                  1 cm3;
   @Options                 output-options;
   @ParametricAnalysis  parametric-analysis;
   @EndTime                 1 s;
}

Dictionary inlet-mixture
{
   @Temperature 750.    K ;
   @Pressure     0.46    atm ;
   @Moles        C6H6 0.0051  O2 0.0375 AR 0.95741;
}
```

This is the only difference with respect to the previous case (Φ=0.19)

The composition is different with respect to the previous case (Φ=0.19)

Task 3: perfectly stirred reactor

```
Dictionary parametric-analysis
{
  @Type                 temperature;

  @NumberOfPoints       40;
  @MinimumValue         850 K;
  @MaximumValue         1350 K;

  @NumberOfThreads      1;
}
```

The parametric analysis is done by varying the reactor temperature

Interval of residence time for parametric analysis (min, max, and number of intervals)

On multi-core machines the calculations can be distributed on more than one core

```
Dictionary output-options
{
  @OutputFolder Output-phi102;
  @StepsFile    1000;
  @StepsVideo   50;
}
```

Name of output folder

Number of integration time steps to write the results on files

Number of integration time steps to write the results on the screen

2. Run the solver for perfectly stirred reactors using the following command (in Microsoft Windows):

```
%OPENSMOKEPP_EXE_FOLDER%\OpenSMOKE_PerfectlyStirredwReactor.exe –input input.102.dic
```

Task 3: perfectly stirred reactor

You may also consider the possibility to use different ODE solvers or different tolerances in order to check if the oscillations are due to numerical problems (in this examples the oscillations are associated to the kinetic mechanism)
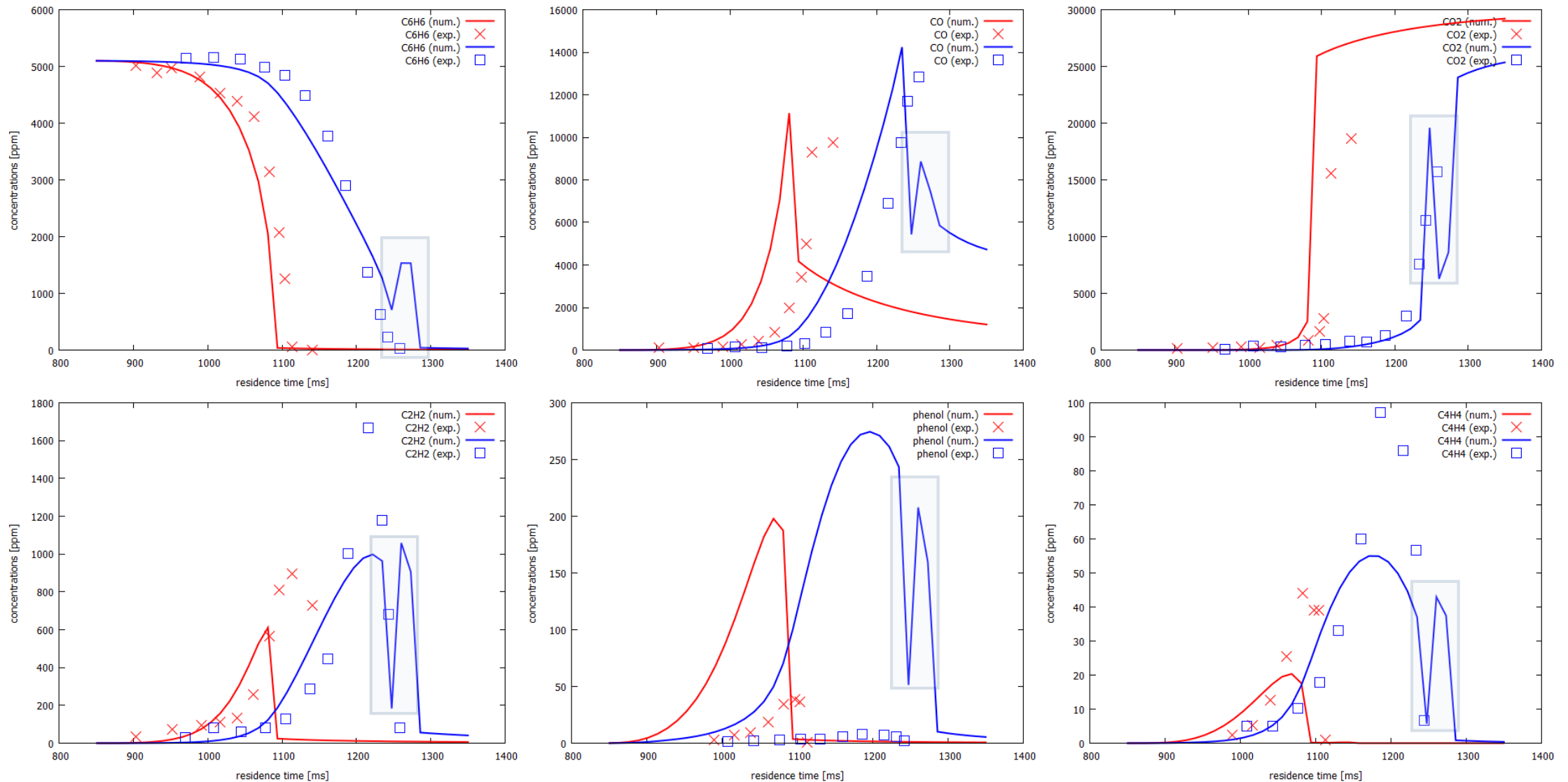
```
Dictionary ode-parameters
{
   @OdeSolver OpenSMOKE;
   @AbsoluteTolerance 1e-10;
   @RelativeTolerance 1e-6;
}
```

Ode solvers available:
OpenSMOKE, CVODE, DVODE, LSODE, RADAU5

In order to use the Dictionary reported above, remember to add the following line to the main dictionary (`PerfectlyStirredReactor`)
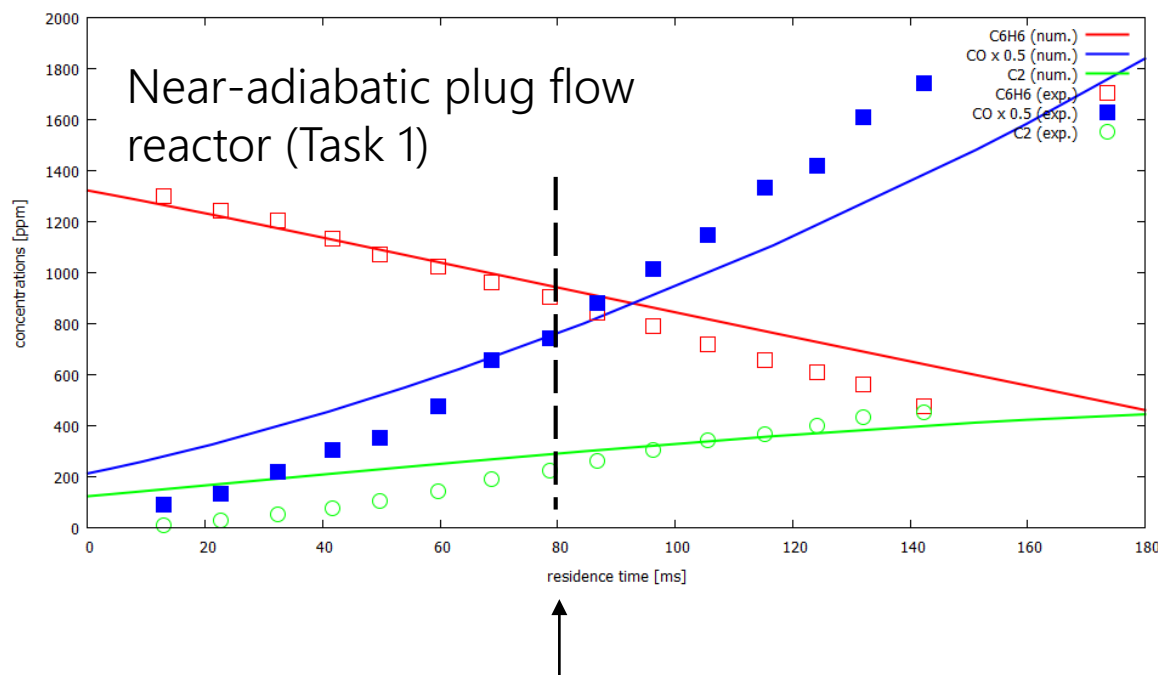
```
@OdeParameters                    ode-parameters;
```

Task 4: analysis of data

Example: analysis of consumption of benzene

Near-adiabatic plug flow reactor (Task 1)

Let us analyze the results at 80 ms

Note: Remember that numerical simulations were shifted of 70 ms, to account for the mixing process. This means that 80 ms on the plot on the left correspond to 150 ms in the numerical simulations

Rate of Production Analysis for C6H6 (@150 ms)
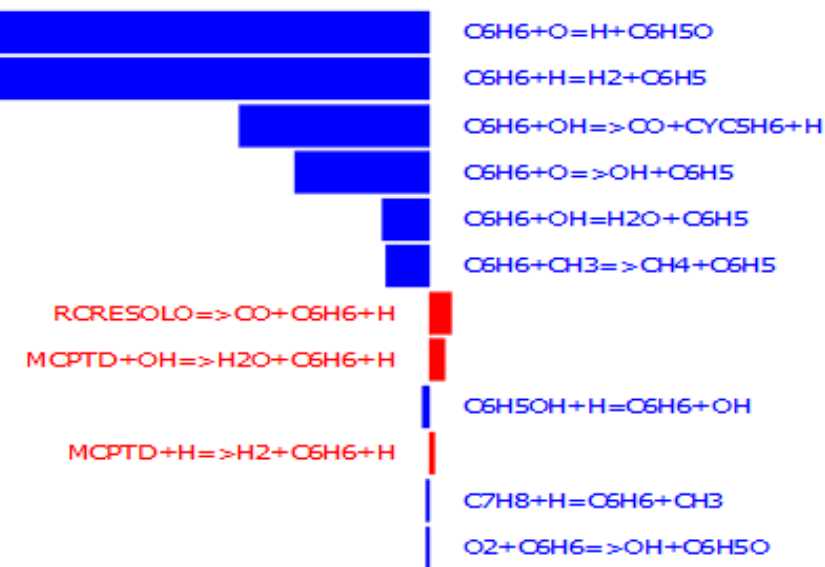
The rate of production analysis allows to recognize the dominant reactions leading to the consumption (in blue) and formation (in red) of benzene

This analysis can be effectively coupled to the path flux analysis to investigate the mechanism governing the evolution of benzene
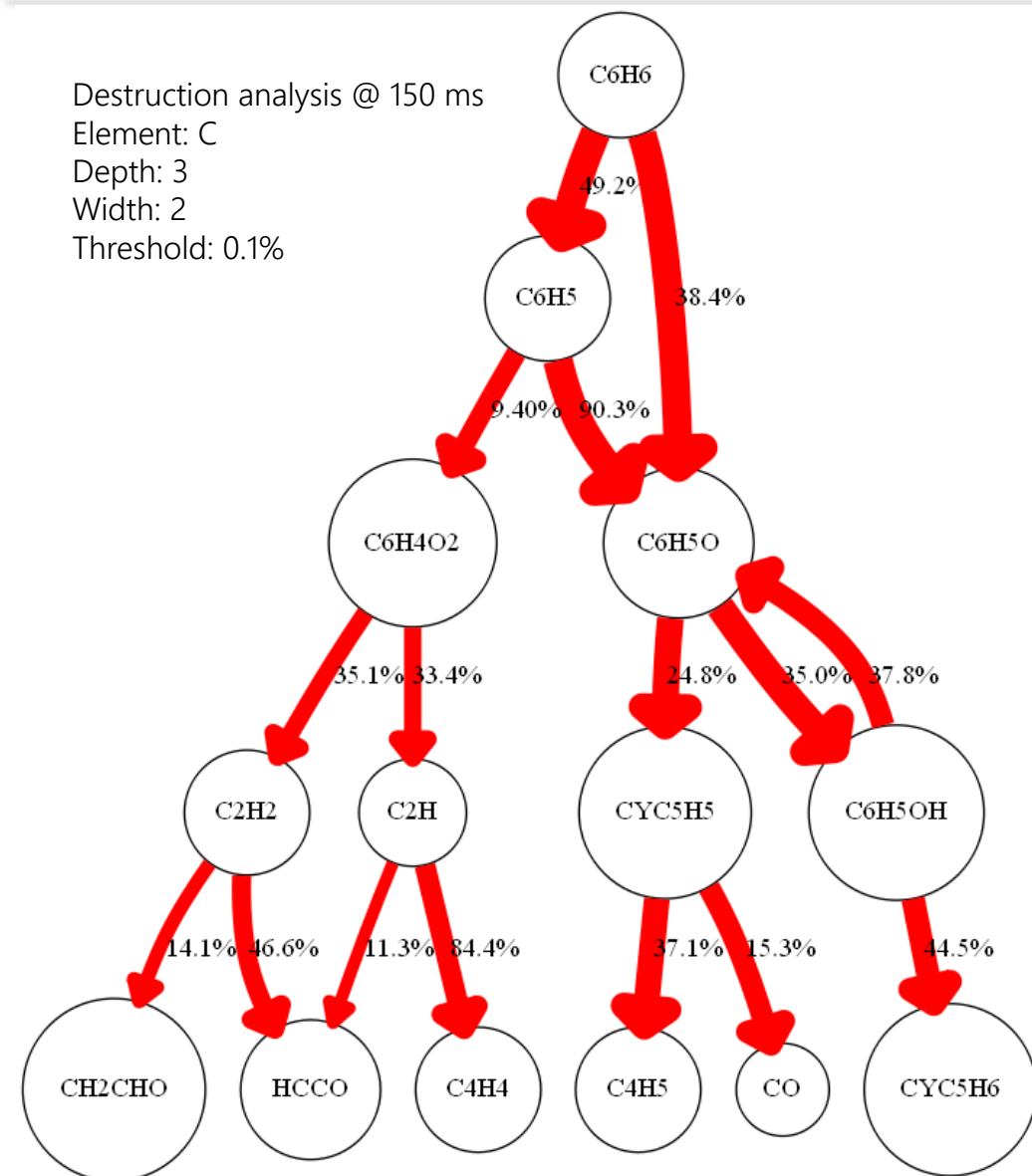
Task 4: analysis of data
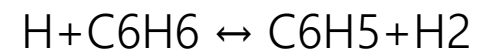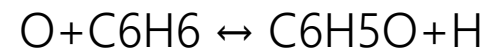

Destruction analysis @ 150 ms
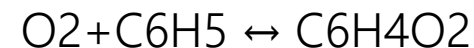Element: C
Depth: 3
Width: 2
Threshold: 0.1%

1. Benzene oxidation mainly proceeds via O and H radical addition to the ring to produce phenoxy radical (C6H5O) and phenyl radical (C6H5):

$$O+C6H6 \leftrightarrow C6H5O+H$$
$$H+C6H6 \leftrightarrow C6H5+H2$$

2. The phenyl radical (C6H5) addition to O2 leads to benzoquinone (C6H4O2):
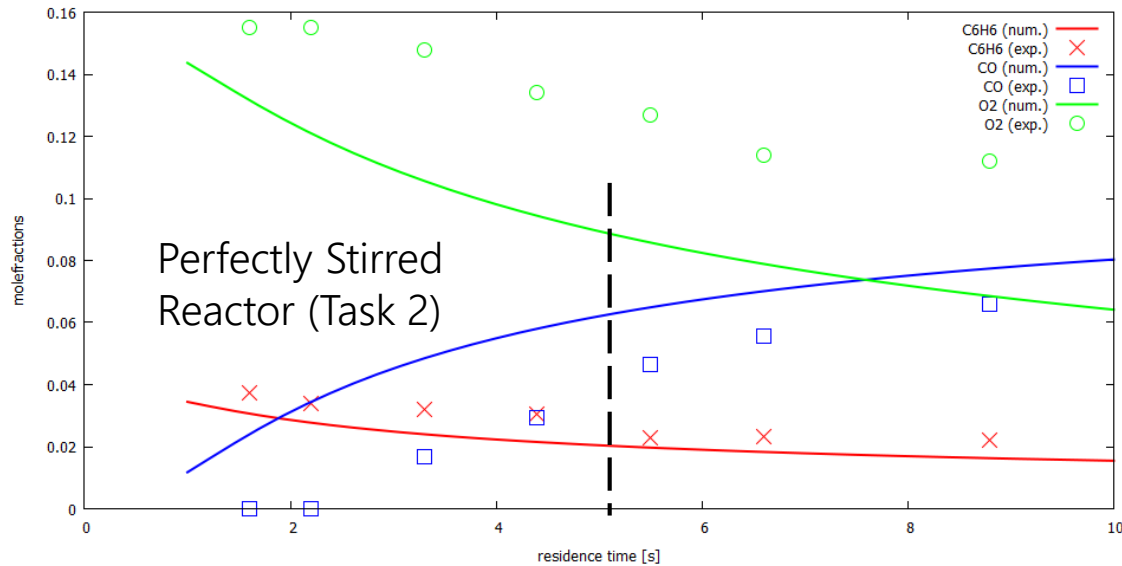
$$O2+C6H5 \leftrightarrow C6H4O2$$

3. Subsequent C6H5O pyrolysis leads to cyclopentadienyl radical (cyC5H5) and CO.

4. Successive O attack on cyC5H5 leads to ring opening and C4H5 formation.

Task 4: analysis of data

Example: analysis of consumption of benzene

Perfectly Stirred Reactor (Task 2)

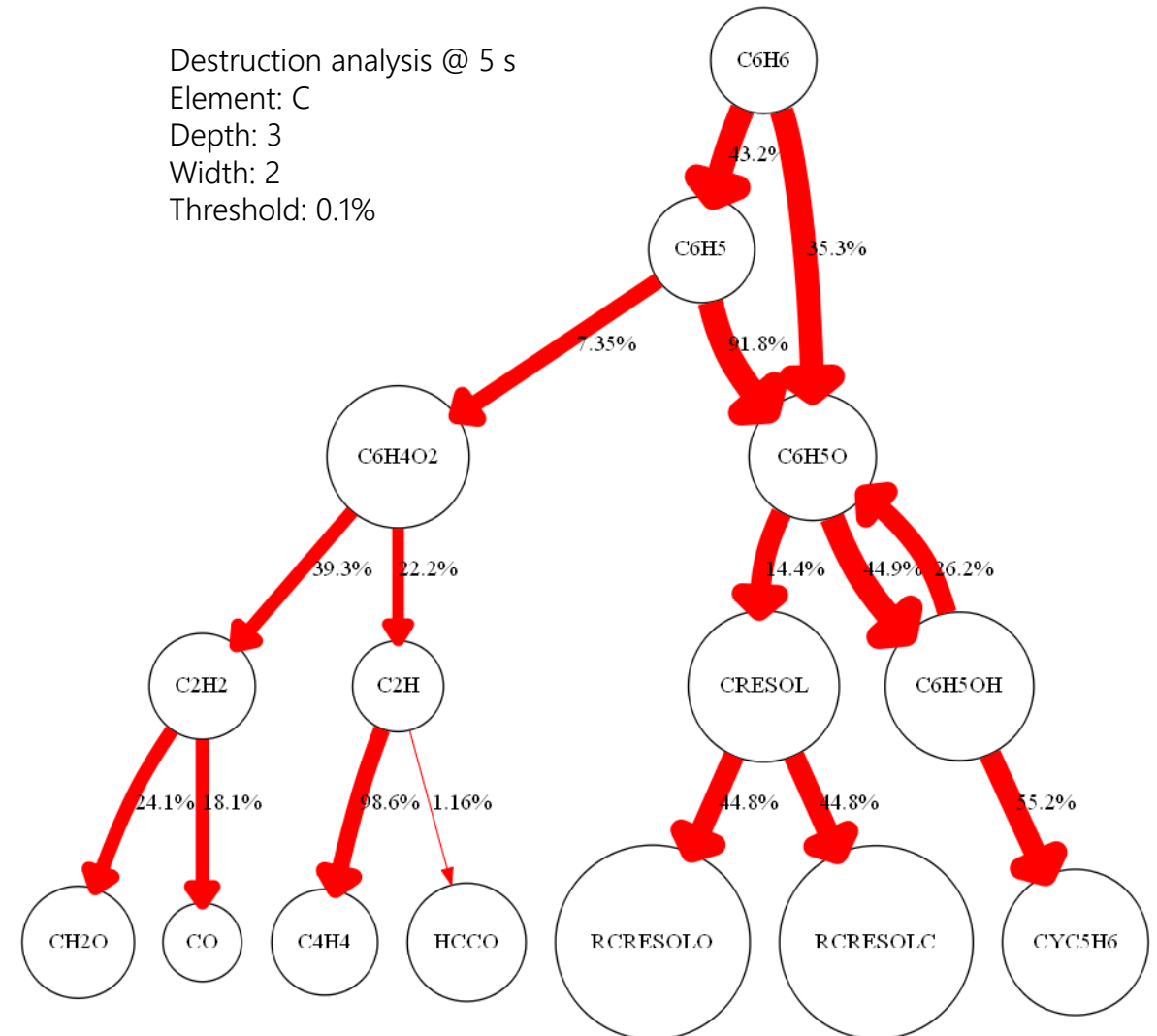Let us analyze the results for the reactor with residence time equal to 5 s

Destruction analysis @ 5 s
Element: C
Depth: 3
Width: 2
Threshold: 0.1%

Reaction Flux Analysis performed with OpenSMOKE (www.opensmoke.polimi.it)

Task 5: benzene oxidation in real applications

Make a set of predictions for benzene oxidation at 800°C and 6% O 2 with a reaction time of 2 s in plug flow reactors. Evaluate the suitability of the current regulations for MSW incinerators.

References

Y. Chai and L.D. Pfefferle. *An experimental study of benzene oxidation at fuel-lean and stoichiometric equivalence ratio conditions*. Fuel, 77(4):313-320, 1998

A. Cuoci, A. Frassoldati, T. Faravelli, and E. Ranzi. *Opensmoke++: An object-oriented framework for the numerical modeling of reactive systems with detailed kinetic mechanisms*. Computer Physics Communications, 192:237-264, 2015. doi: 10.1016/j.cpc.2015.02.014

I. Da Costa, R. Fournet, F. Billaud, and F. Battin-Leclerc. *Experimental and modeling study of the oxidation of benzene*. International Journal of Chemical Kinetics, 35(10):503-524, 2003. doi: 10.1002/kin.10148

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