



## An RCM experimental and modeling study on CH<sub>4</sub> and CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> oxidation at pressures up to 160 bar

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1 An RCM Experimental and Modeling Study on CH<sub>4</sub> and  
2 CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> Oxidation at Pressures up to 160 bar

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## 19 **Abstract**

20           The oxidation of CH<sub>4</sub> and CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> mixtures were studied at pressures relevant to knocking in large  
21 bore natural gas engines. The experiments were carried out in a rapid compression machine (RCM) at end of  
22 compression (EOC) temperatures ranging between 885 – 940 K at compressed gas pressures of 105, 125,  
23 150, and 160 bar at varying equivalence ratios (0.417, 0.526, and 1.0) and dilution percentages (0, 10, and  
24 30% Exhaust Gas Recirculation - EGR) that were defined in a test matrix. This study describes the method  
25 and limitations of performing high-pressure experiments of this magnitude in an RCM, modeling, and  
26 validation of the kinetic mechanism against experimental data. While the recently published AramcoMech  
27 2.0 could well predict the ignition delay times (IDTs) for CH<sub>4</sub> within the uncertainty ranges at comparatively  
28 higher pressures and lower temperatures (885 – 940 K), the predicted reactivity is, in general, lower than  
29 that of AramcoMech 1.3 as shown in our previous screening study. Based on the comparison between both  
30 mechanisms as well as sensitivity analysis on the predicted IDTs, the reaction rate constant for H-atom  
31 abstraction from CH<sub>4</sub> by HO<sub>2</sub> radical was optimized in order to achieve better agreement with the new data  
32 while maintaining the agreement to the previous data sets. The modified mechanism predicts well the IDTs  
33 and the trend of their variation caused by the change in pressure, equivalence ratio, dilution percentage, and  
34 mixture variation with C<sub>2</sub>H<sub>6</sub>.

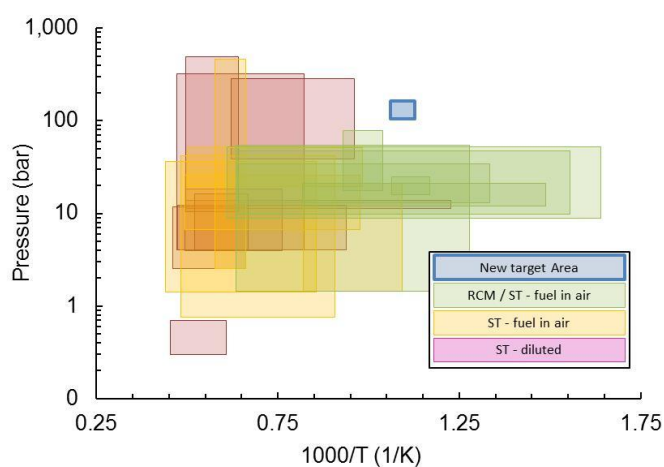
35 **Keywords:** RCM, Methane, Ignition delay, elevated pressures, modeling

## 36 **1. Introduction**

37 Due to the development of new extraction technologies and falling prices, natural gas is becoming an  
38 increasingly popular fuel, especially for commercial engine applications [1]. One of the limiting factors in  
39 achieving higher combustion efficiency in large bore commercial engines is the knocking phenomenon in the  
40 end-gas (unburnt zone). This can be predicted with the aid of software tools coupled with detailed chemical  
41 kinetic mechanisms. An example for one such software chain is the combination of 0-D, 1-D, and 3-D  
42 Computational Fluid Dynamics (CFD) tools developed at FEV GmbH in co-operation with the Institute for  
43 Combustion Engines, RWTH Aachen University [2]. The conventional combustion strategy for commercial  
44 engines (bore < 180 mm) is an open-chamber spark ignited operation mode either with equivalence ratio ( $\phi$ )  
45 close to 1 together with EGR or a lean operation mode ( $\phi < 0.625$ ). For large bore engines (bore > 180 mm),  
46 a pre-chamber is employed (with or without gas injection), where the natural gas is ignited and the high  
47 turbulent jets coming from the pre-chamber then ignite the gas in the main chamber [1]. Typically, the  
48 equivalence ratios in the main chamber range from 0.526 to 0.417 and compression end pressures exceed  
49 100 bar at full engine load. The pressure, temperature, and equivalence ratio which are chosen for the  
50 investigation of this study, represent the conditions in the end-gas region of the engine at the start of  
51 ignition and close to the center of combustion, consequently reflecting real engine application conditions.

52 A kinetic understanding formulated in kinetic mechanisms are required for today's combustor design  
53 tools [2]. Natural gas relevant modeling and experimental studies in this regard have been published  
54 previously. The work by Spadaccini et al. [3] covered a comprehensive literature review on natural gas to the  
55 1990's and this study also involved shock tube experiments to determine IDTs for mixtures of methane with  
56 ethane, propane, or butane at equivalence ratios of 0.45 – 1.25 at pressures of 3 – 15 bar. There is a large  
57 experimental database [3-22] available for IDT shock tube investigations of CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> at higher  
58 temperatures (>1000 K) and pressures varying from 1 to 480 bar. However, for IDT studies at lower  
59 temperatures (600 to 1100 K) and comparatively higher pressures (> 40 bar) the available data is sparse [23-  
60 29]. The recent work by Aul et al. [16] focused on deriving a test condition based on the statistical design of  
61 experiments and it also emphasized the need to validate mechanisms in areas for which little data have been  
62 recorded experimentally. Consequently, this study aims to expand the unexplored area of **lower**

63 **temperatures** and elevated pressures for C1 – C2 hydrocarbons at varying equivalence ratios and dilution  
64 percentages in an RCM. **Figure 1** shows the graphical insight of the conditions tested with both shock tube  
65 and RCM from various studies and the novel targeted regime which is the focus of this paper.



66

67 **Figure 1: The graphical overview of the literature on Natural gas mixtures for the different targeted pressures and temperatures.**

68 Herein, we deliver a new set of high-pressure experiments for CH<sub>4</sub> and CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> mixtures, which according  
69 to the **authors'** knowledge, are the first set of experiments recorded in an RCM at EOC gas pressures up to  
70 160 bar. It builds upon a previous screening study carried out with CH<sub>4</sub> and CH<sub>4</sub>/C<sub>3</sub>H<sub>8</sub> mixtures in the same  
71 facility at pressures ranging from 80 to 120 bar [30]. The extended pressure and equivalence ratio range  
72 cover the relevant conditions of large bore gas engines as described before. These experiments are used for  
73 modeling and validating the chemical kinetic mechanism.

## 74 **2. Experiments**

75 The experiments were performed on a defined test matrix relevant to knocking in the main chamber and  
76 pre-chamber of large bore gas engines. The test matrix involves a variation of pressure, dilution, equivalence  
77 ratio, and mixture composition. The dilution of the gas mixture was considered in order to reflect the effect  
78 of inert EGR. While CO<sub>2</sub> and H<sub>2</sub>O are major combustion products found in the exhaust gas, previous studies  
79 have shown that their chemical effect is minor. The work of Donohoe et al. [31] showed that there is a  
80 significant change in thermal properties of the mixture with steam addition, whereas no relevant chemical  
81 effect is observed. Zeng et al. [32] studied the effect of N<sub>2</sub> and CO<sub>2</sub> on the ignition characteristics of CH<sub>4</sub>/air  
82 mixtures in shock tubes for dilution coefficients of 0%, 20%, and 50%. It was observed that for fuel-lean

83 mixtures there is a diminutive change in the reactivity when the mixture is diluted by 20% of either N<sub>2</sub> or  
 84 CO<sub>2</sub>. For this reason, the EGR is represented by the percentage of diluent in this study instead of considering  
 85 CO<sub>2</sub> and H<sub>2</sub>O as diluents. **Table 1** shows the test matrix which was used for this study. In order to understand  
 86 the representation of % EGR with inert gas diluent mol % a brief explanation of the same is attached to the  
 87 supplementary material.

No.	Pressure [bar]	EGR mol %	$\phi$ -	Mole fraction %			
				CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	diluent	O <sub>2</sub>
1	105	10	0.526	4.74	0	77.26	18.00
2	125	10	0.526	4.74	0	77.26	18.00
3	150	10	0.526	4.74	0	77.26	18.00
4	125	0	0.526	5.24	0	74.86	19.90
5	125	0	0.526	4.17	0.62	75.21	19.99
6	160	30	1	6.63	0	80.13	13.25
7	125	0	0.417	4.19	0	75.69	20.12

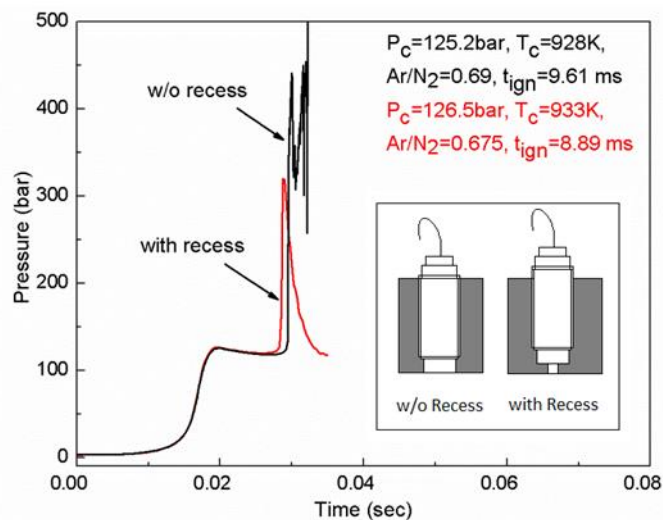
88

89 **Table 1: Test matrix used in the study**

90 The construction of the RCM used in this study has been described in detail by Lee et al. [33]. The facility  
 91 utilizes a pneumatic driving and hydraulic stopping mechanism, and for these high-pressure experiments  
 92 both the driving and hydraulic pressure had to be increased substantially. Mixture preparation was carried  
 93 out in a stainless steel mixing vessel and the partial pressures of individual gases were monitored using two  
 94 pressure sensors ranging from 0 – 500 mbar (STS ATM.1<sup>st</sup>) and 0 – 10 bar (STS ATM.1<sup>st</sup>). The initial  
 95 temperature was recorded with several type T thermocouples that were mounted on the outer surface of  
 96 the reaction chamber and the mean value was considered for the initial temperature. The combustion  
 97 chamber has ports accessible for pressure data acquisition and can withstand pressures up to 1000 bar. For  
 98 the unconventionally high EOC pressures targeted in this study, special care had to be taken for the pressure  
 99 measurements. Typically, for low-pressure experiments, a Kistler (6125C-U20) sensor with low thermal shock  
 100 error is used. However, this Kistler sensor has an overload pressure of only 350 bar which is insufficient to  
 101 withstand the pressure peaks that occur in this study. For this reason, the reaction chamber was fitted with a  
 102 PCB sensor (PCB 113B22) for reactive experiments. This has the advantage of having a similar measuring  
 103 range as that of the Kistler sensor but has a maximum burst pressure of 1034 bar. However, the PCB sensor

104 can be affected by thermal heat shock due to the rapid temperature changes during an experiment. One  
105 possible measure to avoid this is by the addition of a thin layer of silicone in front of the sensor but this may  
106 influence the ignition behaviour of the test mixture and the layer also depletes quickly because of the harsh  
107 conditions of this study. For this reason, the silicone layer was not applied to the PCB sensor during the  
108 reactive experiments. Instead, the pressure in the non-reactive experiments were measured using both the  
109 Kistler and PCB sensors simultaneously so that, the heat shock effect on the PCB sensor can be quantified  
110 and used to correct the pressure measurement of the reactive experiment for each condition. The heat  
111 shock effect was quantified by using the ratio of the compressed pressures recorded by the Kistler sensor to  
112 that of the PCB sensor for each experiment and further taking the average of the ratios to correct for the  
113 amplification factor of the PCB sensor. An example of this procedure is provided in the Supplementary  
114 material. The possible uncertainties induced by this method compared to a directly measured pressure are  
115 included in the uncertainty analysis presented later. Despite the high burst pressure of the PCB sensor, this  
116 sensor was damaged during the first set of experiments. It was speculated that this is due to the very fast  
117 pressure increase at ignition inducing high accelerating forces inside the sensor. In order to reduce the peak  
118 load on the sensor, the new PCB sensor was afterwards mounted in a recessed configuration in contrast to  
119 the Kistler sensor, which was flat mounted during the non-reactive experiments. If the pressure increase is  
120 quantified in kbar/ms, the ignition event with the sensor on the flat mounted configuration observed a  
121 maximum value of 150 kbar/ms whereas, with the recessed mounting it is about an order of magnitude  
122 lower. The recessed mounting configuration degrades the sensor's ability to measure high frequencies and  
123 the cavity effect of this configuration will typically reduce the sensor's resonant frequency. However, the  
124 pressure traces shown in **Figure 2** illustrate the minor differences in both the flat mounted and recessed  
125 configuration. The compression of the gas mixture is a comparatively slow process and the recess  
126 configuration used does not influence the pressure measured at the end of compression. The second  
127 important parameter to be deduced from the pressure reading is the IDT. As mentioned before, the rate of  
128 pressure rise due to the ignition event is reduced when using the recessed configuration and this could, in  
129 theory, influence the measured/deduced IDT. However, the difference in the IDT due to the recessed  
130 configuration only amounts to less than 0.01 ms and is negligible for the measured range of IDTs. A

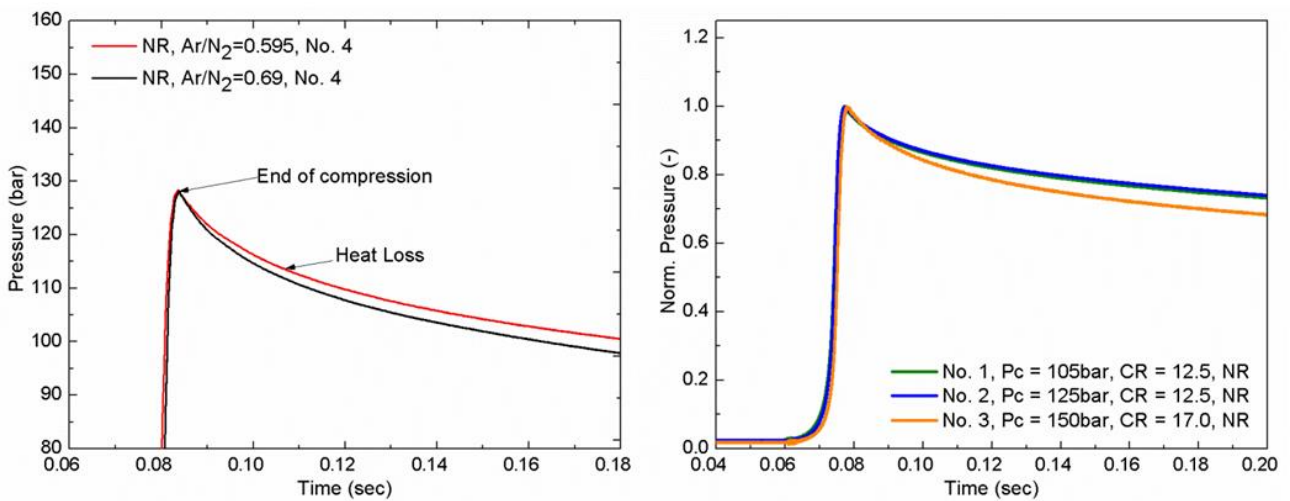
131 comparison of the difference in the IDTs, induced by the two configurations is presented in the  
 132 Supplementary material. The increase in the dead volume due to the recessed configuration is about 5  $\mu$ l  
 133 compared to the smallest EOC volume which is about 34 ml (i.e at the highest compression ratio) and is,  
 134 therefore, negligible. It is important to note that neither the design influences significantly the measurement  
 135 of the IDT nor the pressure at EOC, but it reduces the peak pressure levels by a factor of approximately 50%.  
 136 One also is informed that the change in EOC pressures and temperatures seen in the traces is attributed to  
 137 the change in initial conditions and is not an effect of the recessed configuration. The rapid rate of pressure  
 138 drop seen after the ignition event is due to heat loss and possibly also piston rebound and thermal heat  
 139 shock behavior of the pressure transducer. Since the behaviour after ignition is ~~inessential-not essential~~ to  
 140 this study, ~~we do not more-emphasis-consider is-not-given-to~~ the pressure traces after the ignition event.



141  
 142 **Figure 2: Pressure profile of a reactive experiment with and without recessed adaptor for the pressure sensor (PCB)**

143 -To vary the EOC temperature, either the proportion of the diluent gases (Ar/N<sub>2</sub>, 0–100%) can be  
 144 changed, or the end-wall position can be varied (0–21 mm) to change the compression ratio (~7 to 17). The  
 145 effect of these changes on the heat loss after EOC must be understood. **Figure 3** shows the effect on the  
 146 heat loss by varying the content of argon in the mixture for a fixed end wall position. The higher the argon  
 147 content, higher the heat loss, which can be observed by the drop in pressure after the EOC. This effect of  
 148 different diluent gas composition on the IDTs in an RCM has been discussed previously in more detail by  
 149 Würmel et al. [34]. As the volume of the reaction chamber decreases with the change in end wall position,

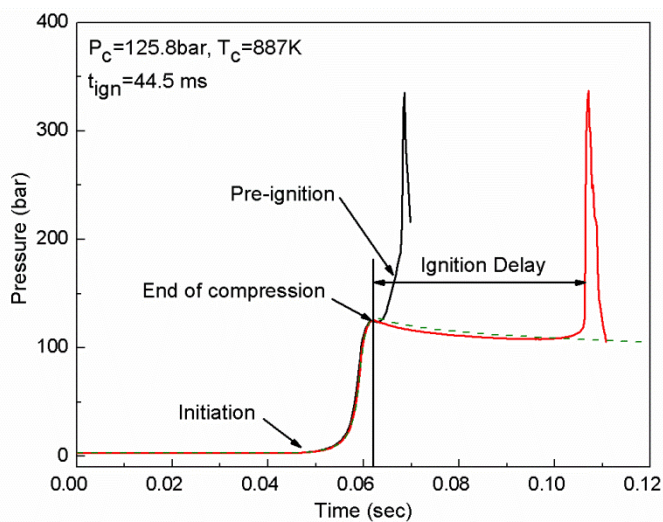
150 the ratio of volume to surface area also decreases leading to a stronger pressure drop due to heat loss.  
 151 **Figure 3** also shows the normalized pressure traces for 105, 125 and 150 bar conditions for a specific  
 152 compressed temperature and it illustrates the effect of heat loss with the change due to end wall position  
 153 and compression ratio, respectively. The combination of changing the diluent gas and the end-wall position  
 154 allows one to tailor the experiments to acclimate varying conditions in a test matrix. The EOC temperature  
 155 was calculated using Gaseq [35] which employs an adiabatic compression/expansion routine and the  
 156 temperature dependent ratio of specific heats.



157  
 158 **Figure 3: Non-Reactive pressure profile (Kistler) at fixed end wall position and varying Argon content in the methane mixture for**  
 159 **125 bar,  $\phi=0.526$ . Normalized pressure traces of the 105, 125 and 150 bar conditions with different compression ratios.**

160 The measurement uncertainty that would contribute to the calculation of the EOC temperature was  
 161 estimated for the conditions tested. In the calibrated pressure and temperature range, the PCB and the  
 162 Kistler sensor have an uncertainty of 0.07% and 0.04% of full scale (FS), respectively. The initial temperature  
 163 measured with a T type thermocouple has an uncertainty of  $\pm 0.5$  K. The initial pressure and mixture  
 164 preparation which were monitored by the two static sensors have an uncertainty of  $\leq \pm 0.05\%$  of FS.  
 165 Considering the possible uncertainties in the thermal data of the species, the initial temperature ( $T_0$ ), initial  
 166 pressure ( $p_0$ ), the corresponding change in the equivalence ratio of the prepared mixture ( $\Delta\phi=0.42\%$ ), and  
 167 the measuring uncertainty in the EOC pressure ( $\Delta P_c=\pm 0.15$  bar); the combined uncertainty leads to a  
 168 deviation of  $\pm 5$  K in the EOC temperature ( $T_c$ ). **A study by Weber et al. [36] focused on the uncertainty**  
 169 **estimation of the compressed temperature in an RCM, where scripts to estimate uncertainty using the**

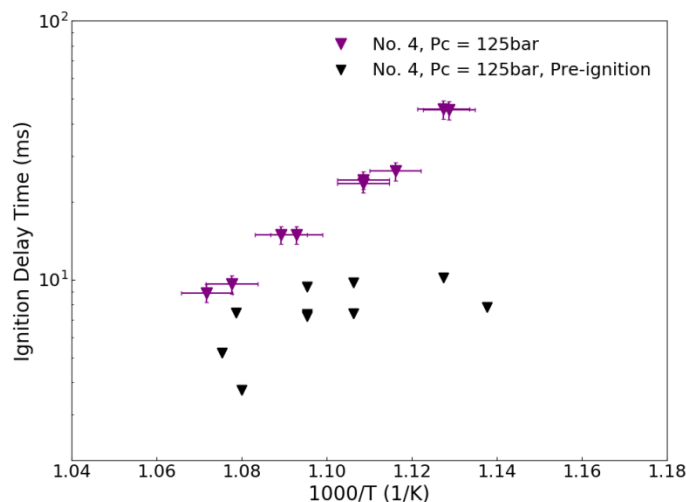
170 independent parameter analysis method and the Monte Carlo method were devised. In the end, Weber et  
 171 al. reported uncertainties in the compressed temperature for propene at relatively higher pressures (40 bar)  
 172 in a similar magnitude to those reported here. A comparative estimation of the uncertainty using the  
 173 method reported here and by Weber et al [36] is available in the Supplementary material. All reactive  
 174 experiments were repeated once showing good repeatability with a variation in IDT for the majority of the  
 175 experiments to be within  $\pm 4\%$  with only one condition showing  $\pm 8\%$  at a constant EOC pressure and  
 176 temperature. All figures below showing the ignition delay times results in the following visualize indicate this  
 177 maximum variation of  $\pm 8\%$  in our measurements as error bars. Comparatively, in the study of Burke et al.  
 178 [37] the scatter of experimental data in the two different RCMs (NUIG and UConn) was found to be  $\pm 15\%$   
 179 and  $\pm 10\%$ , respectively. The variation observed in this study lies within this range. The uncertainties in the  
 180 measurement of the non-reactive experiments are the same as those for at of the corresponding reactive  
 181 experiments as they utilize the same measuring system. Therefore Consequently, the uncertainty in the  
 182 simulations resulting from using an effective volume profile deduced from a measured pressure profile will  
 183 also be the same as the measurement uncertainty.



184  
 185 **Figure 4: Pressure profile of reactive, non-reactive and a pre-ignition experiment for methane at 125 bar and  $\phi=0.526$ .**

186 The test gases used for this study were of high purity and supplied by Praxair and Westfalen [ $\text{CH}_4$ ,  
 187  $\text{C}_2\text{H}_6$  – 99.95% and for diluent gases Ar – 99.996%,  $\text{N}_2$ , and  $\text{O}_2$  – 99.999%]. **Figure 4** also shows the pressure  
 188 profile of a 125 bar experiment and its corresponding non-reactive trace. It should be emphasized that  
 189 during the experimental work, pre-ignition experiments were encountered similar to those observed by

190 Mittal and Sung [38]. Pre-ignition is an inhomogeneous ignition event leading to a steady increase in  
 191 pressure before the main ignition. Experiments were first conducted at 125 bar conditions when the pre-  
 192 ignition occurred and later different pressures and temperatures were scanned to check for the occurrence  
 193 of pre-ignition. An analysis of these measurements revealed that pre-ignition occurred only at higher  
 194 pressures but the reason was due to a different factor. It was found that the reaction chamber was  
 195 contaminated with a thin layer of hydraulic oil which was a consequence of the increase in the hydraulic  
 196 pressure which was necessary for the high-pressure experiments in this study. A thin shim was introduced  
 197 between the hydraulic and the reaction chambers, thereby eliminating the ingress of hydraulic oil and  
 198 reducing the occurrence of pre-ignition. Furthermore, the chamber was cleaned frequently as a precaution.  
 199 However, occasionally the experiments showed pre-ignition and they were not included for further analysis.  
 200 **Figure 5** shows the plot of the IDT against the inverse of EOC temperature for the reliable experimental  
 201 points and the pre-ignition experimental points. In addition, the representative uncertainties in the EOC  
 202 temperature ( $\pm 5$  K) and variation in the IDT ( $\pm 8\%$ ) are presented in **Figure 5**.



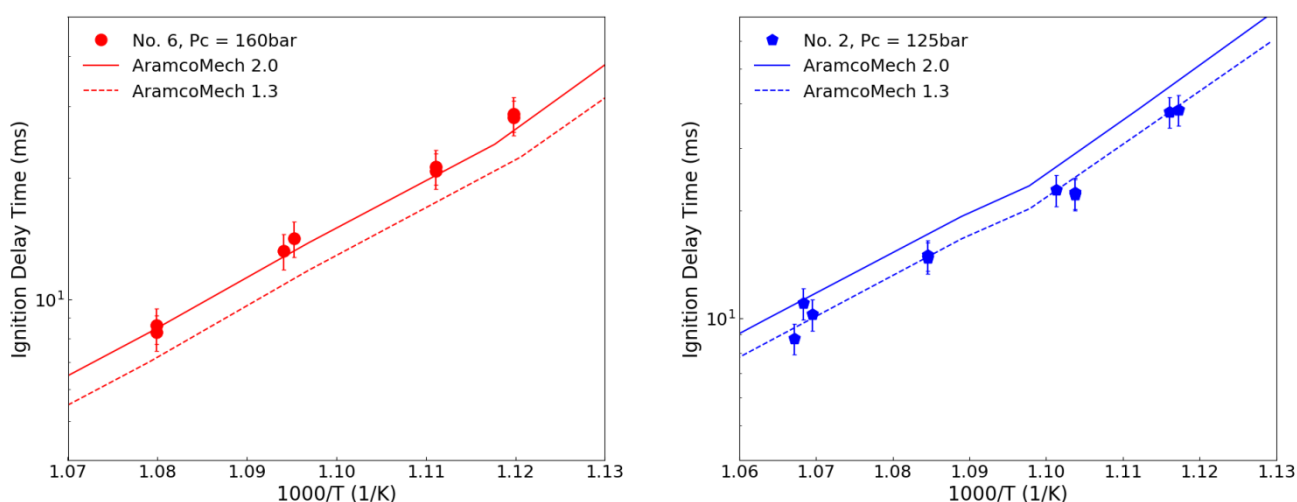
203  
 204 **Figure 5: Ignition delay time data and pre-ignition experimental data for methane at 125 bar,  $\phi=0.526$ .**

205 Performing experiments at such high pressures in this facility were primarily limited by the pressure sensors.  
 206 The design pressure of the reaction chamber is high enough to withstand a higher EOC pressure with similar  
 207 gas mixtures and the effect of the strong ignition pressure peak on the sensor can be reduced with the  
 208 recessed arrangement. However, reactive and non-reactive pressure traces of the 150 and 160 bar  
 209 experiments showed the first signs of oscillations in pressure at EOC, which may be caused either by the

210 large inertial forces generated when the piston stops, or by the vibration induced by the contact between  
 211 the pin and groove assembly. To achieve these high-pressure conditions (160 bar), the driver pressure on the  
 212 pneumatic side had to be increased to 24 bar. Comparing this to the standard EOC pressure conditions (20  
 213 bar) the driver pressure typically used is 8–10 bar. A conclusion on the oscillations observed in the high-  
 214 pressure case is not possible at the moment and further analysis on the dynamics is required. For this  
 215 reason, EOC pressures higher than 160 bar have not been investigated in this study. A solution to this  
 216 problem and investigating higher pressures will be considered in future studies.

### 217 3. Modeling

218 The kinetic model used in this work is from the base chemistry up to  $C_2$  species of the recently published  
 219 AramcoMech 2.0 [39]. Compared to the earlier published AramcoMech 1.3 [40], the most significant change  
 220 in the base chemistry are the updated rate constants for  $H\dot{O}_2+H\dot{O}_2\rightleftharpoons H_2O_2+O_2$  and  $\dot{O}H+H\dot{O}_2\rightleftharpoons H_2O+O_2$ ,  
 221 which are from Hong et al. [41]. Part of the  $CH_3O$  chemistry has been adopted from the recent work of Burke  
 222 et al. [42] on methanol, including the interactions of  $CH_3\dot{O}$  radicals with  $\dot{O}H$ ,  $H\dot{O}_2$ ,  $H_2O_2$ ,  $CH_4$  and  $H\dot{C}O$ .  
 223 Additionally, in the previously published AramcoMech 1.3 [40], the reaction rate constants for  $CH_4+H\dot{O}_2\rightleftharpoons$   
 224  $\dot{C}H_3+H_2O_2$  were taken from the work of Iparraguirre et al [43] with the A-factor increased by 50%. In  
 225 AramcoMech 2.0 [39], this value was restored to the value calculated by Iparraguirre et al. [43].



226

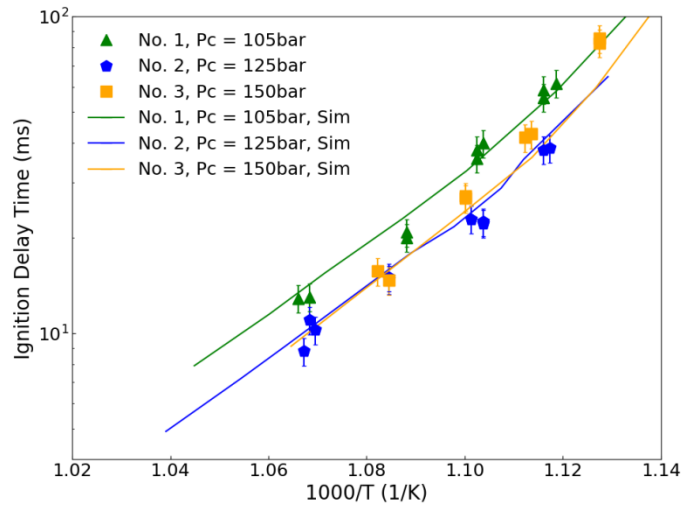
227 **Figure 6: Comparison of experimental data and model predictions at pressures of 160 and 125 bar.**

228 In this work, we found that the predicted IDTs of methane are sensitive to the reaction rate of  
229  $\text{CH}_4 + \text{H}\dot{\text{O}}_2 \rightleftharpoons \dot{\text{C}}\text{H}_3 + \text{H}_2\text{O}_2$ . **Figure 6** shows that AramcoMech 1.3 [40] in general predicts shorter IDTs than  
230 AramcoMech 2.0 [39] and therefore results in an over-prediction of reactivity under some conditions, while  
231 the latter tends to under-predict reactivity in some cases.

232 Through comprehensive comparisons, we found that the best agreement can be achieved by using a  
233 value between those from AramcoMech 1.3 [40] and AramcoMech 2.0 [39]. Thus, the A-factor of  
234  $\text{CH}_4 + \text{H}\dot{\text{O}}_2 \rightleftharpoons \dot{\text{C}}\text{H}_3 + \text{H}_2\text{O}_2$  in the mechanism used in this work is 25% higher than the value reported by  
235 Iparraguirre et al. [43]. The remainder of AramcoMech 2.0 [39] has been used unmodified. Further  
236 comparisons of the current mechanism and AramcoMech 1.3 [40] and AramcoMech 2.0 [39] can be found in  
237 the Supplementary material, which indicates that these modifications have in general, led to improved  
238 model predictions.

## 239 **4. Results and Discussion**

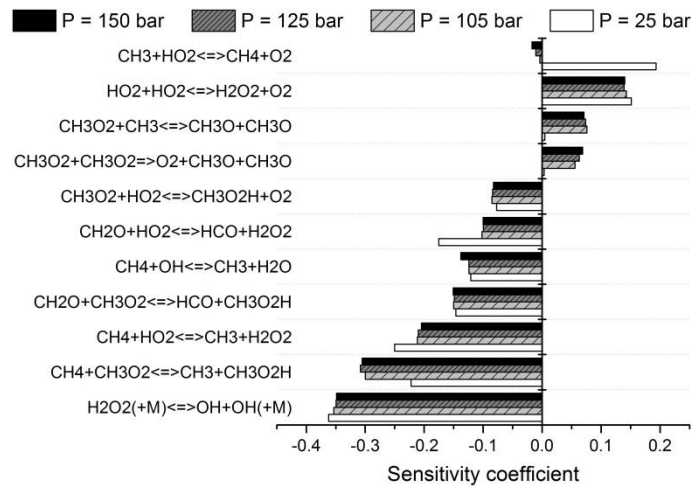
240 Experiments were performed for the range of conditions listed in Table 1. As mentioned earlier, reactive  
241 experiments were carried out using the PCB sensor and the non-reactive experiments used both the PCB and  
242 Kistler sensors. For the purpose of simulation, the non-reactive pressure profiles from the Kistler sensor  
243 were utilized. Non-reactive pressure traces are essential in capturing the facility effects of the RCM  
244 experiments i.e. radical pool generation during the compression phase and heat loss after the EOC, which is  
245 detailed in the work of Sung and Curran [44]. In order to extend the simulations beyond the measured  
246 experimental range, the initial temperature of the measured non-reactive profiles were changed. The  
247 adapted mechanism is used for simulation of IDTs for the various conditions in the test matrix. In addition,  
248 the modified mechanism, experimental data, and the corresponding non-reactive profiles are included in the  
249 Supplementary material.



250

251 **Figure 7: Comparison of experimental data (symbols) and model predictions (line) at varying pressures (105, 125 and 150 bar),  $\phi =$**   
 252 **0.526, with an inert gas dilution of 77.26%. The numbers in the legend (eg: No.1) represent the corresponding conditions in the**  
 253 **test matrix.**

254 The IDT data obtained from the experiments and simulations are plotted on a logarithmic scale as a  
 255 function of inverse EOC temperature. **Figure 7** shows the experimental data and the simulation for 100% CH<sub>4</sub>  
 256 at pressures of 105, 125, and 150 bar with 77.26% inert gas fraction. The reactivity increases as the pressure  
 257 increases because of the increase in the concentration of the reactive species and this trend can be seen in  
 258 the 105 and 125 bar data. In order to achieve higher EOC pressures, the compression ratio had to be  
 259 increased for the 150 bar case and subsequently the ratio of diluent gases (Ar/N<sub>2</sub>). This led to smaller  
 260 compression volumes and different heat transfer coefficients ultimately leading to stronger heat loss and  
 261 consequently longer IDTs for the 150 bar experiments. However, by using the volume profiles deduced from  
 262 the non-reactive experiments, the differences are accounted for in the simulations and all of these shows  
 263 good agreement with the experimental results, where the majority of the simulations are within the  
 264 variation of the experimental results.



265

266 **Figure 8: Brute force sensitivity analysis of IDT,  $\phi = 0.526$ ,  $T_c = 910$  K,  $P_c = 25$  bar, 105 bar, 125 bar, and 150 bar**

267 To highlight the important reactions that affect the reactivity during the ignition process, a series of  
 268 sensitivity analysis have been performed. **Figure 8** shows a brute force sensitivity analysis using Chemkin Pro  
 269 at  $\phi = 0.526$ ,  $T_c = 910$  K,  $P_c = 105$  bar, 125 bar, 150 bar, and 25 bar. In the analysis, the rate constants of each  
 270 reaction were increased and decreased by a factor of two ( $k_+$  and  $k_-$ ), and the simulations were performed  
 271 using two mechanisms with these changes to derive the IDTs ( $\tau_+$  and  $\tau_-$ ). The sensitivity coefficient ( $S$ ) is  
 272 defined as:

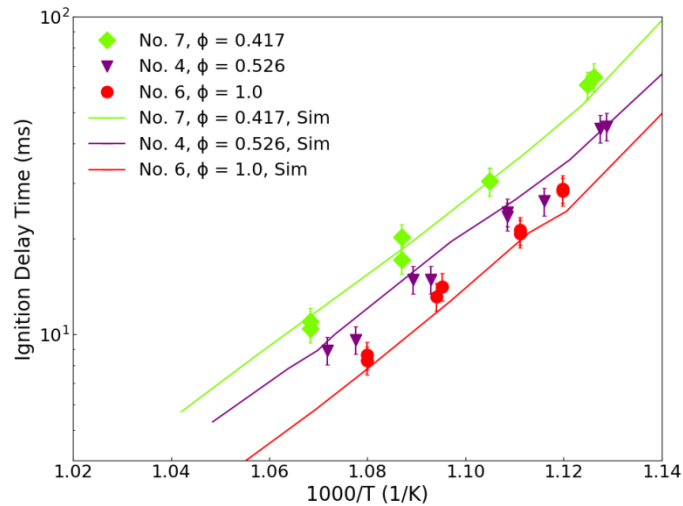
$$273 \quad S = \frac{\ln(\tau_+/\tau_-)}{\ln(k_+/k_-)} = \frac{\ln(\tau_+/\tau_-)}{\ln(2/0.5)}$$

274 Therefore, a reaction with a positive sensitivity coefficient inhibits reactivity while that with a negative  
 275 sensitivity coefficient promotes reactivity.

276 At higher pressures (105 bar, 125 bar, and 150 bar) the most sensitive reactions remain the same.  
 277 The sensitivity factors of each reaction under these different pressures are also similar; however, at lower  
 278 pressures, some more significant changes can be observed. Under all four conditions, the decomposition of  
 279  $H_2O_2$  is the most sensitive reaction, which promotes reactivity by producing two  $\dot{O}H$  radicals. On the other  
 280 hand, the chain termination reaction  $\dot{H}O_2 + \dot{H}O_2 = H_2O_2 + O_2$  is in all cases one of the most inhibiting  
 281 reactions. This is because one  $\dot{H}O_2$  radical could be otherwise converted into  $H_2O_2$  by abstracting one  
 282 hydrogen atom from  $CH_4$  or  $CH_2O$ . Thus  $\dot{H}O_2$  is a critical species in the ignition process of methane at the  
 283 current high-pressure conditions. According to the rate of production analysis,  $\dot{H}O_2$  is mainly produced from  
 284 the reaction of oxygen with radicals including  $\dot{H}CO$ ,  $CH_3\dot{O}$ , and  $\dot{H}$  atom, all of which result from the oxidation

285 of  $\dot{\text{C}}\text{H}_3$  radical via the sequence of  $\text{CH}_3\dot{\text{O}}_2 \rightarrow \text{CH}_3\text{O}_2\text{H} \rightarrow \text{CH}_3\dot{\text{O}} \rightarrow \text{CH}_2\text{O} \rightarrow \text{H}\dot{\text{C}}\text{O}$ . The decomposition of  $\text{CH}_3\text{O}_2\text{H}$   
286 is another important chain branching reaction that produces a  $\dot{\text{O}}\text{H}$  radical and a  $\text{CH}_3\dot{\text{O}}$  radical. This reaction is  
287 not shown in **Figure 8** as sensitive, due to its high rates under all considered conditions. However, several  
288 reactions producing  $\text{CH}_3\text{O}_2\text{H}$  from its precursor,  $\text{CH}_3\dot{\text{O}}_2$  radical, are found to be sensitive in promoting  
289 reactivity as shown in **Figure 8**, while the competing reactions inhibit reactivity.

290 Amongst the most sensitive reactions shown in **Figure 8** the decomposition of  $\text{H}_2\text{O}_2$  is the only reaction  
291 in the current mechanism whose rate constants include a fall-off behaviour. This means that, at lower  
292 pressures,  $\text{H}_2\text{O}_2$  decomposes at a lower rate and therefore restricts the reactivity. Accordingly, it can be seen  
293 in **Figure 8** that most reactions related to  $\text{H}_2\text{O}_2$ , either producing or consuming it, are more sensitive to lower  
294 pressures. On the other hand, the other reactions are more sensitive at higher pressures. These reactions  
295 mainly affect the production and consumption of  $\text{CH}_3\dot{\text{O}}_2$  radical, which is the precursor of  $\text{CH}_3\text{O}_2\text{H}$  as  
296 discussed above. This trend is more obvious in comparing the sensitivity analysis at higher pressures to the  
297 one at 25 bar: the reactions that directly involve  $\text{H}_2\text{O}_2$  are more sensitive under lower pressures while the  
298 others are less sensitive. It needs to be noted that the most inhibiting reaction under 25 bar is the chain  
299 termination reaction between  $\dot{\text{C}}\text{H}_3$  and  $\text{H}\dot{\text{O}}_2$ , which is not sensitive under high pressures. This is because  $\dot{\text{C}}\text{H}_3$   
300 radical could add to  $\text{O}_2$  more easily at high pressures and result in chain branching process as discussed  
301 above. Overall this analysis shows that the ranking of reactivity controlling reactions changes at higher  
302 pressures thereby underlining the importance of fundamental kinetic investigations at application relevant  
303 pressures.



304

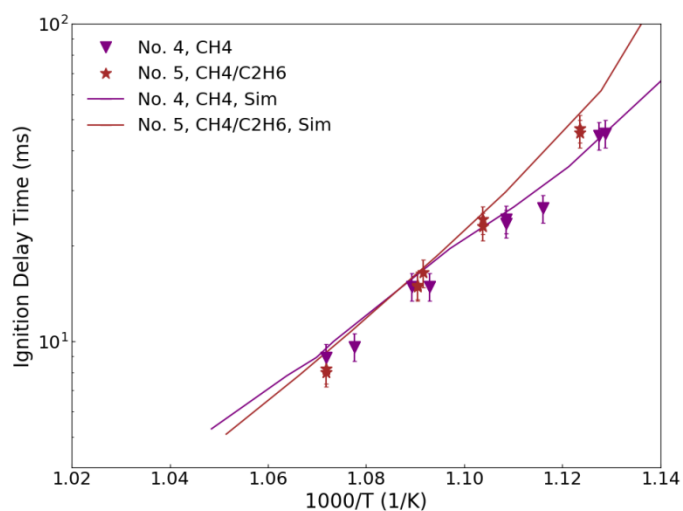
305 **Figure 9: Comparison of experimental data (symbols) and model predictions (line) for variation of equivalence ratio ( $\phi = 0.417$ ,**  
 306  **$0.526$  and  $1.0$ ), at pressures of 125 and 160 bar with an inert gas dilution of 75.69, 74.86 and 80.13%.**

307

308 **Figure 9** depicts the effect of equivalence ratio on reactivity including both experimental results and  
 309 model predictions. The conditions for equivalence ratio 0.417 and 0.526 are fuel/air mixtures, where the  
 310 diluent proportions are varied to change the EOC temperature, whereas an equivalence ratio of 1.0 is a  
 311 dilute condition with excess diluent equivalent to a 30% EGR condition. In this temperature regime, the  
 312 reactivity of the mixture is strongly dependent on the concentration of the fuel, and as the mixture becomes  
 313 rich the reactivity of the system increases. This is in agreement with previous studies [16, 28, 29]. The model  
 captures the trends in reactivity very well.

314

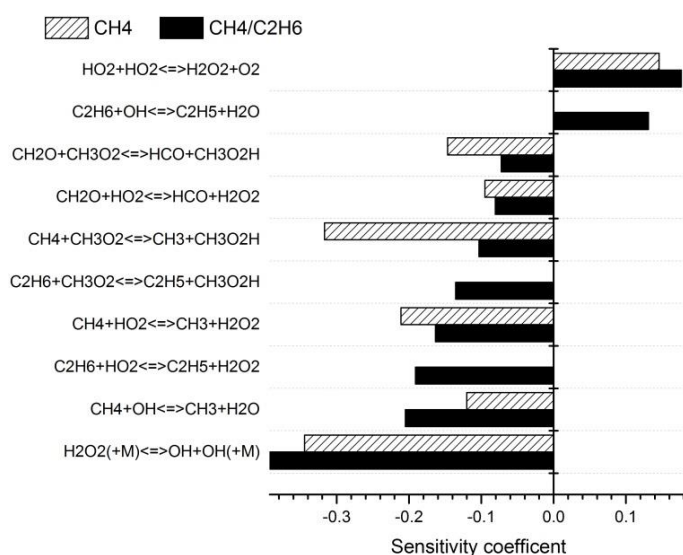
315 **Figure 10** illustrates the effect of the addition of ethane (13% mol) on reactivity at 125 bar and  $\phi =$   
 316 0.526. In general, in the **low-temperature** regimes (890–933 K), the reactivity increases with an increase in  
 317 carbon chain length. This increase in carbon chain length facilitates the **low-temperature chemistry** paving  
 318 the way for opportunities for isomerization reactions and further leading to chain branching reactions.  
 319 Hence, the addition of ethane influences the **low-temperature chemistry** of the mixture, thereby increasing  
 320 its reactivity. However, the experiments carried out for the  $\text{CH}_4/\text{C}_2\text{H}_6$  blend were performed with a higher  
 321 compression ratio and smaller EOC volumes. This leads to an increase in heat loss and consequently results  
 322 in lower average temperatures and longer IDTs, which is more obvious in the **lower temperature region** of  
**Figure 10**. Again, the model captures the change in reactivity well.



323

324 **Figure 10: Comparison of experimental data (symbols) and model predictions (line) for variation of fuel mixtures at a pressure of**  
 325 **125bar,  $\phi=0.526$  and with an inert gas dilution of 74.86 and 75.21%.**

326 In the preceding discussion, the addition of ethane promoted the reactivity of the system and  
 327 shortens the IDTs. **Figure 11** shows a sensitivity analysis of reactions to IDTs with and without ethane  
 328 addition to fuel mixture composition under the same conditions. The reactivity of the mixture and the  
 329 sensitive reactions mostly remain the same because only 13% ethane was added. Amongst the top ten most  
 330 sensitive reactions, there are three reactions involving C2 chemistry.

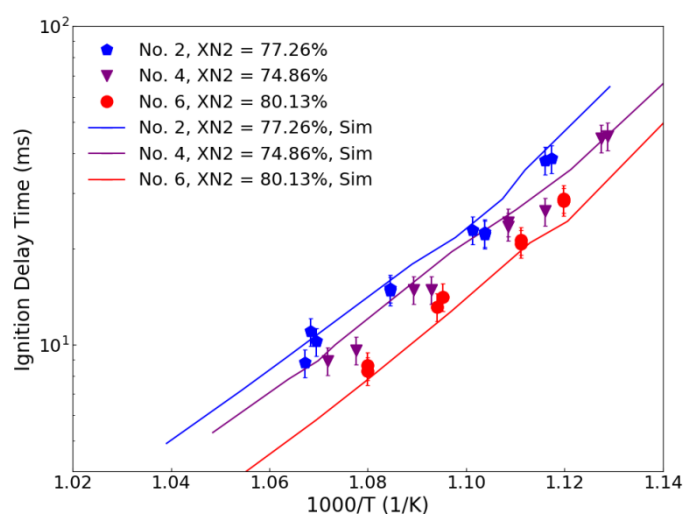


331

332 **Figure 11: Brute force sensitivity analysis of ignition delay time,  $\phi = 0.526$ ,  $T = 910 \text{ K}$ ,  $P_c = 125 \text{ bar}$**

333 Hydrogen atom abstraction from ethane by  $\text{HO}_2$  and  $\text{CH}_3\text{O}_2$  radicals producing  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{O}_2\text{H}$  promote  
 334 reactivity. This trend is consistent with our analysis for conditions without ethane present: the reactions that

335 produce  $\text{H}_2\text{O}_2$  and  $\text{CH}_3\text{O}_2\text{H}$  promote reactivity because these species are critical in leading to chain branching.  
 336 On the other hand, H-atom abstraction from ethane by  $\dot{\text{O}}\text{H}$  radicals inhibits reactivity, as this competes with  
 337  $\text{CH}_4$  for  $\dot{\text{O}}\text{H}$  radicals, which promotes reactivity. In general, the addition of ethane increases mixture  
 338 reactivity. For ethane, hydrogen abstraction is easier than for methane because the ethane molecule has  
 339 more (six as opposed to four) C–H bonds, which are relatively weaker than those of methane. Due to the  
 340 presence of the beta carbon, ethyl can readily lose one hydrogen atom on the beta carbon via  $\beta$ -scission or  
 341 hydrogen abstraction by  $\text{O}_2$ , producing ethylene and a hydrogen atom or hydroperoxyl radical. The  
 342 production of  $\dot{\text{H}}$  atoms and  $\text{HO}_2$  radicals in this way leads to higher reactivity.



343  
 344 **Figure 12: Comparison of experimental data (symbols) and model predictions (line) for methane mixtures at different dilution**  
 345 **percentage at a pressure of 125 and 160 bar with  $\phi = 0.526$  &  $1.0$ .**

346 Finally, **Figure 12** highlights the effect of varying the inert gas fraction representing a varying EGR  
 347 fraction as discussed earlier. Diluting the mixture decreases the concentration of the reactive components  
 348 leading to longer IDTs. The inert gas fraction in the experiments is increased from 74.86% (0%) to 77.30%  
 349 (10%) at 125 bar for fuel-lean mixtures, whereas for the stoichiometric conditions at 160 bar the inert gas  
 350 fraction is 80.13%, representing a 30% dilution. The calculated ignition delay is consistent with the  
 351 experimental data and captures the trend well. In general, for majority of the data sets the deviation of the  
 352 model from the experiments is within the experimental variation, thereby showing that the chemical kinetic  
 353 mechanism is able to predict the IDTs at the targeted regime of higher pressures and lower temperatures.

## 354 5. Conclusions

355 Within this study, a range of experimental data were acquired in an RCM for CH<sub>4</sub> and CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>  
356 mixtures at varying equivalence ratios, dilution percentages, and pressures ranging from 105 to 160 bar in  
357 the temperature range of 845 - 940 K. Although there have been a number of studies on IDT measurements  
358 in the high and intermediate temperature regime, there is very limited data available in the literature at  
359 higher pressures in the RCM regime. The results of this study are the first set of data for CH<sub>4</sub> and CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub>  
360 mixtures at pressures from 105 to 160 bar taken to study knocking characteristics in application relevant  
361 conditions. An explicit description of the limitations of performing high-pressure experiments in an RCM and  
362 the approach used to overcome these limitations has been highlighted in this study. The load on the  
363 pressure sensor during the ignition event is reduced with the introduction of a recessed configuration. The  
364 issue of pre-ignition occurring during the experiments at these high-pressure conditions was resolved with  
365 the addition of a thin shim between the hydraulic and reaction chambers. Two dynamic pressure sensors  
366 have been used to complement the shortcomings of each other while the Kistler is limited by the pressure  
367 limit and the PCB is limited by its inability to account for the heat shock effect. The approach of using the  
368 pressures sensors in tandem to quantify the heat shock effect and determination of the compressed  
369 pressure is established. However, the problem of encountering oscillations at the end of compression so far  
370 limits our ability to achieve pressures higher than 160 bar. The recently published AramcoMech 2.0 was  
371 optimized and used to simulate the conditions in the test matrix. The mechanism not only captures the  
372 reactivity trends at various conditions of the matrix but also predicts quantitatively the measured IDTs. The  
373 majority of the IDT data is predicted within the variation of the experiments. The key reactions promoting  
374 and suppressing reactivity at these conditions were identified using a brute force sensitivity analysis. The  
375 decomposition of H<sub>2</sub>O<sub>2</sub> producing two  $\dot{O}H$  radicals seems to be the most sensitive reaction for all conditions,  
376 including both CH<sub>4</sub> and CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> mixtures. The chain termination reaction of  $\dot{C}H_3$  and  $\dot{H}O_2$  suppresses the  
377 reactivity at lower pressures (25 bar), whereas at higher pressures (150 bar) it remains insensitive for the  
378 CH<sub>4</sub> mixtures. Moreover, the abstraction of hydrogen from ethane by  $\dot{H}O_2$  and  $CH_3\dot{O}_2$  radicals enhances the  
379 reactivity in CH<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> mixtures. Overall, this study highlights the methodology for performing high-pressure

380 experiments in an RCM and also emphasizes the importance of the fundamental understanding of chemical  
381 kinetics at application relevant pressures.

382 **Supplementary Material**

- 383 1. Calculation: EGR % to N<sub>2</sub> dilution
- 384 2. Quantification of heat loss
- 385 3. Flat and Recessed configuration differences
- 386 4. Ignition delay time measurement data
- 387 5. Uncertainty Estimation
- 388 6. Constant volume simulations for the conditions in this study
- 389 7. Experimental Overview: non-reactive profiles
- 390 8. Comparison of the current mechanism, AramcoMech 1.3 and AramcoMech 2.0 mechanism
- 391 9. Mechanism file and thermal data. (separate files)
- 392 10. Non-Reactive profiles (separate folder)

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