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A comprehensive experimental and modeling study of the ignition delay time characteristics of ternary and quaternary blends of methane, ethane, ethylene, and propane over a wide range of temperature, pressure, equivalence ratio, and dilution

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ABSTRACT

The ignition delay time (IDT) characteristics of new ternary and quaternary blended $C_1 - C_3$ gaseous hydrocarbons, including methane/ethane/ethylene and methane/ethane/ethylene/propane, are studied over a wide range of mixture composition, temperature ($\sim 800 - 2000$ K), pressure ($\sim 1 - 135$ bar), equivalence ratio ($\sim 0.5 - 2.0$), and dilution ($\sim 75 - 90\%$) using both experimental data and kinetic modeling tools. In this regard, all of the experimental tests were designed using the Taguchi approach (L_9) to fulfill the experimental matrix required to generate a comprehensive set necessary to validate a detailed chemical kinetic model. High- and low-temperature IDTs were recorded using low/high-pressure shock tubes (L/HPST) and rapid compression machines (RCM), respectively. The model predictions using NUIGMech1.2 are evaluated versus all of the newly recorded experimental data. Moreover, the individual effects on IDT predictions of the parameters studied, including mixture composition and pressure, are investigated over the temperature range. The results show that NUIGMech1.2 can reasonably reproduce the experimental IDTs over the wide range of the conditions studied. The constant-volume simulations using the chemical kinetic mechanism reveal the synergistic/antagonistic effect of blending on IDTs over the studied temperature range so that IDTs in certain temperature ranges are very sensitive to even small changes in mixture composition.

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1. Introduction

The combustion of low-carbon fuels ($C_1 - C_3$) for energy and power generation is a very promising step towards future low-to-zero emission energy production. Thus, gaining a deep understanding of the combustion chemistry of such fuels and their blends is important. Hence, the development of high-fidelity chemical mechanisms which can satisfactorily explain the oxidation and pyrolytic characteristics of low-carbon fuels is demanding. Together with speciation and laminar burning velocity techniques, ignition delay times (IDTs) are important in the validation of chemical kinetic

mechanisms [1, 2]. Developing a comprehensive experimental IDT database that can stochastically and unbiasedly cover a wide range of operating conditions, including pressure, temperature, equivalence ratio, and dilution, is essential in this regard. Such a database can efficiently support the development of high-fidelity chemical kinetics, which can be validated against all available experimental IDT data. To do so, Baigmohammadi et al. [2] studied the IDT characteristics of $C_1 - C_2$ pure hydrocarbons including methane (CH_4), ethane (C_2H_6), and ethylene (C_2H_4) fuels [2] as well as their binary blends [3]. Subsequently Martinez et al. [4] extended this work for higher hydrocarbon by investigating the IDTs of binary blends of C_2H_4 /propane (C_3H_8) and C_2H_6 / C_3H_8 mixtures in a shock tube (ST) and in a rapid compression machine (RCM) over a wide range of temperature, pressure, equivalence ratio, and dilution conditions.

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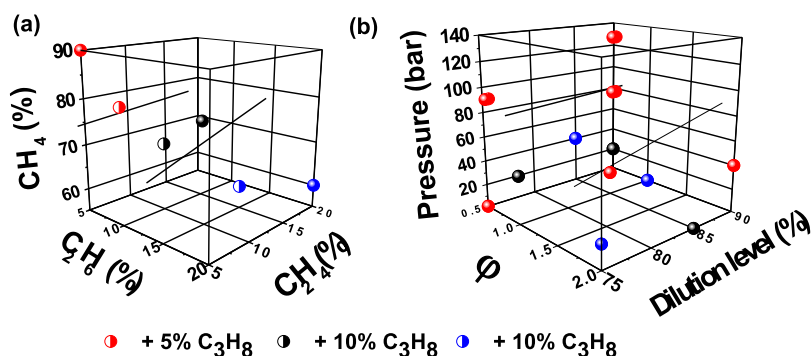


Fig. 1. Experimental tests performed in the current study for% vol. composition of (a) ternary ($\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$) blends represented in solid symbols and quaternary ($\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$) blends represented in half solid symbols, and (b) the input conditions for $\text{C}_1 - \text{C}_3$ blends studied in the current work at various equivalence ratios (x-axis), pressures (y-axis) and dilution levels (z-axis).

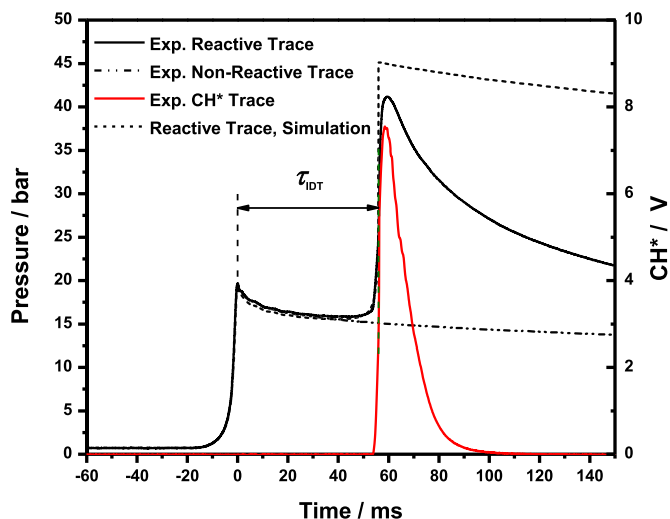


Fig. 2. Definition for measuring IDT in the NUIG-RCM using Kistler pressure trace and PMT-CH* trace mounted on the side wall of the reaction chamber.

As these previous studies focused on the IDT studies of single and binary blended fuel mixtures, *this paper* intends to examine the IDT behaviours of ternary and quaternary blends of $\text{C}_1 - \text{C}_3$ hydrocarbons with relevance for engine and gas turbine applications. Furthermore, although there is enough data recorded in the literature for the IDT characteristics of $\text{C}_1 - \text{C}_3$ alkane blended fuels and natural gas mixtures (NG) [3-11], evidence of the effect of adding an olefin to $\text{C}_1 - \text{C}_3$ alkane blends on IDTs has not been reported to date. Thus, towards developing a comprehensive IDT database, we have designed a set of IDT experiments to cover this void over a wide range of pressure, temperature, equivalence ratio, and dilution (Fig. 1). The new experimental data sets are designed to explore the IDT characteristics of ternary and quaternary blends of $\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ and $\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$ mixtures.

Furthermore, providing stochastically and unbiasedly distributed experimental IDTs over a wide range of pressure, temperature, equivalence ratio, dilution with varying ethylene concentrations can help researchers develop more sophisticated and higher fidelity chemical kinetics. It can also lead to a valuable database capable of resembling the IDT characteristics of modified NG mixtures for a wide range of applications such as industrial furnaces and internal/external combustion engines working under homogeneous charge compression ignition (HCCI), exhaust gas recirculation (EGR), and moderate or intense low oxygen dilution combustion regimes.

To achieve this, the current experimental and simulation study was defined, and the number of desired IDT experiments were op-

timised, covering the target operating conditions discussed above using the Taguchi [5] design of experiments (DOE) approach as shown in Fig. 1. However, high-pressure (> 40 bar) tests were added to the Taguchi matrix to develop the database further. As shown in Fig. 1(a), the composition of the blends is distributed diagonally to cover the target fuel compositions. Fig. 1(b) demonstrates how using the Taguchi approach, we can reasonably populate the physical conditions in the desired cube so that a wide range of conditions can be covered without performing an overwhelming number of IDT experiments. The designed experiments encapsulate equivalence ratios of 0.5, 1.0, and 2.0 in 'air', at pressures (p_5 and p_C) of 1, 20, 40, 90, and 135 bar, for diluent (N_2 and Ar) concentrations of 75%, 85%, and 90% of reactive mixtures in the temperature (T_5 and T_C) range of $\sim 800 - 2000$ K. The detailed kinetic mechanism NUIGMech1.2 is used to evaluate all of the newly measured experimental data, and the important reactions are identified to determine the synergistic/antagonistic effects of various blending effects on the IDTs.

The current study is organized in three stages, including (i) the design of new experiments over a wide range of operating conditions using the Taguchi approach; (ii) experimental measurements; and (iii) simulations using NUIGMech1.2. Comprehensive Supplementary material files containing non-reactive traces for RCM simulations, the original spreadsheets of experimental tests, L/HPST oscilloscope traces, and the combined figures of reactive, non-reactive, and modeling pressure traces are provided along with this paper. Moreover, the general information about the gasses (fuel/oxygen/argon/nitrogen), experimental facilities, and data acquisition systems are also accessible as Supplementary Material.

2. Design of experiments and experimental approach

As mentioned above, all of the new IDT experiments were designed using an L_9 Taguchi matrix to optimally reduce the number of experiments and time required. The Taguchi approach can tackle the issue using a specific design of orthogonal arrays which permits a comprehensive experimental investigation by doing a minimal number of experimental tests. In this regard, the minimum number of experiments is determined as follows:

$$N_{\text{Taguchi}} = 1 + NF(L - 1) \quad (1)$$

where, N_{Taguchi} , NF , and L are the number of experiments, number of factors, and number of levels, respectively. According to the Taguchi approach, its performance is optimal when there are limited interactions between the desired variables. To use the Taguchi method, it is essential to define the controlling factors and levels. According to the factors and levels, several design of experiments (DOE) matrices are derived and are included as Supplementary material. The DOE process was followed for four param-

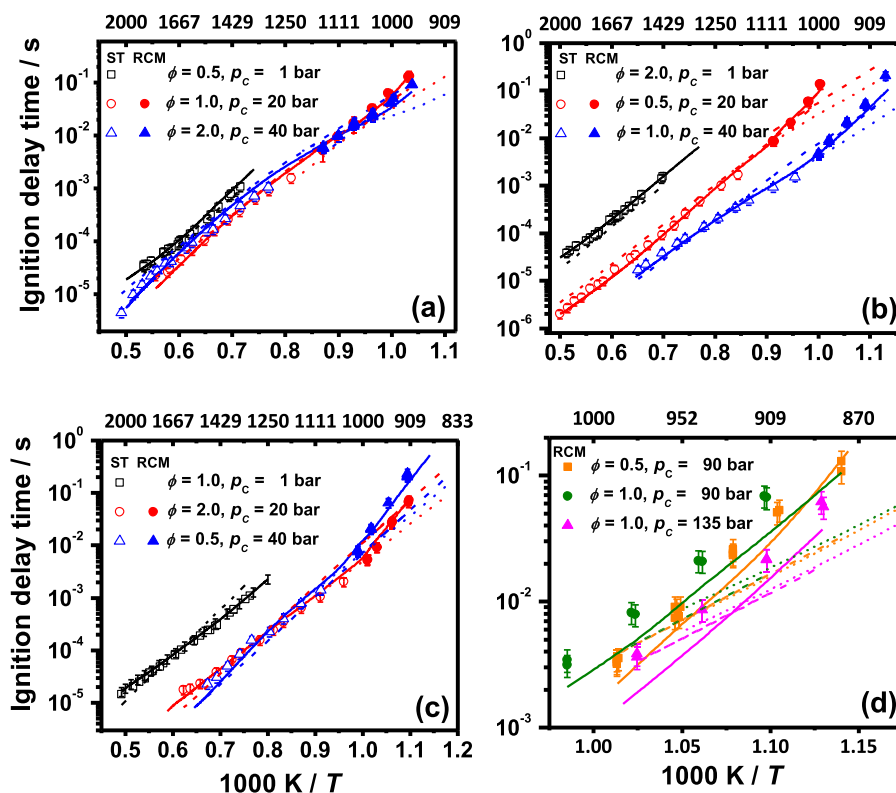


Fig. 3. Experimental and simulated IDT data of $\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ mixtures. (a) 90% $\text{CH}_4/5\% \text{C}_2\text{H}_4/5\% \text{C}_2\text{H}_6$ blend at 75% N_2 (black square symbols/lines), 75% $\text{N}_2+10\% \text{Ar}$ (red circle symbols/lines), and 75% $\text{N}_2+15\% \text{Ar}$ (blue triangle symbols/lines), (b) 75% $\text{CH}_4/12.5\% \text{C}_2\text{H}_4/12.5\% \text{C}_2\text{H}_6$ blend at 75% $\text{N}_2+10\% \text{Ar}$ (black square symbols/lines), 75% $\text{N}_2+15\% \text{Ar}$ (red circle symbols/lines), and 75% N_2 (blue triangle symbols/lines), (c) 60% $\text{CH}_4/20\% \text{C}_2\text{H}_4/20\% \text{C}_2\text{H}_6$ blend at 75% $\text{N}_2+15\% \text{Ar}$ (black square symbols/lines), 75% N_2 (red circle symbols/lines), and 75% $\text{N}_2+10\% \text{Ar}$ (blue triangle symbols/lines), (d) 90% $\text{CH}_4/5\% \text{C}_2\text{H}_4/5\% \text{C}_2\text{H}_6$ blend at 90 bar with 67.8% $\text{N}_2+7.5\% \text{Ar}$ (olive green circle symbols/lines), and at 135 bar with 68.3% $\text{N}_2+17\% \text{Ar}$ (magenta triangle symbols/lines). Solid lines: NUIGMech1.2; dashed lines: derived correlations; and dotted lines: CV – low-temperature simulations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ters of ternary and quaternary fuel combinations, pressure, equivalence ratio, and dilution at three levels, where the details are shown in Fig. 1 and Table 1. As previously discussed by Baigmoammadi et al. [2, 3], the new IDT experimental data presented in Table 1 were collected using low- and high-pressure shock tubes (L/HPST) and RCMs refers to the low pressure shock tube, the high pressure shock tube and the (red) rapid compression machine facilities at C^3 -NUI Galway, respectively, and PCFC refers to the RCM facility at PCFC RWTH Aachen University.

In the RCM facilities, the IDT of the normal studied mixtures (diluent concentration = 75%) and the pressure/time histories of their relevant non-reactive mixtures were recorded using a Kistler 6045A transducer mounted in the reaction chamber wall. However, the IDTs of mixtures at 85% and 90% dilution and at post-compression pressures of 20 and 40 bar were recorded using both the Kistler pressure record and light emission using a photomultiplier (PMT) equipped with a CH^* filter due to the weak pressure signal observed at these diluted conditions. Therefore, as shown in the figure below, the IDT is defined as the maximum gradient in pressure or CH^* after compressing the studied mixture. The following figure illustrates the IDT definition for experiments and simulations of the RCM data measured in the current work. More detailed information of the LPST, HPST, NUIG-RCM and PCFC-RCM data is included in Section 5 of the Supplementary material.

2.1. Uncertainty analysis

The details of the uncertainty analysis are provided as Supplementary material. However, a synopsis is presented here. The presented uncertainty analysis is adopted based on the methods ap-

plied by Petersen et al. [6] and Weber et al. [7]. According to our analyses [2, 3], the average uncertainties in the compressed mixture temperatures (T_5 or T_C) and measured IDTs ($\sigma_{IDT}\%$) in the NUIG STs and RCM are estimated to be approximately $\pm 20 \text{ K}$ and $\pm 25\%$ (in the H/LPSTs) and $\pm 5 - 15 \text{ K}$ and $\pm 20\%$ (in the RCM), respectively over the entire range of cases studied. The uncertainty in the PCFC RCM is estimated using the methods described in Ramalingam et al. [8], and for the compressed temperature, the uncertainty is estimated to be within $\pm 5 \text{ K}$, with a measurement uncertainty of $\pm 0.15 \text{ bar}$ for the compressed pressure and variation of $\pm 15\%$ for the IDTs.

3. Computational modeling

NUIGMech1.2 is developed as a further development/refinement of NUIGMech1.1 with the addition and modification of several important reactions which are discussed in more detail in Section 4.2 below. This mechanism includes 2746 species and 11,279 reactions and reproduces similar good results as those previously published using NUIGMech1.1 for the oxidation of $\text{C}_1 - \text{C}_6$ species [9–14]. These experimental and theoretical studies include natural gas mixtures [10], propane/propene blends [14], propyne [11], and the auto-ignition and pyrolysis studies of $\text{C}_2 - \text{C}_6$ alkenes [12, 13]. All of the simulations are conducted using a Python script based on the CANTERA [15] library for the ST simulation and CHEMKIN-Pro 18.2 [16] software for the RCM simulations. Details of these simulations have already been published [2, 3, 8, 17–20]. The effect of surface reactions on IDTs is ignored in our simulations [2, 3]. The definition of IDT is taken to be the maximum gradient of the CH^* species $\left. \frac{d\text{CH}^*}{dt} \right|_{\max}$ or the maximum gradient of pressure

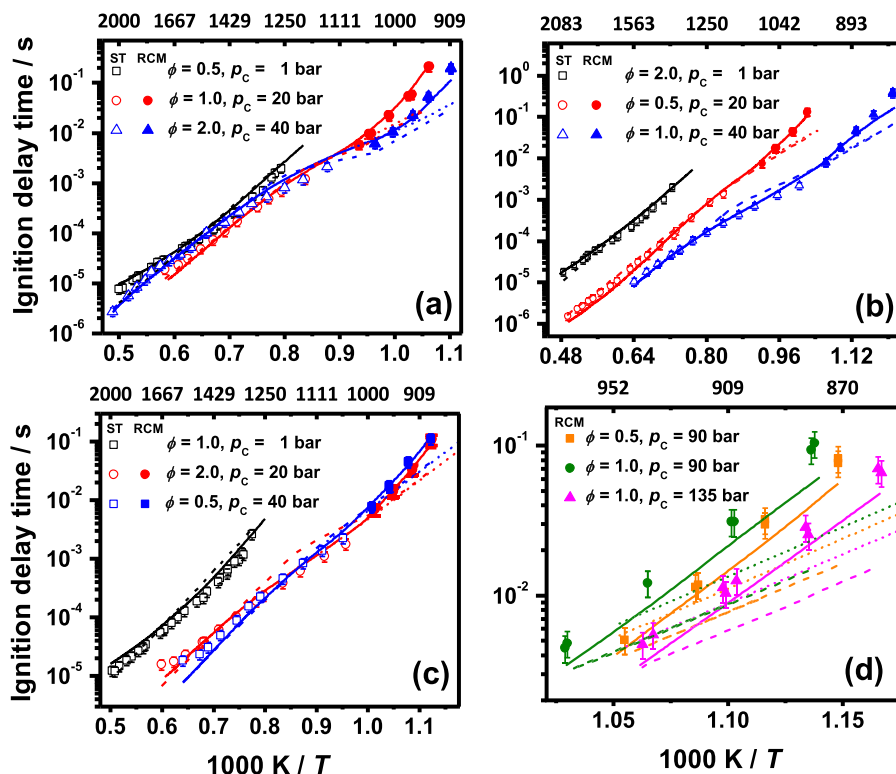


Fig. 4. Experimental and simulated IDT data for $\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$ mixtures. (a) 80% $\text{CH}_4/5\% \text{C}_2\text{H}_4/10\% \text{C}_2\text{H}_6/5\% \text{C}_3\text{H}_8$ blend at 75% N_2 (black square symbols/lines), 85% N_2 (red circle symbols/lines), and 90% N_2 (blue triangle symbols/lines), (b) 70% $\text{CH}_4/10\% \text{C}_2\text{H}_4/10\% \text{C}_2\text{H}_6/10\% \text{C}_3\text{H}_8$ blend at 75% $\text{N}_2+10\% \text{Ar}$ (black square symbols/lines), 90% N_2 (red circle symbols/lines), and 75% N_2 (blue triangle symbols/lines), (c) 60% $\text{CH}_4/15\% \text{C}_2\text{H}_4/15\% \text{C}_2\text{H}_6/10\% \text{C}_3\text{H}_8$ blend at 75% $\text{N}_2+15\% \text{Ar}$ (black square symbols/lines), 75% N_2 (red circle symbols/lines), and 85% N_2 (blue triangle symbols/lines), (d) 80% $\text{CH}_4/5\% \text{C}_2\text{H}_4/10\% \text{C}_2\text{H}_6/5\% \text{C}_3\text{H}_8$ blend at 90 bar with 68.1% $\text{N}_2+7.5\% \text{Ar}$ (orange square symbols/lines), 68.5% $\text{N}_2+17.1\% \text{Ar}$ (olive green circle symbols/lines), and at 135 bar with 68.5% $\text{N}_2+17.1\% \text{Ar}$ (magenta triangle symbols/lines). Solid lines: NUIGMech1.2; dashed lines: derived correlations; and dotted lines: CV – low-temperature simulations. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$\frac{dp}{dt}|_{\max}$ for the ST simulations. For the RCM simulations, the facility effects are included using the volume-time profiles derived from the non-reactive experimental pressure-time traces in which O_2 is replaced by N_2 in the mixture [18, 21].

To identify the controlling chemistry both promoting and inhibiting the reactivity of the system and thus their effect on IDT predictions, we present sensitivity analyses based on the brute force definition, with the definition of sensitivity coefficient (S) in Eqn. (2) [22] being:

$$S = \frac{\ln(\tau^+/ \tau^-)}{\ln(k^+/k^-)} = \frac{\ln(\tau^+/ \tau^-)}{\ln(2.0/0.5)} \quad (2)$$

This sensitivity coefficient is calculated for every reaction included in the chemical kinetic mechanism of interest. The IDT (τ) is perturbed through direct changes in the pre-exponential factor in the Arrhenius equation. S can be either positive or negative, with a positive value corresponding to a reaction that inhibits reactivity giving longer IDTs and vice versa. Moreover, the flux analyses presented in this work are based on rate of production (ROP) analyses performed to track the consumption of the main components in the different mixture compositions as their intermediates species.

A global analysis of regressions implemented to correlate simulated IDTs assuming constant volume conditions using NUIGMech1.2 is presented in Section 4.4. Moreover, the respective correlation equations and their coefficient values for specific conditions, based on various temperatures, pressure, equivalence ratios, and different fuel mixtures composition, are also provided. General correlations are intended to be a practical engineering tool to quickly and accurately calculate IDTs at the required condition. A

more complete and fully detailed Tables S12 – S15 of correlation values, standard errors, and performance are included as Supplementary material.

4. Results and discussions

A comprehensive comparison between the experimental IDTs (Table 1) and those predicted using NUIGMech1.2 is presented below.

4.1. Performance of NUIGMech1.2 and the correlations versus experimental data

The performance of NUIGMech1.2 compared to the new experimental ST and RCM IDT data for various ternary and quaternary blends of $\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ and $\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6/\text{C}_3\text{H}_8$ fuels, Table 1, is shown in Figs. 3 and 4. The symbols refer to the experimental data, with the solid lines from NUIGMech1.2 simulations and the dashed lines representing the correlation equation results. These correlations are derived over well-defined conditions, as discussed in Section 4.4.

Figs. 3 and 4 show that NUIGMech1.2 can reasonably reproduce all of the measured IDTs over the stochastically distributed conditions studied. It not only reproduces the effects of mixture composition and temperature on IDTs, but it can also reliably predict the effects of pressure, equivalence ratio, and the effect of dilution except at very high-pressures (≥ 90 bar) where the model underpredicts the IDTs for the ternary blends of the $\text{CH}_4/\text{C}_2\text{H}_4/\text{C}_2\text{H}_6$ mixtures. A detailed comparison between the performance of NUIGMech1.2 and other available mechanisms is provided in Section 9

Table 1
CH₄/C₂H₄/C₂H₆ and CH₄/C₂H₄/C₂H₆/C₃H₈ mixture compositions in% mole volume in the current study. Where keywords LPST, HPST and RCM.

	No	% CH ₄	% C ₂ H ₄	% C ₂ H ₆	% C ₃ H ₈	% O ₂	% N ₂ + % Ar	ϕ	T _c (K)	p _c (bar)	Facility
CH ₄ /C ₂ H ₄ /C ₂ H ₆ 90%/5%/5%	1	4.29	0.24	0.24	0.0	20.24	75+0	0.5	1396–1874	1	LPST NUIG
	2	4.32	0.24	0.24	0.0	10.20	75+10	1.0	967–1797	20	HPST
	3	4.40	0.20	0.20	0.0	5.20	75+15	2.0	960–2033	40	RCM
CH ₄ /75.3%C ₂ H ₄ /C ₂ H ₆ 75%/12.5%/12.5%	4	5.70	0.90	0.90	0.0	17.50	75+0	1.0	885–1536	40	NUIG
	5	5.22	0.87	0.87	0.0	8.04	75+10	2.0	1432–1951	1	LPST NUIG
CH ₄ /C ₂ H ₄ /C ₂ H ₆ 60%/20%/20%	6	1.33	0.22	0.22	0.0	8.22	75+15	0.5	996–2001	20	HPST
	7	6.67	2.22	2.22	0.0	13.89	75+0	2.0	911–1604	20	RCM
	8	1.5	0.50	0.50	0.0	12.50	75+10	0.5	914–1484	40	NUIG
CH ₄ /C ₂ H ₄ /C ₂ H ₆ 90%/5%/5%	9	1.71	0.57	0.57	0.0	7.14	75+15	1.0	1311–2032	1	LPST NUIG
	10	4.24	0.24	0.24	0.0	20	67.8 + 7.5	0.5	877–987	90	RCM
	11	4.24	0.24	0.24	0.0	10	68.3 + 17	1.0	885–976	135	PCFC
CH ₄ /C ₂ H ₄ /C ₂ H ₆ /C ₃ H ₈ 80%/5%/10%/5%	12	4.24	0.24	0.24	0.0	10	68.3 + 17	1.0	911–1015	90	
	13	3.51	0.22	0.44	0.22	20.61	75+0	0.5	1259–2002	1	LPST NUIG
	14	3.58	0.22	0.45	0.22	10.50	85+0	1.0	941–1717	20	HPST
CH ₄ /C ₂ H ₄ /C ₂ H ₆ /C ₃ H ₈ 70%/10%/10%/10%	15	3.68	0.23	0.46	0.23	5.40	90+0	2.0	908–2049	40	RCM
	16	4.93	0.70	0.70	0.70	17.96	75+0	1.0	826–1561	40	NUIG
	17	4.62	0.66	0.66	0.66	8.41	75+10	2.0	1379–2062	1	LPST NUIG
CH ₄ /C ₂ H ₄ /C ₂ H ₆ /C ₃ H ₈ 60%/15%/15%/10%	18	1.15	0.16	0.16	0.16	8.36	90+0	0.5	977–2024	20	HPST
	19	6.42	1.60	1.60	1.07	14.30	75+0	2.0	890–1668	20	RCM
	20	1.41	0.35	0.35	0.24	12.64	85+0	0.5	891–1560	40	NUIG
CH ₄ /C ₂ H ₄ /C ₂ H ₆ /C ₃ H ₈ 80%/5%/10%/5%	21	1.63	0.41	0.41	0.27	7.28	75+15	1.0	1290–1987	1	LPST NUIG
	22	3.42	0.21	0.43	0.21	20.10	68.1 + 7.5	0.5	871–948	90	RCM
	23	3.43	0.21	0.43	0.21	10.08	68.5 + 17.1	1.0	857–941	135	PCFC
	24	3.43	0.21	0.43	0.21	10.08	68.5 + 17.1	1.0	879–972	90	

of the Supplementary material. Considering similar comparisons of C₁ – C₃ pure and binary fuels mixtures, including methane, ethane, ethylene, and propane, over the wide range of physical and chemical conditions presented previously by the authors [2–4], NUIG-Mech1.2 better reproduces the oxidation behavior of small hydrocarbon species compared to other similar available mechanisms [23–32].

4.2. Effect of blending on ignition

To determine the chemistry controlling ignition times of CH₄/C₂H₄/C₂H₆/'air' and CH₄/C₂H₄/C₂H₆/C₃H₈/'air' blends, Fig. 5(a) depicts the IDTs of single fuel mixtures of CH₄/'air', C₂H₄/'air', C₂H₆/'air', C₃H₈/'air', while binary mixtures of CH₄/C₂H₆/'air' are depicted together with the ternary and quaternary blends at fuel-stoichiometric condition, at a pressure of 40 atm and temperatures in the range 714 – 1667 K.

At first glance, in Fig. 5(a), the CH₄/'air' mixture is the slowest to ignite over the entire temperature range studied in this work, while the C₂H₆/'air' is the next slowest in the low-temperature regime (< 900 K), being ~25% faster than CH₄. However, C₂H₆/'air' becomes the second-fastest mixture to ignite, after ethylene, by inverting its trend at ~ T_c = 1100 K. Overall, C₂H₆/'air' mixtures are approximately an order of magnitude faster to ignite than CH₄ and are ~50% faster compared to the C₃H₈/'air' mixtures, but are slower by a factor of ~1.5 when compared to C₂H₄/'air' mixtures at temperatures higher than 1150 K. The C₂H₄/'air' mixtures are the fastest to ignite at high-temperatures, and exhibit shorter IDTs compared to the C₃H₈/'air' mixtures at temperatures below ~1050 K, with propane being the fastest fuel to ignite in the low-temperature regime.

To determine the chemistry controlling the reactivities of various fuel/'air' mixtures, reaction pathways based on multiple rate of production (ROP) analyses are illustrated in Fig. 6 for (i) the pure fuels in 'air', (ii) the 50% CH₄/50% C₂H₆ binary mixtures, (iii) the 50% CH₄/25% C₂H₄/25% C₂H₆/ ternary mixtures, and (iv) the 50% CH₄/16.66% C₂H₄/16.66% C₂H₆/16.66% C₃H₈ quaternary mixtures at p_c = 40 atm, ϕ = 1.0, for (a) T_c = 800 K and (b) T_c = 1450 K. The ROP analyses are implemented following a standardized elemental carbon balance. The normalised values above the arrow

denote the fractions of the parent fuel proceeding via various reaction pathways. Moreover, sensitivity analyses are performed at p_c = 40 atm, ϕ = 1.0, for (a) T_c = 800 K and (b) T_c = 1450 K to interpret the most sensitive reactions to IDTs and are presented in Fig. 7.

Fig. 7(b) shows that, at 1450 K, the chain branching reaction $\dot{H} + O_2 \leftrightarrow \dot{O} + \dot{O}H$ governs and promotes the ignition of the fuel/'air' mixtures, the rate of which depends on the amount of hydrogen atoms and molecular oxygen available in the mixtures. However, for the CH₄/'air' mixture, methyl ($\dot{C}H_3$) radicals rather than \dot{H} atoms dominate the ignition behavior, with $\dot{C}H_3 + HO_2 \leftrightarrow CH_3\dot{O} + \dot{O}H$ and $\dot{C}H_3 + \dot{O}_2 \leftrightarrow CH_2O + \dot{O}H$ being the most sensitive reactions promoting reactivity, and $\dot{C}H_3 + \dot{C}H_3 (+M) \leftrightarrow C_2H_6 (+M)$ is the most sensitive reaction inhibiting reactivity, as illustrated in Fig. 7(b). At 1450 K, CH₄ is mostly consumed by H-atom abstraction by \dot{H} , \dot{O} and $\dot{O}H$ radicals producing methyl ($\dot{C}H_3$) radicals, Fig. 6(b). Approximately 11% of these $\dot{C}H_3$ radicals react with O₂ through $\dot{C}H_3 + O_2 \leftrightarrow CH_2O + \dot{O}H$ to generate formaldehyde (CH₂O) and $\dot{O}H$ radicals in a reaction that greatly promotes the reactivity of the mixture, as seen by the sensitivity analysis presented in Fig 7(b). The CH₂O then reacts with $\dot{C}H_3$ radical and leads to the formation of CH₄ and formyl ($\dot{H}CO$) radical. Another pathway contributing to the consumption of the $\dot{C}H_3$ radicals (15.8%) is the chain branching reaction $\dot{C}H_3 + HO_2 \leftrightarrow CH_3\dot{O} + \dot{O}H$, which produces methoxy (CH₃ \dot{O}) and $\dot{O}H$ radicals, significantly promoting reactivity, Figs. 6(b) and 7(b). The current mechanism employs the rate coefficients for $\dot{C}H_3 + HO_2 \leftrightarrow CH_3\dot{O} + \dot{O}H$ from the theoretical calculation by Jasper et al. [33]. This reaction channel directly competes with the chain-terminating reaction $\dot{C}H_3 + HO_2 \leftrightarrow CH_4 + O_2$ for hydroperoxyl (HO_2) radicals, as shown in Fig. 7(b), and the current mechanism utilizes the rate constant from Zhu et al. [34] for this inhibiting pathway. At the high temperature of 1450 K, ~7% of methyl ($\dot{C}H_3$) radicals react with O₂ to form methyl peroxy (CH₃ \dot{O}_2) radicals via $\dot{C}H_3 + O_2 \leftrightarrow CH_3\dot{O}_2$. These radicals further dissociate to CH₂O and $\dot{O}H$ radicals, promoting reactivity as illustrated in Fig 7(b). This direct dissociation of CH₃ \dot{O}_2 radicals was not incorporated in the previous mechanism, and in NUIGMech1.2, the rate constant for this reaction is adopted based on an extensive study of rate rules by Villano et al. [35] derived using electronic structure calculations.

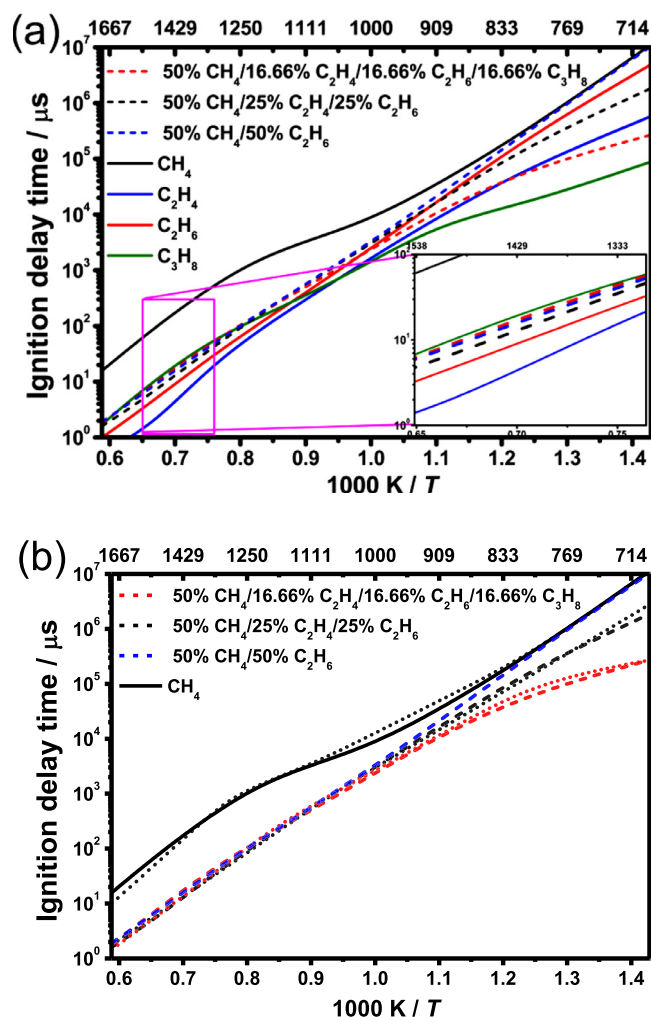


Fig. 5. (a) Comparisons of IDT predictions for various single, binary, ternary, and quaternary fuels in air at $p_c = 40$ atm and $\phi = 1.0$, and (b) the predictions of their corresponding correlations (dotted lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 8(a) shows the importance of the addition of the $\text{CH}_3\dot{\text{O}}_2$ dissociation channel and the updated rate constant for $\dot{\text{C}}\text{H}_3 + \text{CH}_3 (+M) \leftrightarrow \text{C}_2\text{H}_6 (+M)$ on the IDT predictions using NUIGMech1.2 compared to NUIGMech1.1, which slightly under-predicts the IDTs in the intermediate temperature range of 1000 – 1100 K at $p_c = 24$ atm, and for both $\phi = 0.5$ and 1.0. The addition of the $\text{CH}_3\dot{\text{O}}_2 \leftrightarrow \text{CH}_2\text{O} + \dot{\text{O}}\text{H}$ reaction channel results in a decrease in predicted IDTs represented by dashed-dotted lines in Fig. 8(a). Nonetheless, an excellent improvement in IDT prediction is achieved by updating the $\dot{\text{C}}\text{H}_3 + \text{CH}_3 (+M) \leftrightarrow \text{C}_2\text{H}_6 (+M)$ rate constants together with the inclusion of the $\text{CH}_3\dot{\text{O}}_2$ dissociation reaction ($\text{CH}_3\dot{\text{O}}_2 \leftrightarrow \text{CH}_2\text{O} + \dot{\text{O}}\text{H}$) in NUIGMech1.2, as depicted by the solid lines in Fig. 8(a).

According to the ROP and the sensitivity analysis of CH_4/air mixtures, at high temperatures (1450 K) a significant quantity (~55%) of the methyl radicals undergo self-recombination to form C_2H_6 making methane the slowest fuel to ignite compared to the other single fuels. The self-recombination reaction of methyl radicals has been widely studied in the literature. Comparisons of pressure-dependent rate constants and various experimental measurements for $\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}_3 (+M) \leftrightarrow \text{C}_2\text{H}_6 (+M)$ from the literature [37–42] are shown in Fig. 8(b). NUIGMech1.1 employed a rate constant from the experimental and theoretical study of Wang et al. [41] for this reaction. Here NUIGMech1.2 uses the fit derived from

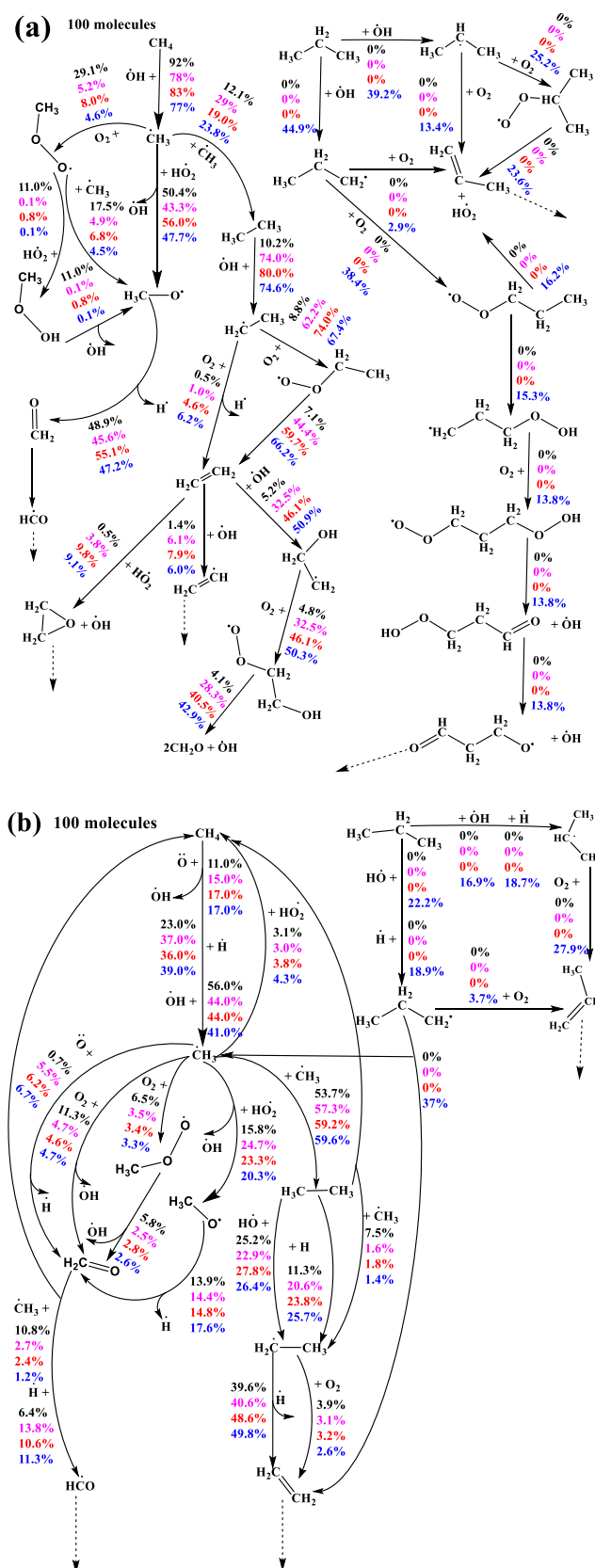


Fig. 6. Flux analyses of pure CH_4 (black), 50% $\text{CH}_4/50\%$ C_2H_6 blend (magenta), 50% $\text{CH}_4/25\%$ $\text{C}_2\text{H}_4/25\%$ C_2H_6 blend (red), and 50% $\text{CH}_4/16.66\%$ $\text{C}_2\text{H}_4/16.66\%$ $\text{C}_2\text{H}_6/16.66\%$ C_3H_8 (blue) mixtures at $p_c = 40$ atm and $\phi = 1.0$, at the time of 20% fuel consumed for (a) $T_c = 800$ K and (b) $T_c = 1450$ K. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

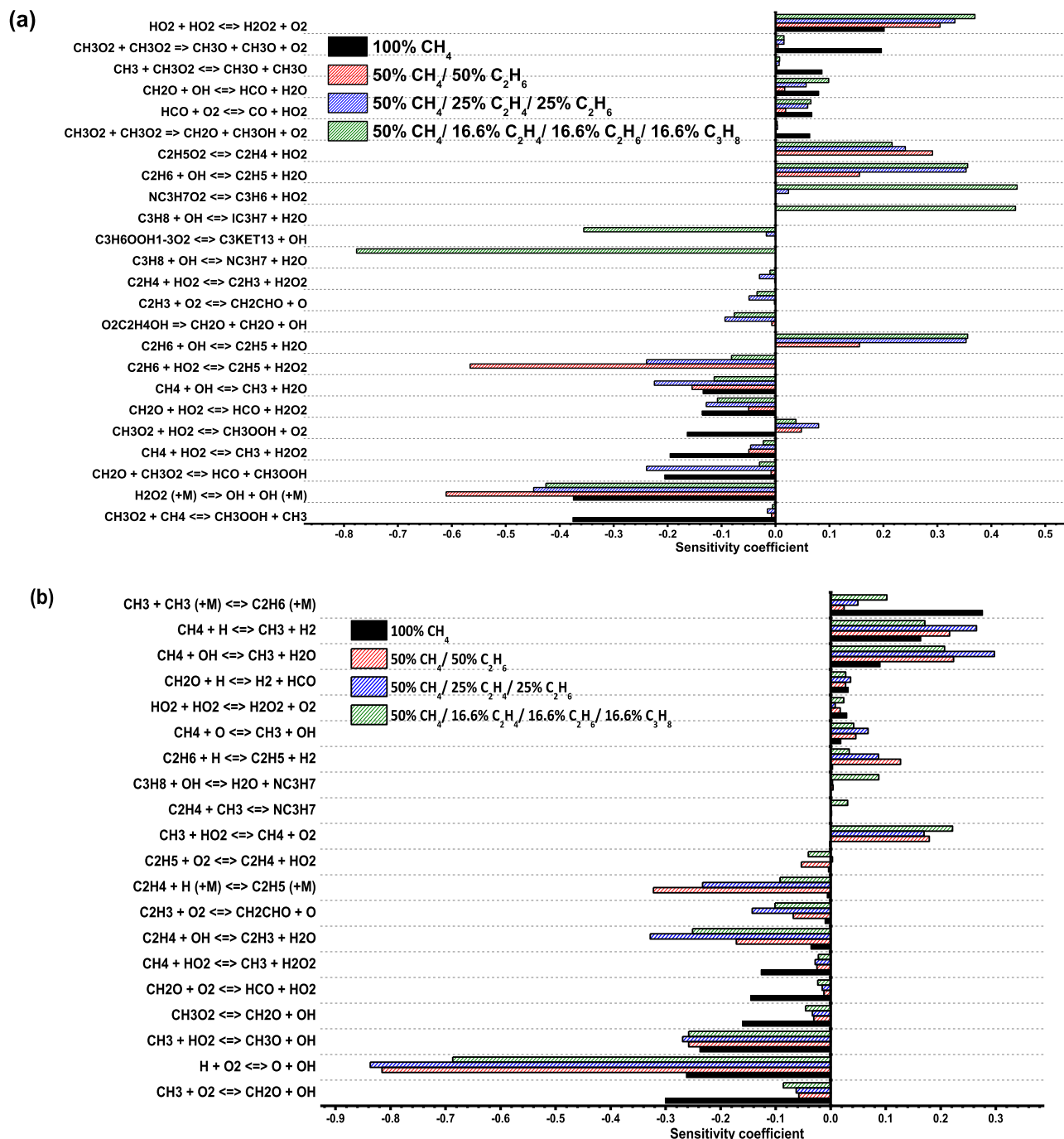


Fig. 7. Sensitivity analyses to IDTs for pure CH₄, 50% CH₄/50% C₂H₆ blend, 50% CH₄/25% C₂H₄/25% C₂H₆ blend, and 50% CH₄/16.66% C₂H₄/16.66% C₂H₆/16.66% C₃H₈ mixtures in 'air' at $p_c = 40$ atm, $\varphi = 1.0$, for (a) $T_c = 800$ K and (b) $T_c = 1450$ K.

a comprehensive experimental review by Blitz et al. [40] for the high-pressure limit rate constant. We have chosen this rate constant as the revised high-pressure limit is in good agreement with the recent experimental study by Sangwan et al. [38] in the temperature range 292 – 714 K as well as with the high level theoretical calculation by Klippenstein et al. [42]. Fig. 8(b) shows that the high-pressure limit reported by Wang et al. [41] is ~17% slower than that measured by Sangwan et al. [38] at 714 K. In NUIG-Mech1.2 the low-pressure limit and the fall-off parameters are taken from Wang et al. [41], as these satisfactory match the experimental measurements from Slagle et al. [37] and Glanzer et al. [39] in the pressure-dependent fall-off regime, Fig. 8(b).

In Fig. 6(a), the ROP analysis of the pure CH₄/air mixture at 800 K shows that ~50% of CH₃ radicals react with HO₂ forming methoxy (CH₃O) radicals by $\dot{\text{C}}\text{H}_3 + \text{H}\dot{\text{O}}_2 \leftrightarrow \text{CH}_3\dot{\text{O}} + \dot{\text{O}}\text{H}$, which further decomposes through $\text{CH}_3\dot{\text{O}} (+\text{M}) \leftrightarrow \text{CH}_2\text{O} + \dot{\text{H}} (+\text{M})$ to produce formaldehyde (CH₂O) and H atoms. A significant quantity of $\dot{\text{C}}\text{H}_3$ (30%) reacts with O₂ to form methyl peroxy radicals through $\dot{\text{C}}\text{H}_3 + \text{O}_2 \leftrightarrow \text{CH}_3\dot{\text{O}}_2$. Approximately ~11% of CH₃O₂ is consumed by its reaction with HO₂, via $\text{CH}_3\dot{\text{O}}_2 + \text{H}\dot{\text{O}}_2 \leftrightarrow \text{CH}_3\text{OOH} + \text{O}_2$ followed by rapid dissociation of the methyl hydroperoxide (CH₃OOH) into methoxy (CH₃O) and OH radicals, thus significantly enhancing reactivity. Furthermore, considerable amounts of CH₃OOH can be produced from CH₃O₂ by $\text{CH}_3\dot{\text{O}}_2 + \text{CH}_4 \leftrightarrow \text{CH}_3\text{OOH} + \dot{\text{C}}\text{H}_3$ and

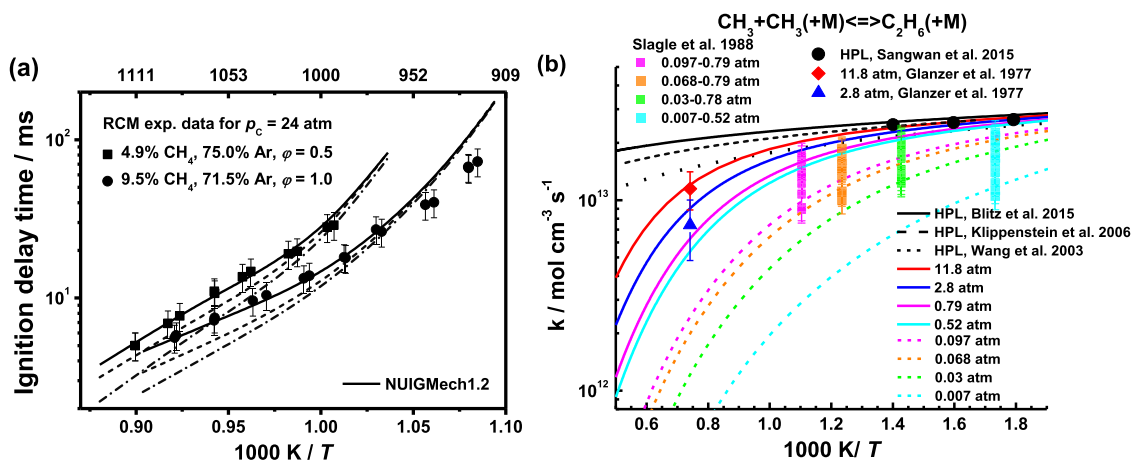


Fig. 8. (a) Effects of addition of $\text{CH}_3\text{O}_2 \leftrightarrow \text{CH}_2\text{O} + \dot{\text{O}}\text{H}$ reaction and updated $\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}_3 (+M) \leftrightarrow \text{C}_2\text{H}_6 (+M)$ rate constant on the IDTs for 4.9% CH_4 at $\phi = 0.5$ [36] and 9.5% CH_4 at $\phi = 1.0$ [36]; —, NUIGMech1.1; - - - , NUIGMech1.1 plus $\text{CH}_3\text{O}_2 \leftrightarrow \text{CH}_2\text{O} + \dot{\text{O}}\text{H}$ [35]; ····, NUIGMech1.2 which includes $\text{CH}_3\text{O}_2 \leftrightarrow \text{CH}_2\text{O} + \dot{\text{O}}\text{H}$ [35] reaction as well as an updated rate constant for $\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}_3 (+M) \leftrightarrow \text{C}_2\text{H}_6 (+M)$. (b) Comparisons of the rate constants for $\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}_3 (+M) \leftrightarrow \text{C}_2\text{H}_6 (+M)$ [37–42].

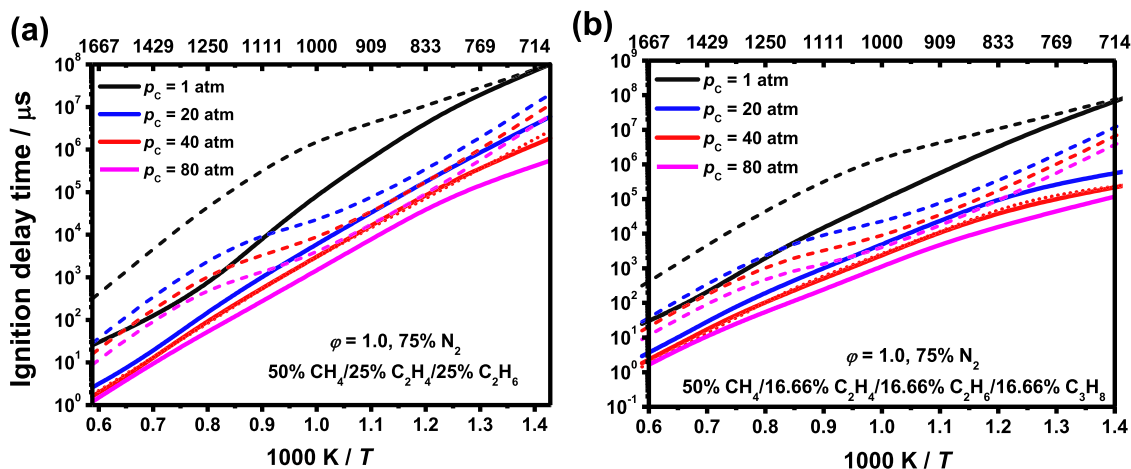


Fig. 9. Effect of pressure over the IDT predictions of (a) 50% $\text{CH}_4/25\% \text{C}_2\text{H}_4/25\% \text{C}_2\text{H}_6$ blend (solid lines), and (b) 50% $\text{CH}_4/16.66\% \text{C}_2\text{H}_4/16.66\% \text{C}_2\text{H}_6/16.66\% \text{C}_3\text{H}_8$ blend (solid lines), pure CH_4 (dashed lines), and corresponding correlations (dotted lines) for fuel in air at $\phi = 1.0$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

$\text{CH}_2\text{O} + \text{CH}_3\text{O}_2 \leftrightarrow \text{HCO} + \text{CH}_3\text{OOH}$ reactions promoting methane ignition at low temperatures, as can be seen in Fig. 7(a). The ROP analysis shows that ~17% of CH_3O_2 radicals further react with $\dot{\text{C}}\text{H}_3$ to produce two methoxy radicals through $\text{CH}_3\text{O}_2 + \dot{\text{C}}\text{H}_3 \leftrightarrow \text{CH}_3\dot{\text{O}} + \text{CH}_3\dot{\text{O}}$. Fig. 7(a) also shows that this reaction along with $\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \leftrightarrow \text{CH}_3\dot{\text{O}} + \text{CH}_3\dot{\text{O}} + \text{O}_2$ competes for CH_3O_2 radicals with the chain propagating reactions $\text{CH}_4 + \text{CH}_3\text{O}_2 \leftrightarrow \text{CH}_3\text{OOH} + \dot{\text{C}}\text{H}_3$ and $\text{CH}_2\text{O} + \text{CH}_3\text{O}_2 \leftrightarrow \text{HCO} + \text{CH}_3\text{OOH}$ producing methyl hydroperoxide, thus decreasing the reactivity of the CH_4/air mixture. NUIGMech1.2 utilizes the rate constant recommended by Lightfoot et al. [43] for $\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \leftrightarrow \text{CH}_3\dot{\text{O}} + \text{CH}_3\dot{\text{O}} + \text{O}_2$ based on flash photolysis measurements at atmospheric and low temperatures conditions, as shown in Fig. S51. For $\text{CH}_3\text{O}_2 + \dot{\text{C}}\text{H}_3 \leftrightarrow \text{CH}_3\dot{\text{O}} + \text{CH}_3\dot{\text{O}}$, the rate coefficients are adopted from the work of Keiffer et al. [44], as shown in Fig. S52. However, further research is recommended in the study of the rate constant of this reaction. Finally, at 800 K, the remaining 12% of $\dot{\text{C}}\text{H}_3$ radicals react through the self-recombination reaction $\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}_3 (+M) \leftrightarrow \text{C}_2\text{H}_6 (+M)$, thus activating the C_2H_6 chemistry.

Unlike the case for CH_4/air mixtures, the most important reaction promoting the reactivity at high temperatures for the binary, ternary and quaternary blends is the chain branching reaction $\dot{\text{H}} + \text{O}_2 \leftrightarrow \dot{\text{O}} + \dot{\text{O}}\text{H}$. This is because C_2H_4 , C_2H_6 , and C_3H_8 mixtures

generate larger concentrations of $\dot{\text{H}}$ atoms compared to CH_4/air mixtures and consequently increases the fuel reactivities of the blended mixtures at the high-temperature conditions, as shown in Fig. 5. In a previous study [4], the important reactions, as well as the choice of their rate constants governing the oxidation behavior of $\text{C}_2\text{H}_4/\text{air}$, $\text{C}_2\text{H}_6/\text{air}$, $\text{C}_3\text{H}_8/\text{air}$ mixtures and their binary blends, were discussed in detail. Thus, in this work, particular emphasis is placed on understanding the synergistic and antagonistic effects of ethane/ethylene/propane fuels on the ignition of methane/fuel mixtures.

The consumption of C_2H_6 is initiated by H-atom abstraction, mainly by $\dot{\text{O}}\text{H}$ radicals and $\dot{\text{H}}$ atoms producing ethyl radicals ($\dot{\text{C}}_2\text{H}_5$), through $\text{C}_2\text{H}_6 + \dot{\text{H}}/\dot{\text{O}}\text{H} \leftrightarrow \dot{\text{C}}_2\text{H}_5 + \text{H}_2/\text{H}_2\text{O}$. Most ethyl radicals decompose to C_2H_4 and $\dot{\text{H}}$ atoms via $\dot{\text{C}}_2\text{H}_5 (+M) \leftrightarrow \text{C}_2\text{H}_4 + \dot{\text{H}} (+M)$. Ethylene can further undergo H-atom abstraction reactions to form vinyl radicals ($\dot{\text{C}}_2\text{H}_3$) which are responsible for the generation of a substantial amount of $\dot{\text{H}}$ atoms by their reaction with O_2 via $\dot{\text{C}}_2\text{H}_3 + \text{O}_2 \leftrightarrow \dot{\text{C}}_2\text{H}_3\text{CHO} + \dot{\text{O}}$ and $\text{CH}_2\text{CHO} \leftrightarrow \text{CH}_2\text{CO} + \dot{\text{H}}$, ultimately leading to the faster ignition of $\text{C}_2\text{H}_6/\text{air}$ mixtures compared to CH_4/air mixtures, as shown in Fig 5(a). The remaining $\dot{\text{C}}_2\text{H}_5$ radicals react with O_2 to produce ethylene through $\dot{\text{C}}_2\text{H}_5 + \text{O}_2 \leftrightarrow \text{C}_2\text{H}_4 + \text{HO}_2$, which directly competes with $\dot{\text{C}}_2\text{H}_5 (+M) \leftrightarrow \text{C}_2\text{H}_4 + \dot{\text{H}} (+M)$, resulting in a shorter IDT for $\text{C}_2\text{H}_6/\text{air}$

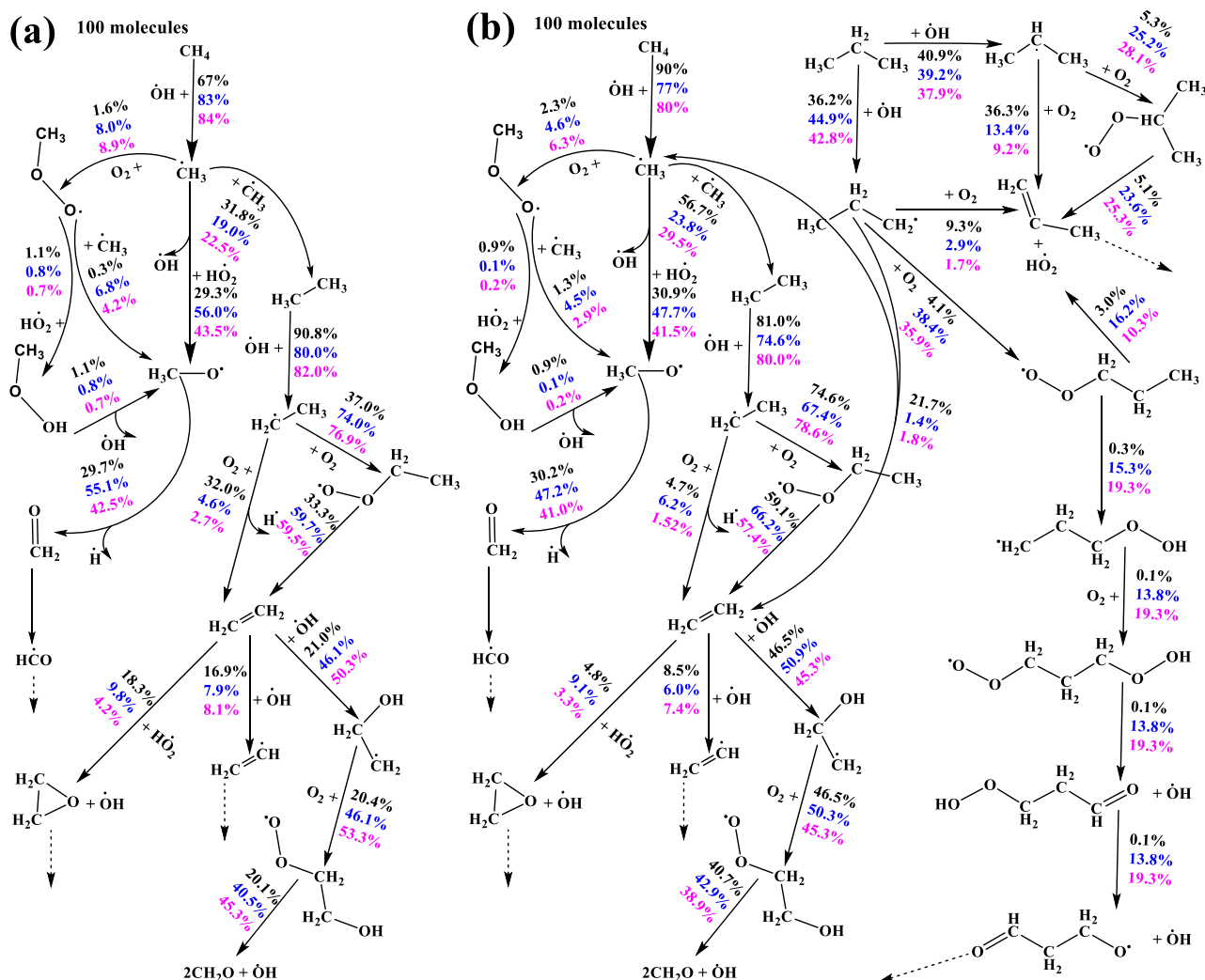


Fig. 10. Flux analyses as function of pressure of 1 atm, 40 atm and 80 atm (black, blue, and magenta percentages respectively), at $T_c = 800$ K, $\varphi = 1.0$, for (a) 50% $\text{CH}_4/25\%$ $\text{C}_2\text{H}_4/25\%$ C_2H_6 , and (b) 50% $\text{CH}_4/16.66\%$ $\text{C}_2\text{H}_4/16.66\%$ $\text{C}_2\text{H}_6/16.66\%$ C_3H_8 in air. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

mixture compared to $\text{C}_2\text{H}_4/\text{air}$ mixture. The effect on IDTs of the addition of ethane to CH_4/air mixtures is presented in Fig 5(a). The reactivity of the mixture increases significantly for the 50% $\text{CH}_4/50\%$ C_2H_6 binary blend at high temperatures (> 1000 K) compared to the pure methane mixture. In Fig. 6(b), the magenta-bold percentages represent the ROP for 50% $\text{CH}_4/50\%$ C_2H_6 binary mixtures at 40 atm, $\varphi = 1.0$ and $T_c = 1450$ K. Flux analyses show that the addition of C_2H_6 to CH_4/air mixtures does not alter the main reaction pathways corresponding to the pure CH_4 chemistry; however, it leads to increased production of $\dot{\text{H}}$ atoms which increases the sensitivity coefficients of $\dot{\text{H}} + \text{O}_2 \leftrightarrow \dot{\text{O}} + \dot{\text{O}}\text{H}$ and $\text{C}_2\text{H}_4 + \dot{\text{O}}\text{H} \leftrightarrow \dot{\text{C}}_2\text{H}_3 + \text{H}_2\text{O}_2$ for the 50% $\text{CH}_4/50\%$ C_2H_6 binary mixtures, Fig. 7(b). On the contrary, the reactions $\text{CH}_4 + \dot{\text{H}} \leftrightarrow \dot{\text{C}}\text{H}_3 + \text{H}_2$ and $\text{CH}_4 + \dot{\text{O}}\text{H} \leftrightarrow \dot{\text{C}}\text{H}_3 + \text{H}_2\text{O}$ compete for the available $\dot{\text{H}}$ atoms and $\dot{\text{O}}\text{H}$ radicals which exhibit higher positive sensitive coefficients for the C_2H_6 blended mixtures in comparison to the pure CH_4 case.

At low temperatures, the pure $\text{C}_2\text{H}_6/\text{air}$ mixture is still faster to ignite compared to the pure CH_4/air mixture, but the difference between the two decreases with a decrease in temperature, Fig. 5(a). Furthermore, for the 50% $\text{CH}_4/50\%$ C_2H_6 binary blend, the IDT predictions overlap with the pure CH_4 ones at low-temperatures. The sensitivity analysis shows that the sensitivities of $\text{H}_2\text{O}_2 (+M) \leftrightarrow \dot{\text{O}}\text{H} + \dot{\text{O}}\text{H} (+M)$ and $\text{H}\dot{\text{O}}_2 + \text{H}\dot{\text{O}}_2 \leftrightarrow \text{H}_2\text{O}_2 + \text{O}_2$ are

strengthened by the addition of 50% C_2H_6 to CH_4/air mixtures. This is because, compared to the pure CH_4 case, H-atom abstraction from C_2H_6 by $\text{H}\dot{\text{O}}_2$ exhibits a relatively larger negative sensitivity coefficient promoting reactivity, which is attributed to the higher rate constant of $\text{C}_2\text{H}_6 + \text{H}\dot{\text{O}}_2 \leftrightarrow \dot{\text{C}}_2\text{H}_5 + \text{H}_2\text{O}_2$, which is approximately an order of magnitude faster than that for $\text{CH}_4 + \text{H}\dot{\text{O}}_2 \leftrightarrow \dot{\text{C}}\text{H}_3 + \text{H}_2\text{O}_2$. However, most of the C_2H_5 radicals formed add to O_2 producing ethylperoxy ($\text{C}_2\text{H}_5\dot{\text{O}}_2$) radicals, followed by the concerted elimination reaction $\text{C}_2\text{H}_5\dot{\text{O}}_2 \leftrightarrow \text{C}_2\text{H}_4 + \text{H}\dot{\text{O}}_2$, which plays an important role in inhibiting the ignition of the C_2H_6 blended mixtures at low temperatures, Fig. 7(a).

C_2H_4 is an essential intermediate of C_2H_6 oxidation and is the fastest fuel to ignite compared to the other single fuels at high temperatures. The effect on IDT predictions of the addition of C_2H_4 to a $\text{CH}_4/\text{C}_2\text{H}_6/\text{air}$ mixture is presented in Fig 5(a). The reactivity of the 50% $\text{CH}_4/25\%$ $\text{C}_2\text{H}_6/25\%$ C_3H_8 ternary blend is $\sim 15\%$ faster than the $\text{CH}_4/\text{C}_2\text{H}_6$ binary blend at high temperatures (> 1000 K). Moreover, at low temperatures, the ternary blend is $\sim 80\%$ faster than the binary blend. The main reason for the increased reactivity of C_2H_4 blended mixtures at high temperatures is attributed to the substantial formation of $\dot{\text{H}}$ atoms due to the reaction sequence, $\text{C}_2\text{H}_4 + \dot{\text{O}} \leftrightarrow \dot{\text{C}}\text{H}_2\text{CHO} + \dot{\text{H}}$, and $\text{C}_2\text{H}_4 + \dot{\text{O}} \leftrightarrow \dot{\text{C}}\text{H}_2 + \text{CH}_2\text{O}$, followed by $\dot{\text{C}}\text{H}_2 + \text{O}_2 \leftrightarrow \text{CO}_2 + \dot{\text{H}} + \dot{\text{H}}$ [4], thus increasing the im-

portance of the $\dot{H} + O_2 \leftrightarrow \dot{O} + \dot{O}H$ and $C_2H_4 + \dot{O}H \leftrightarrow \dot{C}_2H_3 + \dot{H}O_2$ reactions for the ternary blend compared to the binary blend mixtures, Fig. 7(b). On the other hand, at low temperatures (< 1000 K), C_2H_4 is primarily consumed by the addition of $\dot{O}H$ radicals producing hydroxyl-ethyl (\dot{C}_2H_4OH) radicals which add to molecular oxygen to form hydroxyethylene-peroxy ($\dot{O}_2C_2H_4OH$) radicals. The dissociation of $\dot{O}_2C_2H_4OH$ radicals ultimately increases the reactivity of the ethylene blended mixtures at low temperatures by generating two molecules of formaldehyde and $\dot{O}H$ radicals. For the ternary mixtures, $\dot{O}H$ radicals are also formed through the reaction $C_2H_4 + HO_2 \leftrightarrow C_2H_4O1-2$ (oxirane) + $\dot{O}H$, further promoting reactivity.

Propane/air' oxidation at high temperatures (> 900 K) is mainly dominated by H-atom abstraction by $\dot{O}H$ radicals and \dot{H} atoms, leading to the formation of *n*-propyl ($n\dot{C}_3H_7$) and isopropyl ($i\dot{C}_3H_7$) radicals. Most $n\dot{C}_3H_7$ radicals decompose via β -scission $n\dot{C}_3H_7 \leftrightarrow C_2H_4 + \dot{C}H_3$. The methyl radicals so formed can react with hydroperoxyl radicals either via $\dot{C}H_3 + HO_2 \leftrightarrow CH_3\dot{O} + \dot{O}H$, which promotes reactivity, or $\dot{C}H_3 + HO_2 \leftrightarrow CH_4 + O_2$, which inhibits reactivity. Methyl radicals also self-react to form C_2H_6 , further reducing the reactivity of the propane/air mixtures. The effect on IDTs of adding C_3H_8 to $CH_4/C_2H_6/C_2H_4$ /air' mixtures is shown in Fig 5(a). At high temperatures, the 50% $CH_4/16.66\%$ $C_2H_6/16.66\%$ $C_2H_4/16.66\%$ C_3H_8 quaternary blend is $\sim 15\%$ slower than the 50% $CH_4/25\%$ $C_2H_6/25\%$ C_3H_8 ternary mixtures, Fig 5(a). The sensitivity analysis, Fig. 7(b), shows that at 1450 K, the main chain branching reaction $\dot{H} + O_2 \leftrightarrow \dot{O} + \dot{O}H$ is relatively less sensitive to the IDT of the quaternary blends compared to the ternary blends leading to a lower reactivity of the 50% $CH_4/16.66\%$ $C_2H_6/16.66\%$ $C_2H_4/16.66\%$ C_3H_8 /air mixtures. Fig. 6(b) shows that the addition of pure C_3H_8 to $CH_4/C_2H_6/C_2H_4$ ternary blends becomes an important source of methyl radicals produced from the β -scission of $n\dot{C}_3H_7$ radicals, is responsible for the slower reactivity of the quaternary blends compared to the ternary blends at higher temperatures.

Fig. 7(a) shows that at lower temperature the reactivity of the quaternary blends is governed by $C_3H_8 + \dot{O}H \leftrightarrow n\dot{C}_3H_7 + H_2O$ being the most reactivity promoting channel, while the most sensitive reactions inhibiting the reactivity are $C_3H_8 + \dot{O}H \leftrightarrow i\dot{C}_3H_7 + H_2O$ and $n\dot{C}_3H_7O_2 \leftrightarrow C_3H_6 + HO_2$. At $T_c < 900$ K, $n\dot{C}_3H_7$ radicals add to molecular oxygen producing *n*-propyl-peroxy ($n\dot{C}_3H_7\dot{O}_2$) radicals, which then isomerize to hydroperoxyl-propyl ($\dot{C}_3H_6OOH1-3$) radicals that can add to molecular oxygen generating hydroperoxyl-propyl-peroxy ($C_3H_6OOH1-3\dot{O}_2$) radicals. The $C_3H_6OOH1-3\dot{O}_2$ radicals can further isomerize and generate a carbonyl hydroperoxide and an $\dot{O}H$ radical. Finally, the carbonyl hydroperoxide undergoes RO-OH bond cleavage, producing a second $\dot{O}H$ radical and a carbonyl-alkoxy ($R\dot{O}$) radical in a chain branching process that increases the reactivity of propane at low temperatures, Fig. 6(a). The addition of propane to the ternary blends significantly increases the reactivity of the 50% $CH_4/16.66\%$ $C_2H_6/16.66\%$ $C_2H_4/16.66\%$ C_3H_8 quaternary blends, this being just less reactive than the pure C_3H_8 /air' mixture at lower temperatures (< 900 K), Fig. 5(a).

4.3. Effect of pressure on ignition

Fig. 9 illustrates the effect of the pressure on IDTs for 50% $CH_4/25\%$ $C_2H_4/25\%$ C_2H_6 blend, 50% $CH_4/16.66\%$ $C_2H_4/16.66\%$ $C_2H_6/16.66\%$ C_3H_8 blend along with pure methane at $\phi = 1.0$. Fig. 9 indicates that the reactivity of the mixtures increases at high-pressure conditions due to the corresponding increase in concentration with pressure. Furthermore, it is observed that at lower temperatures (< 830 K), the addition of C_2H_4/C_2H_6 and $C_2H_4/C_2H_6/C_3H_8$ fuels to pure methane for the ternary and quaternary blends, results in faster IDTs at high-pressure conditions (20, 40 and 80 atm) compared to the 1 atm case. Figs. 10(a)

and 10(b) illustrate the effect of pressure on IDTs based on reaction path analyses depicted by black numbers for the 1 atm case and blue numbers for the 40 atm case at 800 K for the 50% $CH_4/25\%$ $C_2H_4/25\%$ C_2H_6 and 50% $CH_4/16.66\%$ $C_2H_4/16.66\%$ $C_2H_6/16.66\%$ C_3H_8 blends, respectively. The flux analyses presented in Figs. 10(a) and 10(b) show that for the ternary and quaternary blends, the total fluxes going through the ignition promoting pathways $\dot{C}H_3 + O_2 \leftrightarrow CH_3\dot{O}_2$ and $\dot{C}H_3 + HO_2 \leftrightarrow CH_3\dot{O} + OH$ are around two times higher at 40 and 80 atm compared to 1 atm, while $\sim 32\%$ less flux goes through the methyl radical recombination reaction $\dot{C}H_3 + \dot{C}H_3 (+M) \leftrightarrow C_2H_6 (+M)$ at 40 and 80 atm compared to 1 atm, thus increasing the overall reactivity of the blends at high pressure and low-temperature conditions. Moreover, for the ternary blend, as pressure rises, the carbon fluxes going through the channels generating hydroxyl-ethyl (\dot{C}_2H_4OH) radicals from $C_2H_4 + \dot{O}H$ followed by the O_2 addition and the subsequent dissociation of $O_2\dot{C}_2H_4OH$ leading to two formaldehyde and a hydroxyl radical increases, as seen in Fig. 10(a). These formaldehyde molecules react with HO_2 radicals to generate H_2O_2 , which more strongly promotes the reactivity through the thermal dissociation reaction $H_2O_2 (+M) \leftrightarrow \dot{O}H + \dot{O}H (+M)$ at the high-pressure condition of 40 and 80 atm compared to 1 atm, as shown in Fig. S53.

For the 50% $CH_4/16.66\%$ $C_2H_4/16.66\%$ $C_2H_6/16.66\%$ C_3H_8 quaternary blend, at 1 atm, a considerable amount of $n\dot{C}_3H_7$ (21.7%) undergoes β -scission, via $n\dot{C}_3H_7 \leftrightarrow \dot{C}H_3 + C_2H_4$, while for 40 atm, the percentage contribution through this channel reduces significantly accounting only 0.4% of the total flux. Whereas, at 40 atm $\sim 34\%$ more flux goes through the $n\dot{C}_3H_7 + O_2 \leftrightarrow n\dot{C}_3H_7\dot{O}_2$ pathway compared to 1 atm condition increasing the reactivity for the quaternary blend at high pressures and low temperatures through the generation of two reactive $\dot{O}H$ radicals, as discussed in Section 4.2.

4.4. Correlation analysis

Reliable global correlations that can accurately reproduce experimental measurements are desirable tools for analytical, semi-empirical, or computational fluid dynamics (CFD) calculations of reactive flows. Such correlations are versatile tools that can predict a mixture's sensitivity to any change in the correlated parameters. As discussed previously [2, 3], these correlations significantly reduce the required simulation time in response to any change in the chemical system, a critical parameter in real-time combustion controlling and monitoring systems. A simple form of the correlations applied here follows those previously published [2, 3] and is expressed in Eqn. (3). As previously shown, this type of correlation can reasonably explain the IDT characteristics of single and binary blended $C_1 - C_3$ hydrocarbons over a wide range of conditions [2, 3]. Here, it should be noted that Eqn. (3) explains the general form of the correlations used in the study so that the "F" variable is zero for the tertiary blended $C_1 - C_2$ fuels where no propane is present.

$$\tau_{\text{corr}} = 10^A \exp\left(\frac{B}{T_c}\right) [CH_4]^C [C_2H_4]^D [C_2H_6]^E [C_3H_8]^F [\text{oxygen}]^G [\text{diluent}]^H \quad (3)$$

where A represents the pre-exponential factor coefficient, B represents the activation energy divided by universal gas constant, and C - H represent coefficients for methane, ethylene, ethane, propane, oxidizer, and dilution, respectively.

All of the correlations were derived using NUIGMech1.2 based on thousands of adiabatic constant volume simulations, and their corresponding correlation coefficients are presented below and in Tables S12 - S15 of the Supplementary material. The correlation coefficients were calculated using a non-linear curve fitting routine available in OriginPro 8.5 [45] which provides linear regressions together with residuals, R^2 , χ^2 and standard errors for every coefficient value. Some of the examples of these conditions

are presented in Fig. 5(b) and Fig. 9. However, according to the simple form of Eqn. (3), the correlations are derived over ranges where the dependency of the IDT on the various parameters does not become highly non-linear. Moreover, for relatively long IDTs (> 10 ms) measured using the RCM, the correlation results derived using the adiabatic constant volume calculations differs significantly from the simulations including heat loss effects for the facility. We have already discussed this effect in detail [2,4].

For $1100 \leq T_C \leq 2000$ K:

$$\tau_{\text{corr}} = 10^{-10.94} \exp\left(\frac{2, 120, 8}{T_C}\right) [\text{CH}_4]^{1.004} [\text{C}_2\text{H}_4]^{-0.888} [\text{C}_2\text{H}_6]^{-0.041} [\text{C}_3\text{H}_8]^{0.0} [\text{oxygen}]^{-1.399} [\text{diluent}]^{0.666} \quad (4)$$

$$\tau_{\text{corr}} = 10^{-10.36} \exp\left(\frac{2, 132, 0}{T_C}\right) [\text{CH}_4]^{0.834} [\text{C}_2\text{H}_4]^{-0.222} [\text{C}_2\text{H}_6]^{-0.186} [\text{C}_3\text{H}_8]^{-0.165} [\text{oxygen}]^{-1.496} [\text{diluent}]^{0.48} \quad (5)$$

For $800 \leq T_C \leq 1100$ K:

$$\tau_{\text{corr}} = 10^{-8.049} \exp\left(\frac{1, 681, 7}{T_C}\right) [\text{CH}_4]^{0.31} [\text{C}_2\text{H}_4]^{-0.722} [\text{C}_2\text{H}_6]^{-0.138} [\text{C}_3\text{H}_8]^{0.0} [\text{oxygen}]^{-0.398} [\text{diluent}]^{-0.162} \quad (6)$$

$$\tau_{\text{corr}} = 10^{-8.011} \exp\left(\frac{1, 582, 6}{T_C}\right) [\text{CH}_4]^{0.133} [\text{C}_2\text{H}_4]^{-0.257} [\text{C}_2\text{H}_6]^{-0.105} [\text{C}_3\text{H}_8]^{-0.5} [\text{oxygen}]^{-0.292} [\text{diluent}]^{-0.089} \quad (7)$$

At high temperatures (1100 – 2000 K), the coefficient associated with CH₄ in both blends (CH₄/C₂H₄/C₂H₆/'air' and CH₄/C₂H₄/C₂H₆/C₃H₈/'air') is strongly positive, while those for C₂H₄, C₂H₆, and C₃H₈ are negative. CH₄ produces high concentrations of $\dot{\text{C}}\text{H}_3$ radicals, which are relatively less reactive compared to $\dot{\text{H}}$ atoms produced in the oxidation of C₂H₄, C₂H₆, and C₃H₈. Thus, increasing the CH₄ concentration in the ternary and quaternary blends will increase IDT, and increasing C₂H₄, C₂H₆, and C₃H₈ concentrations will decrease the mixture IDT. Moreover, the coefficient associated with C₃H₈ in the quaternary (CH₄/C₂H₄/C₂H₆/C₃H₈/'air') blend is smaller than the coefficients for C₂H₄ and C₂H₆. This is because, at high temperatures, C₃H₈ produces $\dot{\text{C}}\text{H}_3$ radicals and C₂H₄ molecules from $n\dot{\text{C}}_3\text{H}_7$ radicals that decompose via β -scission reaction by $n\dot{\text{C}}_3\text{H}_7 \leftrightarrow \text{C}_2\text{H}_4 + \dot{\text{C}}\text{H}_3$, whereas C₂H₄ and C₂H₆ oxidation produces higher amounts of $\dot{\text{H}}$ atoms, thus more effectively enhancing the reactivity of the C₂H₄ or C₂H₆ blended mixtures than those of the C₃H₈ blended ones. Therefore, although increasing the concentrations of C₂H₄ and C₃H₈ relative to CH₄ will increase mixture reactivity, the former will dominate the latter.

Furthermore, at high temperatures, the coefficient corresponding to the oxidizer is significantly higher than other coefficients showing the strong sensitivity of oxygen concentrations under the respective conditions. For the low-temperature range, 800 – 1100 K, the coefficients for C₂H₄ and C₃H₈ become strongly negative. This is because, in this temperature range, C₂H₄ and C₃H₈ greatly enhance reactivity by producing higher concentrations of highly active OH radicals compared to the CH₄ and C₂H₆ fuels. Moreover, the coefficient corresponding to the oxidizer in Eqns. (6) and 7 is comparable to other coefficients showing less importance on oxygen concentrations under these specific conditions. A more detailed correlation table is included for all conditions studied in this work as Supplemental material, which includes the coefficients, standard errors related to coefficients R², and χ^2 . For both, low and high temperatures, the corresponding R² and χ^2 parameters are ranging from 0.985 – 0.999 and 1.53×10^{-4} – 1.02×10^{-11} , respectively.

Figures S51 and S52 in the Supplementary material compare the predictions of the quaternary correlations derived in this study with our prior published experimental IDTs of binary blends for C₂H₄/C₃H₈ and C₂H₆/C₃H₈ mixtures at high temperature and high-pressure conditions [4]. The present correlations are also compared with the IDT predictions calculated using the binary correlations derived in our previous work [4]. It can be seen that the global correlation of the quaternary blend is unable to accurately predict the IDTs of the C₂H₄/C₃H₈ and C₂H₆/C₃H₈ binary blends. This is attributed to the fact that the present correlations were derived from simulations of quaternary mixtures with CH₄ as the major fuel component. Eq. (5) shows that, for quaternary mixtures, the coefficient associated with CH₄ is strongly positive compared to the other fuel components in the blend and thus CH₄ dominates the predicted reactivity of the fuel mixture. Since our previously published [4] binary blends did not include CH₄ as an additive component, the predictions of the present correlations differ significantly from those calculated using the binary mixture correlations [4].

Conclusions

In the current study, a detailed experimental and kinetic modeling study of the IDT characteristics of C₁ – C₃ novel ternary and quaternary blends of CH₄/C₂H₄/C₂H₆ and CH₄/C₂H₄/C₂H₆/C₃H₈ mixtures was performed over a wide range of experimental conditions, temperature (~750 – 2000 K), pressure (1 – 135 bar), equivalence ratio ($0.5 \leq \varphi \leq 2.0$), and dilution (~75 – 90%). 24 new IDT datasets, including approximately 360 data points were measured, which were not already available in the literature. Low- and high-temperature IDT characteristics of CH₄/C₂H₄/C₂H₆ and CH₄/C₂H₄/C₂H₆/C₃H₈ combinations were investigated using the ST and RCM facilities at NUIG and PCFC RWTH Aachen University. The results showed that NUIGMech1.2 could predict the IDT characteristics of the blends studied with high fidelity over the wide range of conditions studied here.

Therefore, NUIGMech1.2 was used to perform studies on the blending and pressure effect on ignition. It was observed that for all blends used in this work, as the temperature and the pressure increase, the IDTs decrease. For high temperatures ($T > 1100$ K), CH₄ exhibit the slowest reactivity because its chemistry is mainly driven by methyl chemistry, $\dot{\text{C}}\text{H}_3 + \text{H}\dot{\text{O}}_2 \leftrightarrow \text{CH}_4 + \text{O}_2$, and $\dot{\text{C}}\text{H}_3 + \dot{\text{C}}\text{H}_3 (+M) \leftrightarrow \text{C}_2\text{H}_6 (+M)$; these reaction pathways are responsible for the very slow ignition on pure CH₄ and the ternary and quaternary blends at this temperature. C₂H₆ is the second-fastest mixture to ignite, and this is because the pressure dependent reaction from ethyl radical enhances the reactivity $\dot{\text{C}}_2\text{H}_5 (+M) \leftrightarrow \text{C}_2\text{H}_4 + \dot{\text{H}} (+M)$ at the same time, competition with the concerted elimination reaction $\dot{\text{C}}_2\text{H}_5 + \text{O}_2 \leftrightarrow \text{C}_2\text{H}_4 + \text{H}\dot{\text{O}}_2$ slow down the ignition making C₂H₆ slower than C₂H₄. C₂H₄ mixtures show the fastest reactivity due to the vinyl ($\dot{\text{C}}_2\text{H}_3$) chemistry that makes C₂H₄ the fastest fuel to ignite. Furthermore, C₃H₈ is much slower than C₂H₄ due to the high amount of methyl ($\dot{\text{C}}\text{H}_3$) radicals produced from $n\dot{\text{C}}_3\text{H}_7$ channels.

It was observed that for low temperatures ($T < 1100$ K), methyl chemistry is still responsible for the slow ignition exhibited by CH₄. This is because of the large amount of $\dot{\text{C}}\text{H}_3$ radicals reacting with O₂ to form methyl peroxy radicals $\dot{\text{C}}\text{H}_3 + \text{O}_2 \leftrightarrow \text{CH}_3\dot{\text{O}}_2$, which further react through $\text{CH}_3\dot{\text{O}}_2 + \text{CH}_3\dot{\text{O}}_2 \leftrightarrow \text{CH}_3\dot{\text{O}} + \text{CH}_3\dot{\text{O}} + \text{O}_2$ to inhibit the reactivity. However, here C₂H₆ is the second slowest due to the concerted elimination reaction, $\text{C}_2\text{H}_5\dot{\text{O}}_2 \leftrightarrow \text{C}_2\text{H}_4 + \text{H}\dot{\text{O}}_2$, which becomes very important at this temperature. Additionally, C₂H₄ is the second-fastest in igniting due to hydroxy-ethyl-peroxy ($\dot{\text{O}}_2\text{C}_2\text{H}_4\text{OH}$) and oxirane (C₂H₄O1–2) channels that enhance the reactivity. Moreover, C₃H₈ exhibits the fastest ignition at this temperature due to the considerable amount of OH radicals generated

by the addition of *n*-propyl ($\text{n}\dot{\text{C}}_3\text{H}_7$) radicals to O_2 and going to chain branching reactions.

Finally, several correlations were derived from mimicking the performance of NUIGMech1.2 in predicting the IDT characteristics of the blended fuels over a wide range of pressure, temperature, equivalence ratio, fuel composition, and dilution. The results demonstrated that the derived correlations could be depended upon as agile, fast, and reasonably reliable tools to predict the IDTs of the blends studied over their validity range of pressure, temperature, and mixture composition.

Fig. 2

Supplementary files

All supplementary files are attached to the online version of the article.

1. The Supporting Information file; including all referred items and plots in the manuscript.

2. The Supplementary files (.zip); including all raw data such as datasheets and oscilloscopes voltage and pressure traces etc.

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.2021.111626](https://doi.org/10.1016/j.combustflame.2021.111626).

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