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Exercise 3
Engine Exhaust Oxidation of Unburned Hydrocarbons

Combustion Fundamentals and New Technologies

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

Reactor models

Plug Flow reactor (PFR) from the OpenSMOKE++ Suite

Reaction mechanism

GRI-Mech 3.0

Purpose

Familiarize the student with:

1) the reaction mechanism format;
2) the pre-processing operations to be carried out on kinetic mechanisms;
3) numerical simulations of plug flow reactors;
4) use of electronic chemical kinetics database from NIST for identifying reactions and obtaining rate constants. Furthermore, to caution the student to validate the kinetic model prior to application.

Background (I)

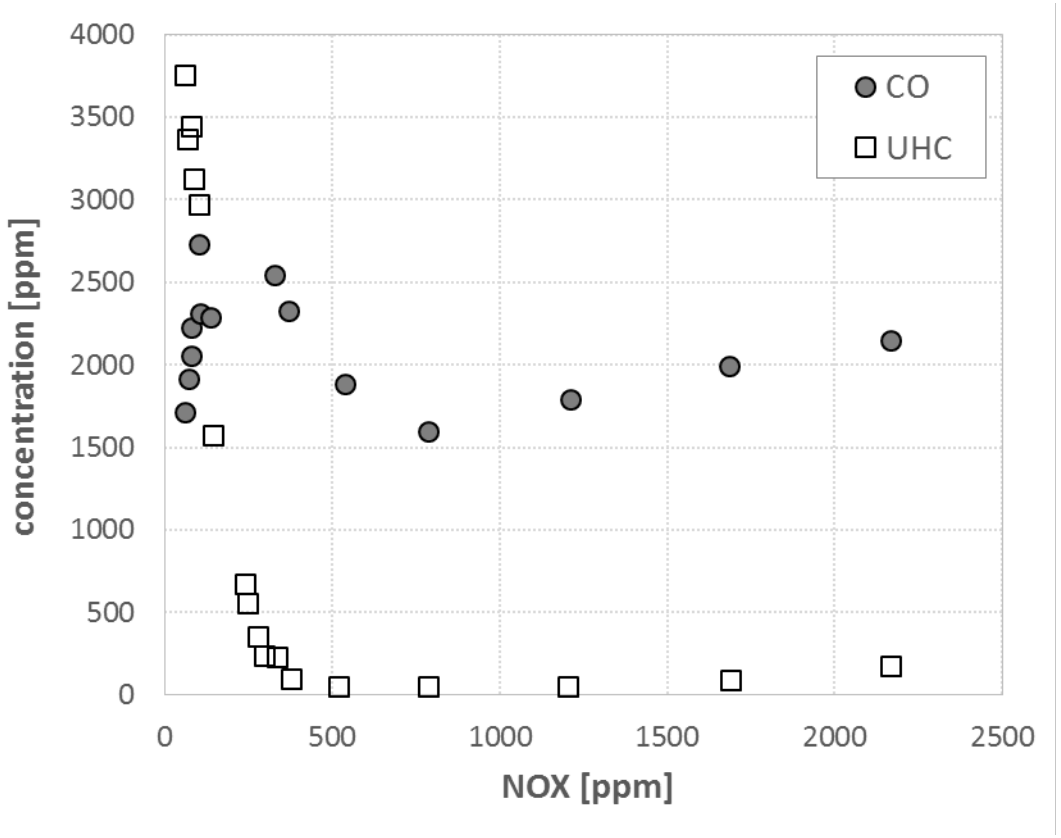
Co-generation of heat and power in lean-burn natural gas engines is attractive due to the comparably low capitol costs of these units and because they are suitable for de–centralised production of power and heat. A further advantage of this technology compared to conventional coal-fired power plants is the reduction of the CO2 emission; the combustion of natural gas produces about 45% less C O 2 per energy unit compared to coal.

However, the emission of unburned hydrocarbons (UHC) from these engines, which may amount to a significant fraction of the fuel input, has become a concern. For natural gas fired engines the UHC consists largely of methane, which is a strong greenhouse gas. The emission sources in these engines include filling of crevice volumes with unburned mixture that the flame cannot propagate into, flame quenching at the walls, exhaust valve leakage, and misfiring of the engine.

Control of unburned hydrocarbon emissions from lean-burn engines may be achieved by modifying the fuel, by modifying engine design and/or operating conditions, or by applying post–cylinder processes such as catalytic oxidation or regenerative incineration.

Background (II)

Another possibility is to enhance the post-cylinder oxidation process, either by modifying reaction conditions in the manifold/exhaust system or by injection of promoting additives. Recent work (Kristensen, 2000) indicates that the main parameters that control the amount of UHC oxidation in the exhaust is temperature, residence time and, perhaps surprisingly, concentration of nitrogen oxides.



Results obtained on a 35 kW test engine equipped with an extended exhaust reactor (Kristensen, 2000). These results show the dramatic impact of NO level on UHC conversion in the exhaust reactor.

P.G. Kristensen, B. Karll, A.B. Bendtsen, P. Glarborg, and K. Dam-Johansen. Exhaust oxidation of unburned hydrocarbons from lean-burn natural gas engines. Combustion science and technology, 157 (1-6):263-292, 2000.

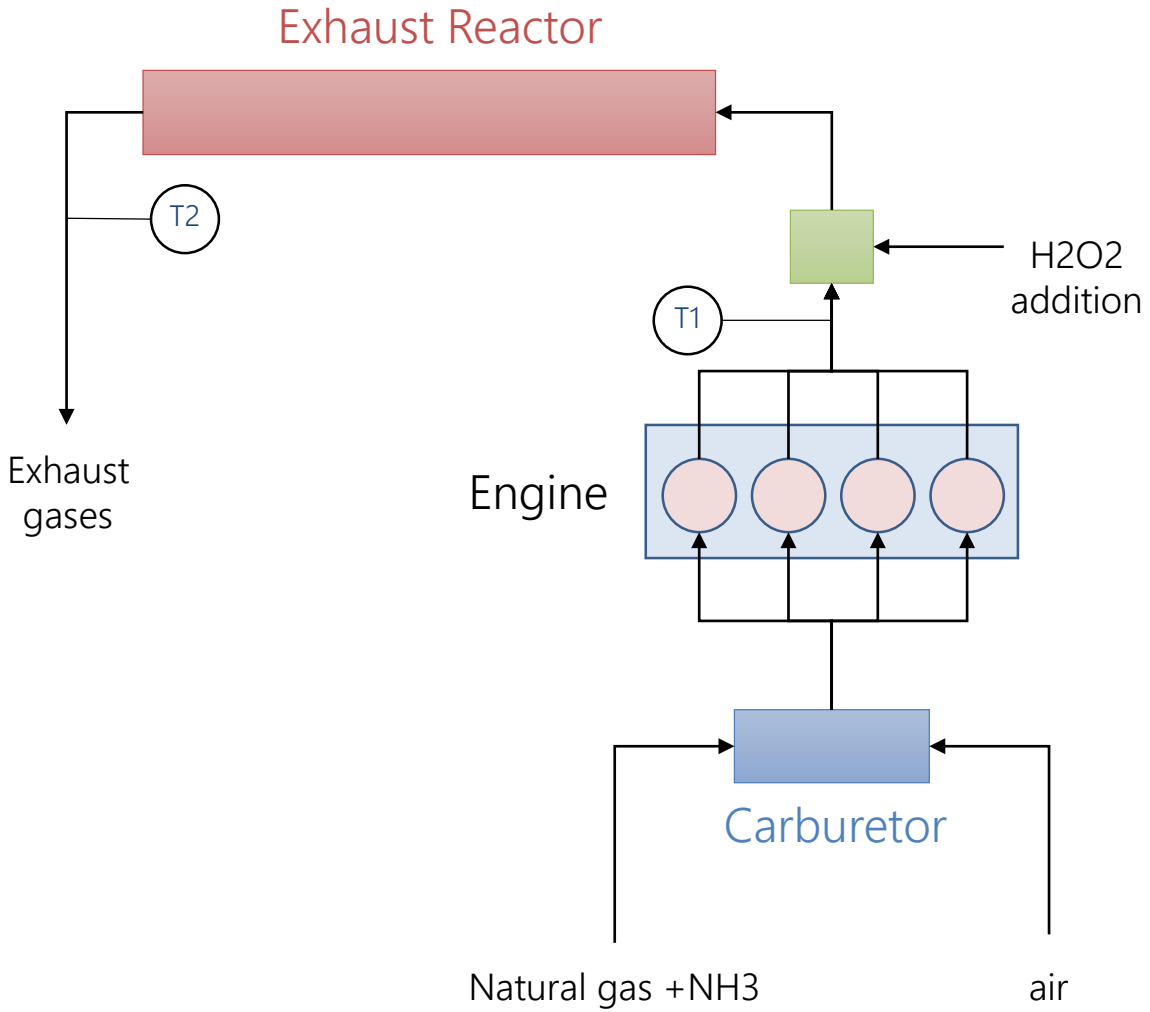
Experimental apparatus

In order to evaluate the potential for oxidation of UHC in the exhaust channel the engine was equipped with an extended exhaust reactor.

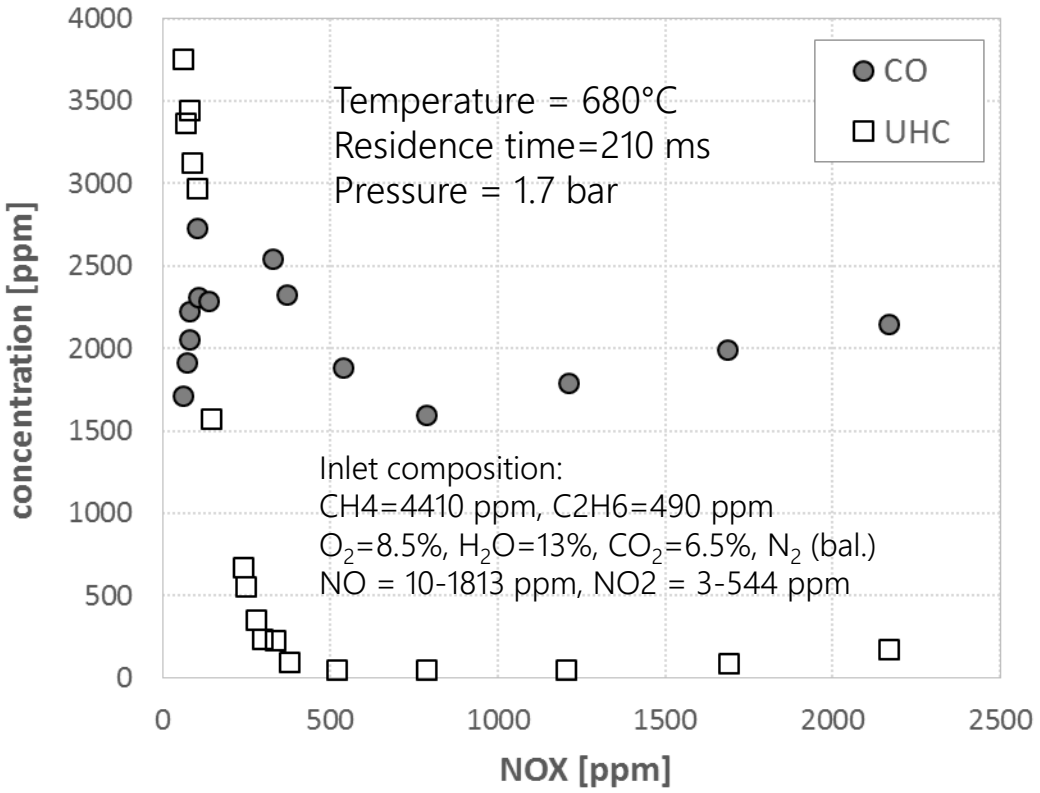
The engine was operated with addition of NH_3 (or NO) in the natural gas intake or with H_2O_2 or air in the exhaust.

The purpose of adding NH3 was to increase the amount of NOx in the exhaust (probe T1), while H_2O_2 was used in an attempt to promote the exhaust oxidation process.

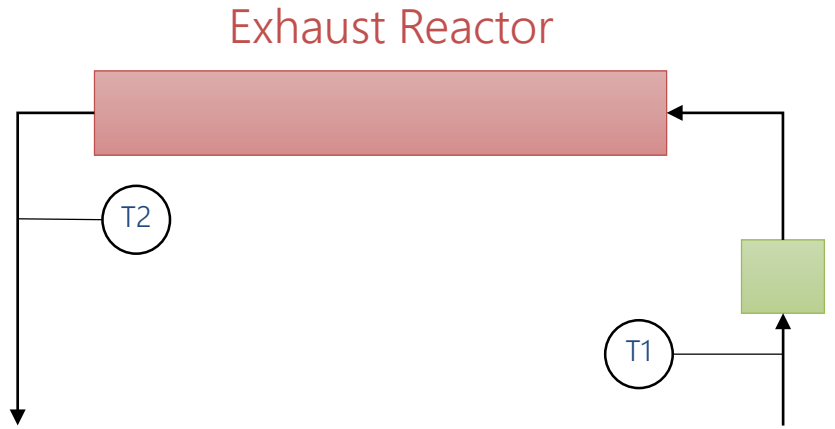
Ammonia was the preferred additive for increasing the NOx level, since gas cylinders with liquid NH3 were available.



Experimental measurements



Measured (at probe T2) stack concentrations of UHC and CO as function of NOx in the exhaust (measured at probe T1).



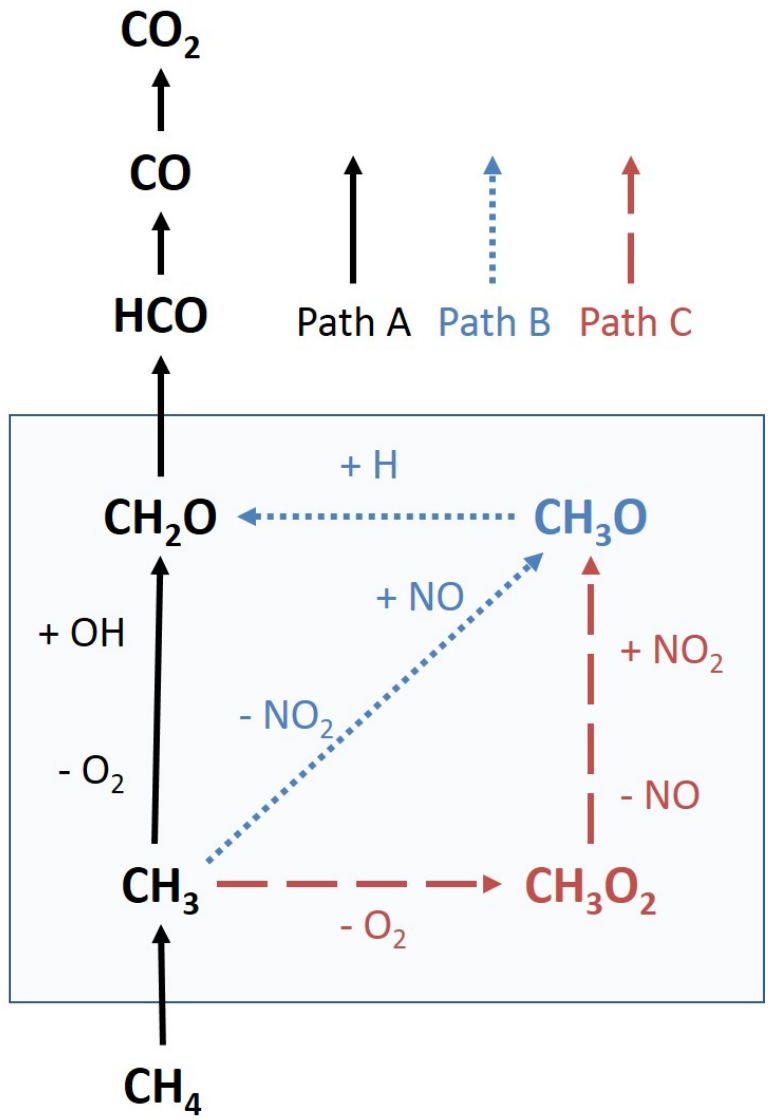
- A strong correlation between UHC, CO and NOx in the exhaust reactor is evident
- As the NOx level increases from about 50 ppm to 300 ppm, the UHC emission decreases from about 4000 ppm to very low levels, while the CO level increases strongly
- Above 500 ppm NOx the UHC is completely oxidized
- At high levels of NOx, above 1000 ppm, both UHC and CO emissions increase slowly with increasing amounts of NOx

Reaction paths in exhaust oxidation of CH_4

The chemistry that is responsible for the promoting effect of NOx on methane oxidation is now fairly well established (Bendtsen, 2000).

The oxidation of methane proceeds through reactions of the methyl radical (CH3), which is comparatively unreactive. Paths B and C, which involves reactions of CH3 and CH3O2 with NO2 and NO, offer low activation energy, overall chain branching oxidation pathways.

In the presence of NOx and at low temperatures (600-800°C), paths B and C compete favorably with path A and promote oxidation.



A.B. Bendtsen, P. Glarborg, and K. Dam-Johansen. Low temperature oxidation of methane: The influence of nitrogen oxides. Combustion science and technology, 151(1):31-71, 2000.

Tasks

Use a proper chemical kinetic mechanism together with the plug-flow code to to evaluate the potential of oxidation of unburned hydrocarbons in the exhaust channel of lean-burn natural gas engines. Then, revise the GRI-Mech 3.0 by adding the missing species and reactions needed to describe the experimental data..

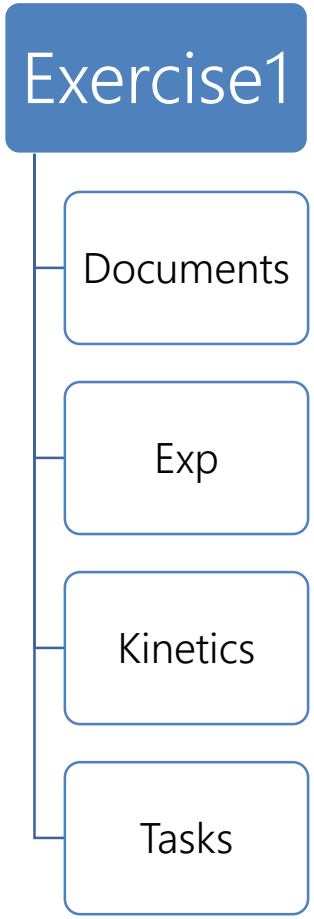
1. Evaluate the ability of three different kinetic mechanisms to describe the chemistry of this process. Test the model against the experimental data using the same operating conditions

2. Examine whether GRI-Mech 3.0 contains the reaction paths described in the previous slide. If necessary, add missing reactions. Compare predictions of the revised model with the experimental measurements.

3. Evaluate the extent of UHC oxidation under exhaust conditions characteristic of a full-scale engine. Conditions are: 2600 ppm CH_4, 160 ppm C_2H_6, 50 ppm CH_2O, 210 ppm NO, 50 ppm NO_2, 7.8% O_2, 11.5% H_2O, and 6.1% CO_2; balance nitrogen. Vary temperature between 580°C and 650°C with a residence time of 50 ms and a pressure of 1.7 bar.

4. 4. Evaluate the possibility of promoting UHC oxidation in the exhaust by injection of hydrogen peroxide (H_2O_2). Conditions as above.

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

This mechanism does not account for paths B and C and therefore it cannot be used for simulating the experimental data of Kristensen et al. (2000). The purpose of this practical session is to extend it by adding the missing reactions!

Number of species: 53
Number of reactions: 325

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.

Bendtsen et al.

The chemical kinetic model of Bendtsen *et al.* (2000), was developed based on flow reactor studies of CH4 oxidation under conditions similar to engine exhaust.

Number of species: 76
Number of reactions: 484

A.B. Bendtsen, P. Glarborg, and K. Dam-Johansen. Low temperature oxidation of methane: The influence of nitrogen oxides. Combustion science and technology, 151(1):31-71, 2000.

POLIMI_C1C3_NOX_1505

Detailed mechanism of the pyrolysis, partial oxidation and combustion of hydrocarbon fuels up to 3 C atoms. Contains reactions of paths B and C.

Number of species: 148
Number of reactions: 3211

A. Cuoci, A. Frassoldati, T. Faravelli, E. Ranzi, Formation of soot and nitrogen oxides in unsteady counterflow diffusion flames, Combustion and Flame 156 (10), pp. 2010-2022 (2009)

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 (**grimech30.dat**) and kinetic mechanism (**grimech30.dat**) files are available in the Kinetics folder

2. Open the **Task0** folder and create a new input file (**input.gri30.dic** in the following) in which you specify the thermodynamic and kinetic files and the destination folder:

```
Dictionary CHEMKIN_PreProcessor
{
        @Kinetics               ../../Kinetics/GRI30/grimech30.dat;
        @Thermodynamics         ../../Kinetics/GRI30/thermo30.dat;
        @Output                 kinetics-GRI30;
}
```

input.gri30.dic

You can choose to use local or absolute paths

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.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.dic` file

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

6. Repeat steps 1-5 also for the Bendtsen and the POLIMI mechanisms.

Task 1: isothermal plug flow reactor

Simulation conditions

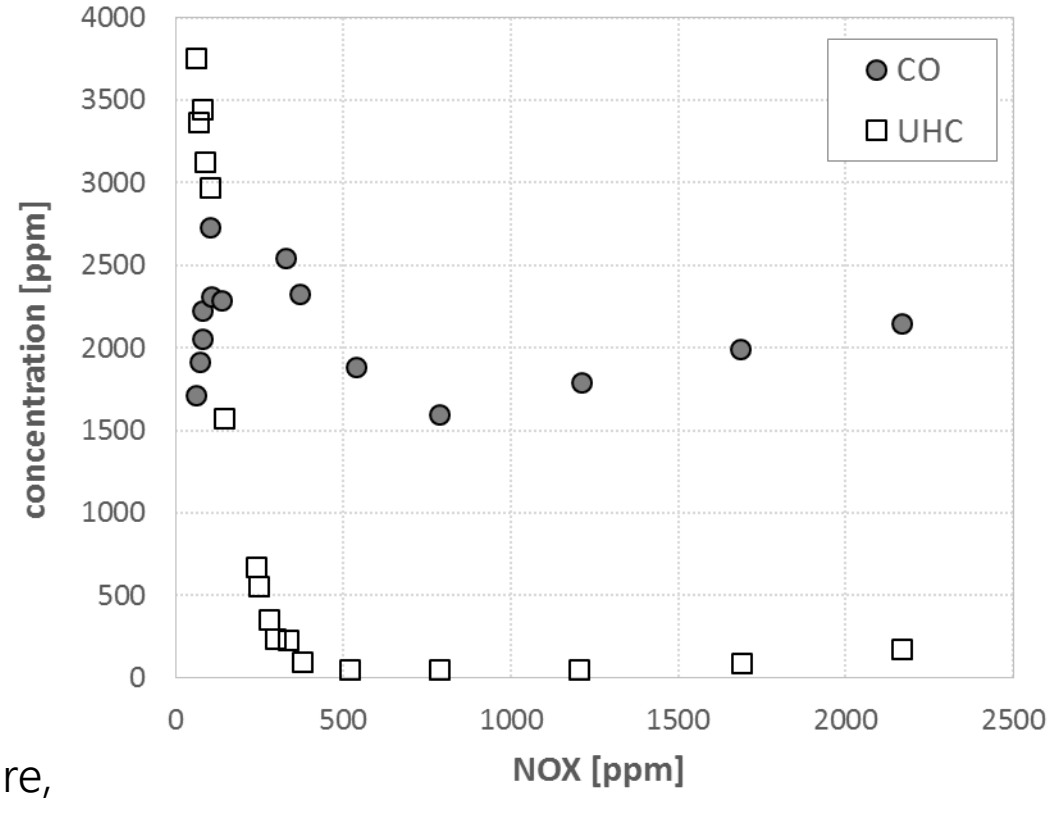
Isothermal plug flow reactor

Temperature = 680°C
Residence time=210 ms
Pressure = 1.7 bar

Inlet composition:
CH4=4410 ppm, C2H6=490 ppm
O_2=8.5%, H_2O=13%, CO_2=6.5%, N_2 (bal.)
NO = 10-1813 ppm, NO2 = 3-544 ppm

Each experimental point correspond to a different inlet mixture, with different amounts of NOX (NO+NO2)

For every point you can keep fixed the ratio NO/NO2=10/3



Task 1: isothermal plug flow reactor

1. Open the `Task1` folder and for each kinetic mechanism to be investigated, create a new input file (`input.dic`) specifying the reaction conditions

```
Dictionary PlugFlowReactor
{
  @KineticsFolder          ../../Task0/kinetics-GRI30;
  @Type                    Isothermal;
  @InletStatus             inlet-mixture;
  @ResidenceTime 210 ms;
  @ConstantPressure        true;
  @Velocity                1 m/s;
  @ParametricAnalysis      parametric-analysis;
}

Dictionary inlet-mixture
{
  @Temperature    680.     C;
  @Pressure       1.7      bar;
  @Moles          CH4      0.00441  C2H6    0.00049
                           O2       0.085    H2O     0.13
                           CO2      0.065    N2      0.71445
                           NO       5.0E-04  NO2     1.5E-04;
}
```

pre-processed kinetic mechanism (Task 0)

Isothermal reactor

We want to simulate several different inlet compositions, so we adopt the parametric analysis

This composition corresponds to the first condition to be simulated

be careful, normalization is done automatically!

Task 1: isothermal plug flow reactor

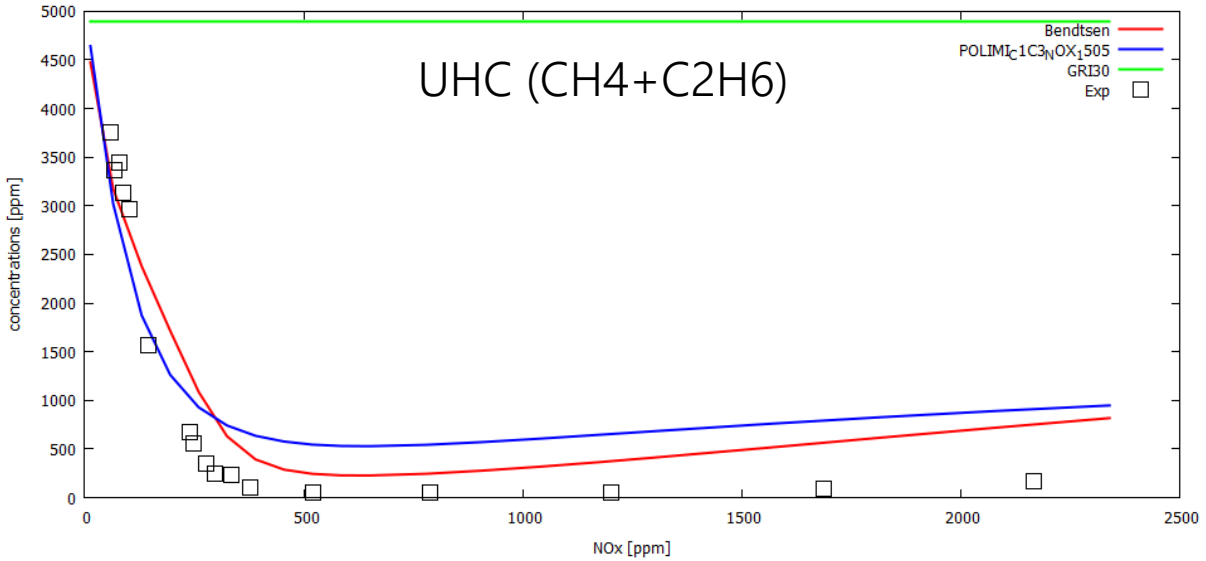
```
Dictionary parametric-analysis
{
   @Type  moles;
   @ListOfValues CH4 4.41E-03 C2H6 4.90E-04 O2 8.50E-02 H2O 1.30E-01 CO2 6.50E-02 NO 1.00E-05 NO2 3.00E-06 N2 7.15087E-01 :
                 CH4 4.41E-03 C2H6 4.90E-04 O2 8.50E-02 H2O 1.30E-01 CO2 6.50E-02 NO 5.00E-05 NO2 1.50E-05 N2 7.15035E-01 :
                 CH4 4.41E-03 C2H6 4.90E-04 O2 8.50E-02 H2O 1.30E-01 CO2 6.50E-02 NO 1.00E-04 NO2 3.00E-05 N2 7.14970E-01 :
                 CH4 4.41E-03 C2H6 4.90E-04 O2 8.50E-02 H2O 1.30E-01 CO2 6.50E-02 NO 1.50E-04 NO2 4.50E-05 N2 7.14905E-01 :
                 CH4 4.41E-03 C2H6 4.90E-04 O2 8.50E-02 H2O 1.30E-01 CO2 6.50E-02 NO 2.00E-04 NO2 6.00E-05 N2 7.14840E-01 :
                 CH4 4.41E-03 C2H6 4.90E-04 O2 8.50E-02 H2O 1.30E-01 CO2 6.50E-02 NO 2.50E-04 NO2 7.50E-05 N2 7.14775E-01 ;
}
```

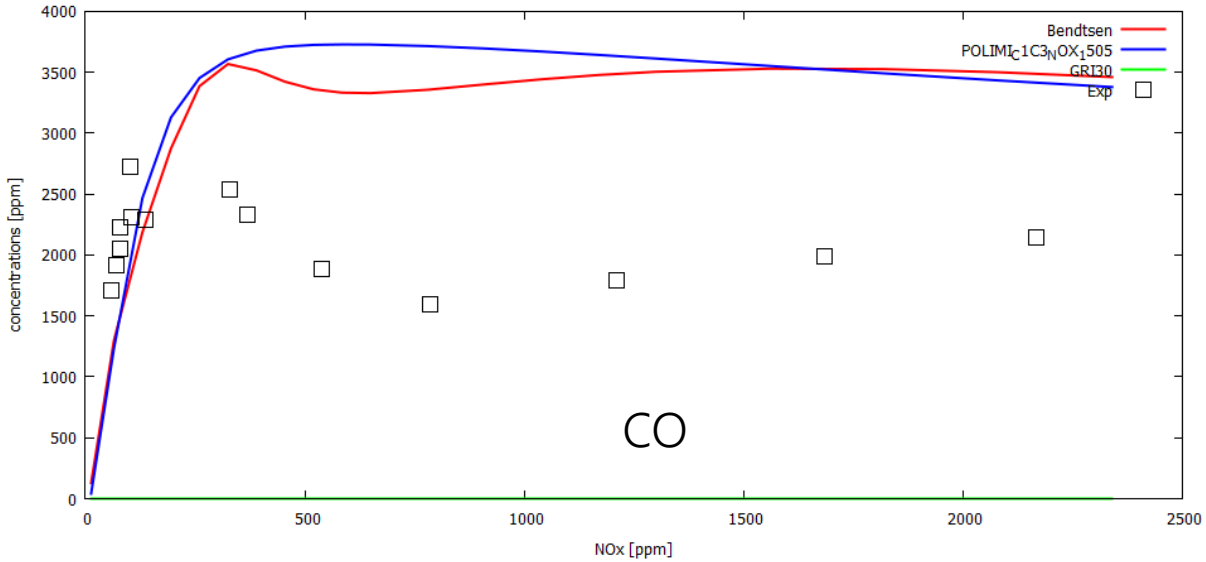
2. Run the solver for plug flow reactors using the following command (in Microsoft Windows):

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

3. If everything works properly, you will find the results in the **`Output`** folder. For each case you can find a dedicated folder, named **`CaseYY`**, where **`YY`** is an index starting from **`0`**. In particular, the **`ParametricAnalysis.out`** file (in the Output folder) reports the final status and the initial status of each simulated reactor

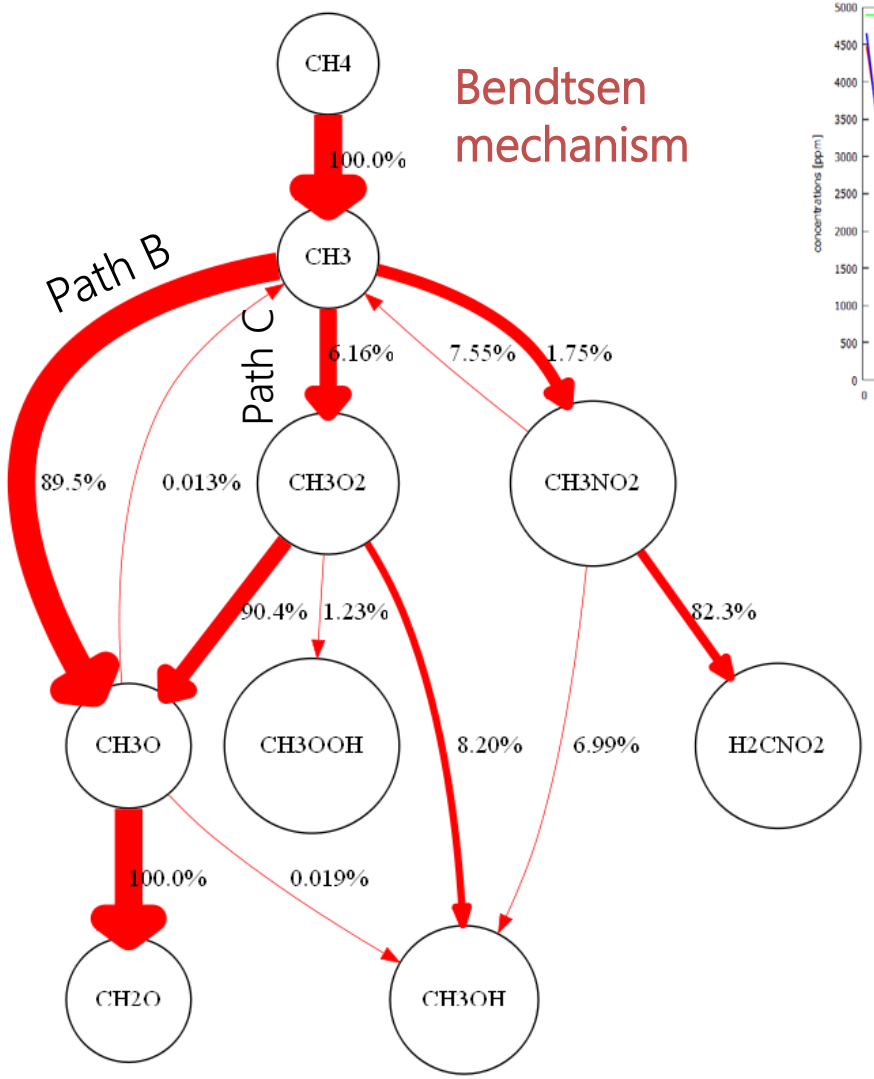
Task 1: plug flow reactor

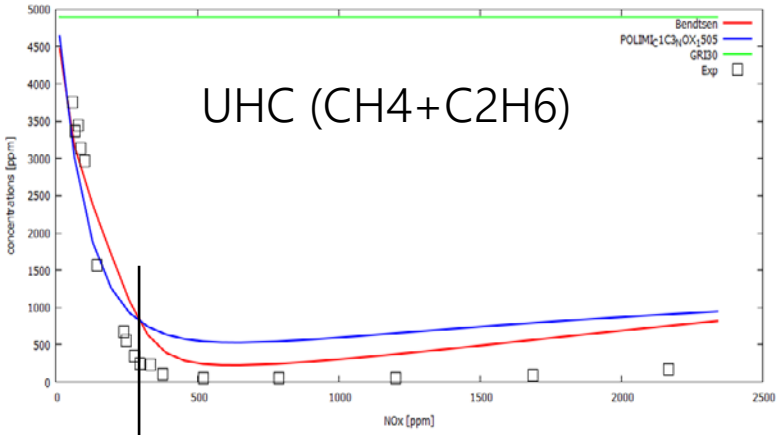




- The GRI-30 mechanism is completely unable to capture the experimental data…
- Analysis of GRI-30 reactions reveals that paths B and C are not accounted for
- Bendtsen's and POLIMI kinetic mechanisms are in reasonable agreement with experimental data, especially when the amount of NOX in the exhaust gases is below 500 ppm

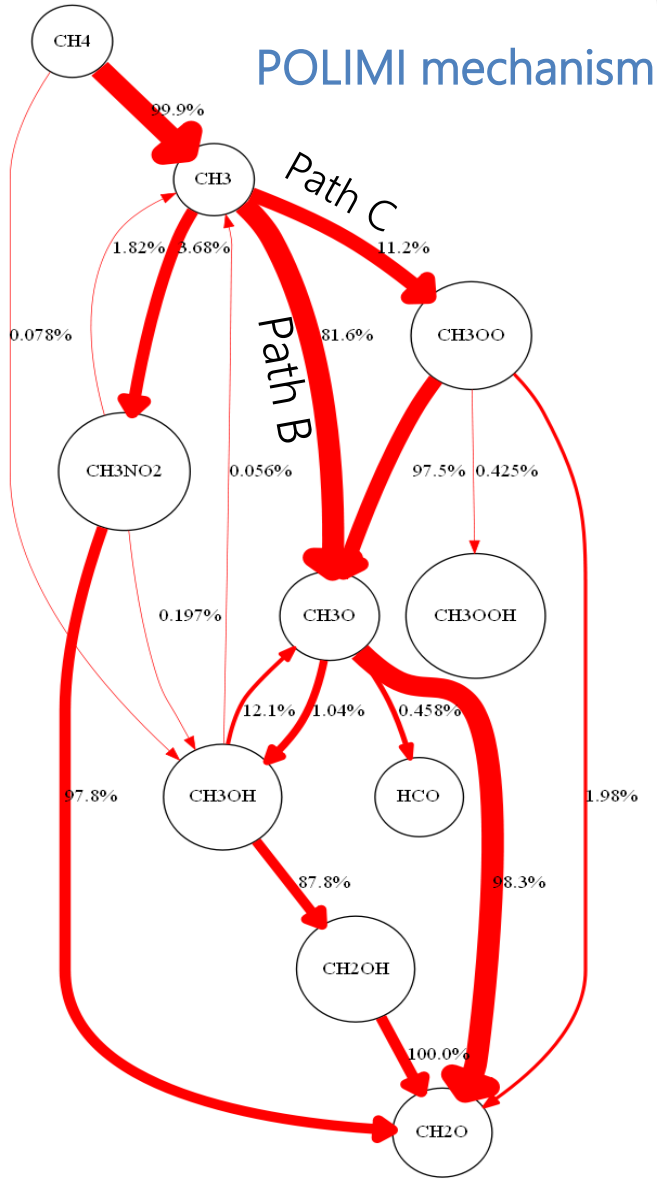
Task 1: plug flow reactor



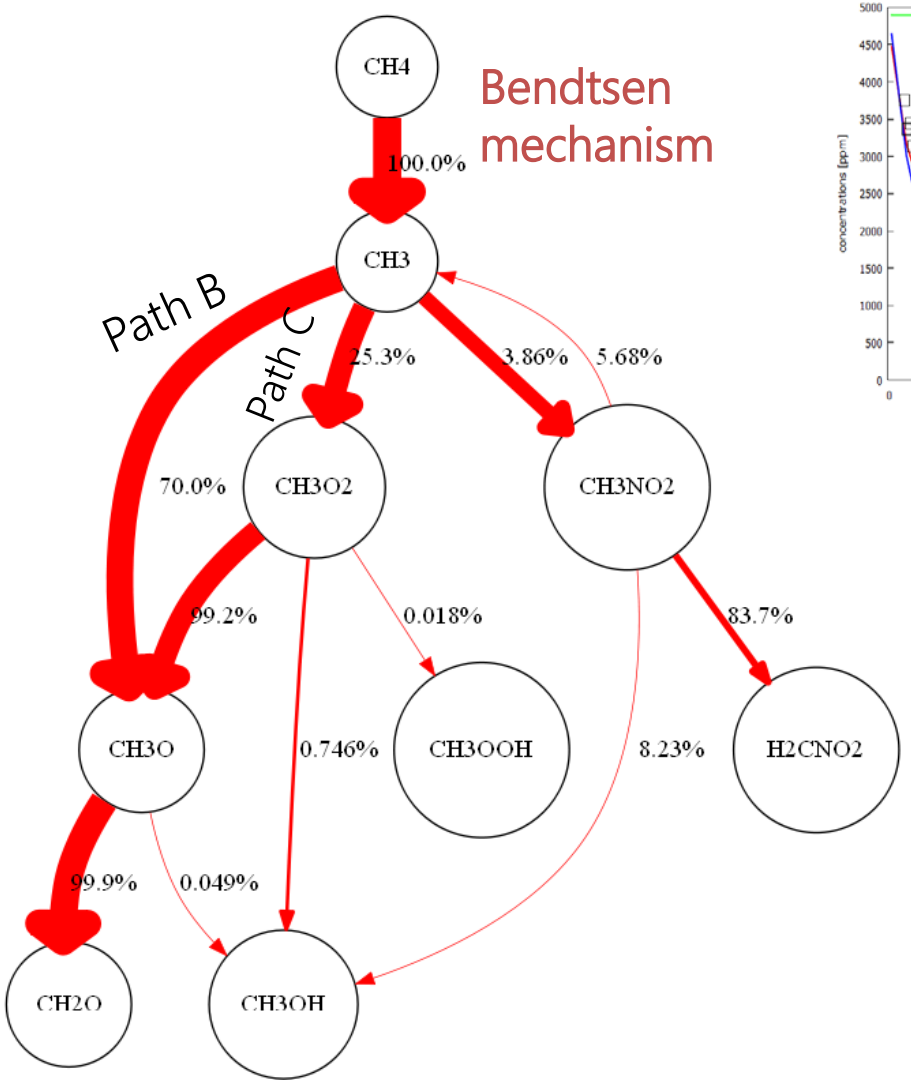


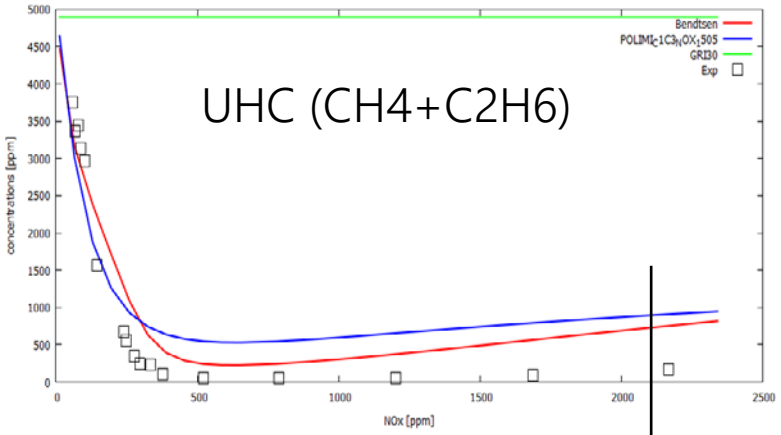
Reaction path analysis for CH4:
inlet NOX 300 ppm

Dest. analysis @ 50 ms
Element: C
Depth: 3
Width: 2
Threshold: 0.1%



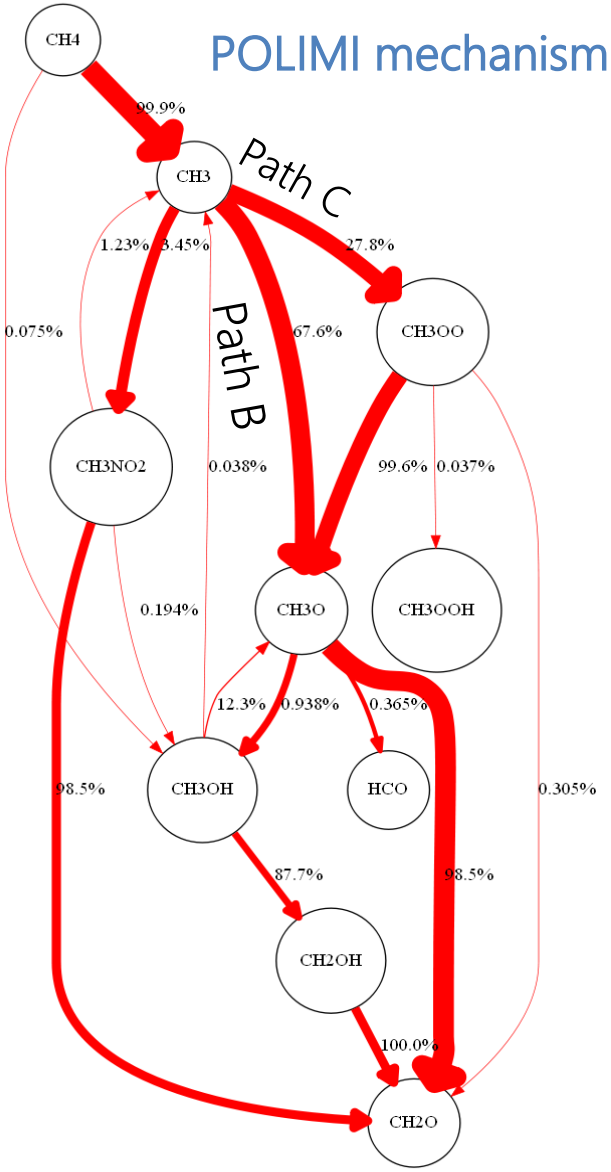
Reaction path analysis





Reaction path analysis for CH4:
inlet NOX 2100 ppm

Dest. analysis @ 50 ms
Element: C
Depth: 3
Width: 2
Threshold: 0.1%



Task 2: extension of GRI-3.0 mechanism (I)

The following three new species have to be added to the GRI-3.0 mechanism in order to describe paths B and C: CH3OO, CH3NO2 and HONO

Path B

CH3+NO2=CH3O+NO

CH3NO2(+M)=CH3+NO2(+M)

HO2+NO=NO2+OH [already available in GRI-3.0]

H+CH2O(+M)=CH3O(+M) [already available in GRI-3.0]

Path C

CH3+O2(+M)=**CH3OO**(+M)

CH3OO+NO=CH3O+NO2

CH3OO+OH=CH3OH+O2

H+CH2O(+M)=CH3O(+M) [already available in GRI-3.0]

HONO (nitrous acid) submechanism

OH+NO+M=**HONO**+M

CH2O+NO2=HCO+**HONO**

HONO+OH=H2O+NO2

CH4+NO2=CH3+**HONO**

CH3NO2+H=**HONO**+CH3

Nitrous acid, HONO, play an important role on chemistry of OH

Task 2: extension of GRI-3.0 mechanism (II)

Thermodynamic data to be added for the three new species:

```
CH3OO      9/08/94 LIG/CC   1H   3O   2    0G   300.000  5000.000 1381.000     1
 8.04008290E+00 6.53779443E-03-2.30284850E-06 3.64660532E-10-2.14511604E-14    2
-2.27775197E+03-1.73557764E+01 1.46355059E+00 2.09318664E-02-1.40862480E-05    3
 4.66682187E-09-6.15228667E-13 1.08022981E+02 1.83173980E+01                   4
CH3NO2            T01/00C   1H   3N   1O   2G   200.000  6000.000 1000.        1
 6.73034758E+00 1.09601272E-02-4.05357875E-06 6.67102246E-10-4.04686823E-14    2
-1.29143475E+04-1.01800883E+01 3.54053638E+00 1.86559899E-03 4.44946580E-05    3
-5.87057133E-08 2.30684496E-11-1.11385976E+04 1.06884657E+01-9.71208165E+03    4
HONO         HNO2 RUS 89H   1N   1O   2    0G   200.000  6000.000  1000.0     1
 0.57919018E+01 0.36515212E-02-0.12928936E-05 0.20688716E-09-0.12315254E-13    2
-0.11565589E+05-0.40558233E+01 0.32141709E+01 0.81276869E-02 0.16602559E-05    3
-0.95285182E-08 0.48715058E-11-0.10753237E+05 0.98219504E+01-0.94355439E+04    4
```

Task 2: extension of GRI-3.0 mechanism (III)

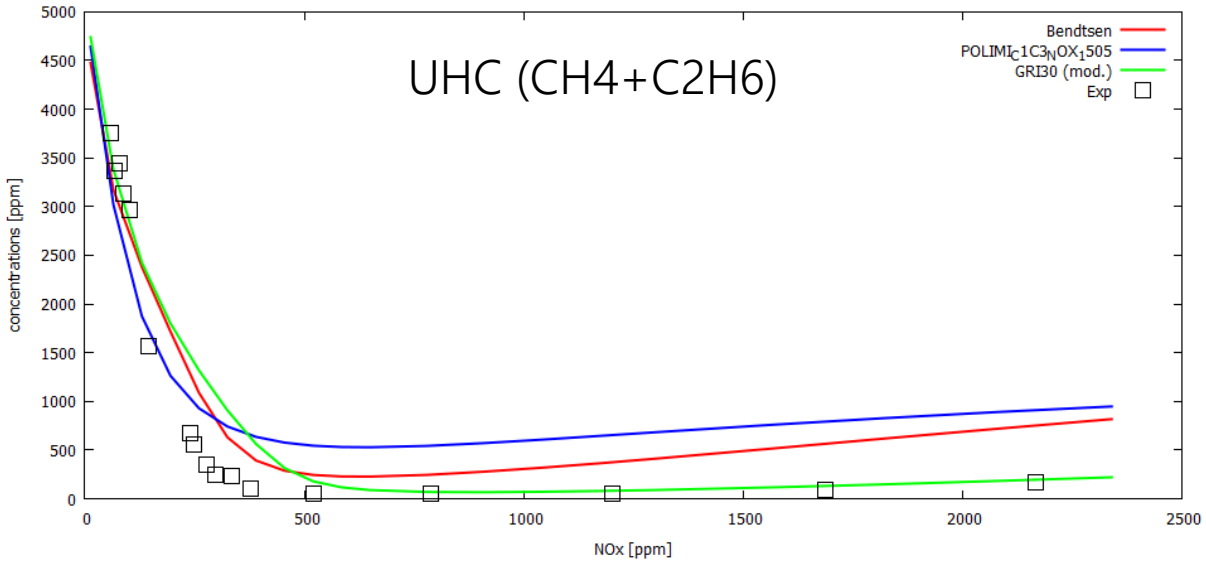
Reactions to be added to the GRI-3.0 kinetic mechanism

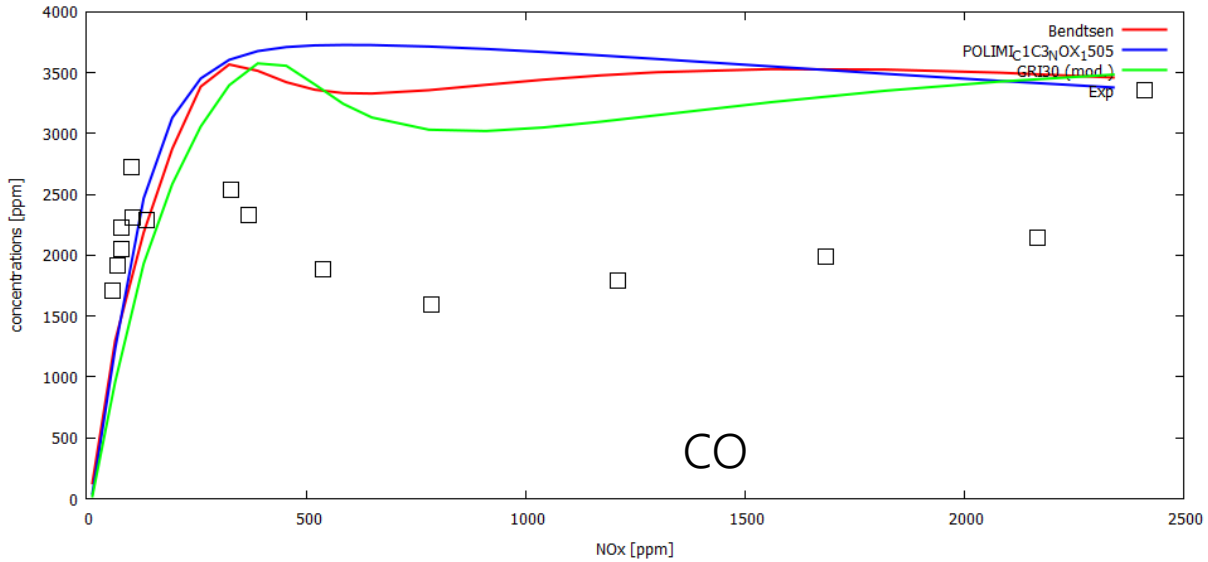
```
!PATH B (2 reactions)
CH3+NO2=CH3O+NO                .1500E+14    0    0
CH3NO2(+M)=CH3+NO2(+M)         1.8E16       0    58500
  LOW/1.3E17 0 42000/
  TROE/ 0.183 1.0E-30 1.0E30 /

!PATH C (3 reactions)
CH3+O2(+M)=CH3OO(+M)         7.8E08   1.20     0
  LOW  / 5.4E25 -3.30  0 /
  N2/1.1/  H2O/10/
CH3OO+NO=CH3O+NO2            2.53E12  0      -358
CH3OO+OH=CH3OH+O2            6.0E13   0         0

! HONO Subset (5 reactions)
OH+NO+M=HONO+M                 5.1E23 -2.51    -68
CH2O+NO2=HCO+HONO              8.0E02  2.77  13730
HONO+OH=H2O+NO2                4.0E12     0      0
CH4+NO2=CH3+HONO               1.2E+13    0  30000
CH3NO2+H=HONO+CH3              3.3E12     0   3730
```

Task 2: extension of GRI-3.0 mechanism (III)

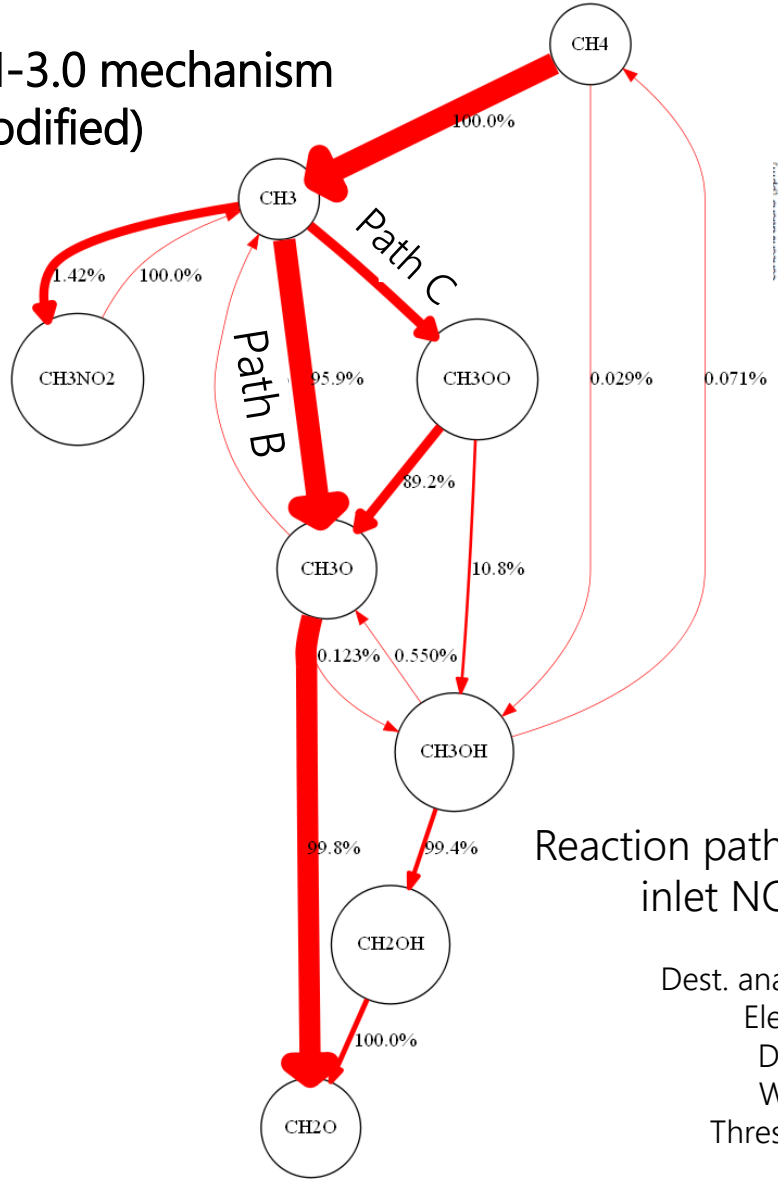


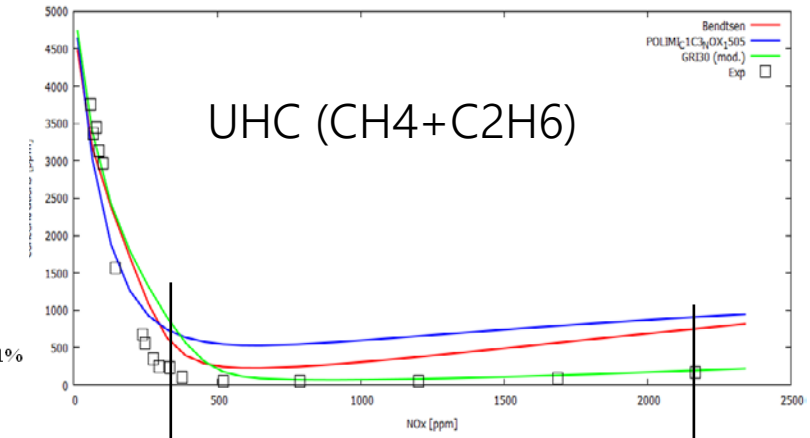


- The modified GRI-3.0 mechanism is now able to capture the experimental measurements with reasonable agreement
- Its performance is very similar to Bendtsen's mechanism

Task 2: extension of GRI-3.0 mechanism (IV)

GRI-3.0 mechanism (modified)



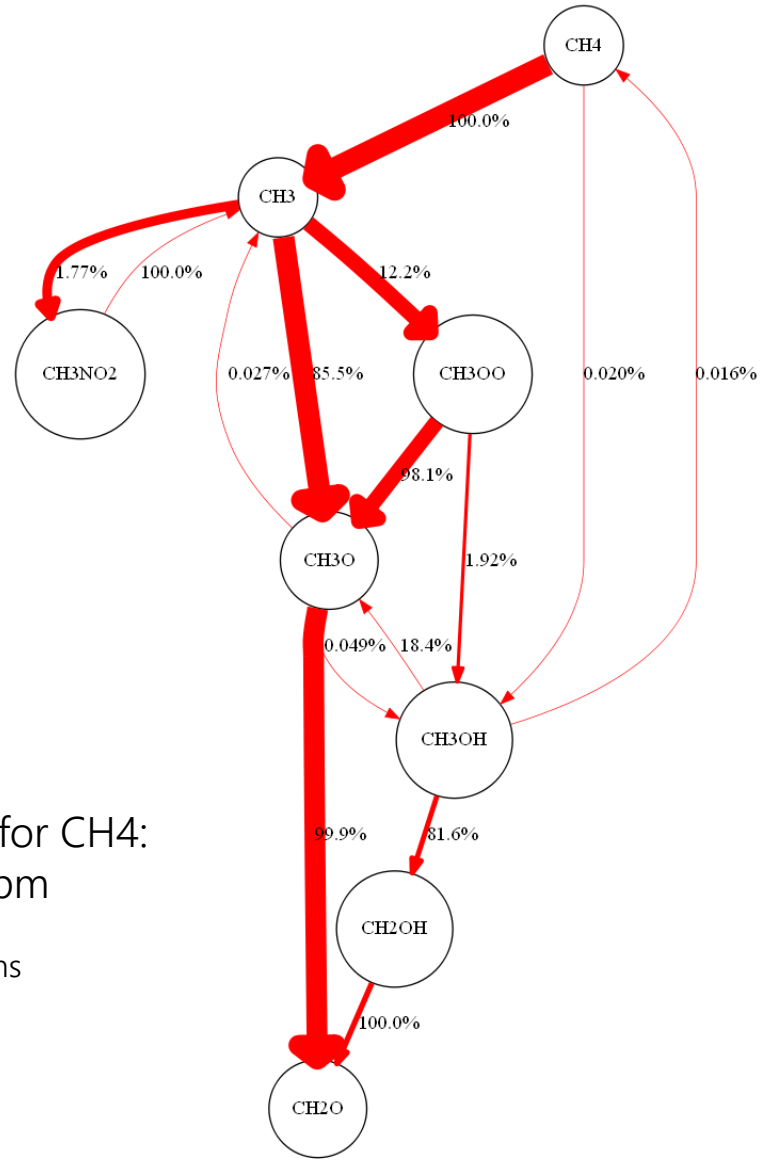


Reaction path analysis for CH4: inlet NOX 300 ppm

Dest. analysis @ 50 ms
Element: C
Depth: 3
Width: 2
Threshold: 0.1%

Reaction path analysis for CH4: inlet NOX 2100 ppm

Dest. analysis @ 50 ms
Element: C
Depth: 3
Width: 2
Threshold: 0.1%



Task 3: PFR in real operating conditions

We want now to evaluate the extent of UHC oxidation under exhaust conditions characteristic of a full-scale engine.

Operating conditions

Inlet composition:
2600 ppm CH_4, 160 ppm C_2H_6, 50 ppm CH_2O
210 ppm NO, 50 ppm NO_2
7.8% O_2, 11.5% H_2O, and 6.1% CO_2; balance nitrogen.

Residence time of 50 ms
Pressure of 1.7 bar.
Vary temperature between 580°C and 650°C

Parametric analysis with respect to reactor temperature (in isothermal conditions)

Task 3: PFR in real operating conditions

1. Open the `Task3` folder and for each kinetic mechanism to be investigated, create a new input file (`input.dic`) specifying the reaction conditions

```
Dictionary PlugFlowReactor
{
  @KineticsFolder          ../../Task0/kinetics-GRI30-modified;
  @Type                    Isothermal;
  @InletStatus             inlet-mixture;
  @ResidenceTime           50 ms;
  @ConstantPressure        true;
  @Velocity                1 m/s;
  @ParametricAnalysis      parametric-analysis;
}

Dictionary inlet-mixture
{
  @Temperature    580.     C;
  @Pressure       1.7      bar;
  @Moles          CH4      2.6E-03   C2H6    1.6E-04
                  CH2O     5.0E-05   O2      7.8E-02
                  H2O      1.15E-01  CO2     6.1E-02   N2  7.4293E-01
                  NO       2.10E-04  NO2     5.0E-05;
}
```

pre-processed kinetic mechanism (Task 0)

Isothermal reactor

To perform the parametric analysis with respect to the reactor temperature

Task 3: PFR in real operating conditions

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

        @NumberOfPoints         9;
        @MinimumValue           580 C;
        @MaximumValue           650 C;

        @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 plug flow reactors using the following command (in Microsoft Windows):

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

Task 3: PFR in real operating conditions

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.

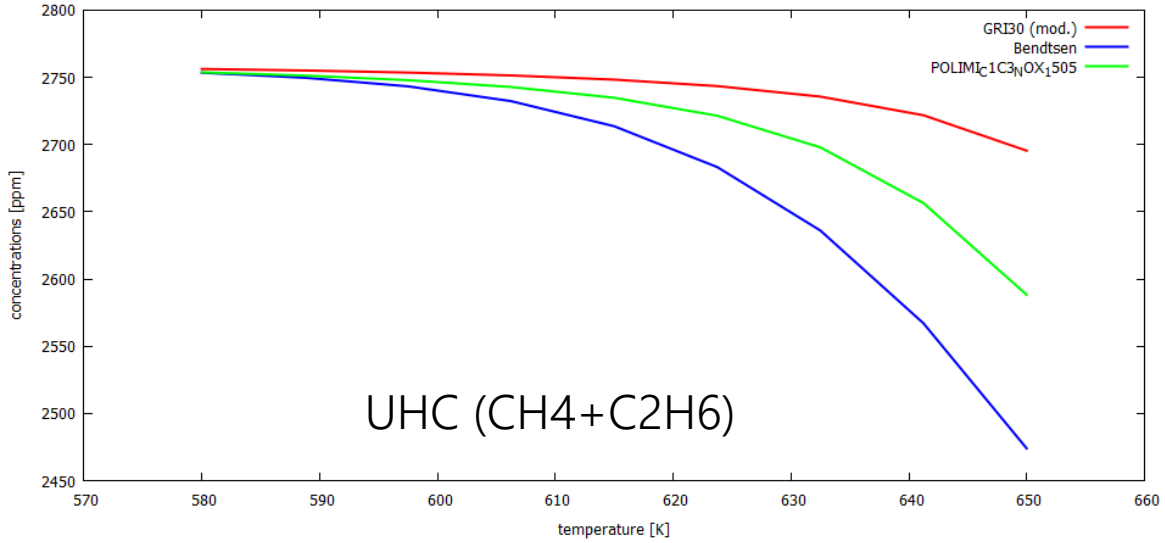
4. In addition, for each reactor simulated during the parametric analysis (9 in this examples), you will find a dedicated folder, with names `Case0`, `Case1`, `Case2`, and so on. For each case the following files are available

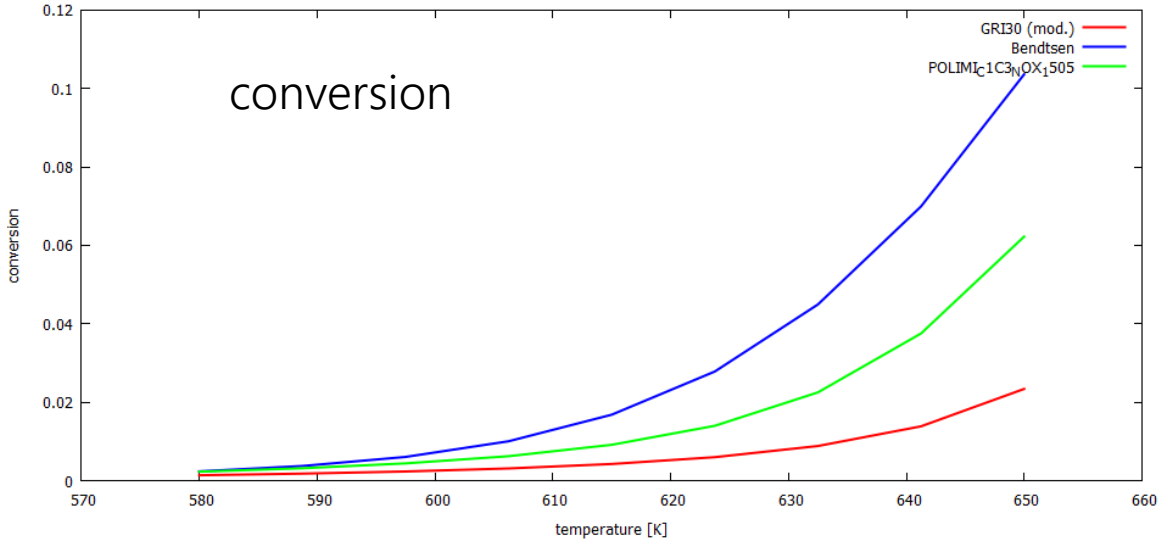
   - FinalSummary.out: this file reports the initial and final status of the reacting mixture (temperature, pressure, density, composition, etc.)

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

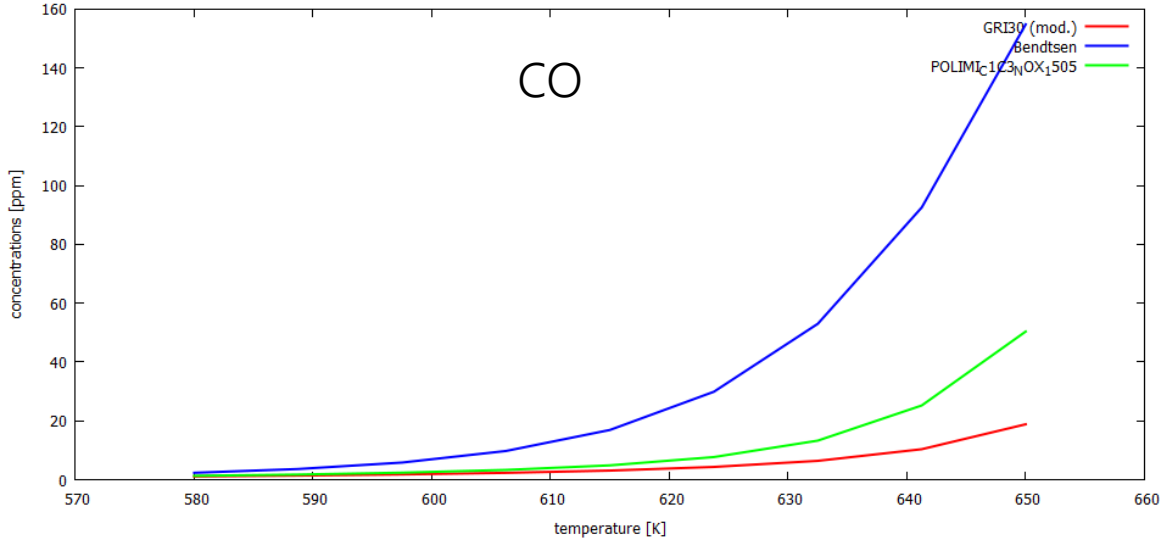
   - Output.xml: XML output file to be used by the OpenSMOKE++ graphical post-processor

Task 3: PFR in real operating conditions





CO



Task 4: Addition of H2O2

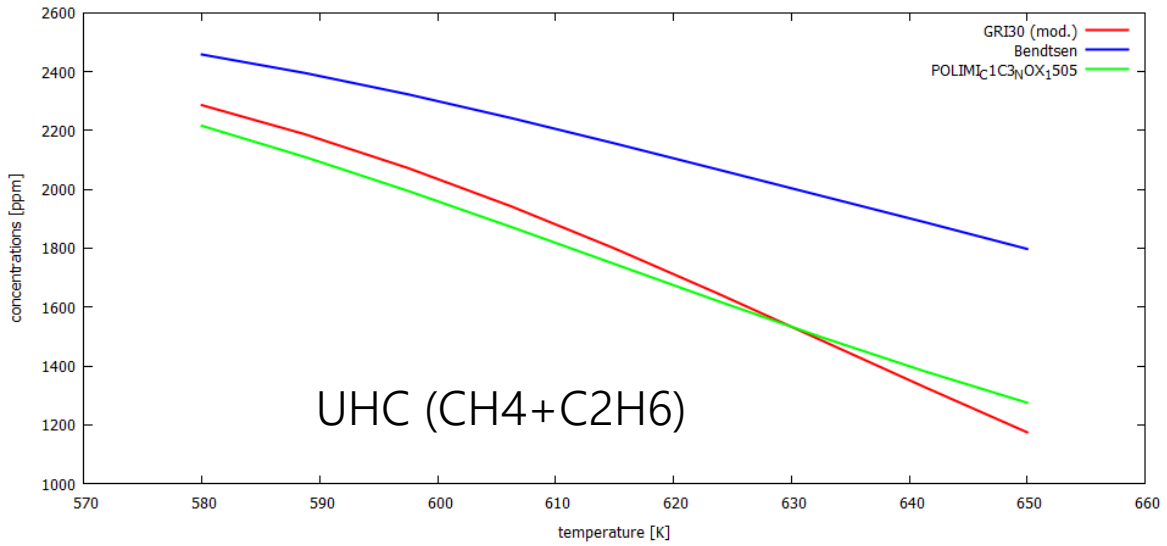
We want now to study the impact of H2O2 addition to the inlet composition in quantities comparable to the UHC level.
We assume the same operating conditions adopted in Task 3, with the addition of 1000 ppm of H2O2

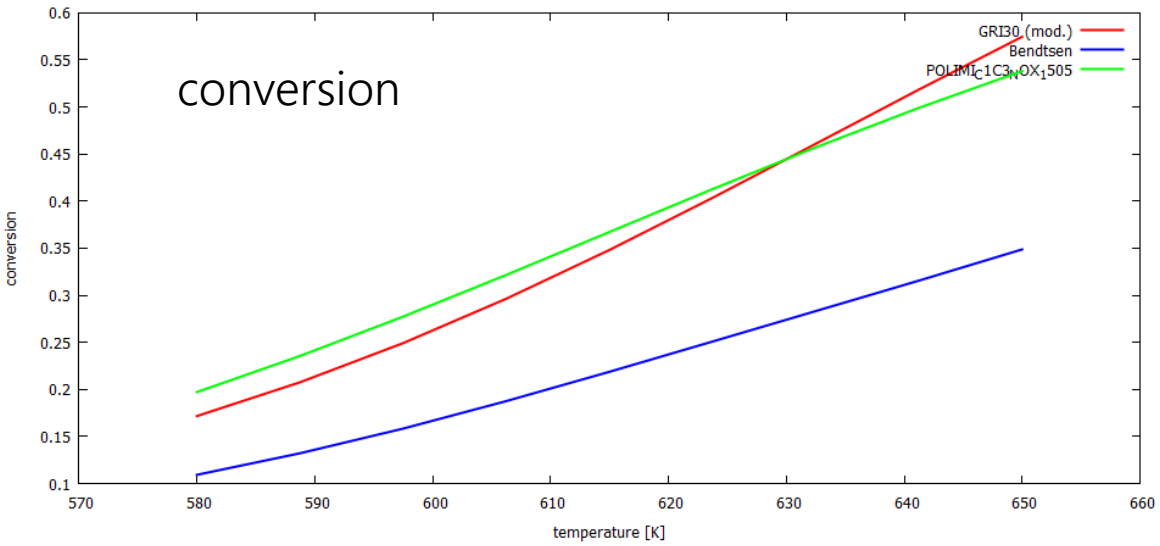
Inlet composition:
2600 ppm CH4, 160 ppm C2H6, 50 ppm CH2O
210 ppm NO, 50 ppm NO2
7.8% O2, 11.5% H2O, and 6.1% CO2; balance nitrogen
1000 ppm H2O2

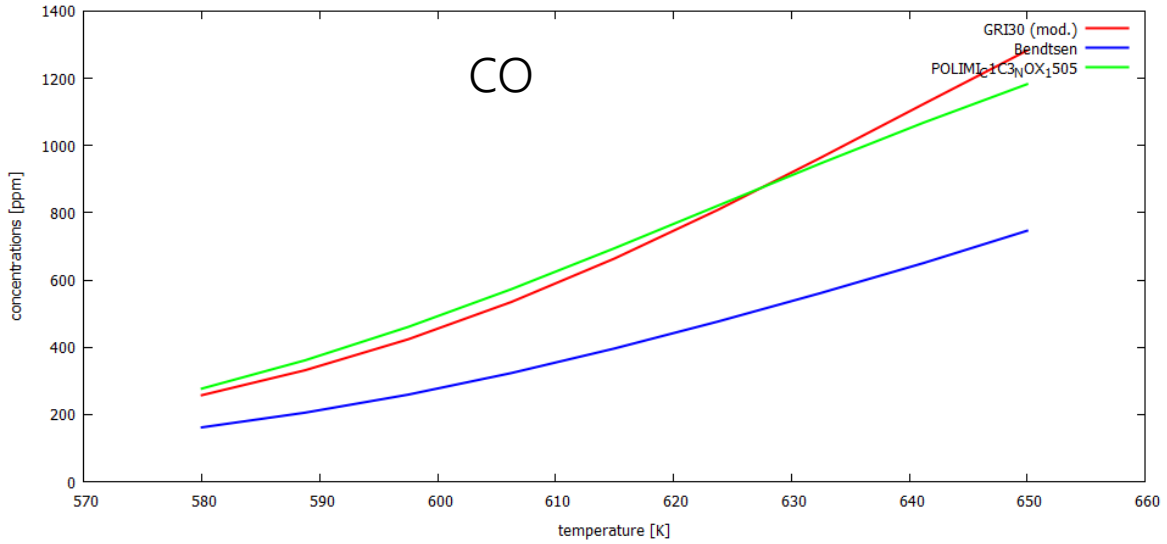
Residence time of 50 ms
Pressure of 1.7 bar.
Vary temperature between 580°C and 650°C

Parametric analysis with respect to reactor temperature (in isothermal conditions)

Task 4: Addition of H2O2

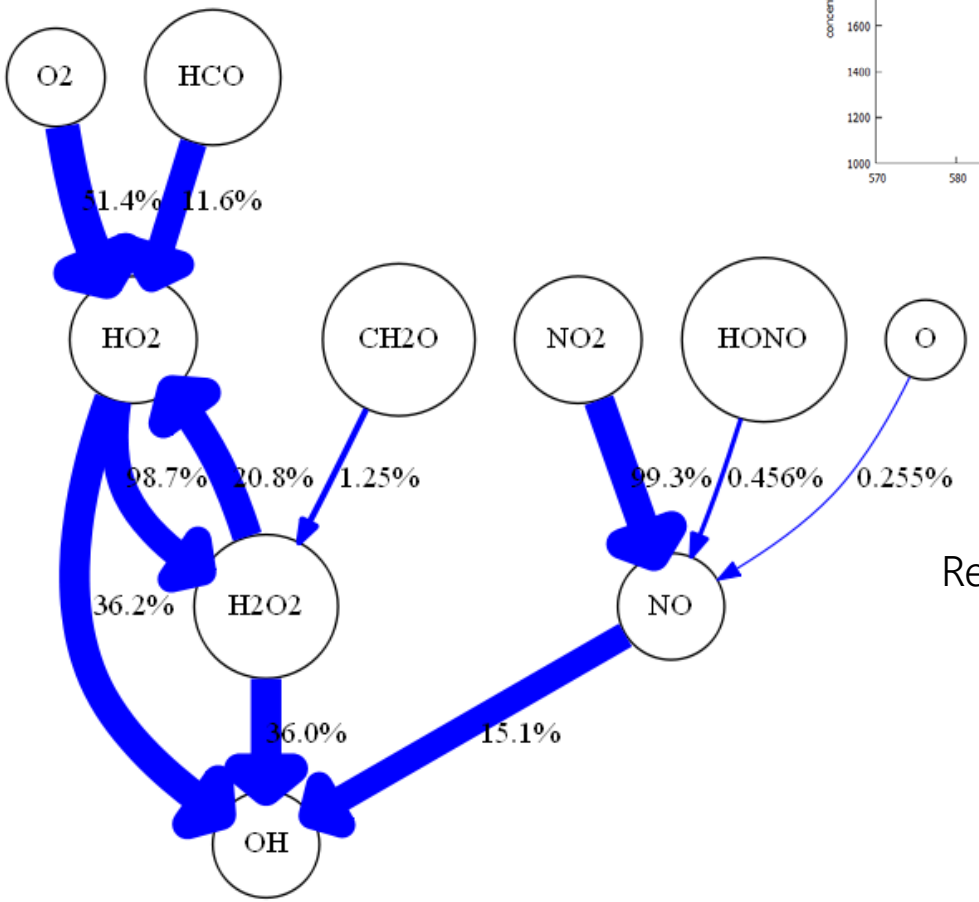


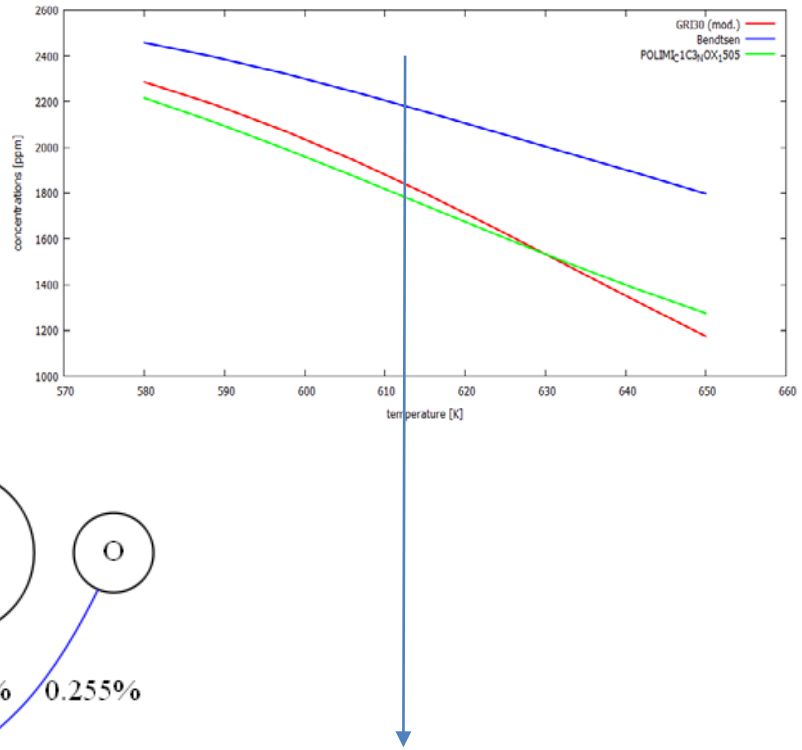




Task 4: Addition of H2O2

with H2O2 addition (Task 4)

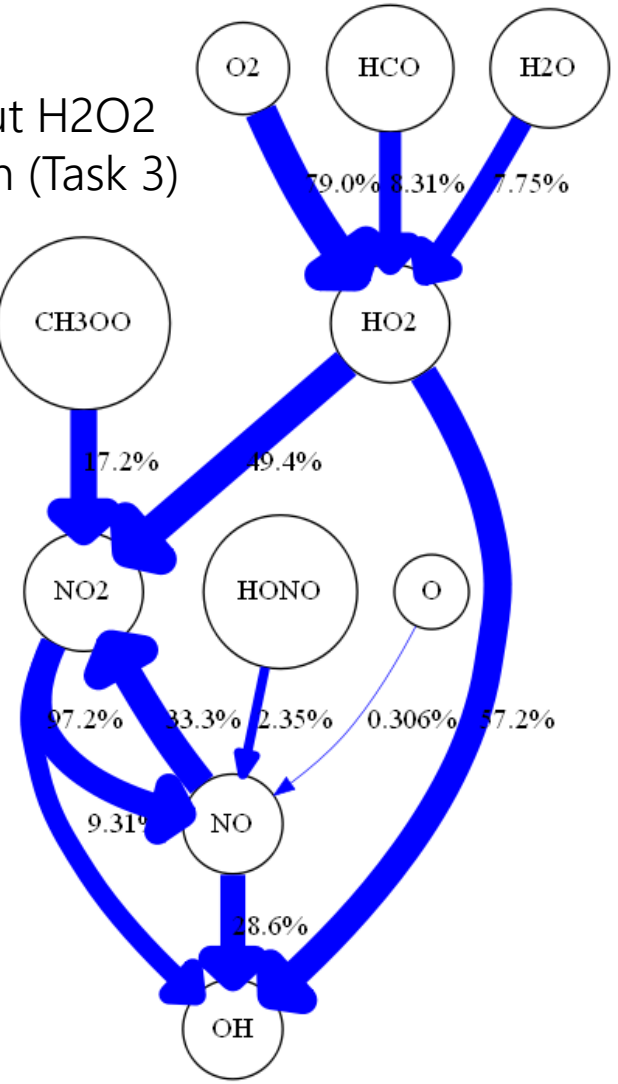




Reaction path analysis for OH:
Temperature = 610 °C
GRI-3.0 modified

Formation analysis @ 5 ms
Element: O
Depth: 2
Width: 3
Threshold: 0.1%

without H2O2 addition (Task 3)



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