

Influence of the amount of ethanol added to acetylene on NO reduction during acetylene-ethanol mixtures oxidation

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Abstract

This work is focused on the experimental and kinetic study of the reduction of NO through acetylene-ethanol mixtures oxidation. The experiments were conducted in an isothermal quartz flow reactor at atmospheric pressure in the 775-1375 K temperature range, and from fuel-rich to stoichiometric conditions. For a given C₂H₂ concentration, the influence of adding different amounts of ethanol on the NO reduction, and the influence of temperature and oxygen concentration on the concentrations of C₂H₂, C₂H₅OH, CO, CO₂, NO and HCN have been analyzed. The experimental results have been simulated and interpreted in terms of a literature detailed gas phase kinetic mechanism for the interactions among NO and acetylene-ethanol mixtures.

Introduction

The emission of nitrogen oxides (NO_x) and soot are important concerns related to diesel engines, and are subjected to stringent emissions regulations aiming to reduce considerably health risks. It has been reported that diesel-ethanol blends can reduce the amount of soot produced under different diesel engine operating conditions [1]. Nevertheless, there is no agreement regarding the NO_x emissions. Some of the studies found in the literature establish that diesel-ethanol blends could reduce the final NO_x emissions [1-4], while other studies [5,6] have indicated that ethanol in diesel combustion processes can increase the NO_x emissions, depending on the load, speed of the engine and type of biofuel used [6].

Since acetylene is recognized as one of the main soot precursors and it is an intermediate product in many combustion processes [7], it results interesting to analyze the role of acetylene-ethanol mixtures on NO emissions. It is well known that hydrocarbons, such acetylene, can interact with NO under fuel-rich conditions allowing the NO reduction by reburn type reactions [8-10]. Therefore, the NO reduction level reached by the use of pure acetylene can be taken as the reference value to evaluate the effect of the addition of ethanol on NO emissions.

In this context, the aim of the present work is to analyze, for a given C₂H₂ concentration, the influence of adding different amounts of ethanol on the NO reduction under fuel-rich to stoichiometric conditions.

Experimental

The experimental installation used in the present work is described elsewhere [e.g. 11-13] and only a brief description is given here. A quartz plug flow reactor, according to the design of Kristensen et al. [14], is placed in a three-zone electrically heated oven, securing a uniform temperature profile throughout the

reaction zone within ±10 K. The temperature in the reaction zone was measured with a type K fine-wire thermocouple placed into a thin tube along the reactor without contact with reactants. The reactor tube has a reaction zone of 8.7 mm inside diameter and 200 mm in length. The fed gases were supplied from gas cylinders and regulated by mass flow controllers, in up to four separate streams: a main flow containing nitrogen and water vapour, which is fed by saturating a nitrogen stream through a bubbling water system at room temperature, and three injector tubes for the rest of reactants (C₂H₂, C₂H₅OH, NO and O₂, all of them diluted in nitrogen) and N₂ to balance up to obtain a total flow rate of 1000 mL (STP)/min. The configuration of the injection system has been chosen following the investigations of Alzueta et al. [8]. At the outlet of the reactor, the product gas is efficiently quenched by means of external refrigeration with air.

The exhaust gas composition was determined using: a Gas Chromatograph, equipped with TCD and FID, for hydrocarbons, ethanol and permanent gases (such as CO and CO₂); a Fourier transform infrared (FTIR) spectrometer for HCN; and continuous CO/CO₂ and NO analyzers for CO, CO₂ and NO concentrations. The uncertainty of the measurements is estimated as ±5% but not less than 10 ppm.

Reaction Mechanism

The experimental results have been analyzed in terms of a detailed gas-phase chemical kinetic model for the oxidation of acetylene-ethanol mixtures in presence of NO described by Abián et al. [15]. This mechanism is based on that developed by Alzueta et al. [16] for acetylene conversion, on the basis of a previous work by Skjøth-Rasmussen et al. [17] for benzene formation, using methane or methane doped with C₂, C₃, and C₄ hydrocarbons, as the initial hydrocarbon, under fuel-rich conditions. With the addition of reactions for ethanol

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conversion from the mechanism of Alzueta and Hernández [12], as well as reactions from the mechanism developed by Glarborg et al. [18], to describe the interactions among C_1/C_2 hydrocarbons and nitric oxide. All calculations were performed using Senkin [19], a plug-flow code, which runs in conjunction with the Chemkin library [20]. The reverse rate constants obtained from the forward rate constants, and the thermodynamic data were taken from the same sources as the different submechanisms. The full reaction mechanism includes 78 species and 532 reversible elementary reactions, and can be obtained directly from the authors.

Results and discussion

A study of the acetylene-ethanol mixture interaction with NO as a function of the amount of ethanol added for a given acetylene concentration of 500 ppm has been carried out. The experiments were performed at atmospheric pressure, in the 775-1375 K temperature range, under stoichiometric ($\lambda=1$) and fuel-rich ($\lambda<1$) conditions. The influence of added ethanol amount on NO reduction has been analyzed for an inlet NO concentration of 500 ppm, varying the ethanol concentration, as an additive, in the range of 0-200 ppm. Table 1 lists the conditions of the different experiments performed. All the experiments were carried out under high diluted conditions to ensure an isothermal reaction zone. Besides analyzing the influence of ethanol amount on NO reduction, the influence of temperature and the air excess ratio (λ) on the concentration of the main products quantified in this study (C_2H_2 , C_2H_5OH , CO, CO_2 , NO and HCN) have been also analyzed. The more relevant results obtained are shown and discussed below.

Figure 1 shows the outlet NO concentrations as a function of the temperature depending upon the added ethanol content to the mixture for the different air excess ratios studied. The obtained results for $\lambda=1$ and $\lambda=0,7$ (Figures 1a and 1b) present no appreciable NO conversion in the low temperature range (750-1100 K). At intermediate temperatures (1100-1275 K, approximately), a pronounced diminution in NO concentration can be observed, and at the highest temperature region (>1275 K), NO concentration is found to be practically constant. This behaviour is not observed for very fuel-rich conditions ($\lambda=0,2$), Figure 1c. In this latter case, NO concentration decreases gradually in all the reaction temperature window and it does not reach a stable minimum concentration.

For a given stoichiometry, the addition of different amounts of ethanol does not result into a significative difference in the maximum NO reduction level. For $\lambda=1$, Figure 1a, the maximum NO reduction is around 35%, while for $\lambda=0,7$, Figure 1b, the reduction of NO reaches maximum levels of 38%. For $\lambda=0,2$, Figure 1c, the obtained NO reduction levels are not competitive with the ones at fuel-leaner conditions, presenting values around 15%.

It is also noticeable in Figure 1 that the onset temperature for NO conversion varies with the presence and absence of ethanol. This fact is specially appreciable in Figure 1b ($\lambda=0,7$). NO reduction starts as largely acetylene reaction does, and taking into account that acetylene conversion window is shifted to higher temperatures in the presence of ethanol [15], NO consumption is initiated at lower temperatures when ethanol is not present in the fuel mixture. Nevertheless, it is important to remark that the amount of ethanol added does not appear to be an important factor for the maximum reduction NO levels reached.

Table 1. Matrix of experimental conditions^a.

Expt.	[NO] (ppm)	[C_2H_2] (ppm)	[C_2H_5OH] (ppm)	λ	[O_2] (ppm)
Set 1	500	500	0	1	1250
Set 2	500	500	0	0,7	875
Set 3	500	500	0	0,2	250
Set 4	500	500	50	1	1400
Set 5	500	500	50	0,7	980
Set 6	500	500	50	0,2	280
Set 7	500	500	100	1	1550
Set 8	500	500	100	0,7	1085
Set 9	500	500	100	0,2	310
Set 10	500	500	200	0,7	1295

^aAll the experiments are run at a given flow rate of 1000 mL (STP)/min, resulting in a residence time dependent on temperature of $195/T(K)$ seconds. Nitrogen is used to balance. Water vapour was kept constant in all the experiments with a concentration of 7000 ppm.

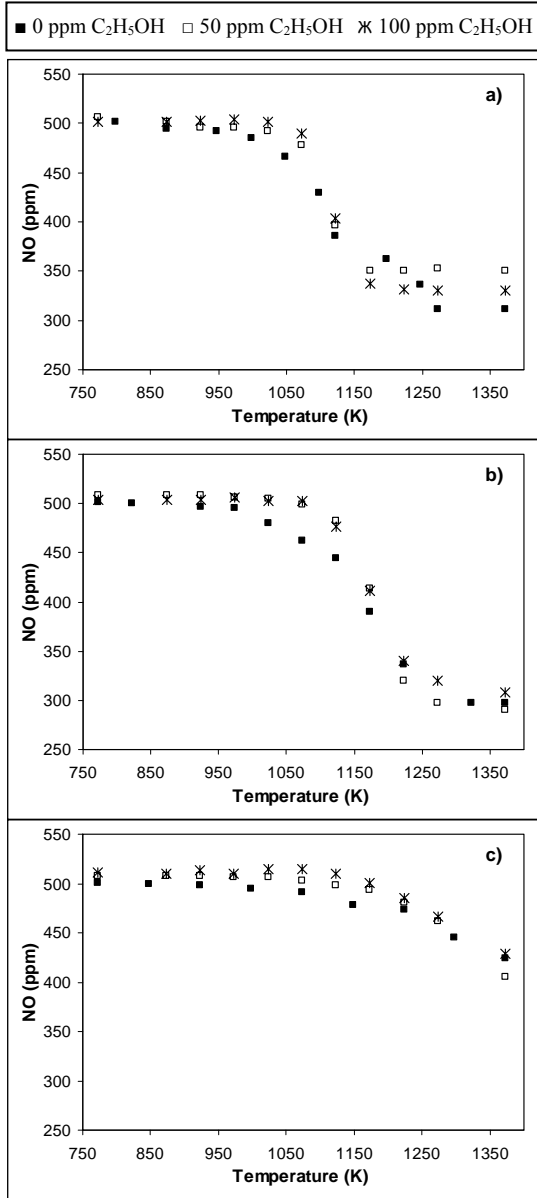


Figure 1. Outlet NO concentration as a function of the temperature for different amounts of ethanol added to the acetylene-ethanol mixture, ranging from 0 to 100 ppm: a) stoichiometric conditions ($\lambda=1$), sets 1, 4, 7 in Table 1; b) moderately fuel-rich conditions ($\lambda=0.7$), sets 2, 5, 8 in Table 1; c) very fuel-rich conditions ($\lambda=0.2$), sets 3, 6, 9 in Table 1.

Figure 2 displays the NO reduction levels (%) as a function of the initial ethanol concentration in the fuel mixture, for the different λ values and selected temperatures representing the different observed temperature intervals. The NO reduction level (%) is defined as the percentage of the quantity NO converted related to the initial NO concentration introduced into the reactor, equation 1.

$$\text{NO reduction (\%)} = \frac{[NO]_{\text{inlet}} - [NO]_{\text{outlet}}}{[NO]_{\text{inlet}}} \times 100 \quad (\text{eq. 1})$$

Although Figure 2 does not provide further information regarding Figure 1, it is very helpful to

analyze the NO reduction data as a function of the amount of ethanol added. It is remarkable that at 1075 K, Figure 2a, NO reductions levels slightly decrease as the amount of ethanol added is increased, whereas at 1175 K and 1375 K, the NO reduction levels remain approximately constant independently of the ethanol content. This fact can be attributed to the progressive shift of the onset of acetylene conversion to higher temperatures as the inlet ethanol amount is increased [15].

These observations reinforce the inference of the non-direct-influence of the amount of ethanol in the reacting mixture on NO reduction.

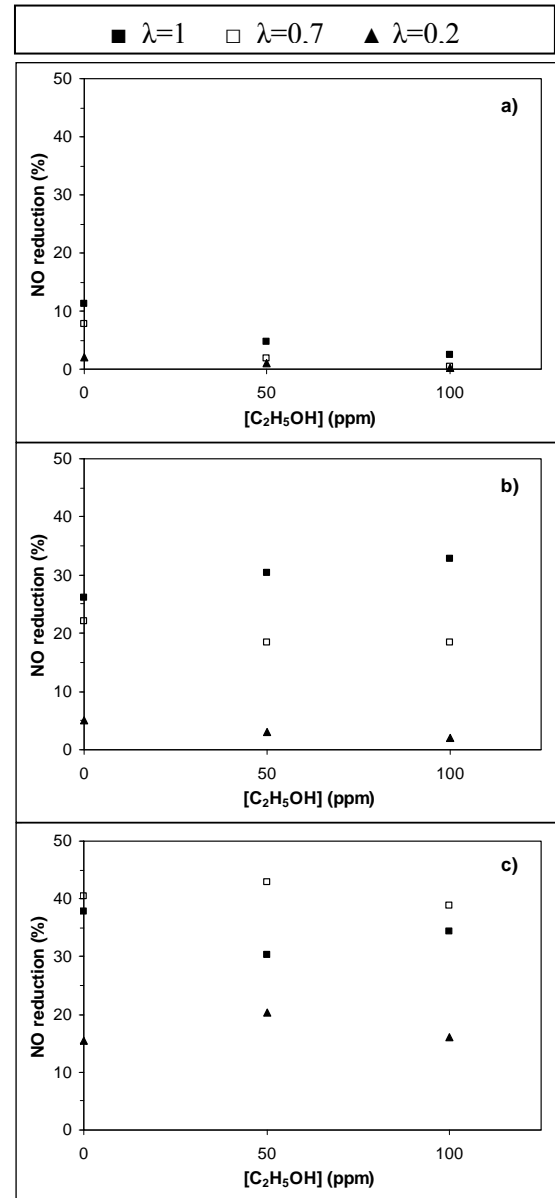


Figure 2. NO reduction (%) as a function of the initial ethanol concentration in the fuel mixture for the different studied stoichiometries ($\lambda=1$, $\lambda=0.7$ and $\lambda=0.2$) and selected temperatures: a) 1075 K, sets 1, 4, 7 in Table 1; b) 1175 K, sets 2, 5, 8 in Table 1; c) 1375 K sets 3, 7, 9 in Table 1.

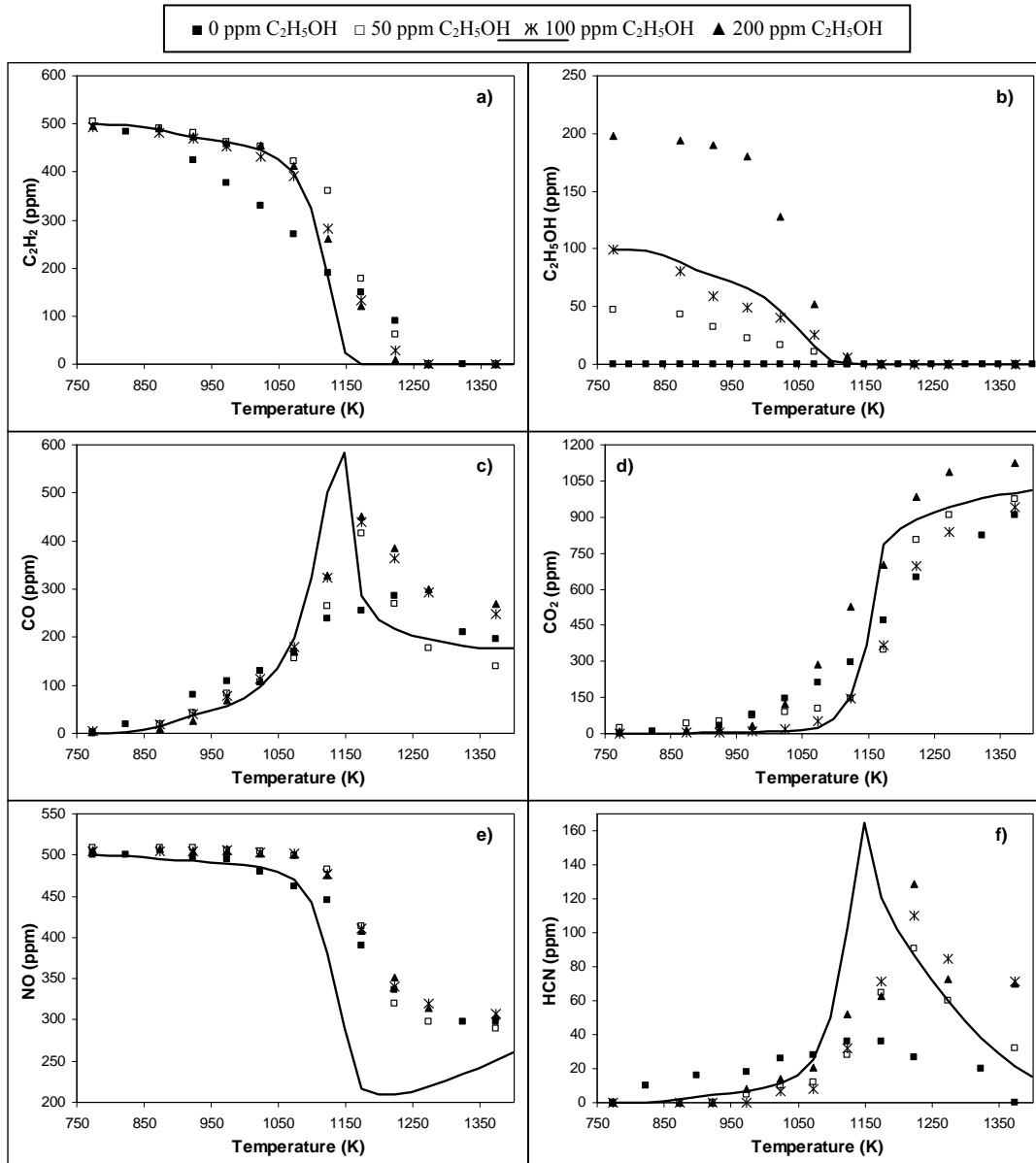


Figure 3. Concentration results of the main output gases quantified as a function of temperature, for different amounts of ethanol added to the mixture (0-200 ppm C_2H_5OH) and moderately fuel-rich conditions ($\lambda=0,7$): a) C_2H_2 , b) C_2H_5OH , c) CO, d) CO_2 , e) NO, f) HCN. The inlet conditions correspond to sets 2, 5, 8, 10 in Table 1. Comparison between experimental data (symbols) and model predictions (lines) for the results obtained under conditions of set 8 in Table 1: $\lambda=0,7$ and 100 ppm C_2H_5OH added to the mixture.

In order to analyze the experimental trends obtained, Figure 3 shows an example of the concentrations of the main outlet gaseous products quantified (C_2H_2 , C_2H_5OH , CO, CO_2 , NO and HCN) as function of temperature, for different initial amounts of ethanol (0-200 ppm) and moderately fuel-rich conditions ($\lambda=0,7$).

As it can be observed from Figure 3, the ethanol concentration does not influence the general evolution of the concentration of the gases represented versus temperature. In those experiments in which ethanol has been added (sets 5, 8, 10 in Table 1), the sharp decay in acetylene concentration (Figure 3a) coincides with the total consumption of ethanol (Figure 3b), as well as with the more

pronounced NO reductions (Figure 3e). Moreover, the ethanol presence shifts the onset for acetylene conversion to higher temperatures. In relation to CO and CO_2 concentrations (Figures 3c and 3d), for a given temperature, as the inlet ethanol concentration increases, generally CO_2 concentration also increases. In the cases in which ethanol has been added to the mixture, CO peak levels reaches approximately the same value for the different ethanol concentrations. This fact might be due to the oxygen content in ethanol which seems to favor the complete oxidation to CO_2 .

Similarly to the trends observed in Figure 1, as the temperature increases, the NO concentration decreases gradually (Figure 3e), at around 1300 K,

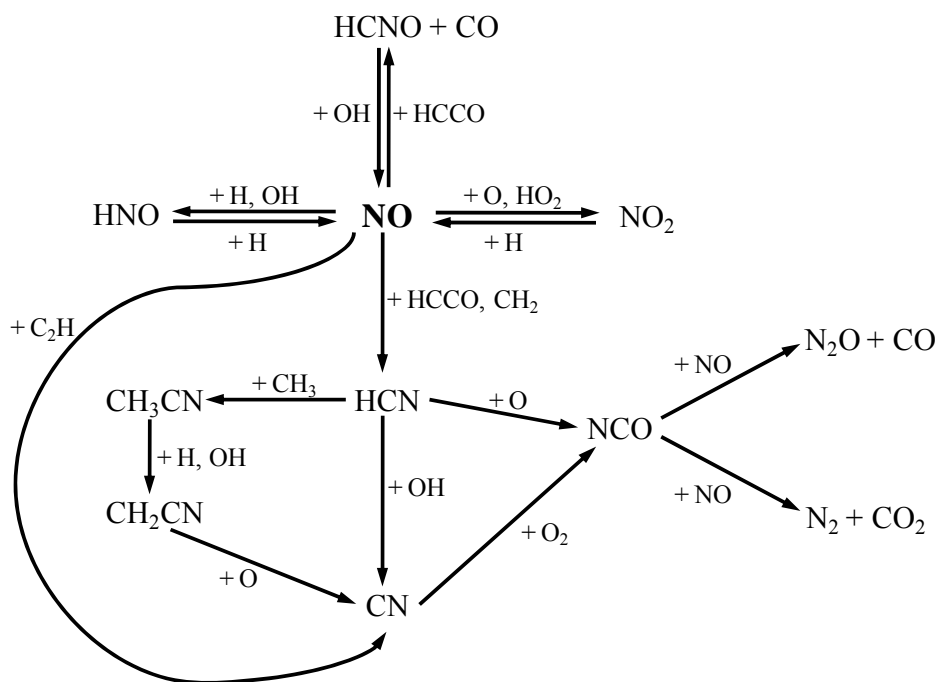


Figure 4. Reaction path diagram for reactive nitrogen conversion in acetylene-ethanol mixtures oxidation under the conditions of sets 2, 5, 8 in Table 1.

remaining approximately constant at higher temperatures which coincides with the total consumption of acetylene.

The formation of HCN peaks at temperatures slightly higher than the onset of NO removal, coinciding with the sharper reduction of NO. This fact can be attributed to the general mechanism of the reburn chemistry in which HCN is an intermediate product in the reduction of NO by hydrocarbon radicals [8,18,21]. An increase in the reaction temperature results into an increase of HCN concentration, which reaches values from 100 to 140 ppm. Nevertheless, for the highest temperatures studied, the concentration of HCN diminishes again, because the oxidation reactions of HCN become faster at those temperatures [21].

The gas-phase chemical kinetic model proposed by Abián et al. [15] for the oxidation of acetylene-ethanol mixtures in presence and absence of NO has been used in the present work. This mechanism was previously used for modeling NO conversion during acetylene-ethanol mixtures oxidation reproducing in a satisfactory way the main experimental trends for C_2H_2 , C_2H_5OH , CO, CO_2 , NO and HCN, and the main acetylene and ethanol consumption routes were identified.

Figure 3 shows an example of the comparison between model predictions (lines) and the experimental data (symbols) for the main output gases quantified (C_2H_2 , C_2H_5OH , CO, CO_2 , NO, HCN) under conditions of set 8 in Table 1, i.e., $\lambda=0,7$ and 100 ppm added ethanol. As it can be observed, the model matches reasonably well the experimental profiles. Notwithstanding, the model somewhat overpredicts the NO reduction in comparison with the experimental

results. In this context, some improvements of such kinetic model are still needed.

In this study, the model has been used to perform NO reaction rate analysis with the aim of identifying the significant reactions and species that significantly contribute to NO reduction as function of ethanol amount added in the initial mixture. According to model predictions, the effect of ethanol is mainly to modify the composition of the radical pool rather to react directly with nitrogen species. This fact is in agreement with the results obtained by Alzueta and Hernández [12] who pointed out that, under the conditions of these experiments, pure ethanol oxidation did not show any reduction of NO by reburn-type reactions.

The calculations indicate that the predicted oxidation of acetylene-ethanol mixtures and their potential for reducing nitric oxide are very sensible to the reactions with O_2 and different radicals (OH, H, O, CH_3 , and HO_2). The most important consumption routes for reactive nitrogen species conversion are shown in Figure 4. The interconversions NO/ NO_2 and NO/HNO by reaction with the radical pool do not contribute to NO removal [18]. The reduction of NO is largely produced by reaction with HCCO, and in a smaller extent with the CH_2 radical (reactions 1 and 2), because acetylene is a direct source of these radicals under the conditions of the present work, being in concordance with the literature [10, 16, 18].



The HCN quantified is formed mainly through the reactions cited above (reactions 1 and 2), and

subsequently it is converted to NCO radicals and latter to N₂O and N₂.

For ethanol no effect is observed, in agreement with the conclusions of Alzueta and Hernández [12].

Conclusions

The influence of the amount of ethanol added to acetylene on NO reduction has been studied in a quartz flow reactor at atmospheric pressure, covering the temperature range of 775-1375 K and different air excess ratios, ranging from fuel-rich to stoichiometric environments. The initial concentrations of acetylene and NO have been kept constant at 500 ppm for both compounds, while the ethanol concentration added, as an additive, has been varied in the range of 0-200 ppm.

Under the conditions studied, the experimental results show that ethanol does not directly affect to the NO reduction, however, it does affect to the acetylene oxidation regime. At low temperatures around 1075 K, it is appreciated that as ethanol concentration is increased in the reacting mixture, the NO reduction level reached is slightly lower. This fact can be attributed to the shift of the onset acetylene conversion which occurs at higher temperatures in the presence of ethanol, affecting the hydrocarbon radical formation. Nevertheless, the maximum NO reduction levels reached are not significantly affected by the ethanol presence in the mixture.

The maximum NO reduction levels reached by the acetylene-ethanol mixtures are around 38%, for $\lambda=1$ and 0,7, and have been found at the highest temperatures studied, above 1225 K.

The experimental results have been analyzed in terms of a detailed gas-phase chemical kinetic model from literature in order to identify the main reaction pathways for NO conversion as function of the inlet ethanol content. The model predictions indicate, under the conditions investigated, NO reduction present any significant dependence with the ethanol concentration in the mixture, which is in agreement with the experimental results. Calculations suggest that hydrocarbon radicals generated from acetylene conversion are the main responsible of the different NO reduction levels reached, being the radical HCCO the main responsible. These results are in agreement with the literature [10,16,18].

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