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Towards a Kinetic Understanding of the NO_x Promoting-Effect on Ignition of Coalbed Methane: A Case Study of Methane/Nitrogen Dioxide mixtures

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Abstract

Nitrogen dioxide (NO_2) is an important impurity in coal-bed methane (CBM) and a dominant component of NO_x pollution in practical engines. Its promoting effect on methane ignition has been studied in the current experimental and kinetic study. Ignition delay times of $NO_2/CH_4/O_2/Ar$ mixtures, with blending ratios of $NO_2:CH_4$ of 30:70, 50:50 and 70:30 for stoichiometric methane mixtures were measured in a shock tube. Experiments cover a range of pressures (1.2 – 10.0 atm) and temperatures (933 – 1961 K). Under all tested pressures, NO_2 addition promotes the reactivity of methane and reduces the global activation energy at all pressures, and these effects are most significant for the mixtures with highest NO_2 concentrations, at the highest pressures and at the lowest temperatures. To simulate the experimental measurements, five literature NO_x sub-mechanisms were integrated with AramcoMech 1.3. The simulations demonstrate that, for the mixtures with low levels of NO_x concentrations, the five models agree well with the experimental ignition delay times. For the mixtures with high NO_x content, however, all five models are unable to reproduce the measured data, and the level of disagreement increases with increasing NO_2 concentration. An updated mechanism is proposed, based on modifications made as a result of

24 sensitivity and reaction flux analyses performed to quantitatively determine the chemical reasons

25 for NO_2 promoting methane ignition. The results indicate that, NO_2 addition perturbs the branching

26 ratio of key reaction pathways by affecting the structure of the free radical pool at the initial ignition

27 stage of methane oxidation. A new reaction cycle *via* the following sequence of reactions $\dot{C}H_3$ +

28 NO_2 <=> $CH_3\dot{O}$ + NO, $CH_3\dot{O}$ + M <=> CH_2O + $\dot{H}$ + M, NO_2 + $\dot{H}$ <=> NO + $\dot{O}H$, and CH_4 + $\dot{O}H$

29 <=> $\dot{C}H_3$ + H_2O is proposed to explain the observed effect of NO_2 addition on the promotion of

30 methane ignition.

31

32 **Keywords:** Shock tube; CH_4; NO_2; Ignition delay time; Kinetic model

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1. Introduction

Coal-bed methane (CBM), a form of natural gas extracted from coal beds, has been considered as a clean alternative fuel for decades[1, 2], especially in coal-rich countries like America, Russia, Canada, Australia and China. However, there are assignable impurity components such as nitrogen oxide (NO_x), sulfur oxide (SO_x), carbon monoxide (CO) and carbon dioxide (CO_2) present in CBM that can significantly influence the combustion and emission performance of internal combustion engines and gas turbines[3-8]. For an internal combustion engine with exhaust gas recirculation, for example, the NO_x formed during fuel combustion will be recirculated into the next combustion cycle and will then influence the combustion phase and induce a potential engine knock by promoting the reactivity of the fresh mixture in the combustion chamber[3, 4, 9, 10].

Previous studies indicate that the presence of NO_x can significantly reduce ignition delay times (τ_{ign}) of methane[6, 7, 11-16], reflecting the importance of NO_x for the combustion of CBM/natural gas in practical combustion devices. Several experimental and modeling investigations of the sensitization effect of NO_x on methane ignition have been conducted. Faravelli et al.[14] developed a detailed NO_x mechanism to examine the impact of NO on hydrocarbon combustion at low-temperature conditions. They reported that the NO significantly promotes the oxidation of hydrocarbons and this observation was more obvious for large alkanes relative to alkenes and methane. Sivaramakrishnan et al.[16] studied the effect of NO addition to fuel-lean $CH_4/C_2H_6/O_2/Ar$ mixtures: 1) at 50 atm in a high-pressure shock tube (HPST); 2) at 10 atm and at 1000 − 1500 K in a jet stirred reactor (JSR). They observed that the mixture reactivity was enhanced by the formation of abundant $\dot{O}H$ radicals with NO addition *via* the reaction $NO + H\dot{O}_2 <=> NO_2 + \dot{O}H$. Rasmussen et al.[13] performed an investigation on the $NO_x/CH_4/O_2$ system using N_2 as diluent over a temperature range of 600 − 900 K at pressures of 20 − 100 bar in a high-pressure laminar flow reactor. They found that NO_x dramatically reduced the initiation temperature, while nitromethane (CH_3NO_2) formed at elevated

3

62   pressures, temporarily inhibited the reactivity of the mixtures. They attributed the promoting effect

63   of NO_x on a chain-propagating NO/NO_2 cycle. Gersen et al.[9] studied the effect of NO_2 addition on

64   ignition delay times of methane, ethane and methane/ethane mixtures in a rapid compression

65   machine (RCM) at pressures of $25 - 50$ bar and at initial temperatures of $900 - 1050$ K. Their

66   results indicated that NO_2 obviously reduced the reactivity of all the mixtures tested, but only

67   exhibited a limited effect on ethane ignition.

68   Recently, Herzler and Naumann[6] investigated the promoting effect of NO_2 on methane/ethane

69   mixtures in a HPST using NO_2 concentrations of $20 - 250$ ppm at pressures of approximately 16 bar

70   and equivalence ratios of $0.25 - 1.0$ over a temperature range of $1000 - 1700$ K. They observed a

71   similar promoting effect of NO_2 as those measured in previous studies. In addition, Herzler and

72   Naumann[6] combined a hydrocarbon mechanism with four NO_x sub-models (Faravelli et al. model[14],

73   Sivaramakrishnan et al. model[16], Rasmussen et al. model[13] and Hori et al. model[5]), and found that

74   all mechanisms predicted similar ignition delay times. More recently, Mathieu et al.[7] explored the

75   effect of NO_2 addition to methane mixtures on ignition delay times at pressures of $1 - 28$ atm and at

76   equivalence ratios of $0.5 - 2.0$ with the mole fraction ratios of $NO_2:CH_4$ varying from 1.7:10 to 7:10

77   in a HPST. They indicated that the addition of NO_2 reduced ignition times of methane mixtures, and

78   the reduction was more obvious at elevated pressure. Moreover, Mathieu et al. proposed an updated

79   NO_x model and compared it with three literature ones (Gersen et al. model[9], Sivaramakrishnan et al.

80   model[16] and Mevel and Shepherd model[17]). Differences in the predictions of the four models were

81   observed at their investigated conditions.

82   Considering the literature review above, these previous studies have focused on mixtures with

83   relatively-low concentrations of nitrogen dioxide. There is no direct experimental evidence to

84   determine whether the available NO_x models can be applied to simulate the auto-ignition behavior

85   of mixtures with high levels of NO_x.

86   The first aim of *this paper* is to provide ignition delay times of $NO_2/CH_4/O_2/Ar$ mixtures with

87 three high blending ratios of NO_2 with NO_2:CH_4 mole fraction ratios of 30:70, 50:50 and 70:30 at

88 pressures from 1.2 to 10.0 atm and over a wide range of temperatures. The second aim is to evaluate

89 the performance of currently available NO_x sub-mechanisms assembled with AramcoMech 1.3

90 compared to our new data. Finally, an updated NO_x model will be proposed and used to conduct a

91 kinetic analysis of the NO_2 sensitizing-effect during the methane ignition process.

2. Experimental

93 All of the current experiments were performed in a stainless steel shock tube, described in a

94 previous study[18-20]. Briefly, the shock tube has an internal diameter of 11.5 cm with a 4.8 m long

95 driven-section and a 4.0 m long driver-section divided by double polyethylene terephthalate (PET)

96 diaphragms. Before each experiment, the shock tube was first evacuated to around 10 Pa using a

97 mechanical vacuum pump and was subsequently vacuumed to below 1 Pa using a roots vacuum

98 pump, with a leak rate of less than 1 Pa/min. The NO_2/CH_4/O_2/Ar mixtures were prepared in

99 advance in a 128 L stainless steel tank using Dalton's law of partial pressure, and allowed to

100 homogenize for more than 12 hours to ensure sufficient mixing and diffusion. The mixing tank was

101 also evacuated to below 1 Pa before mixture preparation. The mixture components used in *this*

102 *study* were CH_4 (> 99.99%), O_2 (> 99.99%), Ar (> 99.99%) and NO_2 (up to 99.99%) diluted to 20%

103 with Ar. Different ratios of high-purity He and N_2 (in purities of up to 99.999% and 99.999%

104 respectively) were used to achieve a tailored condition so as to obtain a longer test time.

105 Four fast-response piezoelectric pressure transducers (PCB 113B26), installed in the last 1.3 m

106 of the shock tube with the same interval of 300 mm, were used to trigger three time-counters

107 (FLUKE PM6690) to record the time intervals, which were used to calculate the incident shock

108 velocities. The shock velocity was extrapolated to the end-wall to obtain the reflected-shock

109 conditions using a chemical equilibrium software GASEQ[21].

110 It was suggested in the work of Petersen et al.[22] that the uncertainty of the reflected temperature

111 was mainly attributable to the uncertainty of the incident shock velocity, which is determined by the

112 uncertainties in the distances of the pressure transduces and shock pass time recorded by the time-

113 counters. We have adopted a standard root-sum-squares (RSS) method used by Petersen et al.[22],

114
$$T_5 = \frac{T_1\left[2(\gamma\text{-}1)M^2+(3\text{-}\gamma)\right]\left[(3\gamma\text{-}1)M^2\text{-}2(\gamma\text{-}1)\right]}{(\gamma+1)^2 M^2} = AM^2+B+CM^{-2}$$
(1)

115
$$M = \frac{V_s}{\sqrt{\gamma R T_1}}$$
(2)

116
$$\delta V_s = \sqrt{\left(\frac{1}{\Delta t}\delta_{\Delta z}\right)^2 + \left(\frac{-\Delta z}{\Delta t^2}\delta_{\Delta t}\right)^2}$$
(3)

117
$$\delta T_5 = \frac{\partial T_5}{\partial M}\delta M = \left(2AM\text{-}2CM^{-3}\right)\frac{\delta V_s}{\sqrt{\gamma_1 R T_1}}$$
(4)

118 where T_5 is the reflected shock temperature (K); T_1 is the initial temperature (K); γ is the adiabatic

119 exponent; V_s is the velocity of the incident shock wave (m/s); and R is the universal gas constant.

120 The uncertainty of the time measured by the FLUKE PM6690 time-counter was estimated to be

121 1000 ns, which is equal to the sum total of random and systematic uncertainties for the FLUKE

122 PM6690 counter timer and resolution time for the pressure transduces. The uncertainty in distance

123 between the pressure transducers was estimated to be 2 × 1000 ns × V_s, which stems mainly from

124 the diameter of the sensing area of the pressure transduces and the shock front thickness. Using Eqs.

125 1 – 4, the largest uncertainty in the reflected temperature is estimated to be 20 K. However, this

126 uncertainty of the reflected shock temperature leads to a 20% uncertainty in measured ignition

127 times, τ_{ign}, based on an Arrhenius type correlation of τ_{ign} using the RSS method, a detailed

128 description of which can be found in our previous study[23].

129   The reflected-shock pressure was detected using a piezoelectric pressure transducer with

130 acceleration compensation (PCB 113B03) located in the endwall. A photomultiplier

131 (HAMAMASSU CR131), installed in the endwall, was used to record OH⋆ light emission through a

132 307 nm narrowband (5 nm) filter. The measured pressure and OH⋆ profiles at the endwall were used

133 to determine the ignition event. The ignition delay time is defined as the time interval between the

134 arrival of the incident shock wave at the endwall and the extrapolation of the maximum slope of

135 OH* emission to the baseline, Fig. 1. Note that an obvious pressure rise (dp/dt = 4%/ms) can be

136 observed before the main ignition due to an interaction between the reflected shock wave and the

137 boundary layer as motioned in our previous study[18], and this has been included in our numerical

138 simulations.

139   To confirm the reliability of the current facility, a confirmatory experiment was conducted for a

140 $NO_2/CH_4/O_2/Ar$ mixture at an identical condition to that already published in the literature[7]. Figure

141 2 shows a comparison between the ignition delay times measured in *this study* and those measured

142 by Mathieu et al. data for the mixture with 70.8% NO_2 addition at φ = 0.5 and p = 1.3 atm. Overall,

143 the current data agrees well with the literature data, by considering both ignition delay times and

144 global activation energy.

145 3. Kinetic model evaluation

146   All of the simulation and kinetic analysis for CH_4/NO_2 mixtures were carried out using the

147 CHEMKIN[24] program with the SENKIN[25] code. As mentioned above, the rate of pressure rise

148 (dp/dt = 4.0%/ms) was considered in the simulations using the SENKIN/VTIM approach as

149 proposed in the literature[26]. The simulated ignition delay time is defined as the time of maximum

150 dT/dt, as this is very similar to the experimental definition.

151   AramcoMech 1.3[27], developed at NUI Galway in 2013, which was selected as the base model

152 for methane oxidation, has been systematically modified and validated against a wide range of

153 experimental targets including shock tube ignition delay times, RCM ignition delay times, laminar

154 flame speed, JSR species mole fraction, and flow reactor speciation. Figure 3 shows a comparison

155 between the experiments and the predictions using AramcoMech 1.3 for mixtures with no NO_2

156 added (N_0), in the temperature range 1400 − 2050 K and at pressures of 1.2 − 10.0 atm. It appears

157   that AramcoMech 1.3 agrees reasonably well with the measured results under all experimental

158   conditions.

159   Regarding the NO_x chemistry, five literature models were chosen, namely those from

160   Sivaramakrishnan et al.[16], Rasmussen et al.[28], Mathieu et al. [7], Gersen et al. [9] and Faravelli et al.[15],

161   with all models containing detailed NO_x sub-models. Specifically, Rasmussen's NO_x sub-model

162   includes 62 species and 501 reactions and was developed based on their studies of NO_x effects on

163   methane[13], ethylene[28] and syngas[29]. This model has been validated against a large set of data

164   obtained in flow reactor, JSR, RCM, shock tube and laminar flames. Gersen's NO_x sub-model,

165   containing 61 species and 479 reactions, is based on the work of Rasmussen et al.[28], with some

166   amendments: 1) the rate constants of the reactions $CH_4 + NO_2 = \dot{C}H_3 + HONO$ and $CH_4 + NO_2 =$

167   $\dot{C}H_3 + HNO_2$ were replaced by the evaluations of Dean and Bozzelli[30]; 2) the rate constants of the

168   reactions $C_2H_6 + NO_2$ and $C_2H_4 + NO_2$ were taken by an analogy with the reaction of CH_4 with

169   NO_2. Sivaramakrishnan's NO_x sub-model includes 38 species and 278 reactions, and has been

170   validated against data from HPST, JSR and flow reactor. Mathieu's[7] NO_x sub-model includes 36

171   species and 305 reactions. The NH_3/NO_x chemistry was taken from Dagaut et al.[31], with the H_2/N_2O

172   chemistry being adopted from Mathieu et al.[32] and the hydrocarbon/NO_x interactions chemistry was

173   taken from Sivaramakrishnan et al[16]. Faravelli's[15] NO_x sub-model contains 30 species and 260

174   reactions. This model has also been validated against experimental data from shock tube, JSR and

175   laminar flame.

176   To better compare the NO_x sub-models, the five literature NO_x sub-models mentioned above

177   were combined with AramcoMech 1.3 in order to minimize the effect of the hydrocarbon sub-

178   mechanism. Herein, the five combined models are called Aramco-S, Aramco-R, Aramco-M,

179   Aramco-G and Aramco-F model, respectively. Figures 4–6 show the comparisons between the

180   measured ignition delay times and the model predictions using the five assembled models. The

181   results indicate that the five models exhibit only slightly different predictions of ignition delay times

182 for mixtures with relatively low NO_2 content, Fig. 4, but there is an obvious difference in the

183 predictions of these models and this discrepancy becomes more significant with increasing

184 concentrations of NO_2, Figs 5 and 6. Previously, Herzler and Naumann[6] performed a similar study,

185 i.e. they combined different NO_x sub-mechanisms (Rassmussen et al.[28], Faravelli et al.[15] and

186 Sivaramakrishnan et al.[16]) to a hydrocarbon sub-mechanism and then simulated the reactivity of

187 NO_x/hydrocarbon mixtures. They found that the different NO_x sub-mechanisms only presented a

188 negligible difference. This observation from Herzler and Naumann[6] is only consistent with that for

189 the N_{30} mixture in *this study* while it is inconsistent for the N_{50} and N_{70} mixtures. Obviously, the

190 different results are mainly attributable to the different NO_2 concentrations used. It can be therefore

191 inferred that all of the recent NO_x models can give good predictions for mixtures with low

192 concentrations of NO_2, but they cannot accurately predict the reactivity for mixtures with high NO_2

193 concentrations.

194   For the N_{30} mixture, Fig. 4, the predictions of all five models agree with the measured ignition

195 delay times at $T < 1280$ K but under-predict the experimental data at $T > 1280$ K in the pressure

196 range of 1.2 – 10.0 atm, and the discrepancies are more obvious with increasing pressures. For the

197 N_{50} mixture, Fig. 5, the five models under-predict the ignition delay times at 1.2 and 4.0 atm at all

198 temperatures tested. When the pressure increases to 10.0 atm, the Aramco-F, Aramco-M and

199 Aramco-S models show an acceptable agreement with the measured data at $T < 1200$ K, but still

200 under-predict at $T > 1200$ K. For the N_{70} mixture, Fig. 6, the Aramco-G, Aramco-F and Aramco-R

201 models moderately agree with the experimental results at $T < 1175$ K but become much faster at $T >$

202 1175 K, while the Aramco-M and Aramco-S models agree moderately at $T > 1175$ K but over-

203 predict the experimental ignition delay times at $T < 1175$ K.

204   As discussed above, the Aramco-M model exhibits generally better agreement compared to the

205 experimental data although it shows an under-prediction at high-temperatures for the N_{30} and N_{50}

206 mixtures and an over-prediction of the ignition delay times at low-temperatures for the N_{70} mixture.

9

207 Thus, the Aramco-M model was selected as the base model to develop a more accurate mechanism

208 for methane/NO_x mixtures.

209 Firstly, the C_2-hydrocarbon/NO_x interaction chemistry in the Aramco-M model was updated

210 using recently published C_2-hydrocarbon/NO_x subsets from Gersen et al[9]. Thereafter, the rate

211 constants of several key reactions, which were recognized though sensitivity analyses, were updated

212 to obtain better simulation agreement against our experimental data. All of the changes/additions to

213 the Aramco-M model are shown in Table 1. The thermochemistry of NO_x related species has been

214 re-calculated at NUI Galway with three quantum-chemical compound methods (CBS-APNO, G3

215 and G4) and the B3LYP/cc-pVTZ level of theory[33], and these new data have been adopted in our

216 updated mechanism. Figure 7 shows the performance of the modified mechanism against the

217 experimental data. It appears that the updated model captures well both the global activation energy

218 and ignition delay times for all of the mixtures tested over the range of physical conditions.

219 Additionally, the updated model has been used to simulate the ignition delay times reported by

220 Mathieu et al.[7] and Herzler and Naumann[6], and the comparisons are provided in the ***Supplementary***

221 ***Material***. Generally, the model exhibits good agreement compared to the literature data.

222 **4. Results and discussion**

223 In *this study*, the ignition delay times were measured behind the reflected shock waves for four

224 stoichiometric $NO_2/CH_4/O_2/Ar$ mixtures with different NO_2 concentrations (N_0, N_{30}, N_{50} and N_{70}) at

225 1.2, 4.0 and 10.0 atm. Here NO_2 was only regarded as a part of the argon used as diluent gas. The

226 detailed compositions of the tested mixtures are shown in Table 2 and all experimental data are

227 provided in the ***Supplemental Material***.

228 4.1 Pressure-dependence of CH_4/NO_2 mixtures

229 As with most hydrocarbons, the trends with respect to the influence of pressure on the ignition

10

230 delay times are in-line for all tested mixtures, Fig. 7. Moreover, the pressure effect increases with

231 increasing the NO_2 blending ratio. Particularly, the reductions in τ_{ign} are a factor of 2.43, 2.36, 2.63

232 and 3.08 (high-temperature) and 1.98, 2.01, 2.12 and 2.35 (low-temperature) for the N_0, N_{30}, N_{50}

233 and N_{70} mixtures, respectively, when the pressure is changed from 1.2 to 10.0 atm. Clearly, the

234 reduction in τ_{ign} with an increase in pressure for the N_{30} mixture is less obvious than the pure

235 methane one but is the reverse of the trend observed for the N_{50} and N_{70} mixtures. Mathieu et al.[7]

236 reported that the reduction in ignition delay times with increasing pressure for NO_2/CH_4 mixtures

237 was less important than for pure methane mixtures. The different observations can be attributed to

238 the different NO_2 concentrations present in the mixtures. In the Mathieu et al. study, the

239 concentration of NO_2 is similar to that of the N_{30} mixture in *this study*, and there is therefore a

240 similar pressure-dependence with methane, Fig. 7a. However, with increasing NO_2 addition as in

241 the N_{50} and N_{70} mixtures, the pressure-dependence of the mixtures is notably affected by the

242 CH_4/NO_2 chemistry, meaning that the reactivity of mixtures containing higher concentrations of

243 NO_2 is more sensitive to a change in pressure compared to methane, Figs. 7b and 7c.

244 4.2 The effect of NO_2 on methane reactivity

245   Figure 8 illustrates the effects of NO_2 addition on methane ignition at pressures of 1.2, 4.0 and

246 10.0 atm. It is seen that the presence of NO_2 significantly reduces τ_{ign} of methane over the entire

247 temperature range. Moreover, the reduction in τ_{ign} increases with increasing NO_2 concentrations.

248 Similar observations have also been found in previous studies of the NO_2 sensitization effect on

249 hydrocarbons[6, 7]. Note that this reduction in τ_{ign} is lessened at elevated pressures, which is also

250 observed by Mathieu et al.[7]. In addition, the reduction in τ_{ign} presents a considerable temperature-

251 dependence. Specifically, at 1.2 atm, Fig. 8a, the N_{30}, N_{50}, and N_{70} mixtures exhibit a 78.5%, 89.0%

252 and 94.1% reduction in τ_{ign} at low-temperatures. At 4.0 atm, Fig. 8b, an 83.8%, 93.5% and 97.5%

253 reduction can be observed for the N_{30}, N_{50} and N_{70} mixtures at low-temperatures. However, at 10.0

254 atm, Fig. 8c, the results shows a reduction of up to 86.1%, 95.1% and 98.3% for the N_{30}, N_{50} and

255 N_{70} mixtures at low-temperatures.

256   For a given mixture, the dependence of ignition delay times on temperature follows a simple

257 Arrhenius behavior, and the correlations are proposed based on the study of Davidson et al.[34], as

258 shown in the following format:

259
$$\tau = Ap^n \exp(E_a / RT) \tag{5}$$

260 Where τ is the ignition delay time (µs), p is the pressure (atm), T is the temperature (K) and E_a is the

261 global activation energy (kcal· K^{-1} mol^{-1}), R is the universal gas constant (equal to 1.9872×10^{-3}

262 kcal K^{-1} mol^{-1}). The correlations obtained are as follows:

263   N_0:

264
$$\tau = -5.7 p^{-0.64} \exp(42.15 / RT) \tag{6}$$

265   N_{30} ($T > 1350$ K):

266
$$\tau = -2.18 p^{-0.56} \exp(26.13 / RT) \tag{7}$$

267   N_{50}:

268
$$\tau = -2.0 p^{-0.69} \exp(24.11 / RT) \tag{8}$$

269   N_{70}:

270
$$\tau = -2.4 p^{-0.72} \exp(22.41 / RT) \tag{9}$$

271   It is observed that the exponent of pressure for the N_{30} mixture is smaller to that of the N_0

272 mixture indicating that ignition delay times are less sensitive to a change in pressure for the N_{30}

273 mixture. For the N_{50} and N_{70} mixtures however, the exponents of pressure are greater than that for

274 the N_0 mixture, indicating that ignition delay times are more sensitive to a change in pressure for

275 high NO_2 concentrations. Moreover, the results show an obvious reduction in the global activation

276 energy with increasing NO_2 concentration, with this reduction becoming moderate with increasing

277 NO_2 concentration.

278 **5. Kinetic analysis**

279 5.1 Sensitivity analysis

280 To identify the key reactions in the CH_4/NO_2 system, a brute force sensitivity analysis to

281 ignition delay time was conducted for the four mixtures tested in *this study* at 1500 K and 4.0 atm

282 using the modified Aramco-M model. Here, a sensitivity coefficient is defined as a perturbation

283 caused by a change in A-factor for each reaction rate constant[35] as follows:

$$S_i = \frac{\tau(2k_i) - \tau(0.5k_i)}{1.5\tau(k_i)}$$

284 (10)

285 where τ is the ignition delay time of the combustible mixture, k_i is rate constant of the ith reaction

286 and S_i is sensitivity coefficient of ith reaction. A negative value means that the reaction promotes

287 reactivity and vice versa.

288 The most-sensitive reactions of the pure methane and CH_4/NO_2 mixtures at 4.0 atm and 1500 K

289 are displayed in Figs. 9 and 10, respectively. For the N_0 mixture, Fig. 9, the chain-branching

290 reaction R1 ($\dot{H} + O_2 <=> \ddot{O} + \dot{O}H$) shows the biggest negative sensitivity coefficient, while the

291 parallel reactions R148 ($\dot{C}H_3 + O_2 <=> CH_3\dot{O} + \ddot{O}$) and R149 ($\dot{C}H_3 + O_2 <=> CH_2O + \dot{O}H$) present

292 relatively-high negative sensitivity coefficients as a two-fold effect: a) the consumption of an

293 unreactive methyl radical can form highly reactive free $\ddot{O}$ atoms or $\dot{O}H$ radicals which promote

294 reactivity; b) the $CH_3\dot{O}$ radical can directly decompose to form another $\dot{H}$ atom *via* $CH_3\dot{O} + M <=>$

295 $CH_2O + \dot{H} + M$. Reaction 129 ($CH_4 + \dot{H} <=> \dot{C}H_3 + H_2$) exhibits the highest positive sensitivity

296 coefficient as a highly reactivity $\dot{H}$ atom is consumed to form a relatively unreactive $\dot{C}H_3$ radical. It

297 appears that the most sensitive reactions associated with the ignition of pure methane involve $\dot{C}H_3$

298 radicals, indicating that the production and consumption of these are critical in controlling methane

299 ignition. Compared to larger hydrocarbons, in methane oxidation these fuel radicals do not readily

300 react with O_2 *via* R148 and R149 to form further free radicals due to lower conversion rates of $\dot{C}H_3$

301 radicals. It is well known that fuel radicals reacting with O_2 is typically one of the global rate

13

302 limiting steps during low-temperature hydrocarbon combustion. Therefore, as mentioned in

303 previous studies[36, 37], the two reactions above are responsible for the longer ignition delay times of

304 methane oxidation compared to other hydrocarbons.

305   Unlike pure methane, several of the newly-added reactions exhibit a high sensitivity coefficient

306 for the mixtures with NO_2 added to methane, Fig. 10. This means that NO_2 addition is responsible

307 for a significant perturbation in the radical pool generated during methane oxidation. Methyl

308 radicals can be preferentially oxidized by NO_2 *via* R1017 ($\dot{C}H_3 + NO_2 <=> CH_3\dot{O} + NO$) in the

309 mixtures containing NO_2 rather than by O_2 *via* R148 and R149 for the pure methane mixture,

310 leading to R1017 becoming the second-most important reaction in terms of increasing reactivity and

311 reducing the importance of R148 and R149. This reduction increases with an increase in NO_2

312 concentration. Figure 11 shows a comparison of the rate constants for R1017, R148 and R149. It

313 appears that the rate constant of R1017 is greater than that of R148 and R149 by orders of

314 magnitude. As a result, the consumption of $\dot{C}H_3$ radicals is dramatically promoted *via* R1017,

315 leading to an increased concentration of $\dot{H}$ atoms through the decomposition of $CH_3\dot{O}$ radicals.

316 Furthermore, R952 ($NO_2 + \dot{H} <=> NO + \dot{O}H$) is the most inhibiting reaction due to its competition

317 for $\dot{H}$ atoms with R1. Note that methane preferentially undergoes H-atom abstraction by $\dot{O}H$

318 radicals rather than by $\dot{H}$ atoms in the presence of NO_2, causing the dramatic decreases in the

319 sensitivity of R129 and the obvious increase in sensitivity of R130 ($CH_4 + \dot{O}H <=> \dot{C}H_3 + H_2O$).

320   For the mixtures containing a high concentration of NO_2, N_{50} and N_{70}, methane is almost

321 completely consumed *via* H-atom abstraction by $\dot{O}H$ radicals. An obvious reduction in the

322 sensitivity coefficients of R129 and R190 ($\dot{C}H_3 + \dot{C}H_3 (+ M) <=> C_2H_6 (+ M)$) with NO_2 addition is

323 observed as less methane is consumed *via* R130 and fewer $\dot{C}H_3$ radicals react *via* R190.

324 Particularly, the sensitivity coefficient of R1 increases for the N_{30} mixture but decreases with

325 increasing NO_2 concentration. The initial added NO_2 is mainly consumed through R952, and a

326 small amount reacts through R1017. For the N_{30} mixture, the initial added NO_2 is quickly consumed

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327 completely *via* R952 and R1017, and the production of Ḣ atoms and ȮH radicals in the presence of

328 NO_2 enhances reaction R1. For the N_{50} and N_{70} mixtures, however, the high initial NO_2

329 concentration persists for a long time before ignition, so R952 competes with R1 for Ḣ atoms, and a

330 reduction in sensitivity coefficient of R1 can be seen with increasing NO_2 concentration.

331 5.2 Kinetic effect of NO_2 addition on reaction pathway of methane

332   To further understand the chemical interaction between NO_2 and CH_4, a reaction pathway/flux

333 analysis was performed using the updated Aramco-M model at 4.0 atm and 1500 K, and at 20%

334 CH_4 consumption. For the pure methane mixture, the fuel molecules are largely consumed *via* H-

335 atom abstraction reactions by Ḣ and Ö atoms and ȮH radicals to form ĊH₃ radicals, Fig. 12.

336 Subsequently, ĊH₃ radicals are consumed *via* three reaction pathways: the first (56.8%) in which

337 ĊH₃ radicals undergo a radical-radical self-recombination termination reaction to generate ethane,

338 inhibiting reactivity; the second (12.5%) in which ĊH₃ radicals react with O_2 to form formaldehyde

339 and ȮH radicals *via* a chain propagation reaction which actually promotes reactivity; the third

340 (6.3%) in which ĊH₃ radicals react with HȮ₂ radicals in a chain branching reaction to produce ȮH

341 and CH₃Ȯ radicals which readily decompose to formaldehyde and Ḣ atoms. Note that in the

342 presence of NO_2, almost all of the methane fuel (84.5%, 95.1 and 96.3% for the N_{30}, N_{50} and N_{70}

343 mixtures, respectively) is consumed *via* H-atom abstraction by ȮH radicals. In addition, with

344 increasing NO_2 addition, the consumption of the ĊH₃ radicals *via* the self-recombination reaction

345 reduces to 13.8%, 2.4% and < 1.0% for the N_{30}, N_{50} and N_{70} mixtures, respectively. It can

346 significantly drive the ignition because less ĊH₃ radicals are transformed into stable C_2H_6

347 molecules *via* the chain termination of R190. This means that more ĊH₃ radicals, 63.2%, 84.4% and

348 89.1%, are oxidized by NO_2 to form CH₃Ȯ radicals *via* R1017. As a result, more Ḣ atoms are

349 generated from CH₃Ȯ radical decomposition with increasing concentrations of NO_2 and thus will

350 accelerate fuel consumption *via* H-atom abstraction.

351 5.3 Rate of production analysis with NO_2 addition

352   As described above, the production of $\dot{O}H$ radicals is critical to the promoting effect of NO_2 on

353 methane ignition. Here, the mole fractions of $\dot{O}H$ radicals produced as a function NO_2 addition at

354 4.0 atm and 1500 K are plotted in Fig. 13. It appears that the peak in $\dot{O}H$ mole fraction is

355 comparable for the four mixtures tested near the main ignition. However, the $\dot{O}H$ radical mole

356 fraction obviously increases with increasing NO_2 concentration during the induction time. It means

357 that there is a chemical environment to rapidly consume methane before the main ignition. To

358 demonstrate the simulated observation, rates of production of CH_4 and $\dot{O}H$ radicals were carried out

359 under the same condition, Fig. 14. The results indicate that reaction R1 largely contributes to the

360 production of $\dot{O}H$ radicals, while reactions R3 ($\dot{O}H + H_2 \iff \dot{H} + H_2O$) and R27 ($CO + \dot{O}H \iff$

361 $CO_2 + \dot{H}$) mainly consume $\dot{O}H$ radicals for the mixture without NO_2. For all of the key reactions

362 presented in Fig. 14a, the contributed rate peaks are displayed in the position nearby the main

363 ignition. However, the rates of consumption and production of $\dot{O}H$ radicals *via* reactions R1, R3 and

364 R27 decrease with increasing NO_2 addition, while the development of $\dot{O}H$ radicals *via* reaction

365 R130 consuming $\dot{O}H$ radicals and reaction R952 producing $\dot{O}H$ radicals is observed to be more

366 important. Particularly, for the N_{70} mixture, reactions R952 and R130 displace R1, R3 and R27 in

367 becoming the most important $\dot{O}H$ radical production and consumption reactions, respectively. It is

368 worth noting that the peaks contributed by R952 and R130 in the rate of production analysis appear

369 during the induction time rather than at the main ignition. This indicates that the free radical pool

370 will be pre-established at the initial stage of ignition by NO_2 addition, leading to methane can be

371 consumed *via* R130 at the ignition induced time. This confirms the simulation result observed in

372 Fig. 13. In fact, methane is largely consumed by H-atom abstraction by $\dot{H}$ and $\ddot{O}$ atoms and $\dot{O}H$

373 radicals and *via* R129, R131 ($CH_4 + \ddot{O} \iff \dot{C}H_3 + \dot{O}H$) and R130, for the mixtures with low NO_2

374 content. However, for the mixtures with high NO_2 content, namely the N_{50} and N_{70} mixtures, only

375 R130 is observed to be competitive in consuming methane, Fig. 14b. There is a clearly different

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376 oxidation cycle pathway from pure methane in the presence of NO_2, namely, the $\dot{C}H_3$ radicals

377 formed by R130 goes to feed R1017 to produce more $CH_3\dot{O}$ radicals which readily decompose to

378 generate reactive $\dot{H}$ atoms and promote the formation of $\dot{O}H$ radicals *via* R952. The abundant $\dot{O}H$

379 radicals formed from R952 further accelerate the methane oxidation *via* R130. This also explains

380 why R130 becomes the important reaction promoting reactivity in Fig. 9 for high concentrations of

381 NO_2 present in the CH_4/NO_2 mixtures.

6. Conclusions

383 Ignition delay times of $NO_2/CH_4/O_2/Ar$ mixtures with mole blending ratio of $NO_2:CH_4 = 0$,

384 30:70, 50:50 and 70:30 were measured behind reflected shock waves at pressures ranging from 1.2

385 to 10.0 atm and for temperatures ranging from 933 to 1961 K. A kinetic analysis was performed

386 using a modified model to interpret the promoting effect of NO_2 on methane ignition. The main

387 conclusions are summarized as follows,

388 1) The addition of NO_2 significantly reduces ignition delay times of methane oxidation. The

389 reduction is more prominent with decreasing temperature and increasing pressure. The

390 promoting effect of NO_2 is more remarkable for the mixtures with higher NO_2

391 concentration. Moreover, the addition of NO_2 reduces the global activation energy of

392 methane and the reduction becomes more moderate with increasing NO_2 addition.

393 2) Five assembled models (Aramco-M, Aramco-G, Aramco-R, Aramco-S and Aramco-F) were

394 used to simulate the measured ignition delay times. For the mixtures with low NO_2

395 concentrations, (N_0 and N_{30}) the five models present similar predictions and agree with the

396 experimental data. However, the five models do not predict well the experimental

397 measurements for the mixtures with higher NO_2 content (N_{50} and N_{70}).

398 3) An updated model is proposed to simulate the current data and other literature data and has

399 been used to conduct a kinetic analysis. NO_2 addition benefits the free radical pool

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400 especially $\dot{O}H$ radical formation in the initial ignition stage of methane, and perturbs the

401 branching ratios of key reactions. Compared to pure methane, the formation of $\dot{O}H$ radicals

402 occurs mainly *via* the inter-conversion of NO_2 and NO *via* R952 ($NO_2 + \dot{H} <=> NO + \dot{O}H$)

403 rather than R1 ($\dot{H} + O_2 <=> \ddot{O} + \dot{O}H$), while more stable $\dot{C}H_3$ radicals prefer to undergo

404 reaction R1017 ($\dot{C}H_3 + NO_2 <=> CH_3\dot{O} + NO$) in a chain-propagation process rather than

405 radical self-recombination via R190 ($\dot{C}H_3 + \dot{C}H_3 (+ M) <=> C_2H_6 (+ M)$).

Acknowledgements

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References

413 1. Tian, L.; Cao, Y.; Chai, X.; Liu, T.; Feng, P.; Feng, H.; Zhou, D.; Shi, B.; Oestreich, R.;

414 Rodvelt, G. Best practices for the determination of low-pressure/permeability coalbed methane

415 reservoirs, Yuwu Coal Mine, Luan mining area, China. *Fuel* **2015,** 160, 100-107.

416 2. Rightmire, C. Coalbed methane resource. **1984**.

417 3. Nicolle, A.; Dagaut, P. Occurrence of NO-reburning in MILD combustion evidenced via

418 chemical kinetic modeling. *Fuel* **2006,** 85 (17), 2469-2478.

419 4. Dubreuil, A.; Foucher, F.; Mounaı, C.; Dayma, G.; Dagaut, P. HCCI combustion: Effect of NO

420 in EGR. *Proc. Combust. Inst.* **2007,** 31 (2), 2879-2886.

421 5. Hori, M.; Matsunaga, N.; Marinov, N.; William, P.; Charles, W. In *An experimental and kinetic*

422 *calculation of the promotion effect of hydrocarbons on the NO-NO$_2$ conversion in a flow reactor*,

423 Symposium (International) on Combustion, **1998**; Elsevier: 1998; pp 389-396.

424 6. Herzler, J.; Naumann, C. Shock Tube Study of the Influence of NO$_x$ on the Ignition Delay

425 Times of Natural Gas at High Pressure. *Combust. Sci. Technol.* **2012,** 184 (10-11), 1635-1650.

426 7. Mathieu, O.; Pemelton, J. M.; Bourque, G.; Petersen, E. L. Shock-induced ignition of methane

427 sensitized by NO$_2$ and N$_2$O. *Combustion and Flame* **2015**.

428 8. Dayma, G.; Dagaut, P. Eeffects of air contamination on the combustion of hydrogen—effect of

429 NO and NO$_2$ addition on hydrogen ignition and oxidation kinetics. *Combust. Sci. Technol.* **2006,**

430 178 (10-11), 1999-2024.

431 9. Gersen, S.; Mokhov, A.; Darmeveil, J.; Levinsky, H.; Glarborg, P. Ignition-promoting effect of

432 NO$_2$ on methane, ethane and methane/ethane mixtures in a rapid compression machine. *Proc.*

433 *Combust. Inst.* **2011,** 33 (1), 433-440.

434 10. Chong, J.; Tsolakis, A.; Gill, S.; Theinnoi, K.; Golunski, S. E. Enhancing the NO$_2$/NO$_x$ ratio in

435 compression ignition engines by hydrogen and reformate combustion, for improved aftertreatment

436   performance. *Int. J. Hydrogen Energy* **2010,** 35 (16), 8723-8732.

437   11. Dabora, E. Effect of NO_2 on the ignition delay of CH_4-air mixtures. *Combust. Flame* **1975,** 24,

438   181-184.

439   12. Konnov, A. Implementation of the NCN pathway of prompt-NO formation in the detailed

440   reaction mechanism. *Combust. Flame* **2009,** 156 (11), 2093-2105.

441   13. Rasmussen, C. L.; Rasmussen, A. E.; Glarborg, P. Sensitizing effects of NO_x on CH_4 oxidation

442   at high pressure. *Combust. Flame* **2008,** 154 (3), 529-545.

443   14. Faravelli, T.; Frassoldati, A.; Ranzi, E. Kinetic modeling of the interactions between NO and

444   hydrocarbons in the oxidation of hydrocarbons at low temperatures. *Combust. Flame* **2003,** 132 (1),

445   188-207.

446   15. Frassoldati, A.; Faravelli, T.; Ranzi, E. Kinetic modeling of the interactions between NO and

447   hydrocarbons at high temperature. *Combust. Flame* **2003,** 135 (1), 97-112.

448   16. Sivaramakrishnan, R.; Brezinsky, K.; Dayma, G.; Dagaut, P. High pressure effects on the

449   mutual sensitization of the oxidation of NO and CH_4–C_2H_6 blends. *Phys. Chem. Chem. Phys.* **2007,**

450   9 (31), 4230-4244.

451   17. Mével, R.; Shepherd, J. Ignition delay-time behind reflected shock waves of small

452   hydrocarbons–nitrous oxide (–oxygen) mixtures. *Shock Waves* **2015,** 25 (3), 217-229.

453   18. Zhang, Y.; Huang, Z.; Wei, L.; Zhang, J.; Law, C. K. Experimental and modeling study on

454   ignition delays of lean mixtures of methane, hydrogen, oxygen, and argon at elevated pressures.

455   *Combust. Flame* **2012,** 159 (3), 918-931.

456   19. Zhang, Y.; Huang, Z.; Wei, L.; Niu, S. Experimental and kinetic study on ignition delay times

457   of methane/hydrogen/oxygen/nitrogen mixtures by shock tube. *Chinese Sci. Bull.* **2011,** 56 (26),

458   2853-2861.

459   20. Zhang, J.; Pan, L.; Zhang, Z.; Mo, J.; Huang, Z. Shock tube and kinetic modeling study of

460   isobutanal oxidation. *Energy Fuels* **2013,** 27 (5), 2804-2810.

461 21. Morley, C. Gaseq: a chemical equilibrium program for Windows. *http:// www. gaseq. co. uk*

462 **2005**.

463 22. Petersen, E. L.; Rickard, M. J.; Crofton, M. W.; Abbey, E. D.; Traum, M. J.; Kalitan, D. M. A

464 facility for gas-and condensed-phase measurements behind shock waves. *Measurement Sci.*

465 *Technol.* **2005,** 16 (9), 1716.

466 23. Zhang, Z.; Hu, E.; Pan, L.; Chen, Y.; Gong, J.; Huang, Z. Shock-Tube Measurements and

467 Kinetic Modeling Study of Methyl Propanoate Ignition. *Energy Fuels* **2014,** 28 (11), 7194-7202.

468 24. Kee, R. J.; Rupley, F. M.; Miller, J. A. *Chemkin-II: A Fortran chemical kinetics package for the*

469 *analysis of gas-phase chemical kinetics*; Sandia National Labs., Livermore, CA (USA): **1989**.

470 25. Lutz, A. E.; Kee, R. J.; Miller, J. A. *SENKIN: A fortran program for predicting homogeneous*

471 *gas phase chemical kinetics with sensitivity analysis*; Sandia National Labs., Livermore, CA (USA):

472 1988.

473 26. Chaos, M.; Dryer, F. L. Chemical‐kinetic modeling of ignition delay: Considerations in

474 interpreting shock tube data. *Int. J. Chem. Kinet.* **2010,** 42 (3), 143-150.

475 27. Metcalfe, W. K.; Burke, S. M.; Ahmed, S. S.; Curran, H. J. A hierarchical and comparative

476 kinetic modeling study of $C_1- C_2$ hydrocarbon and oxygenated fuels. *Int.l J. Chem. Kinet.* **2013,** 45

477 (10), 638-675.

478 28. Lopez, J. G.; Rasmussen, C. L.; Alzueta, M. U.; Gao, Y.; Marshall, P.; Glarborg, P.

479 Experimental and kinetic modeling study of C_2H_4 oxidation at high pressure. *Proc. Combust. Inst.*

480 **2009,** 32 (1), 367-375.

481 29. Rasmussen, C. L.; Hansen, J.; Marshall, P.; Glarborg, P. Experimental measurements and

482 kinetic modeling of $CO/H_2/O_2/NO_x$ conversion at high pressure. *Int. J. Chem. Kinet.* **2008,** 40 (8),

483 454-480.

484 30. Dean, A. M.; Bozzelli, J. W. Combustion chemistry of nitrogen. In *Gas-phase combustion*

485 *chemistry*, Springer: **2000**; pp 125-341.

486   31. Dagaut, P.; Glarborg, P.; Alzueta, M. U. The oxidation of hydrogen cyanide and related

487   chemistry. *Prog. Energy Combust. Sci.* **2008,** 34 (1), 1-46.

488   32. Mathieu, O.; Levacque, A.; Petersen, E. Effects of N_2O addition on the ignition of H_2–O_2

489   mixtures: Experimental and detailed kinetic modeling study. *Int. J. Hydrogen Energy* **2012,** 37 (20),

490   15393-15405.

491   33. Bugler, J.; Somers, K. P.; Simmie, J. M.; Guthe, F.; Curran, H. J. *Proc. Combust. Inst.* **2015**,

492   submitted.

493   34. Davidson, D.; Oehlschlaeger, M.; Herbon, J.; Hanson, R. Shock tube measurements of iso-

494   octane ignition times and OH concentration time histories. *Proc. Combust. Inst.* **2002,** 29 (1), 1295-

495   1301.

496   35. Zhang, J.; Wei, L.; Man, X.; Jiang, X.; Zhang, Y.; Hu, E.; Huang, Z. Experimental and

497   modeling study of n-butanol oxidation at high temperature. *Energy Fuels* **2012,** 26 (6), 3368-3380.

498   36. Takita, K.; Abe, N.; Masuya, G.; Ju, Y. Ignition enhancement by addition of NO and NO_2 from

499   a N_2/O_2 plasma torch in a supersonic flow. *Proc. Combust. Inst.* **2007,** 31 (2), 2489-2496.

500   37. Chen, Z.; Qin, X.; Ju, Y.; Zhao, Z.; Chaos, M.; Dryer, F. L. High temperature ignition and

501   combustion enhancement by dimethyl ether addition to methane–air mixtures. *Proc. Combust. Inst.*

502   **2007,** 31 (1), 1215-1222.

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508 **Table. 1**. List of updated reactions rate constants.

Reactions	Reaction rate constant			Reference
	A	*n*	E_a	
$\dot{C}H_3+NO_2 <=> CH_3O+NO$	1.28E+13	-0.2	0.0	[16]
$CH_2O+NO_2 <=> HCO+HONO$	1.40E-07	5.640	9220.0	[28]
$NO_3+NO_2 <=> NO_2+NO+O_2$	2.35E+10	0.000	2960.0	[16]
$HONO+OH <=> NO_2+H_2O$	1.70E+12	0.000	-520.0	[16]
$NO_2+O <=> NO+O_2$	1.00E+14	-0.520	0.000	[9]

509 Units = $cm^3 \ mole^{-1} \ s^{-1} \ cal^{-1}$.

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511 **Table 2.** The compositions of mixtures measured in the present experiment.

Mixture	Mole blending ratio	CH_4	NO_2	O_2	AR
N_0	100% CH_4	0.0190	0.0000	0.0381	0.9429
N_{30}	30% NO_2/70% CH_4	0.0190	0.0081	0.0384	0.9345
N_{50}	50% NO_2/50% CH_4	0.0187	0.0187	0.0371	0.9255
N_{70}	70% NO_2/30% CH_4	0.0189	0.0435	0.0379	0.8997

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Figures captions

**Fig.1.** Typical measured pressure and OH* profiles at the end-wall for N_{30} mixture at 4.0 atm and 1315 K.

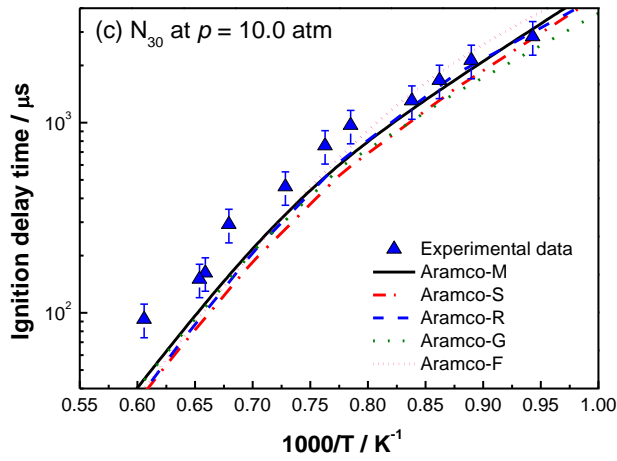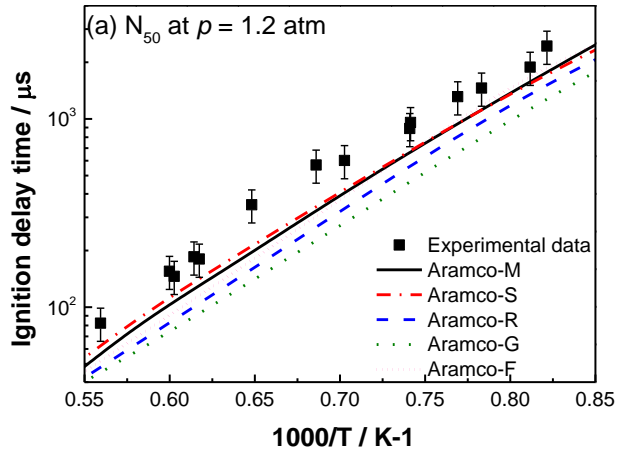**Fig.2.** Comparison between the measured data and the predictions using Aramco 1.3 for N_0 at different pressures.
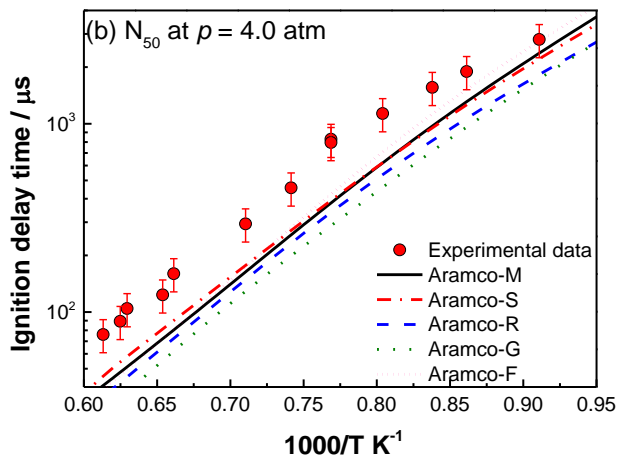
Fig.3. Comparison between the measured data and the predictions with five assembled models for N_{30} mixture at different pressures. (a) 1.2 atm, (b) 4.0 atm, (c) 10.0 atm.
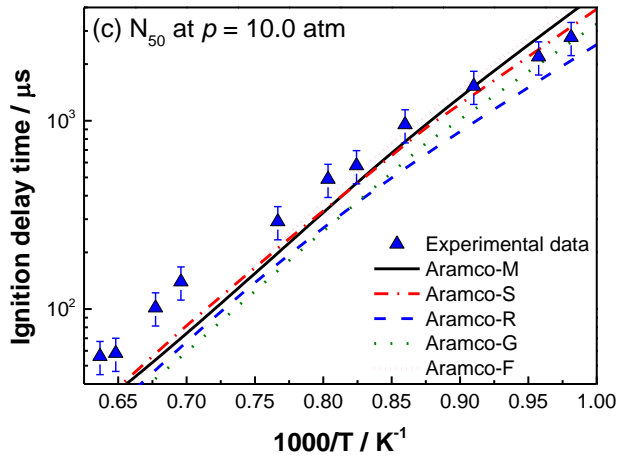
Fig.4. Comparison between the measured data and the predictions with five assembled models for N_{50} mixture at different pressure. (a) 1.2 atm, (b) 4.0 atm, (c) 10.0 atm.

Fig.5. Comparison between the measured data and the predictions with five assembled models for N_{70} mixture at different pressures. (a) 1.2 atm, (b) 4.0 atm, (c) 10.0 atm.
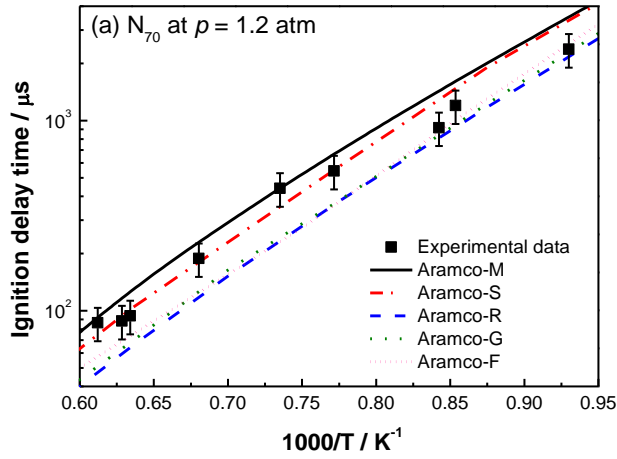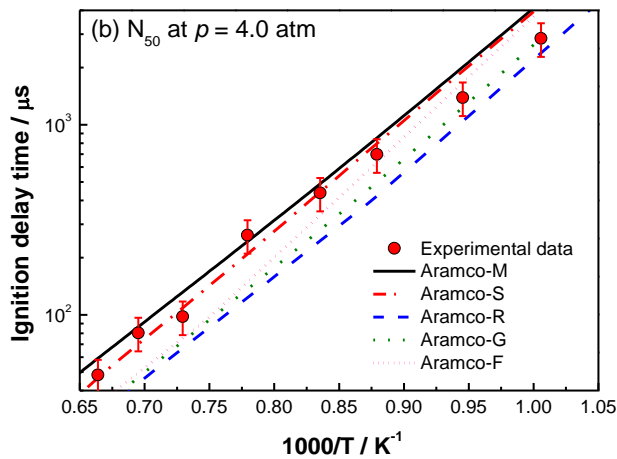
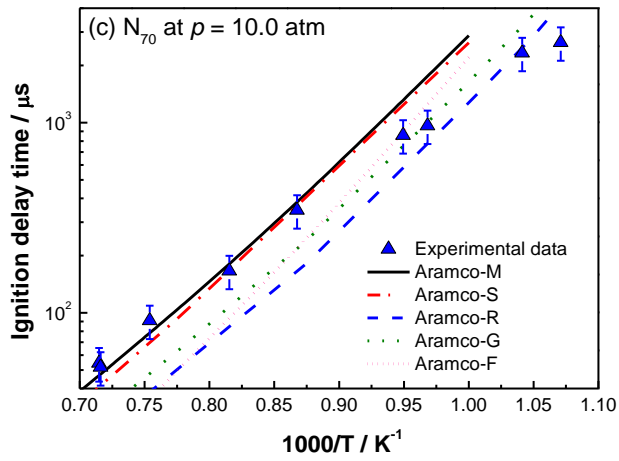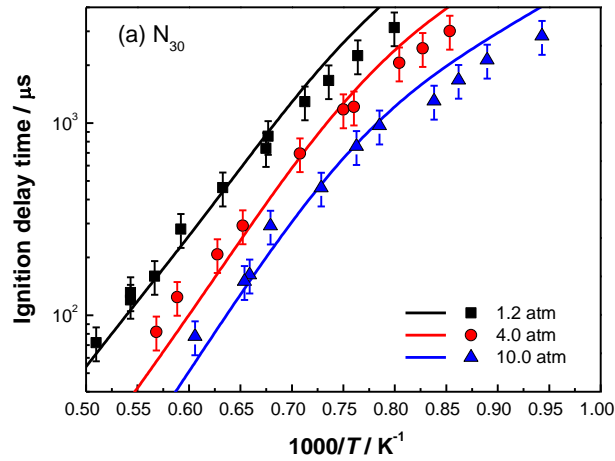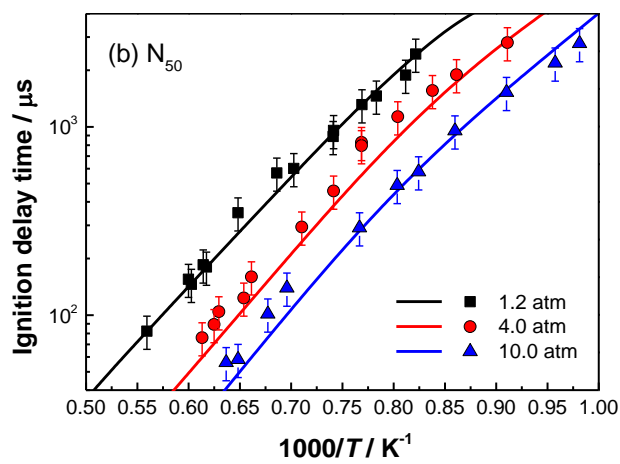**Fig.6.** Comparison between the measured ignition delay times and the model predictions with updated model for the CH_4/NO_2 mixtures. (a) N_{30}, (b) N_{50}, (c) N_{70}.

Fig.7. Comparison of the current and literature data for CH_4/NO_2 with 70.8% blend ratio at 1.3 atm and $\phi = 0.5$.

Fig.8. Effect of NO_2 blending ratio on the ignition delay time of methane at pressure from 1.2 to 10.0 atm. Symbols: experiments; Lines: simulations with updated model. (a) 1.2 atm; (b) 4.0 atm; (c) 10.0 atm.

Fig.9. Normalized sensitivity analysis for neat CH_4 at $p = 4.0$ atm and $T = 1500$ K using updated model.

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533 **Fig.10.** Normalized sensitivity analysis for N_{30}, N_{50} and N_{70} at $p = 4.0$ atm and $T = 1500$ K using

534 updated model. The normalized sensitivity coefficient of R1: $\dot{H} + O_2 <\Leftrightarrow> \ddot{O} + \dot{O}H$ is divided by 2.

535 **Fig.11.** Comparison of the rate constants for the reactions R148, R149 and R1017.

536 **Fig.12.** Reaction pathway analysis of four mixtures at 4 atm and 1500 K using updated model. N_0:

537 black, N_{30}: red, N_{50}: blue, and N_{70}: green.

538 **Fig.13.** Mole fraction of $\dot{O}H$ growth during ignition of CH_4/NO_2 mixtures at $p = 4.0$ atm and $T =$

539 1500 K using updated model.

540 **Fig.14.** Rate of productions for $\dot{O}H$ and CH_4 in CH_4/NO_2 ignition process at $p = 4.0$ atm and $T =$

541 1500 K using updated model. (a) rate of $\dot{O}H$ production analysis; (b) rate of CH_4 production

542 analysis.

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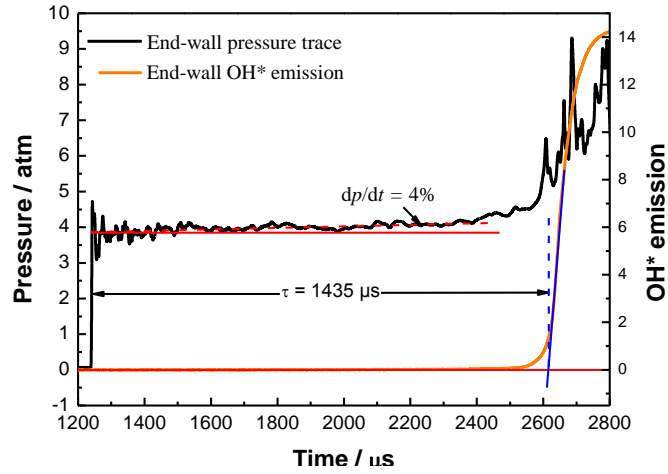
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Fig.1. Typical measured pressure and OH* profiles at the end-wall for N_{30} mixture at 4.0 atm and

1315 K.

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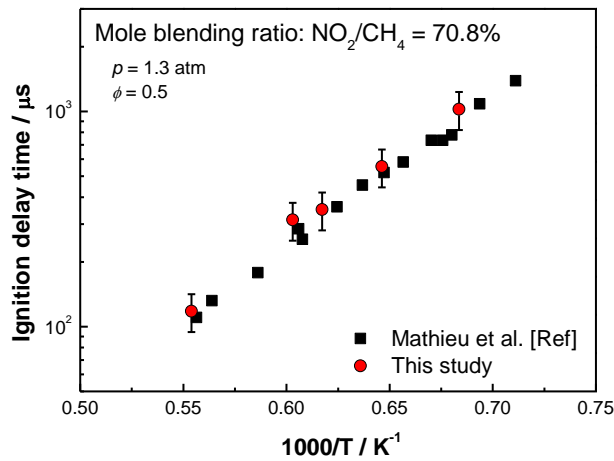
Fig.2. Comparison of the current and literature data for CH_4/NO_2 with 70.8% blend ratio at 1.3 atm

and $\varphi = 0.5$.

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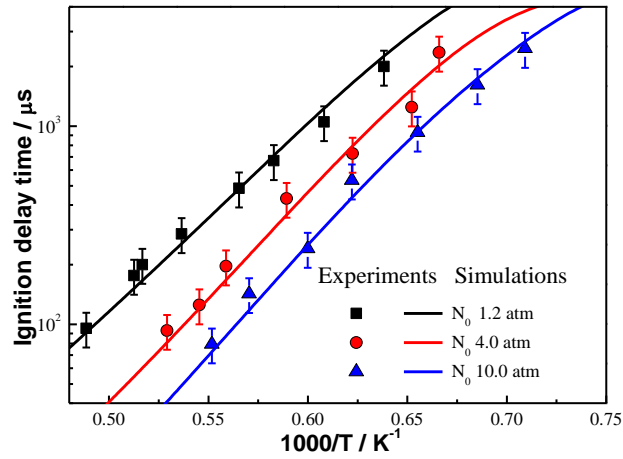
Fig.3. Comparison between the measured data and the predictions using AramcoMech 1.3 for N_0 at

different pressures.

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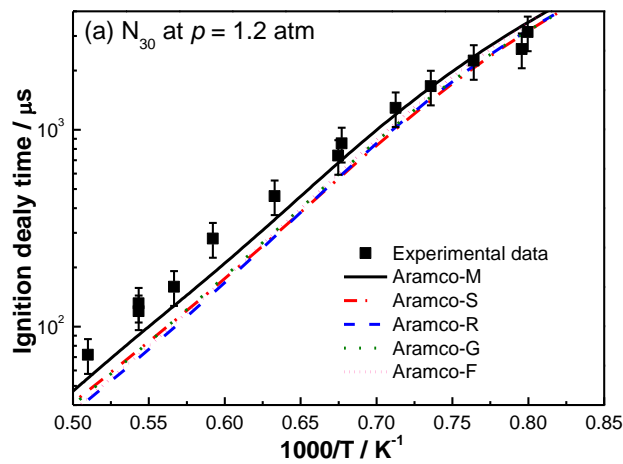
557
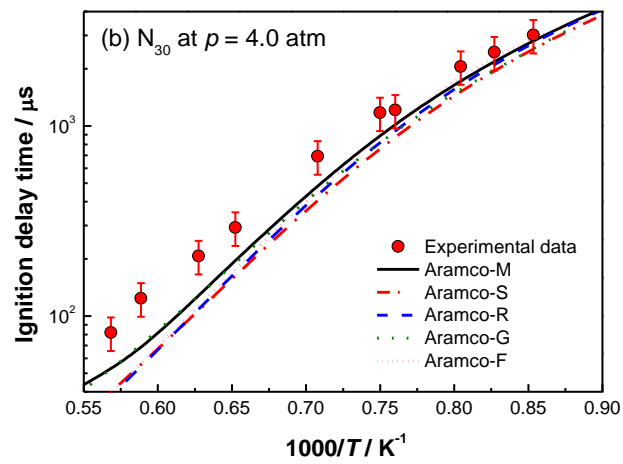
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Fig.4. Comparison between the measured data and the predictions with five assembled models for

N_{30} mixture at different pressures. (a) 1.2 atm, (b) 4.0 atm, (c) 10.0 atm.

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(c) N_{50} at p = 10.0 atm

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Fig.5. Comparison between the measured data and the predictions with five assembled models for

N_{50} mixture at different pressure. (a) 1.2 atm, (b) 4.0 atm, (c) 10.0 atm.

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(a) N_{70} at p = 1.2 atm

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(b) N_{50} at p = 4.0 atm

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Fig.6. Comparison between the measured data and the predictions with five assembled models for

N₇₀ mixture at different pressures. (a) 1.2 atm, (b) 4.0 atm, (c) 10.0 atm.

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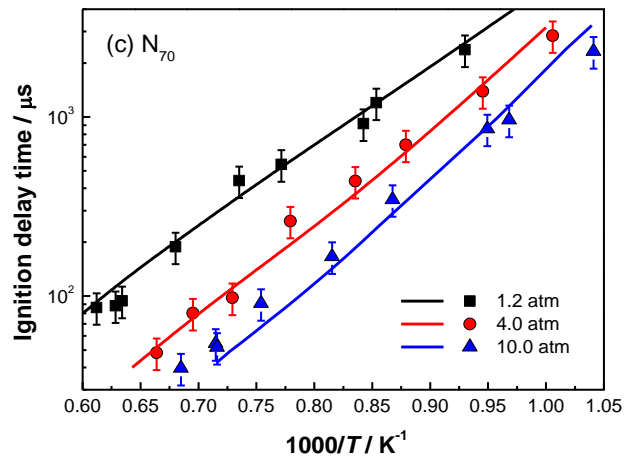
Fig.7. Comparison between the measured ignition delay times and the model predictions with updated model for the CH_4/NO_2 mixtures. (a) N_{30}, (b) N_{50}, (c) N_{70}.

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Fig.8. Effect of NO_2 blending ratio on the ignition delay time of methane at pressure from 1.2 to 10.0 atm. Symbols: experiments; Lines: simulations with updated model. (a) 1.2 atm; (b) 4.0 atm; (c) 10.0 atm.

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Fig.9. Normalized sensitivity analysis for neat CH_4 at p = 4.0 atm and T = 1500 K using updated model.

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Fig.10. Normalized sensitivity analysis for N_{30}, N_{50} and N_{70} at $p = 4.0$ atm and $T = 1500$ K using updated model. The normalized sensitivity coefficient of R1: $\dot{H} + O_2 <=> \ddot{O} + \dot{O}H$ is divided by 2.

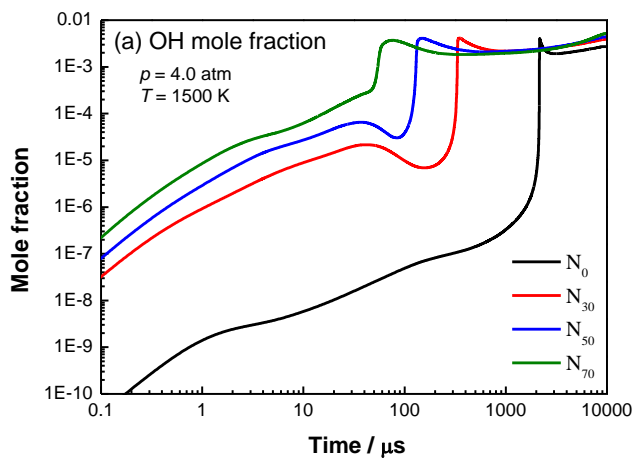**Fig.11.** Comparison of the rate constants for the reactions R148, R149 and R1017.

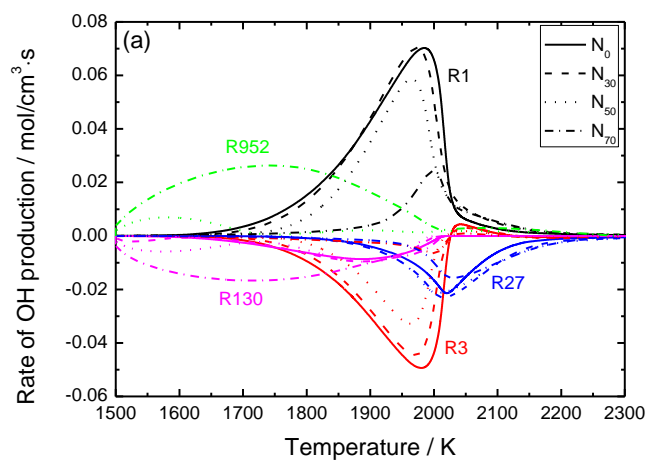**Fig.12.** Reaction pathway analysis of four mixtures at 4 atm and 1500 K using updated model. N_0: black, N_{30}: red, N_{50}: blue, and N_{70}: green.

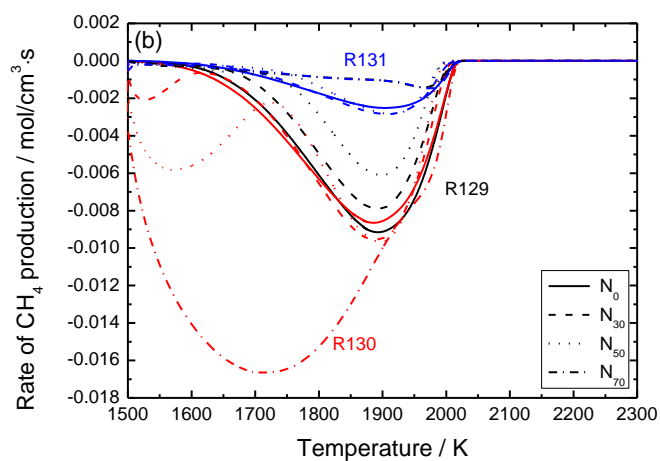**Fig.13.** Mole fraction of $\dot{O}H$ growth during ignition of CH_4/NO_2 mixtures at $p = 4.0$ atm and $T = 1500$ K using updated model.

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610 **Fig.14.** Rate of productions for ȮH and CH$_4$ in CH$_4$/NO$_2$ ignition process at p = 4.0 atm and T =

611 1500 K using updated model. (a) rate of ȮH production analysis; (b) rate of CH$_4$ production

612 analysis.

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