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High-pressure ethanol oxidation and its interaction with NO

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ABSTRACT

Ethanol has become a promising biofuel, widely used as a renewable fuel and gasoline additive. Describing the oxidation kinetics of ethanol with high accuracy is required for the development of future efficient combustion devices with lower pollutant emissions. The oxidation process of ethanol, from reducing to oxidizing conditions, and its pressure dependence (20, 40 and 60 bar) has been analyzed in the 500–1100 K temperature range, in a tubular flow reactor under well controlled conditions. The effect of the presence of NO has been also investigated. The experimental results have been interpreted in terms of a detailed chemical kinetic mechanism with the GADM mechanism (*Glarborg P, Alzueta MU, Dam-Johansen K and Miller JA, 1998*) as a base mechanism but updated, validated, extended by our research group with reactions added from the ethanol oxidation mechanism of Alzueta and Hernández (*Alzueta MU and Hernández JM, 2002*), and revised according to the present high-pressure conditions and the presence of NO. The final mechanism is able to reproduce the experimental trends observed on the reactants consumption and main products formation during the ethanol oxidation under the conditions studied in this work. The results show that the oxygen availability in the reactant mixture has an almost imperceptible effect on the temperature for the onset of ethanol consumption at a constant pressure, but this consumption is faster for the highest value of air excess ratio (λ) analyzed. Moreover, as the pressure becomes higher, the oxidation of ethanol starts at lower temperatures. The presence of NO promotes ethanol oxidation, due to the increased relevance of the interactions of CH_3 radicals and NO_2 (from the conversion of NO to NO_2 at high pressures and in presence of O_2) and the increased concentration of OH radicals from the interaction of NO_2 and water.

1. Introduction

Minimizing particulate matter and nitrogen oxides (NO_x) emissions from combustion, especially from transport, is a pressing need to improve the air quality, preserve the environment and comply with the increasingly restrictive laws. A prospective solution is fuel reformulation since its effects on emissions are immediate and can be implemented, without significant changes, in the design of the equipment. This reformulation implies the total or partial replacement of the conventional fuel by alternative ones, that may have been obtained in a more environmentally friendly way, for example, alcohols such as ethanol or butanol from biomass or wastes by biorefinery processes [1].

Ethanol (C_2H_5OH) is one of the most studied alcohols and its use, directly or as a gasoline additive, is spread worldwide. However, the cetane number, flash point and calorific value of ethanol are lower than those corresponding to diesel fuel, so it cannot be used directly in diesel engines. Therefore, ethanol must be blended with diesel fuel or biodiesel [2] and, working under the appropriate conditions, the emissions of CO, particulate matter and NO_x could be reduced [3].

The ethanol oxidation has been investigated in several works using laminar flames, shock tubes, flow reactors and rapid compression machines, as it has been summarized in the study of Mittal et al. [4]. More recently, Barraza-Botet et al. [5] carried out ignition and speciation studies in ethanol combustion in a rapid compression facility. For modeling predictions, they [5] used the detailed mechanism of Burke et al. [6,7] developed for C_1-C_3 hydrocarbons and oxygenated species oxidation, obtaining a good agreement with the experimental results.

However, despite its relevance for its applicability to internal combustion engines, the ethanol oxidation in flow reactors under high-pressure conditions has not been previously studied. Therefore, reliable experimental data for validation of the kinetic models in this high-pressure regime become of high importance.

In this context, the aim of the present work is to extend the experimental database on ethanol oxidation with the study of its conversion under high-pressure conditions, in a flow reactor, for different air excess ratios, both in the absence and presence of nitric oxide (NO).

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NO may be formed in the combustion chamber of a diesel engine, mainly through the thermal NO mechanism and, once it has been formed, NO may interact with ethanol or its derivatives. The experimental results are analyzed in terms of a detailed chemical kinetic mechanism to identify the main reaction routes occurring and to better understand the possible ethanol-NO interactions.

2. Experimental methodology

The ethanol oxidation experiments, both in the absence and presence of NO, have been carried out in a high-pressure flow reactor designed to approximate gas plug flow. The experimental set up is described in detail in Marrodán et al. [8] and only a brief description is provided here. A controlled evaporator mixer (CEM) has been used to feed an aqueous solution of ethanol (10% by weight) into the reaction system. The oxygen required to carry out each oxidation experiment depends on the air excess ratio analyzed (λ, defined as the inlet oxygen concentration divided by stoichiometric oxygen), and it has been supplied from gas cylinder through a Bronkhorst Hi-Tech mass flow controller. In the case of the experiments in the presence of NO, 500 ppm of NO have been added to the feed gas flow. Table 1 lists the conditions of the different experiments.

The gas reactants are premixed before entering the reaction system, which consists of a tubular quartz reactor (inner diameter of 6 mm and 1500 mm in length) enclosed in a stainless-steel tube that acts as a pressure shell. The longitudinal temperature profile in the reactor was experimentally determined. An isothermal zone (± 10 K) of 56 cm was obtained in the reactor, which was considered as reaction zone. Nitrogen to balance up to obtain a total flow rate of 1 L (STP)/min has been used, resulting in a gas residence time dependent of the pressure and the temperature according to: t_r (s) = 261 P(bar)/T(K).

The products were analyzed using an on-line 3000A Agilent micro-chromatograph equipped with TCD detectors and an URAS26 ABB continuous IR NO analyzer. The uncertainty of the measurements is estimated as ± 5%, but not less than 10 ppm.

3. Modeling

Simulations of the experimental results obtained in the ethanol high-pressure oxidation, in the absence and presence of NO, have been made using a gas-phase chemical kinetic model and the software Chemkin-Pro [9]. The detailed mechanism used in this work has been built up by our research group from the GADM mechanism [10], progressively updated (e.g. [11,12]) and modified to consider the different experimental conditions, such as the high-pressure and/or the different compounds involved [13–17]. In the case of ethanol, the reaction subset proposed by Alzueta and Hernández [18] in an atmospheric ethanol oxidation study has been included in the mechanism compiled in this work. Formic acid (HCOOH) has been identified as an intermediate in oxidation of dimethyl ether [19], which is an isomer of ethanol, so the reaction subset for formic acid oxidation proposed by Marshall and Glarborg [20] has also been included in the mechanism. The thermodynamic data for the species involved are taken from the same sources as the original mechanisms. The complete mechanism (137 species and 798 reactions) is provided as Supplementary Material in CHEMKIN format.

Table 1
Matrix of experimental conditions.

Set	Ethanol (ppm)	O_2 (ppm)	NO (ppm)	λ	P (bar)
1	5000	10,500	0	0.7	20
2	5000	10,500	0	0.7	40
3	5000	10,500	0	0.7	60
4	5000	15,000	0	1	20
5	5000	15,000	0	1	40
6	5000	15,000	0	1	60
7	5000	60,000	0	4	20
8	5000	60,000	0	4	40
9	5000	60,000	0	4	60
10	5000	10,500	500	0.7	20
11	5000	10,500	500	0.7	40
12	5000	10,500	500	0.7	60
13	5000	15,000	500	1	20
14	5000	15,000	500	1	40
15	5000	15,000	500	1	60
16	5000	60,000	500	4	20
17	5000	60,000	500	4	40
18	5000	60,000	500	4	60

4. Results and discussion

A study of ethanol oxidation at high pressure (20, 40 and 60 bar), in the 500–1100 K temperature range, has been carried out, for different air excess ratios (λ = 0.7, 1 and 4), both in the absence and in the presence of NO.

4.1. Oxidation of ethanol in the absence of NO

Fig. 1 shows an example of the results for ethanol consumption and CO and CO_2 formation as a function of temperature for the conditions of set 4 in Table 1, i.e., 20 bar, stoichiometric conditions (λ = 1) and in the absence of NO. From now on, experimental results are denoted by symbols, and modeling calculations by lines. In general, there is a good agreement between the experimental results and model predictions. Under these conditions, the ethanol conversion starts at approximately 725 K, the same temperature as for the onset of CO formation whose concentration peaks at 775 K. At the highest temperatures, ethanol and CO are completely oxidized to CO_2.

Fig. 2 shows the concentration of ethanol and of the main products quantified (CO, CO_2, CH_3CHO, C_2H_4, CH_4, CH_3OH, H_2), for different air excess ratios (from λ = 0.7 to λ = 4), at a constant pressure of 20 bar, and in the absence of NO. The oxygen availability in the reactant mixture does not modify significantly the temperature for the onset of ethanol conversion at a given pressure. In an ethanol oxidation study at atmospheric pressure, Alzueta and Hernández [18] observed that the ethanol oxidation occurs at lower temperatures for very oxidizing conditions (λ = 35), and small differences between λ = 0.7 and λ = 1 were found.

The biggest discrepancies can be found in the experimental and modeling results for CH_4, for reducing and stoichiometric conditions, and CH_3OH, minor products compared to CO and CO_2. The same tendencies can be observed for the other pressures studied in this work, although these results are not shown.

In order to further evaluate the influence of air excess ratio on ethanol oxidation, given the little influence found for λ = 1 and λ = 4,

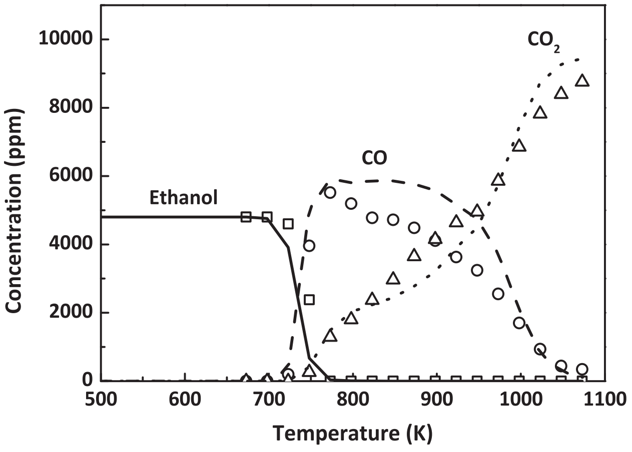

Fig. 1. Concentration of ethanol, CO and CO_2 as a function of temperature, for the conditions named as set 4 in Table 1 (λ = 1, 20 bar).

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