Exercise 2: Oxidation of Aromatic Compounds

Reactor models

Plug Flow reactor (PFR) and Perfectly Stirred reactor (PSR) from the `OpenSMOKE++ Suite` [2]

Reaction mechanism

Oxidation of benzene (C_6H_6/O_2): `POLIMI_PRF_PAH_LT_1412` [6]

Purpose

Familiarize the student with the numerical simulation of plug flow reactors and perfectly stirred reactors. 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 enviromental 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 [6] 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.

Task

Evaluate the capabilities of the `POLIMI_PRF_PAH_LT_1412` reaction mechanism [6] for describing the overall oxidation behavior of benzene by comparing predictions with experimental results obtained in a turbulent flow reactor [5] and well-stirred reactors [3][1]. Based on the mechanism, evaluate current regulations, applying to municipal waste incinerators, that aim to ensure complete oxidation of aromatic species.

1. Compare modeling predictions in plug flow reactors with the `POLIMI_PRF_PAH_LT_1412` mechanism with the experimental results [5] for benzene and phenol shown in Figure 1. The experimental data were obtained in a turbulent flow reactor [5] under near-adiabatic conditions. The species concentrations were measured as function of residence time in the reactor. The initial mixing of reactants in the reactor is known to affect the chemical induction time. For this reason modeling results should be shifted in time to match the measured benzene level at the point of the highest concentration gradient. This approach has been shown to be valid, since the induction chemistry has only a negligible effect on the post-induction species profiles [4].

2. Compare modeling predictions in well-stirred reactors with the `POLIMI_PRF_PAH_LT_1412` mechanism with the experimental results of Da Costa et al. [3] for benzene and phenol shown in Figure 2. Low-temperature partial oxidation of benzene was studied by Da Costa et al. [3] in a continuous jet-stirred quartz reactor with an internal volume of 88 cm3. The mole compositions of the reacting flow were helium/oxygen /benzene = 80.5:15.5:4 (equivalence ratio equal to1.9). Experiments were carried out at a constant temperature (923 K) and atmospheric pressure, with residence times ranging from 1 to 10 s. The main products analyzed by gas chromatography were phenol, carbon
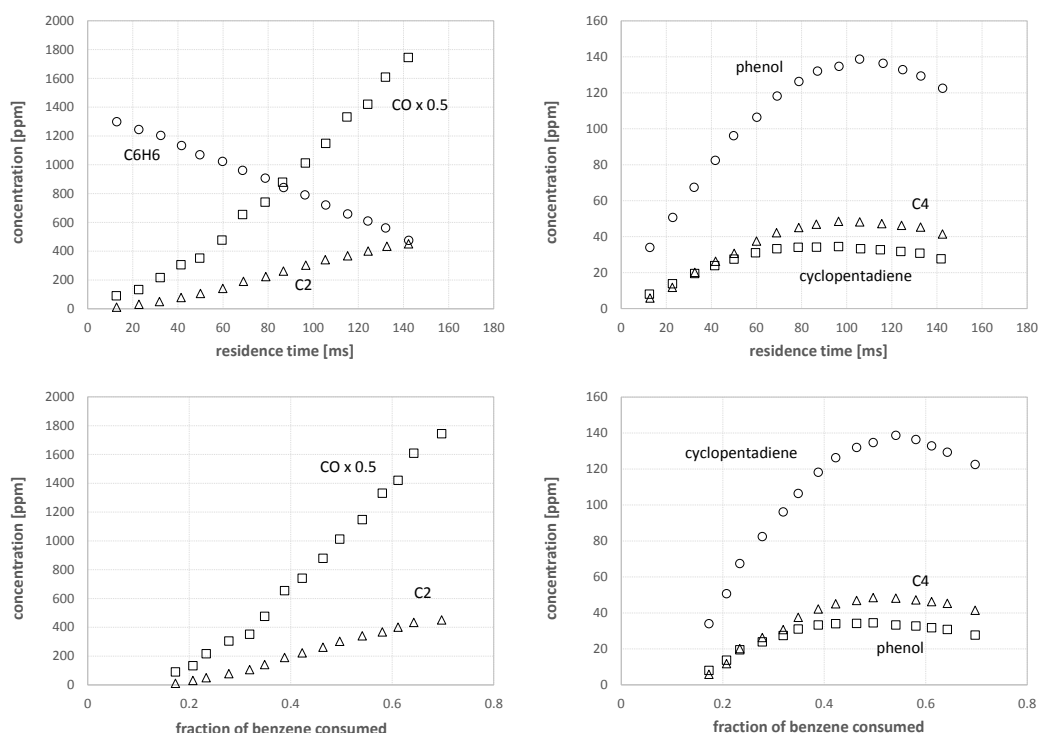
Fig. 1: Experimental data [5] for oxidation of benzene in an adiabatic flow reactor. Inlet composition is: C_6H_6=1571 ppm, O_2=15900 ppm; balance N_2. Inlet temperature is 1098 K, atmospheric pressure. C2 is the sum of acetylene (C_2H_2) and ethylene (C_2H_4). C4 is the sum of vinyl acetylene (C_4H_4) and butadiene (C_4H_6).

monoxide and dioxide, methane, C2 species (acetylene and ethylene), propyne, propene, and 1,3-butadiene. These conditions are particularly mild (corresponding to benzene conversions of under 50%) compared with the ones of the next perfectly stirred reactor (Task 3) and provide useful information on the relative role of the decomposition and recombination reactions of the phenoxy radical.

3. Compare modeling predictions in well-stirred reactors with the `POLIMI_PRF_PAH_LT_1412` mechanism with the experimental results for benzene and phenol shown in Figure 3. The experimental data were obtained by Chai and Pfefferle [1] in a micro-jet reactor, which approaches a well-stirred reactor under the conditions investigated. The experiments covered the temperature range 900–1300 K at nominal residence times of 50 ms and pressures of 350 torr and Φ=0.19 and Φ=1.02.

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% O_2 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.

Procedure

Task 0: preprocessing of kinetic mechanism and thermodynamic data

Run the `OpenSMOKE_CHEMKINPreProcessor` utility on the reaction mechanism (`POLIMI_PRF_PAH_LT_-1412.CKI` file) and the thermodynamic data (`POLIMI_TOT_NOX_1412.CKT` file). Open the log file to make sure no errors were encountered in the reaction mechanism.
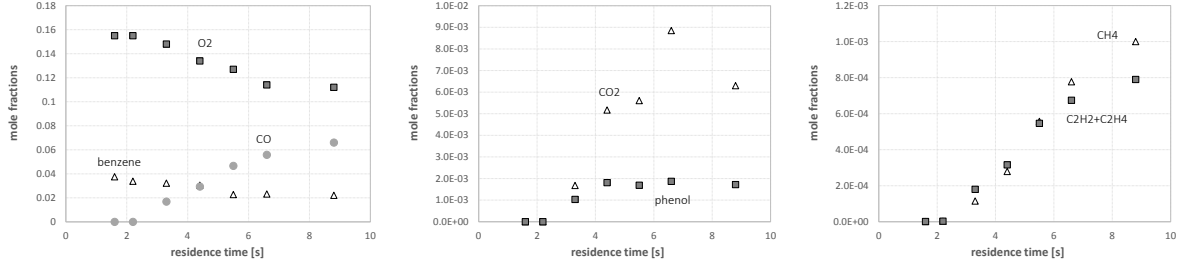
Fig. 2: Experimental data [3] for oxidation of benzene in a jet-stirred reactor with internal volume of 88 cm^3. The mole compositions of the reacting flow were helium/oxygen /benzene = 80.5/15.5/4 (equivalence ratio equal to 1.9). Experiments were carried out at a constant temperature (923 K) and atmospheric pressure.
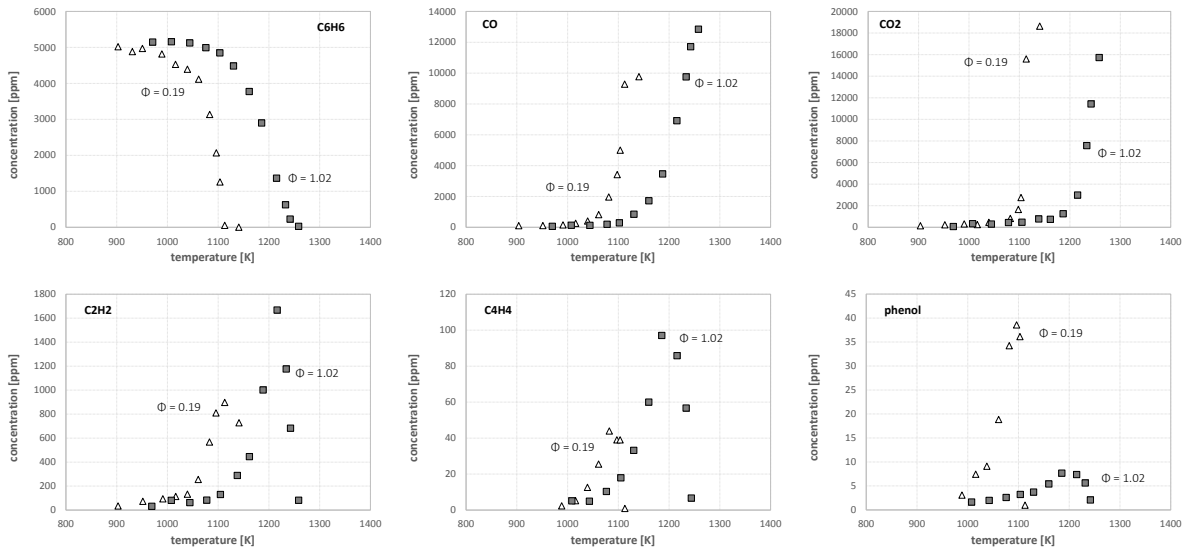

Fig. 3: Experimental data [1] for oxidation of benzene in a jet-stirred reactor. Inlet compositions are: C_6H_6=5100 ppm and O_2=20.13% (vol.) for case at Φ=0.19 and C_6H_6=5100 ppm and O_2=3.75% (vol.) for case at Φ=1.02. Balance Ar. Pressure is 0.46 atm.; nominal residence time 50 ms.

Task 1: simulation of adiabatic plug flow reactor

Edit the `input.dic` file, specifying the reaction conditions corresponding to those of Figure 1. Run the `OpenSMOKE_PlugFlowReactor` solver under adiabatic conditions and compare with the experimental results. Remember to match the measured benzene level at the point of the highest concentration gradient, since time 0 may be different in experiments and modeling.

Task 2: simulation of well-stirred reactor at atmospheric pressure

Simulate the data of Figure 2 assuming perfectly stirred reactor conditions (use `OpenSMOKE_Perfectly-StirredReactor` solver).

Edit the `input.dic` file, specifying the reaction conditions corresponding to Figure 2. Run `Open-SMOKE_PerfectlyStirredReactor` for a number of fixed temperature conditions, using the parametric analysis to make a batch of runs. Compare with the experimental results.

Task 3: simulation of well-stirred reactor at 350 torr

Simulate the data of Figure 3 assuming perfectly stirred reactor conditions (use `OpenSMOKE_Perfectly-StirredReactor` solver).

Edit the `input.phi019.dic` and `input.phi019.dic` files, specifying the reaction conditions corresponding to Figure 3. Run `OpenSMOKE_PerfectlyStirredReactorr` for a number of fixed temperature conditions, using the parametric analysis to make a batch of runs. Compare with the experimental results.

Task 4: analysis of numerical results

Based on the comparisons made, evaluate the ability of the model to predict benzene and phenol under the conditions investigated.

Task 5: evaluation of suitability of current regulations

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

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