HAP/VOC ABATEMENT ASSISTED BY H$_2$O AND H$_2$ IN MILD COMBUSTION CONDITION

P. Sabia, M. de Joannon
sabia@irc.cnr.it
Istituto di Ricerche sulla Combustione - C.N.R., Naples – ITALY

Abstract
Mild combustion is a clean technology that relies on mixtures highly diluted and pre-heated to oxidize fuels in homogeneous conditions. High dilution levels allows for limited temperature gradient thus for reducing and controlling the emission of pollutant species such as NO$_x$ and particulate matter from energy production systems. Furthermore it can be employed also as a cleaning process in the post-combustion zone of industrial systems for the abatement of pollutant species present in exhausted gas flows.

This paper deals with the oxidation/abatement of Hazardous Air Pollutants (HAP) and Volatile Organic Compound (VOC) species in Mild combustion regime.

The system abatement efficiency may be increased whether an appropriate diluent and/or a fuel “enhancer” are employed. In case of water dilution or hydrogen as auxiliary fuel, pollutants oxidation can be more proficient since water and hydrogen propensity to give radicals in the thermal conditions typical of Mild combustion process.

Therefore the attention has been focused on the effect of the diluent nature and the hydrogen addition to mixtures on the evolution of the oxidation process, by considering auto-ignition and oxidation times. The analysis has been carried on by means of numerical simulations realized using both nitrogen and/or water as diluent and several amounts of hydrogen.

Results show that steam and hydrogen significantly affect the characteristic kinetic times (auto-ignition and oxidation times). Rate of production analysis were numerically performed to understand the chemical mechanisms involved in system diluted in water and/or in presence of hydrogen in a wide mixture inlet temperature range.

Introduction
In industrial processes HAP and/or VOC emission control is realized through several technologies, i.e thermal or catalytic oxidation, absorption or condensation [1, 2] in dependence of VOC/PAH concentration in the exhausted flue gases. Whether it ranges from 20 up to 2000 ppm, catalytic or thermal oxidizers are the suitable abatement technologies.

The former envisages the use of a platinum, palladium or manganese dioxide catalysts to convert the contaminants in carbon dioxide and water in a restricted range of temperature (300 -500°C), whereas thermal oxidation relies on combustion chamber high temperatures (725-825°C) and adequate retention time (0.5-1 s). Both the technologies are designed to achieve from 95% to 99% of removal efficiency [3, 4].

In both thermal and catalytic oxidizers the heat released from the oxidation of HAP/VOC compounds in the exhausted flue gases is not sufficient to raise the temperature of the waste stream up to the desired temperature so that a gas flow pre-heating and auxiliary fuels and air are commonly required. Such strategy may lead to working temperatures that could case, in
thermal oxidizers, the formation of undesirable by-products, such as NO\(_x\), while, in catalytic oxidizers, the deactivation of catalysts.

In case of HAP/VOC thermal incineration, pollutants can be oxidized in operative conditions typical of Mild Combustion [5] regime whether reactants pre-heating is boosted at a temperature higher than the HAP/VOC auto-ignition temperature and the mixture dilution level is high enough to reach not flammable mixtures. Such approach would imply a fine control of working temperatures thus avoiding the formation of undesired by-products.

Moreover, the system abatement efficiency may be increased whether an appropriate diluent and/or a fuel enhancer are employed. As matter of fact, in case of mixture steam dilution or hydrogen addition, HAP abatement can be enhanced since such compounds can release radical species and speed up oxidation reactions.

In this framework, the paper aims to show a preliminary analysis of HAP oxidation in Mild combustion regime. The effect of diluent nature and hydrogen as auxiliary fuel has been evaluated by comparing numerical results obtained for mixtures diluted with nitrogen and/or water in presence of several amounts of hydrogen.

**Numerical tools**

Numerical simulations have been run using the PLUG [6] application of the Chemkin 3.7.1 [7] software and the oxidation kinetic mechanism ht0704.cki [8, 9] (available at www.chem.polimi.it/CRECKModeling/kinetic.html). PLUG simulates the behavior of plug-flow chemical reactors. More specifically, such application is designed to model the non-dispersive, one-dimensional flow of a chemically reacting, ideal-gas mixture in a conduit of essentially arbitrary geometry. Such configuration has been chosen in order to study the oxidation process as function of the axial coordinate or, equivalently, of the residence time. Benzene has been chosen as representative species of HAP and/or VOC. It has been selected because it is the simplest aromatic hydrocarbon with a relatively well-known oxidation mechanism [10]. To value the abatement efficiency of more complex aromatic compounds, in systems assisted by water and hydrogen, anthracene has been selected.

**Results**

The main flow enters the reactor in premixed conditions with a velocity equal to 100 m/s at inlet temperatures \((T_{in})\) ranging from 850K up to 1500K. The concentration of HAP species to be oxidized has been set equal to the 25% of the lower flammability limit concentrations, since thermal oxidation plants operate under such condition for safety requirements [11]. The mixture is then composed by air, thus ultra-lean conditions have been considered. Nitrogen has been substituted in several amounts with steam up to work with a system completely diluted in steam, while keeping constant the overall dilution degree. Its amount has been changed in such a way to represent 0%, 25%, 50%, 75% and 100% of the overall dilution degree. Furthermore small amounts of hydrogen, equal to 100%, 200% and 300% with respect to fuel concentration, substitute nitrogen in inlet mixtures in order to assess the effect of such fuel on HAP oxidation characteristic times.

The auto-ignition and the oxidation times have been considered in order to study the evolution and the completion of the oxidation process. These parameters are important in the designing of thermal HAP destruction plant since they influence both the abatement efficiency and the plant dimensioning.

Figure 1 shows the temperature profiles versus the reactor residence time for both the fuels in curves parametric in water content. Figure 1a and 1b are relative to benzene respectively pre-heated at 900K and 1300K, while 1c and 1d to anthracene at the same reference inlet temperatures.
At 900K for C₆H₆/O₂/N₂ mixture, after an induction period, the reactor temperature increases rather slowly and then abruptly jumps to the steady state value. For steam diluted systems the trend is similar but curves are slightly shifted toward lower residence times with respect to system fully diluted in N₂.

![Temporal temperature profiles](image)

**Figure 1.** Temporal temperature profiles for C₆H₆ and C₁₀H₁₄ in curves parametric in water content for Tₑₐ₃ equal to 1000K and 1300K.

Also for a steam dilution level equal to 75% and 100%, the system slowly reaches the steady state, although in these cases the temperature jump does not occur. It is worth noting that the systems diluted in steam at 25% reaches the steady condition for the lowest residence times. Furthermore, as soon as steam concentration increases, systems attain a lower final temperature because of the greater steam heat capacity in comparison with nitrogen. Such trend is also recognizable for the systems pre-heated up to 1300K, but in this case, steam accelerates the benzene oxidation respect to the system diluted in nitrogen.

Similar considerations apply to the case of anthracene oxidation (Fig1b, Fig1d). At 900K temperature temporal profiles for systems diluted in steam almost coincide for low residence times, then they reach the stationary condition steeply or slowly in dependence of the steam amount. The nitrogen-diluted system reaches the steady condition for the lowest residence
time. At 1300K any profile presents a first jump of temperature, followed by a smooth one. Then systems reach temperature stationary values in dependence of their heat capacity.

Figure 2. Auto-ignition times for C₆H₆ and C₁₄H₁₀ as function of α for several steam amount.

Figure 2a and 2b shows the auto-ignition times respectively for C₆H₆ and C₁₄H₁₀ as a function of the parameter 1000/T (α) on curves parametric in steam amount. The auto-ignition delay time (τ) has been defined as the time needed by the system to increase its temperature of 10K with respect to T_in.

For benzene systems, auto-ignition time decreases as α decreases. For very low T_in, τ slightly decreases as much as steam amount increases. In fact, for α=1.17 it goes from 0.95 s down to 0.47 s respectively for the system with 0% and 100% of steam. Auto-ignition times diminish congruently with this trend. For systems diluted with steam, τ values almost coincide for high temperatures, while τ for the nitrogen-diluted system remains higher respect to the others up to 1450K, then it abruptly decreases for higher temperatures.

In case of C₁₄H₁₀ the trend is different. In fact, for low temperatures the longest auto-ignition time competes to the system diluted in N₂, while the shortest one is relative to the system diluted in steam and nitrogen in equi-molar fraction. At 900K, between α=1.1 and α=0.9, the system fully diluted with steam shows the longest τ, then, as much as the steam content is diminished, τ decreases. For α<0.9, the N₂ diluted system presents the longest ignition delay time, followed by the system diluted with steam, whereas the system with a water content equal to 25% shows the shortest τ.

Figure 3 reports temperature profiles versus residence time on curves parametric in the H₂ content for systems diluted in N₂ at 900K and 1300K. Figures 3a and 3b are relative to C₆H₆ mixtures.

At 900 K they show a first short induction period where temperature increases slowly, but then, it abruptly jumps up to the steady condition. The final temperature depends on H₂ content. The higher it is, the higher is the steady temperature system, thus, in case of N₂ dilution, it goes from 1260K, for the system without H₂, to 1630K for the system with H₂=300%. Furthermore the system without H₂ presents the shortest auto-ignition and oxidation time (τox). H₂ does not have a specific effect on the oxidation times since t_ox relative
to the system with H₂=200% is slightly higher than the case with H₂=100% but lower than the case H₂=300%.

Figure 3. Temporal temperature profiles for C₆H₆ and C₁₀H₁₄ on curves parametric in H₂ content for Tₘ equal to 900K and 1300K.

At 1300K the temperature profiles are quite different in comparison with the ones reported in figure 3a. They show a first short induction period, where temperature increases quite abruptly, followed by a slow growth, afterward a second smooth temperature increment that leads the system to the steady condition. The auto-ignition and oxidation times decrease increasing the hydrogen concentration whereas the steady temperature increases. Similar considerations apply for C₁₄H₁₀, as shown in figure 3c and 3d.

Figure 4a shows the auto-ignition time for benzene and anthracene mixtures fully diluted in nitrogen versus the parameter α on curves parametric in the H₂ content. It is possible to recognize two different behaviors. Curves intersect at α=1.05. For α>1.05, even if values are relatively close to each other, the system with H₂=300% shows the highest auto-ignition time, while the shortest one competes to the system without H₂. For α<1.05, such trend inverts, and the difference among values becomes more appreciable. For very high Tₘ the C₁₄H₁₀/O₂/N₂ auto-ignition times drop down and assume values lower than the other systems.
In case of anthracene the behavior is similar to benzene, but the intersection among curves happens for $\alpha=1.1$. Such point is identifiable for any considered steam amount and marks the shift between operative conditions in which $\text{H}_2$ delays auto-ignition of the mixture to conditions in which $\text{H}_2$ promotes the its ignition.

**Figure 4.** Auto-ignition times for the systems $\text{C}_6\text{H}_6/\text{N}_2$ and $\text{C}_{14}\text{H}_{10}/\text{N}_2$ as function of $\alpha$ for several $\text{H}_2$ amount.

Figure 5 shows the auto-ignition times for anthracene and benzene systems fully diluted in steam. In both cases the trend is very similar to the one described for figure 4, but the intersection point of the curves occurs for higher $T_{\text{in}}$.

**Figure 5.** Auto-ignition times for the systems $\text{C}_6\text{H}_6/\text{H}_2\text{O}$ and $\text{C}_{14}\text{H}_{10}/\text{H}_2\text{O}$ as function of $\alpha$ for several $\text{H}_2$ amount.

Such point is identifiable for any dilution level and it shifts towards higher temperatures as much as the water content increases.
Discussion

In order to understand the effect of steam dilution and hydrogen addition on the evolution of the oxidation process a rate of production analysis has been realized. In particular, computations have been carried out considering the system C$_{14}$H$_{10}$/O$_2$ diluted in nitrogen and/or water and with H$_2$ content equal to 0% and 300% for inlet temperature equal to 900K and 1300K. Similar analyses have been realized for benzene systems and are reported elsewhere [12]. Without exploiting deep insight the benzene and anthracene oxidation mechanisms in such operative conditions, the analysis has been focused on the most influential reactions, identified, in a previous work [12] as the reactions typical of the subsystem H$_2$/O$_2$. They are reported below:

1) \[ H + O_2 \rightarrow OH + O \]  
(branching reaction)

2) \[ H + O_2 + M \rightarrow HO_2 + M \]  
(breaking reaction)

3) \[ O + H_2O \rightarrow OH + OH \]  
(water break-down)

Fig. 6a shows the rates of reaction 1), 2) and 3) for the system C$_{14}$H$_{10}$/O$_2$/N$_2$ and the relative temperature profile as function of the residence time for T$_{in}$=900K. The rates of reactions 1) and 2) are relative to the consumption of the H radicals while the rate of reaction 3) is referred to the production of OH radicals.

Before the occurrence of the temperature jump, the breaking reaction provides radicals for initiating the oxidation process. Subsequently the branching reaction (1), followed by reaction 4) O + H$_2$ => OH + H and 5) OH + H$_2$ => H$_2$O + H, leads the system to the ignition. Reaction 3) in such operative condition covers a relative important role just in the ignition delay period.

In fig.6b the rates of the three reactions are reported for the system C$_{14}$H$_{10}$-H$_2$/O$_2$/N$_2$ as function of the residence time for T$_{in}$=900K.

In this case it is recognizable the same pathway described in the case of figure 6a, even if it is worth noting that H$_2$ delays the ignition time, which occurs for a relatively longer time in comparison with the first system, and doubles the rates of reactions considered. For very low residence times, H$_2$ promotes reaction 1) and 2) while depressing the reaction rates among radicals and anthracene, in particular with O. In fact preliminary numerical reaction rates analysis on the oxidation of anthracene has shown that O is very effective in the first steps of the combustion process. H$_2$ reacts with O radicals and delays the first attack to the aromatic compound. This implies a lower overall reaction rate, since the depletion of radicals species coming from the fuel pyrolysis and oxidation.

Fig. 6c reports the rates of reactions 1), 2) and 3) for the system C$_6$H$_6$/O$_2$/H$_2$O. In this case the steam break-down and the breaking reaction plays a crucial role as source of radicals. At the same time reaction 2) is faster than reaction 1) for any residence time. The reaction 3) produces HO$_2$ radicals that are relatively less reactive than OH radicals. They mainly form H$_2$O$_2$ that, in turn, decomposes forming OH radicals. This pathway is relatively slower respect to the branching chain implying a lower reactive condition.

Reaction 2) is furthered respect to reaction 1) because water third-body efficiency ($\beta$) in three-body reactions is significantly high. In fact in the selected kinetic mechanism $\beta_{H_2O}$ in reaction 2) is ten times higher than $\beta_{N_2}$. It is worth noting that in correspondence of the water
break-down there is a first increase of temperature. Moreover the temperature gradually increases up to the stationary state.

**Figure 6.** Rates of reactions 1), 2) and 3) for $\text{C}_{14}\text{H}_{10}/\text{O}_2/\text{N}_2$ (a), $\text{C}_{14}\text{H}_{10}-\text{H}_2(300\%)\text{/O}_2/\text{N}_2$ (b) and $\text{C}_{14}\text{H}_{10}/\text{O}_2/\text{H}_2\text{O}$ (c), with temperature profiles as function of the residence time at $T_{in}=900\text{K}$.

Fig. 7 shows the rates of reactions for the same systems at $T_{in}=1300\text{K}$. In general the high inlet temperature implies that the oxidation reactions are mainly promoted by the branching reaction of the system $\text{H}_2/\text{O}_2$.

In case of system $\text{C}_{14}\text{H}_{10}/\text{O}_2/\text{N}_2$ (fig.7a) reaction 1) and 2) show two different peaks. In correspondence of such peaks, the temperature profile shows two jumps of temperature. Reaction 3) shows two negative minimum values, and then it becomes positive.

Same considerations apply for the system $\text{C}_{14}\text{H}_{10}-\text{H}_2/\text{O}_2/\text{N}_2$ (fig.7b) where the general trend described in the previous case is still recognizable. In particular it is worth noting that $\text{H}_2$ promotes significantly reaction 1) and leads to lower ignition and oxidation times respect to the system pre-heated at 900K.

The rates of production of selected reactions for the system $\text{C}_{14}\text{H}_{10}/\text{O}_2/\text{H}_2\text{O}$ are reported in fig.7c. It is evident that the dilution in water implies a change in the evolution of the oxidation
process. In fact the water breakdown appears to be the predominant reaction. Steam decreases
the auto-ignition and the oxidation times respect to the system diluted in nitrogen, but not
respect to the system C14H10-H2/O2/N2.

Steam reacts with radicals O, giving rise to radicals OH and enhancing the reactivity of
the system respect to the system diluted in nitrogen. At the same time such reaction leads to a
depletion of O radicals thus to a decrease of the H2/O2 branching reactions rates promoted by
high inlet temperatures.

![Figure 7](image_url)

**Figure 7.** Rates of reactions 1), 2) and 3) for C14H10/O2/N2 (a), C14H10-H2(300%)/O2/N2 (b)
and C14H10/O2/H2O (c), with temperature profiles as function of the residence time at Tm=1300K.

**Conclusions**

This study represents a preliminary evaluation of the effect of H2O and H2 on the
oxidation of C6H6 and C14H10 in Mild condition by evaluating the auto-ignition and the
oxidation times. Results show that, for low temperatures, steam dilution implies lower auto-
ignition times but longer oxidation times with respect to the system diluted with nitrogen,
whereas for high temperatures steam reduces both the characteristic times. It is worth noting
that there is an optimum value of steam content that allows for the attainment of the steady state condition within the shortest residence time.

Hydrogen addition to systems diluted in nitrogen delays the characteristic times of systems, for low temperatures, whereas promotes the auto-ignition and oxidation reactions at high temperatures. The rate of production analysis has shown that the H$_2$/O$_2$ reactions, that promote the ignition and the oxidation of hydrocarbons, are sensibly modified by the presence of H$_2$O and H$_2$.

References