

Innovative technique for the control of NO_x formed in combustion processes

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Abstract

NO_x formed in combustion processes is mainly constituted by nitrogen monoxide (NO) while nitrogen dioxide (NO_2) accounts for marginal concentration only. However, being NO_2 characterized by higher water solubility and equilibrium constant in the neutralization reaction operated with basic reactants, it is easily removed via dry or wet processes. On this basis an innovative process alternative to the conventional DeNO_x SCR and SNCR can be envisaged, where the oxidation of NO to NO_2 makes the successive abatement of the oxidized fraction relatively easier. The scope of the work is the study of the oxidation of NO to NO_2 , considered as the controlling step of the proposed process, operated with hydrogen peroxide (H_2O_2). A mathematical model of the oxidation has been developed in the Chemkin v. 3.7 environment, describing the gas phase kinetics in the energy recovery section of a generic combustion process through the Miller and Bowman (1989) kinetic mechanism. The base model has been improved with the introduction of the oxidation steps induced by the injection of hydrogen peroxide drawn from the literature. The NO oxidation reaction was investigated in a temperature range of 250-700°C, with a 20% excess of oxidizing agent with respect to the NO/oxidizer oxidation reaction stoichiometry. The experimental maximum conversion results are less than the calculated one of about 20%. The results of the model have been validated through experimental runs conducted in a bench scale pilot plant.

Keywords: DeNO_x, flue gas treatment, NO_x chemistry.

1 Introduction

Flue gas formed in combustion processes contains NO_x in the form of nitrogen monoxide (NO) and dioxide (NO_2) in variable amounts, the former being the



predominant chemical species. Oxidation of NO to NO₂ can constitute a promising alternative control strategy in NO_x emission being NO₂ easily absorbed in existing scrubber for sulphur dioxide removal. In comparison with nitrogen monoxide, nitrogen dioxide is in fact characterized by higher solubility and reactivity in water or alkali solutions. The NO₂ Henry constant is five times the value reported for NO [1], and the reactivity of this gas further increases its solubility. So, once oxidized in NO₂ form, NO_x could in principle be removed by a simple wet scrubbing. Several oxidation processes have actively been studied. Lyon et al. [2] proposed the use of methanol, Murakami et al. [4, 5] the use of methanol, formaldehyde and hydrogen peroxide, Hjuler et al. [3] the injection of methanol, ethane, acetone, acetaldehyde or methylamine. In this study the results of an experimental campaign to investigate the effectiveness of hydrogen peroxide as an oxidizing agent are reported. The obtained oxidation conversions were interpreted, through a kinetic mechanism, modelling the gas phase reaction in the ChemkinTM environment.

2 Experimental section

2.1 Experimental test setup

The experimental test setup is shown in Figure 1. The gas with a known NO concentration is fed through a flow rate controller from a cylinder to a preheater consisting in a quartz tube (20 mm diameter and 450 mm length) inserted in a tubular furnace with adjustable temperature. The tube is filled with alumina cylinders (1 × 8 mm) to improve the heat transfer and obtain the temperatures scheduled for the tests. At the exit of the preheating section, the oxidizing agent is injected through a capillary silica duct (0.53 mm diameter) fed by a

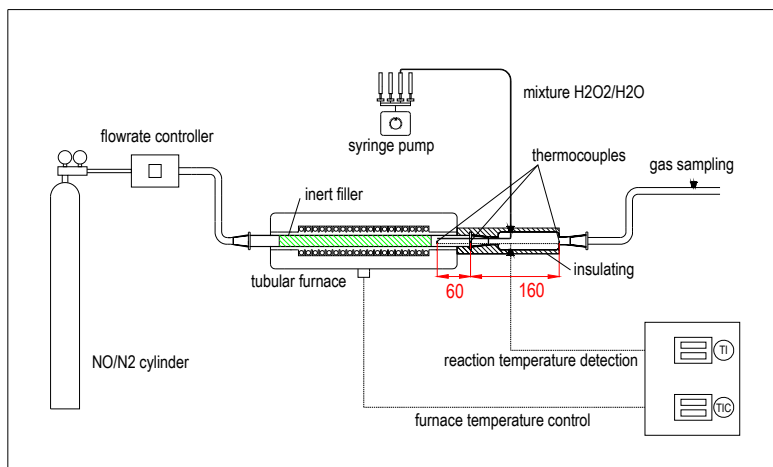


Figure 1: Experimental test setup.

programmable syringe pump at the set flow rate. The reaction zone consists of two quartz tube sections, both of 110 mm in length, but with different diameters (from 20 mm to 32 mm), to allow an easy insertion of the oxidant supply line. The sections outside the furnace are insulated with rock wool to limit heat dispersion and gas cooling. However, in preliminary runs, evidence was obtained of a progressive cooling of the reaction mixture in the reaction volume. So, three thermocouples were inserted in different locations to monitor the temperature trend. From the exit of the reaction zone, the gas is conveyed through an 8 mm tubing up to a sampling port. During all the reactions the pressure in the system is considered atmospheric.

2.2 Materials and operative parameters

A cylinder of certified mixture containing 2000 ppmv of NO in N₂ supplied by Siad was used as a gas feed. Hydrogen peroxide 38% was supplied by Carlo Erba and, before use, the concentration of H₂O₂ was determined by iodometric titration. The conversion in the oxidizing process was computed measuring the NO₂ concentration in the gas mixture exiting the reaction volume by a GC/MS Agilent 5973 instrument. In all the tests the gas flow rate was set to 1.0 L min⁻¹ and the H₂O₂/NO molar ratio was maintained equal to 1.2 by setting the oxidizing solution flow rate at 8.6 µL min⁻¹. The injected solution instantly vaporizes and, due to the order of magnitude of the used volume, the heat of vaporization was considered negligible with respect to the established temperature profiles.

The operative conditions for each test at the injection point are reported in Table 1. In the same table the observed experimental conversions are also reported.

Table 1: Operative conditions at the injection point.

T_{inj} [°C]	Q_{gas} [L min ⁻¹]	U [cm s ⁻¹]	μ [mPa s]	ρ [g L ⁻¹]	Re []	Conv [%]
250	1.755	9.316	27.054	0.6524	44.93	13.73
260	1.789	9.494	27.410	0.6402	44.35	33.62
270	1.822	9.672	27.762	0.6284	43.78	44.44
350	2.091	11.097	30.406	0.5424	39.98	77.90
370	2.158	11.453	31.019	0.5307	39.19	81.91
420	2.326	12.343	32.467	0.4924	37.44	76.11
450	2.426	12.878	33.279	0.4719	36.53	73.28
520	2.661	14.125	35.004	0.4303	34.73	67.31
610	2.963	15.728	36.876	0.3864	32.96	38.60
690	3.232	17.153	38.214	0.3543	31.81	12.69
700	3.265	17.331	38.360	0.3507	31.69	11.22

The temperature detection at the locations highlighted in Figure 1 allowed the reconstruction of the temperature profiles developed in each test; essential information in the experimental results interpretation. As reported in Table 1, the



calculated Reynolds number values indicate that the reactive flow is always in the laminar regime, an occurrence which plays a relevant role in the data analysis.

3 Modelling the experimental rig

The pilot plant was modelled as a plug flow reactor (PFR) by the PLUG routine available in the package ChemkinTM v. 3.71 [6]. This routine allows the insertion by the user of both the effective temperature profiles and the geometry variation of the reaction volume, according to the description reported in Figure 1. The inlet gas, considered premixed in its components, is defined in composition by the molar fractions reported in Table 2.

Table 2: Gas phase flow rate and composition in the experimental tests.

	Flow rate [moles min ⁻¹]	Molar fraction []
N ₂	0.040790	0.9883180
NO	0.000082	0.0019806
H ₂ O	0.000302	0.0073247
H ₂ O ₂	0.000098	0.0023767

Further data necessary in running the simulations are reported in Table 1.

The kinetic mechanism to model the gas phase chemistry is that proposed by Miller and Bowman [7], particularly suitable to study nitrogen chemistry, which includes the mechanisms and the connected kinetic parameters for the thermal-, prompt- and fuel-NO formation and for the formation and destruction of NO₂. The selection of this mechanism is due to its completeness and accuracy.

4 Results and discussion

The comparison of the experimental conversions and the calculated ones is reported in Figure 2. As can be noted, the values of the experimental conversions are lower than the conversions obtained in the simulation.

A simple explanation of the difference between experimental and calculated conversions can be drawn in terms of mixing of the two flows fed to the reactor. In the experimental setup the gas flow from the preheater is in the laminar regime and this occurrence influences the actual mixing which develops from the oxidizer injection point. In the simulations, otherwise, the hypothesis is made that the two flows are premixed at the reaction volume inlet. The influence of the mixing in the reactive flows behaviour is widely reported in the literature, in particular in the processes that involve NO_x [8, 9]. The fundamental but simplified approach here considered is based on the description of the mixing process after Zwietering [10].

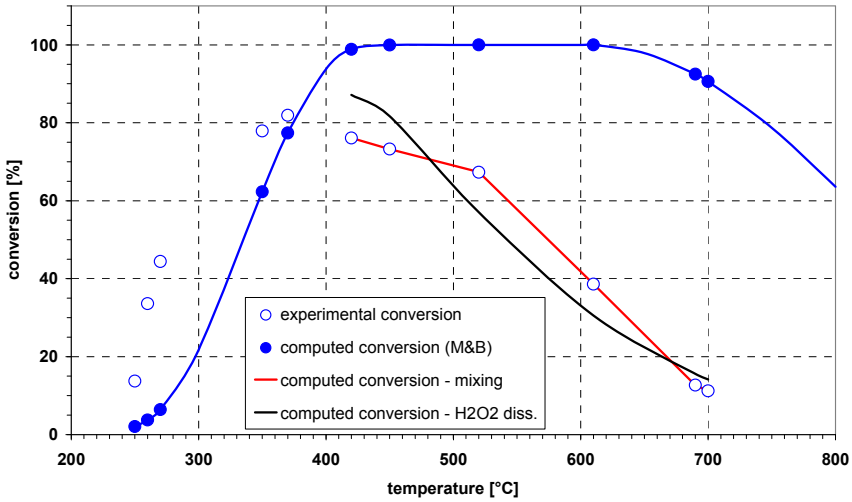


Figure 2: Comparison between experimental and calculated conversions.

In the present case, the gas flow fed to the reaction zone is continuously diluted by the oxidizing mixture which becomes available for the reaction. The mass flow of the gas stream at a given time can be expressed as

$$\frac{dm_{bulk}}{dt} = km_{inj} \quad (1)$$

where m_{bulk} is the mass flow across the system, m_{inj} the injected mass flow and k a fictitious constant accounting for the mixing. In this hypothesis, the mass flow across the reaction system at a given time can be expressed as

$$m_{bulk}(t) = m_{bulk,0} + m_{inj,0}[1 - \exp(-kt)] \quad (2)$$

The k constant can be computed from a value of time that would correspond to a given percentage of injected reactant incorporated into the main flow, that is with reference to an experimentally determined or estimated mixing time according to

$$k = \frac{\ln\left(\frac{m_{inj,0}}{m_{inj,t}}\right)}{t} \quad (3)$$

In the present case, the mixing time is defined as the time necessary to mix the injected H_2O_2 solution with the gas flow in the H_2O_2/NO stoichiometric ratio.

Because of the actual molar ratio is 1.2, the ratio between the injected molar flow rate at the end of the useful mixing and the fixed one is

$$\frac{1.0}{1.2} = 0.83 \quad (4)$$

Thus, time mixing corresponds to the mixing of the 83% of the injected oxidizing flow rate, t_{83} , from which follows

$$\ln\left(\frac{m_{inj,0}}{m_{inj,t}}\right) = \ln\left(\frac{100}{17}\right) \quad (5)$$

In this relationship, the quantity 17 represents the flow rate not mixed within the defined mixing time, as referred to an initial flow rate equal to 100. Finally, the following equation is obtained linking the k constant to the defined mixing time

$$k = \frac{\ln(100/17)}{t_{83}} \quad (6)$$

In this approach no attempt is made to describe the physical phenomena occurring in the mixing region, however a fundamental mixing characteristic is captured, that is the oxidizing mixture initially reacts in understoichiometric condition, progressively transferring to condition more and more close to the stoichiometric one.

A major advantage of this simplified approach is an easy implementation in the model inserting the fictitious reaction



describing the transformation of the non reactive species H_2O_2^* in the reactive species H_2O_2 with a kinetics represented by the k constant. The PLUG routine of the ChemkinTM package was used to compute the values of the k constant necessary to reproduce by simulation the obtained experimental conversions. The results of these calculations are reported in Figure 2 (red curve). From the computed k constant values, the corresponding mixing times t_{83} were easily calculated as reported in Table 3. These calculations were performed starting from the injection temperature of 420°C, being the experimental and calculated conversions at 370 practically coincident.

The comparison of the mixing times computed at the highest injection temperatures (4.14, 16.30 and 18.60 s at the temperatures 610, 690 and 700°C, respectively) with the residence times of the reacting mixture in the reaction volume, reported as temperature function in Figure 3, clarify the reason why experimental conversions far lower than the simulated ones are observed.

Considering as an example the injection temperature 610°C, in Figure 3 it can be easily noted that the reacting mixture stays in the temperature favourable range for a very short period. Practically, the mixture cools down from the injection temperature to 300°C in about 1 s. However, this residence time in the favourable range of temperature would still be enough to obtain a quantitative conversion of NO to NO₂. The simulation performed when the mixing phenomena are not considered shows an almost instantaneous conversion, as reported in Figure 4.

Table 3: k constant values and corresponding mixing times.

T_{inj} [°C]	k [s ⁻¹]	t_{83} [s]
420	3.66E+00	4.84E-01
450	2.25E+00	7.88E-01
520	1.26E+00	1.41E+00
610	4.27E-01	4.15E+00
690	1.09E-01	1.63E+01
700	9.55E-02	1.86E+01

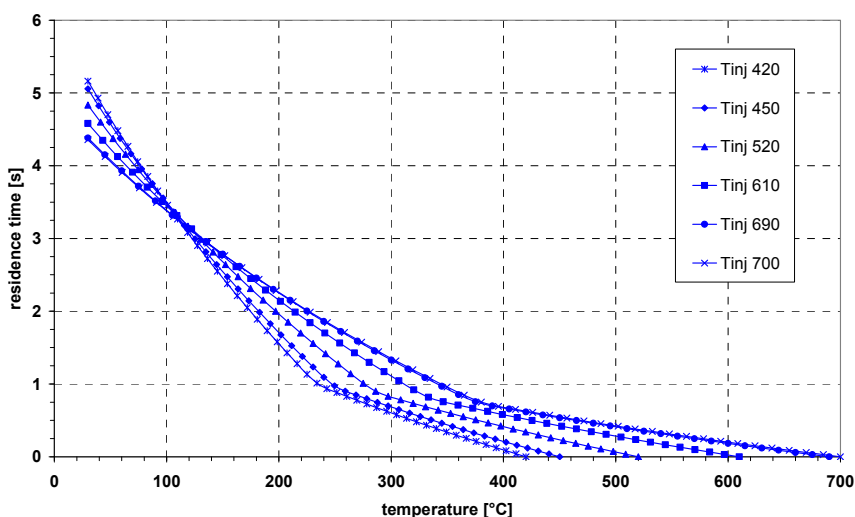


Figure 3: Residence time vs. temperature within the reaction volume.

However, when mixing is taken into account, the time necessary to obtain the mixing of a stoichiometric amount of oxidizing agent is equal to 4.15 s in the considered case, so a period much longer than the residence time in the favourable range of temperature. In other words, in this residence time just a marginal part of the stoichiometric amount of oxidizer is able to mix with the gas flow rate, producing an observed conversion much lower than expected.

The amount of injected oxidizer which effectively mixes with the gas flow rate, m_{inj} , computed via eq. (2) with the k constant determined for the examined case is reported in Figure 4. Within the favourable temperature range ($T_{inj} \div 300^{\circ}\text{C}$), the gas goes about 120 mm in the reaction volume. At this length, only about 42% of the oxidizer is able to mix with the main gas stream, constraining the resulting conversion at a value absolutely lower than that obtained in the case of complete premixing. From this length ahead, the mixing process proceeds, however outside the favourable temperature range, so that conversion increases only marginally. Discontinuities found on the curves representing the oxidizer mixed amount and the conversion when mixing is considered depends on the geometry variation in the reaction volume.

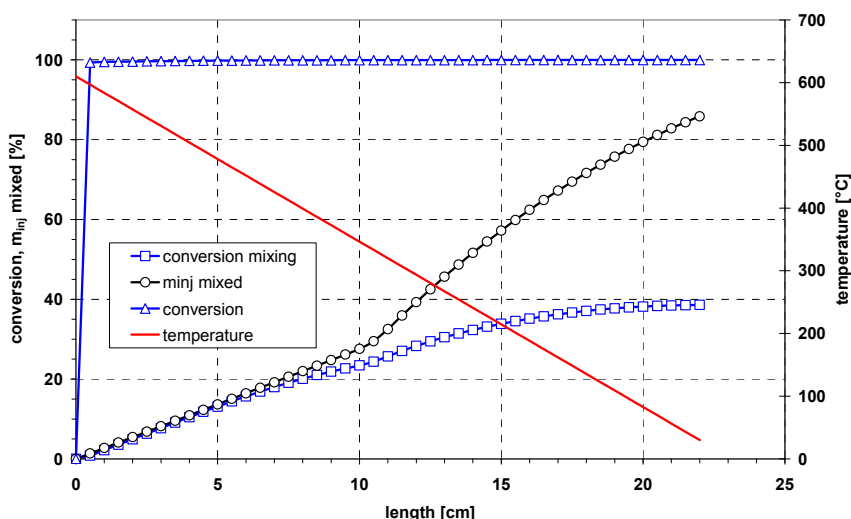
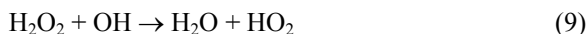


Figure 4: Computed conversions when mixing phenomena are considered or not for an oxidizer injection temperature of 610°C .

The difference between measured and computed conversions can also be explained considering the possible dissociation of hydrogen peroxide in the injection duct and before the mixing happens, according to the reaction



This reaction limits the formation of the active species in NO oxidation, the radical hydroperoxide formed in the reaction



To quantify the influence of the hydrogen peroxide dissociation, reaction (8) has been inserted in the adopted kinetic mechanism and the associate constant rate was varied to reproduce the observed conversions. In Figure 5 the obtained values of the constant rate are reported in the Arrhenius plot, allowing to regress the pre-exponential factor, k_0 , and the activation energy, E , of reaction (8). In

particular, the regressed activation energy of $38667 \text{ kcal kmol}^{-1}$ stays in the range $18000 - 48000 \text{ kcal kmol}^{-1}$ reported in the literature [11]. The introduction of reaction (8) in the kinetic model allows for better representation of the experimental data as shown in Figure 2 (black curve).

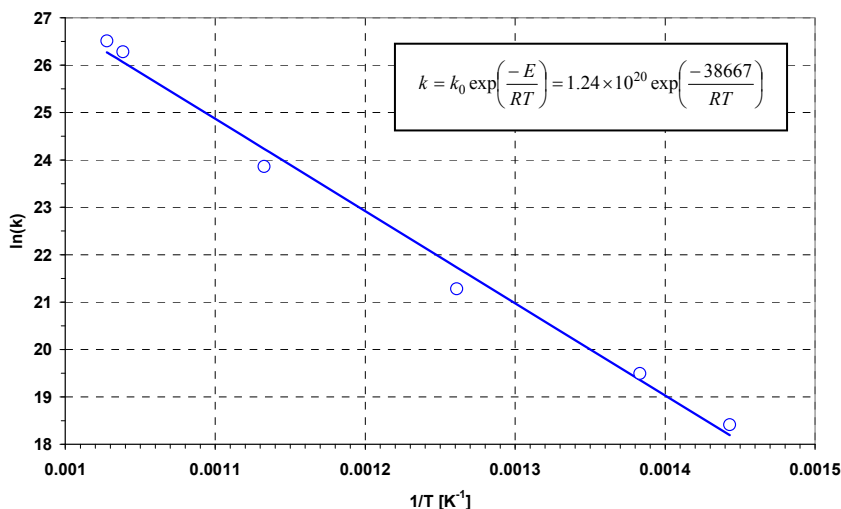


Figure 5: Regression of the Arrhenius parameters of reaction (8).

5 Conclusions

In this work the ability of hydrogen peroxide to oxidize nitrogen oxide to nitrogen dioxide has been investigated. A set of experimental runs has demonstrated that the optimal range of temperature where the selected oxidizer shows its maximum effect is between 350 and 520°C . The observed conversions have been interpreted in the ChemkinTM v. 3.71 environment with the kinetic mechanism after Miller and Bowman. Two effects can explain the differences between the measured and modelled conversions: the mixing dynamics and the oxidizer dissociation. These effects have been considered separately, but obviously they can occur simultaneously. To quantify the influence of both, further experimental work is needed with substantial modification to the experimental setup.

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