VOC Destruction by Water Diluted Hydrogen Mild Combustion.  
A Preliminary Study

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1. Introduction

Thermal destruction of Volatile Organic Compounds (VOC) is a mature technology, largely applied in the case where the recovery and re-use or disposal of the organic pollutants is not considered an advantageous alternative in the process cycle. Modern catalytic or thermal oxidizers are designed to achieve from 95\% to 99\% of removal efficiency on the basis of the temperature and residence time used in the process [1,2]. The typical combustion chamber temperatures in thermal oxidation devices range from of 950K up to 1100K. Coupled with the required inlet VOC concentrations, fixed at 25\% or 50\% of the low explosion limit according to the specific application for safety regulations, such temperatures do not allow for sustaining the reaction process. Therefore, an auxiliary fuel, such as natural gas, propane and light fuel oil is needed. If the system configuration and VOC concentration allow for a heat recovery from VOC oxidation process for inlet reactant pre-heating, then the quantity of auxiliary fuel decreases. Unfortunately, the contemporary use of an auxiliary fuel and reactant pre-heating can lead to the potential formation of undesirable by-products, such as NO\textsubscript{x}. However, for a pre-heating of reactants at a temperature higher than the VOC autoignition temperature, thermal oxidation can fall in the Mild Combustion regime if mixtures sufficiently diluted are used. In this case both the clean and cleaning characteristics of the Mild combustion are simultaneously effective in the same process.

Moreover, a not secondary advantage of such a combustion regime is its potential application together with complementary pollutant abatement techniques for compounds different from the ones involved in thermal destruction. For instance, it is well discussed in literature [3] that the working temperature range of Mild combustion processes coincides with the temperature range characteristic of Selective Non-Catalytic Reduction of NO\textsubscript{x}. Moreover, the suitable choice of the diluent can improve the abatement efficiency of the system. This is the case of water diluted Mild Combustion where the diluent can favor the VOC oxidation for its propensity to give radicals in these thermal conditions. The use of a fuel enhancer, such as hydrogen, can play the same role increasing the efficiency of the system by reducing the characteristic time of the process. Furthermore, the water used as diluent allows for separating particles from flue gas in a downstream condensation unity. The heterogeneous nucleation of water molecules on organic or inorganic particles present in the stream captures submicromic particulate matter, which generally escapes from standard separation unit.

Although several applications of regenerative burners for VOC destruction are reported in literature, and are already available for industrial pollutant treatment, there are very few information in the scientific literature about VOC thermal oxidation in Mild Combustion regime.

In this framework, the paper aims to show a preliminary analysis of VOC oxidation in Mild combustion regime. The two simplest compounds, representative of oxygenated and aromatic VOC are chosen for this study. Therefore, the oxidation process of formaldehyde and benzene is followed in preheated, diluted condition of Mild combustion. The effect of diluent has been evaluated by comparing results obtained using both nitrogen and/or water as diluent.
In both case the effect of hydrogen on the evolution of the process has been evaluated.

2. Numerical tools

The numerical simulations have been run using the PLUG [4] application [5] of the Chemkin 3.7 software. PLUG simulates the behavior of plug-flow chemical reactors. More specifically, the 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. Formaldehyde and benzene have been chosen as representative of the VOC. The former species has been selected because of its relatively simple oxidation mechanism, hence it can be a suitable species to realize a preliminary study of the oxidation process in a system that works with so high inlet temperatures and with high dilution levels, while the latter compounds represents the aromatics compounds class, that notoriously exhibit a very complex oxidation kinetic [6]. The oxidation kinetic mechanisms used are the c1c3ht0512.cki [7] for formaldehyde and the ht0512.cki [7] for benzene.

3. Results

The flow enters the reactor in premixed conditions with a velocity of 100 m/s for several inlet temperatures, which ranges from 900K up to 1400K, while the mixture composition is changed. In particular fuel concentration has been set equal to the 25% of the lower flammability limit concentrations, since this is a realistic approach in fact thermal oxidation plants operate with such fuel concentration limits for safety requirements. The mixture is then composed by air, hence ultralean conditions have been considered. Nitrogen amount has been substituted in several percentages, while keeping constant the overall dilution degree, with steam up to work with a system completely diluted with steam. In such a way it has been possible to value the effect of the diluent nature on the evolution of the oxidation process. The autoignition time and the temporal temperature profile, as well as the fuel yields in species such as carbon monoxide and carbon dioxide, have been considered in order to study the evolution and the completion of the oxidation process. The yields will not be presented in the paper for the lack of the room.

![Figure 1](image)

**Fig.1** Autoignition times as function of steam percentage for the systems CH$_2$O/O$_2$/N$_2$ and C$_6$H$_6$/O$_2$/H$_2$O (b) at 1000K and 1300K.

Furthermore small amounts of hydrogen have been added to inlet mixtures in order to assess
the effect of such fuel on the time of the VOC destruction and mainly its interaction with steam. Hydrogen substitutes the diluent but its low overall concentration does not significantly change the heat capacity of the system.

Figure 1 shows the autoignition times for formaldehyde and benzene systems at 1000K and 1300K as function of steam percentage. It has been changed in such a way to represent the 0%, 20%, 40%, 80% and 100% of the overall dilution degree. The autoignition delay time (τ) has been defined as the time needed by the system to increase its temperature of 10K, respect to the inlet one.

As expected the ignition delay times of formaldehyde systems are lower than the ones relative to benzene mixtures for both the temperatures here considered.

At 1000K, as the steam percentage increases, τ slightly decreases. In fact for formaldehyde systems it goes from 1.1 $10^{-2}$ sec to about 7 $10^{-3}$ sec, while it goes from 1.5 $10^{-2}$ sec to 7.6 $10^{-3}$ sec for benzene mixtures. At 1300K the autoignition time for CH$_2$O still decreases by increasing the steam content, but in this case it firstly decreases from 1.8 $10^{-3}$ sec to 1.4 $10^{-3}$ sec for a steam relative percentage equal to 40%, then for the system diluted in steam it slightly increases up to 1.45 $10^{-3}$ sec.

Figure 2 shows the temperature profiles as function of the residence time in the reactor for both the fuels as function of the steam amount.

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**Fig.2**  Autoignition times as function of steam percentage for the systems CH$_2$O/O$_2$/N$_2$ and C$_6$H$_6$/O$_2$/H$_2$O at 1000K and 1300K.

Figure 2a and 2b are relative to formaldehyde systems respectively pre-heated up to 1000K and 1300K.

In any case the reactor temperature increases and reaches a steady state but the temperature temporal profiles suggest different evolutions of the oxidation process. In fact in general the reactor temperature slowly increases then abruptly jumps to the steady condition. Nevertheless for the system diluted in steam up to 80% and 100% there is a further change of the temperature profile slope. For the former system the slope change is relatively smooth, in the latter case this tendency is more evident and the system reaches the steady condition very slowly. It is worth noting that the systems diluted in steam up to 20% reaches the steady condition for the lowest residence times. Furthermore, as soon as the steam concentration increases systems reach a lower final temperature. This behavior is also recognizable for the system pre-heated up to 1300K but in this case the temperature profiles suggest that steam accelerates the formaldehyde oxidation, in fact the system diluted in nitrogen reaches the
steady condition later than all the other mixtures.
The same considerations apply to benzene oxidation (Fig2c, Fig2d). In these cases systems need a longer time to ignite and the evolution of the oxidation process is relatively slower but the steam addition effect on the autoignition time and on the steady state delay time is more evident. At 1000K the system diluted in steam up to 40% reaches the steady condition for the lowest residence time. Also in these cases the steady temperature is inversely proportional to the heat capacity of the system.

Figure 3 shows the autoignition time as function of hydrogen amount for three systems respectively diluted in nitrogen, in water and in nitrogen and steam, with a water relative percentage equal to 40%. It has been fixed equal to 100%, 200% and 300% respect to the fuel concentration.

Figure 3a is relative to formaldehyde mixtures. The autoignition time $\tau$, for any hydrogen concentration, is as much lower as the steam content is increased from 0% to 100%. At 1000K as the hydrogen concentration is increased the autoignition time $\tau$ slightly decreases. In particular the system diluted in nitrogen is more sensitive to the hydrogen content in fact the ignition delay time decreases from $9 \times 10^{-3}$ sec to $8.35 \times 10^{-3}$ sec, while for the other two systems the variation is less pronounced.

At 1300K $\tau$ shows the same trend identified for 1000K but system is much more sensitive to hydrogen presence. For the system $\text{CH}_2\text{O}/\text{O}_2/\text{N}_2$ $\tau$ goes from $1.7 \times 10^{-4}$ sec to $9.4 \times 10^{-5}$ sec, while for the system $\text{CH}_2\text{O}/\text{O}_2/\text{N}_2-40\%\text{H}_2\text{O}$ the autoignition time goes down from $8.9 \times 10^{-5}$ sec to $4.7 \times 10^{-5}$ sec. Furthermore for the last system it changes from $6.9 \times 10^{-5}$ sec to $3.6 \times 10^{-5}$ sec.

Figure 3b shows the autoignition time for benzene mixtures as function of hydrogen content. It is noteworthy to highlight that at 1000K and in absence of hydrogen the system diluted in nitrogen has the highest autoignition time while the lowest one competes to the system diluted in steam. As soon as hydrogen is added, $\tau$ relative to the system $\text{C}_6\text{H}_6/\text{O}_2/\text{N}_2$ slightly
decreases, while in the other two cases increases. For a hydrogen percentage equal to 100%, in case of steam dilution level up to 40% of the overall dilution degree, $\tau$ becomes higher than the system diluted in $N_2$, while for the maximum $H_2$ content, the highest $\tau$ competes to the system $C_6H_6/O_2/N_2/H_2O$. Once again at 1300K and in absence of $H_2$, the highest autoignition time competes to the system diluted in nitrogen but the lowest one is relative to the system with a steam level equal to 40%. As the hydrogen content increases, $\tau$ decreases in any system, but it is evident that hydrogen affects the evolution of the oxidation process in a more significant way for the system diluted in nitrogen, since for a hydrogen content equal to 100% the autoignition time change is the highest one. Further hydrogen addition does not imply a substantial change of $\tau$. In the other two cases $\tau$ decreases as the hydrogen content is augmented but they are not very sensitive. For $H_2$ concentration equal to 300%, autoignition times for the three systems are very close to each other but oxidation starts earlier for the system fully diluted in water, whilst the system with a relative water concentration of 40% shows the lowest autoignition time.

Figure 4 show temperature profiles as function of the residence time on curves parametric in hydrogen content for the systems diluted in nitrogen and in water at 1000K. Profiles relative to the systems diluted in nitrogen and water have been neglected since they do not add any further information.

![Temperature temporal profiles](image)

**Fig.4** Temperature temporal profiles as function of hydrogen percentage for the systems $CH_2O/O_2/N_2 (a)$, and $CH_2O/O_2/H_2O (b)$, $C_6H_6/O_2/N_2 (c)$ $C_6H_6/O_2/H_2O (d)$ at 1000K.

Figure 4a and 4b present the cases relative to formaldehyde mixtures. Temperature profiles are similar. They show a first short induction period, where temperature increases slowly, but then, it abruptly jumps and reaches the steady condition. The final temperature depends on hydrogen content. The higher it is, the higher is the steady temperature system, thus, in the case of nitrogen dilution, it goes from 1260K, for the system without hydrogen, to 1630K for the system with a hydrogen percentage respect to the $CH_2O$ molar concentration equal to 300%, while, in case of steam dilution, it goes, for the same hydrogen contents, from 1210K to 1520K. Comparing the system for a fixed hydrogen concentration, the final temperature depends on the heat capacity of the system, thus systems diluted in water have a lower final temperature value.

Figure 4c and 4d are relative to aromatic compound mixtures. In the case of nitrogen dilution, temperature profiles show the same trend identified in the aldehyde case but the oxidation
characteristic times are relatively lower. In case of dilution with steam (Fig.4d) hydrogen addition delays the autoignition time but anticipates the systems stationary condition. All the curves intersect at the same residence time that corresponds to about 1100K. Hydrogen modifies also temperature profiles, in fact in the absence of hydrogen temperature presents a first increase followed by a gradual increase up to the final value. In case of H₂ concentration equal to 300% the system ignition is delayed but the temperature jumps to the final value with a relative sharp slope. The profiles relative to the other hydrogen concentrations collocate between these two curves in such a way to describe the evolution of the oxidation process as function of the hydrogen concentration from the two conditions just described.

4. Discussion

In order to understand the effect of steam dilution and of hydrogen addition a preliminary rate of production analysis has been realized taking into account the most influential reactions on the evolution of the oxidation process. In particular, such numerical analysis has been carried out considering the systems C₆H₆/O₂ since benzene mixtures have shown to be more sensitive to these two parameters. Therefore systems diluted in nitrogen and in water and with a hydrogen content equal to 0% and 300% at 1000K have been considered.

The most influential reactions are the following [8]:

1) H + O₂ ⇒ OH + O  
2) H + O₂ + M ⇒ HO₂ + M  
3) O + H₂O ⇒ OH + OH

![Image](Fig.5)

**Fig.5** Rates of reactions 1), 2) and 3) for the systems C₆H₆/O₂/N₂ (a), C₆H₆-H₂(300%)/O₂/N₂ (b) and C₆H₆/O₂/H₂O (c), C₆H₆-H₂(300%)/O₂/H₂O (d) and relative temporal temperature profiles as function of the residence time.

Fig 5a shows the rates of reaction 1), 2) and 3) for the system C₆H₆/O₂/N₂ and the relative temporal temperature profile as function of the residence time. 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. The figure 5a illustrates that the branching reaction is the dominant reaction for this operative condition. It is followed by reaction 4) O + H₂ ⇒ OH + H and 5) OH + H₂ ⇒ H₂O + H. This pathway increases the pool of radicals that allow for sustaining the oxidation process. In figure 5b the rates of the three reactions are reported for the system C₆H₆-H₂/O₂/N₂ as function of the residence time. In
this case it is recognizable the same pathway but hydrogen promotes the ignition, which occurs for a lower residence time in comparison with the first system, and doubles the rates of production.

Figure 5c reports the rates of reactions 1), 2) and 3) for the system C₆H₆/O₂/H₂O. In this case the steam break-down plays a crucial role as source of radicals. In fact reaction 3) provides for OH radicals that can lead the system to ignite. At the same time reaction 2) is faster than reaction 1) for any residence time. The breaking reaction produces HO₂ radicals, which are relatively less reactive than OH radicals, they mainly form H₂O₂ that, in turn, decomposes forming OH radicals. This pathway is relatively slower respect to the one that starts from reaction 1), this implies that the system is less reactive.

In these operative conditions reaction 2) is favored respect to reaction 1) because water third-body efficiency (α) in three-body reactions is significantly high. In fact in the kinetic mechanism used for these numerical simulations α_{H₂O} in reaction 2) is ten times higher than α_{C₆H₆}. It is worth noting that in correspondence of the break-down of the water there is a first increase of temperature. Moreover the temperature gradually increases up to the stationary state.

Figure 5d shows temperatures profiles for the system C₆H₆H₂/O₂/H₂O as function of the residence time. Hydrogen modifies the evolution of benzene oxidation, in fact in this case the reaction 2) is the fastest one among the considered reactions. Before the autoignition time the system reactivity is damped. In fact the reaction rate of benzene is lowered since OH radicals, formed mainly through the steam break-down reaction, react with the hydrogen available in the system. This produces water and H radicals that, in turn, react mainly through reaction 2).

Benzene is oxidized with a lower velocity since O radicals, mainly produced by the reaction of C₆H₆ with molecular oxygen, are not available in the system because they react with H₂, giving rise to OH radicals and H radicals. The former radical reacts with benzene producing water, the latter one produces HO₂ by means of reaction 2).

Once the ignition reaction starts, the pool of radical increases and they sustain the oxidation process. Steam plays again an important role in fact enhances the OH radical concentration by means of reaction 3).

5. Conclusions

This study represents a preliminary evaluation of the effect of the steam and of hydrogen on the oxidation of formaldehyde and benzene in Mild condition by evaluating the autoignition time and the steady state attainment. These parameters are important in the design of thermal VOC destruction plant since they influence the abatement efficiency then the plant dimension. It has come out that steam dilution implies not only lower autoignition times but also longer times for the attainment of the steady state. However for very high water content there is an increase of the autoignition time. This implies that there is an optimum value of steam content that allows for the attainment of the steady state condition by the minor residence time.

Hydrogen addition to systems diluted in nitrogen promotes the oxidation reactions and anticipates the steady state condition. In systems diluted in steam hydrogen delays the autoignition of the mixture but anticipates the attainment of the full destruction of the VOC. The rate of production analysis has shown that the H₂/O₂ reactions that promote the ignition and the destruction of volatile organic compounds are sensibly modified by the presence of water and hydrogen.
References