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# Experimental study and numerical validation of oxy-ammonia combustion at elevated temperatures and pressures

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## Abstract

The combustion of fossil fuels, which are mostly based on hydrocarbon chains, produces large quantities of carbon dioxide which is a major contributor to the global warming. Due to alarming concerns, initiatives are taken to promote the use of ‘zero-carbon fuel’. The use of ammonia as an alternative fuel in combustors like gas turbines and spark-ignition engines have already been tested. As high pressures and temperatures are encountered in these combustors, it is essential to find laminar flame speed data for ammonia combustion at these conditions. The present study focuses on performing experiments at elevated conditions for different equivalence ratios in a constant volume spherical chamber. A literature study was performed to select and evaluate the most recent kinetic mechanisms for ammonia combustion under these conditions. A sensitivity analysis highlighting the key reactions for two of the schemes has been performed. A range of exponential factors for temperature and pressure which is used to calculate the flame speeds for a given reference conditions :  $\alpha$  and  $\beta$  have been determined.

*Keywords:* Ammonia, laminar flame speed, constant volume chamber, elevated conditions

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## 1. Introduction

1 In the recent times, there is an extensive use of carbon-based fuels to  
2 meet with the ever-increasing demand for energy. This has resulted in a  
3 rapid depletion of fossil fuels along with an increase in carbon emissions  
4 and other green-house gases which is the primary cause of global warming  
5

6 leading to climate change. Attempts are being made to curb the excessive  
7 usage of these conventional fuels by using alternative green fuels. Many  
8 countries have signed conventions like Kyoto protocol [1] and Paris agreement  
9 [2] which aim to reduce the emission of the green-house gases. Ammonia has  
10 received recent interests as it is carbon-free and relatively safe to store and  
11 transport. The use of ammonia as an alternative fuel in combustors like  
12 gas turbines [3] and especially in spark-ignition engines [4] has already been  
13 tested. Ammonia flames are characterized by a low combustion intensity, low  
14 laminar burning velocities and narrow flammability limits. Flame speed of  
15 ammonia in air at stoichiometry is as low as  $7\text{ cm/s}$  at standard atmospheric  
16 conditions [5]. The low heating value (LHV) of ammonia is  $18.8\text{ MJ/kg}$   
17 which is lower than most of the commonly used fuels like hydrogen and  
18 methane [6]. Nevertheless, ammonia is favoured in spark-ignition engines as  
19 it has a high octane number. It has an energy density of  $22.5\text{ MJ/kg}$  and  
20 can be stored in liquid form under  $0.8\text{ MPa}$  at atmospheric temperature  
21 [7]. Ammonia is produced by the Haber-Bosch process which is the most  
22 economic way for mass production. This process can be made carbon-free  
23 to make it a green fuel. Hydrogen is obtained from the electrolysis of water  
24 with the help of solar and wind energy (renewable sources of energy) whereas  
25 nitrogen is obtained from air. Zamfirescu et al. [8] have shown that ammonia  
26 is the cheapest fuel per 100 km driving range and is cost-effective when  
27 compared to other fuels like hydrogen which also has an added disadvantage  
28 of risks in transportation. The flammability limits of ammonia ( $\varphi=0.63$ -  
29  $1.4$ ) compared to hydrogen ( $\varphi=0.1$ - $7.1$ ) [5] is quite low which makes it safer  
30 to store and transport but at the same time difficult to ignite making it  
31 an advantage and a disadvantage simultaneously. The economic statistics  
32 report by the ARPA-E, U.S. department of energy [9] show that ammonia  
33 is the most feasible form of energy delivery options for transportation when  
34 compared to both hydrogen and gasoline. The adiabatic flame temperature  
35 and the auto-ignition temperature of ammonia are at  $1800^\circ\text{C}$  and  $650^\circ\text{C}$   
36 respectively making it a potential contender among other green fuels due to  
37 its anti-knock characteristics.

38 Despite the numerous properties which make ammonia a desirable fuel,  
39 there are a few added disadvantages in addition to the low flammability limit  
40 and the low LHV. It is known that ammonia is hazardous when released  
41 into the atmosphere due to its high toxicity. From the investigations made  
42 by Westlye et al. [10] on a spark-ignition engine, it was concluded that  
43 there may be unburned ammonia emissions along with intermediary oxides

44 of nitrogen which are harmful to the environment. To reduce the impact  
45 of these emissions, a selective catalytic reduction (SCR) was developed to  
46 promote complete combustion and also to ensure that the exhaust emissions  
47 do not pollute the environment.

48 The low speed of ammonia flames [11, 12] leads to an early blow-off and a  
49 difficulty in ignition. Ammonia is often combined with hydrogen or methane  
50 to increase the overall performance like the flame speeds, flammability lim-  
51 its and power output. Literature is available on different conditions for the  
52 combined fuel mixture [6, 13]. Data at high pressure and high temperature is  
53 available for ammonia mixed with hydrogen or methane [14, 15, 16, 17, 18].  
54 However, for pure ammonia combustion, analyses have been made for a nar-  
55 row range of pressure and temperature conditions for different equivalence  
56 ratios [12]. As high pressures and high temperatures conditions are encoun-  
57 tered in spark-ignition engines and gas turbines, it is essential to find flame  
58 speed data for these conditions. The data available in the literature is at-  
59 tached as a supplementary document. It can be seen that the maximum  
60 flame speed for ammonia combustion is available for a pressure of 10 bar and  
61 a temperature of 473 K [18].

62 The present study focuses on performing experiments at high tempera-  
63 tures and pressures conditions for different equivalence ratios in a constant  
64 volume condition. The results of these experiments provide laminar flame  
65 speeds for a pressure range of 2 to 37 bar and a temperature range of 369 to  
66 584 K at 3 different equivalence ratios (i.e. 0.8, 1.1 and 1.3). These results  
67 are further used to assess the most recent chemical kinetic schemes available  
68 in the literature at identical conditions. It is important to identify the key  
69 reactions and to ensure that the pressure and temperature dependence is well  
70 accounted for at elevated conditions.

## 71 **2. Methodology**

### 72 *2.1. Experimental set-up*

73 The accuracy of the measurement of the flame speeds is quite important  
74 as it affects the overall performances. Flame speed is a sizing parameter that  
75 influences the design of spark-ignition engines and gas turbines. The exper-  
76 iments were performed in the OPTIPRIME facility [19] of ICARE-CNRS,  
77 Orléans, France. One of the most common methods to measure the flame  
78 speeds is spherical flame propagating outwards in a constant volume cham-  
79 ber which has been deployed as the principal apparatus here. This method

80 allows making measurements at high initial temperatures and pressures [20].  
81 The most interesting aspect of the set-up is that a 360° fused silica ring en-  
82 ables a full radial visibility. The flame front can be tracked from the ignition  
83 point which is at the centre of the spherical chamber to the walls where the  
84 flame propagates and finally extinguishes. The idea behind the vast visibility  
85 range is to be certain that the flame front remains spherical throughout the  
86 process without being influenced by gravity effects or instabilities and also to  
87 obtain the flame radius evolution over time. The apparatus also consists of  
88 a K-type thermocouple to measure the initial temperature and two pressure  
89 transducers (AVL GU21D) to measure the pressure simultaneously with the  
90 flame radius evolution from its ignition point.

## 91 *2.2. Experiment conditions and measurement of flame speeds*

92 The tests were performed for a mixture of ammonia-oxygen at 3 different  
93 equivalent ratios: 0.8, 1.1 and 1.3 at an initial temperature of 300 K. For the  
94 rich mixtures, the initial pressure ranged between 1 bar and 4 bar whereas  
95 for the lean mixture, it was at 1 bar and 2 bar. 30 % of the oxidiser mixture  
96 consists of oxygen and the remaining 70 % is the diluent for all the conditions.  
97 The diluent is required because these flames are quite unstable in nature as  
98 both hydrodynamic and thermo-diffusive instabilities are favoured in these  
99 temperature and pressure conditions. The Lewis number of ammonia flames  
100 is close to 1 and so, in order to increase the Lewis number, there is a need of  
101 adding bath gases with high thermal diffusivity. A combination of argon and  
102 helium was used to stabilise the flame. The ratio of the diluent was chosen  
103 such that the mixture could be readily ignited and the flame sustains till it  
104 hits the wall. It is difficult to ignite mixtures with a high helium content at  
105 low pressures as helium possesses a high thermal diffusivity. In the case of  
106 the high-pressure conditions, occurrence of instabilities is promoted and so,  
107 a large percentage of helium is required to stabilise the flame. The initial  
108 conditions used are represented in Table 1. The adiabatic flame temperature  
109 has been calculated and reported in Table 1. At this equilibrium condition,  
110 it is seen that the dissociation reaction of  $\text{H}_2\text{O}$  to  $\text{OH}$  is favoured.

111 Pressure was recorded during the experiment using the pressure transduc-  
112 ers. The pressure in the chamber increases up to almost 10 times the initial  
113 pressure. Images were captured at the rate of 12000 fps using a CMOS cam-  
114 era (PHANTOM V1611) for all conditions. The images used to determine  
115 the flame speed spanned over the ignition point to the point where the flame  
116 front hits the wall. On using a code written in Matlab, the radius of the

Table 1: Initial conditions for the test cases along with the adiabatic flame temperature (AFT)

$\varphi$	$P_0$ (bar)	Diluent	AFT(K)
0.8	1	49% Ar 21% He	2895
0.8	2	49% Ar 21% He	2944
1.1	1	49% Ar 21% He	2976
1.1	2	49% Ar 21% He	3036
1.1	1	21% Ar 49% He	2976
1.1	2	21% Ar 49% He	3036
1.1	3	21% Ar 49% He	3069
1.1	4	70% He	3093
1.3	1	49% Ar 21% He	2885
1.3	2	49% Ar 21% He	2927
1.3	2	21% Ar 49% He	2928
1.3	3	21% Ar 49% He	2950
1.3	4	21% Ar 49% He	2965
1.3	4	70% He	2965

117 flame at each frame was determined. The flame speed was calculated using  
 118 the obtained radius and the corresponding pressure by the equation 1

$$S_u = \frac{dR_f}{dt} - \frac{(R_0^3 - R_f^3)}{3\gamma_u R_f^2 P} \frac{dP}{dt} \quad (1)$$

119 where  $R_f$  and  $R_0$  represent the flame radius and the inner chamber radius  
 120 respectively,  $P$  is the pressure in the chamber and  $\gamma_u$  is the heat capacity  
 121 ratio of unburnt gas. Further details on this method can be found in [20, 21,  
 122 22, 23, 24].

### 123 2.3. Chemical Kinetics Schemes

124 Several numerical schemes are available in the literature. On performing  
 125 a literature review [34, 35], it was understood that Okafor [30] gave the most  
 126 congruent results for lean mixtures and Klippenstein [25] and Zhang [27]  
 127 gave the best results for the fuel-rich mixtures. Konnov [36] and Mathieu [33]  
 128 seem to over-estimate and under-estimate the flame speeds respectively when  
 129 compared to the experimental data [5]. The most recent kinetic schemes were  
 130 selected and are represented in Table 2. These mechanisms were used in the  
 131 premixed laminar flame speed calculator available in Chemkin-Pro. The

Table 2: Chemical kinetic schemes used in this study

Kinetic Schemes	Species	Reactions	Reference
Klippenstein et al.	33	211	[25]
Dagaut et al.	42	250	[26]
Zhang et al. (2017)	37	229	[27]
Shrestha et al.	34	264	[28]
Nakamura et al.	38	232	[29]
Modified Okafor*	60	359	[30]
Otomo et al.	32	213	[31]
Stagni et al.	31	203	[32]
Mathieu and Petersen	55	278	[33]

\* Okafor scheme was modified to add helium using the third body coefficients of argon.

132 flame speed was calculated for a pressure-temperature pair which evolved  
 133 isotropically mimicking the experimental combustion process.

134 Among the 9 chosen mechanisms, it was seen that 2 mechanisms- Naka-  
 135 mura [29] and Stagni [32] predicted and captured the experimental results  
 136 at all conditions better than the other mechanisms. Although, the 9 chosen  
 137 mechanisms could aptly produce the trend, i.e. the flame speed increases  
 138 with an isotropic increase of temperature and pressure for all the test condi-  
 139 tions; there is a variation in the flame speed values. Sensitivity analyses were  
 140 performed for a few mechanisms to understand the role of the key reactions.

### 141 3. Results and discussions

#### 142 3.1. Experimental and numerical flame speeds

143 The experiments were performed in the isochoric condition. The isochoric  
 144 method helps to retrieve a wide band of flame speed data at elevated condi-  
 145 tions [20, 21, 22, 23, 24]. This range has been chosen such that the stretch  
 146 effects that occur in the initial phase and the heat losses endured when the  
 147 flame front hits the wall do not affect the propagation of the flame front and  
 148 hence, the flame speed. Table 3 represents the range of pressure and temper-  
 149 ature for which the flame speeds have been determined. It is assumed that  
 150 the temperature of fresh gases evolves isentropically while the flame front  
 151 propagates. A relative accuracy of less than 0.5% on the flame radius was  
 152 propagated on the flame speed leading to a maximal error lower than 5% [20].  
 153 The experiment traces have been widened to account for this uncertainty.

Table 3: Initial pressure and equivalence ratio with the range of pressure and temperature for which the flame speed has been measured. The initial temperature,  $T_0$ , was maintained at 300K

$\varphi$	$P_0$ (bar)	P range (bar)	T range (K)
0.8	1	2-6	369-502
0.8	2	4-16	374-555
1.1	1	2-9	371-572
1.1	2	4-16	371-557
1.1	3	6-30	372-584
1.1	4	8-37	371-575
1.3	1	2-8	370-544
1.3	2	4-17	370-555
1.3	3	6-26	370-557
1.3	4	8-36	369-563

154 The experimental flame speeds and the flame speeds from the chosen  
155 mechanisms were calculated and plotted for all the conditions given in Table  
156 1. A very similar trend for all the given conditions was noted. However, most  
157 of the schemes failed to give the flame speed value within the experimental  
158 range. Generally, it was seen that the schemes of Klippenstein, Zhang (2017)  
159 and Dagaut over-estimate the flame speeds when compared to the experimen-  
160 tal flame speed whereas Mathieu and Otomo under-estimate the flame speed.  
161 The other 4 mechanisms more or less fall within  $\pm 5\%$  error bar of the ex-  
162 perimental results. Out of the 14 cases, 3 of them are represented here in the  
163 Figures 1, 2 and 3. The 3 chosen conditions represent a fuel-lean condition,  
164 a fuel-rich condition and a high-pressure condition to illustrate the above  
165 mentioned observations. The chosen conditions help to demonstrate a fuel-  
166 rich versus fuel-lean mixture at similar initial conditions and a low pressure  
167 versus high pressure condition at the same equivalence ratio.

168 Figure 1 depicts the flame speed at  $\varphi=1.3$ ,  $P_0=4$  bar and  $T_0=302$  K with  
169 a diluent mixture of 21% Ar and 49% He. Figure 2 represents the flame  
170 speed at  $\varphi=1.3$ ,  $P_0=1$  bar and  $T_0=296.8$  K and Figure 3 represents the  
171 flame speed at  $\varphi=0.8$ ,  $P_0=1$  bar and  $T_0=296.2$  K. Both the cases use the  
172 same diluent mixture: 49% Ar and 21% He. The flame speeds of the lean  
173 fuel-air ratio case,  $\varphi=0.8$  is higher than that of the rich case,  $\varphi=1.3$ . The y  
174 axis represents the flame speed whereas the x axis is split as temperature and



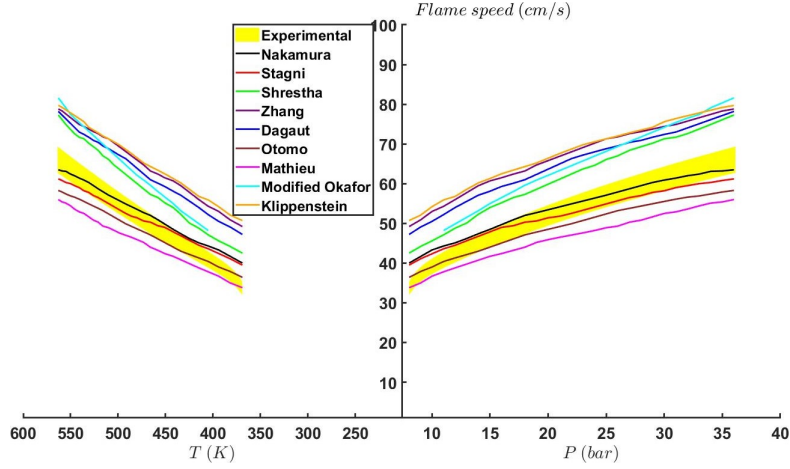


Figure 1: Laminar flame speeds at  $P_0=4$  bar,  $T_0=302.3\text{K}$ ,  $\varphi = 1.3$ , 21% Ar and 49% He. The experimental flame speeds have been thickened in yellow to account for the uncertainties incurred. The y axis represents the flame speed whereas the x axis is split as temperature and pressure. This is done as the flame speed is function of both pressure and temperature which evolves isotropically during the combustion process. The orange colour represents Klippenstein [25], violet represents Zhang (2017) [27], blue represents Dagaut [26], brown represents Otomo [31], pink represents Mathieu [33], cyan represents Modified Okafor [30], green represents Shrestha [28], red represents Stagni [32] and black represents Nakamura [29]

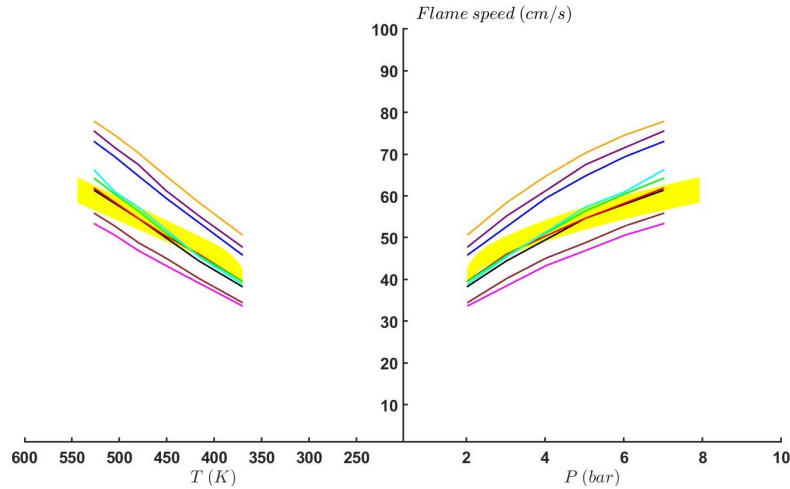


Figure 2: Laminar flame speeds at  $P_0=1$  bar,  $T_0=296.8\text{K}$ ,  $\varphi = 1.3$ , 49% Ar and 21% He

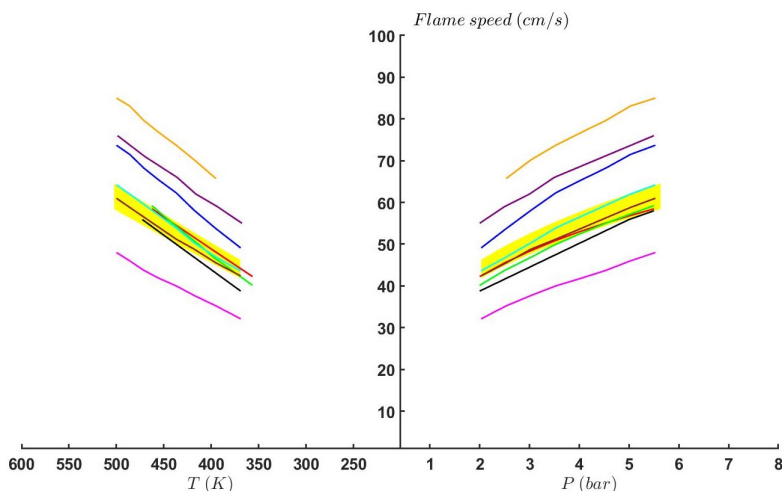


Figure 3: Laminar flame speeds at  $P_0=1$  bar,  $T_0=296.2$ K,  $\varphi = 0.8$ , 49% Ar and 21% He

175 pressure. This is done as the flame speed is function of both pressure and  
 176 temperature which evolves isotropically during the combustion process. On  
 177 analysing all the cases, it was concluded that both Nakamura and Stagni can  
 178 predict the flame speed closest to the experimental values. The experimental  
 179 flame speeds along with the flame speeds from Nakamura and Stagni for  
 180 all the cases are provided as supplementary document. Since, the study  
 181 mainly focusses on 3 mechanisms, the following legend is maintained for  
 182 convenience: red represents Stagni, black represents Nakamura and green  
 183 represents Shrestha.

### 184 3.2. Sensitivity analyses

185 Sensitivity analyses were performed on a few mechanisms to understand  
 186 the behaviour and to highlight the key reactions. It was seen that the most  
 187 dominant reaction irrespective of the mechanism and the initial conditions is  
 188  $O_2 + H \rightleftharpoons O + OH$ . It is interesting to note that the sensitivity coefficient  
 189 on the flow rate for the reactions for all the schemes are quite different even  
 190 though the rate constant,  $k$  are quite similar. On comparing the rate constants  
 191 of this reaction  $O_2 + H \rightleftharpoons O + OH$  for Klippenstein and Nakamura  
 192 and the flame speeds it can be confirmed that the discrepancy in the magni-  
 193 tude of flame speeds does not arise from the small difference in values of the  
 194  $k$ . The vast difference in the flame speeds for different mechanisms may be  
 195 attributed to the global summation effect of those reactions that do not fall

196 under the top 10 important reactions. Since, Nakamura and Stagni estimate  
197 the flame speeds closer to the experimental results, a deeper study has been  
198 made on them.

199 Figures 4a, 4b and figures 5a, 5b depict the sensitivity analyses for Naka-  
200 mura and Stagni mechanisms at  $\varphi = 0.8$  and  $\varphi = 1.1$  for an initial pressure of  
201 1 bar and a diluent mixture of 49% Ar and 21% He respectively. Figures 6a,  
202 6b represent the sensitivity analyses for Nakamura and Stagni mechanisms  
203 respectively at  $\varphi = 1.1$ ,  $P_0=3$  bar with a diluent mixture of 21% Ar and 49%  
204 He whereas figures 7a, 7b represent the analyses at  $\varphi = 1.1$ ,  $P_0=4$  bar and  
205 a diluent mixture of 70% He. Figures 8a, 8b and figures 9a, 9b display the  
206 sensitivity results at  $\varphi = 1.3$  for a  $P_0=2$  bar with a diluent mixture of 21%  
207 Ar and 49% He and for a  $P_0=4$  bar with a diluent mixture of 70% He respec-  
208 tively. The analyses illustrate the use of different equivalence ratios, initial  
209 pressures and diluent mixtures. The sensitivity analyses for the remaining  
210 conditions are provided as a supplementary material. It is interesting to  
211 note that even though the flame speed predicted by Nakamura and Stagni  
212 are quite close, the top 10 important reactions are not exactly the same.  
213 The two common reactions apart from the dominant reaction are :  $\text{HNO} +$   
214  $\text{H} \rightleftharpoons \text{NO} + \text{H}_2$  and  $\text{NH}_2 + \text{NO} \rightleftharpoons \text{NNH} + \text{OH}$ . It is noticed that the  
215 reaction  $\text{H}_2 + \text{O} \rightleftharpoons \text{H} + \text{OH}$  exists within the top 10 important reactions  
216 in all cases for both the mechanisms except for the lean cases of Nakamura.  
217 The rich cases for both the mechanisms witnessed another 2 common reac-  
218 tions:  $\text{NH}_2 + \text{H} \rightleftharpoons \text{NH} + \text{H}_2$  and  $\text{NH}_2 + \text{O} \rightleftharpoons \text{HNO} + \text{H}$ . A standard set  
219 of reactions is noted for each equivalence ratio apart from the above stated  
220 common reactions irrespective of the initial pressure except for  $\text{H} + \text{O}_2 +$   
221  $(\text{M}) \rightleftharpoons \text{HO}_2 + (\text{M})$  which is found only for those with an initial pressure of  
222 2 bar or more. However, none of the stated reactions play a role as significant  
223 as the  $\text{O}_2 + \text{H} \rightleftharpoons \text{O} + \text{OH}$  reaction does. Also, from the sensitivity analyses  
224 charts it can be seen that the flame speed is not highly sensitive to pressure.  
225 The sensitivity analyses show that these mechanisms predict a weak depen-  
226 dence of flame speed on pressure. On comparing with methane flames [20],  
227 the recombination reaction,  $\text{CH}_3 + \text{H} \rightleftharpoons \text{CH}_4$  is one of the main reactions  
228 which becomes more sensitive at higher pressure and equivalence ratio. The  
229 equivalent recombination reaction in ammonia flames,  $\text{NH}_2 + \text{H} \rightleftharpoons \text{NH}_3$  is  
230 not as sensitive as it is for the methane flames. Indeed, the mass burning  
231 rate is a parameter that indicates the reactivity. It increases as both the  
232 pressure and temperature increase for both ammonia and methane flames.  
233 It is known that when the pressure increases, the H radicals produced in the

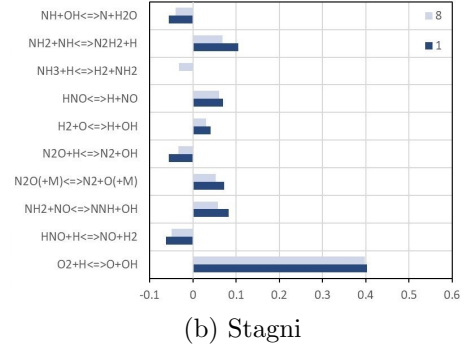
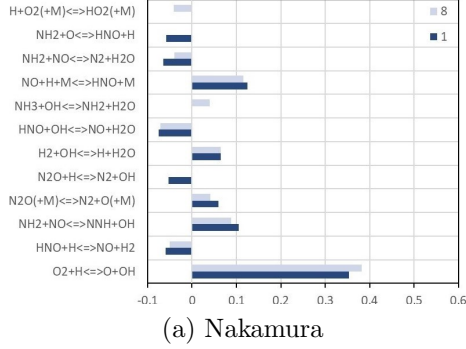


Figure 4: Sensitivity analyses at  $P_0=1$  bar,  $\varphi = 0.8$ , 49% Ar and 21% He with the minimum pressure at 1 bar (dark blue) and the maximum at 8 bar (light blue)

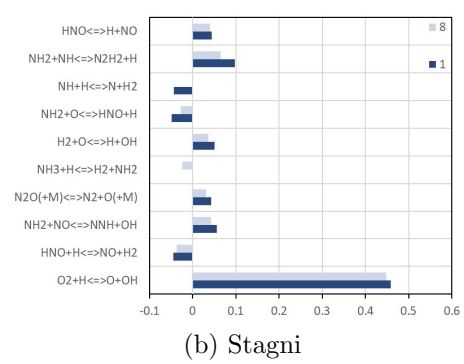
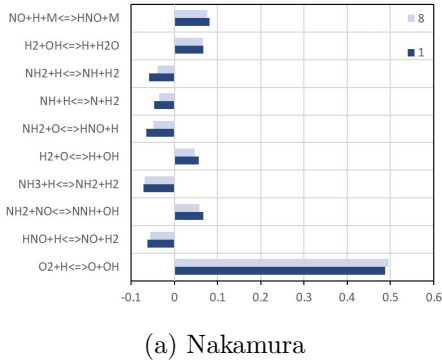


Figure 5: Sensitivity analyses at  $P_0=1$  bar,  $\varphi = 1.1$ , 49% Ar and 21% He with the minimum pressure at 1 bar (dark blue) and the maximum at 8 bar (light blue)

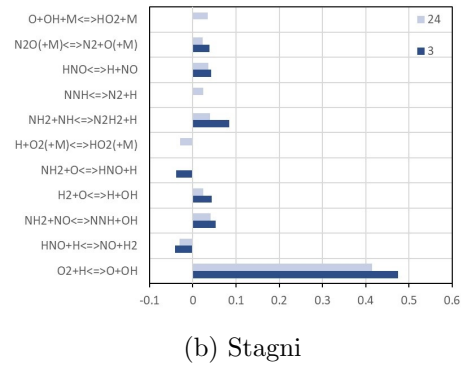
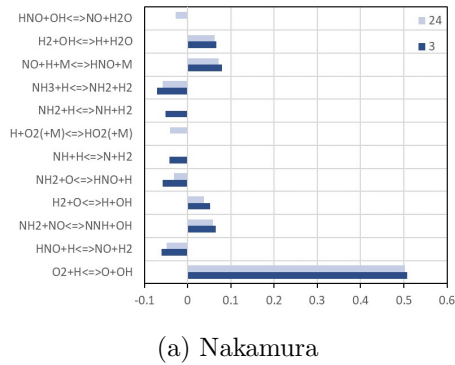
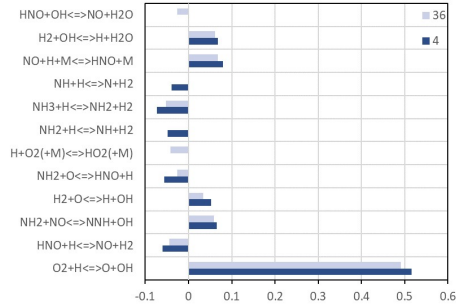
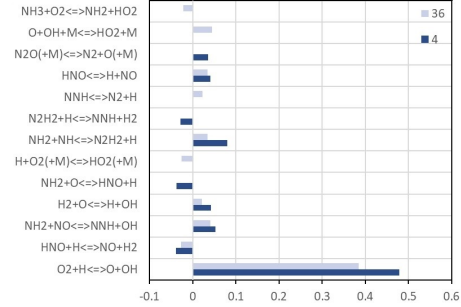


Figure 6: Sensitivity analyses at  $P_0=3$  bar,  $\varphi = 1.1$ , 21% Ar and 49% He with the minimum pressure at 3 bar (dark blue) and the maximum at 24 bar (light blue)

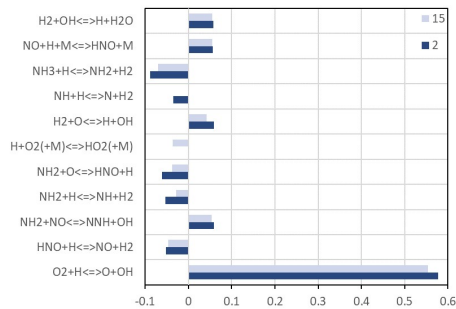


(a) Nakamura

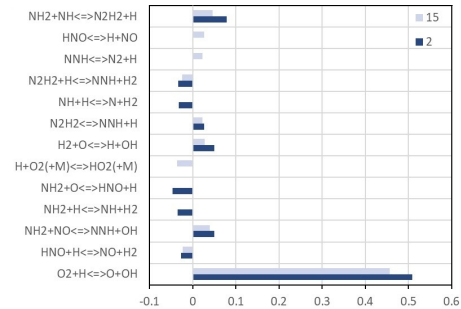


(b) Stagni

Figure 7: Sensitivity analyses at  $P_0=4$  bar,  $\varphi = 1.1$ , 70% He with the minimum pressure at 4 bar (dark blue) and the maximum at 36 bar (light blue)

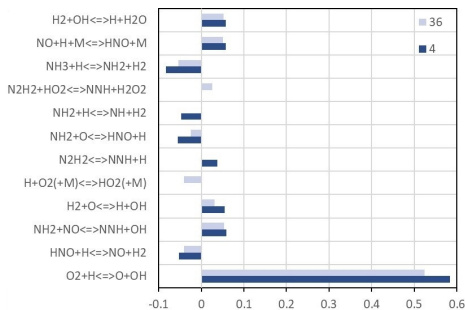


(a) Nakamura

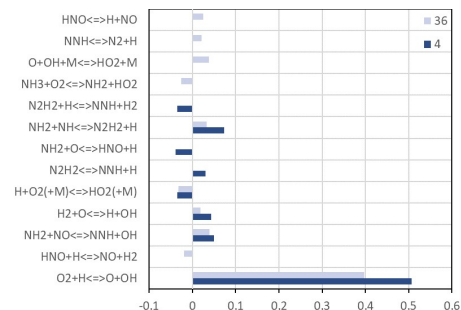


(b) Stagni

Figure 8: Sensitivity analyses at  $P_0=2$  bar,  $\varphi = 1.3$ , 21% Ar and 49% He with the minimum pressure at 2 bar (dark blue) and the maximum at 15 bar (light blue)



(a) Nakamura



(b) Stagni

Figure 9: Sensitivity analyses at  $P_0=4$  bar,  $\varphi = 1.3$ , 70% He with the minimum pressure at 4 bar (dark blue) and the maximum at 36 bar (light blue)

234 methane flames are more efficiently consumed leading to a decrease of flame  
235 speed. Here, to assess for ammonia flames, it may not be easy to conclude  
236 on the effect of the recombination reaction as the pressure and temperature  
237 increase simultaneously. To evaluate this effect, isothermal and isobaric sen-  
238 sitivity analyses have been carried out with one of the cases represented in  
239 the supplementary document. It is seen that  $O_2 + H \rightleftharpoons O + OH$  is indeed  
240 the most sensitive reaction and the recombination reaction is not as sensitive  
241 as compared to the case of the methane flames. The dominance of the driving  
242 reaction whose rate constant is pressure-independent and the absence of the  
243 equivalent sensitive recombination reaction can possibly explain the ability  
244 of all the mechanisms to produce the experimental trend invariably.

245 Figures 1 and 2 represent the flame speed variation over pressure and tem-  
246 perature for a low-pressure and a high-pressure initial condition respectively.  
247 As shown in these figures, irrespective of a high-pressure and a low-pressure  
248 initial condition, it can be seen that the flame speed variation over a pres-  
249 sure difference of 30 and 6 bar are translated as a variation of about 180 K  
250 in the temperature scale. In other words, the flame speed change is much  
251 higher when the temperature changes by a small amount as compared to a  
252 variation in pressure. The temperature increase is higher at the beginning of  
253 the compression and this effect decreases at higher pressure. All of these sug-  
254 gest that the combustion of ammonia is more temperature-sensitive rather  
255 than being pressure-sensitive, thereby implying that the mechanisms may  
256 be temperature-driven and not pressure-driven. In order to understand the  
257 working of these mechanisms further study has been made.

### 258 3.3. Isotherms and isobars

259 Figure 10a depicts the variation of flame speed over pressure at  $T=300$   
260 K and Figure 10b over temperature at  $P=1$  bar for 3 selected mechanisms:  
261 Nakamura, Stagni and Shrestha for  $\varphi = 0.8, 1.1$  and  $1.3$  at a diluent mixture  
262 of 49% Ar and 21% He. Isotherms were plotted at  $T=300$  K and at  $T=500$   
263 K and isobars were plotted for  $P=1$  bar and  $P=3$  bar. Similar results were  
264 obtained for both conditions. Isotherms at  $T=500$  K and isobars at  $P=3$  bar  
265 are provided as supplementary data. It is important to note that the flame  
266 speed axis range for the isobars are 4 times the range of the isotherms. It  
267 can be seen that as the pressure increases, the flame speed does not vary  
268 much. The drastic change in the flame speed is between 1-5 bar for all the  
269 mechanisms. As for the case of flame speed variation over the temperature,  
270 it is seen that the flame speed increases with temperature and the change

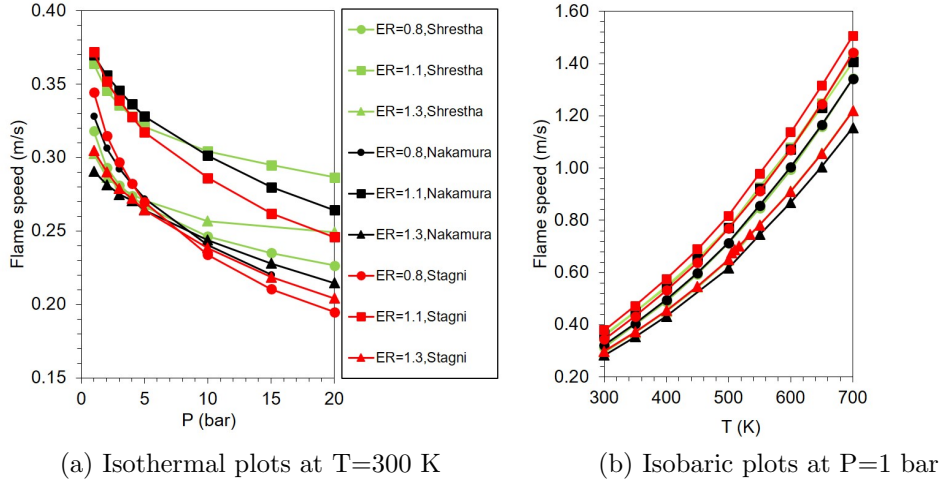
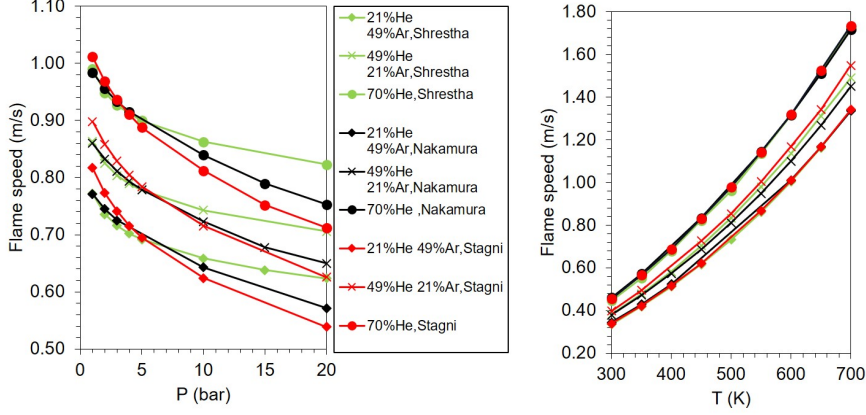


Figure 10: Comparison study of Nakamura, Stagni and Shrestha for  $\varphi = 0.8, 1.1$  and  $1.3$  at a diluent mixture of 49% Ar and 21% He, circles represent  $\varphi = 0.8$ , squares represent  $\varphi = 1.1$  and triangles represent  $\varphi = 1.3$  whereas the colours green, black and red represent the mechanisms of Shrestha, Nakamura and Stagni respectively.

271 is prominent at higher temperature. This essentially proves that the mech-  
 272 anisms are indeed driven by temperature. On evaluating the performance  
 273 of the 3 mechanisms, it can be said that the temperature effect is the same  
 274 in the 3 mechanisms. Figure 10a suggests that the pressure effect is slightly  
 275 more important in Stagni when compared to the other 2 mechanisms and  
 276 the least in Shrestha.

277 The effect of the bath gases is studied and is displayed in figures 11a and  
 278 11b. Isotherms at T=300 K and 500 K and isobars at P=1 bar and 3 bar  
 279 gave similar results. Isothermal plots at T=500 K are displayed in Figure  
 280 11a and isobaric plots at P=3 bar are shown in Figure 11b. The isotherms  
 281 at T=300 K and isobars at P=1 bar are provided as supplementary data.  
 282 It may be concluded that for the Shrestha mechanism the variation of the  
 283 flame speed with pressure is independent of the bath gas composition while  
 284 both Nakamura and Stagni show a slight dependence.

285 The pressure and temperature dependencies may be expressed as given in  
 286 the equation 2 using a reference flame speed and the corresponding conditions  
 287 if the exponential factors  $\alpha$  and  $\beta$  are known.



(a) Isothermal plots at T=500 K

(b) Isobaric plots at P=3 bar

Figure 11: Comparison study of Nakamura, Stagni and Shrestha for  $\varphi = 1.1$  for different bath gases compositions, circles represent 70% He, crosses represent 49% He and 21% Ar and diamonds represent 21% He and 49% Ar whereas the colours green, black and red represent the mechanisms of Shrestha, Nakamura and Stagni respectively.

$$\frac{S_u}{S_u^o} = \left(\frac{T_u}{T_u^o}\right)^\alpha \left(\frac{P_u}{P_u^o}\right)^\beta \quad (2)$$

288

289 Using the isothermal and isobaric curves, the values for  $\alpha$  and  $\beta$  are  
 290 estimated. It is observed that  $\alpha$  varies linearly with the temperature for all  
 291 the 3 mechanisms and the value ranges between 1.5 and 2. This range of  
 292 value is quite common to most of the fuels [37].  $\beta$  variation for Nakamura  
 293 and Stagni is quadratic whereas it is almost a constant for Shrestha as seen  
 294 in the Figure 12. Beta trends represented in the Figure 12 is calculated using  
 295  $P_0=1$  bar,  $T_0= 500$  K and the corresponding flame speed depending on the  
 296 equivalence ratio and the diluent mixture. The values of  $\beta$  lies between -  
 297 0.04 and -0.17 which is much lower than most of the fuels [37]. The low  
 298 value of beta results from the pressure independent behaviour. It is worth  
 299 emphasising that the pressure in-dependency increases with an increase in  
 300 pressure.

### 301 3.4. Alpha and beta values for the experiment and numerical flame speeds

302 From the experimental test conditions, it is possible to have at least two  
 303 conditions with the same equivalence ratio, initial temperature and diluent



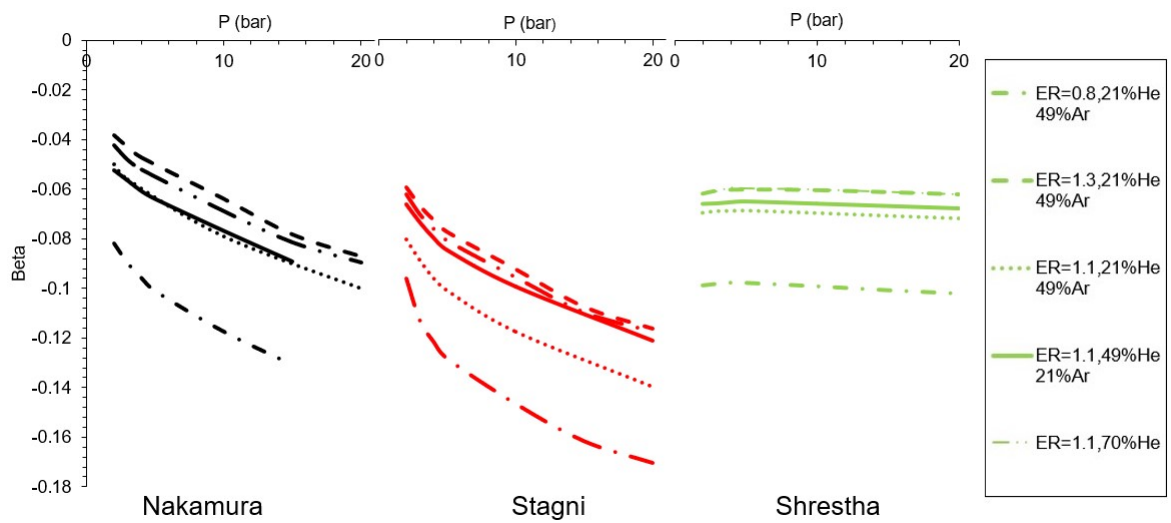


Figure 12: Beta trends from isotherms at  $T=500$  K calculated using  $P_0=1$  bar,  $T_0= 500$  K and the corresponding flame speed depending on the equivalence ratio and the diluent mixture.  $\varphi=0.8$ , 21% He 49% Ar is represented by dash dot,  $\varphi=1.3$ , 21% He 49% Ar by dash,  $\varphi=1.1$ , 21% He 49% Ar by round dot,  $\varphi=1.1$ , 49% He 21% Ar by solid and  $\varphi=1.1$ , 70% He by long dash dot dot and the colours black, red and green represent Nakamura, Stagni and Shrestha respectively.

304 mixture but with a different initial pressure giving rise to two (P,T) pairs.  
305 A certain range of pressure is common to both the conditions but the corre-  
306 sponding temperatures are different due to the initial conditions. The flame  
307 speeds can be obtained for two different temperatures at an isobaric condi-  
308 tion. Considering one of the flame speed curves (here, the flame speed  
309 corresponding to the initial condition with the lower pressure) as the ref-  
310 erence curve, an estimation of  $\alpha$  can be made using equation 2 and can be  
311 optimised to get the most precise value. A similar process can be used to esti-  
312 mate the  $\beta$  values from flame speeds corresponding to two different pressures  
313 at isothermal conditions.

314 The values of  $\alpha$  and  $\beta$  from Nakamura and Stagni lies within the exper-  
315 iment range. The values of  $\beta$  ranges between -0.07 to -0.21 and the values  
316 of  $\alpha$  range between 1.5 and 1.92 depending on the initial conditions. Both  
317  $\alpha$  and  $\beta$  are not constant values, therefore an estimation of the flame speed  
318 using equation 2 can be made by interpolating the values within the given  
319 range for the given set of conditions. It can be intuitively said that having a  
320 low  $\beta$  value is advantageous as pressure oscillations would have fewer effects  
321 on the flame stabilization in systems like gas turbines.

#### 322 4. Conclusion

323 Experiments to measure flame speeds corresponding to the conditions  
324 encountered in spark-ignition engines and gas turbines have been performed.  
325 The study was done for 3 different equivalence ratios: 0.8, 1.1 and 1.3 at an  
326 initial temperature of 300 K and an initial pressure ranging from 1 to 4 bar.  
327 The data available in the literature gives the flame speeds for a maximum  
328 pressure of 10 bar and a temperature of 473 K. From this study, the laminar  
329 flame speeds for a pressure of 37 bar and a temperature of 584 K have been  
330 obtained. These tests were performed in constant volume condition which is  
331 the most efficient way to obtain a wide range of data for elevated conditions.

332 A literature study had been made to select the most recent kinetic schemes  
333 for ammonia combustion. These schemes have been evaluated for the same  
334 conditions as that of the experiments. It was seen that the chosen schemes  
335 could produce the experimental trend- increase of flame speed with an isotropic  
336 increase of pressure and temperature for all the conditions. On performing  
337 a sensitivity analyses, it was understood that the most dominant reaction  
338 is  $\text{O}_2 + \text{H} \rightleftharpoons \text{O} + \text{OH}$ . Despite the high sensitivity of this reaction and  
339 the rate constant of this reaction being similar for all mechanisms, only 4

340 mechanisms: Shrestha, Nakamura, Modified Okafor and Stagni could pre-  
341 dict the flame speeds with the  $\pm 5\%$  error bar of the experimental flame  
342 speeds. The recombination reaction of the ammonia flames is pressure in-  
343 sensitive. In order to understand the working of the mechanisms, various  
344 simulations were performed at isobaric and isothermal conditions. The re-  
345 sults of these simulations prove that the mechanisms are temperature-driven  
346 and not pressure-driven as the change in flame speed for a small increase in  
347 temperature is much higher than the change in flame speed obtained from  
348 the same increase in pressure. The maximum influence of pressure is seen  
349 only from 1-5 bar after which the flame speeds do not vary a lot. The in-  
350 crease in the flame speed is attributed only to the increase of temperature  
351 which promotes the chemical reactivity. The impact of adding the bath gases  
352 has been noted for some of the mechanisms. The change in the flame speed  
353 response to pressure for Shrestha seems to have a lesser effect from the bath  
354 gases composition whereas Stagni and Nakamura seem to be influenced by  
355 the constituents of the bath gases.

356 A range of exponential factors  $\alpha$  and  $\beta$  required to calculate the flame  
357 speeds at a given pressure and temperature using a reference condition was  
358 determined. It is interesting to note that  $\beta$ , the exponential factor for the  
359 pressure is much smaller than most of the fuels emphasising the pressure  
360 in-dependency behaviour. This implies that ammonia is an ideal fuel for  
361 spark-ignition engines and gas turbines since pressure oscillations would have  
362 limited effects on the flame speed.

363 It can be concluded that the performance of oxy-ammonia flames is in  
364 par with the conventional fuels and has a promising future. Ammonia being  
365 a non-carbon based fuel, indeed has the potential to replace the hydrocarbon  
366 fuels without a large compromise in performance.

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