Iran First International Combustion School (ICS2019)
Tehran, 24-26 August 2019

Combustion modeling: Training Sessions

1. Numerical simulation of 0D reacting systems: batch reactor (ignition delay times) and perfectly stirred reactor (speciation)

Alberto Cuoci

The OpenSMOKE++ Suite

- The **OpenSMOKE++ Suite** (developed by the CRECK Modeling Group at Politecnico di Milano) is a collection of standard solvers for simulating reacting systems with detailed kinetic mechanisms, with hundreds of species and thousands of reactions.

- The solvers currently available move from ideal reactors (batch reactors, continuously stirred tank reactors, plug flow reactors, …) to laminar premixed and diffusive laminar flames. Heterogeneous catalytic reactions are also accounted for.

- The OpenSMOKE++ Suite can be freely downloaded from the following website address, after registration from an Academic email address: https://www.opensmokepp.polimi.it/

- Details are available in the following paper:

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

Organization of ICS2019 Training Session Material

TrainingSessions

- TS1
- TS2
- Docs
- KineticMechanisms

`TS1, TS2, …`
Folders containing the input files needed to carry out the tasks corresponding to the training sessions 1, 2, etc

`Docs`
OpenSMOKE++ User's Guide and additional documentation files

`KineticMechanisms`
Collection of several detailed kinetic mechanisms in CHEMKIN format (thermodynamics, transport and kinetic files) adopted for running the simulations

OpenSMOKE++ User's Guide & Tutorials

- The OpenSMOKE++ User's Guide is available in the Docs folder
- All the available options for each solver are reported there, together details about the installation process
- Additional examples and tutorials are available at the following web address: https://github.com/acuoci/OpenSMOKEppTutorials

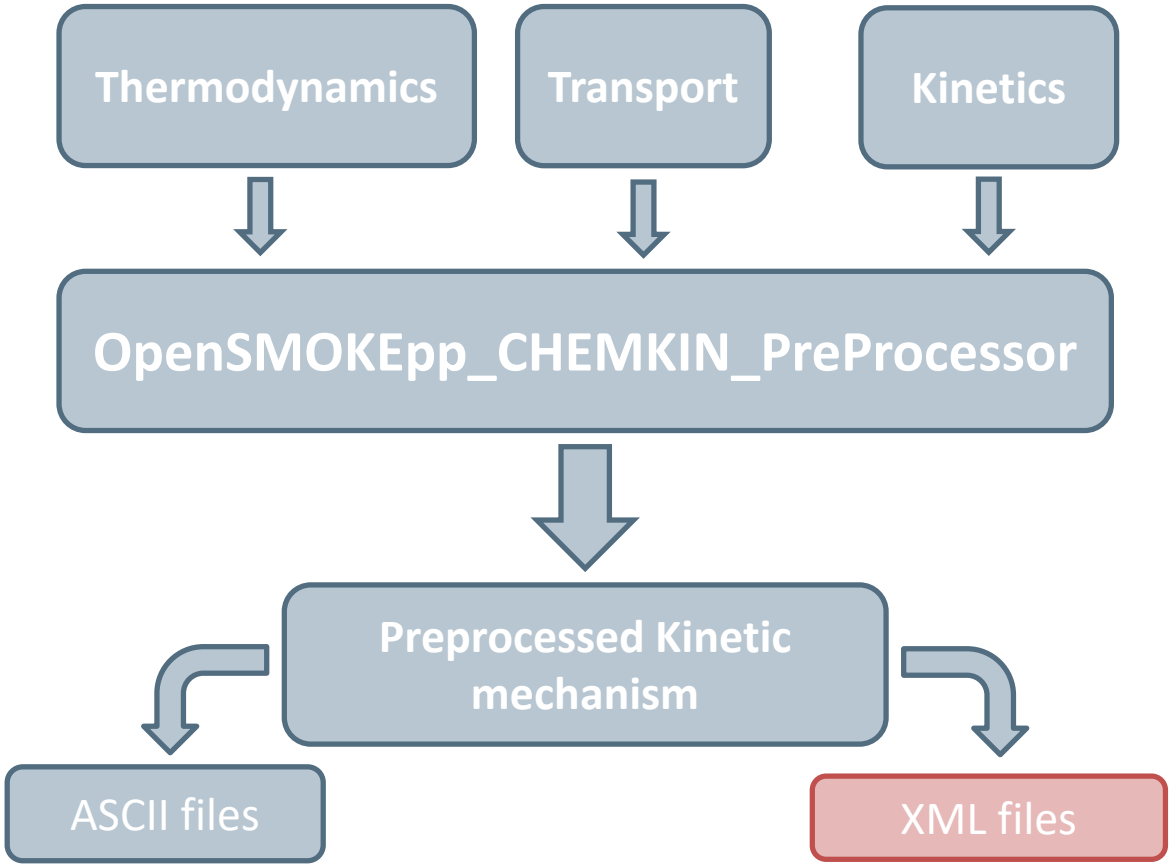
Outline

0. **Pre-processing of a kinetic mechanism**

1. **Ignition delay times (adiabatic batch reactor)**
   a) n-heptane
   b) iso-octane
   c) n-heptane/iso-octane

2. **Jet Stirred Reactors: speciation (isothermal perfectly stirred reactor)**
   a) toluene
   b) n-heptane/iso-octane

Task 0: pre-processing kinetic mechanisms



Objective: get familiar with the pre-processing operations and analysis of pre-processed results

Task: preprocess a complete kinetic mechanism (together with thermodynamics and transport properties)

We will use the `POLIMI_PRF_PAH_LT_1412.CKI` kinetic mechanism (~300 species, ~12000 reactions), a reduced mechanism for gasoline obtained from the complete POLIMI mechanism

Task 0: pre-processing kinetic mechanisms

1. Preparation of input data

Go to the `Task0` folder, containing the `input.dic`. This file contains instructions for pre-processing the complete kinetic mechanism

```
Dictionary CHEMKIN_PreProcessor
{
        @Thermodynamics
        ../../KineticMechanisms/POLIMI_1412/Thermodynamics/POLIMI_TOT_NOX_1412.CKT;
        @Transport
        ../../KineticMechanisms/POLIMI_1412/Transport/POLIMI_TOT_NOX_1412.TRC;
        @Kinetics
        ../../KineticMechanisms/POLIMI_1412/Kinetics/POLIMI_PRF_PAH_LT_1412.CKI;
        @Output
        kinetics-POLIMI_PRF_PAH_LT_1412;
}
```

`@Transport`
path to the CHEMKIN file containing the transport data to be pre-processed

`@Kinetics`
path to the CHEMKIN file containing the kinetic mechanism to be pre-processed

Task 0: pre-processing kinetic mechanisms

2. Run the kinetic preprocessor

3. Analyze the pre-processing results

If everything was done properly, the `kinetics-POLIMI_PRF_PAH_LT_1412` output folder will be created, containing the following files (in addition to the usual files associated to thermodynamics):

`Kinetics_Summary.out`
This file simply contains the kinetic mechanism written in a more readable format

`kinetics.xml`
`reaction_names.xml`
these are the only file needed by OpenSMOKE++ Suite solvers. They contain the pre-processed thermodynamic (and transport) data together with the whole reaction mechanism in XML format

Task 2: Ignition Delay Times (IDT) from batch reactors

Objective: estimate the ignition delay times (IDT) for n-heptane, iso-octane and n-heptane/iso-octane mixtures at several pressures and compare the numerical results with experimental data

Task: use the batch reactor model for estimating the ignition delay times

a) n-heptane
b) iso-octane
c) n-heptane/iso-octane

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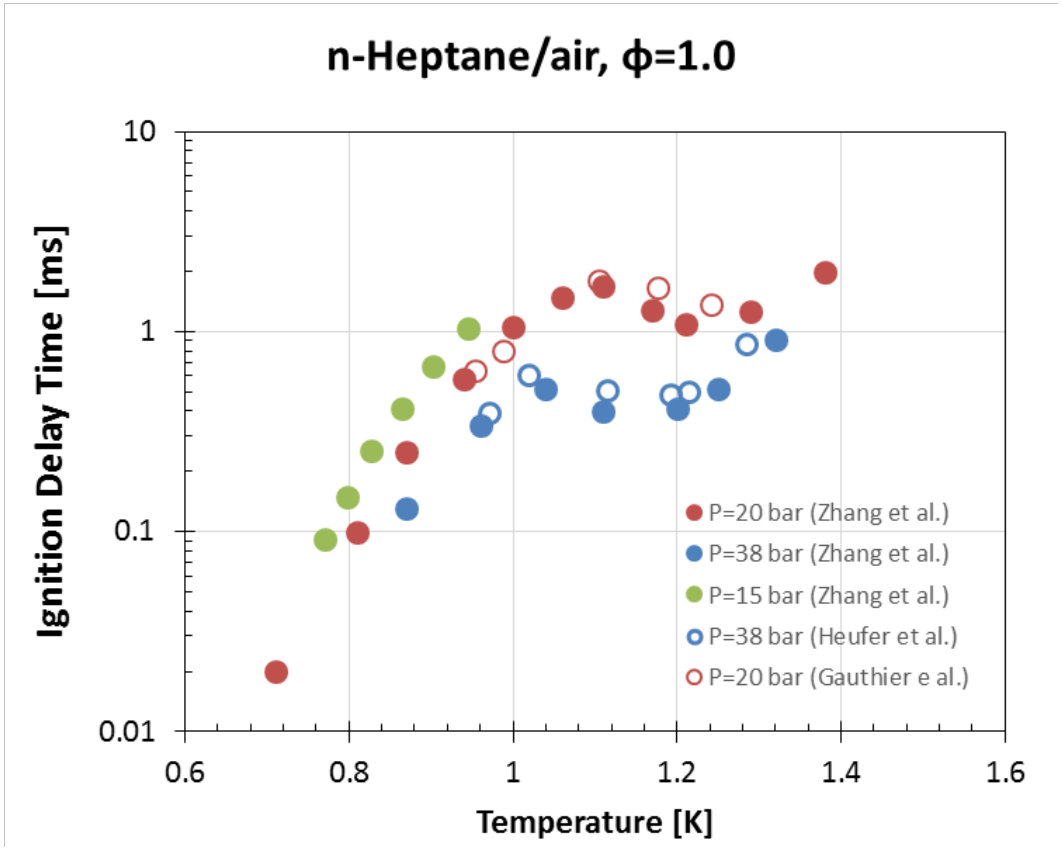
a) **n-heptane**
b) iso-octane
c) n-heptane/iso-octane

n-heptane: experimental data



In the experiments, ignition delay times of stoichiometric n- heptane/air mixtures have been measured in two different high-pressure shock tubes in the temperature range of 726–1412 K and at elevated pressures (15, 20 and 38 bar).

Zhang et al., *An updated experimental and kinetic modeling study of n-heptane oxidation*, Combustion and Flame 172 (2016), p. 116-135

n-heptane: preparation of input files (I)

1. Preparing the input for batch reactor calculations

The `Task1/a.IDT_heptane` folder contains also the input files for simulating adiabatic batch reactors, in order to estimate the ignition delay times. The input file is split in several Dictionaries.

```
Dictionary BatchReactor
{
        @KineticsFolder
        ..\..\Task0\ kinetics-POLIMI_PRF_PAH_LT_1412;
        @Type              NonIsothermal-ConstantVolume;
        @InitialStatus     initial-mixture;
        @EndTime           0.1 s;
        @ParametricAnalysis   parametric-analysis;
        @IgnitionDelayTimes   ignition-delay-times;
        @Options              output-options;
}

Dictionary initial-mixture
{
        @Temperature              1000 K;
        @Pressure                 15 bar;
        @EquivalenceRatio         1.0;
        @FuelMoles                NC7H16 1.00;
        @OxidizerMoles            O2 0.21  N2 0.79;
}
```

Main Dictionary, specifying the type of batch reactor to be simulated

Dictionary specifying the reference conditions of the mixture

n-heptane: preparation of input files (II)

```
Dictionary parametric-analysis
{
        @Type                temperature;
        @NumberOfPoints      3;
        @MinimumValue        1050 K;
        @MaximumValue        1300 K;
}

Dictionary output-options
{
        @OutputFolder    15bar;
}

Dictionary ignition-delay-times
{
        @Temperature      true;
        @Pressure         true;
        @Species          OH CH;
}
```

Automatic change of temperature in a given range (parametric analysis)

Name of the output folder

Calculation of ignition delay times

n-heptane: running the simulations

2. Run the batch reactor simulations

Always from the same `Task1/a.IDT_heptane` folder, we can now run the `OpenSMOKEpp_BatchReactor` solver.

Run the `Run.bat` file by double-clicking on it or, from the Command Prompt, type:

```
"..\..\..\OpenSMOKE++Suite\OpenSMOKEpp_BatchReactor.exe" --input
input_phi1_15bar.dic
"..\..\..\OpenSMOKE++Suite\OpenSMOKEpp_BatchReactor.exe" --input
input_phi1_20bar.dic
"..\..\..\OpenSMOKE++Suite\OpenSMOKEpp_BatchReactor.exe" --input
input_phi1_38bar.dic
```

3. Analysis of output

Temperature, pressure and composition profiles for each simulated reactor are available in Output.out file. From its content it is possible to reconstruct the ignition delay time (IDT)

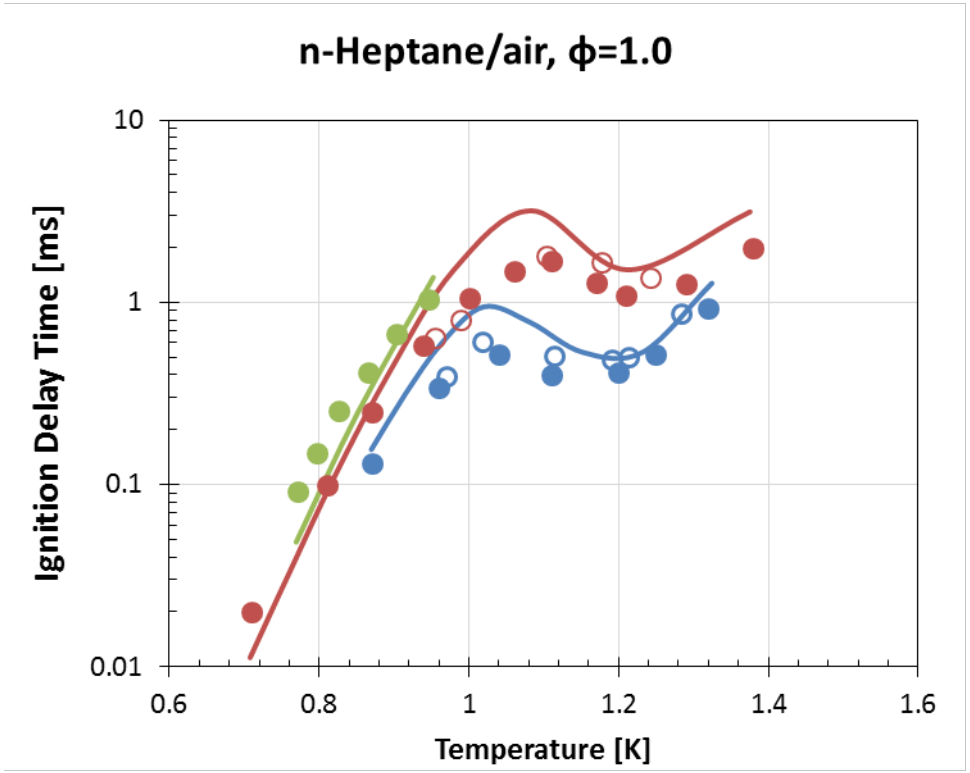
n-heptane: post-processing

4. Automatic recognition of IDTs

In the output folder of each parametric case, the ignition delay times automatically calculated by the OS++ solver are available in the `ParametricAnalysisIDT.out` file.

In addition, for each case in the parametric analysis, a file `IDT.out` is written in the dedicated forlders `Case0, Case1, Case2`, etc.

n-heptane: comparison with experimental data



Zhang et al., *An updated experimental and kinetic modeling study of n-heptane oxidation*, Combustion and Flame 172 (2016), p. 116-135

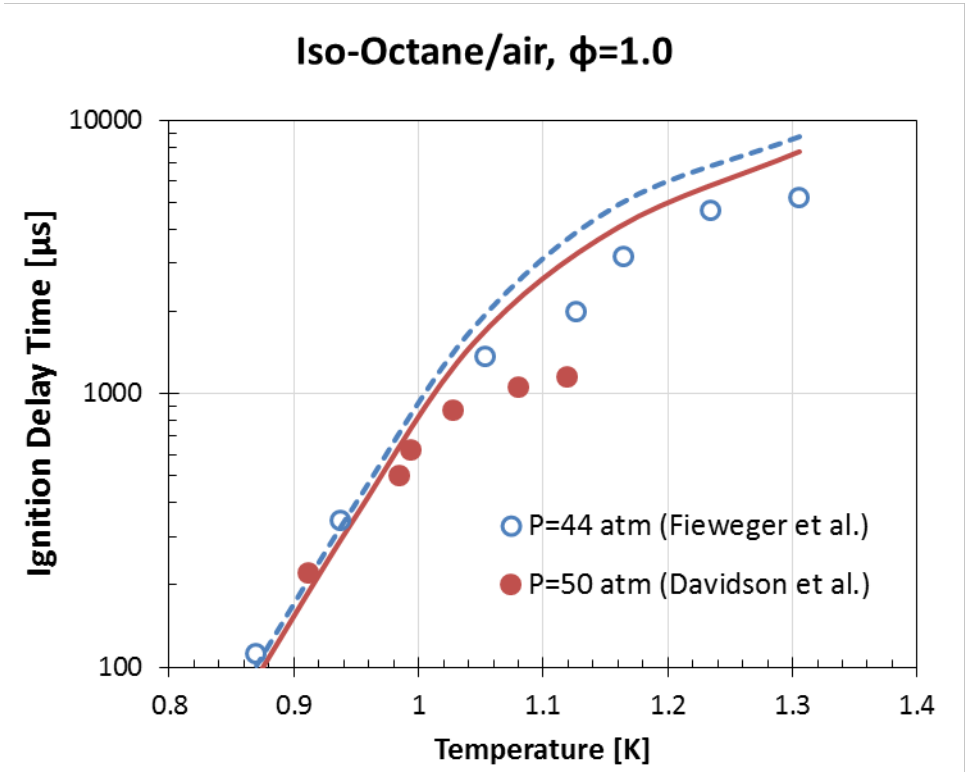
Task 2: Ignition Delay Times (IDT) from batch reactors

Objective: estimate the ignition delay times (IDT) for n-heptane, iso-octane and n-heptane/iso-octane mixtures at several pressures and compare the numerical results with experimental data

Task: use the batch reactor model for estimating the ignition delay times

a) n-heptane
b) iso-octane
c) n-heptane/iso-octane

i-octane: comparison with experimental data



Ignition delay times were measured in a shock tube for iso-octane/air and toluene/air at conditions similar to those found in homogeneous charge compression ignition (HCCI) engines.

Davidson et al., *Shock tube ignition measurements of iso-octane/air and toluene/air at high pressures*, Proceedings of the Combustion Institute, 30 (2005), p. 1175-1182

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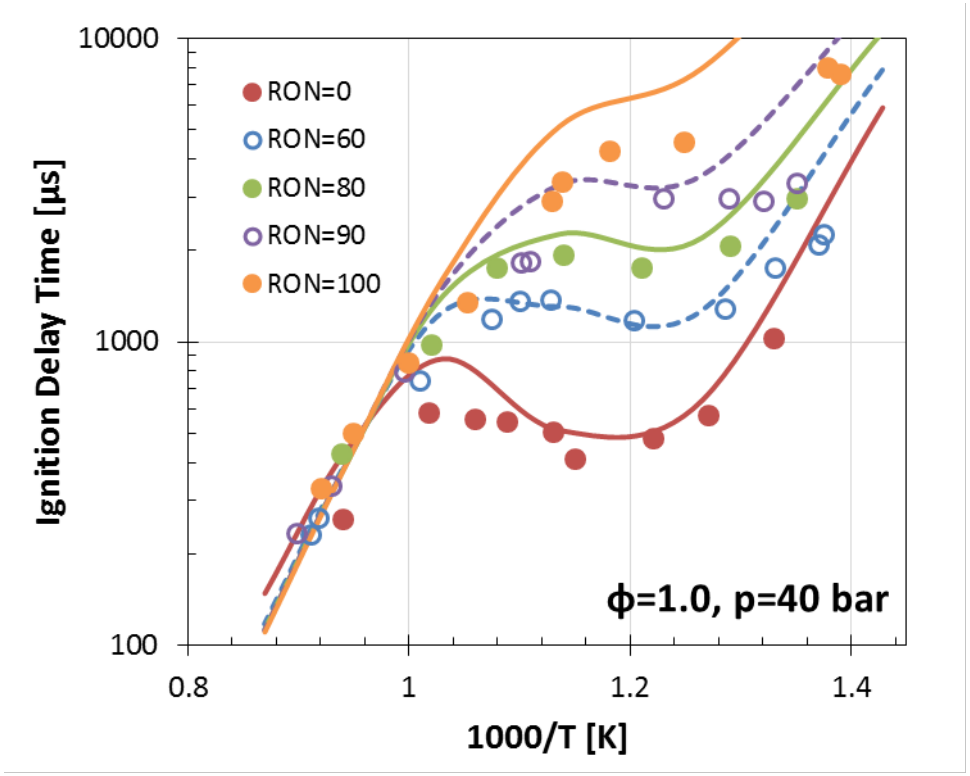
Objective: estimate the ignition delay times (IDT) for n-heptane, iso-octane and n-heptane/iso-octane mixtures at several pressures and compare the numerical results with experimental data

Task: use the batch reactor model for estimating the ignition delay times

a) n-heptane
b) iso-octane
c) n-heptane/iso-octane

n-heptane/i-octane mixtures



Ignition delay times were measured under relevant engine conditions by the shock tube technique

Fieweger et al., *Self-Ignition of S.I. Engine Model Fuels: A Shock Tube Investigation at High Pressure*, Combustion and Flame, 109 (1997), p. 599-619

Task 2: Speciation in a Jet Stirred Reactor

Objective: analyze the formation of selected chemical species in an isothermal Jet Stirred Reactor (modeled as a perfectly stirred reactor) in a wide range of temperature and compare the numerical predictions to the experimental data available

Task: use the perfectly stirred reactor model for analyzing the speciation in experimental jet stirred reactors

a) toluene
b) n-heptane/iso-octane

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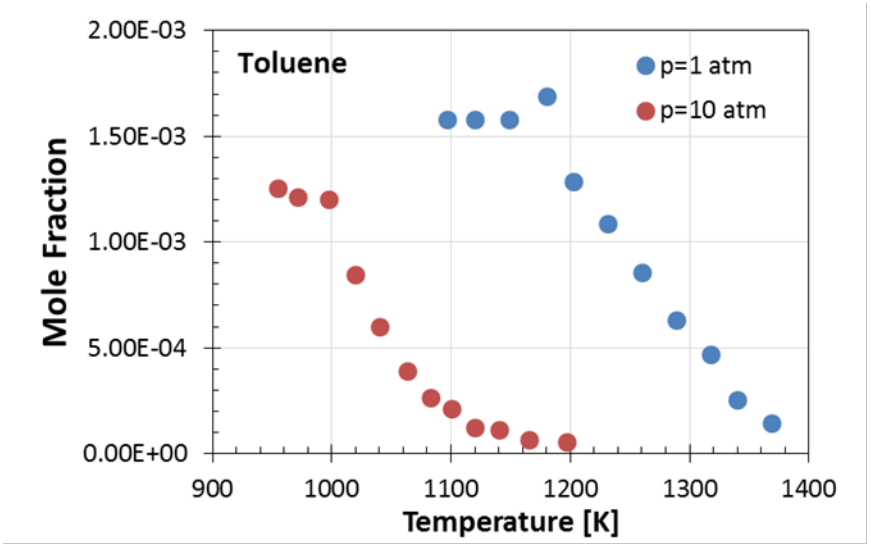
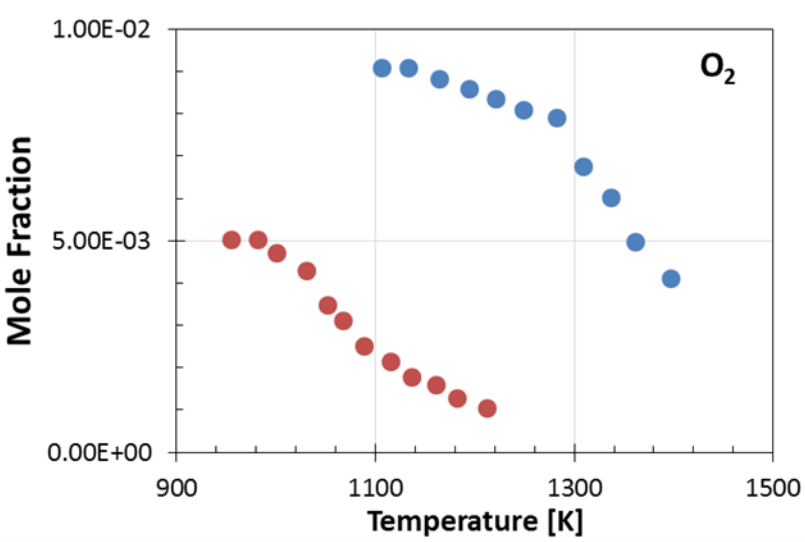
Task: use the perfectly stirred reactor model for analyzing the speciation in experimental jet stirred reactors

a) **toluene**
b) n-heptane/iso-octane

Toluene: experimental data (I)

The oxidation of toluene was investigated in a jet stirred reactor (JSR) at the pressure of 10 atm, residence time of 0.6 s, equivalence ratios of 0.5, 1.0 and 1.5, and temperatures from 950 to 1200 K using gas chromatography combined with flame ionization detector, thermal conductivity detector and mass spectrometry

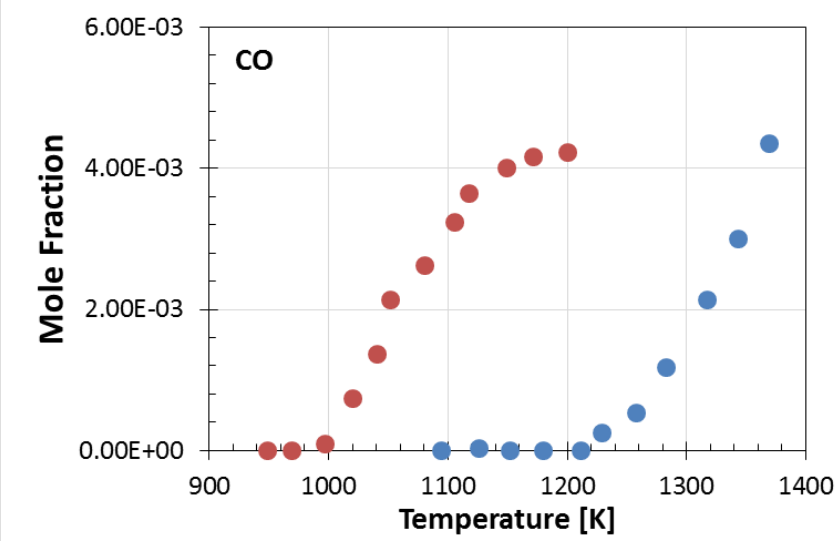


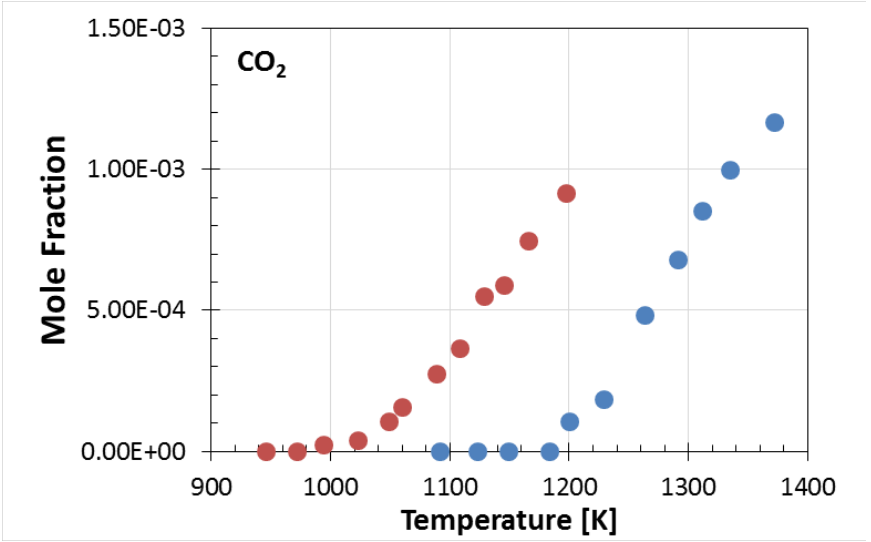


Yuan et al., *Investigation on the pyrolysis and oxidation of toluene over a wide range conditions. I. Flow reactor pyrolysis and jet stirred reactor oxidation*, Combustion and Flame, 162 (2015), p. 3-21

Toluene: experimental data (II)

The oxidation of toluene was investigated in a jet stirred reactor (JSR) at the pressure of 10 atm, residence time of 0.6 s, equivalence ratios of 0.5, 1.0 and 1.5, and temperatures from 950 to 1200 K using gas chromatography combined with flame ionization detector, thermal conductivity detector and mass spectrometry





Yuan et al., *Investigation on the pyrolysis and oxidation of toluene over a wide range conditions. I. Flow reactor pyrolysis and jet stirred reactor oxidation*, Combustion and Flame, 162 (2015), p. 3-21

Toluene: preparation of input files (I)

1. Preparing the input for jet stirred reactor calculations

The `Task2\a.JSR_toluene` folder contains also the input files for simulating Jet Stirred Reactors. The input file is split in several Dictionaries.

```
Dictionary PerfectlyStirredReactor
{
@KineticsFolder
..\..\Task0\kinetics-POLIMI_PRF_PAH_LT_1412;
@Type                       Isothermal-ConstantPressure;
@InletStatus                inlet-mixture;
@ResidenceTime              1.0 s;
@Volume                     30.5 cm3;
@ParametricAnalysis         parametric-analysis;
@Options                    output-options;
@OdeParameters              ode-parameters;
}
Dictionary initial-mixture
{
@Temperature      900.      K;
@Pressure         1.        atm;
@MoleFractions    C7H8      0.00157  O2       0.0091
                  N2        0.98933;
}
```

Main Dictionary, specifying the type of jet stirred reactor to be simulated

Dictionary specifying the reference conditions of the mixture

Toluene: preparation of input files (II)

```
Dictionary parametric-analysis
{
        @Type               temperature;
        @ListOfValues       900  950 1000 1050 1100 1150
                            1200 1250 1300 1350 1400 1450 K;
}

Dictionary output-options
{
    @OutputFolder1atm_Phi1.5;
    @OutputSpecies          C7H8 O2 CO CO2;
}

Dictionary ode-parameters
{
        @AbsoluteTolerance 1e-14;
        @RelativeTolerance 1e-7;
}
```

Automatic change of temperature in a given range (parametric analysis)

Name of the output folder

Better to adopt strict tolerance for description of low-temperature conditions

Toluene: running the simulations

2. Run the jet stirred reactor simulations

Always from the same `Task2\a.JSR_toluene` folder, we can now run the `OpenSMOKEpp_PerfectlyStirredReactor` solver.

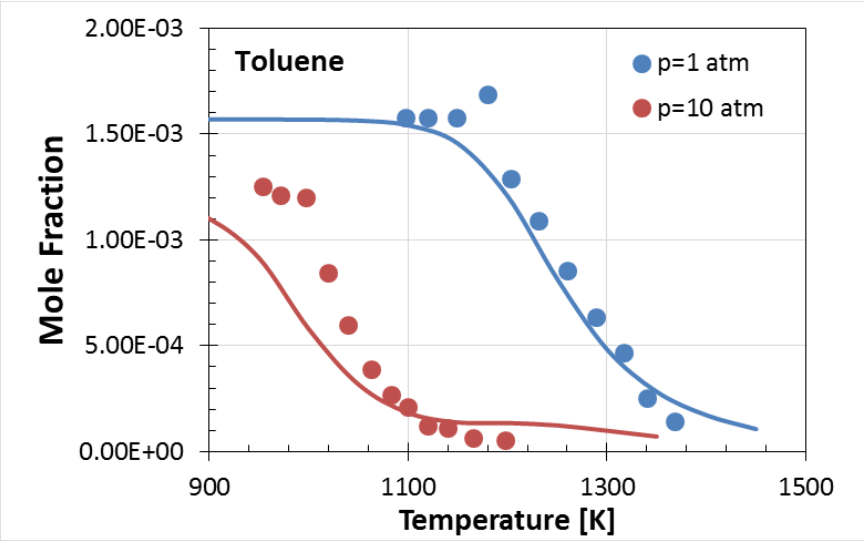
Run the `Run.bat` file by double-clicking on it or, from the Command Prompt, type:

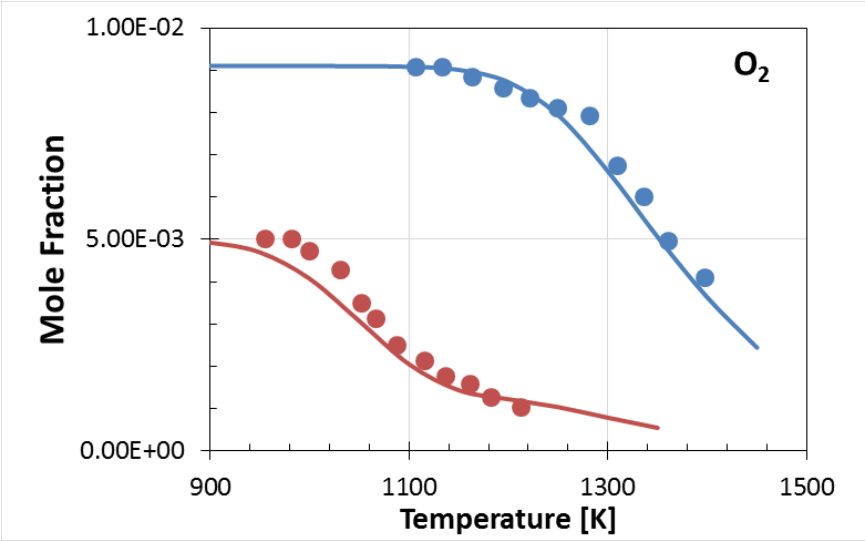
```
"..\..\..\OpenSMOKE++Suite\OpenSMOKEpp_PerfectlyStirredReactor.exe"
--input input_1atm_phi15.dic

"..\..\..\OpenSMOKE++Suite\OpenSMOKEpp_PerfectlyStirredReactor.exe"
--input input_10atm_phi15.dic
```

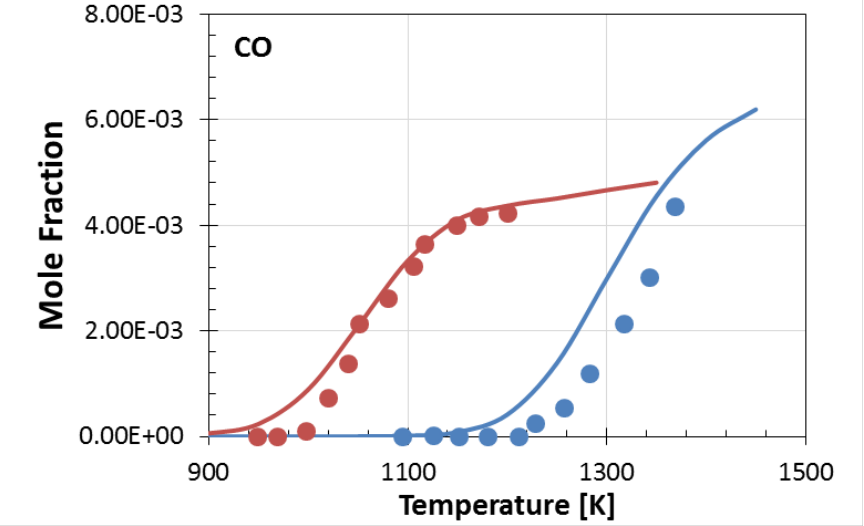
3. Analysis of output

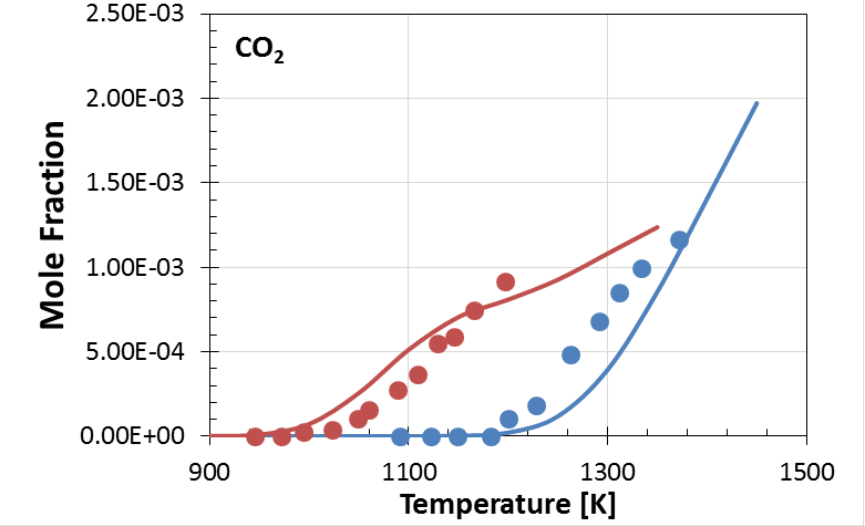
Temperature and composition at the exit of each simulated condition are available in the `ParametricAnalysis.out` file.

Toluene: comparison with experimental data









Task 2: Speciation in a Jet Stirred Reactor

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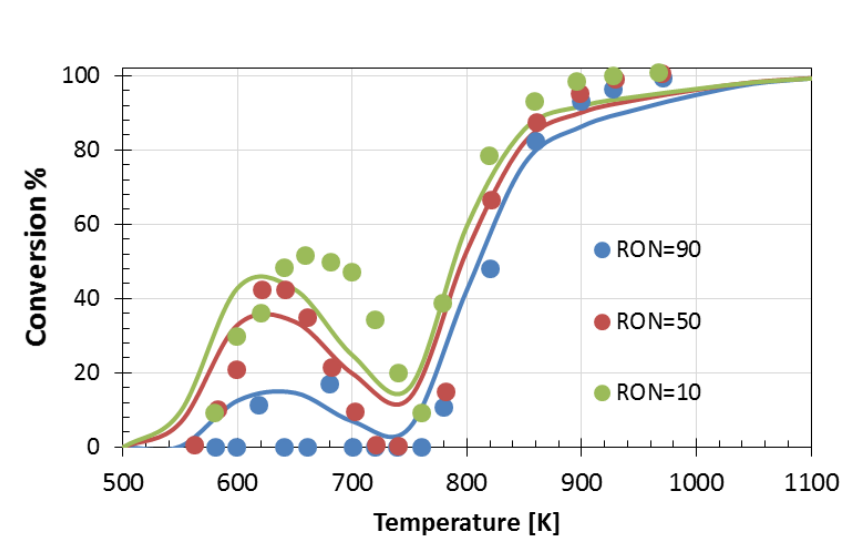
Task: use the perfectly stirred reactor model for analyzing the speciation in experimental jet stirred reactors

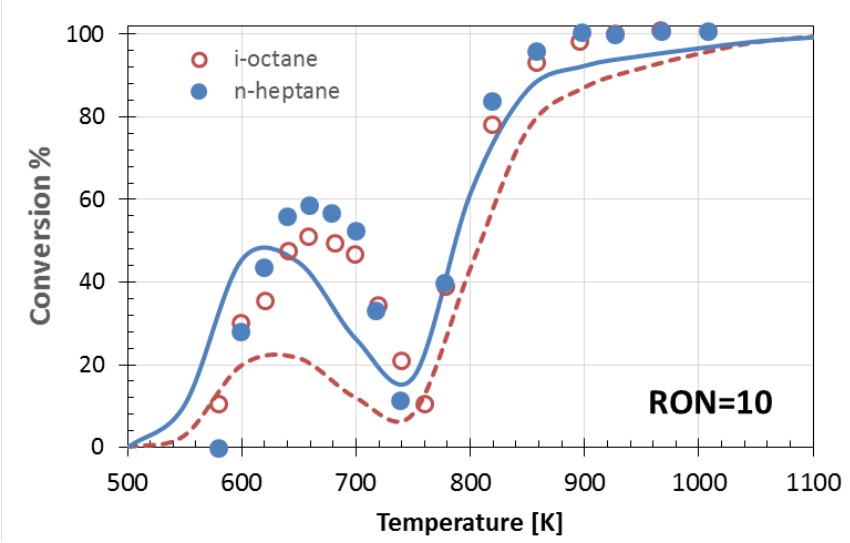
a) toluene

b) n-heptane/iso-octane

n-heptane/i-octane: comparison with experimental data (I)

Experimental results obtained in a perfectly jet-stirred reactor in a temperature range from 580 to 1150 K and high pressure (10 atm), which includes the negative temperature coefficient region

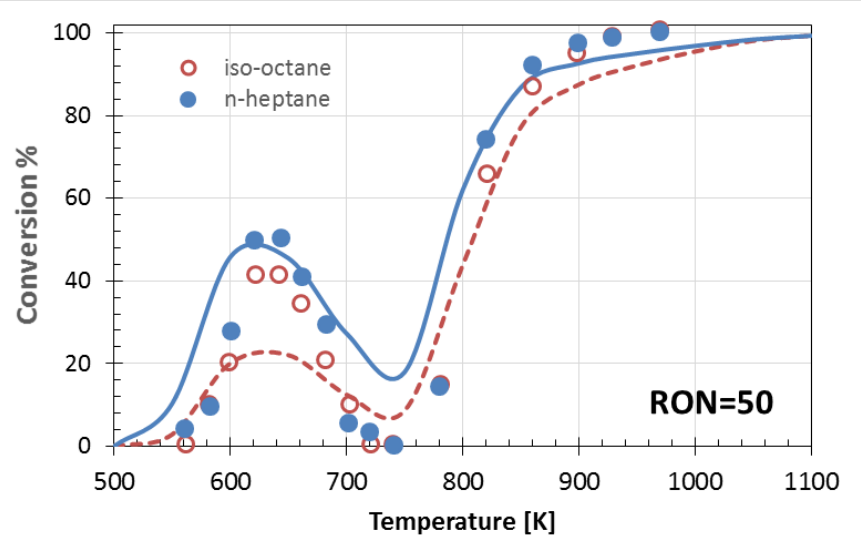


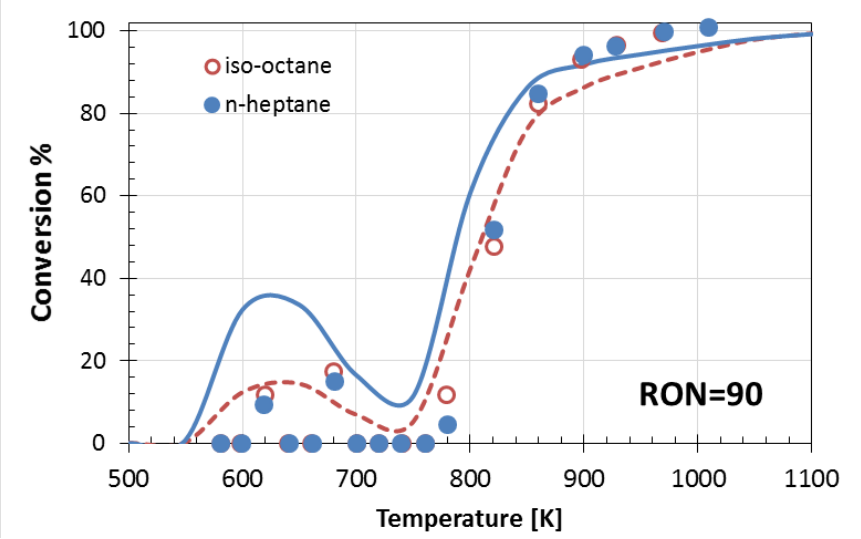


Glaude et al., *Modeling the oxidation of mixtures of primary reference automobile fuels*, Energy & Fuels, 16 (2002), p. 1186-1195

n-heptane/i-octane: comparison with experimental data (II)

Experimental results obtained in a perfectly jet-stirred reactor in a temperature range from 580 to 1150 K and high pressure (10 atm), which includes the negative temperature coefficient region





Glaude et al., *Modeling the oxidation of mixtures of primary reference automobile fuels*, Energy & Fuels, 16 (2002), p. 1186-1195

References (I)

CHEMKIN®

Reaction Design, *Chemkin Theory Manual*, CK-THE-15151-1601-UG-1, January 2016
Web: https://www.ems.psu.edu/~radovic/ChemKin_Theory_PaSR.pdf

Reaction Design, *CHEMKIN, A software package for the analysis of gas-phase chemical and plasma kinetics*, CK-TUT-10112-1112-UG-1, CHE-036-1, CHEMKIN Collection Release 3.6, September 2000
Web: https://www3.nd.edu/~powers/ame.60636/chemkin2000.pdf

Reaction Design, *TRANSPORT, A software package for the evaluation of gas-phase, multicomponent transport properties*, TRA-036-1, CHEMKIN Collection Release 3.6, September 2000
Web: https://www3.nd.edu/~powers/ame.60636/transport.pdf

Reaction Design, *CHEMKIN Tutorials Manual*, CK-TUT-10112-1112-UG-1, December 2011
Web: https://www.ems.psu.edu/~radovic/ChemKin_Tutorial_2-3-7.pdf

References (II)

OpenSMOKE++ Development

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

Cuoci, A., Frassoldati, A., Faravelli, T., Ranzi, E. *Numerical modeling of laminar flames with detailed kinetics based on the operator-splitting method* (2013) Energy and Fuels, 27 (12), pp. 7730-7753, DOI: 10.1021/ef4016334

Cuoci, A., Frassoldati, A., Faravelli, T., Ranzi, E. *A computational tool for the detailed kinetic modeling of laminar flames: Application to C2H4/CH4 coflow flames* (2013) Combustion and Flame, 160 (5), pp. 870-886, DOI: 10.1016/j.combustflame.2013.01.011

M.Maestri, A.Cuoci, *Coupling CFD with detailed microkinetic modeling in heterogeneous catalysis,* Chemical Engineering Science 96(7), pp. 106-117 (2013) DOI: 10.1016/j.ces.2013.03.048