An Experimental and Kinetic Modeling Study of Laminar Flame Speed of Dimethoxymethane and Ammonia Blends

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Abstract

Ammonia (NH₃) is considered a promising carbon-neutral fuel, with high hydrogen content, that can diversify the global energy system. Blending ammonia with a highly reactive fuel is one possible strategy to enhance its combustion characteristics. Here, an investigation of blends of NH₃ and dimethoxymethane (DMM), a biofuel with high fuel-born oxygen content and no carbon-carbon bonds, is reported. Unstretched laminar burning velocity (S_L) and Markstein length of different NH₃/DMM blends were experimentally determined using spherically propagating premixed flames. The DMM mole fraction was varied from 0.2 to 0.6 while measuring S_L at 298 K, 0.1 MPa and equivalence ratios (Φ) over a range of 0.8 to 1.3. The addition of DMM was found to immensely enhance the combustion characteristics of ammonia. DMM 20% (by mole fraction) in NH₃/DMM blend increased S_L more than a factor of 3 over neat ammonia; such enhancement was found to be comparable with 60% CH₄ in NH₃ ($\Phi = 0.9 - 1.1$) blends. Increasing Φ was found to significantly decrease the burned gas Markstein length for lean cases, whereas a negligible effect was observed for rich mixtures. A composite chemical kinetic model of DMM/NH₃, aimed

at interpreting the high-temperature combustion chemistry, was able to reliably predict S_L for neat NH_3 and DMM flames. Also, the predictive capability of the kinetic model to describe S_L for DMM/ NH_3 blends is reasonably good. Sensitivity analysis and reaction paths analysis indicated that the NH_3 /DMM blends could be understood as the dual oxidation processes of the individual fuels which are competing for the same radical pool.

Keywords: *Ammonia; Dimethoxymethane; Laminar flame speed; Markstein length; Kinetic model.*

Nomenclature

A	flame area	T_b	burnt gas temperature
CN	cetane number	T_i	mixture initial temperature
C_p	specific heat at constant pressure of the mixture	T^o	inner layer temperature
CVSV	Constant Volume Spherical Vessel	T_u	unburnt mixture temperature
DME	Dimethyl ether	Ze	Zeldovich number
DMM	Dimethoxymethane	χ_{DMM}	DMM mole fraction in the fuel blend
K	total stretch rate	σ	the expansion coefficient: ρ_u/ρ_b
L_b	burned gas Markstein length	Φ	mixture equivalence ratio
Le	Lewis number	λ	thermal conductivity of the mixture
OMEs	Oxymethylene dimethyl ethers	t	time from ignition
P_i	mixture initial pressure	ρ_b	burnt gas density
R_f	schlieren flame radius	ρ_u	unburnt mixture density
S_L	unstretched laminar burning velocity relative to the unburnt gas	ξ_E	normalized enhancement factor
S_n	stretched propagating flame speed	δ_L	preheat flame thickness
S_s	unstretched laminar burning velocity relative to the burnt gas		

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3 **1. Introduction**
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6 Greenhouse gas emission from the burning of fossil fuels has steadily risen since the industrial
7 revolution. The adoption of carbon-free fuels will not only help diversify the global energy system
8 but also reduce our dependence on fossil fuels. Hydrogen is a carbon-free fuel; however, the high
9 cost of hydrogen transport and storage makes its sustainable utilization very challenging. On the
10 contrary, due to the high percentage of hydrogen in ammonia (17.7% by weight), it can be regarded
11 as a carbon-free hydrogen carrier with a lower cost of storage and transport [1, 2]. Similar to
12 hydrogen, ammonia can be produced from renewable resources [3]. Consequently, one possible
13 step ahead towards carbon-free combustion can be the utilization of ammonia in combustion-based
14 energy devices. However, there are some barriers of using ammonia as a fuel due to its low
15 flammability limits, relatively low energy density (LHV 18.6 MJ/kg), high ignition energy, and
16 high NO emissions [1, 4].
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31 There is a growing interest in investigating the combustion characteristics of ammonia blends.
32 Blending ammonia with hydrocarbon fuels results in fuels of higher energy density and flame
33 speeds, and lower CO₂ emissions than the conventional hydrocarbon. Recently, Kobayashi *et al.*
34 [5] provided an extensive review of the combustion behavior of different ammonia blends. There
35 are a couple of fundamental studies on the combustion behavior of ammonia blended with
36 hydrocarbons and hydrogen. For example, over a pressure range of 0.1-0.5 MPa, the relatively low
37 laminar burning velocity, S_L , of neat ammonia was found to exhibit similar trends as that of the
38 hydrocarbon fuels showing maximum S_L at $\Phi \approx 1.1$ [1]. In CH₄/NH₃ blend, the laminar burning
39 velocity was seen to increase with the increase of CH₄ concentration in the mixture [2, 6], and the
40 same trend was reported for C₃H₈/NH₃ flames [7] as well. Blending NH₃ with hydrogen enhanced S_L
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exponentially with the increase of hydrogen mole fraction in the blend [8]. Recently, Otomo *et al.* [9] proposed a chemical kinetic model to predict S_L and ignition delay times of H_2/NH_3 blends.

In addition, the use of alternative fuels or new fuel formulations for future internal combustion engines is another pathway to alleviate the oil crisis and to achieve high efficiency and clean combustion. To this end, oxygenated fuels can be promising candidates [10, 11]. Recently, synthetic oxymethylene dimethyl ethers (OMEs, $CH_3O-(CH_2O)_n-CH_3$, $n=1-5$) has attracted considerable interest [10]. Comparing with diesel fuel, OMEs exhibited higher engine efficiency with lower HC, CO, NO_x, soot emissions due to its higher fuel-born oxygen, higher ignitability, higher volatility, absence of carbon-carbon bonds [11]. OMEs was used as pilot fuels for natural gas dual-fuel combustion [12]. Methanol is the building block of OMEs production; the former chemical can be produced from coal, natural gas, or biomass through syngas [13]. Depending on the feedstock type, and subsequent gasification, syngas can also be obtained from renewable resources via different methodologies [14]. A cost assessment showed that OME production is competitive with conventional diesel on a tonnage base [15]. Therefore, OMEs has a substantial advantage over other alternative fuels in need of massive public subsidies.

Recently, studies in Internal Combustion Engines (ICE) have focused on using ammonia blended with oxygenated fuels, driven by the demand for alternative fuels [16, 17]. In these studies, ammonia was blended with dimethyl ether, DME, $(CH_3O-(CH_2O)_n-CH_3)$, $n=0$) and tested in a compression-ignition engine, where DME served as a co-fuel to initiate the combustion. Their results showed that a higher fraction of ammonia in the blends caused longer ignition delays and limited the engine load. These observations highlight the need to characterize the combustion properties of NH_3 blended with different co-fuels as combustion promoters. Although both methanol and DME are attractive oxygenated-fuels for future sustainability, methanol is toxic, and

DME is gaseous. Therefore, DMM (dimethoxymethane, $\text{CH}_3\text{O}-\text{CH}_2\text{O}-\text{CH}_3$, OME1) offers an excellent chemical feedstock for more convenient storage and handling. DMM, an oxygenated biofuel (42% wt O_2) with a high H/C ratio, has recently drawn considerable attention [18, 19]. Pure DMM burns clean with no soot [20], and also, there are promising reports of DMM reducing soot/PAH substantially when blended with diesel fuels [21-23]. However, the physical properties of DMM include low boiling point, low cetane number (CN), low viscosity, lubricity and high volatility lead to the need for the modifications of fuel supply/injection systems. Hence, the use of DMM as a blend with diesel or with additives. Omari et al. [24] indicated that an optimum blending ratio (DMM/diesel wt%) of 35% is the best compromise between soot reduction and the deterioration of fuel properties such as heating value and CN. At present, DMM production relies on the catalytic oxidation of methanol and methanol condensation with formaldehyde [25]. Several other routes utilizing methanol or CO_2 and H_2 to produce DMM in one step have been proposed [26, 27].

From the kinetic modeling perspective, numerous hydrocarbon mechanisms blended with the sub-mechanism of NH_3 oxidation have been used to predict the combustion characteristics of NH_3 dual fuel systems. Recently, Han *et al.* [28] used the available kinetic models to validate their measurements of the atmospheric laminar burning velocity of NH_3 blended with H_2 , CO , and CH_4 . They showed that none of the available kinetic models (GRI-Mech 3.0 [29], Okafor *et al.* [2], and SanDiego [30]) could accurately capture the experimental data which they attributed to the uncertainty in the rate parameters of the N-containing reactions. In a recent review, Kobayashi *et al.* [5] also reported considerable discrepancy between the experiments and the predictions of the laminar burning velocity of NH_3 -air flames.

This work is aimed at characterizing the combustion behavior of NH_3/DMM blends over a wide range of conditions to test their applicability in modern combustion devices. To achieve these goals, measurements of laminar burning velocity for various NH_3/DMM mixtures were carried out in a Constant Volume Spherical Vessel (CVSV). To understand the combustion behavior of NH_3/DMM blends, a chemical kinetic model was constructed from Shrestha *et al.* [31] for NH_3 base model, and the DMM sub-mechanism was added from Sun *et al.* [32]. Such studies of NH_3 in dual-fuel combustion applications offer a fundamental combustion database for stepwise movement towards the low-carbon mobility future. Therefore, this work aims at improving the NH_3 oxidation model by validating against the newly measured experimental data on the laminar flame speeds of DMM/NH_3 blends over a wide range of conditions.

2. Experimental Setup

The Constant Volume Spherical Vessel, CVSV, at KAUST (shown in Fig. 1) has an inner diameter of 330 mm and is equipped with two orthogonal pairs of quartz windows of 120 mm in diameter. The initial temperature of the mixture was recorded at two locations inside the vessel to ensure the thermal homogeneity of the mixture. Mixtures of ammonia (> 99.98% purity), DMM (> 99.5% purity), and dry air were prepared in the vessel according to the required partial pressures of the gaseous components. The dry air on a molar basis has a composition of 20.947% O_2 , 78.084% N_2 , 0.9% argon, and the remaining 0.1% are carbon dioxide, helium, neon, and hydrogen. The required amount of liquid DMM was injected inside the vessel using a gas-tight micro-syringe under vacuum, which immediately evaporates to the required partial pressure of DMM. Then gaseous ammonia was added followed by dry air. A pressure transducer (Keller; PAA-33X, which guarantees the accuracy of 0.005% in full scale) fitted to the vessel was used to monitor the partial pressure of the reactants during the mixture preparation as well as the initial mixture pressure

before ignition. The maximum deviation between the initial mixture pressure inside the vessel and the required initial pressure was about 3%. Before filling the CVSV, it was evacuated up to 0.001 MPa and purged with nitrogen to remove combustion residuals. Mixtures were ignited by using two spark electrodes (1.2 mm diameter), forming a V-shape configuration at the center of the vessel with a 1 mm gap. An average spark ignition energy was set to 24 mJ. To ensure mixture homogeneity, CVSV is equipped with a fan located inside the vessel at the top flange. The fan was stopped approximately 45 s before ignition event to prevent any perturbation to the flame propagation. Clear flame propagation was recorded by schlieren photography with a high-speed camera (Photron; FastCam Ultima APX 120K) at 4000 fps and 512×512 pixels with a spatial resolution of approximately 315 $\mu\text{m}/\text{pixel}$. The uncertainty of the counted pixels associated with each flame radius in the digital photos is ± 1 pixel. This leads to a maximum uncertainty of $\pm 1.6\%$ at the minimum flame radius of 20 mm and a minimum uncertainty of $\pm 0.7\%$ at the maximum flame radius of 45 mm. For a given condition, the measurements were repeated three to five times to check the repeatability of the data. The experimental data were found within the estimated experimental uncertainty (97% confidence level). The unstretched laminar burning velocity and burned Markstein length (described in Section 3.2) were determined as the average value of the results obtained from each experiment. The experimental fluctuation was defined as the difference between the maximum and minimum values of the experimental results.

The uncertainties in the laminar burning velocity measurements using the spherical flame outward propagation include the confinement effect, flame instability, ignition energy, buoyancy, and nonlinearity of the stretch rate-flame speed relationship [33]. Uncertainties in the measured laminar burning velocity were between ± 0.6 cm/s and ± 1.3 cm/s, depending on the equivalence ratio and DMM/ NH_3 mixture fraction. The maximum observed flame radius was around 45 mm;

thus, there was no pressure rise in the chamber. This radius gives a volume of the burned gases less than 2.1% of the CVSV volume, which avoids pressure rise and confinement effects [34]. The uncertainty in the measured laminar burning velocity accounts for the all sources of experimental errors, based on the combination of the experimental and statistical errors (with a 0.97% self-confidence calculated from Student's law and standard deviation). In the current study, the uncertainty was estimated using the Taylor Series Method of uncertainty propagation, as described in [35]. In addition, the appearance of the flame (shown in Section 3) does not show any tendency to become unstable within the acquired flame radius; thus, the flame instability did not contribute to the experimental uncertainty. The ignition energy effect and the suitability of the nonlinear or linear methodologies for the flame speed-stretch rate relationship were carefully considered to avoid their impacts on the reported data (discussed in Section 3.2). The effect of buoyancy is noticeable for the flames with laminar burning velocity < 15 cm/s [36]. In the current blends, few flames had unstretched laminar burning velocity < 15 cm/s, furthermore, these flames did not show any change in the flame symmetry or upward drifting during their propagation, see Section 3.1. Consequently, the buoyancy effects were considered insignificant in this study. Details of radiation-induced uncertainty of the experimental setup can be found elsewhere [37, 38], which showed the uncertainty having a value of $< 4\%$ for the lowest measured laminar burning velocity at 14-15 cm/s.

Figure 1. Schematic diagram of the experimental setup

For the spherically propagating laminar flames, the stretched propagating flame speed, S_n , is evaluated as $S_n = dR_f/dt$, where R_f is the schlieren flame radius, and t is time. The spherical propagating flame is subjected to curvature or aerodynamic strains. Hence, S_n represents the stretched laminar flame speed of a spherical flame and is dependent on the total stretch rate, κ . The total stretch rate in spherical flame, κ , is defined as the time change of flame area per unit area: $(1/A) (dA/dt) = (2/R_f)S_n$, where A is the flame surface area. Various correlations between S_n and κ have been proposed to estimate the unstretched laminar burning velocity relative to the burnt gas, S_s , which enable the elimination of the effect of stretch by extrapolating S_n to zero stretch rate [39]. The asymptotic analysis showed that the difference between the unstretched laminar burning velocity, S_s , and the stretched flame speed, S_n , is linearly proportional to the flame stretch rate as given by $S_s - S_n = L_b \kappa$ [40], where the proportionality constant L_b is the burned gas Markstein length. On the other hand, the nonlinear relationship [41] was found to be most appropriate for extracting

S_s from the measured data using the following correlation (section 3.2 will detail the selection of the methodology for the flame speed extrapolation):

$$\left(\frac{S_n}{S_s}\right)^2 \ln\left(\frac{S_n}{S_s}\right) = -2 \frac{L_b k}{S_s}$$

In this correlation, S_s and L_b can be deduced from the linear extrapolation in a plot of $\ln(S_n)$ versus κ/S_n^2 , with an intercept on the $\ln(S_n)$ axis equal to $\ln(S_s)$ and the slope of a value equal to $(-S_s L_b)$. After extracting S_s , the unstretched laminar burning velocity relative to the unburnt gas, S_L , is obtained by the mass balance over the unstretched flame as $S_L = S_s/\sigma$, where σ is the expansion coefficient, *i.e.*, the ratio of the unburnt mixture density, ρ_u , to the burnt gas density, ρ_b .

The laminar flame speed measurements were conducted on various NH₃/DMM blends, where the DMM mole fraction in the blends, χ_{DMM} , was varied over 0.2, 0.3, 0.4 and 0.6. For these blends, the mixture equivalence ratio was varied from 0.8 to 1.3 while keeping the mixture temperature, T_i , and pressure, P_i , at 298 ± 3 K, and 0.10 MPa, respectively. The unburnt and burnt mixture properties are listed in Table 1. The unburnt mixture density, ρ_u , and the burnt gas density, ρ_b , for the different blend at the various equivalence ratio, Φ , are illustrated in Table 1. The λ , c_p , α , and ν are the thermal conductivity, specific heat at constant pressure, thermal diffusivity and kinematic viscosity, respectively. The combustion literature reported several definitions of an equivalent Lewis number for a mixture with two fuel components. The first formulation of the effective Lewis number introduced by law et al. [42], was based on the weighted average non-dimensional heat release of the two fuel components. The second formulation of the effective lewis number was derived based on a volumetric fraction-weighted average of the fuel diffusivities [43]. While the third definition was based on the volumetric fraction-weighted average formulation, see Muppala et al. [44]. Recently, Nicolas et al.[45] investigated the impacts of the previous formulations of the

effective Lewis number on hydrogen/hydrocarbon/air mixture flames. They showed that the volumetric weighted average approach was found to be the most consistent for the tested hydrogen/hydrocarbon/air flames and leading to a qualitatively accurate prediction of both Markestén length sign and slope inversion. Thus, in the current study, Le number was evaluated using the average mole-weighted formula of the deficient reactants: $(\frac{\chi_{DMM}Le_{DMM} + \chi_{NH_3}Le_{NH_3}}{\chi_{DMM} + \chi_{NH_3}})$, in this correlation, χ_{NH_3} represents NH_3 mole fraction in the blend [2, 46], which is similar to the volumetric fraction-weighted approach. Lewis numbers characterizing mixtures with a single fuel “ i ”, were computed as: $Le_i = \frac{D_T}{D_{im}}$. D_T is the mixture thermal diffusivity and D_{im} is the mass diffusivity of the deficient reactant “ i ” relative to the gas mixture. The mixture thermal diffusivity was calculated as: $D_T = \frac{\lambda}{\rho_u c_p}$, with λ and C_p being the mixture-averaged thermal conductivity and specific heat, respectively. The mixture thermal conductivity and ordinary diffusion coefficients of the species were obtained using the full multicomponent transport model, solving the so called L matrix. Subsequently, the mass diffusion coefficients of each species of interest (DMM, NH_3 , and O_2) were evaluated as mixture-averaged diffusion coefficients into the mixture. The specific heat at constant pressure, C_p , was evaluated as the mass fraction-weighted: $C_p = \sum_{i=1}^N C_{p,i} Y_i$, with Y_i and $C_{p,i}$ being the mass fraction and specific heat of the i^{th} species, respectively. As shown in Table 1, Le for lean mixtures is greater than unity which is found to increase with increasing χ_{DMM} , but it remains constant for rich mixtures.

Table 1: The unburnt and burnt mixture properties used in this study. The initial temperature and pressure of the mixture were 298 K and 0.1 MPa, respectively.

χ_{DMM}	Φ	ρ_u	ρ_b	$\lambda \times 10^{-3}$	c_p	$\alpha \times 10^{-5}$	$\nu \times 10^{-5}$	Le
--	--	(kg/m ³)	(kg/m ³)	(W/mK)	(J/kg/K)	(m ² /s)	(m ² /s)	(--)
0.2	0.9	1.1711	0.1542	26.431	1102	2.064	1.475	1.162
	1.0	1.1721	0.1472	26.428	1101	2.050	1.465	--
	1.1	1.1723	0.1457	26.425	1119	2.035	1.455	1.031
	1.2	1.1731	0.1471	26.421	1127	2.022	1.445	1.026

	1.3	1.1733	0.1490	26.421	1135	2.009	1.435	1.021
0.3	0.9	1.1961	0.1548	26.173	1092	2.030	1.454	1.252
	1.0	1.1984	0.1478	26.148	1100	2.012	1.442	--
	1.1	1.2007	0.1460	26.123	1107	1.995	1.430	1.031
	1.2	1.2030	0.1473	26.098	1115	1.978	1.418	1.026
	1.3	1.2052	0.1491	26.073	1122	1.962	1.407	1.021
0.4	0.8	1.2088	0.1655	26.041	1078	2.027	1.455	1.342
	0.9	1.2130	0.1551	25.999	1086	2.006	1.441	1.330
	1.0	1.2171	0.1483	25.958	1093	1.986	1.427	--
	1.1	1.2211	0.1463	25.917	1100	1.926	1.414	1.031
	1.2	1.2251	0.1474	25.877	1107	1.949	1.401	1.026
	1.3	1.2289	0.1492	25.839	1114	1.931	1.388	1.021
0.6	0.8	1.2288	0.1656	25.841	1071	2.000	1.439	1.469
	0.9	1.2354	0.1555	25.778	1078	1.977	1.423	1.455
	1.0	1.2419	0.1490	25.716	1084	1.954	1.408	--
	1.1	1.2484	0.1468	25.655	1091	1.933	1.393	1.031
	1.2	1.2547	0.1476	25.596	1097	1.912	1.379	1.026
	1.3	1.2609	0.1493	25.539	1103	1.892	1.365	1.021

3. Results and Discussion

3.1 Flame appearance and observations

Figure 2 illustrates the propagation of the spherical laminar flames corresponding to the various elapsed time after the ignition event for $\chi_{DMM} = 0.2$ and 0.6 at the equivalence ratio (Φ) of 0.9 to 1.3 (see Fig. 2a and Fig. 2b, respectively). No flame instability was observed, which is true for all studied cases. However, at $\Phi = 0.8$ and $\chi_{DMM} = 0.2$ (not shown in Fig. 2), the hot spot generated by the spark was observed between the spark electrodes at $t = 0$ ms. But after a few milliseconds, the boundaries of the flame kernel become extinguished as a result of the high local stretch rate. Under these conditions, the flame kernel tends to readily quench due to low heat release from the chemical reaction. For $\chi_{DMM} = 0.2$ and $\Phi = 0.9$, the flame was found to be most susceptible to the buoyancy effects because it had the lowest flame propagation speed. The center of this flame was close to the spark electrodes up to the flame radius of 60 mm with no appreciable deformation of the flame appearance. This indicates that the buoyancy effect on the flame shape was negligible.

As seen in Fig. 2a, after an elapsed time of 30 ms, the flame radius for $\Phi = 1.1$ was found to be larger than that of $\Phi = 0.9$, and 1.3. The minor flame cracks observed at $\Phi = 1.1$ and 1.3 for $\chi_{DMM} = 0.6$ are believed to be consequences of the large deposit ignition energy along with the thinner flame thickness at high χ_{DMM} . In addition, these little observed cracks did not develop into more cracks at larger flame radius where the stretch rate decreases and its stabilizing influence is diminished. Clearly, increasing the mole fraction of χ_{DMM} increases the flame propagation speed (see images in Fig. 2a, and Fig. 2b for a given elapsed time, for example at $t = 20$ ms).

Figure 2. Schlieren images of NH₃/DMM flames recorded at (a) $\chi_{DMM}=0.2$ and (b) $\chi_{DMM}=0.6$, for the equivalence ratio (Φ) of 0.9, 1.1 and 1.3.

3.2 Laminar flame speed experimental data for NH₃/DMM blends

Figure 3 illustrates the typical behaviors of the stretched flame speed, S_n , and the flame stretch rate, κ , with the flame radius, R_f , for two flames with $\chi_{DMM} = 0.3$ and 0.6 and various Φ . In the CVSV, the elapsed time of the flame propagation can be subdivided into three regions: an ignition affected region, a stationary propagation region, and a chamber affected region. As shown in Figs. 3a-3b, S_n exhibits excessively large values after spark ignition, associated with high flame curvature and hence stretch rates (see Figs. 3c-3d). Then both S_n and κ decrease sharply to minimum value due to the ignition transition from the deposited spark energy. This trend is more evident for lean flames ($\Phi = 0.8$, and 0.9) indicating that such flames are more prone to the stretch rate. The ignition transient regime develops into the stationary propagation regime, where S_n eventually approaches a steady-state value, and κ steadily decreases to roughly merge at higher values of R_f (see Figs. 3c-3d). The development from the ignition regime to the stable regime transpires faster at higher χ_{DMM} . The large inner diameter of CVSV relative to the schlieren imaging region minimizes the effect of the chamber confinement on the flame propagation as confirmed by the S_n and κ versus R_f plots.

Figure 3. Variations of the stretched flame speed, S_n , and the flame stretch rate, κ with R_f at $\chi_{DMM} = 0.3$ and 0.6 for various Φ

The transition from the spark energy deposition to the steady flame propagation after ignition shows different trajectories depending on the flame conditions. This can be illustrated by plotting S_n versus κ for two flames at $\Phi = 0.8$ and 1.2 , while keeping the same χ_{DMM} at 0.4 (see Fig. 4). For these flames, the Lewis number, Le , changes from 1.342 to 1.026 for $\Phi = 0.8$ and 1.2 , respectively (see Table 1). As can be seen, S_n versus κ plot exhibits a ‘Z’ like trajectory for the lean mixture in contrary to the rich flames which follow nearly a linear path. Similar ‘Z’ like trajectory was reported for rich CH_4/NH_3 -air flames [2], where Le was equal to 1.1 . The lower branch of this Z path stems from the influence of ignition; whereas the middle and upper branches are caused by the thermos-diffusive and radiative heat loss. Also, the energy deposited by the spark may partially affect the middle part of the trajectory [47]. Note that the nonlinear behavior of S_n versus κ transforms into linearity by increasing Φ from 0.8 to 1.2 . This change can be attributed to the combined effects of both the Lewis number and the preheat flame thickness. A detail discussion will follow in the next section.

Figure 4. Stretched flame speed, S_n , versus flame stretch rate, κ , for two flames with different Lewis number, Le .

Only R_f values between 20 mm (to avoid the effect of ignition energy that was overdriving the flame) and 45 mm (to ensure that the recorded images within the isobaric region of the vessel pressure signal) were used to extract S_s (see Fig. 5) to reduce the uncertainties due to the stretch extrapolation. However, at least 50 data points are used to extract S_s . The ‘Z’ like trajectory behavior of S_n - κ relationship was found to decrease as Φ increases which is true for both blends of $\chi_{DMM} = 0.3$ and 0.6. Additionally, for a given Φ , S_n - κ plot was observed to behave more linearly trajectory after ignition for higher χ_{DMM} flames. This is more obvious for the lean flames, *e.g.*, $\Phi = 0.9$ (see Figs 5a-5b), indicating that the NH_3 rich blends exhibit a more tendency to ‘Z’ like trajectory in S_n - κ relationship. Similar observations were reported for CH_4/NH_3 flames [2, 46]. Therefore, the stretch effect needs to be eliminated by extrapolating the S_n to zero stretch rate. Different stretch extrapolation relations have been proposed [48], and it is believed that the method for S_n - κ extrapolation is one of the major sources of uncertainties. As illustrated by Wu et al. [48], to reduce the uncertainty due to the extrapolation, the ratio of $2L_{b,lin}/R_{f,mid}$ should lie between -0.1 and 0.15, where $L_{b,lin}$ is the Markstien length deduced from the linear extrapolation, and $R_{f,mid}$ is the middle radius of the data under consideration. Thus, to limit the extrapolation effect, the mixture Lewis number should be around unity or to have a wide range of usable flame radii [38]. For the mixture blends of extreme Lewis number, *i.e.*, the blend with $\chi_{DMM} = 0.6$ and $\Phi = 0.8$ and 1.2, the linear and non-linear extrapolation plots are presented in Fig. 5b. For the full radius range, *i.e.*, 20-45 mm, the values of $2L_{b,lin}/R_{f,mid}$ are 0.09 and 0.04 for $\Phi = 0.8$ and 1.2, respectively which lie within the range of Wu’s criterion. This indicates that with the current large vessel, the linear and nonlinear extrapolations provide negligible difference. Since the nonlinear model is expected to be more general than the linear model and can be applied for arbitrary mixtures with

wide range of Le number, the nonlinear correlation was applied in this work to deduce the unstretched laminar burning velocity and burned gas Markstein length.

Figure 5. Stretched laminar flame speed, S_n , versus κ for different Φ : (a) at $\chi_{DMM} = 0.3$, (b) at $\chi_{DMM} = 0.6$. The symbols represent the measured data, while the curves are the nonlinear extrapolation of the measurements, and the dashed lines show the linear extrapolation at $\chi_{DMM} = 0.6$, for $\Phi = 0.8$ and 1.2 .

The sensitivity of S_n to the stretch rate at the different blend ratios is evaluated by measuring the burned gas Markstein length, L_b . Figure 6 plots the variation of L_b with Φ for the different DMM/NH₃ blends. For comparison, the values reported by Hayakawa *et al.* [1] for neat NH₃-air flames are also plotted. As seen, DMM/NH₃ blends show a different trend than the neat NH₃-air flames. Unlike neat NH₃, the L_b values (all positive) for DMM/NH₃ blends show a steeper decline with increasing Φ . For neat NH₃, L_b values are negative for $\Phi < 0.9$, which keeps increasing to positive values as the mixture gets richer. Another notable difference was found with the Lewis number (Le). For lean NH₃ flames, Le was found to be less than unity and increased to greater than unity for rich mixture; whereas Le values are higher than 1 for all DMM/NH₃ blends investigated here. Thereby, for the neat NH₃/air flames, the burned gas Markstein lengths at lean mixtures were

negative because temperature and burning velocity of stretched flames increase due to the thermos-diffusive effects. As indicated in Table 1, Le values of lean mixtures are significantly larger for high χ_{DMM} . For rich mixtures, the variation in Le with χ_{DMM} is not noticeable. This explains the variation of L_b with Φ observed, which shows a decrease in L_b with increasing Φ . For example, when Le is close to unity (rich mixtures in Table 1), the flame stretch, *i.e.*, the thermos-diffusive effects, do not significantly alter the propagating flame speed, S_n . Figure 6 further illustrates the variation of L_b with χ_{DMM} . For lean flames, L_b increases with increasing χ_{DMM} . On the contrary, the rich flames show a negligible variation of L_b with χ_{DMM} (0.3-0.6). However, the rich flames of $\chi_{DMM} = 0.2$ show relative higher L_b values than that of $\chi_{DMM} > 0.3$ blends.

Earlier studies [49, 50] have shown that L_b is a function of Le (Lewis number), σ (thermal expansion coefficient), Ze (the Zeldovich-number) and δ_L (the preheat flame thickness), as given by the relationship: $L_b = \delta_L[f_1(\sigma) + Ze (Le - 1)f_2(\sigma)]$. Here, f_1 and f_2 are functions of σ and have positive values. The first term in this relationship is always positive and is important in equidiffusive mixtures. The second term accounts for thermos-diffusive effects on the flame speeds of those mixtures with non-equidiffusive, and it takes negative (positive) values for flames with Le less (greater) than unity. For the DMM/ NH_3 blends considered here, σ does not vary significantly. For the lean mixtures, it appears that the positive dependence of L_b on χ_{DMM} stems from the combined effects of δ_L , Ze , and Le . Figure 7 illustrates the variation of both δ_L and Ze with Φ for various χ_{DMM} . δ_L is calculated as $(\lambda/\rho_u C_p S_L)$, where λ and C_p are the thermal conductivity and the specific heat capacity at a constant pressure of the mixture, respectively. Zeldovich-number, Ze , which may express the sensitivity of the flame speed to the variation in the maximum flame temperature [51], is defined as $4(T_b - T_u)/(T_b - T^o)$, where T_b and T_u are the burned and unburned temperatures, while T^o is the inner layer temperature [51, 52]. Within the temperature profile of

premixed flames, the inner layer temperature marks the transition from inert preheat zone to the reaction zone, and therefore, it is the point where the second derivative vanishes and the slope is maximum. Mixture properties, T_b , and T^o used for estimating Ze and δ_L were calculated using the composite chemical kinetic model used for simulation of the laminar burning velocity and premixed flames while keeping the same grid constraints, as described in section 3.3. The Zeldovich number could also be evaluated as $E(T_b - T_u)/RT_b^2$; E is the mixture activation energy, and R is the universal gas constant [53]. E can be determined from the relationship $E/R = -2d \ln(\rho_u S_L)/d(1/T_b)$ [54]. Evaluation of E/R requires the calculation of $\ln(\rho_u S_L)$ at different T_b . T_b is estimated by a small variation in T_u for each χ_{DMM} [55]. Here, the two formulae to evaluate Ze yield nearly identical values.

Figure 6. Relationship between L_b and Φ for different DMM/ NH_3 blends and neat NH_3 flames [1].

Figure 7. Equivalence ratio (Φ) dependence of the preheating zone thickness, δ_l (a), and Zel'dovich number, Ze (b) for various NH_3/DMM blends.

As illustrated in Fig. 7a, δ_l decreases with increasing χ_{DMM} (*i.e.*, less $\text{NH}_3\%$) for a given Φ , and the thinnest δ_l occurs at $\Phi = 1.1$ except for $\chi_{\text{DMM}} = 0.6$, where δ_l remains nearly constant after $\Phi = 1.1$. Ze also decreases with χ_{DMM} with a minimum value occurring at $\Phi = 1$ (see Fig. 7b). According to the previous L_b relationship, the increment in both δ_l and Ze will promote the effect of a non-unity Le to yield higher values of L_b . Such combined effects are more prominent for the leaner blends, where both δ_l and Ze in addition to Le , have higher values. Interestingly, L_b is found to increase with χ_{DMM} even though the values for both δ_L and Ze show a decline with increasing χ_{DMM} for a given Φ under lean conditions (see Fig. 6). This indicates that Le has a more dominant effect on L_b than both δ_L and Ze combined. The effect of the Ze on L_b is negligible for the rich mixtures. Besides, Le is close to unity for rich mixtures ($\chi_{\text{DMM}} = 0.3$ to 0.6) which reduces the impact of both δ_L and Ze on L_b for these blends. However, higher values of L_b are observed for richer blends with $\chi_{\text{DMM}} = 0.2$ in contrast to the blends with $\chi_{\text{DMM}} > 0.2$ (see Fig. 6). For this particular blend, δ_l and

Ze show a relative increase at higher Φ relative to the other rich mixture blends as illustrated in Fig. 7.

3.3 Laminar burning velocity prediction from chemical kinetic simulations

A robust chemical kinetic model is not available in the literature for DMM/ NH_3 blends. Therefore, a composite kinetic model was constructed by combining the base mechanism for NH_3 from Shrestha *et al.* [31], and DMM sub-mechanism from Sun *et al.* [32]. Shrestha *et al.* [31] tested the robustness of their kinetic model for C, H, N, O system by validating against several experimental targets, *e.g.*, laminar burning velocities, ignition delay times, speciation from jet-stirred and flow reactors, and premixed-flame data [56]; whereas Sun *et al.* [32] developed the mechanism for the oxidation of poly(oxymethylene) dimethyl ethers (which also includes DMM) and validated against their measurements of the laminar burning velocities and speciation data in low-pressure premixed flames. Simulations of the laminar burning velocity and the premixed flames were performed with the PREMIX module in ANSYS CHEMKIN-Pro package. Up to 300 grids were used to obtain converged solutions with the constraints for GRAD and CURV as 0.1 and 0.01, respectively. Figure 8a shows the comparison between the model predictions and experimental data for the laminar burning velocity (S_L) of DMM/ NH_3 blends. The measured S_L of neat DMM/air-flame [57] is also presented. In this work, additional measurements were carried out for neat DMM-air flames to compare our data with the well-established data from Gillespie *et al.* [57]. As can be seen, the experimental data from present work is in excellent agreement with that of Gillespie *et al.* [57] indicating the reliability of the current work (see ref. [58] for further illustration of our laminar flame speed for neat DMM data at elevated temperatures and pressures). The present kinetic model performs excellently in predicting S_L for neat DMM for all the equivalence ratio investigated. However, the predictions for DMM/ NH_3 blends are somewhat

overpredicted. The overprediction in the worst-case scenario is ~20% for the leans flames, in particular for $\chi_{\text{DMM}} = 0.6$ flames. The discrepancies between the model prediction and the measurements are highest for $\chi_{\text{DMM}} = 0.6$ cases; the possible cause of this higher discrepancy is explained in detail with the help of reaction flow analysis in Section 3.4. The model predictions show better agreement with the data for stoichiometric and rich mixtures ($\chi_{\text{DMM}} = 0.2, 0.3$, and 0.4). Interestingly, the experimental S_L data for the rich NH_3/DMM -air mixtures do not exhibit the same degree of attenuation with Φ as that of the lean mixtures. Overall, the model follows the experimental trend very well of increasing laminar burning velocities with the increase of χ_{DMM} . The attempts to investigate neat NH_3 flames were futile because the small flame kernel generated after the spark ignition could not sustain. Since for neat NH_3 flames, and $Le < 1$, the extinguishing of the flame kernel may be attributed to the limited spark energy and heat loss.

Figure 8b compiles literature S_L data [1, 28, 59-65] for neat NH_3 -air mixtures and compares with the present model predictions. The model prediction is reasonably good for lean-to-stoichiometric NH_3/air flames at 1 atm and 298 K. For rich conditions ($\Phi > 1.1$), the model predicts somewhat higher values of S_L . However, there is a considerable discrepancy among the fuel-rich experimental data, particularly for mixtures with $\Phi > 1.1$. Most of the experimental data exhibit a maximum value of S_L near $\Phi = 1.1$ for NH_3 -air mixtures. This phenomenon is well captured by the current model. Furthermore, in Fig. 8 it is seen that the predicted laminar burning velocity for neat NH_3 towards lean conditions are slower compared to most of the experimental data; however, this trend is reversed when NH_3 is blended with DMM. Blending NH_3 with the DMM significantly affects some of the key radical pool concentration in the flame (see Figure S1 of the radical pool profiles in the in supporting information) which primarily controls the system reactivity.

Since nitrogen chemistry is mostly controlled by the more complex radicals pool (e.g. N_xH_y radicals), the reverse trend on the laminar burning velocity (towards the lean side) could be due to an unbalance in the radical pool in the blended system. This can be further supported using temperature versus equivalence ratio illustration (see Figure S2 of adiabatic flame temperature versus Φ , in the supporting information). It can be observed that the temperature difference in the flames between the neat NH_3 and the blended system is higher towards the lean side compared to the rich side. As stated earlier, the current model predicts the laminar burning velocity of the neat DMM very well than DMM/ NH_3 blends. This may highlight the importance of some of the cross elementary reactions between nitrogen and carbon family, which may be missing in the current kinetic model. This warrants further optimization/investigation of the composite model, which is currently underway.

The heat release during the oxidation of fuel directly controls the adiabatic flame temperature. Since DMM has a higher lower heating value than that of ammonia, one expects that DMM/ NH_3 blends will have the higher adiabatic-flame temperature with increasing χ_{DMM} (see Fig. S2). Consequently, the laminar burning velocities are higher for larger χ_{DMM} in DMM/ NH_3 blends. Note that the burning velocity is directly proportional to the square root of the product of the thermal diffusivity (α) and the rate of reaction (RR) ($S_L \propto \sqrt{\alpha \cdot RR}$ [66]), and RR is a strong function of the flame temperature. Clearly, the DMM content in DMM/ NH_3 blends strongly impact the flame temperature and hence the laminar flame speed. The thermal diffusivity (α) does not change much for varying χ_{DMM} (see Table 1). Therefore, its impact on the adiabatic flame temperature for varying χ_{DMM} is not significant.

Figure 8. Comparison of the measured S_L with simulated values: **(a)** for various DMM/NH₃ blends, neat DMM, and **(b)** for neat NH₃. The error bars represent the uncertainty in our measurements (experimental methodologies: heat flux method [28], [57] - constant volume chamber vessel [1], [59-62] [64-65], and cylindrical flow tube [63]).

Figure 9a plots the degree of enhancement of the laminar burning velocity of ammonia by blending with various mole fractions of DMM and CH₄. The S_L data for CH₄/NH₃ blends were taken from Han *et al.* [28]. The addition of ignition promoter (DMM or CH₄) causes roughly a linear increase in S_L for a given equivalence ratio between 0.9 and 1.1. Evidently, DMM is a better ignition promoter as it greatly enhances S_L compared to CH₄ for a given condition. To quantify the degree of enhancement, we used the normalized enhancement factor ξ_E [28], which is defined as:

$$\xi_E, \% = [S_L(\chi_M, \Phi) - S_{L, NH_3}(\Phi)] / S_{L, NH_3}(\Phi).$$

Here, $S_{L, NH_3}(\Phi)$ and $S_L(\chi_M, \Phi)$ are the laminar burning velocities of NH₃/air flames and the NH₃-M blends (M = DMM or CH₄) for a given Φ , respectively. Figure 9b illustrates the enhancement factor ξ_E versus Φ for χ_{DMM} or $\chi_{CH_4} = 0.2$ and 0.6. Again, DMM shows promising results with a higher degree of enhancement as compared to CH₄ for all Φ . The ξ_E for $\chi_{DMM} = 0.2$ comes nearly equal to that of $\chi_{CH_4} = 0.6$ for a given Φ between 0.9 and 1.1, and ξ_E values for DMM are even higher for $\Phi > 1.1$ (see Fig. 9b). Interestingly, methane shows big enhancement effects on the lean side, whereas DMM displays high degree of

enhancement for both lean and rich mixtures (for $\chi_{DMM} = 0.6$, $\xi_E = 540\%$ and 470% for $\Phi = 0.8$ and 1.3 , respectively).

For $\chi_{DMM} = 0.2$, the enhancement factor remains nearly constant at $\sim 200\%$ for $0.9 \leq \Phi \leq 1.1$. Relative to methane, the presence of activated methylene groups next to oxygen atoms ($-\text{O}-\text{CH}_2-$) in the chemical structure of DMM leads to the formation of hydroperoxides in the early stage of combustion (see Fig. S1 in SM). These hydroperoxides decompose into OH radicals, which are one of the key radicals for the decomposition of NH_3 and DMM as well as the radical derivatives. Also, the $(-\text{CH}_2\text{O}-)$ chain leads to the enhancement of the carbon flux to CH_2O and fewer to carbon atoms ending up in CH_3 , which is not the case of the methane chemistry blended with NH_3 ; where all the CH_4 is consumed first by H abstraction to form CH_3 .

Figure 9. (a) Variation of S_L with χ_{DMM} or χ_{CH_4} relative to neat NH_3 (solid lines are the simulation results), (b) enhancement factor, ξ_E , versus Φ for a given χ_{DMM} or χ_{CH_4}

3.4 Ammonia-DMM flame chemistry

Despite some discrepancy between the model predictions and measurements for the blended system, the present model accurately follows the experimental trend highlighting its capability in describing the flame kinetics. To explore the essential reaction pathways for laminar burning

velocity prediction that could be of interest for future study for developing a comprehensive model, a reaction flow analysis and sensitivity analysis are conducted and discussed. For brevity, we will analyze the stoichiometric NH_3/DMM -air flames, where we also observed the highest discrepancy between model prediction and experiment for $\chi_{\text{DMM}} = 0.6$. The discussion will be based on the results obtained from the current composite kinetic model. The major reaction pathways are identified by employing integrated mass flux analyses based on C-atoms and N-atoms for stoichiometric NH_3/DMM blends of two cases: $\chi_{\text{DMM}} = 0.2$ and 0.6 (see Fig. 10). Reaction path analyses (Fig. 10a) reveals that DMM mainly undergoes H-atom abstraction at the terminal carbon atom by reactive H and OH species mostly to form $\text{CH}_3\text{OCH}_2\text{OCH}_2$ via, reactions R1 and R2, respectively.

As the χ_{DMM} in the blend increases, more reactive intermediate species (H, O, and OH) are formed (see Fig. 11). Not surprisingly, a higher yield of $\text{CH}_3\text{OCH}_2\text{OCH}_2$ radicals is achieved for higher mole fraction of DMM, e.g., 82% and 91% for $\chi_{\text{DMM}} = 0.2$ and 0.6 , respectively. Regardless of χ_{DMM} , all $\text{CH}_3\text{OCH}_2\text{OCH}_2$ radicals undergo thermal unimolecular dissociation to form CH_3OCH_2 (67%) and CH_2O (33%). The formed CH_3OCH_2 radical will readily decompose to CH_2O (50%) and CH_3 (48%). Also, a portion of CH_3 reacts with O-atom to form CH_2O via reaction R3, and a small fraction of CH_3 reacts with NO_2 to form CH_3O through reaction R4. However, it is interesting to see that as χ_{DMM} increases from 0.2 to 0.6 , HO_2 radical also participates in converting CH_3 to CH_3O via reaction R5, which is not seen for $\chi_{\text{DMM}} = 0.2$.

The importance of HO₂ radical at higher χ_{DMM} is shown as the reaction R5 can be linked to the path NNH→N₂ (see Fig. 10b). At $\chi_{DMM} = 0.2$ NNH is mainly decomposed to N₂+H via thermal dissociation channel, however, at $\chi_{DMM} = 0.6$ NNH reacts mostly with O₂ to form N₂+HO₂ and minor contribution is via thermal dissociation channel and vice versa. The HO₂ radical formed (at $\chi_{DMM} = 0.6$), reacts with CH₃ via reaction R5 to give CH₃O, which further thermally dissociates to give CH₂O+H. In this sequence, the less reactive HO₂ radical is consumed to form more reactive H-atom. The reaction NNH+O₂=N₂+HO₂ becomes vital in producing the HO₂ radical, and the reaction rate of this reaction certainly controls its formation. This partially explains why the present model predicted higher flame velocity at the stoichiometric condition $\chi_{DMM} = 0.6$ compared to $\chi_{DMM} = 0.2$ and the reaction rate of this reaction requires further investigation based on the present analysis. However, no attempt is made to investigate the sensitivity of the reaction rate of this reaction (NNH+O₂=N₂+HO₂) on model prediction, which is beyond the scope of the present study. This also further leads to the conclusion as to why the current model predicted higher flame velocity at lean condition (excess oxygen) for all the χ_{DMM} investigated compared to rich condition (see Figure 8). As can be seen in Fig. 10a, higher hydrocarbon intermediates (C₂ species) are formed following the reaction sequence: DMM→CH₃OCH₂OCH₂→CH₃OCH₂→CH₃(+CH₃). Unsurprisingly, the formation of C₂ species is favoured by 4% more for $\chi_{DMM}=0.6$ as compared to $\chi_{DMM} = 0.2$, leading to the conclusion that higher DMM content in the blend favours higher hydrocarbon formation. Formaldehyde (CH₂O) follows the usual route by reacting with H atom and OH radical to form formyl radical (HCO) which subsequently undergoes thermal dissociation to form CO and H atom. The formed CO then reacts with OH radicals to form CO₂ (see the reaction sequences R6-R9 below).

Figure 10b shows the reaction path analysis for NH_3 consumption. The reaction is initiated by H-abstraction with OH radicals and H-atom to form amidogen (NH_2) radical (reactions R10 and R11).

Figure 10. Integrated reaction flow analysis for the degradation of DMM based on C-atom (a) and for NH_3 based on N-atom (b) of the stoichiometric DMM- NH_3 flames at $\chi_{\text{DMM}} = 0.2$ and 0.6 using the current composite model. The radicals indicated along the arrows are ordered from top to bottom according to their contribution to the particular reaction pathway.

Consecutive reactions of NH_2 with OH and H yield NH, whereas its reaction with O atom generates HNO radical (see reaction sequences R12-R15). The flow analysis reveals that the pathway leading to HNO is favoured more at higher DMM content in the blend. For example, increasing χ_{DMM} from 0.2 to 0.6, HNO formation path is favoured 15% more, and the reaction pathway leading to imidogen radical (NH) is inhibited by 5%. This observation is also in line with the sensitivity plot

shown in Fig. 12, where R12 shows the highest negative sensitivity. The reaction flow analysis (Fig. 10b) also indicates that a small fraction of NH_2 reacts with NO to form NNH (7%, and 9% for $\chi_{\text{DMM}} = 0.2$ and 0.6, respectively). This chain propagating reaction $\text{NH}_2 + \text{NO} = \text{NNH} + \text{OH}$ (R15) appears among the most sensitive reactions for the laminar burning velocity (see Fig. 12).

Imidogen (NH radical) further undergoes several reaction channels (R16-R24) to finally yield N_2 . One possible route occurs via H-atom abstraction of NH radicals by H and OH, forming N atoms which eventually lead to N_2 by reacting with NO. In another route, NH can also react with OH and O_2 to form HNO which can react with OH, and H to form NO, and NO can eventually yield N_2 via reactions R22, R23, and R24. The reaction of NH radical with NO forming N_2O is also a major channel for NH loss, reaction (R25). The N_2O formed exclusively goes to N_2 by reacting with H-atom ($\text{N}_2\text{O} + \text{H} = \text{N}_2 + \text{OH}$).

The model suggests that cross-reactions between the carbon and nitrogen family plays a minor role. For example, reaction $\text{CH}_3 + \text{NH}_2 = \text{CH}_3\text{NH}_2$ contributes $\sim 1\%$ and $\sim 2\%$ of NH_2 consumption for $\chi_{\text{DMM}} = 0.2$ and 0.6 , respectively, and reaction $\text{CH}_3 + \text{NH} = \text{CH}_2\text{NH} + \text{H}$ contributes $\sim 2\%$ and 5% for $\chi_{\text{DMM}} = 0.2$, and 0.6 , respectively, for NH loss (not shown in Fig. 10). This may indicate that the interactions between C and N containing species are insignificant for the prediction of the laminar burning velocity and the flame structure. The sensitivity analysis displayed in Fig. 12 further justifies this argument.

Therefore, the oxidation of NH_3/DMM -air blends can be understood as parallel oxidations processes of the individual fuel components. However, in the process of dual-fuel oxidation, both components share the same OH , H , and O radical pool, thereby influencing the chemistry of DMM and NH_3 indirectly. These parallel oxidation processes are in line with the reactions flow analyses of NH_3/CH_4 -air flames at $\Phi = 1$, undertaken by Okafor *et al.*[2]. For these NH_3 -dual fuel systems, similar reactions involving OH , H , and O species govern the kinetics, and hence they will have a significant influence on the laminar burning velocity. To explore the impact of χ_{DMM} on these key radicals, OH , O , H , and CO radicals and temperature profiles were computed for the un-stretched adiabatic DMM/NH_3 -air flames at $\Phi = 1$ and $\chi_{\text{DMM}} = 0.2, 0.6$ (see Fig. 11). Here, the x-axis represents the computational domain. As seen, the mole fractions of all radicals decrease with decreasing χ_{DMM} (increasing $\text{NH}_3\%$). In addition to the decline of the radical concentrations, the mole fraction profiles are also shifted towards the post-reaction zone for low χ_{DMM} , which is also evident in the temperature profile. The relatively low flame speed for low χ_{DMM} can be attributed to the decrease in the temperature, mainly in the reaction zone. Therefore, the overall reactivity may slow down by the enhanced chain-terminating reactions stemming from NH_3 chemistry. An increase in χ_{DMM} promotes the reactivity as demonstrated by the chain branching reaction,

CO+OH=CO₂+H, which is the second most sensitive reaction in positive direction influencing S_L , and its influences increase with χ_{DMM} (see Fig. 12).

Figure 12 shows the top 15 sensitive reactions for the un-stretched laminar burning velocity of DMM/NH₃-air flame at $\Phi = 1$, and various χ_{DMM} . For the sake of comparison, the sensitive reactions of neat NH₃-air flames are also presented. In all cases, the chain branching reaction (O₂+H=OH+O) appears to be the most sensitive reaction. For neat NH₃, the most influential reactions for S_L , through controlling H and OH radical concentrations, include R15, R20, R21, R22 and R26 (see Fig. 12a).

From nitrogen chemistry, the chain propagating reaction, R15 appears to be the second most crucial reaction affecting the radical concentration after O₂+H=OH+O reaction, whereas reactions R20, R21, and R22 show negative influence on the radical pool [2, 46]. Reaction R26 does not show sensitivity towards DMM/NH₃ blends; however, it is the third most sensitive reaction (in a positive direction) for neat NH₃ flame (see Fig. 12a-b). For the neat ammonia flame, reaction R26 shows a positive influence on S_L , where HNO radical is produced via the recombination of NO and H-atom. However, the high HNO concentration may also promote the rate of H-atom and OH radical consumption through the reactions of R20 and R21. This is in line with the sensitivity analysis where these reactions (R20 and R21) have a negative impact on the laminar burning velocity. The same effect has been noticed for reaction R14. Though R14 produces H-atom, it exerts a negative impact on the flame speed through increased production of HNO radicals.

Figure 12b illustrates the sensitivity analysis for DMM/NH₃ blends. Some reactions, e.g., R14, R15, and R20, appear to be sensitive for both neat NH₃ and DMM/NH₃ blends which influence H,

OH and O radical pool, and promote the production of HNO. In addition, R16 and R18 also appear to be sensitive reactions for $\chi_{DMM}=0.2$ blend. These reactions form HNO and NO radicals which have a negative influence on OH radical concentration, and thereby on S_L . Reaction R14 displays the highest sensitivity in the negative direction, but its sensitivity decreases with the increase in χ_{DMM} . The production of HNO via R14 and R16 enhances the negative effect on the flame speed via R20.

Figure 11. Temperature, and OH, O, H and CO radicals profiles for unstretched adiabatic DMM/NH₃-air flames at $\Phi = 1$ and $\chi_{DMM} = 0.2$ and 0.6

Figure 12. First-order normalized sensitivity of unstretched laminar burning velocity of stoichiometric: (a) NH_3 -air flames and (b) NH_3/DMM -air flames at various χ_{DMM} . Positive sensitivity means that the reactions enhance the flame speed, and the negative sensitivity indicates that the reaction retards the flame speed.

As shown in Fig. 12b, the impact of the reactions from the nitrogen chemistry decreases with increasing χ_{DMM} . For high χ_{DMM} , DMM chemistry dominates by enhancing the flame speed of the blends via the core of H_2/CO mechanism. As can be seen, $\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$ (R9), and $\text{HCO} (+\text{M}) = \text{H} + \text{CO} (+\text{M})$ (R8) are the second and the third most sensitive reactions. Reaction R8 facilitates H-atom production, and at the same time, it also promotes CO production. The formed CO reacts with OH radicals via R9 to produce more H-atoms, which eventually enhances the flame speed. Reactions of H atoms with HCO ($\text{HCO} + \text{H} = \text{CO} + \text{H}_2$) and OH ($\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$) are the second and the third most sensitive reactions in the negative direction. These are termination reactions and hence retard the flame speed. As seen in Fig. 11, the temperature begins to rise as CO starts to evolve in the system, revealing that the reactions involving CO are more sensitive for the temperature profile. In CO/NH_3 -air mixtures with low χ_{NH_3} , Han *et al.* [28] showed that H-atoms, formed by the decomposition of NH_3 , were found to enhance the combined CO oxidation and

H₂/O₂ mechanisms by the increase of H and OH radical pools which led to the rapid increase of S_L . Their findings can be integrated into the current outcome where blends with higher χ_{DMM} produce a higher yield of CO at early times, which then expedites the flame speed (see Fig. 11). However, at low χ_{DMM} , the shortage of H and OH radical pools and low CO concentration prevents early CO initiation, which explains the observed trend of decreasing S_L with the increase of χ_{NH_3} . Therefore, the reactions of the carbon family are more important for expediting the laminar flame speed of the studied blends. As expected, the sensitivities of N-containing reactions are significantly decreased for $\chi_{DMM} > 0.2$ blends. Furthermore, it may be observed that the reactions involving HO₂ radical show increased sensitivity with the increase of χ_{DMM} (see Fig. 12b). The reason may be due to the presence of activated methylene group bound to the oxygen atoms (-O-CH₂-) in DMM, which leads to the formation of hydroperoxy alkyl radical in the early stage of the combustion as pointed out by Shrestha *et al.* [67].

A close inspection of Fig. 8 revealed that rich mixtures show less attenuation in S_L as compared to the lean mixtures. This observation can be explained with the aid of Fig. 13, where the mole fraction profiles of OH, O, H and CO radicals are presented for $\Phi = 1.2$. The decreased concentration of OH and O for rich flames, as opposed to the stoichiometric mixture, is not surprising. However, rich flames ($\Phi = 1.2$) show a significant increase of CO and H concentration as compared to that for $\Phi = 1$ (see Fig. 11 and 13). For the rich mixtures, CO+OH = CO₂+H (R9) plays a crucial role in enhancing the flame speed.

Figure 13. OH, O, H, and CO radicals profiles for unstretched adiabatic DMM/NH₃-air flames for $\Phi = 1.2$, and $\chi_{DMM} = 0.2$ and 0.6

Figure 14 shows sensitivity analysis for the unstretched laminar burning velocity for various DMM/NH₃ flames at $\Phi = 1.2$. As seen, $\text{HCO} (+\text{M}) = \text{H} + \text{CO} (+\text{M})$ appears to be the second most sensitive reaction in the positive direction followed by the $\text{CO} + \text{OH}$ reaction. Our reaction path analysis reveals that $\text{HCO} (+\text{M}) = \text{H} + \text{CO} (+\text{M})$ is the dominant path for the formyl radical consumption. A similar conclusion was made by earlier studies [68, 69] indicating that the net HCO to CO conversion facilitates the H-atom radical production, and hence promotes the chain branching reactions. This explains the observed higher concentrations of CO and H radicals for rich NH₃-DMM flames, and thus their effects on the enhancement of laminar flame speed (S_L).

Figure. 14. First-order normalized sensitivity of unstretched laminar burning velocity of NH_3/DMM -air flames for various χ_{DMM} and $\Phi = 1.2$.

NO_x emission during ammonia combustion is a major concern which needs a closer attention before NH_3 can be realized as a potential future fuel for practical applications. Here, we briefly assess the impact of χ_{DMM} on NO emissions for DMM/NH_3 blends. Fig. 15 illustrates the predicted NO mole fraction for varying DMM mole fractions in a stoichiometric mixture. As seen, NO production increases initially approaching its peak at $\chi_{\text{DMM}} = 0.3$ before it starts decreasing for higher DMM content in the NH_3/DMM blends. Neat DMM shows negligible NO emissions as expected. In ammonia flames, NO is generated via the oxidation pathways of NH_i ($i=0, 1, 2$) radicals, mainly through an HNO intermediate. NH_i radicals plays a critical role to reduce NO via $\text{NH}_i + \text{NO}$ reaction. The key combustion species for converting NH_i into NO are O , OH , H and O_2 . Under flame conditions, the increased concentration of these species favors the conversions of NH_i to NO , and may inhibit the reduction of NO by NH_i radicals. Higher NO formation for the low mole fractions of DMM highlights the role of NH_i species, and also the prompt NO channel via CH route (see Fig. S3 for NH_2 and CH radicals profiles for unstretched adiabatic neat NH_3 ,

DMM, and DMM/NH₃-air flames at $\Phi = 1$). The negligible NO formation in the neat DMM flames compared to the DMM/NH₃ blends indicates that the prompt NO contribution to the NO formation is minor compared to the fuel NO pathway. However, we note here that the results displayed in Fig. 15 strongly depends upon the adiabatic flame temperatures and the equivalence ratio. In rich ammonia flames, the combination reaction of NH_i radicals dominate which eventually lead into the formation of N₂. Consequently, NO production is low for NH₃ rich flames. Therefore, one can conclude that the NO level is mainly governed by the levels of O/H and NH_i radicals. Moreover, the oxidation of HCN can also affect NO formation. HCN is found to decrease with increasing χ_{DMM} (See Fig. S4 in the supplementary material). This warrants further investigation to explore the cross-reactions between carbon and nitrogen family impacting the NO emissions for various DMM/NH₃ blends at different equivalence ratio. To conclude, the addition of DMM to NH₃ does not necessarily decrease the NO emission in the flame as one would expect. However, the model suggests that NO would start to decrease after reaching a certain mole fraction of DMM which is an interesting observation. This warrants further verification through speciation measurements.

Figure 15. NO mole fraction at the post-flame zone as a function χ_{DMM} at $\Phi = 1$, $P_i = 0.1$ MPa, and $T_i = 298$ K.

Conclusions

Combustion characteristics NH_3 blended with dimethoxymethane (DMM) were investigated using a constant volume chamber. This study finds that DMM/ NH_3 blend can be a promising renewable fuel with enhanced combustion characteristics. In this work, the un-stretched adiabatic laminar burning velocity (S_L) was measured for various DMM/ NH_3 blends ($\chi_{\text{DMM}} = 0.2$ to 0.6) at 298K and 0.1 MPa , and $\Phi = 0.8$ to 1.3 . In addition, numerical simulations using an assembled chemical kinetic model of NH_3 and DMM sub-mechanisms were used to predict measured S_L . Some of the key findings are:

1. Addition of DMM was found to enhance the un-stretched laminar burning velocity significantly. For example, S_L relative to neat NH_3 -air flames (NH_3 -air flames data were taken from [28]) is enhanced by $\sim$ factor of 3 for the blend containing $\chi_{\text{DMM}} = 0.2$ at $\Phi = 1.1$, and by $\sim 125\%$ compared to CH_4/NH_3 blend at $\chi_{\text{DMM}} = \chi_{\text{CH}_4} = 0.6$, $\Phi = 1.1$. Interestingly, the highest enhancement of the flame speed with DMM was found at the richest and leanest limits.
2. The sensitivity of the flame to the stretch rate increases with a shift of Φ towards leaner mixtures and lower ammonia concentrations. This is indicated by a decrease in the burned gas Markstein length, L_b , with an increase in Φ (especially in the lean mixture blends).
3. Blending DMM with NH_3 leads to an opposite evolution of L_b with Φ relative to the observed L_b / Φ evolution in neat NH_3 flames which showed negative values of L_b at lean NH_3 -air flames.
4. The significant decrease in L_b for the lean blend flames with Φ was driven mainly by the decline in lewis number (Le), while both preheat flame thickness (δ_L), and Zeldovich-number

- (Ze) showed minor impacts. At the same Φ (lean mixtures), despite the notable decrease in both δ_L and Ze with χ_{DMM} , L_b was found to increase because of the significant rise of Le .
5. For DMM/ NH_3 rich flames ($Le \approx 1$, with no change with χ_{DMM}), at high $\chi_{DMM} = 0.3-0.6$, δ_L shows a negligible variation with Φ . However, for rich mixture at $\chi_{DMM} = 0.2$, δ_L is relatively high and increases with Φ , leading to a slight increase of the flame sensitivity to the stretch rate. Moreover, the flame speed-stretch rate relationship shows different trajectories depending on Le number.
 6. The proposed NH_3 /DMM chemical kinetic model performs excellently to predict S_L for neat DMM flames and shows a reasonably good S_L prediction for neat NH_3 flames. Also, the model does reasonably well to capture the experimental data of DMM/ NH_3 blends.
 7. Reaction path analyses indicate that the oxidation of NH_3 /DMM blend can be treated as a parallel oxidation process of the individual fuels, which compete for the same radical pool (OH , H , O) thus making the chemical system to be interwoven.
 8. The dominant rate-limiting reactions in DMM/ NH_3 flames, which govern the oxidation of NH_3 are $\text{NH}_2 + \text{NO} = \text{NNH} + \text{OH}$ and $\text{NH}_2 + \text{O} = \text{HNO} + \text{H}$. These reactions have the most control over the radical pools for NH_3 oxidation and thus impact significantly to S_L . The early arrival of CO radical in the flame compensates the shortage of the O and OH radicals for the rich flames, which enhances the flame laminar burning velocity.

Acknowledgements

The research reported in this publication was supported by the Office of Sponsored Research (OSR) at King Abdullah University of Science and Technology (KAUST).

Supporting information material

The supporting information material file contains four supporting figures. In Fig. S1, the OH, H, O, and HO₂ radicals profiles for unstretched adiabatic DMM/NH₃-air flames at $\Phi = 1$ for varies DMM/NH₃ blends are presented. The variation of the adiabatic flame temperature of DMM/NH₃-air flames with Φ for the different DMM/NH₃ blends are shown in Fig. S2. Figure S3 illustrates the NH₂ and CH radicals profiles for unstretched adiabatic DMM/NH₃-air flames for $\Phi = 1$ premixed mixtures. Finally, the HCN radicals profiles for unstretched stoichiometric DMM/NH₃-air flames are presented for varies DMM/NH₃ blending ratios.

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