

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.

Keywords: ethanol; oxidation; high-pressure; nitrogen oxides; modeling.

28 **1. Introduction**

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

36 Ethanol (C₂H₅OH) is one of the most studied alcohols and its use, directly or as a gasoline additive, is spread
37 worldwide. However, the cetane number, flash point and calorific value of ethanol are lower than those
38 corresponding to diesel fuel, so it cannot be used directly in diesel engines. Therefore, ethanol must be
39 blended with diesel fuel or biodiesel [2] and, working under the appropriate conditions, the emissions of CO,
40 particulate matter and NO_x could be reduced [3].

41 The ethanol oxidation has been investigated in several works using laminar flames, shock tubes, flow
42 reactors and rapid compression machines, as it has been summarized in the study of Mittal et al. [4]. More
43 recently, Barraza-Botet et al. [5] carried out ignition and speciation studies in ethanol combustion in a rapid
44 compression facility. For modeling predictions, they [5] used the detailed mechanism of Burke et al. [6,7]
45 developed for C₁-C₃ hydrocarbons and oxygenated species oxidation, obtaining a good agreement with the
46 experimental results.

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

51 In this context, the aim of the present work is to extend the experimental database on ethanol oxidation
52 with the study of its conversion under high-pressure conditions, in a flow reactor, for different air excess
53 ratios, both in the absence and presence of nitric oxide (NO). NO may be formed in the combustion chamber
54 of a diesel engine, mainly through the thermal NO mechanism and, once it has been formed, NO may

55 interact with ethanol or its derivatives. The experimental results are analyzed in terms of a detailed chemical
56 kinetic mechanism to identify the main reaction routes occurring and to better understand the possible
57 ethanol-NO interactions.

58

59 **2. Experimental methodology**

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

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

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

78

79 **3. Modeling**

80 Simulations of the experimental results obtained in the ethanol high-pressure oxidation, in the absence and
81 presence of NO, have been made using a gas-phase chemical kinetic model and the software Chemkin-Pro

82 [9]. The detailed mechanism used in this work has been built up by our research group from the GADM
83 mechanism [10], progressively updated (e.g. [11,12]) and modified to consider the different experimental
84 conditions, such as the high-pressure and/or the different compounds involved [13-17]. In the case of
85 ethanol, the reaction subset proposed by Alzueta and Hernández [18] in an atmospheric ethanol oxidation
86 study has been included in the mechanism compiled in this work. Formic acid (HCOOH) has been identified
87 as an intermediate in oxidation of dimethyl ether [19], which is an isomer of ethanol, so the reaction subset
88 for formic acid oxidation proposed by Marshall and Glarborg [20] has also been included in the mechanism.
89 The thermodynamic data for the species involved are taken from the same sources as the original
90 mechanisms. The complete mechanism (137 species and 798 reactions) is provided as Supplementary
91 Material in CHEMKIN format.

92

93 **4. Results and discussion**

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

97

98 **4.1. Oxidation of ethanol in the absence of NO**

99 Figure 1 shows an example of the results for ethanol consumption and CO and CO₂ formation as a function
100 of temperature for the conditions of set 4 in Table 1, i.e., 20 bar, stoichiometric conditions ($\lambda=1$) and in the
101 absence of NO. From now on, experimental results are denoted by symbols, and modeling calculations by
102 lines. In general, there is a good agreement between the experimental results and model predictions. Under
103 these conditions, the ethanol conversion starts at approximately 725 K, the same temperature as for the
104 onset of CO formation whose concentration peaks at 775 K. At the highest temperatures, ethanol and CO
105 are completely oxidized to CO₂.

106 Figure 2 shows the concentration of ethanol and of the main products quantified (CO, CO₂, CH₃CHO, C₂H₄,
107 CH₄, CH₃OH, H₂), for different air excess ratios (from $\lambda=0.7$ to $\lambda=4$), at a constant pressure of 20 bar, and in
108 the absence of NO. The oxygen availability in the reactant mixture does not modify significantly the

109 temperature for the onset of ethanol conversion at a given pressure. In an ethanol oxidation study at
110 atmospheric pressure, Alzueta and Hernández [18] observed that the ethanol oxidation occurs at lower
111 temperatures for very oxidizing conditions ($\lambda=35$), and small differences between $\lambda=0.7$ and $\lambda=1$ were found.
112 The biggest discrepancies can be found in the experimental and modeling results for CH_4 , for reducing and
113 stoichiometric conditions, and CH_3OH , minor products compared to CO and CO_2 . The same tendencies can
114 be observed for the other pressures studied in this work, although these results are not shown.

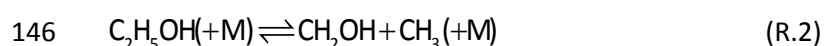
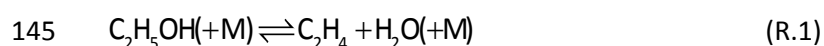
115 In order to further evaluate the influence of air excess ratio on ethanol oxidation, given the little influence
116 found for $\lambda=1$ and $\lambda=4$, model calculations for $\lambda=35$, very fuel-lean conditions, have been carried out. The
117 theoretical results obtained for $\lambda=35$ (Figure 2) are almost the same than those for $\lambda=4$, for ethanol,
118 acetaldehyde (CH_3CHO) and CO and CO_2 concentrations, but lower amounts of CH_4 , C_2H_4 and CH_3OH are
119 predicted. So, it can also be deduced that for the high-pressure conditions studied in this work, there is
120 almost no influence of the oxygen availability on the temperature for the onset of ethanol oxidation.

121 Figure 3 shows the influence of the pressure change (20, 40 and 60 bar) on the ethanol consumption and CO
122 formation, which has been selected as one of the main products of ethanol oxidation. Independently of the
123 stoichiometry analyzed, the consumption of ethanol starts at lower temperatures as the pressure is
124 increased, approximately 100 K when moving from 20 to 60 bar. This behavior is also observed in the
125 formation of CO , which peaks at lower temperatures for the highest pressure analyzed. The oxidation of CO
126 to CO_2 is favored by an increase in pressure, as well as by an increase in the lambda value.

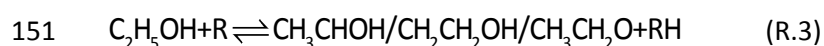
127 Considering the experimental procedure utilized in this work, a change in the pressure maintaining the total
128 gas flow rate, also implies a change in the gas residence time (t_r (s)= $261 P(\text{bar})/T(\text{K})$). Therefore, with the
129 present mechanism, that describes well the experimental results, we have made different simulations to try
130 to distinguish between the effect of gas residence time or pressure. This evaluation can be found as
131 Supplementary Material, Figure S.1. The results indicate that both the pressure and the residence time have
132 an appreciable effect on the ethanol conversion, which is shifted to lower temperatures when any of the
133 above variables is increased. Accordingly, the results presented in Figure 3 correspond to the joint effect of
134 pressure and residence time.

135 In general, modeling predictions are in good agreement with the experimental observations. Consequently,
136 in this work, reaction rate analysis has been performed to identify the main ethanol consumption routes and
137 products formation and the obtained results have been represented in a reaction pathway diagram in Figure
138 4 (left).

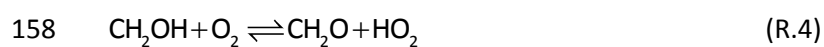
139 The ethanol consumption is initiated by its thermal dehydration to ethylene (reaction R.1), as this latter has
140 been detected by gas chromatography, and also by its thermal decomposition through bond cleavage to
141 CH_2OH and CH_3 radicals (reaction R.2). For example, for 20 bar and $\lambda=0.7$, at 725 K, 86% of the ethanol is
142 being consumed through reaction R.2, and for $\lambda=4$, 95% of the ethanol consumption is produced through
143 reaction R.1. This fact could explain the almost negligible effect of the oxygen availability on the
144 temperature for the onset of ethanol consumption.



147 In earlier studies involving ethanol oxidation in flow reactors [18,21], and in flames and jet stirred reactors
148 [22], the main reaction pathways for ethanol consumption were identified. The proposed reaction routes are
149 based on a hydrogen abstraction that may occur on three different sites, leading to the formation of three
150 different $\text{C}_2\text{H}_5\text{O}$ radical isomers (reaction R.3, where R can be O, H, OH, CH_3 or HO_2 radicals).



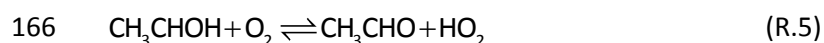
152 Under the conditions of the present work, these reactions also take place, especially that one involving HO_2
153 radicals, as it was previously observed in the oxidation of other oxygenated compounds, such as
154 dimethoxymethane [23], under high-pressure conditions. The hydroxymethyl radical (CH_2OH), formed in
155 reaction R.2 from ethanol, reacts with molecular oxygen to produce formaldehyde and more HO_2 radicals
156 (reaction R.4), which interact with ethanol (reaction R.3) producing the CH_3CHOH radical, the dominant
157 radical under the present conditions.



159 An example of the evolution along the reactor of the main consumption reactions for ethanol can be
160 observed in Figure 4 (right), for 20 bar, $\lambda=1$ and 725 K. At the beginning of the reactor, the ethanol

161 consumption is mainly through its thermal dehydration (reaction R.1), but hydrogen abstraction reaction by
162 HO₂ (reaction R.3) becomes more relevant with the distance.

163 The CH₃CHOH radical reacts with molecular oxygen (reaction R.5) producing acetaldehyde, which has been
164 quantified by gas chromatography. Acetaldehyde interacts with the radical pool producing the acetyl radical
165 (CH₃CO), which thermally decomposes to CO and CH₃ radicals.



167 The reaction pathways involving the other two C₂H₅O radicals are of minor relevance compared to those
168 already described, and very similar to those described in previous ethanol oxidation works (e.g. [22]).

169 As it has been mentioned in the introduction, the mechanism of Burke et al. [6,7] has been used in previous
170 ethanol studies, e.g. [5]. Therefore, it has been considered interesting to compare the experimental results
171 obtained in this work with those predicted with the present model and the Burke et al. model. This
172 comparison can be found as Supplementary Material, Figures S2-S10.

173 It can be observed that, in general, the model proposed in this work fits better the experimental results
174 corresponding to the ethanol conversion onset temperature and the concentrations of ethanol, CO, CO₂, H₂
175 and C₂H₄, while the Burke et al. model fits better the concentrations corresponding to CH₄ and CH₃OH.

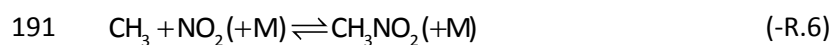
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177 **4.2. Oxidation of ethanol in the presence of NO**

178 In the present work, the influence of the presence of NO in the reactant mixture on ethanol oxidation has
179 also been analyzed. When burning any fuel in an air atmosphere at high temperatures, NO may be formed
180 through the thermal NO formation mechanism by nitrogen fixation from the combustion air [24]. NO may be
181 reduced by its interaction with ethanol and/or its derivatives, or may promote the ethanol oxidation in a
182 mutually sensitized oxidation [25]. Therefore, the interaction between ethanol and NO has been considered
183 in the present work from both experimental and modeling points of view.

184 As it can be drawn from the discussion of the main reaction pathways for ethanol conversion in the absence
185 of NO, a high concentration of CH₃ radicals is also expected in the presence of NO. Furthermore, under the
186 present experimental conditions, it has been observed that, due to the high-pressure conditions and the
187 presence of O₂, NO added to the reactant mixture is converted to NO₂ before entering the reactor. From the

188 interaction between CH₃ radicals and NO₂ (reaction -R.6), the mechanism initially compiled in this work
189 predicted an accumulation of nitromethane (CH₃NO₂), whose formation was not detected experimentally.
190 Another possible interaction between CH₃ radicals and NO₂ leading to CH₃ONO may occur (reaction -R.7).



193 In a high-pressure flow reactor study, Rasmussen and Glarborg [16] analyzed the effects of NO_x on CH₄
194 oxidation, through ab initio calculations. Their calculations indicated that the formation of CH₃ONO is
195 energetically unfavorable, but, if formed, it would dissociate to NO and methoxy radical (CH₃O).

196 Therefore, because of the high CH₃ and NO₂ concentrations expected and no CH₃NO₂ detection, the CH₃ONO
197 reaction to CH₃ and NO₂ (reaction R.7) has been included in our mechanism. There is not much information
198 in bibliography regarding this reaction and its kinetic parameters. So, the value of 7.00 x 10¹⁰ cm³ mol⁻¹ s⁻¹
199 proposed by Canosa et al. [26] has been adopted for reaction R.7. As it can be seen in Figure 5, in the
200 concentration profiles of ethanol and CO, the predictions of the model improved considerably after including
201 reaction R.7 in the mechanism.

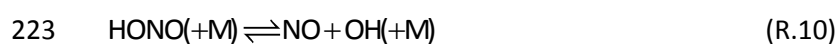
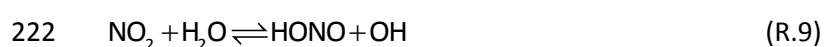
202 Figure 6 (top) shows a comparison between the experimental results (symbols) and model predictions (lines)
203 obtained during ethanol oxidation, in the presence of NO, for different air excess ratios and different
204 pressures. Compared to Figure 3, the presence of NO promotes ethanol oxidation shifting the onset of
205 ethanol oxidation to lower temperatures, a difference of 100-125 K approximately. As also occurred in the
206 absence of NO, the available oxygen in the reactant mixture does not modify the temperature for the onset
207 of ethanol conversion at a constant pressure of 20 bar. The same tendency was observed for the other
208 pressures analyzed (results not shown), but the higher the pressure the lower the ethanol conversion onset
209 temperature. Figure 6 (bottom) shows the experimental and theoretical NO concentration results for
210 different air excess ratios and 20 bar, and also other pressures for λ=4. Modeling predictions are shifted to
211 higher temperatures, approximately 50 K, compared to experimental results. At low temperatures, as
212 previously mentioned, the NO fed to the system is converted to NO₂ through reaction R.8, and it is not thus
213 experimentally detected until approximately 750 K. Unlike what was observed for ethanol, both λ and

214 pressure values influence the NO concentration, in the way that increasing the amount of oxygen in the
215 reactant mixture or increasing the pressure, results in a lower amount of NO experimental or predicted.



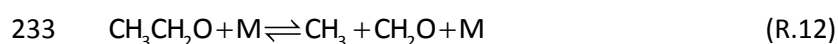
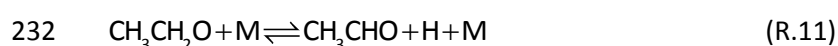
217 Once formed, NO₂ reacts with CH₃ radicals originated from ethanol to produce CH₃ONO (reaction -R7), which
218 decomposes rapidly into CH₃O+NO. As a consequence, NO is detected again, especially for 20 bar and λ=0.7,
219 because an increase in the value of pressure or lambda favors reaction R.8.

220 NO₂ can also react with H₂O to produce HONO and OH radicals (reaction R.9), which promote ethanol
221 conversion. The HONO formed decomposes to produce NO (reaction R.10).



224 The same reactions (R.9 and R.10), but in the reverse sense, were the cause of a slightly inhibiting effect of
225 ethanol conversion by NO observed in the ethanol oxidation at atmospheric pressure [18], under certain
226 conditions.

227 In the presence of NO, the ethanol consumption routes are the same as those already described in the
228 absence of NO. However, in the presence of NO, the reaction pathways involving the CH₃CH₂O radical
229 (formed through R.3) acquire more relevance, becoming the predominating reaction pathways. This radical
230 decomposes through reactions R.11 and R.12 to produce acetaldehyde or CH₃ radicals and formaldehyde,
231 respectively.



234 First-order sensitivity analyses for ethanol and CO have been performed for different air excess ratios and 20
235 bar, in the absence of NO and in the presence of NO.

236 The obtained ethanol results are in agreement with the ethanol consumption pathways previously described
237 and can be found as Supplementary Material, Figure S11. In the absence of NO, the most sensitive reaction
238 is the hydrogen abstraction reaction by HO₂ (reaction R.3), which is the main reaction pathway for ethanol
239 consumption. The reaction H₂O₂(+M)=OH+OH(+M) is also very sensitive due to the generation of OH radicals

240 which can promote the consumption of ethanol by H abstraction reactions. In the presence of NO, the
241 formation of $\text{CH}_3\text{CH}_2\text{O}$ radical from ethanol (reaction R.3, $\text{C}_2\text{H}_5\text{OH}+\text{OH}=\text{CH}_3\text{CH}_2\text{O}+\text{H}_2\text{O}$) and its thermal
242 decomposition (reactions R.11 and R.12) present a high sensitivity coefficient, becoming the dominant
243 ethanol consumption under these conditions. The CH_3 radicals generated in reaction R.12 may interact with
244 ethanol promoting its consumption. The formation of HONO from the interaction of $\text{CH}_2\text{O}+\text{NO}_2$
245 ($\text{CH}_2\text{O}+\text{NO}_2=\text{HCO}+\text{HONO}$) and its subsequent decomposition (reaction R.10, $\text{HONO}(+\text{M})=\text{NO}+\text{OH}(+\text{M})$)
246 producing OH radicals are sensitive in the presence of NO, because of the OH radicals generated that
247 promote ethanol conversion.

248 Moreover, the first-order sensitivity analysis for CO (Figure 7) indicates that, in the absence of NO, the most
249 sensitive reaction is the thermal dehydration of ethanol to ethylene (reaction R.1). The subsequent reaction
250 of ethylene with O_2 presents a high sensitivity for all the values of lambda analyzed. Hydrogen abstraction
251 reactions from ethanol with different radicals are also sensitive. In the presence of NO, as in the case of the
252 sensitivity results for ethanol, hydrogen abstraction reactions by OH radicals to produce $\text{CH}_3\text{CH}_2\text{O}$ radical and
253 its subsequent decomposition are highly sensitive. The interaction of NO_2 with CH_2O to produce HONO and
254 HCO presents the highest sensitivity coefficient for all the lambdas analyzed.

255

256 **5. Conclusions**

257 The oxidation of ethanol has been analyzed from both experimental and modeling points of view. The
258 influence on the process of the available oxygen in the reactant mixture (different air excess ratios: $\lambda=0.7$, 1
259 and 4), the change of pressure (20, 40 and 60 bar) and the presence or absence of NO has been analyzed in a
260 tubular flow reactor, in the 500-1100 K temperature range.

261 In general, there is a good agreement between experimental and modeling predictions. The results show
262 that, for the conditions studied in this work, at a constant pressure, the temperature for the onset of ethanol
263 oxidation is roughly independent of the amount of oxygen available in the reactant mixture, but the ethanol
264 conversion starts at lower temperatures as the pressure is increased. A reaction rate analysis indicates that
265 the ethanol consumption is mainly initiated by thermal dehydration or decomposition.

266 When NO is fed to the high-pressure system, it converts to NO₂ before entering in the reactor. In view of the
267 high expected concentration of NO₂ and CH₃ radicals (from the ethanol conversion), the reaction
268 $\text{CH}_3\text{ONO} \rightleftharpoons \text{CH}_3 + \text{NO}_2$ has been included in our mechanism, with clear improvements of the model
269 predictions. In the presence of NO, the ethanol conversion is promoted due to the increased concentration
270 of OH in the radical pool from the interaction of NO₂ and water. As observed in the absence of NO, the
271 stoichiometry does not have a clear influence on the ethanol oxidation regime, whereas an increase in the
272 pressure shifts the temperature for the onset of ethanol consumption to lower temperatures.

273

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278

279 **References**

- 280 [1] Sarathy SM, Oßwald P, Hansen N, Kohse-Höinghaus K. Alcohol combustion chemistry. *Prog. Energy*
281 *Combust. Sci.* 2014;44:40-102.
- 282 [2] Alviso D, Krauch F, Román R, Maldonado H, dos Santos RG, Rolón JC, Darabiha N. Development of a
283 diesel-biodiesel-ethanol combined chemical scheme and analysis of reactions pathways. *Fuel* 2017;
284 191:411-426.
- 285 [3] An H, Yang WM, Li J. Effects of ethanol addition on biodiesel combustion: a modeling study. *Appl.*
286 *Energy* 2015;143:176-188.
- 287 [4] Mittal G, Burke SM, Davies VA, Parajuli B, Metcalfe WK, Curran HJ. Autoignition of ethanol in a rapid
288 compression machine. *Combust. Flame* 2014;161:1164-1171.
- 289 [5] Barraza-Botet CL, Wagnon SW, Wooldridge MS. Combustion chemistry of ethanol: ignition and
290 speciation studies in a rapid compression facility. *J. Phys. Chem. A* 2016;120:7408-7418.

- 291 [6] Burke SM, Metcalfe W, Herbinet O, Batton-Leclerc F, Haas FM, Santner J, Dryer FL, Curran HJ. An
292 experimental and modeling study of propene oxidation. Part 1: speciation measurements in jet-
293 stirred and flow reactors. *Combust. Flame* 2014;161:2765-2784.
- 294 [7] Burke SM, Burke U, Mc Donagh R, Mathieu O, Osorio I, Keesee C, Morones A, Petersen EL, Wang W,
295 DeVerter TA, et al. An experimental and modeling study of propene oxidation. Part 2: ignition delay
296 time and flame speed measurements. *Combust. Flame* 2015;162:296-314.
- 297 [8] Marrodán L, Millera Á, Bilbao R, Alzueta MU. High-pressure study of methyl formate oxidation and its
298 interaction with NO. *Energy Fuels* 2014;28:6107-6115.
- 299 [9] ANSYS Chemkin-Pro 17.2, Release 15151; Reaction Design: San Diego, 2016.
- 300 [10] Glarborg P, Alzueta MU, Dam-Johansen K, Miller JA. Kinetic modeling of hydrocarbon/nitric oxide
301 interactions in a flow reactor. *Combust. Flame* 1998;115:1-27.
- 302 [11] Glarborg P, Alzueta MU, Kærsgaard K, Dam-Johansen K. Oxidation of formaldehyde and its interaction
303 with nitric oxide in a flow reactor. *Combust. Flame* 2003;132:629-638.
- 304 [12] Glarborg P, Østberg M, Alzueta MU, Dam-Johansen K, Miller JA. The recombination of hydrogen
305 atoms with nitric oxide at high temperatures. *Proc. Combust. Inst.* 1999;27:219-227.
- 306 [13] Rasmussen CL, Hansen J, Marshall P, Glarborg P. Experimental measurements and kinetic modeling
307 of CO/H₂/O₂/NO_x conversion at high-pressure. *Int. J. Chem. Kin.* 2008;40:454-480.
- 308 [14] Rasmussen CL, Glarborg P. Measurements and kinetic modeling of CH₄/O₂ and CH₄/C₂H₆/O₂
309 conversion at high pressure. *Int. J. Chem. Kin.* 2008;40:778-807.
- 310 [15] Rasmussen CL, Andersen KH, Dam-Johansen K, Glarborg P. Methanol oxidation in a flow reactor:
311 implications for the branching ratio of CH₃OH+OH reaction. *Int. J. Chem. Kin.* 2008;40:423-441.
- 312 [16] Rasmussen CL, Glarborg P. Sensitizing effects of NO_x on CH₄ oxidation at high pressure. *Combust.*
313 *Flame* 2008;154:529-545.
- 314 [17] Giménez-López J, Rasmussen CT, Hashemi H, Alzueta MU, Gao Y, Marshall P, Goldsmith CF, Glarborg
315 P. Experimental and kinetic modeling study of C₂H₂ oxidation at high pressure. *Int. J. Chem. Kin.*
316 2016;48:724-738.

- 317 [18] Alzueta MU, Hernández JM. Ethanol oxidation and its interaction with nitric oxide. *Energy Fuels*
318 2002;16:166-171.
- 319 [19] Fischer SL, Dryer FL, Curran HJ. The reaction kinetics of dimethyl ether. I: High-temperature pyrolysis
320 and oxidation in flow reactors. *Int. J. Chem. Kinet.* 2000;32:713-740.
- 321 [20] Marshall P, Glarborg P. Ab initio and kinetic modeling studies of formic acid oxidation. *Proc.*
322 *Combust. Inst.* 2015;35:153-160.
- 323 [21] Abián M, Esarte C, Millera Á, Bilbao R, Alzueta MU. Oxidation of acetylene-ethanol mixtures and their
324 interaction with NO. *Energy Fuels* 2008;22:3814-3823.
- 325 [22] Leplat N, Dagaut P, Togbé C, Vandooren J. Numerical and experimental study of ethanol combustion
326 and oxidation in laminar premixed flames and jet-stirred reactor. *Combust. Flame* 2011;158:705-725.
- 327 [23] Marrodán L, Royo E, Millera Á, Bilbao R, Alzueta MU. High-pressure oxidation of dimethoxymethane.
328 *Energy Fuels* 2015;29:3507-3517.
- 329 [24] Abián M, Alzueta MU, Glarborg P. Formation of NO from N₂/O₂ mixtures in a flow reactor: toward
330 and accurate prediction of thermal NO. *Int. J. Chem. Kinet.* 2015;47:518-532.
- 331 [25] Taylor PH, Cheng L, Dellinger B. The influence of nitric oxide on the oxidation of methanol and
332 ethanol. *Combust. Flame* 1998;115:561-567.
- 333 [26] Canosa C, Penzhorn RD, Sonntag C. Product quantum yields from the photolysis of NO₂ at 366 nm in
334 presence of ethylene. The role of NO₃^{*}. *Ber. Bunsenges Phys. Chem.* 1979;83:217-225.
- 335

336 **Table captions**

337 **Table 1.** Matrix of experimental conditions.

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Set	Ethanol (ppm)	O ₂ (ppm)	NO (ppm)	λ	P (bar)
1	5000	10500	0	0.7	20
2	5000	10500	0	0.7	40
3	5000	10500	0	0.7	60
4	5000	15000	0	1	20
5	5000	15000	0	1	40
6	5000	15000	0	1	60
7	5000	60000	0	4	20
8	5000	60000	0	4	40
9	5000	60000	0	4	60
10	5000	10500	500	0.7	20
11	5000	10500	500	0.7	40
12	5000	10500	500	0.7	60
13	5000	15000	500	1	20
14	5000	15000	500	1	40
15	5000	15000	500	1	60
16	5000	60000	500	4	20
17	5000	60000	500	4	40
18	5000	60000	500	4	60

339

340 **Figure captions**

341 **Figure 1.** Concentration of ethanol, CO and CO₂ as a function of temperature, for the conditions named as
342 set 4 in Table 1 ($\lambda=1$, 20 bar).

343

344 **Figure. 2.** Influence of the air excess ratio on the concentration profiles of ethanol and main products (CO,
345 CO₂, CH₃CHO, C₂H₄, CH₄, CH₃OH, H₂) during ethanol oxidation, as a function of temperature, for the
346 conditions named as sets 1, 4 and 7 in Table 1 (20 bar).

347

348 **Figure. 3.** Influence of the pressure change on the concentration profiles of ethanol and CO, as a function of
349 temperature, for the conditions named as sets 1-9 in Table 1.

350

351 **Figure 4.** Left: reaction path diagram for ethanol consumption and product formation. Right: normalized
352 rate-of-consumption coefficients for ethanol along the reactor (for the conditions of set 4 in Table 1: 20 bar,
353 $\lambda=1$ and 725 K).

354

355 **Figure 5.** Improvement in modeling predictions for ethanol and CO concentration, with and without reaction
356 R.7 in our mechanism, for the conditions named as set 16 in Table 1.

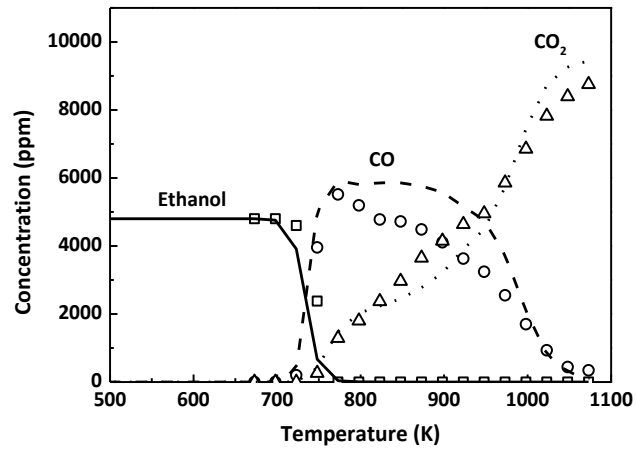
357

358 **Figure 6.** Influence of the air excess ratio and pressure on the concentration profiles of ethanol (top) and NO
359 (bottom) for the conditions named as sets 10, 13 and 16-18 in Table 1.

360

361 **Figure 7.** Sensitivity analysis for CO for different air excess ratios and 20 bar. Top: in the absence of NO (at
362 698 K). Bottom: in the presence of NO (at 648 K). (*) The sensitivity coefficients have been divided by two.

363

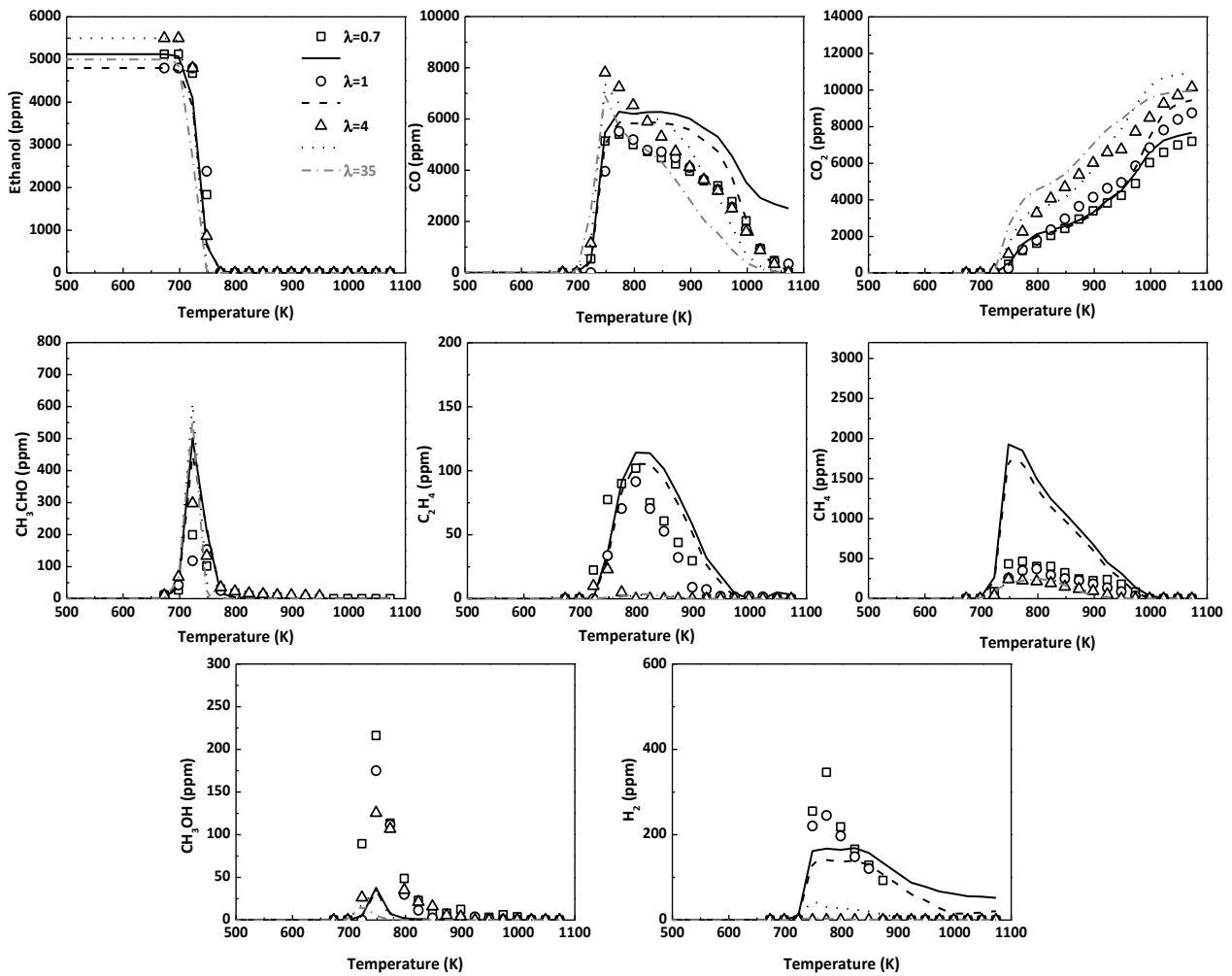


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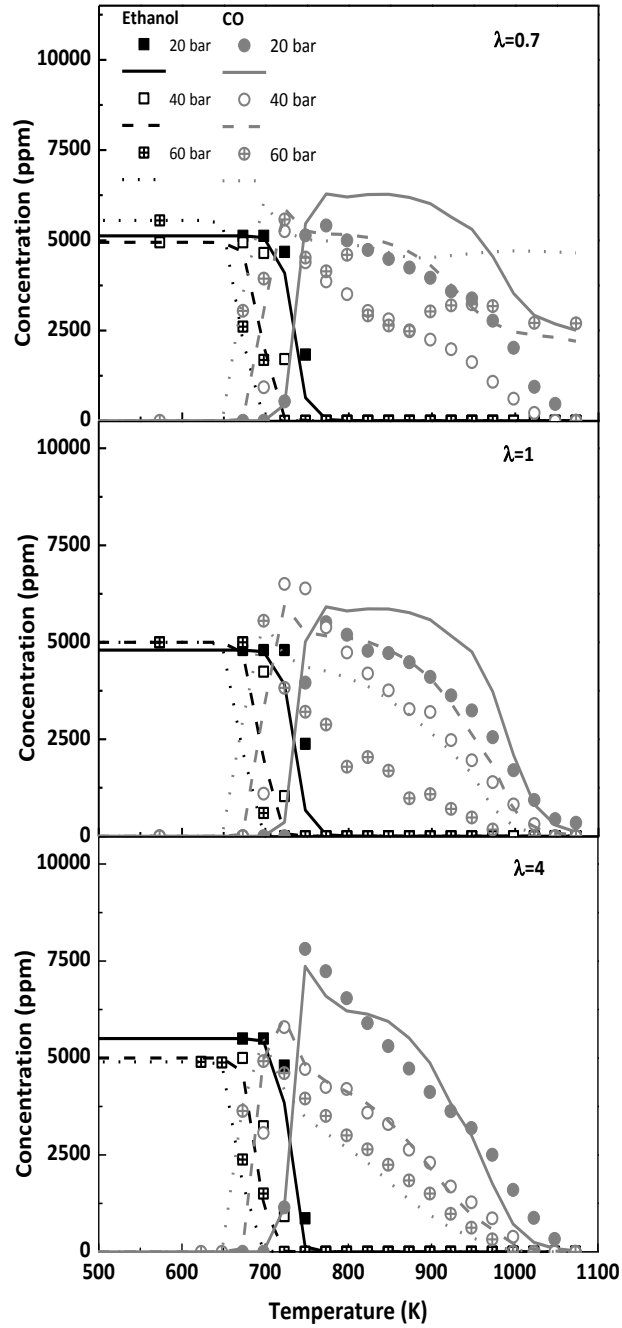
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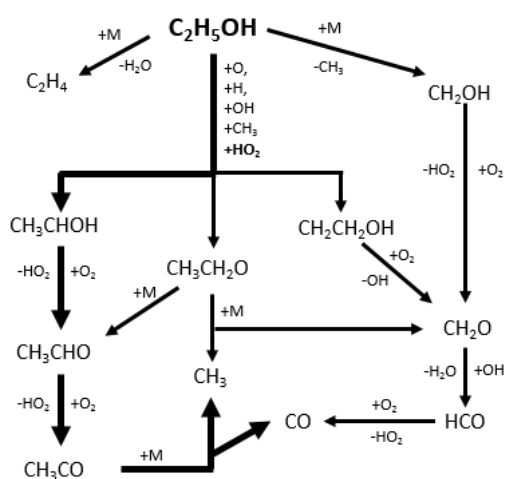
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 370 conditions named as sets 1, 4 and 7 in Table 1 (20 bar).
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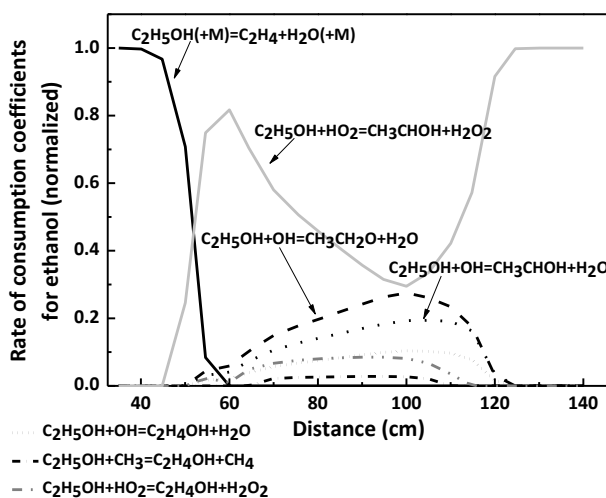


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 373 temperature, for the conditions named as sets 1-9 in Table 1.

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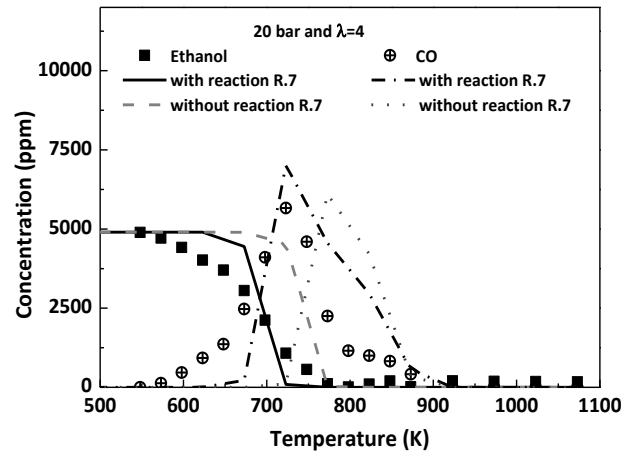
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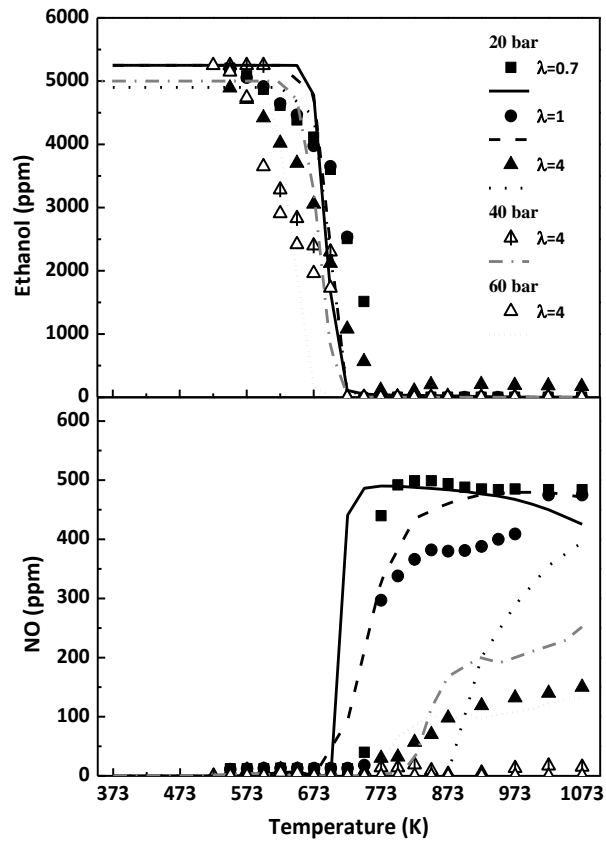
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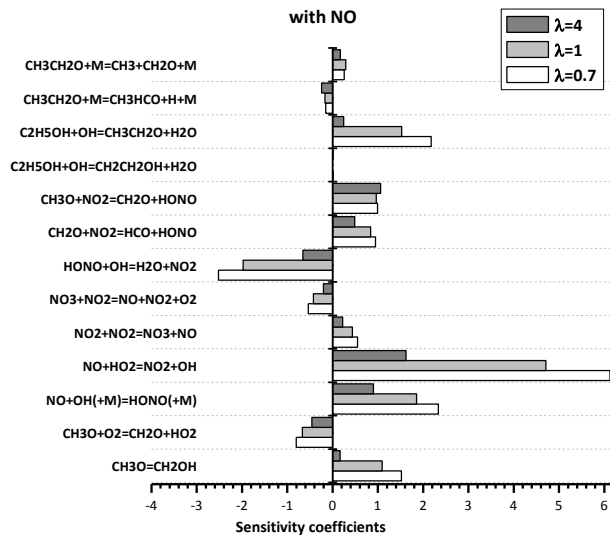
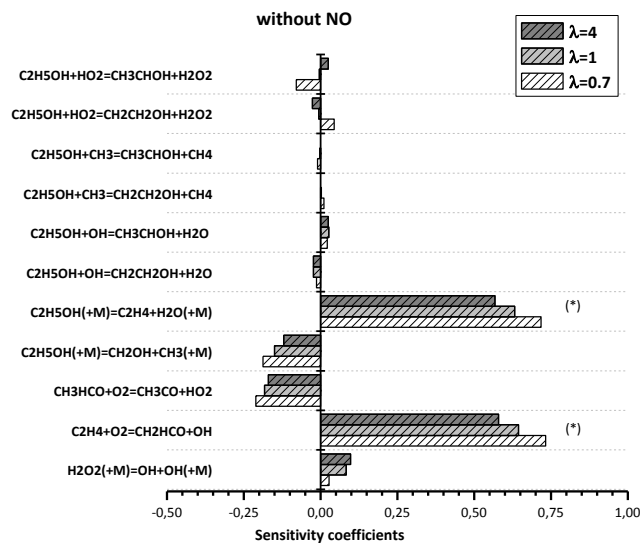
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- 389 **List of Supplementary Materials** (L. Marrodán et al., High-pressure ethanol oxidation and its interaction with
390 NO *Fuel* 2017)
- 391 1/ Kinetic model: mechanism (CHEMKIN file)
- 392 2/ Supplementary material (PDF file)
- 393 3/ Experimental data (Excel file)