Exercise 3: Engine Exhaust Oxidation of Unburned Hydrocarbons

Reactor models

Plug Flow reactor (PFR) from the `OpenSMOKE++ Suite` [2]

Reaction mechanism

GRI-Mech 3.0 [3]

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 [5] for identifying reactions and obtaining rate constants. Furthermore, to caution the student to validate the kinetic model prior to application.

Background

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 CO_2 emission; the combustion of natural gas produces about 45% less CO_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. 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 [4] 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. Figure 1 shows results obtained on a 35 kW test engine equipped with an extended exhaust reactor [4]. These results show the dramatic impact of NO level on UHC conversion in the exhaust reactor.

The chemistry that is responsible for the promoting effect of nitrogen oxides on methane oxidation is now fairly well established [1]. A reaction path diagram in shown in Figure 2. The oxidation of methane proceds through reactions of the methyl radical (CH_3), which is comparatively unreactive. Paths B and C in Figure 2, which involves reactions of CH_3 and CH_3O_2 with NO_2 and NO, offer low activation energy, overall chain branching oxidation pathways. In the presence of nitrogen oxides and at low temperatures (600-800°C), paths B and C compete favorably with path A and promote oxidation.

Task

Use a proper chemical kinetic mechanism together with the plug-flow code `OpenSMOKE_PlugFlowReactor` to to evaluate the potential of oxidation of unburned hydrocarbons in the exhaust channel of lean-burn
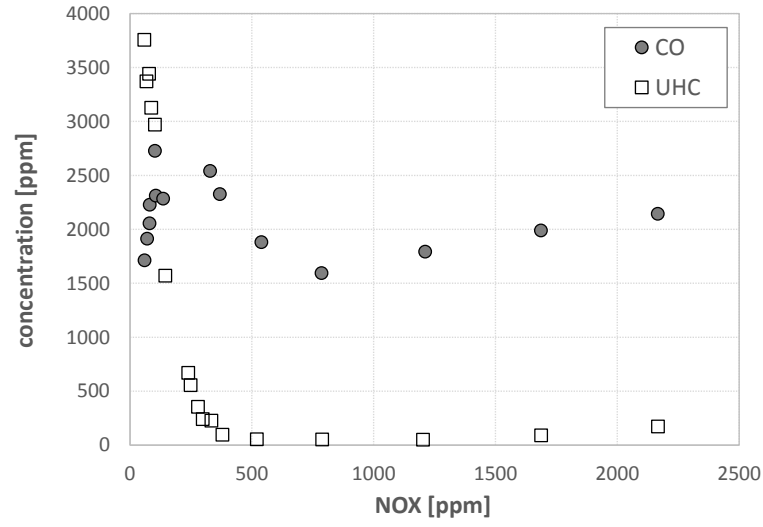
Fig. 1: Measured stack concentrations of UHC and CO as function of NOx in the exhaust [4]. The level of NOx was increased by adding NO to the natural gas. Due to analyser saturation, CO concentrations above 2540 ppm occurring at levels of NOx of 200-300 ppm are not shown. Data are shown for excess air levels of 8% (above 200 ppm NOx) and 9% (0-300 ppm NOx).
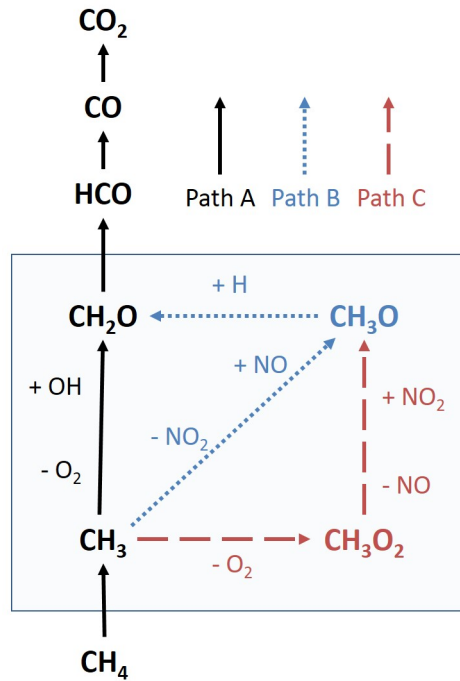

Fig. 2: The reaction paths active in exhaust oxidation of methane. Path A dominates in the absence of nitrogen oxides, path B in the presence of $NO2$, path C is active if NO, but no $NO2$, is present and at elevated pressures [1].

natural gas engines. Then, revise the GRI-Mech 3.0 [3] by adding the missin 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: `POLIMI_C1C3_NOX_1505` [6], GRI-Mech 3.0 [3], and Bendsten's mechanism [1]. Test the model against the data on Figure 1. Use the following conditions: inlet composition $CH_4 = 4410ppm$, $C_2H_6 = 490ppm$, $O_2 = 8.5$, $H_2O = 13$, $CO_2 = 6.5$, $NO = 10 - 1813ppm$, $NO_2 = 3 - 544ppm$, balance nitrogen; $T = 680°C$, reactor residence time=210 ms, pressure=1.7 bar.

2. Examine whether GRI-Mech 3.0 contain the reactions depicted as significant in Figure 2. If necessary, add missing reactions involving CH_3, CH_3O_2 and NO_2/NO. Find rate constants in an appropriate database, such as the NIST Chemical Kinetics Database [5]. Compare predictions of the revised model with the results of Figure 1.

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

Procedure

Task 0: preprocessing of kinetic mechanism and thermodynamic data

Run the `OpenSMOKE_CHEMKINPreProcessor` utility on the three mechanisms available: `POLIMI_C1C3_-NOX_1505` [6], GRI-Mech 3.0 [3], and Bendsten's mechanism [1]. Open the `log` file to make sure no errors were encountered in the reaction mechanism.

Task 1: simulation of isothermal plug-flow reactor

For each mechanism available, edit the `input.dic` files, specifying the reaction conditions corresponding to those of Figure 1. Run the `OpenSMOKE_PlugFlowReactor` solver under isothermal conditions for selected values of the inlet NO concentrations (10 different values are sufficient) and compare with the experimental results.

Task 2: revision of GRI mechanism

- Write down the species and reactions involved in the pathway diagram of Figure 2. Edit the reaction mechanism GRI-Mech 3.0 [3] (`grimech30.dat` file) and examine which of these species/reactions that are missing from the mechanism.

- Find rate constants for the missing reactions in an appropriate database, here the NIST Chemical Kinetics Database [5].

- Edit the reaction mechanism (`grimech30.dat` file) and add the missing species/reactions. Save the revised mechanism under a new name. Run the `OpenSMOKE_CHEMKINPreProcessor` utility on the revised reaction mechanism. Open the `log` file to make sure no errors were encountered in the reaction mechanism.

- Compare predictions of the revised model with the results of Figure 1 and the previous model predictions.

Task 3: isothermal plug-flow reactors in real conditions

Perform a few plug-flow calculations for the specified conditions of a full scale engine and assess the potential for UHC reduction in the exhaust channel.

Task 4: addition of H_2O_2

Repeat the calculations of Task 3, this time adding hydrogen peroxide (H_2O_2) to the inlet composition in quantities comparable to the UHC level. Evaluate process potential for UHC oxidation.

References

[1] 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.

[2] 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.

[3] 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.

[4] 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.

[5] J.A. Manion, R.E. Huie, R.D. Levin, D.R. Burgess Jr., V.L. Orkin, W. Tsang, W.S. McGivern, J.W. Hudgens, V.D. Knyazev, D.B. Atkinson, E. Chai, A.M. Tereza, C.Y. Lin, T.C. Allison, W.G. Mallard, F. Westley, J.T. Herron, R.F. Hampson, and D.H. Frizzell. Nist chemical kinetics database, nist standard reference database 17, version 7.0 (web version), release 1.6.8, national institute of standards and technology, gaithersburg, maryland, 20899-8320. Technical report, 2013.

[6] E. Ranzi, A. Frassoldati, R. Grana, A. Cuoci, T. Faravelli, A.P. Kelley, and C.K. Law. Hierarchical and comparative kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels. *Progress in Energy and Combustion Science*, 38(4):468–501, 2012.