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VOC destruction by water diluted hydrogen mild combustion

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Abstract

This study represents a preliminary numerical evaluation of the effect of steam dilution and hydrogen addition on the oxidation of formaldehyde and benzene, chosen as representative of the volatile organic compounds (VOC), in mild condition by evaluating the autoignition time and the steady state attainment. These parameters are important in the design of thermal VOC destruction plants since they influence the abatement efficiency and, therefore, the plant dimension.

It has come out that, in comparison with the system diluted in nitrogen, steam induces lower autoignition times and, on the other hand, longer times for the attainment of the steady state. In contrast, for very high water content the autoignition time slightly increases. In particular results have shown that is possible to identify an optimum value of steam content that allows for the attainment of the steady state condition by the lowest residence time.

Hydrogen addition to systems diluted in nitrogen promotes the oxidation reactions and anticipates the steady state condition. In steam diluted systems hydrogen delays the autoignition of the mixtures even though anticipates the attainment of the complete destruction of the VOC.

The rate of production analysis has showed that the H_2/O_2 reactions, that promote the ignition and the destruction of VOC, are sensibly modified by the presence of water and hydrogen.

Keywords: Formaldehyde oxidation; Benzene oxidation; Steam dilution; Hydrogen addition

1. Introduction

Thermal destruction of volatile organic compounds (VOC) is a mature technology, largely applied in case 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% up to 99% of removal efficiency in dependence of the temperature and residence time used in the process (Donley and Lewandowski, 1996; Haden Drysys International Ltd, 1997). The typical combustion chamber temperatures in thermal oxidation devices range from 950 K up to 1100 K. Coupled with the required inlet VOC concentrations, fixed at 25% or 50% of the low flammability limit according to the specific application for safety regulations (AWMA, 1992), 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 finalized to 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_x. The use of the auxiliary fuel can be completely avoided by pre-heating the reactants at a temperature higher than the VOC autoignition

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temperature so that the oxidation process can evolve without an external support. In this case, in order to keep the maximum temperature lower than the threshold temperature of NO_x and soot formation, a high dilution level has to be used. These working conditions (i.e. high pre-heating and dilution of reactants) are characteristic of mild combustion (Cavaliere and de Joannon, 2004), an innovative combustion technology that shows very peculiar behavior and several advantages in process and pollution control. For instance, it is characterized by the absence of a traditional flame with a reaction volume covering a wide region of the combustion chamber. This allows to avoid the presence of strong thermal gradients and hot spots, in fact the process is characterized by nearly homogeneous concentration and temperature profiles. The presence of a high radical concentration due to the peculiar reaction conditions favors the oxidation of pollutant species injected in the system. Therefore, the clean and cleaning characteristics of mild combustion (Cavaliere and de Joannon, 2004), are simultaneously effective in the same process.

In addition, a mild combustion process can coexist in the same unit with complementary pollutant abatement techniques. For instance, it is discussed in literature (Cavaliere and de Joannon, 2004) that the working temperature range of mild combustion coincides with the narrow temperature range where selective non-catalytic reduction of NO_x is feasible. Therefore the two processes can contemporaneously evolve in the same cleaning section of an industrial plant.

A further improvement in pollutant abatement consists of a suitable choice of the diluent that can increase the efficiency of the system. This is the case of species that can be involved in the reaction process, such as happens for water. For instance, in water diluted mild combustion the diluent can favor the VOC oxidation for its propensity to give radicals in the thermal working conditions characteristic of this process. Furthermore, in case of water dilution, the diluent can be condensed in a downstream unit allowing for separation of particles from flue gas. 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.

Similar considerations apply for the use of a clean fuel enhancer, such as hydrogen. It can play the same role as water with the production of a significant amount of radicals that increase the efficiency of the system by reducing the characteristic time of the process.

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

In this framework, the paper aims to show an analysis of VOC oxidation in mild combustion regime by evaluating, in addition, the effect of the diluent and of a fuel enhancer on the efficiency of the process. The two simplest compounds, representative of oxygenated and aromatic VOC, were chosen for this study. Therefore, the oxidation process of formaldehyde and benzene was followed in preheated, diluted condition of mild combustion. The effect of diluent was evaluated by comparing results obtained using nitrogen and/or steam as diluent. In any case the effect of hydrogen addition on the evolution of the process was analyzed.

2. Numerical tools

The numerical simulations were run using the PLUG (Kee et al., 2003a) application of the Chemkin 3.7 software (Kee et al., 2003b) that 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 arbitrary geometry.

Formaldehyde and benzene were chosen as representative of the VOC. The former species was 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 (Westbrook and Dryer, 1984).

The oxidation kinetic mechanisms used were the c1c3ht0512.cki (www.chem.polimi.it/CRECKModeling/c1c3ht0512.cki) for formaldehyde and the ht0512.cki (www.chem.polimi.it/CRECKModeling/ht0512.cki) for benzene.

The kinetic mechanisms were opportunely validated for several operative conditions and different reactor configurations, such as well described in literature (Ranzi et al., 1994; Faravelli et al., 1997; Granata et al., 2005). A further validation analysis has been here reported by considering experimental data collected in operative conditions very close to the ultralean conditions typical of a VOC abatement process considered in this paper. Fig. 1 shows a comparison between temperature profiles measured in an adiabatic turbulent plug flow reactor as function of the residence time for benzene (Venkant et al., 1982) and

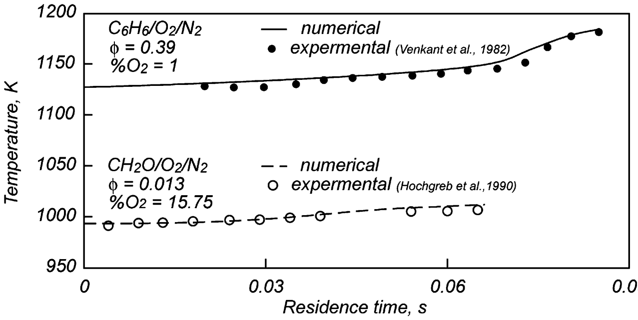

Fig. 1. Comparison of experimental data and numerical computation in ultralean conditions.