

Ethanol as fuel additive: high-pressure oxidation of its mixtures with acetylene

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Abstract

An experimental and modeling study of acetylene-ethanol mixtures under high-pressure conditions (10 and 40 bar) has been carried out in the 575-1075 K temperature range. The influence of the oxygen inlet concentration (determined by λ) and the amount of ethanol present in the reactant mixture on the oxidation process has also been evaluated. The predictions of the proposed model are in satisfactory agreement with the experimental data. The onset for acetylene conversion is almost the same independently of the oxygen or ethanol concentrations in the reactant mixture, but it is shifted to lower temperatures when the pressure is increased. Under the conditions of this study, the ethanol presence does not modify the main reaction routes for acetylene conversion.

INTRODUCTION

Fuel reformulation seems to be a promising strategy for minimizing particulate matter and nitrogen oxides emissions from diesel engines. This reformulation implies the total or partial replacement of the fuel by alternative ones, preferably from renewable sources, including alcohols such as ethanol or butanol [1]. Some advantages of this reformulation are its immediate effects on diminishing pollutant emissions and its implementation without significant changes in the design of the equipment.

Among all possible biofuels, ethanol is one of the most widely studied and used, directly or as a gasoline additive. However, its application in diesel engines is restricted because its cetane number, flash point and calorific values are lower compared to diesel. Therefore, ethanol should be blended with diesel or biodiesel to overcome all these difficulties. Regarding to the exhaust pollutant emissions, although there is a bit of controversy, some authors indicate that, working under the proper conditions, CO, soot and nitrogen oxides emissions could be reduced [2].

This controversy makes necessary a systematic study at laboratory scale under well controlled operating conditions to acquire a better knowledge of the possible effects of the ethanol addition to fuel. A possibility is to consider acetylene-ethanol mixtures. In this work, acetylene (C_2H_2) has been set as the main fuel since it is recognized as one of the main soot precursors and it is an important intermediate in combustion of hydrocarbons.

In this context, the aim of the present work is to analyze the oxidation of C_2H_2 -ethanol mixtures under high-pressure conditions from both experimental and modeling points of view. The experimental results have been used to validate a chemical kinetic mechanism able to describe the oxidation of both compounds and their mixtures under the conditions studied. This will extend the applicability of the model to other operating conditions and it can be used as a predicting tool.

METODOLOGY

The experimental section of this work, which has been carried out in a high-pressure gas phase experimental set up described in detail in Marrodán et al. [3], includes a study of the oxidation of C₂H₂ (approximately 500 ppm) and ethanol (50-200 ppm) blends. The oxygen inlet concentration has been varied from reducing to oxidizing conditions by modifying the value of lambda, defined as the inlet oxygen concentration divided by the stoichiometric oxygen, that is $\lambda=0.7, 1$ or 20 . Nitrogen is used to balance up to obtain a total gas flow rate of 1000 (STP) mL/min. Reactant mixtures are highly diluted minimizing the reaction thermal effects. An isothermal reaction zone of 56 cm was obtained (± 10 K), resulting in a gas residence time that depends on pressure and temperature in the way: $t_r[s]=261 \cdot P[\text{bar}]/T[\text{K}]$. To evaluate the influence of pressure on the oxidation process, two different pressures, 10 and 40 bar, have been studied, whereas the influence of the temperature has been analyzed in the 575-1075 K temperature range. On the other hand, model calculations have been performed using the software CHEMKIN-PRO [4], with the proposed chemical kinetic mechanism and thermodynamic data for the involved species as input files. A more complex description of the detailed mechanism used in this work was presented in [5] and can be obtained directly from the authors.

RESULTS AND DISCUSSION

Figure 1 compares experimental results (symbols) and modeling predictions (lines) obtained for the conversion of C₂H₂ and formation of CO (as one of the major oxidation products), for 10 bar, when 50 ppm of ethanol have been added to the reactant mixture and for the different values of lambda analyzed. The mechanism used provides, in general, good agreement between experimental results and modeling predictions, reproducing well the experimental trends obtained under the conditions of this study.

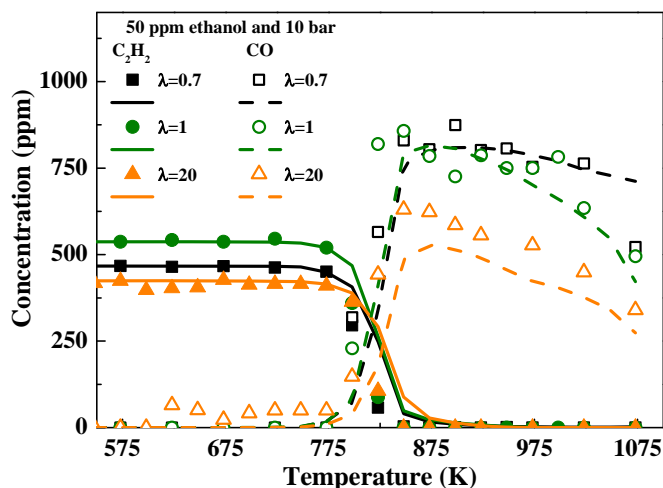


Figure 1 Influence of temperature and oxygen concentration (λ) on C₂H₂ conversion and CO formation. Comparison between experimental results (symbols) and modeling calculations (lines).

As it is shown in Figure 1, the inlet oxygen concentration does not clearly modify the acetylene oxidation regime and CO formation. Similar results are obtained for higher

amounts of ethanol added to the reactant mixture (results not shown). The temperature for the onset of C_2H_2 oxidation and, therefore, the onset for CO formation are almost independent of the value of lambda analyzed. Under the conditions of this work, the ethanol is consumed completely for the stoichiometries analyzed and its conversion starts at almost the same temperature independently of the inlet oxygen concentration. Other study of C_2H_2 -ethanol mixtures, but under atmospheric pressure conditions [6], also indicates that the onset temperature of acetylene and ethanol conversion is almost the same for all the values of lambda analyzed. However, unlike what is observed at high pressure, for atmospheric pressure, the temperature range for the full consumption of acetylene and ethanol is different depending on the value of lambda analyzed. Thus, at atmospheric pressure and the leanest conditions studied, the full conversion of acetylene is produced at approximately 100 K below compared to $\lambda=0.7$ and stoichiometric conditions, while for $\lambda=0.2$, acetylene is not completely consumed even for the highest temperatures analyzed, 1375 K.

As it can be seen in Figure 2, for the conditions studied in this work, the C_2H_2 oxidation regime is not influenced by the amount of ethanol added to the reactant mixture. Only an increase in working pressure, from 10 to 40 bar, appears to shift the onset of C_2H_2 oxidation to lower temperatures, approximately 100 K. The C_2H_2 conversion at 40 bar starts at 725 K, which is approximately the same temperature than that obtained under similar experimental conditions by Giménez et al. [7] in a high-pressure (60 bar) oxidation study of C_2H_2 .

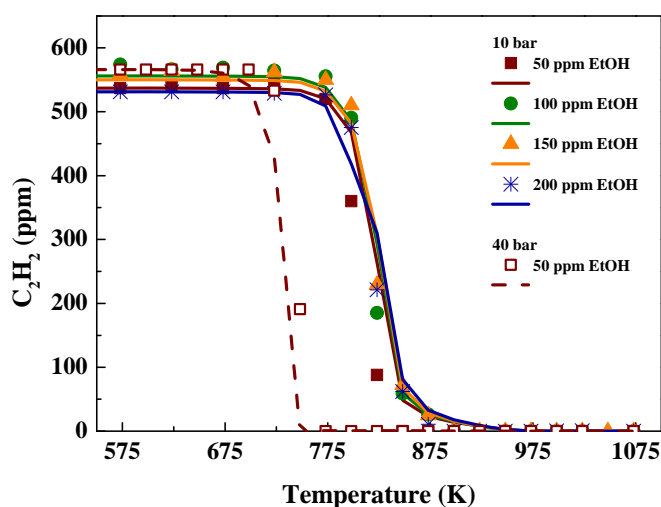


Figure 2 Influence of the amount of ethanol added to the reactant mixture, pressure (10 or 40 bar) and temperature for stoichiometric conditions ($\lambda=1$). Comparison between experimental results (symbols) and modeling calculations (lines).

A reaction rate analysis has been performed to identify the main C_2H_2 and ethanol consumption routes. In the case of acetylene, it is mostly consumed by recombination with OH to form the CHCHOH adduct for all the values of lambda analyzed and, only for reducing conditions, the C_2H_2 combination with H to form vinyl (C_2H_3) becomes relevant. These reaction routes are almost the same than those described in a high-pressure C_2H_2 oxidation work [7], so apparently the addition of ethanol to the reactant mixture does not modify the C_2H_2 oxidation regime. On the other hand, ethanol conversion is initiated by its

thermal dehydration to ethylene and it is mainly consumed by hydrogen abstraction reactions, as it was previously described in earlier studies concerning ethanol oxidation [e.g. 5, 6].

CONCLUSIONS

The influence of temperature (575-1075 K), pressure (10 or 40 bar), inlet oxygen concentration ($\lambda=0.7, 1$ or 20) and amount of ethanol added to the reactant mixture (50-200 ppm) has been evaluated in the high-pressure oxidation of acetylene-ethanol mixtures. The experimental results and modeling predictions are in good agreement. Neither the oxygen concentration nor the amount of ethanol added to the reaction mixture have a clear influence on the conversion of C_2H_2 . Only an increase in pressure (when moving from 10 to 40 bar) shifts the onset for acetylene conversion to lower temperatures. The reaction routes for acetylene remain practically unaltered by the addition of ethanol in comparison to those obtained in the high-pressure oxidation study of acetylene.

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