A kinetic study of the oscillating combustion of hydrogen and syngas in well-stirred reactors.

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Introduction

The establishment of permanent oscillations ("limit cycles") has been often observed in the oxidation of several hydrocarbons in premixed, non-adiabatic systems like well-stirred reactors [1-3]. In such cases, the interaction between mass flow, heat exchange and chemical kinetics results in a periodic extinction and reignition of the system.
Several operating parameters have been found to influence the establishment of periodic limit cycles: beyond the fuel type and the dilution level, the oscillatory behavior is affected by the reactor temperature, pressure and residence time. Thus, the high number of parameters makes theoretical analysis a necessary step to understand the causes of such phenomena.
The simplest system to be studied is the combustion of hydrogen in a premixed reactor. Such configuration was first studied by Baulch et al. [2, 4, 5]. The oxidation of CO was also separately analyzed [6, 7]. In this work, a kinetic analysis of the hydrogen and syngas oxidation in isothermal, well stirred reactors is carried out. By adopting detailed kinetic mechanisms, the boundaries of the oscillating regions are defined through a parametric study. The Rate of Production (ROP) Analysis is adopted to understand the critical reaction paths.

Oxidation of hydrogen in well-stirred reactors

Baulch et al. [2, 4, 5] explained oscillations of hydrogen in well-stirred reactors through the competition of two competing reactions: (i) branching $H + O_2 \rightarrow OH + O$ and (ii) third-body reaction $H + O_2 (+M) \rightarrow HO_2 (+M)$. They represent the main pathways for O_2 decomposition. The first increases the system reactivity, while the second is a propagation reaction converting H radical into HO_2, which is more stable. Therefore, when the third body reaction prevails on the branching one, the system decreases its reactivity. The amount of active radicals produced is not able to sustain the incoming reactants consumption. The result is a re-accumulation of H_2 and O_2 in the system and a reduction of the products until a new ignition occurs. If the two phenomena remain of the same order of magnitude, limit cycles might be established. Figure 1a shows an example of such competition.
Each limit cycle can be divided in two parts. The "kinetic" region is confined in the time interval where the ignition of the system occurs. On the contrary, the "convective" section corresponds to a condition of inhibition where the products are removed and reactants are accumulated in the reactor. The switch between the two occurs when the reactivity within the reactor is not sustained, i.e. when the third body reaction is favored over branching. This can be further analyzed by looking at the profiles of 3 of the main radicals (Figure 1b).
A ROP analysis in different time steps shows the relative importance of third body reaction over branching. Figure 2 shows the pathways of the consumption of H radical.

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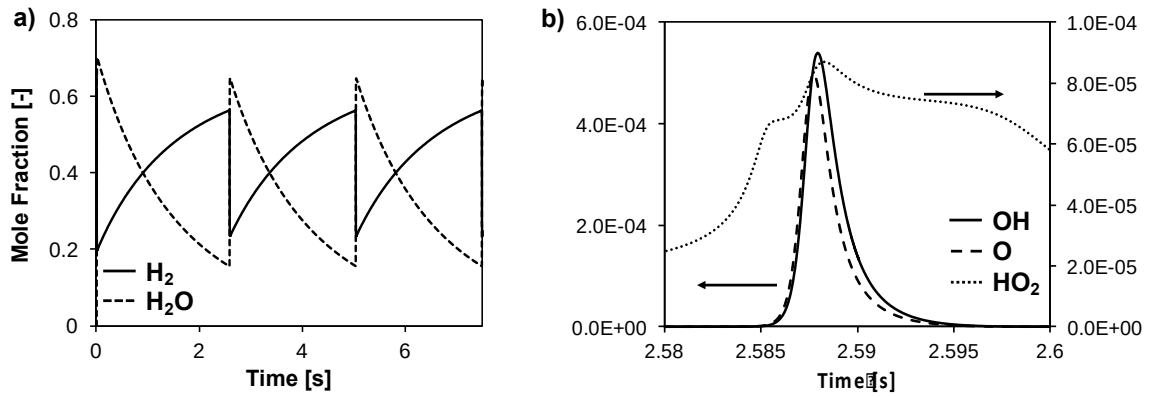

Figure 1: Time profiles of characteristic species in a well-stirred reactor. Inlet mixture: 0.6667 of H_2 and 0.3333 of O_2. Pressure of 0.1 atm and constant temperature of 800 K. Residence time $\tau = 2$ s.

The weight of the third body reaction grows over time with respect to the branching one. Analyzing the kinetic model used to perform the reactor simulation, it is possible to observe that the third-body efficiencies of several species are greater than one. Above all, the efficiency of water amounts to 10. Thus, the main reason for the increase of the importance of the third-body reaction is the accumulation of water.

In order to understand the effect of this aspect, the kinetic constant of this reaction must be considered: $k_{third} = k \cdot \sum_{i=1}^{NC} \frac{P \cdot y_i}{R \cdot T} \varepsilon_i$, where ε_i is the third-body efficiency. Since the amount of water in mole fractions is between 0.6 and 0.7 (Figure 1), the kinetic constant is enhanced by a factor around 6-7. By forcing to 1 the third body efficiency of H_2O, the steady state is reached and the oscillations disappear.

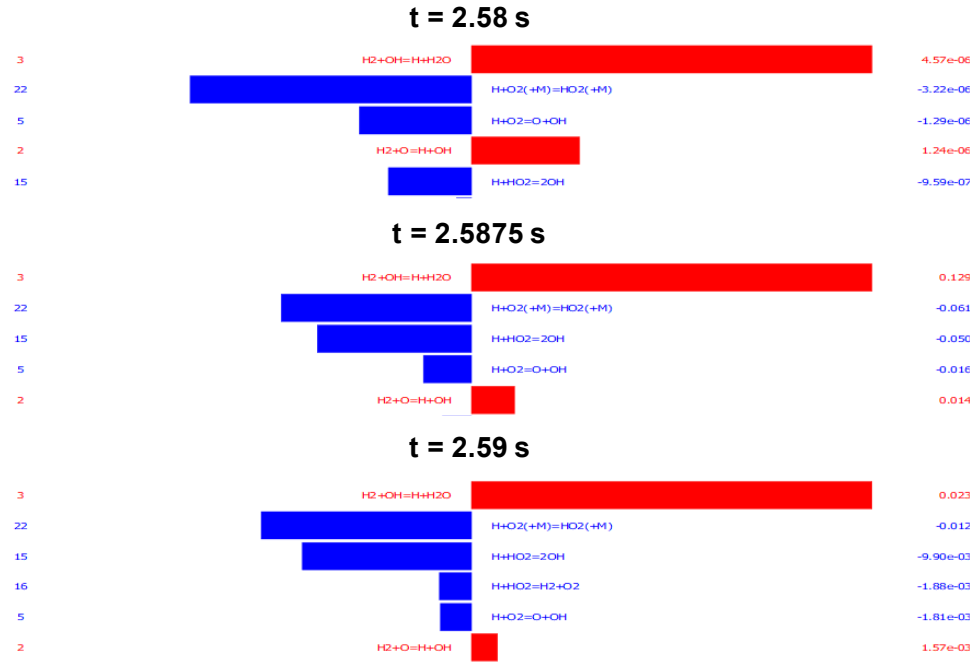

Figure 2. ROP analysis at different time steps.

Figure 3a shows, through a P-T diagram, the closed region where oscillations occur for the stoichiometric oxidation of H_2.

The Lower Oscillating Limit (LOL) and the Upper Oscillating Limit (UOL) delimit the presence of the oscillations. By changing the residence time τ, the oscillating region is modified; if τ is increased, the region of interest is concentrated mainly at low pressures,

while the temperature window is shifted to lower values. This behavior is related to the higher contact time and, correspondingly, the lower flow rate.

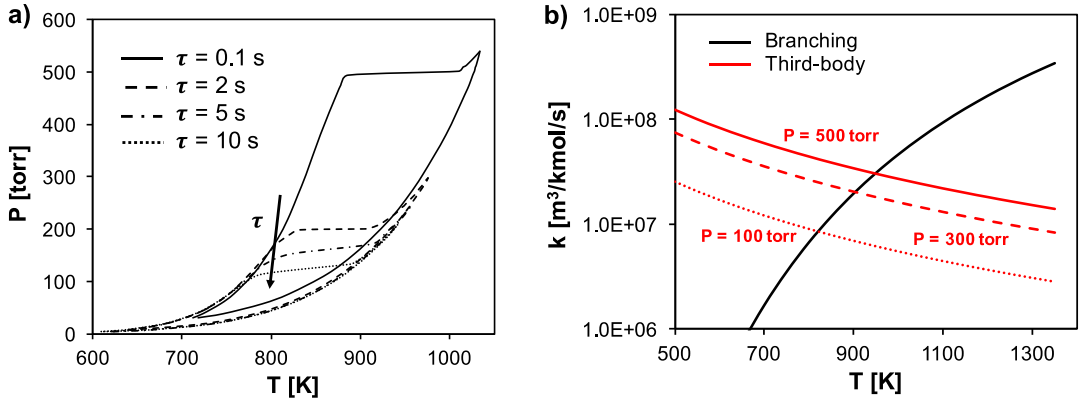

Figure 3. a) Oscillation regions for an isothermal, constant-pressure well-stirred reactor. Inlet mixture is H_2/O_2 at stoichiometric conditions; b) Kinetic constants of branching and third-body reaction as a function of temperature and pressure. Note: third-body kinetic constant does not include the efficiencies of third body.

In Figure 3b, the behavior of the kinetic constants of branching and third-body reactions as a function of temperature and pressure is showed. The branching reaction is pressure-independent: it increases by increasing the temperature. On the contrary, the presence of third body makes the second reaction affected by the pressure variation. In particular, its value is shifted upward by increasing the pressure. The trend decreases with the temperature. The intersection point moves to higher temperatures as the pressure increases.
When the pressure exceeds 500-600 torr, the oscillations disappear. As shown in Figure 3b, if the pressure is increased the intersection point is moved at higher temperatures. Therefore, the competition between the two reactions is anyway present. Yet, in these conditions the high reactivity of the hydrogen prevails. Even if the branching reaction is not favored over the third-body reaction, the reactants do not accumulate when the system is inhibited and stationary state is however attained.

Oxidation of syngas in well-stirred reactors

The oxidation of a mixture of carbon monoxide and hydrogen in a well-stirred reactor can occur with periodic ignition and inhibition of the system. If the amount of hydrogen if sufficiently high, the cause of oscillations is the same competition analysed in the previous section between branching and third-body reaction. This can be shown by the analysis of P-T maps obtained at three different residence times, as shown in Figure 4.
They are very similar in shape to those obtained for hydrogen. A slight difference is present in the temperature window. For the syngas case, it is narrower than hydrogen. In particular the LOL curve is shifted to higher temperatures. The reason can be found recalling the third body reaction kinetic constant. The presence of CO in the inlet stream implies the formation of carbon dioxide in the reactor. Both these species have an efficiency higher than 1, i.e. 1.9 for CO and 3.8 for CO_2. Therefore, the effect on the correction factor of the kinetic constant moves the intersection point in Figure 3b up to higher temperatures with respect to the corresponding case for H_2.

Considering the opposite situation, for which H_2 is lower than CO, a peculiar behavior is found, as previously observed by Griffiths et al. [7]: they analyzed CO oxidation with a small amount of H_2 at temperatures at which the branching reaction is much more favored than the third-body one.

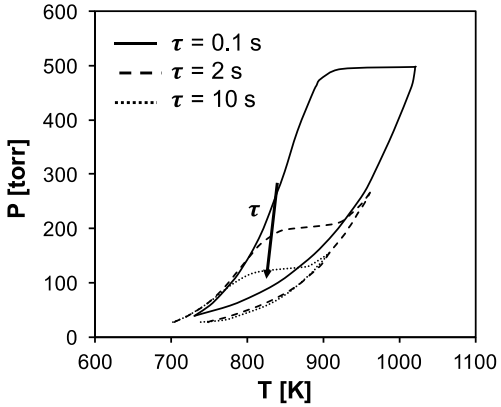

Figure 4. P-T diagram for stoichiometric oxidation of syngas. Inlet mixture composition: 0.4445 H_2, 0.2222 CO and 0.3333 O_2. Investigated residence times: 0.1 s, 2 s and 10 s.

In this case, being CO the main fuel, the chemistry is mainly controlled by the CO/CO_2 mechanism. As the oscillation occurs only if there is an inhibition of the system, the main termination reaction present is: O + CO (+M) → CO_2 (+M): it is a third-body reaction and it inhibits the system. Figure 5a better explains such competition through a ROP analysis.

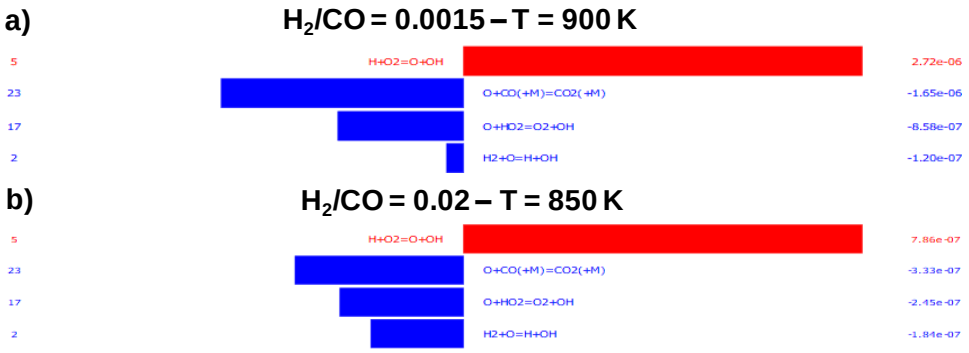

Figure 5. Rate of Production Analysis for O close to H_2O and CO_2 peaks. P = 0.1 atm.

The two alternative paths to the CO reaction for O consumption are the propagation reaction O + HO_2 → O_2 + OH and the branching reaction H_2 + O → H + OH. Both increase the reactivity of the system: each OH radical produced reacts mainly with CO obtaining H and carbon dioxide. Therefore, as soon as OH radicals are formed, they are converted into H radicals, resulting in an increase of the active species. Since the third-body reaction is more favorite, it prevents this effect, causing the oscillating behavior. The source of inhibition of the system is related to the high amount of CO_2 produced. Indeed, if ε_{CO_2} is forced to 1, the oscillation phenomenon disappears.

As the relative amount of hydrogen in the inlet mixture is increased, the temperature at which the system ignites is decreased. Therefore, the third body reaction between H and O_2 progressively assumes higher importance than the corresponding branching. As a consequence, HO_2 radicals are increased, favoring the consumption of O through the propagation reaction. In addition, the branching reaction has a greater importance due to the higher abundance of hydrogen itself. This results in a higher reactivity developed even if the third body reaction CO+O is still high as shown in Figure 5b.

Conclusions

In this work, a detailed kinetic analysis of the oscillatory phenomenon for the hydrogen and syngas combustion in well-stirred reactors was performed. For both fuels, P-T maps were generated with the purpose to understand the influence of these two parameters in addition

to the residence time. Oscillations occur at relatively small temperatures in the range of 600-1050 K and relatively small pressures, below 550 torr. In these operating conditions, there is a chemical competition between the two consumption paths of oxygen: (i) branching $H + O_2 \rightarrow OH + O$ and (ii) third body reaction $H + O_2 (+M) \rightarrow HO_2 (+M)$. When the second process prevails, the reactivity developed in the reactor is limited. Therefore, consumption of incoming reactants is not supported and they accumulate in the system. The accumulation of water favours this phenomenon, due to a third body efficiency of 10. A further analysis was performed in order to explain the behaviour of the oxidation of CO in presence of H_2 traces. In this case, since the controlling chemistry is related to carbon monoxide, the source of oscillations is the termination reaction $O + CO (+M) \rightarrow CO_2 (+M)$. In conclusion, termination reactions are the source of inhibition of the system. This result will be used as starting point to explain the cause of the oscillating combustion of higher hydrocarbons.

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