Ammonia combustion at elevated pressure and temperature conditions

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ARTICLE INFO

ABSTRACT

This numerical study examines the combustion characteristics of premixed ammonia–air mixtures, with equivalence ratios around unity, at elevated pressure and temperature conditions which are encountered in SI engine operations. The laminar burning velocity, final flame temperature and species concentrations were determined using Konnov's mechanism [18]. A flat, freely propagating flame was considered. Both equivalence and compression ratios have an important impact on both the laminar burning velocity and the adiabatic flame temperature. Furthermore, only the variation of the equivalence ratio has a major impact on the formation of nitrogen monoxide. It was found that the compression ratio and the final temperature do not have a significant impact on NO yields for equivalence ratios above unity.

1. Introduction

The search for alternatives to fossil fuels is an important concern of our society. Many studies are devoted to the evaluation of their energy efficiency together with their environmental impact. Among these, oxygenated fuels, biodiesel and hydrogen have been put forward. Even though hydrogen has been recognized as a promising fuel, implementing a global hydrogen-based economy is at present a non-feasible approach unless a suitable storage medium could be found [1]. Furthermore, large investments are required to develop a hydrogen distribution infrastructure due to safety issues. Hydrogen is volatile and has a low flash point; therefore it presents an explosion danger associated with air. In addition, its flame is invisible and hydrogen has a very low volumetric energy density with respect to liquid fuels used in transportation vehicles. Compared with gasoline, the volumetric energy density is four times less if hydrogen is stored in liquid state at $-235\,°C$ or 16 times less if it is stored at $25\,°C$ and $200\,bar$. To bypass such difficulties, we suggest the use of ammonia in a modified spark ignition (SI) engine. Since hydrogen must still be produced to obtain ammonia in large amount, it can be seen as a hydrogen vector. Similar to hydrogen, ammonia can be used as a clean energy carrier and storage medium because it can potentially be burnt in an environmentally benign way, exhausting only water, nitrogen and a few quantity of nitrogen oxides. The feasibility of applying ammonia as an alternative fuel for transportation has been investigated during the past decades [2–6] and the outcome seems to be quite promising. In fact, ammonia has several properties which make it suitable as an alternative fuel for a SI engine. It has a high octane rating (>130) [7] which makes it possible to apply high compression ratios to achieve high engine-cycle efficiencies and in comparison with liquid hydrogen fuel, its storage needs 30% less space [8]. If we compare a same tank of ammonia or hydrogen, the first one contains indeed more energy. In addition, hydrogen must in this case be stored at pressures around 700 bars, which complicates strongly the use of such a fuel in practical system compared to ammonia which is stored at pressures around 8 bar.

However, the successful application of ammonia as an alternative transportation fuel should be grounded in a detailed understanding of the combustion characteristics of NH_3 in SI engine operation conditions. The determining of the structure of pure rich, stoichiometric and lean NH_3–air flames, and the one of seeded ammonia flames with nitrogen monoxide or hydrogen have been the subject of several studies in the past [9–15]. Concerning the use of ammonia in SI engines, a first study was performed in 1941 by Macq [2]. However, the NH_3 was decomposed into H_2 on a catalyst before combustion. The combustion conditions were not the same as in the present work. Hydrogen was shown to help to start the combustion process when it is present in quantities higher than 5%. Liu et al. have performed a numerical study [16], on which the present work is based, giving different results on parameters to apply on the engine to reach the best efficiency and to reduce the formation of NO. However, in the Liu et al. study, the Lindstedt's [17] mechanism was used. It has been proven in a previous work that Lindstedt's model leads to a large disagreement between experimental and simulated results in stoichiometric

NH₃–air flames at low pressure [14]. The numerical study conducted by Liu et al. [16] examined the combustion characteristics of premixed NH₃–air mixtures at elevated pressures and temperatures as encountered during SI engine operation. Therefore, we present in this work a similar methodology by using Konnov's combustion mechanism which gives a better agreement [18]. However a short comparison of the results obtained with Lindstedt's and Konnov's mechanism has also been performed. As it has been shown in previous works [14,15], a high compression ratio (CR) is needed to use NH₃ as a fuel in a SI engine. Therefore, compression ratios between 12:1 and 20:1 have been investigated. Furthermore, the flame which will propagate in such practical systems will have an equivalence ratio of approximately 1.0 [14]. These are the operating conditions that have been considered in this study. The laminar burning velocity, the flame temperature and species concentration profiles have been calculated by using the Cosilab software [19].

2. Specific objectives

The aim of this work is to examine some combustion characteristics of premixed NH₃–air mixtures at elevated pressures and temperatures conditions. This gives information on the feasibility of the use of ammonia as a fuel. The goal of this study is to determine the combustion conditions which yield maximum efficiency while minimizing the emission of pollutants.

3. Numerical simulation

In the flame simulations, laminar, one-dimensional, premixed, and freely propagating flames have been assumed. In nature or laboratory, premixed, freely propagating flames occur under a variety of conditions. Here the adjective "freely" implies that such flames are free from external disturbances as they are typically imposed on a flame by the presence of near-by walls or by flame-anchoring devices such as burner-nozzles or rods. Nevertheless, a premixed, freely propagating flame can be of a complex three-dimensional shape such as a spherical – or approximately spherical flame, and it may exhibit instability or even be turbulent. Such complexities are absent from one-dimensional premixed, freely propagating flames, in particular, if they are laminar and these are the flames with which we are concerned here. Although these flames are model flames that in reality rarely exist, they are valuable research "tools" and hence worthwhile to be considered for study.

One of the critical elements needed for the simulation is a proper reaction mechanism which describes the essential fundamental reaction paths to be followed by the overall reaction. Konnov's mechanism was applied in this study [18]. It has been validated for decomposition, oxidation, ignition, and flame structure of H₂, CO, CH₂O, CH₃OH, CH₄, N₂O, NO, NO₂ and NH₃. This model is not specific for ammonia flames; it considers carbon based species until C₆ but takes into account the presence of nitrogen. Only the reactions of interest were taken and not those with carbon to obtain a model with 31 species and 245 elementary reactions. To reproduce the conditions occurring in SI engines, initial pressure and temperature have been adjusted in order to correspond to compression ratios (CR) from 12:1 to 20:1. However, in a second part of this paper, these two parameters have been varied separately to study the effects of each one on the combustion characteristics of an NH₃–air mixture.

The pressure and unburned mixture temperature have been determined by assuming an isentropic compression process after which the ammonia–air mixture was ignited, supposing an adiabatic and isobaric combustion process. The mixture was considered to be at STP (1 atm. 293,15 K) condition before compression.

The pressure and unburned temperature calculations corresponding to each compression ratio are summarized by the following ideal gas law equations:

$$PV^\gamma = \text{constant} \Rightarrow P_1 V_1^\gamma = P_2 V_2^\gamma \tag{1}$$

$$P_1 V_1 / T_1 = P_2 V_2 / T_2 \tag{2}$$

P_1 and T_1 being the initial Standard Temperature and Pressure Conditions (STP), it can be written that:

$$V_2 = 1/CR \tag{3}$$

$$P_2 = P_1 * (CR)^\gamma \tag{4}$$

$$T_2 = (CR)^{\gamma-1} * T_1 \tag{5}$$

The critical factor for the calculation of final pressures and temperatures is thus the ratio of specific heats, γ. The specific heat at constant pressure, C_p, is calculated from the mixture composition, expressed in mole fractions, $x(i)$, and the individual specific heats, $C_p(i)$; $C_p = \sigma[x(i) C_p(i)]$. The ratio of specific heats, γ then follows from $\gamma = C_p/(C_p - R)$. Gamma is a function of temperature and look-up tables can be easily constructed relating gamma to temperature for any mixture. Ranges of initial pressures and unburned mixture temperatures corresponding to every compression ratio are listed in Table 1.

The initial composition of the flame has been chosen to be close to the one presumed to occur in spark ignition engine operation, the equivalence ratio turns thus around 1.0. The chemical equation for the stoichiometric reaction of ammonia–air is

$$NH_3 + 0.75(O_2 + 3.76N_2) \rightarrow 3.32N_2 + 1.5H_2O \tag{6}$$

The ammonia–air equivalence ratio (φ) was determined according to the Eq. (6) here above and the mole fractions of each reactant are listed in Table 2 for equivalence ratio values from 0.7 to 1.2.

The simulation was run at equivalence ratios listed in Table 2 for each compression ratio value except for 0.7; 0.8 and 0.9 for which it has only been done at STP conditions. Then, in a second

Table 1
Ranges of calculated pressure and unburned mixture temperature for each compression ratio.

Compression ratio, CR	Pressure before combustion, P_2 (atm.)	Unburned mixture temperature, T_2 (K)
12	28.04–28.48	700.9–711.7
13	31.13–31.62	718.3–729.7
14	34.28–34.84	734.7–746.7
15	37.51–38.11	750.1–762.6
16	40.79–41.49	764.7–777.9
17	44.15–44.93	778.7–792.5
18	47.47–48.37	791.7–806.2
19	50.96–51.94	804.6–819.5
20	54.45–55.47	816.7–832.1

Table 2
Ammonia–air mixtures (mole fractions) at several equivalence ratios.

φ	NH₃	O₂	N₂
0.70	0.1639	0.1757	0.6604
0.80	0.1831	0.1716	0.6453
0.90	0.2013	0.1678	0.6309
0.95	0.2102	0.1659	0.6239
1.00	0.2188	0.1641	0.6171
1.05	0.2273	0.1623	0.6104
1.10	0.2356	0.1606	0.6038
1.15	0.2436	0.1589	0.5975
1.20	0.2516	0.1572	0.5912

part of this study, the pressure and the temperature have been varied separately to put forward the effects of each parameter on the combustion characteristics of ammonia.

The computation yields the profiles of gases velocities, flames temperatures and species concentrations throughout the flame. The laminar burning velocity was obtained at the adiabatic flame boundary. Additionally, the flame temperature at the end of the computational domain was taken as the adiabatic flame temperature. Finally, to study the influence of the combustion characteristics; such as the equivalence ratio, the initial temperatures and pressures, etc.; on the exhaust gas composition, the maximum concentration of nitrogen monoxide and the final quantities at the end of the combustion process are plotted as a function of the equivalence and compression ratios.

4. Results and discussion

4.1. Standard Temperature and Pressure Conditions

Figs. 1–3 show the laminar burning velocities, adiabatic flame temperatures and NO mole fractions for fresh gas mixtures at STP for equivalence ratios ranging from 0.7 to 1.2. As presented in Fig. 1, the maximum laminar burning velocity is attained in the rich side with an equivalence ratio of 1.12 and equals to 15 cm/s. This occurrence of peak laminar burning velocity agrees with the result of Checkel et al. [20] who measured a maximum pressure rise of ignited NH_3–air mixture at an ammonia volume
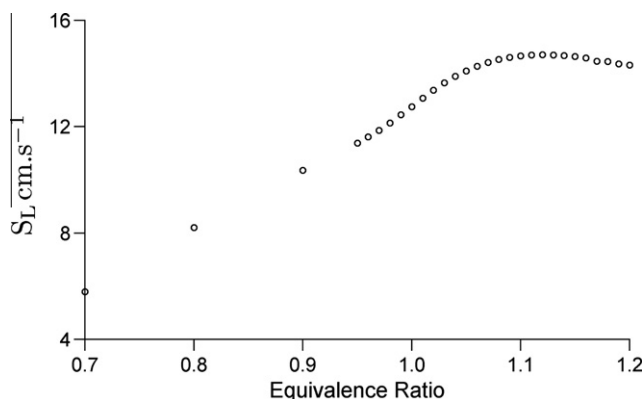

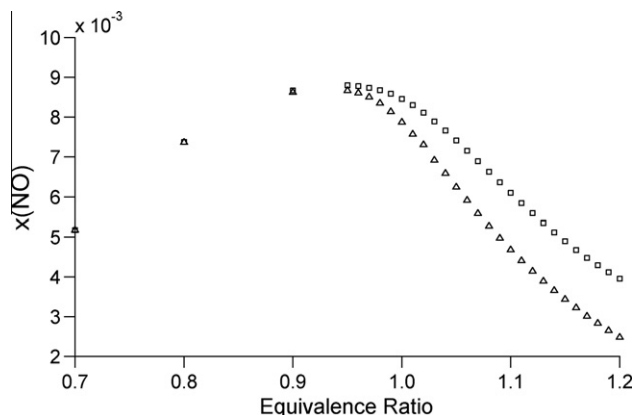Fig. 1. Laminar burning velocity of ammonia–air mixture at STP.

Fig. 2. Highest (□) and burnt gases (△) nitrogen monoxide mole fraction of ammonia–air mixture burning at STP.
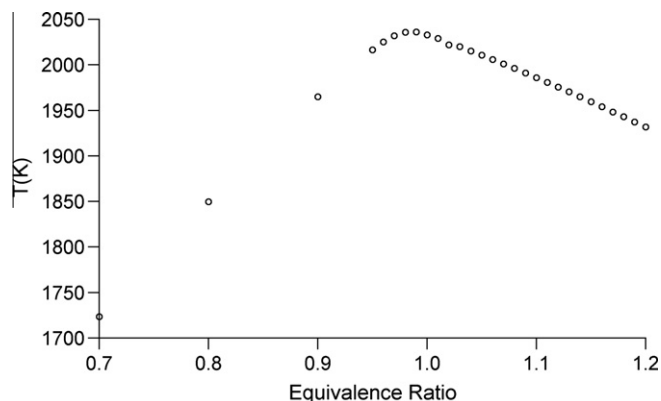

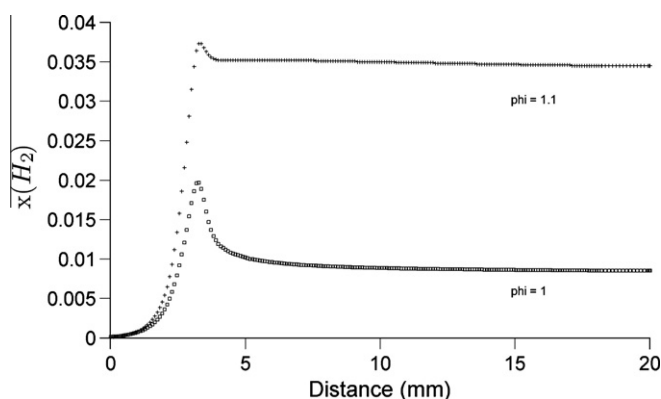Fig. 3. Adiabatic flame temperature for each equivalence ratio at STP.

Fig. 4. Hydrogen mole fraction profiles at equivalence ratio of 1.0 and 1.1 for STP.

concentration of approximately 23.5% ($\varphi = 1.1$) Fig. 2 shows the maximum and the burnt gases mole fractions of the nitrogen monoxide profile for each equivalence ratio at STP. These two values reach a maximum and are identical at $\varphi = 0.95$ ($x(NO) = 9.0 \times 10^{-3}$). For an equivalence ratio lower than 0.95, both values decrease and overlap and for φ higher than 0.95, they decrease too but the $x(NO)$ in the burnt gases region falls more strongly. This implies that the equivalence ratio is a very important parameter which must be well controlled in SI engine operation to minimize the nitrogen monoxide formation.

Fig. 3 illustrates the adiabatic flame temperature as a function of equivalence ratio at STP. This graph shows a peak at an equivalence ratio equals to 0.99 instead of at $\varphi = 1.12$ as the laminar burning velocity. This is likely due to the maximum energy release and the dissociation of surplus ammonia into nitrogen and hydrogen at that equivalence ratio [16].

The H_2 mole fraction profiles for stoichiometric and rich ($\varphi = 1.1$) mixtures at STP are shown in Fig. 4. In rich mixtures, H_2 is produced in the flame front and reaches a partial equilibrium value in the burnt gases region. Under stoichiometric conditions, H_2 is mainly an intermediate peaking in the flame front and declining in the post-combustion zone to reach an equilibrium state. Since the dissociation of NH_3 is endothermic, the adiabatic flame temperature of a rich mixture is expected to be lower than that of the leaner mixture as observed in Fig. 3.

4.2. Effects of the compression ratio

In Figs. 5–7, the influence of the compression ratio on the laminar burning velocities, the adiabatic flame temperature and the
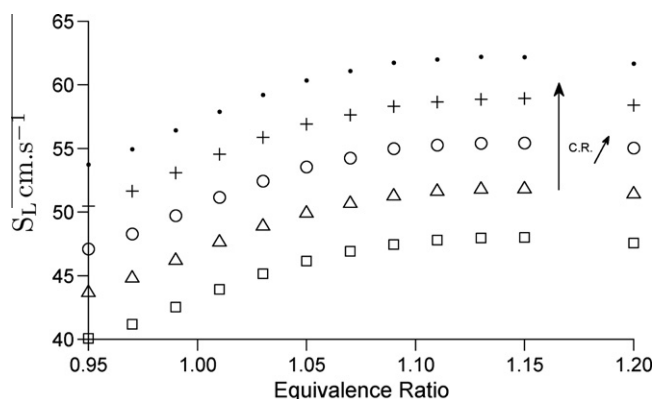
Fig. 5. Laminar burning velocities at several compression ratios (C.R.). □: C.R. = 12; △: C.R. = 14; ○: C.R. = 16; +: C.R. = 18; ●: C.R. = 20.
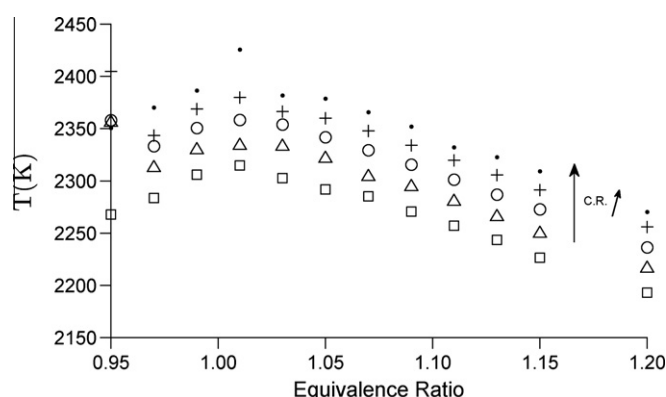

Fig. 6. Adiabatic flame temperature at several compression ratios (C.R.). □: C.R. = 12; △: C.R. = 14; ○: C.R. = 16; +: C.R. = 18; ●: C.R. = 20.
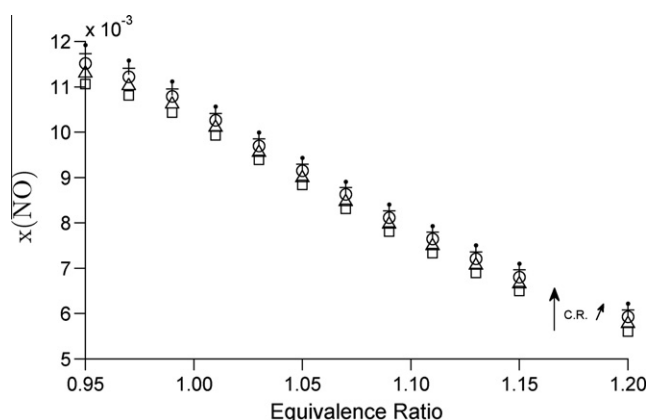

Fig. 7. Highest nitrogen monoxide mole fraction at several compression ratios (C.R.). □: C.R. = 12; △: C.R. = 14; ○: C.R. = 16; +: C.R. = 18; ●: C.R. = 20.

NO formation is illustrated for several equivalence ratios. For all these figures, although simulations were performed for all the equivalence and compression ratios, only a selection is shown in the figures.

In Fig. 5, it can be seen that the variation of compression ratio has no effect on the position of the maximum value of the laminar burning velocity. This maximum value for laminar burning velocity is consistently found to be at equivalence ratio of approximately 1.15. However, in the vicinity of stoichiometric mixtures, the variation of the compression ratio has a significant effect on increasing the laminar burning velocity. An increase in compression ratio from 12:1 to 20:1 leads to a 130% increase in laminar burning velocity.

Fig. 6 presents the variation of adiabatic flame temperature as a function of compression ratio and equivalence ratio. It was found that adiabatic flame temperature increased slightly with compression ratio. However, in this case too, a change in compression ratio does not have an impact on the position of the maximum value of the adiabatic flame temperature, which is consistently found at an equivalence ratio of 1.01. The maximum adiabatic flame temperature varies from 2040 K at STP to 2390 K at 50 bars and 732 K (CR = 20) for an equivalence ratio of 1.01.

Fig. 7 presents the variations of the highest NO mole fraction with the compression ratio and the equivalence ratio. Increasing the compression ratio does not have a significant impact on the NO formation for the range of CR investigated in this work because it leads only to a slight increase of the adiabatic temperature and as a consequence to a slight increase of the thermal NO formation. However, a huge decrease of the highest NO concentration is observed for rich mixtures (φ = 1.2), with a NO maximum mole fraction of only 0.005. This is 50% less than the amount of NO found for an equivalence ratio of 0.95. This characteristic shows the advantage to use slightly rich mixtures as practical fuel to reduce NO production in SI engines. A similar trend is observed for the burnt gas NO mole fraction.

In summary, at a given equivalence ratio (for 0.95 < φ < 1.2), the combined effects of a simultaneous increase in the initial temperature and pressure (effect of increasing the CR) contribute to an important increase of the laminar burning velocity but increases the adiabatic flame temperature and the NO formation slightly.

A comparison of results obtained with Lindstedt's and Konnov's mechanism has also been performed for several conditions of pressure, temperature and equivalence ratio and leads systematically to a diminution of 33% of the burning velocities for the Linstedt's mechanism together with a reduction of 50% of the nitrogen monoxide formation in the burnt gases.

4.3. Separated influences of the initial temperature and pressure

In order to determine the impact of initial pressure and temperature on the laminar burning velocity, adiabatic flame temperature and nitrogen monoxide formation, the initial pressure and temper-
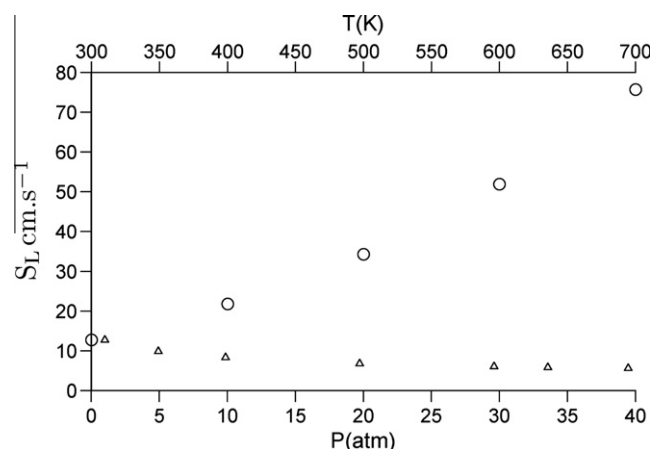

Fig. 8. Separated effects of temperature (○) and pressure (△) variation on the laminar burning velocity.

ature have been varied separately. In a first set of simulations pressure was fixed at 1 atm. and temperatures ranged from 300 to 700 K, then temperature was fixed at 300 K and pressures ranged from 5 to 40 atm. in a second set.

For all these numerical simulations, the flame considered had an equivalence ratio of 1.0. As shown in Figs. 8 and 9, the increase of the unburned mixture temperature for a constant pressure has a positive effect on the laminar burning velocity and on the adiabatic flame temperature. However, the increase of pressure for a constant initial temperature has rather a slightly negative effect on the laminar burning velocity and almost no effect on the adiabatic flame temperature.

Fig. 10 illustrates an increase of the initial temperature (at a constant pressure of 1 atm.) which increases NO formation. This result is due to the increase of the final temperature of the flame as it can be seen in Fig. 9, and therefore the increase of the thermal NO formation. When only the initial pressure is increased, the final temperature of the flame is not really affected (Fig. 9). Unexpectedly, the maximum concentration and final NO mole fraction in the flame decrease. Such a result indicates that the temperature is not the only parameter to take into account for the NO formation. Indeed, for ammonia combustion, the NO formation is due to thermal NO but also to fuel NO. For an increase of the initial temperature at a constant initial pressure, the final flame temperature is increased and therefore the formation of the thermal NO. But for an increase in the initial pressure at a constant initial temperature, the final flame temperature remained unchanged, thus the thermal NO formation is the same. However, the nitrogen monoxide formation decreases with this pressure augmentation, therefore, it seems that pressure influences the kinetic reactions of the fuel NO formation pathways and thus these influences must be investigated to understand the NO formation in ammonia flames at elevated pressure and temperature conditions.

5. Conclusion

A numerical simulation was performed in this study to investigate the characteristics of ammonia–air combustion at several pressure and temperature conditions (1–49 atm., 298–732 K) which could be encountered during the SI engine operation. The laminar burning velocity was found to peak at ammonia–air equivalence ratio of 1.12, while the peak value of the adiabatic flame temperature was predicted to be at stoichiometric condition. ($\varphi = 1.01$). Both equivalence and compression ratios have an important impact on the laminar burning velocity and on the adiabatic flame temperature. On the other hand, only the variation of the equivalence ratio had a major effect on the NO formation. The compression ratio and the final temperature do not have a significant impact on the NO formation for equivalence ratios above 1.0 and for the range of pressures and temperatures investigated in this work. As expected, rich mixtures yield to lower NO_x emissions and the same can be said for an increase of the pressure at constant initial temperature.

Fig. 9. Separated effects of temperature (○) and pressure (△) variation on the adiabatic flame temperature.

Fig. 10. Separated effects of temperature and pressure variation on the maximum and the burnt gases nitrogen monoxide mole fraction in the flame. T variation: Δ: x(NO) max; +: burnt gases x(NO). P variation: ○: x(NO) max; □: burnt gases x(NO).

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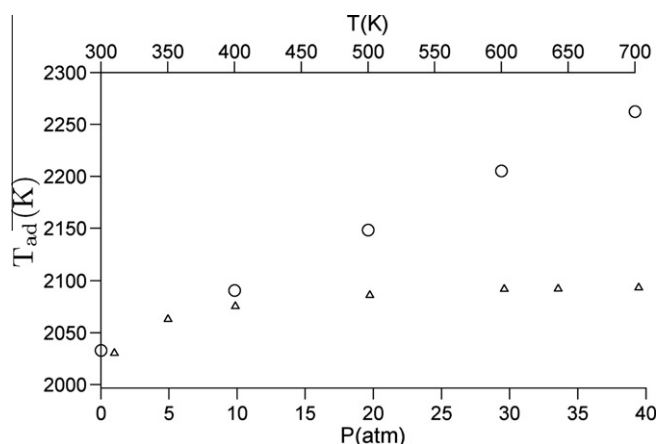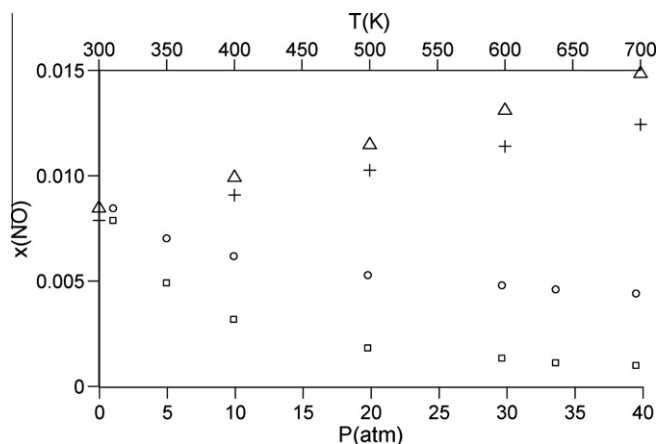
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