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The influence of ammonia on the laminar burning velocities of methylcyclohexane and toluene: An experimental and kinetic modeling study

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ABSTRACT

Laminar burning velocities of methylcyclohexane and toluene blended with ammonia have been determined using the heat flux method at atmospheric pressure and initial temperature of 338 K, over equivalence ratios ranging from 0.7 to 1.3 and ammonia blending fractions in the binary fuel mixtures from 0 to 90%. It was observed that the addition of ammonia to methylcyclohexane and toluene leads to a decrease in laminar burning velocity that is not proportional to the ammonia mole fraction. Such a burning velocity reduction is due to synergistic thermal and kinetic effects. In addition, ammonia has a slightly higher impact on the burning velocities of toluene due to fuel structure effects. The CRECK detailed kinetic model has been used to interpret the experimental measurements and minor modifications on methylcyclohexane, toluene, and methyl-phenoxy radical chemistry allowed even improved agreement. New experimental results have been compared with predictions of this refined kinetic mechanism. The model provided good predictions of the measurements capturing the effect of equivalence ratio and ammonia fraction ranges investigated. Finally, a mass fraction-based mixing rule was shown to be predictive for binary blends of NH_3 with methane and several hydrocarbons typically used to formulate surrogates for practical fuels.

1. Introduction

Recently ammonia (NH_3) has received revitalized interest as a promising renewable and carbon-free energy carrier. This consideration has motivated numerous test studies focused on direct NH_3 utilization in internal combustion engines, stationary gas turbines, and industrial furnaces as recently summarized by Valera-Medina et al. [1]. Such investigations mainly focused on overcoming the nitrogen-based pollutant emissions and the unfavorable combustion characteristics of NH_3 compared to conventional hydrocarbon fuels such as its low flame temperature, low laminar burning velocity, high auto-ignition temperature, narrow flammability range, high heat of vaporization, low lower heating value (on a mass basis), high minimum ignition energy, high ignition delay time, low radiation intensity, and slow chemical conversion rate.

In order to address these challenges, several investigators have considered enhancing the combustion by doping NH_3 with H_2 [2–16], which could be produced in situ from NH_3 partial dissociation, leading to better ignitability, increased laminar burning velocity and extended flammability range. Another potential combustion promoter that has been tested is methane, the main fuel for gas turbines power generation [7, 17-19]. Contemporary studies also extensively investigated the performances of dual fueled combustion of NH_3 with diesel [3, 20-23], biodiesel [20], and dimethyl ether [24, 25] in compression-ignition engines; gasoline [4, 6, 26-28] or gasoline/alcohols [29] in spark-ignition engines; and kerosene in gas turbines [19]. These co-firing approaches are of practical interest either to reduce carbon-based emissions, or to enhance combustion when NH_3 is the primary fuel.

Such studies have succeeded in demonstrating the potential of NH_3 as a flexible fuel in conventional combustion systems without major design modifications and, for this purpose, the relevance of auxiliary fuels to be co-fired with NH_3 to counteract its unfavorable combustion properties has been underlined. However, despite the encouraging progress that has been reached in the implementation of NH_3 in current combustion-based applications, the optimal design and reliable operation of practical combustors over a wide range of conditions also require a thorough understanding of

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the combustion chemistry of NH_3-containing mixtures. While various chemical kinetic models have been proposed and validated for hydrocarbons and NH_3 individually, it is not the case for their blends. Such a gap between kinetic studies of neat fuels and engine studies of fuel mixtures emphasizes the need for fundamental experimental data of high fidelity on these blends to provide additional useful validation targets for a comprehensive model validation.

One of the key fundamental properties to characterize the combustion behavior of any fuel or fuel blend is the laminar burning velocity (S_L). Its knowledge is invaluable for the design of combustion devices, for turbulent combustion modeling, and for the validation of chemical reaction mechanisms. As a matter of fact, in an effort to advance this understanding, recent works by several research groups considerably extended the experimental S_L database of NH_3-based mixtures [16, 30-47]. The availability of these target data boosted the development of new detailed kinetic mechanisms that provided important insights into the underlying oxidation process of NH_3 and its blends with hydrogen, syngas, and natural gas. Nevertheless, the information available in archival literature is still insufficient considering that, to the best of our knowledge, dedicated studies focused on the interactions of NH_3 with practical hydrocarbon fuels, such as gasoline, diesel, or kerosene, are only limited to our recent publication [48], where S_L for blends of n-heptane, isooctane, and methane with NH_3 were experimentally and numerically explored and the results interpreted on the basis of thermal, kinetic and transport effects. It was shown that the influence of NH_3 on the high-temperature combustion behavior of high-molecular-weight fuels is quite general because the co-oxidation of NH_3 and large-carbon-number hydrocarbons occurs with little mutual interaction and the controlling role is held by the oxidation rates of small fragments in the main reaction zone of the flame, similar to NH_3_CH_4 systems. However, it is not certain whether this is also true for flames of NH_3 in combination with other reference fuel classes typically present in real transportation fuels, such as aromatics and naphtenes, where the fuel-specific intermediate distribution plays a more important role compared to *n*- and isoparaffins. Additional experiments and analyses can answer this question, which is the goal of the present work. Therefore, two essential components of any road or jet engine fuel surrogate [49, 50], namely methylcyclohexane (MCH) and toluene, are selected in this study as the representatives of cycloparaffins and aromatics. The specific objective is to measure the S_L of their blends with NH_3 over a broad stoichiometry range using the heat flux method to comparatively examine the effect of NH_3 enrichment on flame propagation in the case of hydrocarbons with the same carbon atom number (i.e., C7) but different molecular structures. Furthermore, the results are interpreted in terms of a chemical kinetic model presented and minorly updated for the scopes of this work.

2. Experimental details

Premixed laminar flames were stabilized at atmospheric pressure on a flat flame burner compliant with the heat flux method. The stationary flames generated through this method can essentially be considered adiabatic, one-dimensional, and stretchless. A detailed description of the method, experimental setup, operation, data processing, and uncertainty analysis can be found elsewhere [51], thus only the key elements are outlined here.

All heat flux burners employed so far in our laboratory are made of brass and it is well known that NH_3 can be corrosive towards such a material. Hence, the burner with the worst performances due to an old design, designated as burner “E2” by Alekseev et al. [51], was employed. This burner was already successfully used for measuring S_L of NH_3-containing mixtures [47, 48] where the influence of NH_3 adsorption on the brass surface was considered to be negligible. However, its use leads to a higher uncertainty of the measured S_L than commonly reported for measurements performed with the heat flux method (usually < 1 cm/s) [48].

The burner plate and the plenum chamber were both heated using circulating water throughout two separate jackets. During the experiments, the temperature of the plate edge was maintained at 368 K, while the temperature of the plenum chamber at 338 K (± 1 K). The latter fixes the desired initial temperature of the fresh gas mixture (T_g). This temperature was chosen in order to cover a wide range of equivalence ratios, which is constrained by the vaporization limit of the mixtures.

The positive temperature difference between the burner plate and the inlet mixture allows compensating the heat loss necessary for stabilizing the flame and the heat gain of the unburned gas from the plate. When the two terms are balanced, the net heat flux is zero and an adiabatic flame with respect to the burner is created. For this condition, the radial temperature distribution over the burner plate is uniform and equal to the temperature of the burner plate. This is recorded by eight Chromel-Constantan shielded thermocouples, whose junctions (0.5 mm diameter) are inserted into different holes of the burner surface at specific radii from the center. By changing the flow rate of the fresh gas mixture, an appropriate value can be found to achieve such a condition, where the velocity of the unburned gas corresponds to S_L. Hermanns [52] found that the temperature difference between the burner plate and T_g should be higher than 30 K to avoid flame instabilities. However, as explained, this ΔT has been set to 30 K in the present experiments. Consequently, most of the investigated flames exhibited corrugation or cellularity around adiabatic conditions. In these cases, S_L was determined by extrapolation from flat sub-adiabatic conditions. An example of evaluating S_L from sub-adiabatic flames and the associated uncertainties can be found in [51].

A mixing panel provides controlled flow rates and compositions of the fresh mixtures. The liquid fuels feeding system consists of a stainless steel reservoir pressurized with nitrogen to feed the fuel through a Coriolis liquid mass flow controller into a Controlled Evaporator Mixer (CEM), both from Bronkhorst High-Tech. The total uncertainty of the liquid flow rate is a sum of 0.5 g/h plus the stated flow repeatability of the liquid flow controller, which is within 0.2% of the set-point. Neat MCH and toluene were used as delivered respectively by Alfa Aesar and Merck in sealed bottles and their purity was $\geq$ 99%. The gasses, NH_3 (99.98%) and synthetic air (21% O_2, 1% relative uncertainty), were delivered by AGA and their required flow rates were controlled through two Bronkhorst High-Tech digital thermal mass flow controllers. The air flow was also used as a carrier gas to facilitate the vaporization process as a mixing component and to transport the vapor. The two gas flow controllers were calibrated shortly before the measurements using a positive displacement calibrator (MesaLabs Definer 220). The total uncertainty of the gas flow rates is a sum of 1% stated accuracy of the calibrator plus the stated flow repeatability of the mass flow controllers, which corresponds to 0.2% of the set operating conditions. To prevent fuel condensation throughout the fueling system, an electrically heated pipe was used to connect the evaporator to the plenum chamber and its temperature was set equal to T_g.

Detailed analysis and quantification of the experimental uncertainties were reported earlier [51] and the relative combined standard uncertainty of S_L in the present measurements was estimated to be between 4.4 and 6.4%, depending on the experimental conditions. Measurements were conducted for single-component MCH/air and toluene/air mixtures and binary blends of them with NH_3. For the blends, two volume contents of NH_3 were considered, namely 0.25 and 0.50, with a maximum combined standard uncertainty in the NH_3 mole fraction of 0.006. For these mixtures, the equivalence ratio (Φ) was adjusted from 0.7 to 1.3 with uncertainty between 0.013 and 0.021. Then, in stoichiometric mixtures, the mole fraction of NH_3 was varied from 0 to 0.9 with a step of 0.1. Due to the very low reactivity of NH_3, it was not possible to increase its mole fraction above 0.9 with the present installation. In particular, when the S_L falls below about 10 cm/s, which is the case of pure NH_3, stabilization of the flame on a heat flux burner is only possible by increasing the difference between the temperature of the burner plate and T_g to values higher than 70 K, for example using oil instead of water as the heating fluid [41]. The experimental values of the S_L measured in the present study with the associated uncertainties are given in the Supplementary Material (Tables S1-S8).

3. Modeling details

Numerical simulations were performed by solving the one-dimensional, freely propagating, adiabatic flame problem with the Premixed Laminar Flame-Speed module of the ANSYS Chemkin 17.0 software. The steady-state mass, species, and energy conservation equations were solved with non-uniform mesh spacing, using a mixture-averaged transport formula, without radiative heat transfer and including thermal diffusion. A grid-independent solution was ensured by setting the parameters GRAD and CURV to 0.03, resulting in a number of grid points around 500–700 over the domain of 3 cm. This numerical tool was used to compute S_L and to perform kinetic analyses to study the effect of NH_3 concentration on the propagation of MCH/NH_3 and toluene/NH_3 mixtures.

To the best of our knowledge, the CRECK model is the only one suitable for predicting S_L in flames of NH_3 and hydrocarbons with chain lengths above C_3. Moreover, it has been shown that this model accurately captures the S_L of methane, n-heptane, isooctane, and their blends with NH_3 [48]. Thus, it is meaningful to validate and expand its application range to blends of MCH and toluene with NH_3, which has never been done before owing to the lack of validation data.

3.1. Kinetic model

The CRECK kinetic model (2003, March 2020) [53] developed at Politecnico di Milano accounts for the combustion chemistry of a variety of species relevant to gasoline, bio-fuels and bio-oils, diesel, bio-diesel and aviation fuels [54]. The modular structure of the CRECK model allows to seamlessly couple additional modules such as NO_x [55] and NH_3 chemistry [56], as well as a discrete sectional soot formation model, also developed at CRECK [57–59]. The model thus obtained constitutes a suitable tool also for the analysis of compositional effects on the formation of pollutants.

At the core of the kinetic model is the Aramco C0–C2 mechanism from Metcalfe et al. [60] and the C3 subset from Burke et al. [61]. Updates from [62] have been recently reported for the C0–C1 chemistry. A discussion of the low- and high-temperature combustion mechanisms and of the general principles used to represent heavier components can be found in Ranzi et al. [54]. Recent updates to mono-aromatic and poly-aromatic hydrocarbons are reported in [63–66]. Specifically, the MCH and toluene subsets are respectively from Mairinger et al. [67] and from Pelucchi et al. [68]. Some minor modifications to the MCH and toluene subsets have been applied so as to better match the new experimental data presented in this work, as discussed in Section 3.2. A wide range of validation of the updated model is reported in the Supplementary Material (Figs. S1-S33) and includes speciation data in different ideal reactors as well as ignition delay times in shock tubes and rapid compression machines and other laminar burning velocity measurements [69–93]. The objective of such effort is to always guarantee the best compromise between performances over a wide range of experimental conditions (T, p, Φ, and fuels or fuel mixtures) and new theoretical findings, or experimental evidences [94].

The kinetic model thus obtained is provided, with thermodynamic and transport properties, as Supplementary Material to this study. The high temperature mechanism that we suggest for flame simulations contains 396 species and 12,819 reactions, including NH_3/NO_x subset [55, 56]. The global high and low temperature mechanism, covering both the high and low temperature oxidation regimes for MCH, toluene and other reference fuels contains 520 species and 15,924 reactions and is also attached for sake of completeness.

3.2. Modifications to the original CRECK kinetic model

Table 1 shows reactions belonging to MCH and toluene subsets for which rate constants have been modified for the purposes of this study, with respect to the original CRECK mechanism (March 2020, version 2003) [64, 67, 68]. Figure 1 shows comparisons between rate constants from the previous CRECK mechanism and from the literature. The full set of validation targets, covering both high and low temperature oxidation conditions is reported in the Supplementary Material. Table 1 also reports the references to the specific studies from which the rate constants have been adopted, detailing the extent of the adjustments compared to the starting CRECK kinetic model. Most of the modifications deal with the production or consumption of $\dot{H}$. Indeed, as discussed by Ranzi et al. [95], reactions producing $\dot{H}$ such as radical decomposition reactions, initiation reactions breaking a C–H bond generally increase S_L, as they provide $\dot{H}$ atoms to the branching reaction dominating the chemistry of flames, i.e. $\dot{H}+O_2=\dot{O}H+\ddot{O}$. Conversely, reactions consuming $\dot{H}$ such as H-abstraction and recombination reactions inhibit flame propagation. This can be clearly seen from Fig. 2, which reports the first order normalized sensitivity of S_L for stoichiometric MCH/air and toluene/air flames computed using the CRECK original mechanism.

Rate coefficients have been modified by a maximum factor of 2, which is well within the uncertainties of theoretical studies, where available, and well below expected uncertainties for rate constants derived by analogy or less accurate estimates. H-abstraction reactions by $\dot{H}$ from MCH (denoted in the model as MCYC6) have been theoretically determined by Wang et al. [96] using CBS-QB3. Uncertainties in single point energies calculations with CBS-QB3 are in the order of ~2.5 kcal/mol as reported by Simmie and Somers [99]. This uncertainty in energy barriers already reflects into a factor of ~1.9–3.5 over the temperature range $T = 1000$–2000 K, even neglecting uncertainties in frequencies, and therefore partition functions, determination. The rate constants proposed by Wang et al. [96] were originally adopted as reported in Mairinger et al. [67] and increased by a factor of 2 in this study for (R1). Li et al. [97] theoretically investigated the H-abstraction reactions by $\dot{H}$ from toluene (denoted in the model as C_7H_8) (R2 and R3) using the G4 method that provides a slightly improved accuracy (~1 kcal/mol) compared to CBS-QB3 [99]. For this reason, rate constants by Li et al. [97] were increased by a factor of 2 in the work of Pelucchi et al. [68] on toluene pyrolysis and oxidation. In this study, we have chosen to adopt the original values by Li et al. [97] to further improve the agreement with the new S_L measurements presented in this study without significantly affecting other validation targets.

Methyl-phenol (CRESOL, CH3-Ph–OH where pH represents the aromatic ring) and methyl-phenoxy radical (CH3-Ph-$\dot{O}$) play a key role in toluene oxidation kinetics as deeply discussed pre-

Table 1
Rate constants modified in the context of this work. Units are cm^3, mol, s, cal.

	Reaction	A	n	Ea [cal/mol]	Reference | Notes
R1	$\dot{H}+MCYC6 \leftrightarrow H_2+RMCYC6$	$6.74\ 10^6$	2.46	5238.05	[96] | A x 2 [a]
R2	$\dot{H}+C_7H_8 \leftrightarrow C_7H_7+H_2$	$1.07\ 10^6$	2.27	4392.37	[97] | A / 2 [b]
R3	$\dot{H}+C_7H_8 \leftrightarrow CH_3C_6H_4+H_2$	$2.00\ 10^8$	1.83	14,381.82	[97] | A / 2 [b]
R4	$RCRESOL\dot{O} \rightarrow C_6H_6+\dot{H}+CO$	$9.00\ 10^{13}$	0.00	52,000.00	[64, 68] | A x 1.5 [b, c]
R5	$\dot{H}+RCRESOL\dot{O} \leftrightarrow CRESOL$	$1.00\ 10^{14}$	0.00	0.00	[64, 68] | A / 1.5 [b, c]
R5$_{rev}$		$8.90\ 10^{14}$	0.00	85,864.98	[64, 68] | A / 1.5 [b, c]

Notes: [a] modification since Mairinger et al. [67]
[b] modification since Pelucchi et al. [68]
[c] modification since Pelucchi et al. [64].R4 and R5 are high pressure limit rate constants.

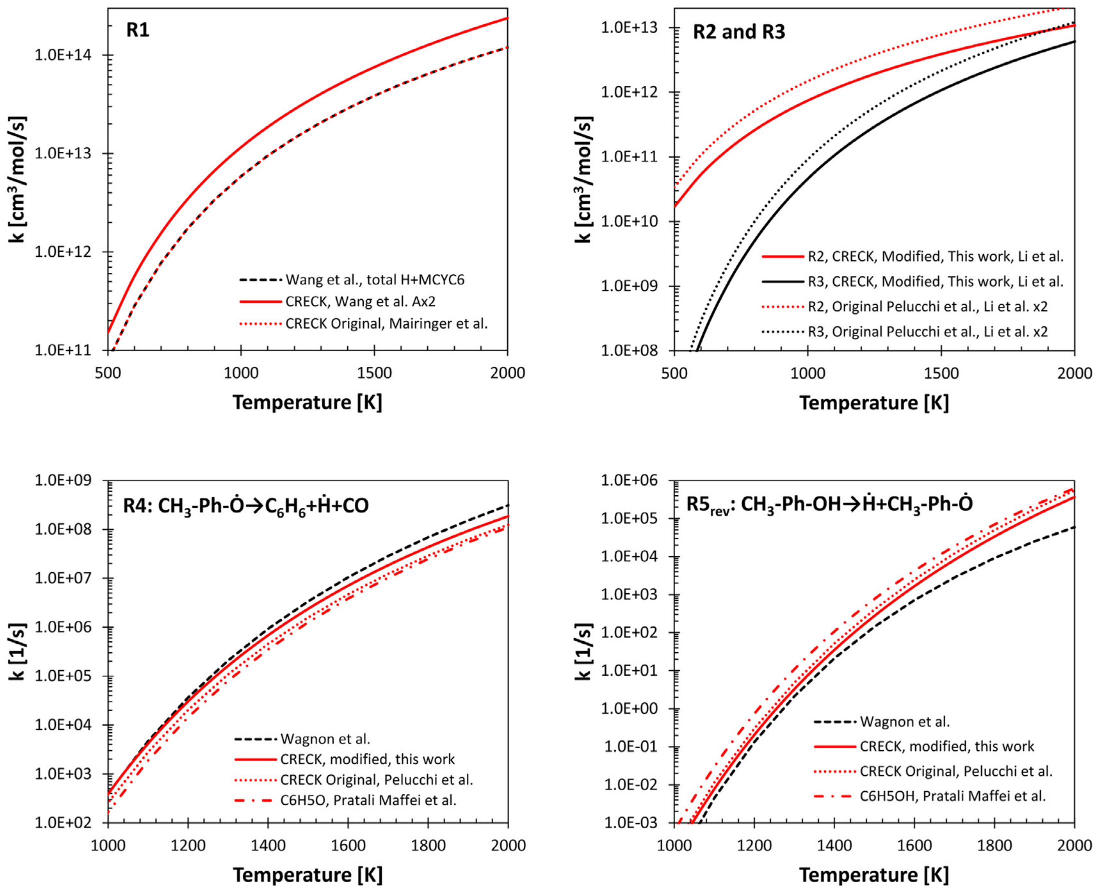

Fig. 1. Comparisons between rate constants from the CRECK original mechanism [64, 67, 68] and rate constants in the modified mechanism here presented. Literature values of the same or analogous reactions (e.g. phenol/phenoxy) are also reported [66, 98].

viously [68, 100]. Resonantly stabilized methyl-phenoxy radical ($RCRESOL\dot{O}$) is formed by the addition of methyl-phenyl radical to O_2 ($O_2+CH_3C_6H_4 \leftrightarrow RCRESOL\dot{O}+\dot{O}$) as discussed by da Silva et al. [100]. Successive reactivity of methyl-phenoxy radical in flames can lead to termination, when recombination with $\dot{H}$ occurs (R5), or branching through a decomposition reaction (R4), analogous to phenoxy radical decomposition to cyclopentadienyl radical (C_5H_5) and CO recently investigated in [66]. R4 is implemented in a lumped form so as to avoid the inclusion of α-hydrofulvenyl radical. Based on the sensitivity analysis we decreased by a factor of 1.5 the termination channel (R5) and increased by the same amount the branching channel (R4). Our final values fall well within an average factor of ~3 from the recent theoretical determination of $C_6H_5\dot{O}+H \leftrightarrow C_6H_5OH$ and $C_6H_5\dot{O} \leftrightarrow C_5H_5+CO$ by Pratali Maffei et al. [66], and within a factor of ~2–5 from the estimates by Wagnon et al. [98]. Overall, it is our belief that such modifications to cresol chemistry are generally within expected uncertainties of available rate constants from the literature. However, systematic theoretical studies for such reaction classes (i.e. radical recombination reactions, unimolecular initiation reactions, addition to O_2 of phenyl-like radicals, etc.) should be performed for aromatic and oxygenated aromatic compounds such as benzene, toluene, phenol and phenolic species with multiple substitutions, along the same lines of recent theoretical investigations [65, 66].

4. Results

4.1. Validation of the experimental and modeling methodology

First, to assess the accuracy of the present measurements, a comparison with benchmark S_L data available in the literature for pure MCH and toluene is carried out and it is presented in Figs. 3 and 4 at an initial temperature of 338 K and atmospheric pressure, over a Φ range of 0.7–1.3. There have been several determinations of S_L for the aforementioned fuels, though only two studies have

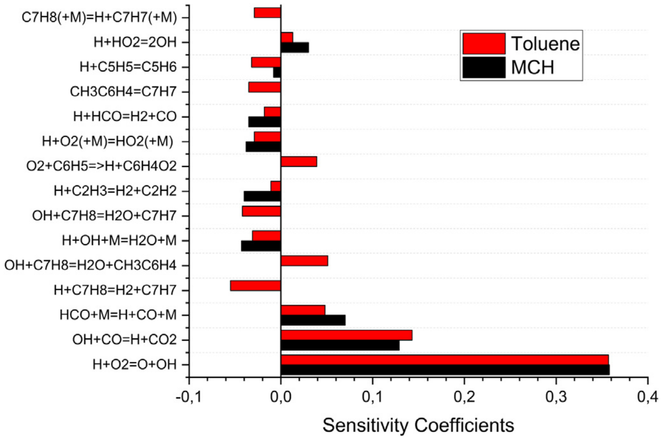

Fig. 2. S_L sensitivity coefficients calculated for stoichiometric MCH-air (black bars) and toluene-air (red bars) mixtures at 1 atm and 338 K using the CRECK original mechanism.

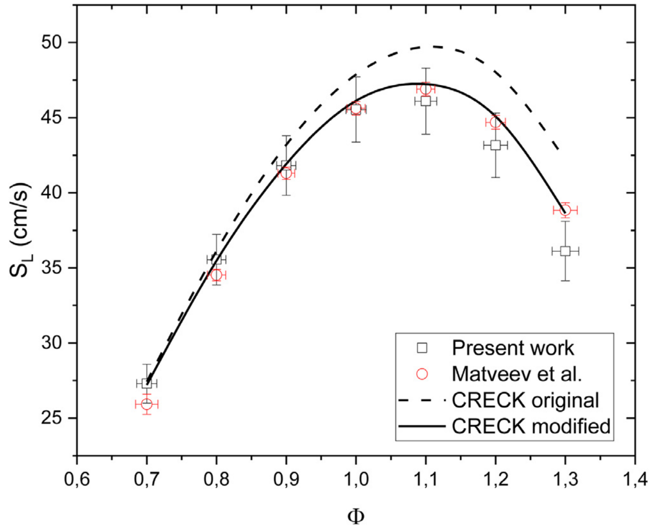

Fig. 3. Experimental (symbols) and simulated (lines) S_L of MCH-air flames versus Φ at T_g=338 K and p = 1 atm. Black squares: present work. Red circles: Matveev et al. [101]. Dashed line: CRECK original. Solid line: CRECK modified.

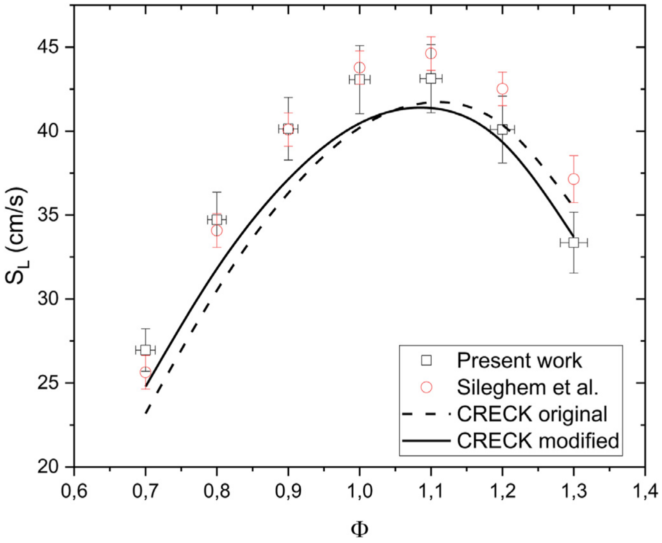

Fig. 4. Experimental (symbols) and simulated (lines) S_L of toluene-air flames versus Φ at T_g=338 K and p = 1 atm. Black squares: present work. Red circles: Sileghem et al. [102] (corrected according to re-evaluation reported in [51]). Dashed line: CRECK original. Solid line: CRECK modified.

been conducted at the same initial conditions as the present work. In particular, the S_L for MCH have been reported by Matveev et al. [101], while the S_L for toluene have been provided by Sileghem et al. [102]. Similar to the data from this study, both the literature data sets have been obtained using the heat flux method, but in different laboratories.

A classical evolution as a function of Φ, with the peak value of S_L at Φ=1.1 is obtained for both fuels. It can be seen from Figs. 3 and 4 that MCH-air mixtures exhibit higher S_L than toluene-air mixtures throughout the whole range of Φ, which is consistent with earlier literature reports [103, 104].

The experimental data measured in the current work are found in very good qualitative and quantitative agreement with those obtained before in other studies, especially for $\Phi < 1.1$. This confirms the reproducibility of the heat flux experiments within the evaluated uncertainties and gives confidence in the experimental setup and the measurements performed herein for reliable validation of kinetic models. However, it should be noted that for both fuels the agreement deteriorates in the case of rich mixtures where the present S_L are slightly lower compared to the previous measurements and, at Φ=1.3, the experimental data do not overlap within the evaluated uncertainties. Before validating the kinetic model using these data, one must examine the possible factors which may cause these differences for rich flames. A similar systematic shift on the fuel-rich side with the burner used in this work was already observed in [48] in the case of pure n-heptane and isooctane. It was suggested that instabilities manifested as cellular flames are the reason for the observed discrepancy under rich conditions. In particular, in the previous studies reported in Figs. 3 and 4 [101, 102], cell formation was observed at $\Phi > 1.3$, in contrast to our previous [48] and current measurements where such instabilities were also observed at lower Φ. It can be inferred that the burner used in the present work, due to the old design, produces less accurate S_L data in the fuel-rich region when liquid fuels are tested, but a maximum discrepancy of about 3 cm/s at $\Phi = 1.3$ is anyhow considered acceptable to extract fundamental information from these data.

In addition, the above data were adopted to evaluate the performance of the proposed model. Thus, the computed S_L are shown in Figs. 3 and 4 together with the corresponding experimental data. Simulations for pure MCH and toluene were performed using the original CRECK and the model updated in the present work, named as CRECK modified. As shown in Figs. 3 and 4, the chemical kinetic simulations with both the original and the modified CRECK models confirm the general shape of the S_L data and predict the peak at around Φ=1.1, which is consistent with the experimental data.

Regarding MCH (Fig. 3), the comparison demonstrates that the S_L are largely better predicted by the modified CRECK over the entire Φ range. In particular, the modifications illustrated in Table 1 lead to a decrease in S_L of 0.2 cm/s at Φ=0.7, 2.5 cm/s at Φ=1.1, and 3.6 cm/s at Φ=1.3 respectively.

Regarding toluene (Fig. 4), it is seen that the modifications adopted in the kinetic mechanism yield an increase of the predicted S_L under lean conditions (1.6 cm/s at Φ=0.7) and a decrease under rich conditions (1.8 cm/s at Φ=1.3). The S_L computed for the fuel-rich mixtures with the refined mechanism are somewhat lower than the data of [102], but they agree quite well with the present experimental data. Despite the improvement of the predictions on the lean side, the S_L are still underpredicted for Φ below 1.1, but the discrepancy between the experimental data and the modified CRECK is smaller compared to the original version. Moreover, the shape of the evolution of the S_L with Φ seems to be better captured by the modified model.

Therefore, while noticeably good agreement between experimental and computed MCH data can be reached as shown in Figs. 3, 4 indicates that the toluene oxidation mechanism may need

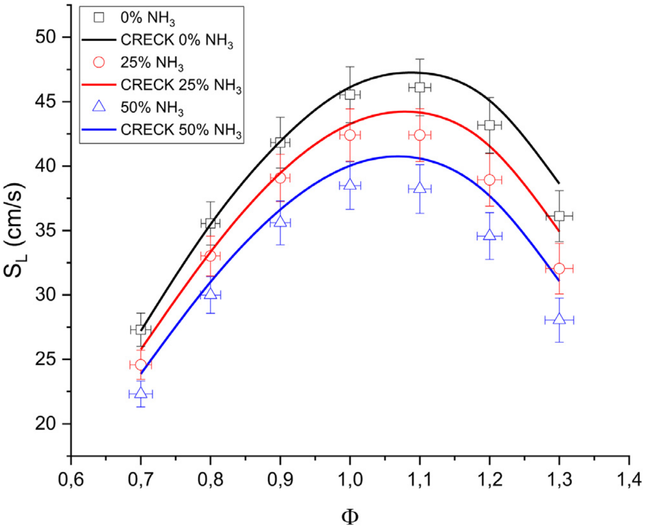

Fig. 5. Experimental (symbols) and simulated (lines) S_L of MCH/NH_3-air flames versus Φ at T_g=338 K and p = 1 atm. Black squares and solid line: NH_3 mole fraction=0. Red circles and solid line: NH_3 mole fraction=0.25. Blue triangles and solid line: NH_3 mole fraction=0.5.

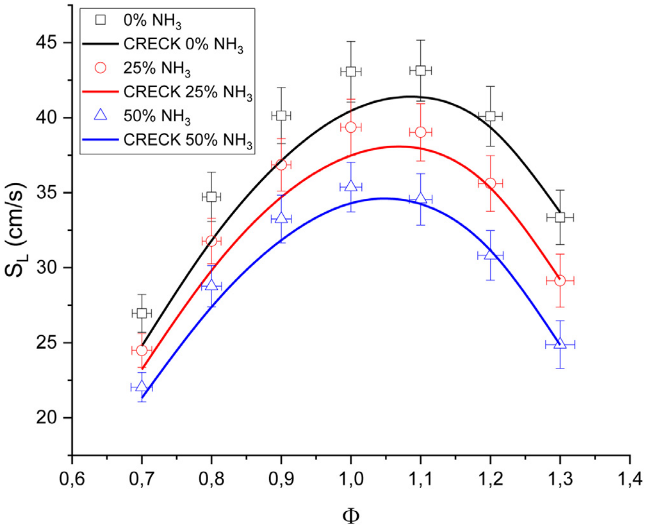

Fig. 6. Experimental (symbols) and simulated (lines) S_L of toluene/NH_3-air flames versus Φ at T_g=338 K and p = 1 atm. Black squares and solid line: NH_3 mole fraction=0. Red circles and solid line: NH_3 mole fraction=0.25. Blue triangles and solid line: NH_3 mole fraction=0.5.

further improvement. This requires additional systematic theoretical studies for reaction classes concerning oxygenated aromatic intermediates, as already discussed in Section 3.2. However, the overall improvement observed on the basis of the comparative experimental and computed results, without deterioration of the predictive performances against other targets (see Supplementary Material) also including other S_L measurements [85, 86, 92, 93, 102, 103], proves that the modified CRECK model is applicable for the present study. Thus, it was adopted for the following analysis.

4.2. Influence of NH_3

In the present section, first, the S_L results for pure MCH and toluene, as well as their binary blends with 25% (± 0.4%) and 50% (± 0.6%) of NH_3, are presented for the same Φ range (0.7–1.3). Next, effects of the addition of up to 90% (± 0.4%) of NH_3 on MCH and toluene are systematically investigated at Φ=1. All the experiments were carried out at initial conditions of 338 K and 1 atm.

S_L measured for the blends are shown in Figs. 5 (MCH/NH_3) and 6 (toluene/NH_3) for the same initial conditions. The results illustrate that NH_3 addition to the fuels causes a decrease of S_L over the entire range of Φ as expected and that the peak S_L shifts towards the stoichiometric mixture for increasing amounts of NH_3 concentration in the blends. The peak S_L for pure MCH and toluene is 46 and 43.1 cm/s respectively; at 25% NH_3, it is 42.4 and 39.4 cm/s, while at 50% NH_3 it is 38.5 and 35.4 cm/s. This suggests that the addition of NH_3 has a similar effect on MCH and toluene. Moreover, it can be seen from Figs. 5 and 6 that, with the increase of NH_3 vol fraction, the percentage decrease in S_L is slightly higher under rich conditions. Similar observations were reported in [48] for NH_3/n-heptane and NH_3/isooctane mixtures.

Along with the measured S_L plotted against Φ, Figs. 5 and 6 also show the results of one-dimensional simulations using the present updated CRECK mechanism. The calculated values reasonably agree with the experimental data within the limits of experimental uncertainty, with a slight overprediction under rich conditions for MCH/NH_3 blends and a slight underprediction under lean conditions for toluene/NH_3 blends, regardless of the value of the NH_3 mole fraction. It is clear that the discrepancy in the case of toluene/NH_3 blends originates from the underprediction of the S_L for neat toluene, as already discussed in the previous section.

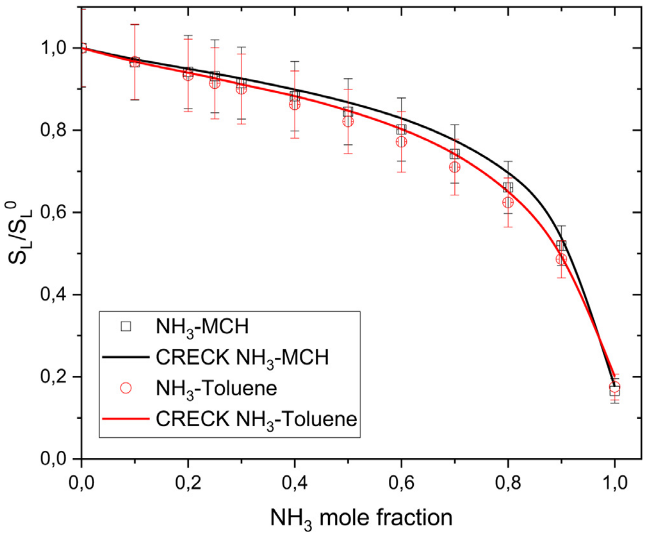

Fig. 7. Experimental (symbols) and simulated (lines) stoichiometric S_L (Φ=1) versus NH_3 mole fraction at T_g=338 K and p = 1 atm, normalized by S_L of pure fuel/air mixtures ($S_L{}^0$). Black squares and solid line: MCH/NH_3-air mixtures. Red circles and solid line: toluene/NH_3-air mixtures. The value of S_L for pure NH_3 is from [41].

On the other hand, the small discrepancy in the case of MCH/NH_3 blends is consistent with the analysis presented in Fig. 3, where the present experimental values were shown to be lower than the reference literature data at Φ > 1.1. Despite this, the elucidation of NH_3 enrichment effects, which is the primary purpose of this study, is not affected by these differences and it can be concluded that the current mechanism accurately captures the S_L variation with NH_3 addition.

In order to more clearly examine the effect of NH_3 addition on S_L of MCH and toluene, the NH_3 mole fraction in the binary blends was increased up to 0.9 with a step of 0.1 considering the stoichiometric mixture as a reference. Measured and predicted values of the S_L of stoichiometric mixtures were normalized with respect to the S_L of pure hydrocarbons ($S_L{}^0$) and the results are plotted in Fig. 7 as a function of the NH_3 quantity in the binary fuel mixtures. It was not possible to cover higher NH_3 ratios experimentally, as explained in Section 2. Therefore, S_L obtained by Han et al. [41] for pure NH_3 is also plotted for comparison and is found to be consistent with the trend of the present results. Results show that from pure MCH or toluene to pure NH_3, S_L decreases nonlinearly with the increase of NH_3 mole fraction in the fuel blend over the entire composition range. Therefore, any mixing rule to be developed or identified would not be a simple mole fraction-based weighted average of the neat constituents S_L. For example, with the addition of 50% NH_3, the S_L is reduced by only 15% from pure MCH and 18% from the pure toluene case. While at 90% of NH_3, the S_L is decreased by nearly 48 and 51% from the two baseline conditions.

Although in Fig. 6 the kinetic mechanism was shown to slightly underpredict the stoichiometric S_L of toluene/air mixtures, the computed normalized profiles capture very well the monotonically decreasing trend and the nonlinear evolution of S_L as a function of NH_3 percentage for both fuels. This means that the underlying mechanism responsible for the observed effect of NH_3 on the S_L of MCH and toluene is accounted for in the kinetic model and it is unraveled in the next section.

Moreover, any decisive information about fuel structure effects cannot be inferred from the experiments as the relative difference between the two data sets is within the experimental uncertainty. However, relying on the computations, the effect of NH_3 in decreasing S_L seems to be slightly more pronounced for toluene than for MCH under the tested conditions. This aspect is also discussed in the next section.

5. Discussion

5.1. Numerical analysis

For the challenge of implementing NH_3 in current combustion-based applications, the variability and dependence of key characteristics such as the S_L on NH_3 concentration in the fuel blends must be understood. In [48], it was found that the propagation process of NH_3-hydrocarbons laminar flames appears to be governed by two dominant synergistic factors dependent on the NH_3 concentration in the fuel blend: 1) the decrease of the adiabatic flame temperature (T_{ad}) as a result of the low energy content of NH_3 (thermal effect) and 2) the chemical inhibition of the overall reactivity caused by the radical scavenging of NH_3 (chemical effect). Therefore, before making any detailed analysis on the molecular structure effects, these two general features of the systems involved shall be verified. To do so, further numerical simulations have been carried out to separate these contributions. In particular, a fictitious species (H_3N) with identical molecular structure, transport, and thermodynamic properties to NH_3 has been defined. This virtual species however does not appear in the elementary reactions of the kinetic mechanism, and thus, it acts as a diluent. Then, simulations have been performed by numerically making the T_{ad} of H_3N/hydrocarbons mixtures equal to that of NH_3/hydrocarbons mixtures in the range explored experimentally for the various fuels at Φ=1, by modifying the H_3N dilution, without altering the transport properties of the reacting mixtures. The sensitivity of S_L to the decrease of T_{ad} has been evaluated case by case with respect to the pure fuels as a reference by comparing the computed data. The results are reported in Fig. 8, where the ordinate axis indicates the predicted values of the S_L of stoichiometric mixtures normalized with respect to the S_L of pure hydrocarbons ($S_L{}^0$) similar to Fig. 7 and the abscissa axis indicates the decrease of T_{ad} ($T_{ad}{}^0$-T_{ad}). The solid lines represent the variations of S_L that have been obtained for hydrocarbon/NH_3 mixtures, and the dashed lines represent the variations of S_L that have been obtained for hydrocarbon/H_3N mixtures. In other words, the difference between dashed lines and the pure hydrocarbons primarily reflects the thermal effects, while the difference between solid and dashed lines isolates purely kinetic effects.

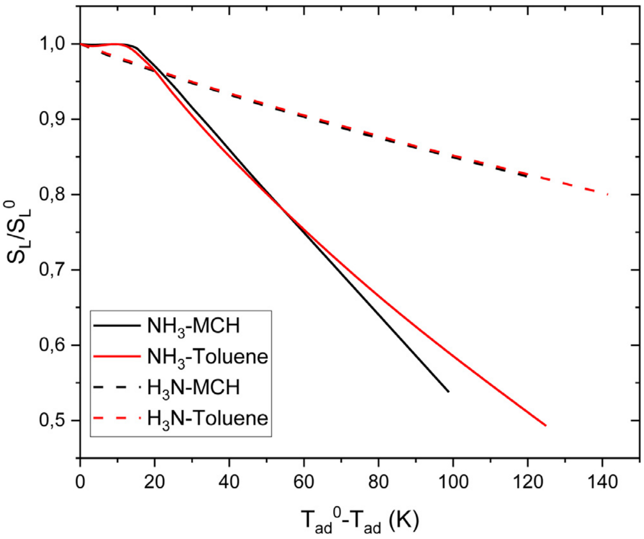

Fig. 8. Simulated stoichiometric S_L normalized by S_L of pure fuel/air mixtures ($S_L{}^0$) at T_g=338 K and p = 1 atm versus $T_{ad}{}^0$-T_{ad} when blending the fuels with NH_3 (solid lines) and H_3N (dashed lines). Black lines: MCH mixtures. Red lines: toluene mixtures.

These computational tests show that the thermal and chemical effects caused by NH_3 addition both contribute to the reduction of S_L. In detail, for a T_{ad} decrease lower than 20 K, which corresponds to low NH_3 addition ratios (<10%), there is no global effect of NH_3 on S_L (solid lines) but the thermal effect (dashed lines) diminishes S_L by about 3%. It means that the negative thermal effect is counterbalanced by a positive kinetic effect, that instead increases S_L. It was observed in [48] that the promoting effect of NH_3 addition on S_L of heavy hydrocarbons is due to an increase in the hydrogen concentration in the flame zone. This was considered as a combined kinetic and transport effect because of the high reactivity and diffusivity of hydrogen. Then, for a constant T_{ad} decrease of about 20 K, which corresponds to an NH_3 addition ratio of ~10%, the thermal effect plays the dominant role as the solid and dashed lines cross. The chemical effect increases with rising NH_3 blending ratios. For a T_{ad} decrease between 35 and 40 K, which corresponds to NH_3 concentrations of about 40–50%, the chemical and thermal effects become comparable. For higher NH_3 ratios, the chemical effect is the main reason for the S_L reduction and, for a T_{ad} reduction higher than 60 K, which corresponds to NH_3 fractions higher than 70%, the ratio chemical/thermal effect is slightly more pronounced for the MCH/NH_3 mixtures. It is interesting to note that the high nonlinearity of the S_L decrease with the increase of NH_3 fraction in the fuel blend observed in Fig. 7 mainly occurs when the chemical effect becomes dominant.

To gain more insight into these effects, Fig. 9 shows the impact of NH_3 fraction in fuel blends on the calculated T_{ad} (left axis) and peak mole fraction of $\dot{H}$ radicals in the reaction zone (X_H, right axis) for the stoichiometric case using the present model. T_{ad} represents the thermal effect on S_L, while X_H reflects the effect of chemical kinetics. The analysis in Fig. 9 has been limited only to the $\dot{H}$ radical because, as discussed in Section 3.2, its generation and consumption reactions play a key role in accelerating and suppressing flame propagation. However, a similar result would have been obtained by showing the peak mole fraction of $\dot{O}H$ radicals. As expected, both T_{ad} and X_H significantly decrease as the NH_3 content in fuel blends increases and the profiles for both fuels have similar tendencies, which closely follow the variation of S_L as a function of the composition of the fuel blends shown in Fig. 7. Figure 9 further shows that the T_{ad} of the MCH/air flame is somewhat lower than that of the toluene/air flame by approx-

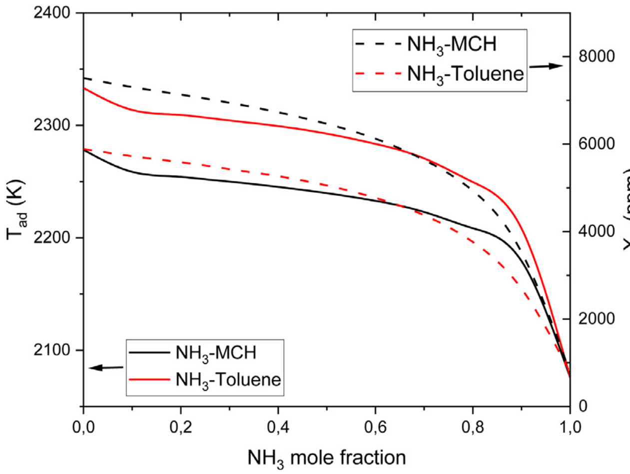

Fig. 9. Simulated stoichiometric T_{ad} (solid lines) and peak X_H (dashed lines) versus NH_3 mole fraction at T_g=338 K and p = 1 atm. Black lines: MCH/NH_3-air mixtures. Red lines: toluene/NH_3-air mixtures.

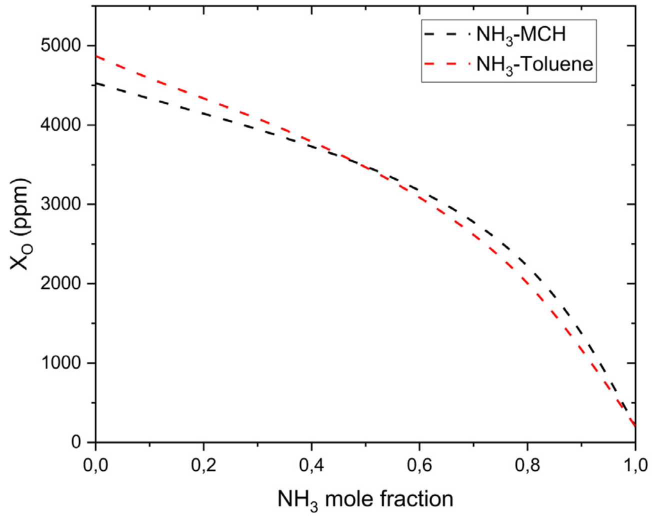

Fig. 10. Simulated stoichiometric peak X_O versus NH_3 mole fraction at T_g=338 K and p = 1 atm. Black line: MCH/NH_3-air mixtures. Red line: toluene/NH_3-air mixtures.

imately 55 K due to the different C/H ratio, which is opposite to their S_L order. On the other hand, it can be seen that the X_H of the MCH/air is higher than that of the toluene/air flame by about 1600 ppm, which is consistent with their S_L order. In fact, the S_L of toluene is known [95] to be lower due to the Ḣ radical scavenging effect of the resonantly stabilized benzyl and phenoxyl radicals. This negative chemical effect overwhelms the positive thermal effect. However, these differences are negligible if compared to the T_{ad} and X_H of NH_3, which are respectively more than 200 K and more than 5000 ppm lower than that of the other two fuels. This confirms that both the thermal and chemical inhibition by NH_3 addition play a critical role in the decrease of the S_L of NH_3/hydrocarbons mixtures.

Not yet explained is the fact that S_L of toluene is slightly more sensitive to NH_3 addition compared to MCH, as shown from the computations reported in Fig. 7. The cause must imply secondary kinetic effects since the analysis reported in Fig. 9 shows that the ratios $T_{ad}{}^{NH3\text{-}Toluene}/T_{ad}{}^{NH3\text{-}MCH}$ and $X_H{}^{NH3\text{-}MCH}/X_H{}^{NH3\text{-}Toluene}$ keeps constant over a broad range of NH_3 mole fraction. First, it is noteworthy that, despite the present kinetic mechanism includes the kinetic interactions among nitrogenous and C_1–C_2 species, these are found to be irrelevant with respect to the prediction of S_L, as no cross-reactions involving nitrogen and carbon radicals show up in the sensitivity analysis, indicating that they do not play a significant role under the conditions of the present flames, in agreement with [48]. It should be noted that co-oxidation reactions between large radical species of toluene and amine radicals leading to substituted NH_2-aromatics are overlooked in the present model. In this regard, Altarawneh et al. [105], who explored the NO_x formation from co-combustion of NH_3 and benzene, have shown that the inclusion of the aniline sub-mechanism might be required to improve the predictions of NO_x formation in NH_3-containing flames. However, because the present mechanism well predicts the effect of NH_3 on S_L of toluene, it is unlikely that the interaction between aromatics and amine radicals can be relevant with respect to the prediction of S_L.

Therefore, any disparity in flame structure and kinetic behavior between the MCH and toluene mixtures with NH_3 shall be indirect. To further explore this, Fig. 10 plots the impact of NH_3 content on the simulated peak mole fraction of Ö radicals in the reaction zone (X_O) for the stoichiometric case. From Fig. 10, two considerations must be done. The first is that for pure toluene X_O is higher than that for pure MCH, contrary to Ḣ (Fig. 9) and ȮH radicals. In particular, for pure toluene flames, X_O is comparable to X_H. Second, it is seen that the X_O profiles deviate from those of T_{ad} and X_H plotted in Fig. 9. In particular, the X_O trend of NH_3/toluene mixtures is steeper than that of NH_3/MCH mixtures, corresponding to a stronger Ö radical scavenging effect, which impacts the S_L. This deserves further consideration and it is shown in the following discussion to be mostly responsible for the difference in the effect of NH_3 on S_L observed numerically.

To further investigate the effect of NH_3 on the observed disparity, sensitivity and rate of production analyses were carried out with the proposed mechanism and the simulation results were analyzed focusing attention on the reactions involving the Ö radical. As already seen from Fig. 2, the sensitivity analysis shows that the chain branching reaction $\dot{H}+O_2=\dot{O}H+\ddot{O}$ plays a dominant role in all the three fuels flame propagation and it is the main source of Ö. However, the importance of this reaction does not strongly depend on the NH_3 content. The radicals generated by this reaction directly contribute to the oxidation of the fuels and small fuel fragments. In fact, it was seen from Fig. 2 that the S_L of both MCH and toluene flames are largely sensitive to the reactions associated with the C_0–C_2 fuel fragments, whose oxidation kinetics mainly controls the heat release and the overall burning rate. This is indeed a quite general behavior in premixed flames of hydrocarbon fuels, for which the rapid fuel breakdown and the oxidation of fuel fragments can be decoupled [95]. However, unlike the MCH flame, the fuel-specific reactions in the sub-mechanism of toluene also have notable enhancement and inhibition role in the flame propagation kinetics, as identified through the sensitivity analysis. This is mainly related to the stability of the aromatic ring and related products. Among the sensitivity coefficients for various reactions, it is seen that while the NH_3 addition has a similar effect on the reactions involving the interaction of Ö with the H_2/C_1–C_2 systems for both fuels, the major difference in the kinetic behavior between NH_3/MCH and NH_3/toluene blends lies in the reactions involving the toluene immediate oxidation intermediates, which exhibit a strong influence on S_L. This can be seen in Fig. 11, which depicts the S_L sensitivity coefficients for the reactions populating the top portion of the sensitivity spectrum, calculated as a function of NH_3 mole fraction for binary NH_3/toluene mixtures, at Φ=1 and T_g=338 K.

For MCH, even though the ring opening and subsequent cracking are rather complicated, the influence of fuel-related reactions is certainly much smaller due to the relatively large production of

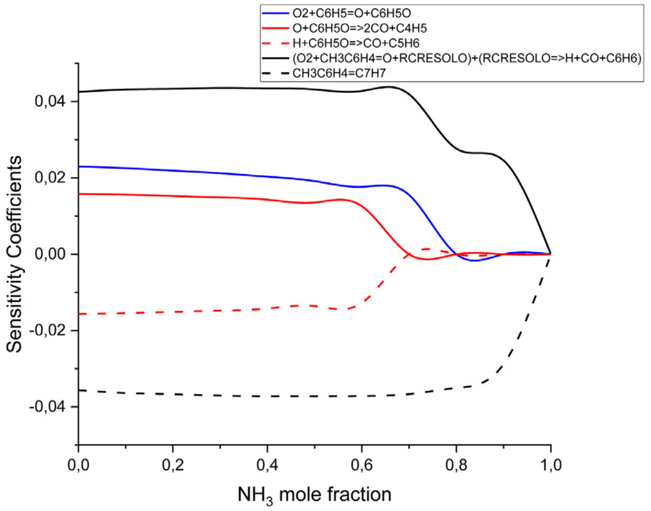

Fig. 11. S_L sensitivity coefficients of important reactions involving the $\ddot{O}$ radical vs. NH_3 mole fraction calculated at Φ=1, T_g=338 K and p = 1 atm for toluene/NH_3-air mixtures. Solid lines: reactions with positive S_L sensitivity. Dashed lines: reactions with negative S_L sensitivity.

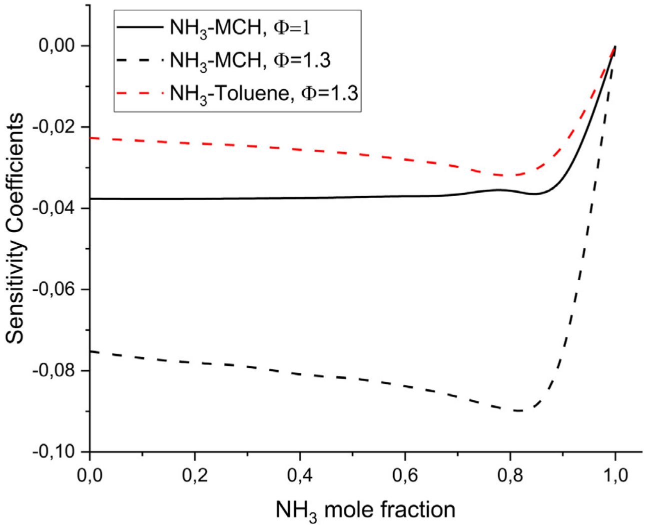

Fig. 12. S_L sensitivity coefficients of the reaction $H+CH_3(+M)=CH_4(+M)$ vs. NH_3 mole fraction calculated at T_g=338 K and p = 1 atm. Black lines: MCH/NH_3-air mixtures. Red line: toluene/NH_3-air mixtures. Solid line: Φ=1. Dashed lines: Φ=1.3.

ethylene and vinyl radical, which enhance the overall reactivity of MCH compared to toluene.

As already discussed in Section 3.2, during the oxidation of toluene, the benzyl (C_7H_7 in Fig. 11) and methyl-phenyl ($CH_3C_6H_4$ in Fig. 11) radical isomers are the primary products from H-abstraction. The benzyl radical is resonantly stabilized, and the benzylic C–H bond is weaker than the phenylic C–H bonds [106]. For these reasons, the reactions of benzyl radical are usually slow and strongly influential in reducing the concentration levels of chain carriers (Fig. 2). As a matter of fact, the isomerization reaction $CH_3C_6H_4=C_7H_7$ (black dashed line in Fig. 11) exhibits a significant negative influence on S_L. As an example, the negative sensitivity of such a reaction is even larger compared to the chain termination reaction $\dot{H}+O_2(+M)=HO_2+(M)$. On the other hand, the addition of the methyl-phenyl radical to O_2 leads to the formation of $\ddot{O}$ and methyl-phenoxy radicals and the subsequent reactivity of the latter can lead to branching through a decomposition reaction, which constitutes an important contribution to the formation of active $\dot{H}$ radicals. This sequence indeed has a very high positive sensitivity and it was reported in Fig. 11 as a single line (black solid) to show that the full sequence is specular with respect to $CH_3C_6H_4=C_7H_7$. Though the sensitivity coefficients of these two individual reactions are not as large as those of the most important reaction $\dot{H}+O_2=\dot{O}H+\ddot{O}$, they are higher compared to $H_2+\ddot{O}=\dot{H}+\dot{O}H$.

As expected, the NH_3 blending modifies the sensitivity coefficients in a nonlinear way. Moreover, it can be seen that for the pure toluene flame the absolute value of the sensitivity of the methyl-phenyl branching sequence is higher than that of the parallel isomerization that forms stable benzyl radicals. However, with increasing NH_3, the relative weight of the isomerization channel increases, showing that the competition between these promoting and inhibiting paths is emphasized. In fact, for an NH_3 mole fraction of 0.8, the absolute sensitivity coefficients of the isomerization reaction become higher than that of the branching sequence. This further promotes the depletion of the radicals pool. Additionally, the results of the sensitivity analysis also reveal that another reaction critical to chain termination is the recombination of $\dot{H}$ atom with the resonantly stabilized phenoxy radical, $\dot{H}+C_6H_5O=>CO+C_5H_6$ (red dashed line). It can be seen from Fig. 11 that such a reaction strongly competes with the oxidation of phenoxy by $\ddot{O}$ (red solid line), which exhibits specular positive sensitivity coefficients. Phenoxy and $\ddot{O}$ radicals are formed via the important oxidation path of phenyl by O_2 (blue line). The oxidation of the phenyl radical becomes less important as the NH_3 mole fraction increases. This suggests that as soon as $\ddot{O}$ atoms become scarce, the competition discussed above becomes more intense and, for NH_3 mole fraction equal to 0.4, $C_6H_5O+\dot{H}$ prevails over $C_6H_5O+\ddot{O}$, thereby further reducing S_L. The results of this analysis clearly indicate that the different impact of NH_3 chemistry on the S_L of toluene flames compared to that observed for MCH flames should be correlated to the $\ddot{O}$ radical scavenging effect of NH_3, which further slows down the overall reaction rate by promoting the chain-terminating reactions of the stable benzyl and phenoxyl radicals.

In addition, it was seen from Figs. 5 and 6 that, with the increase of NH_3 vol fraction, the percentage decrease in the S_L of both MCH and toluene is slightly higher under rich conditions. Therefore, further sensitivity analyses were carried out and the simulation results were analyzed focusing on the reactions for which the impact of NH_3 addition is higher under rich conditions. It was observed that, with increasing Φ, the scavenging effect of NH_3, together with the decrease of T_{ad}, further promote the inhibiting effect of chain-terminating reactions in the same way for both MCH and toluene. This can be clearly seen in the case of the methyl recombination reaction $H+CH_3(+M)=CH_4(+M)$. Thus, Fig. 12 depicts the S_L sensitivity coefficients for this reaction calculated as a function of NH_3 mole fraction for binary NH_3/MCH and NH_3/toluene mixtures, at Φ=1 and 1.3. Note that the case of Φ=1 is not reported for NH_3/toluene mixtures because such a reaction does not show up in the sensitivity analysis. This channel, which is highly sensitive at $\Phi>1$, slows down the system reactivity because it competes with the methyl oxidation routes. For pure MCH and toluene at Φ=1.3, or for NH_3/MCH and NH_3/toluene blends at Φ=1, this competition is less stressed.

5.2. Implications for practical applications

As S_L is a key, but usually unknown, parameter in practical combustion devices, there is also interest to explore if simple mixing rules to estimate S_L can be developed so that the relative proportion of NH_3 and hydrocarbons that ensure the successful engine operation can be readily determined. To propose a generalized relationship in order to estimate the S_L of NH_3/hydrocarbons mixtures on the basis of those of the individual components, the mea-

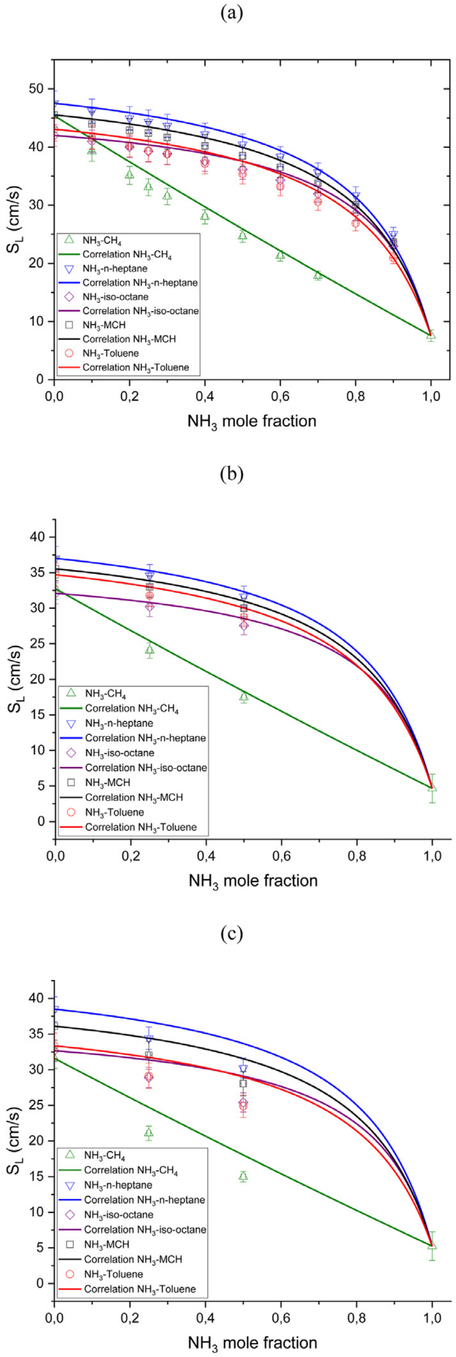

Fig. 13. Experimental (symbols) and calculated (lines) S_L versus NH_3 mole fraction at T_g=338 K, p = 1 atm, and (a) Φ=1, (b) Φ=0.8, (c) Φ=1.3. Black squares and line: MCH/NH_3-air mixtures. Red circles and line: toluene/NH_3-air mixtures. Green up triangles and line: CH_4/NH_3-air mixtures [48]. Blue down triangles and line: n-heptane/NH_3-air mixtures [48]. Purple diamonds and line: isooctane/NH_3-air mixtures [48]. The values of S_L for pure NH_3 are from [41].

sured lean (Φ=0.8), stoichiometric, and rich (Φ=1.3) S_L are plotted in Figs. 13a-c versus the quantity of NH_3 in mole fraction replacing MCH and toluene in the binary fuel/air mixtures. Also shown in the figure are results from [48] for blends of NH_3 with CH_4, n-heptane, and isooctane, obtained under equivalent experimental conditions (T_g=338 K and p = 1 atm).

As already observed in Fig. 7, the evolution is nonlinear and antagonist with the mole fraction of NH_3. However, our previous study [48] suggested that the S_L for flames of NH_3 in combination with methane, n-heptane, and isooctane has a quasi-linear correlation with the NH_3 mass fraction in the fuel blend, instead of mole fraction. Thus, it is interesting to test if the relationship between the S_L of any hydrocarbon class, including naphtenes and aromatics, and the NH_3 ratio can be expressed as $(1-Y_{NH3})(S_L{}^0)+(Y_{NH3})(S_L{}^{NH3})$, where $S_L{}^0$ is the value at zero NH_3 addition and Y_{NH3} is the NH_3 mass fraction. The lines in Fig. 13 show the relationship approximated by this equation. A similar plot as a function of the NH_3 mass fraction is reported in Fig. S34 of the Supplementary Material. It can be observed that the S_L values calculated in this simple way are within the uncertainty of the measured ones for most of the examined mixtures. Thus, it can be concluded that the addition of NH_3 similarly affects the S_L of hydrocarbons, independent of the carbon number (C_1-C_8) and fuel class (linear, branched, and cyclic alkanes, aromatics). The reason for this similarity is that, as explained above, the influence of NH_3 on S_L of hydrocarbons is mostly dominated by flame temperature and activation energy, with little kinetic coupling. This finding can also help to develop reduced mechanisms for surrogate fuels to implement in CFD modeling. However, it must be noted that the proposed mixing rule is less valid under rich conditions, or when applied to the S_L of binary mixtures of NH_3 with CH_4 or toluene, independent on Φ. The reason is that for these mixtures the addition of NH_3 implies secondary kinetic effects as explained in the previous section. Regarding NH_3/CH_4 blends, it was observed in [48] that the higher impact of NH_3 addition on S_L of CH_4 compared to heavy hydrocarbons is due to a decrease in the hydrogen concentration in the flame zone, which induces an inhibiting effect only in the case of CH_4. This was considered as a combined chemical and transport effect because of the high reactivity and diffusivity of hydrogen.

Therefore, it is clear that this correlation, despite more convenient, is only approximate and such deviations do need to be kept in mind when quantitative information concerning fuel similarities or dissimilarities at specific operating points is needed. In these cases, predictions from detailed kinetic models are more valuable. Notwithstanding, the fact that this predictive relationship can be applied equally well to the S_L computed for all the mixtures further points out that the mutual interference between the components of a binary blend of NH_3 with hydrocarbons, when present, has only a minor effect with respect to the whole NH_3 contribution to S_L, at least under the conditions explored in the present and previous work [48]. Further confirmations at higher temperatures and pressures would be worthwhile in order to deduce whether the above correlation can be used to provide support for practical engines and gas turbines design and operation.

6. Conclusions

This work focuses on a combined experimental and modeling investigation on the influence of NH_3 on the propagation of MCH and toluene laminar flames. These hydrocarbons are typical of the component classes found in actual internal combustion engines and aviation fuels. The overall objective was to provide experimental data and a chemical kinetic model for blends of NH_3 with large hydrocarbons, which would be relevant to examine the optimal operation in realistic applications such as internal combustion engines. Specifically, an extensive experimental database on S_L for NH_3/MCH/air and NH_3/toluene/air was acquired at atmospheric pressure and 338 K, for equivalence ratios ranging from 0.7 to 1.3, and NH_3 blending levels in the fuel from 0% to 90%, using the heat flux method. About 60 new data points are presented, that significantly enrich the literature data. A comprehensive chemical kinetic model has been developed based on the existing CRECK chemical kinetic mechanism where the high temperature combustion chemistry was improved with minor adjustments, paying attention to the proper description of the consumption of methylcyclohexane, toluene, and methyl-phenoxy radical. The main findings are summarized as follows:

1. The present results on pure MCH/air and pure toluene/air flames are in reasonably close agreement with previous measurements from the literature obtained with the same method, although small discrepancies are observed under rich conditions.
2. A monotonic decrease in S_L with increasing NH_3 content is observed. The results show that both the equivalence ratio and the NH_3 fraction have an important impact on the S_L of NH_3/hydrocarbon fuel blends. In particular, when the equivalence ratio is held constant, the S_L decreases nonlinearly with increasing the NH_3 mole fraction, but this influence becomes quasi-linear when the NH_3 concentration is considered on a mass basis. This behavior is qualitatively consistent with previous investigations for blends of NH_3 with alkanes. In addition, NH_3 has a slightly higher effect on the S_L of toluene compared to MCH.
3. A comparison of the present measurements with detailed chemical kinetic simulations using the current refined reaction mechanism showed an overall good agreement over the whole range of investigation. On the other hand, the results presented herein showed that additional systematic theoretical studies for reaction classes concerning aromatic compounds and oxygenated aromatic intermediates are still required to improve the prediction of S_L in the case of toluene/air flames.
4. With the refined model, detailed analyses have also been conducted to provide fundamental insights into the physical and chemical blending effects of NH_3 with different classes of compounds that cause the S_L variation in binary mixtures. It was found that, similar to alkanes, the synergistic thermal and chemical effects of NH_3 play a predominant role in the decrease of the S_L for both NH_3/MCH and NH_3/toluene mixtures. The thermal effect is due to the decrease of the adiabatic flame temperature with increasing the NH_3 fraction, while the flame structure analyses revealed that the decrease in chemical reactivity is mainly caused by the reduction of $\dot{H}$, $\ddot{O}$, and $\dot{O}H$ concentrations in the flame. The observed higher inhibition of NH_3 on toluene flames compared to MCH is most likely referable to their different molecular structures. In particular, the $\ddot{O}$ radical scavenging effect of NH_3 further slows down the overall reaction rate by exerting a promoting effect on the chain-terminating reactions of the stable benzyl and phenoxyl radicals. The elucidation of fuel structure effects was the primary reason for the selection of MCH and toluene in this work.
5. A mass fraction-based mixing rule was also proposed and tested against the data collected in the present study and from the literature. This mixing rule, although simple, was shown to be predictive for binary blends of NH_3 with methane and several hydrocarbons typically used to formulate surrogates for practical fuels, suggesting that the kinetic coupling between NH_3 and toluene, despite present, is limited.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2021.111839.

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