An experimental and kinetic modeling study of the ignition delay characteristics of binary blends of ethane/propane and ethylene/propane in multiple shock tubes and rapid compression machines over a wide range of temperature, pressure, equivalence ratio, and dilution

Citation for published version (APA):
Martinez, S., Baigmohammadi, M., Patel, V., Panigrahy, S., Sahu, A. B., Nagaraja, S. S., Ramalingam, A., Mohamed, A. A. E. S., Somers, K. P., Heufer, K. A., Pekalski, A., & Curran, H. J. (2021). An experimental and kinetic modeling study of the ignition delay characteristics of binary blends of ethane/propane and ethylene/propane in multiple shock tubes and rapid compression machines over a wide range of temperature, pressure, equivalence ratio, and dilution. Combustion and Flame, 228, 401-414.
https://doi.org/10.1016/j.combustflame.2021.02.009

Document license:
CC BY

DOI:
10.1016/j.combustflame.2021.02.009

Document status and date:
Published: 01/06/2021

Document Version:
Publisher’s PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

• A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher’s website.
• The final author version and the galley proof are versions of the publication after peer review.
• The final published version features the final layout of the paper including the volume, issue and page numbers.

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

• Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
• You may not further distribute the material or use it for any profit-making activity or commercial gain
• You may freely distribute the URL identifying the publication in the public portal.

If the publication is distributed under the terms of Article 25fa of the Dutch Copyright Act, indicated by the “Taverne” license above, please follow below link for the End User Agreement:
www.tue.nl/taverne

Take down policy
If you believe that this document breaches copyright please contact us at:
openaccess@tue.nl
providing details and we will investigate your claim.

Download date: 11. Jun. 2022
An experimental and kinetic modeling study of the ignition delay characteristics of binary blends of ethane/propane and ethylene/propane in multiple shock tubes and rapid compression machines over a wide range of temperature, pressure, equivalence ratio, and dilution

Sergio Martinez, Mohammadreza Baigmohammadi, Vaibhav Patel, Snehasish Panigrahy, Amrit B. Sahu, Shashank S. Nagaraja, Ajoy Ramalingam, A. Abd El-Sabor Mohamed, Kieran P. Somers, Karl A. Heuffer, Andrzej Pekalski, Henry J. Curran

Combustion Chemistry Centre, School of Chemistry, Ryan Institute, MaREI, NUI Galway, University Road, Galway H91 TK33, Ireland

Physico-Chemical Fundamentals of Combustion, RWTH Aachen University, 52056 Aachen, Germany

Shell Research Limited, Shell Centre London, London SE1 7NA, United Kingdom

**ARTICLE INFO**

Received 12 November 2020
Revised 4 February 2021
Accepted 8 February 2021
Available online 2 March 2021

Keywords: Ethane Ethylene Propane Shock-tube Rapid compression machine Ignition delay time

**ABSTRACT**

In this work, the ignition delay time characteristics of C₂ – C₄ binary blends of gaseous hydrocarbons including ethylene/propane and ethane/propane are studied over a wide range of temperatures (750 – 2000 K), pressures (1 – 135 bar), equivalence ratios (0.5 – 2.0) and dilutions (75 – 90%). A matrix of experimental conditions is generated using the Taguchi (L₀) approach to cover the range of conditions for the validation of a chemical kinetic model. The experimental ignition delay time data are recorded using low- and high-pressure shock tubes and two rapid compression machines (RCM) to include all of the designed conditions. These novel experiments provide a direct validation of the chemical kinetic model, NUIG Mech11, and its performance is characterized via statistical analysis, with the agreement between experiments and model being within ~ 26.4% over all of the conditions studied, which is comparable with a general absolute uncertainty of the applied facilities (~ 20%). Sensitivity and flux analyses allow for the key reactions controlling the ignition behavior of the blends to be identified. Subsequent analyses are performed to identify those reactions which are important for the pure fuel components and for the blended fuels, and synergistic/antagonistic blending effects are therefore identified over the wide range of conditions. The overall performance of NUIG Mech11 and the correlations generated are in good agreement with the experimental data.

© 2021 The Authors. Published by Elsevier Inc. on behalf of The Combustion Institute. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/)

1. Introduction

According to the U.S. Energy Information Administration (EIA) report 2019 [1], it is projected that global energy consumption will increase by approximately 28% in 2050 compared to 2018 levels, with fossil fuels providing approximately 77% of the total energy demand. Liquid fuels, natural gas, and coal are the most important sources amongst all fossil fuels. Liquid fuels, such as gasoline, diesel, etc. are predicted to represent around 33% of energy consumption, with natural gas at close to 30%, coal near 18%, with the remaining 19% corresponding to nuclear, hydropower, and renewable sources [2].

The combustion of fossil fuels is the main sources of CO₂, SOₓ, and NOₓ emissions, among other pollutants. In this regard, natural gas is considered preferable to other fossil fuels including liquid fuels and coal as it is a cleaner energy source, having the highest hydrogen/carbon ratio among them. Widely used in the domestic, transportation, and industrial sectors, liquefied natural gas (LNG) is typically composed of methane (82–100%) but can contain substantial amounts of ethane, propane and butane, while
liquified petroleum gas (LPG) includes mainly propane, and butane. To reduce emissions, it is necessary to improve the efficiency of combustion systems for which a detailed understanding of the controlling chemistry is essential. The oxidation kinetics of small hydrocarbons plays an important role as the base of any mechanism for alternative fuels. For these reasons, the combustion community is interested in enhancing our understanding of the chemistry controlling the oxidation of hydrocarbons to increase the efficiency of engines and to reduce emissions of pollutants such as soot, NOx, UHCs (unburned hydrocarbons), and greenhouse gases in general. A hierarchical [3–6] (bottom-up) strategy has proven to be a good way to develop reliable chemical kinetic mechanisms and improve our understanding of the chemistry controlling pyrolysis and oxidation.

Combustion properties of fuels such as ignition delay time (IDT), speciation profiles, flame speed, among others become invaluable for the optimization of combustors. Relevant experiments and modeling studies for mono-fuels and some blends, such as ethylene, ethane, and propane, have been carried out with different methods and are available in the literature [7–14].

Dagaut et al. [15–17] studied species profiles consumed and produced during the oxidation ethylene, ethane, and propane in a jet-stirred reactor (JSR) using fuel mixtures diluted with nitrogen, at equivalence ratios (φ) of 0.1 – 4.0, at pressures ranging from 1 to 10 atm in the temperature range 800–1250 K. Their work showed the importance of small molecule sub-mechanisms including CO2, CH2O, CH4, C2H2, C2H4, and C3H6 on the combustion of higher hydrocarbons.

Lowry et al. [18] measured laminar premixed flame speeds of pure methane, ethane, and propane, and their binary blends with methane, at φ = 0.7 – 1.3, in a constant-volume cylindrical vessel, in the pressure range 1–10 atm, at room temperature (298 K). They highlighted the need to extensively study the synergistic effect of blends in comparison to pure fuels.

Baigmohammadi et al. [5,6] measured IDTs for pure ethylene, ethane, and propane, and binary alkane/alkene blends in a shock tube (ST) and in a rapid compression machine (RCM) at φ = 0.5–2.0, at pressures ranging from 20 to 40 atm in the temperature range of 800–2000 K. They showed that the synergistic effect on the reactivity of the mixture is important not only based on the fuel blends but in each variable considered during combustion such as pressure, temperature, dilution, etc. These previous studies [5,6,15–17] also used chemical kinetic mechanisms to predict the experimental data presented and identify the most relevant chemical reactions controlling the oxidation of these fuels.

Despite the large amount of data available for pure ethylene, ethane, and propane fuels, there are comparatively fewer studies of their blends, Table 1.

The current study aims to address the lack of data for mixtures by providing IDT data for binary C2H4/C2H6 and C2H2/C3H6 blends over a wide range of temperatures, pressures, equivalence ratios, and dilutions relevant to engine and gas turbine conditions. It also aims to validate a detailed chemical kinetic model using the novel experiments and literature data. We first provide a summary of the experimental conditions and approaches taken for this study, followed by details of the modeling work. The results and discussion section encompasses all of the comparisons of the model performance with the experimental data. Additionally, a comparison of the most important reactions for the pure fuels and their binary blends are presented to determine the kinetics controlling the reactivity of the blends.

| Facility | Fuel | pc / atm | Tc / K | Year | Reference |
|----------|------|----------|--------|------|-----------|
| ST/RCM   | C4H6 | 1 - 40   | 773 - 2200 | 1999 - 2020 | [5, 8, 19-22] |
| ST/RCM   | C6H6 | 1 - 40   | 830 - 1862 | 1971 - 2020 | [5, 9, 23-25] |
| ST/RCM   | C2H6 | 1 - 40   | 689 - 2615 | 1977 - 2013 | [26-31] |
| ST/RCM   | C2H6/C3H6 | 1 - 40 | 800 - 2000 | 2020 | [6] |

2. Design of experiments and experimental approaches

All of the measured IDTs collected and presented in this study were obtained using two different shock tubes (ST) and two rapid compression machines (RCMs). For those experiments carried out at NUI Galway at pressures ranging from 1 to 40 bar and intermediate-to-high-temperatures (> 1000 K), low- (LPST) (pc = 1 bar) and high-pressure (pc ≥ 20 bar) shock tubes (HPSTs) were applied. The IDT experiments corresponding to the relatively high-pressure (20 ≤ pc ≤ 40 bar) and low-temperature (< 1000 K) regimes were taken using a twin-piston RCM. Some experiments at working pressures of 40 bar and greater were measured using a single-piston RCM at the Physico-Chemical Fundamentals of Combustion (PCFC-RWTH [32,33]) Aachen University to enhance the fidelity of the experimental IDTs. Details of these facilities and their operating characteristics are available in the literature [6,34,35].

For the IDT experiments performed at NUIG, ethane, ethylene, and propane gases with a purity of 99.95% were supplied by Air liquid UK, BOC Ireland provided all other gases with purities of 99.99% for oxygen, nitrogen, argon, and 99.96% for helium. At the PCFC-RWTH Aachen University, the alkane/alkene gases were supplied by Westfalen AG with a 99.95% purity. All other gases were supplied by Westfalen AG and Praxair with purities of oxygen ≥ 99.995%, nitrogen ≥ 99.95%, and argon ≥ 99.996%.

To stochastically distribute the experimental IDTs, the experimental conditions for this study were generated using the Taguchi [36] approach by applying an L0 matrix based on four parameters of propane concentration, pressure, equivalence ratio, and dilution and also three different levels for each parameter studied. This approach has already been described by Baigmohammadi et al. [5,6].

For the mixture conditions studied, the propane concentration in the fuel blends varies from 10 to 50%, at pressures ranging from 10 to 135 bar, for φ of 0.5 – 2.0 and at dilutions of 75 – 90% (75% N2 + 0–15% Ar). However, the ratio between the diluents were changed at low-temperature regime (RCM) depending on the desired compressed gas temperature. A synopsis of the designed conditions is presented in Figure 1 and Table 2.

In the current study, most of the measured IDTs in the HPST and RCMs [10,33,37–42] are defined as the time between the end of compression and the maximum gradient in pressure (\(\frac{\Delta P}{\Delta t}\)) behind the reflected shock. However, we define the ignition event as the maximum gradient in CH⁺ (\(\frac{\Delta P}{\Delta t}\)) behind the reflected shock in the LPST measured by a photomultiplier and also when the test mixture is highly diluted in the HPST. The corresponding uncertainties involved in the measured IDTs are discussed by Baigmohammadi et al. [5,6]. Based on the analysis, the uncertainties in compressed mixture temperatures (σTc,5) and measured IDTs change for every individual experimental point depending on the initial temperature, pressure, and/or mixture composition. In this regard, the average uncertainties of the compressed temperatures and the measured IDTs in NUIG-L/HPSTs are estimated to be approximately ± 10 K and ± 25%, respectively. However, the compressed temper-
ature uncertainty and the measured IDT variation in the NUIG and PCFC RCMs are evaluated to be about ± 5 – 15 K and ± 20% over the entire range of conditions.

3. Computational modeling

In the current study, NUIGMech1.1 is used to simulate the experimental targets. This mechanism comprises 2746 species and 11,270 reactions, which is developed based on series of recent experimental [4–6,43–47] and theoretical studies [48–50]. These works are outcome of continuous evolution of the detailed NUIG-Mech1.1 model which is extensively validated in the prior studies for oxidation of C1−C2 hydrocarbons [5,6], natural gas mixtures [44], propane/propane blends [47], propyne [45], iso-butene [51], as well as auto-ignition and pyrolysis of C2−C6 alkenes [4,46]. The current work is a part of simultaneous development of the overall NUIGMecah1.1 mechanism. For the purpose of comparison, AramcoMech3.0 [52] is also utilized to perform simulations against the IDT experimental data from this study. Modifications of the most important reactions explicit to ethane, ethylene and propane chemistry in NUIGMech1.1 have not been mentioned in detail in previous publications [5,6,43,50], and thus are discussed in this study.

The experimental results were simulated using Python scripts based on the Cantera 2.4 [53] library and the CHEMKIN-Pro 18.2 [54] software. Cantera is suitable for automatization making data manipulation faster; however, Chemkin-Pro is faster for simulations involving large mechanisms and thus is more suitable for simulations when a full mechanism is required. As mentioned above, the definition of IDT is taken as the maximum gradient of pressure or radical concentration with respect to time for the ST simulations. In the RCM simulations, facility effects are included using the volume-time profiles derived from non-reactive experimental pressure-time traces in which O2 is replaced by N2 in the mixture [35,56].

The global model uncertainties, εMAD and εMAPE, are calculated based on the differences between the experimental data and mechanism simulated data using the Mean Absolute Deviations (MAD), and the Mean Absolute Percentage Error (MAPE), Eqs. (1) and (2), respectively. However, to analyze the data with an individual error, the Relative Percentage Error (RPE), εRPE, was used (Eq. (3)) to generate the histograms presented in this work. The

![Fig. 1. Experimental Taguchi [36] L9 matrix of conditions. For 90%/10%, 70%/30%, and 50%/50% ratios (a) red: binary C2H4/C2H6 blends, blue: binary C2H4/C3H8 blends. (b) pressure, equivalence ratio, and dilution parameters. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)](image-url)
mathematical expressions used are the following:
\[
\varepsilon_{\text{MAD}} = \frac{1}{n} \sum_{i=1}^{n} |\text{IDT}^\text{mod} - \text{IDT}^\text{exp}| \\
\varepsilon_{\text{MAPE}} = \frac{1}{n} \sum_{i=1}^{n} \left( \frac{|\text{IDT}^\text{mod} - \text{IDT}^\text{exp}|}{\text{IDT}^\text{exp}} \right) \times 100 \\
\varepsilon_{\text{RPE}} = \frac{\text{IDT}^\text{mod} - \text{IDT}^\text{exp}}{\text{IDT}^\text{exp}} \times 100
\]

where \( n \) is the total number of experimental measurements. Further details about the statistical analysis are provided as Supplementary material.

To identify the reactions controlling IDTs, brute-force sensitivity analyses were performed at the experimental conditions presented in this study. The sensitivity coefficient \( S \) [57] is defined as:
\[
S = \frac{\ln(\tau^+/\tau^-)}{\ln(k^+/k^-)} = \frac{\ln(\tau^+)}{\ln(k^+)} = \frac{\ln(k^-)}{\ln(2.0/0.5)}
\]

The sensitivity coefficient \( S \) calculated using the brute force method is based on the IDT \( \tau \), with the pre-exponential factor in the Arrhenius equations for each reaction perturbed in the sensitivity analysis. The sensitivity coefficient can be negative or positive, where a negative value refers to a reaction promoting reactivity (decreasing IDT), while a positive value refers to a reaction inhibiting reactivity (increasing IDT). Furthermore, rate of production (ROP) analyses were carried out to track the consumption of the blends and the production of intermediate species.

A global correlation discussion based on constant volume (CV) IDT simulations using NUIGMech1.1 is presented in the “Regression analysis” section (Section 4.5), together with general equations sorted by various temperature and pressure conditions. The aim of these correlations is to provide an easy and quick way to determine the IDT behavior of binary fuels. This does not require any kind of software pre-set up, and the coefficients of interest can be directly substituted in the equations provided in the respective section. A complete table of coefficient values and further details are provided as Supplementary material.

4. Results and discussions

All of the experimental results for the ethane/propane (C2H6/C3H8) and ethylene/propane (C2H4/C3H8) blends are presented in Section 4.1 together with simulations using NUIGMech1.1 and AramcoMech3.0 [52]. Henceforth, in all figures, the open symbols represent experimental LPST and/or HPST data, and the solid symbols represent the experimental low-temperature RCM data. Sections 4.2 – 4.4 present results for the effects of blend composition, pressure, and equivalence ratio using NUIGMech1.1 and their
corresponding correlations. Finally, Section 4.5 discusses the correlation performance.

4.1. Ethylene/propane and ethane/propane blends

Figures 2 and 3 present experimental data and model predictions of IDTs over the range of conditions studied for the binary C2H4/C3H8 and C2H6/C3H8 blends. Figures 2 and 3 show that NUIGMech1.1 is in better agreement than AramcoMech3.0 with the experimental data. Statistical analyses were conducted using the IDTs from the experiments, and those calculated using both NUIG-Mech1.1 and AramcoMech3.0. A total sample of 328 IDTs was used to determine the mean, standard deviation (σ), mean absolute deviation (MAD), relative percentage error (RPE), and mean absolute percentage error (MAPE). Figure S10(a) and S10(b), with “S” notation referring to the Supplementary material, provide the RPE frequency distribution for NUIGMech1.1 and AramcoMech3.0 relative to the IDT experiments. It can be inferred that the differences between NUIGMech1.1 and AramcoMech3.0 are a consequence of the poor predictions of AramcoMech3.0 in the low-temperature regime for the C2H4/C3H8 blends. Furthermore, the absolute value of MAPE calculated over the entire dataset using NUIGMech1.1 was 26.4%, while that for AramcoMech3.0 is 31.9%, indicating the greater accuracy of NUIGMech1.1. As it can accurately predict the IDT data measured over a wide range of temperatures, pressures and equivalence ratios, CV simulations are performed using NUIG-Mech1.1 to understand the effects of these operating conditions on the IDTs of the pure fuels and their binary blends.

4.2. Synergistic/antagonistic effect of blends

First, the ignition behavior of the pure fuels is analyzed to determine the important reactions controlling the reactivity. In Fig. 4, the IDT predictions for C2H4/air, C2H6/air, and C3H8/air mixtures at fuel-lean conditions, at pc = 40 bar and Tc in the range 740 – 1660 K are shown. At lower temperatures (Tc < 1050 K), C2H4 is the fastest fuel to ignite, however, the trend reverses at higher temperatures, and propane is the slowest to react compared to both C2H6 and C3H8. The reactivity of C2H6 is observed to be higher than C3H8 at all temperatures studied here.

To explore the controlling chemistry at high-temperature conditions, ROP analyses for C2H4/air, C2H6/air, and C3H8/air mixtures
are illustrated in Fig. 5 at \( T_C = 1430 \) K and \( p_C = 40 \) bar. The ROP analyses are performed following an elemental carbon (C) balance. The percentage value above the arrow refers to the percentage of the fuel proceeding through that pathway. The reaction paths represent the promoting (red color) and inhibiting (blue color) channels of the corresponding fuels. At high temperatures, the reactivity of all fuels is governed by the dominating chain branching reaction \( H + O_2 \rightarrow HO + OH \), which depends on the concentrations of H atoms and O\(_2\). In the case of \( C_2H_4/air \) ignition, at 1430 K, the fuel mainly undergoes H-atom abstraction by OH and H producing vinyl (\( C_2H_3 \)) radicals. This radical reacts with \( O_2 \) to generate vinyloxidation.

Ethylene is an important intermediate formed during \( C_2H_6 \) oxidation. At 1430 K, \( C_2H_6 \) consumption is initiated by H-atom abstraction primarily by OH and H forming ethyl (\( C_2H_5 \)) radicals. There has been a wide variety of experimental investigations for these rate constants, as shown in Fig. S13. NUIGMech1.1 has an updated rate constant for H-atom abstraction by OH based on the fit recommended by Krasnoperov and Michael [69]. For H-atom abstraction by H atoms, we have adopted the theoretical calculations from Sivaramakrishnan et al. [70]. \( C_2H_5 \) radicals decompose promptly to \( C_2H_4 \) and H atoms, which undergo chain branching by reacting with \( O_2 \) via \( H + O_2 \rightarrow HO + OH \), promoting reactivity. However, at 1430 K, approximately 15% of \( C_2H_5 \) radicals react with \( O_2 \) to form \( C_2H_4 \) via H-atom abstraction that competes...
with C$_2$H$_6$ radical decomposition. The subsequent reaction pathways associated with the C$_2$H$_4$ consumption flux are governed by the high-temperature chemistry of C$_2$H$_4$ as discussed in the previous paragraph. At higher temperature conditions, C$_2$H$_4$ + O$_2$ $\leftrightarrow$ C$_2$H$_4$ + HO$_2$, as well as the H-atom abstraction by H from the fuel which competes with the main chain branching reaction H + O$_2$ $\leftrightarrow$ O + OH, are responsible for the lower reactivity of C$_2$H$_6$ compared to C$_2$H$_4$.

Similar to ethane and ethylene, propane oxidation is mainly driven by H-atom abstraction by OH radicals and H atoms, generating primary (iC$_3$H$_7$) and secondary propyl (iC$_3$H$_7$) radicals. Due to the importance of H-atom abstraction by OH from propane, there have been a large number of measurements performed, Fig. S14. The rate constants adopted in this work are best fits from the more recent direct measurements by Sivaramakrishnan et al. [71], who investigated the branching fraction for the abstraction of the secondary C-H bond in the temperature range 927 – 1146 K, together with the measurement by Droge and Tully [72] over the temperature range 298–900 K (Fig. S14). At 1430 K, approximately 15% of the C$_3$H$_8$ is consumed by unimolecular decomposition producing C$_2$H$_4$ and methyl (CH$_3$) radicals, Fig. S(c). Substantial concentrations of CH$_3$ radicals are also formed from nC$_3$H$_7$ radicals. Methyl radicals are consumed by reaction with HO$_2$ to produce methoxy radicals through the chain branching reaction CH$_3$ + HO$_2$ $\rightarrow$ CH$_3$O + OH, which promotes reactivity. The route through the chain-terminating reaction CH$_3$ + HO$_2$ $\rightarrow$ CH$_4$ + O$_2$ inhibits reactivity. This competition between chain branching and termination significantly influences IDT predictions for C$_3$H$_8$. The rate constants for these reactions are taken from the theoretical calculations of Jasper et al. [73] and Zhu and Lin [74] respectively. The rate constants and the branching ratio of the two CH$_3$ + HO$_2$ channels agree well with the most recent experimental measurements by Hong et al. [75] (Fig. S15). The self-recombination of CH$_3$ radicals producing C$_3$H$_8$ further contributes to a reduction in the reactivity of propane. The presence of high concentrations of CH$_3$ radicals ultimately decreases the reactivity of C$_3$H$_8$ compared to C$_2$H$_4$ at high-temperature conditions.

The effects on IDTs of the addition of C$_2$H$_4$ to C$_2$H$_4$/air and C$_2$H$_4$/air mixtures are presented in Fig. 4. The reactivities of the mixtures increase significantly for the 90% C$_2$H$_4$/10% C$_3$H$_8$ and 90% C$_2$H$_4$/10% C$_3$H$_8$ binary blends at lower temperatures in the range 740–1000 K. The addition of only 10% C$_3$H$_8$ to the C$_2$H$_4$/air and C$_2$H$_4$/air mixtures shortens IDTs by a factor of 2.8 and 2.0 respectively, at 790 K. To interpret the influence of C$_3$H$_8$ addition on the ignition of the C$_2$H$_4$/air and C$_2$H$_4$/air mixtures, sensitivity analyses were performed at 790 K, Fig. 7. Moreover, Figure 8 illustrates the flux analyses performed for these mixtures in the same condition. The black color represents the flux for the pure C$_2$H$_4$/air or C$_2$H$_4$/air mixtures, and the red color represents the flux for the C$_3$H$_8$ blended binary mixtures. The flux analysis presented in Fig. 8 shows that adding propane to the mixture does not alter the reaction pathways of ethylene and ethane chemistry nor does it significantly affect their flux values.

At 790 K, for both pure C$_2$H$_4$ and the 90% C$_2$H$_4$/10% C$_3$H$_8$ blend, ethylene is primarily consumed by the addition of OH radical to the double bond forming hydroxethyl radicals, which accounts for approximately 70% of the overall C$_2$H$_4$ consumption. These radicals add to molecular oxygen producing hydroxethyl-peroxy radicals (O$_2$C$_2$H$_4$OH), which subsequently decompose, producing two formaldehyde molecules and an OH radical or form vinyl alcohol and HO$_2$ radicals, the former being the most favorable product channel promoting reactivity for the C$_2$H$_4$/air mixture, Fig. 8(a). Besides OH addition, HO$_2$ addition to ethylene producing oxirane (C$_2$H$_4$O1–2) and an OH radical and this reaction also has a large promoting effect on the reactivity of ethylene at low temperatures, especially for fuel-rich conditions.

The importance of the C$_2$H$_4$ + HO$_2$ $\rightarrow$ C$_2$H$_4$O1–2 + OH and O$_2$C$_2$H$_4$OH $\rightarrow$ products reaction systems on C$_2$H$_4$ oxidation is shown in Fig. 8(a), which also presents the performance of the current mechanism and AramcoMech3.0 as can be seen by the red solid lines and black dashed lines, respectively for the 90% C$_2$H$_4$/10% C$_3$H$_8$ mixtures at $p_c$ = 20 atm, and ϕ = 2.0. AramcoMech3.0 severely under-predicts the IDTs, particularly in the low temperature region in the range 800–900 K. AramcoMech3.0 implemented a reaction rate for C$_2$H$_4$ + HO$_2$ $\rightarrow$ C$_2$H$_4$O1–2 + OH based on the recommendation by Zsély et al. [11]. Recently Zádor et al. [77] and Klippenstein [76] studied the potential energy surfaces of the C$_2$H$_4$O$_2$ system using high-level quantum chemistry calculations. NUIGMech1.1 has adopted the rate constant for C$_2$H$_4$ + HO$_2$ from Klippenstein [76], which is approximately a factor of three lower than the rate constant recommended by Zsély et al. [11] at 800 K, Fig. 9(b). Updating this rate constant in AramcoMech3.0 leads to a significant improvement in IDT predictions as depicted by the dashed-dotted line in Fig. 9(a). Another important reaction pathway controlling ethylene IDT is the consumption of O$_2$C$_2$H$_4$OH radicals through the Waddington
mechanism $\text{O}_2\text{C}_2\text{H}_4\text{OH} \rightarrow 2\text{CH}_2\text{O} + \text{OH}$ and the $\text{HO}_2$ elimination channel producing $\text{C}_2\text{H}_5\text{OH}$ which inhibits reactivity. In NUIG-Mech1.1 the rate constant for the dissociation of $\text{O}_2\text{C}_2\text{H}_2\text{OH}$ radicals is adopted from Zádor et al. [78]. AramcoMech3.0 utilized an estimated rate constant for the Waddington pathway that is an order of magnitude higher than the rate determined by Zádor et al. [78], while surprisingly, the $\text{HO}_2$ elimination channel was not included in the mechanism. The last agreement represented by the solid black line in Fig. 9(a) is attained by updating both $\text{C}_2\text{H}_4 + \text{HO}_2$ and dissociations of $\text{O}_2\text{C}_2\text{H}_2\text{OH}$ reactions in AramcoMech3.0 that leads to significant improvement in the agreement of the simulations compared to the experimental measurements.

As seen in Fig. 8(a), OH radicals can abstract hydrogen atoms from ethylene producing $\text{C}_2\text{H}_3$ radicals. These add to $\text{O}_2$ generating vinyl-peroxy radicals, which subsequently dissociate to formaldehyde, $\text{CO}$, and $\text{H}$ atoms. Some $\text{C}_2\text{H}_3$ radicals also produce $\text{CH}_3\text{CHO}$ and $\text{O}$ atoms increasing the reactivity of ethylene ignition, as shown in Fig. 7(a). For the $\text{C}_2\text{H}_4/\text{air}$ mixture, the fuel is mainly consumed by $\text{H}$-atom abstraction by $\text{OH}$ and $\text{HO}_2$ radicals forming $\text{C}_2\text{H}_3$ radicals. These react with $\text{O}_2$ to produce ethylperoxy ($\text{C}_2\text{H}_5\text{O}_2$) radicals, which subsequently decompose to $\text{C}_2\text{H}_4$ and $\text{HO}_2$ radicals. Figure 7(b) shows that the concerted elimination reaction $\text{C}_2\text{H}_2\text{O}_2 \leftrightarrow \text{C}_2\text{H}_4 + \text{HO}_2$ is important in inhibiting the autoignition of $\text{C}_2\text{H}_4$.

Figure 7(a) and 7(b) shows that $\text{C}_2\text{H}_4$ specific reactions become important when propane is added to the $\text{C}_2\text{H}_4/\text{air}$ and $\text{C}_2\text{H}_4/\text{air}$ mixtures. At 790 K, $\text{H}$-atom abstraction from $\text{C}_2\text{H}_4$ by $\text{OH}$ producing $\text{nC}_2\text{H}_7$ and $\text{H}_2\text{O}$ is the most sensitive reaction promoting reactivity, while abstraction leading to $\text{iC}_2\text{H}_7$ radicals inhibits reactivity. At 790 K, $\text{C}_2\text{H}_4/\text{air}$ and $\text{C}_2\text{H}_4/\text{air}$ mixtures.
blend) of iC\textsubscript{3}H\textsubscript{7} radicals react with O\textsubscript{2} to form C\textsubscript{2}H\textsubscript{4} and H\textsubscript{2}O radicals, which reduces reactivity. However, –38.3% (C\textsubscript{2}H\textsubscript{4}/C\textsubscript{3}H\textsubscript{8} blend) and –37.8% (C\textsubscript{2}H\textsubscript{4}/C\textsubscript{3}H\textsubscript{8} blend) of nC\textsubscript{3}H\textsubscript{7} radicals add to O\textsubscript{2} forming n-propyl-peroxy (nC\textsubscript{3}H\textsubscript{2}O\textsubscript{2}) radicals which undergo isomerization generating hydroperoxyl-propyl (C\textsubscript{3}H\textsubscript{2}OOH\textsubscript{1–3}) radicals. These then further add to O\textsubscript{2} producing hydroperoxyl-peroxy radicals (C\textsubscript{3}H\textsubscript{2}OOH\textsubscript{1–3O\textsubscript{2}}), which isomerize to produce carbonylhydroperoxides and OH radicals. The carbonylhydroperoxides can further dissociate, producing a carbonyl-alkoxy radical and a second OH radical, which is a chain branching pathway, resulting in higher reactivity of the C\textsubscript{3}H\textsubscript{5} blended mixtures compared to the pure C\textsubscript{2}H\textsubscript{4}/air or C\textsubscript{3}H\textsubscript{8}/air mixtures.

4.3. Effect of pressure on ignition

Figure 10 presents the influence of pressure on the IDTs for the 50% C\textsubscript{2}H\textsubscript{4}/50% C\textsubscript{3}H\textsubscript{8} and 50% C\textsubscript{2}H\textsubscript{4}/50% C\textsubscript{3}H\textsubscript{8} binary blended mixtures as well as for pure C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}H\textsubscript{6} at $\varphi = 0.5$ and 75% N\textsubscript{2} dilution. The model predicts that the reduction in reactivity due to the addition of C\textsubscript{3}H\textsubscript{8} with C\textsubscript{2}H\textsubscript{4} at 1 atm is more than for the corresponding 20 atm and 40 atm cases at intermediate and higher temperature conditions. The self-recombination of methyl radicals is responsible for the lower reactivity of the propane blended mixtures as discussed in Section 4.2. In the case of the C\textsubscript{2}H\textsubscript{4}/C\textsubscript{3}H\textsubscript{8} blend at 1250 K, as the pressure decreases to 1 atm the CH\textsubscript{3} + CH\textsubscript{3} (+M) ↔ C\textsubscript{2}H\textsubscript{6} (+M) reaction more strongly inhibits reactivity, accounting for 35% of the total flux through methyl radicals, while at 40 bar this reaction contributes only 12% to CH\textsubscript{3} consumption. Furthermore, from Fig. 10 it is observed that the overall reactivity of the system increases with pressure due to the corresponding increase in the concentration of the reactants. At 800 K, upon increasing the pressure from 1 to 20 atm, there is an order of magnitude increase in reactivity observed for both the C\textsubscript{2}H\textsubscript{4}/C\textsubscript{3}H\textsubscript{8} and C\textsubscript{2}H\textsubscript{6}/C\textsubscript{3}H\textsubscript{8} mixtures. There is approximately a four-fold increase in reactivity by increasing the pressure from 20 to 40 atm. To determine the reactions controlling IDT predictions at these conditions, sensitivity analyses are presented in Fig. 11 and Fig. S16 for the binary mixtures at $p_c = 1$, 20, and 40 atm.

Figure 11 shows that at low temperature (800 K) and high-pressure conditions (20 and 40 atm), the reactivity of the binary blends is mainly controlled by H-atom abstraction from C\textsubscript{3}H\textsubscript{8} by OH radicals, with the formation of nC\textsubscript{3}H\textsubscript{7} radicals promoting reac-
tivity and iC\textsubscript{3}H\textsubscript{7} radicals inhibiting reactivity. However, at 800 K and 1 atm, H-atom abstraction from C\textsubscript{3}H\textsubscript{8} no longer influences IDT predictions, but rather the competition between the reactions generating and consuming hydrogen peroxyde, via H\textsubscript{2}O\textsubscript{2} + HO\textsubscript{2} ↔ H\textsubscript{2}O\textsubscript{2} + O\textsubscript{2} and H\textsubscript{2}O\textsubscript{2} (+M) ↔ OH + OH (+M), respectively control the reactivity of the binary blends. The flux analyses presented in Figure 12 show that, at 40 atm pressure, the percentage contribution of nC\textsubscript{3}H\textsubscript{7} radical β-scission forming C\textsubscript{3}H\textsubscript{4} and CH\textsubscript{3}O reduces, while the importance of nC\textsubscript{3}H\textsubscript{7} radical addition to O\textsubscript{2} increases compared to the 1 atm case. Since the addition of nC\textsubscript{3}H\textsubscript{7} radicals to O\textsubscript{2} and the subsequent chain branching channels produces two reactive OH radicals and thus increases reactivity, the formation of nC\textsubscript{3}H\textsubscript{7} radicals, and other low-temperature reactions those are not favorable at low pressures become significant in controlling the overall reactivity of the binary mixtures at higher pressures. At the higher temperature of 1600 K, the reactivity is only controlled by the chain branching reaction, H + O\textsubscript{2} ↔ O + OH irrespective of pressure, as seen in Figs. 11(b) and S16. The reactions that consume H atoms such as, C\textsubscript{3}H\textsubscript{8} + H ↔ nC\textsubscript{3}H\textsubscript{7} + H\textsubscript{2}, C\textsubscript{3}H\textsubscript{8} + H ↔ iC\textsubscript{3}H\textsubscript{7} + H\textsubscript{2}, C\textsubscript{3}H\textsubscript{8} + H ↔ C\textsubscript{2}H\textsubscript{5} + H\textsubscript{2}, CH\textsubscript{3}O + H ↔ H\textsubscript{2}O + H\textsubscript{2} and H + O\textsubscript{2} (+M) ↔ HO\textsubscript{2} (+M) compete with H + O\textsubscript{2} ↔ O + OH and thus inhibit the reactivity of the binary mixtures (Fig. 11).

4.4. Effect of equivalence ratio on ignition

Figure 13 presents the effect of equivalence ratio on IDTs for the pure fuels, 50% C\textsubscript{3}H\textsubscript{8}/50% C\textsubscript{3}H\textsubscript{8} and 50% C\textsubscript{2}H\textsubscript{6}/50% C\textsubscript{3}H\textsubscript{8} binary mixtures at p\textsubscript{c} = 20 atm, 75% N\textsubscript{2}, and at ϕ = 0.5, 1.0, and 2.0. It is observed that at temperatures above 1250 K, the reactivities of both the pure fuels and the binary mixtures are fastest for the fuel-lean mixtures and slowest for the fuel-rich mixtures. However, at a temperature below 1250 K, fuel-rich mixtures are fastest to ignite, and the fuel-lean mixtures are slowest. To determine the governing chemistry under these conditions, sensitivity analyses were per-

![Fig. 11.](image-url) Sensitivity analyses to IDT predictions as function of pressure at ϕ = 0.5, 50% C\textsubscript{3}H\textsubscript{8}/50% C\textsubscript{3}H\textsubscript{8} (a) 800 K and (b) 1600 K.

![Fig. 12.](image-url) Flux analyses at 800 K, ϕ = 0.5, p = 1 (black), and 40 atm (red), with 75% N\textsubscript{2} as diluent for (a) 50% C\textsubscript{3}H\textsubscript{8}/50% C\textsubscript{3}H\textsubscript{8}, and (b) 50% C\textsubscript{2}H\textsubscript{6}/50% C\textsubscript{3}H\textsubscript{8}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
formed, the results of which are presented as a function of equivalence ratio in Figs. S17 and S18 at 800 K and 1600 K. At high temperatures (> 1250 K), IDTs are mainly controlled by the concentration of O\textsubscript{2} in the binary blends through the main chain branching reaction \( \text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH} \), and its influence increases as the mixture becomes leaner. Thus, fuel-lean mixtures are fastest to ignite at high temperatures. However, at low temperatures (< 1250 K), the reactivity is mainly governed by the addition of the fuel derived alkyl radicals to \( \text{O}_2 \) and the following low-temperature chemistry leading to chain branching, which is limited by the fuel concentration through H-atom abstraction from propane by \( \text{OH} \) radicals. Thus, at a lower temperature, the dependence on the equivalence ratio is reversed, with fuel-rich mixtures being the most reactive.

4.5. Regression analysis

Global regression equations have been developed using NUIG-Mech1.1 with approximately 17,280 CV simulations for each blend mixture spanning over five parameters: \( \phi_C (1 - 40 \text{ atm}) \), \( T_C \ (800 - 2000 \text{ K}) \), \( \phi \ (0.2 - 2.0) \), dilution (75% - 90%) and fuel ratio composition (50% \( \text{C}_2\text{H}_4 \) or \( \text{C}_2\text{H}_6 \)/50% \( \text{C}_3\text{H}_8 \), and 70% \( \text{C}_2\text{H}_4 \) or \( \text{C}_2\text{H}_6 \)/30% \( \text{C}_3\text{H}_8 \)). The regression equations developed using the predictions with the ST experimental data in Fig. S20 and S21 of the Supplementary material. The expression (\( \tau_{corr} \)) used is analogous to the Arrhenius rate expression and is defined as shown in Eq. (4) below:

\[
\tau_{corr} = 10^A e^\frac{E}{RT} [\text{C}_2\text{H}_4]^\alpha [\text{C}_2\text{H}_6]^\beta [\text{C}_3\text{H}_8]^\gamma [\text{oxidizer}]^\delta \text{[diluent]}^\zeta
\]  

(4)

where \( A \) represents the pre-exponential factor coefficient, \( B \) represents the activation energy, and \( C - G \) are the concentration dependencies of ethylene, ethane, propane, oxidizer, and dilution, respectively. A synopsis of the derived correlations for the binary fuels studied in the pressure range 20 \( \leq \phi_C \leq 40 \text{ atm} \) over three regimes of temperature is presented below. However, details of the coefficients of the derived correlations along with their corresponding \( \chi^2 \) and \( R^2 \) for the \( \text{C}_2\text{H}_4/\text{C}_2\text{H}_6 \) and \( \text{C}_2\text{H}_6/\text{C}_3\text{H}_8 \) mixtures are presented in Table S6 and S7, respectively.

For 1500 \( \leq T_C \leq 2000 \text{ K} \):

\[
\tau_{corr} = 10^{-10.34} e^\frac{-316.33}{T} [\text{C}_2\text{H}_4]^{-0.502} [\text{C}_2\text{H}_6]^{0.403} [\text{oxidizer}^{-1.080}] \text{[diluent]}^{0.354}
\]  

(5)

For 1100 \( \leq T_C \leq 1500 \text{ K} \):

\[
\tau_{corr} = 10^{-9.402} e^\frac{206.65}{T} [\text{C}_2\text{H}_4]^{0.113} [\text{C}_2\text{H}_6]^{0.413} [\text{oxidizer}^{-1.344}] \text{[diluent]}^{0.131}
\]  

(6)

For 800 \( \leq T_C \leq 1100 \text{ K} \):

\[
\tau_{corr} = 10^{-9.727} e^\frac{14132.32}{T} [\text{C}_2\text{H}_4]^{-0.443} [\text{C}_2\text{H}_6]^{-0.392} [\text{oxidizer}^{-0.427}] \text{[diluent]}^{-0.017}
\]  

(9)

\[
\tau_{corr} = 10^{-9.52} e^\frac{16.02.7}{T} [\text{C}_2\text{H}_4]^{-0.145} [\text{C}_2\text{H}_6]^{-0.555} [\text{oxidizer}^{-0.186}] \text{[diluent]}^{-0.145}
\]  

(10)

At high temperatures (1500–2000 K), the coefficient for ethylene is strongly negative, while those for ethane and propane are positive. This is because at high temperatures increasing the ethylene concentration increases the concentration of vinyl radicals, which react with \( \text{O}_2 \) (\( \text{C}_2\text{H}_2 + \text{O}_2 \leftrightarrow \text{CH}_2\text{CHO} + \text{O} \)) in a reaction which is chain branching. On the other hand, both ethane and propane compete with \( \text{O}_2 \) for \( \text{H} \) atoms, and if their concentrations increase, the rate of \( \text{H} + \text{O}_2 \leftrightarrow \text{O} + \text{OH} \) decreases, reducing reactivity. For ethane/propane mixtures, both coefficients are positive, but it is less positive for ethane than for propane, as the oxidation of ethane leads to higher concentrations of ethylene. Thus, increasing the concentration of ethane relative to propane will increase reactivity and vice versa.

At low temperatures (800–1100 K), the coefficients associated with ethylene, ethane, and propane become negative, with ethane being less negative than propane. At lower temperatures, propane promotes reactivity through the addition of \( n \)-propyl radicals to
O₂ that proceeds to chain branching through the low-temperature reaction sequence that generates two highly active OH radicals. Thus, for the ethane/propane mixtures, increasing the propane concentration will increase mixture reactivity. However, for ethylene/propane mixtures, the coefficient of ethylene is comparable to that of propane, as ethylene and propane exhibit similar reactivities in the temperature range between 900 and 1100 K, as seen in Fig. 4.

It is interesting to note that, at high temperatures Eqs. (5) and (6), the magnitude of the oxidizer coefficients (−1.08 and −1.344 for C₂H₆/C₃H₈ and C₂H₆/C₃H₈ blends, respectively) are significantly larger, by a factor of two or more, than for the corresponding fuel coefficients, thus showing a higher sensitivity towards oxidizer concentrations at these conditions. As we approach the lower temperature regimes Eqs. (9) and (10), the coefficients associated with each fuel become higher and are even larger than the corresponding oxidizer coefficients, thus representing the increasing importance of fuel-based kinetics. These characteristics observed in the correlations corroborate the discussion of the underlying kinetics in Section 4 above and enable the correlations to capture the IDT trends effectively.

5. Conclusions

An experimental and kinetic modeling study of the IDT characteristics of C₂ – C₃ binary blends of C₂H₆/C₃H₈ and C₂H₆/C₆H₆ mixtures over a wide range of experimental conditions, pressures (1–135 atm), temperatures (−750–2000 K), equivalence ratios (0.5 ≤ ϕ ≤ 2.0) and 75–90% of dilution percentage were presented. The performance of NUIG Mech1.1 and its corresponding derived correlations were evaluated against the experimental data collected. Results show that NUIG Mech1.1 is in good agreement within −26.4% of model uncertainty to the measured IDTs over the studied conditions, compared to −35% for Aramco Mech3.0. Moreover, correlations can predict the experimental IDTs appropriately under specific regimes, becoming a useful tool in predicting the behavior of C₂ – C₃ binary blends at specific conditions.

Finally, the effects of blend composition, pressure and equivalence ratio on IDTs were investigated for various mixtures containing C₂H₆, C₃H₈ and C₆H₆ as reactants. It was observed that for all mixtures, as the temperature and pressure increase, IDTs decrease. For the effect of equivalence ratio, an expected crossover point was observed at Tₕ – 1250 K, wherein the controlling chemistry switches such that the trends invert their behavior. The reactivity of C₂H₆ was found to be higher than for C₃H₈ throughout the temperature range examined in this study. At higher temperatures, vinoxy radicals and oxygen atoms formed from the reaction of vinyl radicals with O₂, proceed via dissociation and bimolecular reactions with C₂H₆, to produce a substantial amount of H atoms resulting in faster ignition of C₂H₆/air mixtures. The concerted elimination reaction between C₂H₅ and O₂ is responsible for the reduction in ethane reactivity. It was observed that C₂H₆ blend fuels were the fastest to ignite at lower temperatures (< 1250 K), however, the trend is reversed at higher temperatures, and C₃H₈ exhibited the slowest reactivity compared to both C₂H₆ and C₃H₈ at T > 1250 K. In the case of C₂H₆, at low temperatures n-propyl radical formation, followed the classical low-temperature chain branching pathways via its addition to O₂ generate OH radicals promoting reactivity, while methyl radical recombination and reaction with HO₂ leading to CH₄ and O₂ reduces reactivity at higher temperatures.

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.

Acknowledgments

The authors would like to express their gratitude to Science Foundation Ireland (SFI) via their Research Centre Programme through project numbers 15/IA/3177 and 16/SP/3829, KAV-ICHEC via the project ngche079c, and to Shell Research Ltd. The authors from PCFC RWTH Aachen University would like to recognize the funding support from the German Research Foundation (Deutsche Forschungsgemeinschaft, DFG) through the project number -322460823 (HE7599/2–1).

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2021.02.009.

References

[1] U.S.E.I. Administration, International energy outlook 2019 with projections to 2050, IEA2019, 2019.
[2] S. Bilgen, Structure and environmental impact of global energy consumption, Renew. Sustain. Energy Rev. 38 (2014) 900–902.
[3] W.K. Metcalfe, S.M. Burke, S.S. Ahmed, H.J. Curran, A hierarchical and comparative kinetic modeling study of C₁–C₂ hydrocarbon and oxygenated fuels, Int. J. Chem. Kinet. 45 (2013) 638–675.
[4] S.S. Nagaraja, J. Liang, S. Dong, S. Panigrahy, A. Sahu, G. Kukkadapu, S.W. Wagner, W.J. Pitz, H.J. Curran, A hierarchical single-pulse shock tube pyrolysis study of C₂–C₅ 1-alkenes, Combust. Flame 219 (2020) 456–466.
[5] M. Baigomhammedi, V. Patel, S. Martinez, S. Panigrahy, A. Ramalingam, U. Burke, K.P. Somers, K.A. Heuer, A. Pekalski, H.J. Curran, A comprehensive experimental and simulation study of ignition delay time characteristics of single fuel C₁–C₂ hydrocarbons over a wide range of temperatures, pressures, equivalence ratios, and dilutions, Energy Fuels 34 (3) (2020) 3755–3771.
[6] M. Baigomhammedi, V. Patel, S. Nagaraja, A. Ramalingam, S. Martinez, S. Panigrahy, A.A.E. Mohamed, K.P. Somers, U. Burke, K.A. Heuer, A. Pekalski, H.J. Curran, Comprehensive experimental and simulation study of the ignition delay time characteristics of binary blended methane, ethane, and ethylene over a wide range of temperature, pressure, equivalence ratio, and dilution, Energy Fuels 34 (7) (2020) 8808–8823.
[7] M.M. Kopp, N.S. Donato, E.L. Petersen, W.K. Metcalfe, S.M. Burke, H.J. Curran, Oxidation of ethylene-air mixtures at elevated pressures, part 1: experimental results, J. Propuls. Power 30 (2014) 790–798.
[8] M.M. Kopp, E.L. Petersen, W.K. Metcalfe, S.M. Burke, H.J. Curran, Oxidation of ethylene-air mixtures at elevated pressures, part 2: chemical kinetics, J. Propuls. Power 30 (2014) 799–811.
[9] C.J. Aul, W.K. Metcalfe, S.M. Burke, H.J. Curran, E.L. Petersen, Ignition and kinetic modeling of methane and ethane fuel blends with oxygen: a design of experiments approach, Combust. Flame 160 (2013) 1153–1167.
[10] S.M. Gallagher, H.J. Curran, W.K. Metcalfe, D. Healy, J.M. Simmge, G. Bourque, A rapid compression machine study of the oxidation of propane in the negative temperature coefficient regime, Combust. Flame 153 (2008) 316–333.
[11] L.G. Zsély, T. Nagy, J.M. Simmge, H.J. Curran, Reduction of a detailed kinetic model for the ignition of methane/propane mixtures at gas turbine conditions using simulation error minimization methods, Combust. Flame 158 (2011) 1469–1479.
[12] A. Burcat, R.W. Crossley, K. Scheller, Shock tube investigation of ignition in ethane-oxygen-argon mixtures, Symp. (Int.) Combust. 18 (1972) 115–123.
[13] H. Hashemi, J.G. Jacobson, C.T. Rasmussen, J.M. Christensen, P. Glarborg, S. Gersen, M. van Essen, H.B. Levinsky, S.J. Klippenstein, High-pressure oxidation of ethane, Combust. Flame 182 (2017) 150–166.
[14] S. Gersen, A.V. Mokhov, J.H. Darmeweal, H.B. Levinsky, P. Glarborg, Ignition-promoting effect of NO₂ on methane, ethane and methane/ethane mixtures in a rapid compression machine, Proc. Combust. Inst. 33 (2011) 433–440.
[15] P. Daguin, J.C.C. Boettner, M. Cathonnnet, Ethylene pyrolysis and oxidation: a kinetic modeling study, Int. J. Chem. Kinet. 22 (1990) 641–664.
[16] P. Daguin, M. Cathonnnet, J.C. Boettner, F. Gaillard, Kinetic modeling of propane oxidation, Combust. Sci. Technol. 56 (1987) 23–63.
[17] P. Daguin, M. Cathonnnet, J.C.C. Boettner, Kinetics of ethane oxidation, Int. J. Chem. Kinet. 23 (1991) 437–455.
[18] B. Lowry, J. de Vries, M. Krejci, E. Petersen, Z. Serinyel, W. Metcalfe, H. Curran, G. Bourque, Laminar flame speed measurements and modeling of pure alkanes and alkane blends at elevated pressures, Proceedings of ASME Turbo Expo 2010: Power for Land, Sea and Air (2010) 1–10.
[19] C.J. Brown, G.O. Thomas, Experimental studies of shock-induced ignition and transition to detonation in ethylene and propane mixtures, Symp. (Int.) Combust. 117 (1999) 861–870 1999.
A. Ramalingam, S. Panigrahy, Y. Fenard, H. Curran, K.A. Heuer, A chemical kinetic perspective on the low-temperature oxidation of propane/propane mixtures through experiments and kinetic analyses, Combust. Flame 223 (2021) 369–375.

Y. Sun, C.W. Zhou, K.P. Somers, H.J. Curran, An ab initio/transient state theory of the reactions of CH$_3$H species of relevance to 1,3-pentadiene, Part I: potential energy surfaces, thermochemistry and high-pressure limiting rate coefficients, J. Phys. Chem. A 109 (2005) 7590–7613.

Y. Sun, C.-W. Zhou, K.P. Somers, H.J. Curran, An ab initio/transient state theory of the reactions of CH$_3$H species of relevance to 1,3-pentadiene, Part II: pressure dependent rate constants and implications for combustion modeling, J. Phys. Chem. A 124 (2020) 4001–4018.

J. Power, K.P. Somers, C.-W. Zhou, S. Peukert, H.J. Curran, A theoretical, experimental and modeling study of the reaction of hydrogen atoms with 1- and 2-Pentene, J. Phys. Chem. A 123 (2019) 8506–8526.

N. Sivadas, S. Panigrahy, C.M. Pitz, K.A. Heuer, Energy of isooctane kinetics on the reactivity of di-isobutylene and iso-octane, Combust. Flame 222 (2020) 186–195.

C.W. Zhou, Y. Li, U. Burke, C. Banyon, K.P. Somers, S. Ding, S. Khan, J.W. Hargis, T. Sikes, O. Mathieu, E.L. Petersen, M. AlAbbad, A. Farooq, Y. Yan, Z. Huang, J. Lopez, L. Loparo, S.S. Vasu, W.J. Pitz, H.J. Curran, The influence of iso-butane kinetics on the reactivity of di-isobutylene and iso-octane, Combust. Flame 222 (2020) 186–195.

D.G. Goodwin, R.L. Speth, H.K. Moffat, B.W. Weber, Cantera: an object-oriented software toolkit for chemical kinetics, thermodynamics, and transport processes, https://www.cantera.org, doi:10.5281/zenodo.1702341.

K. Lee, S.H. Yoo, W.K. Kang, K.H. Jung, Reaction of O$_3$P$^\cdot$ atoms with CF$_3$ – CVT (X, Y = F, F, Br), Discharge flow-chemistry/micromachining technique, Chem. Phys. Lett. 323 (2001) 401–418.

S.J. Vermeulen, V.S. Artemyev, V.I. Venedeyov, The mechanism of O$_3$P$^\cdot$ oxidation with ethylene and other simple olefins, Int. J. Chem. Kin. 24 (1992) 545–561.

O. Horie, R. Taeg, B. Remmann, N.L. Arthur, P. Pottinger, Kinetics and mechanisms of combustion, Flash of the reactions of O$_3$P$^\cdot$ with SiH$_4$, SiH$_2$Cl$_2$, SiH$_2$Cl$_2$, and CH$_3$SiH$_3$, J. Phys. Chem. 95 (1991) 4393–4400.

D.M.V. Fondeire, J. Peeters, The kinetic coefficient of the CH$_3$H$^+$O reaction extended over extensive pressure and temperature ranges, Physico-chemical behaviour of atmo-...spheric pollutants, Springer, Dordrecht (1984), pp. 274–282.

R.B. Kleemann, J.W. Sutherland, M.A. Wickramaaratnam, G. Yarwood, Flash photolysis–shock tube kinetic study of the reaction of atomic oxygen with 3P$^\cdot$ ethylene, 10525. Interg. Tetterou.284.K. J. Phys. Chem. 94 (8) (1990) 3354–3357.

M. Mahmud, P. Marshall, A. Fontijns, A high-temperature photophotometry kinetic study of the reaction of oxygen (3P$^\cdot$) atoms with ethylene from 290 to 1510K, J. Phys. Chem. 91 (6) (1987) 1568–1573.

T.L. Nguyen, L. Vreeveek, X.J. Hou, M.T. Nguyen, J. Peeters, Potential energy surfaces, product distributions and thermal rate coefficients of the reaction of O$_3$P$^\cdot$ with CH$_3$H$_2$X (X = H, D): a comprehensive theoretical study, J. Phys. Chem. A 109 (33) (2005) 7485–7499.

L.N. Krzasevoper, J.V. Michael, Shock tube studies using a novel multipass absorption cell: rate constant results for OH + H$_2$ and OH + CH$_3$H$_2$J. Phys. Chem. A 108 (2004) 5634–5648.

R. Sivaramakrishnan, J.V. Michael, B. Rusic, High-temperature rate constants for H+CH$_3$H and CH$_3$, Int. J. Chem. Kinet. 44 (3) (2012) 194–205.

R. Sivaramakrishnan, C.F. Goldsmith, S. Peukert, J.V. Michael, Direct measurements of channel specific rate constants in OH + CH$_3$IIH$_2$ promt dissociations of propyl radicals, Proc. Combust. Inst. 37 (2019) 231–238.

A.T. Drooge, F.P. Tully, Hydrogen atom abstraction from alkanes by hydroxyl 3. Propane, J. Phys. Chem. 90 (1986) 1949–1954.

A.W. Jasper, S.J. Klippenstein, L.B. HARDING, Theoretical rate coefficients for the reaction of methyl radical with hydroperoxy radical and for methylhydroperoxyl, J. Phys. Chem. A 103 (2009) 729–736.

R. Zhu, C. Lin, The CH$_3$ + HO$_2$ Reaction: First-principles prediction of its rate constant and product branching probabilities, J. Phys. Chem. A 105 (2001) 6243–6248.
[75] Z. Hong, D.F. Davidson, K.-Y. Lam, R.K. Hanson, A shock tube study of the rate constants of HO$_2$ and CH$_4$ reactions, Combust. Flame 159 (2012) 3007.
[76] S.J. Klippenstein, From Theoretical reaction dynamics to chemical modeling of combustion, Proc. Combust. Inst. 36 (2017) 77–111.
[77] J. Zádor, R.X. Fernandes, Y. Georgievskii, G. Meloni, C.A. Taatjes, J.A. Miller, The reaction of hydroxyethyl radicals with O$_2$: a theoretical analysis and experimental product study, Proc. Combust. Inst. 32 (2009) 271–277.
[78] J. Zádor, S.J. Klippenstein, J.A. Miller, Pressure-dependent OH yields in alkene+HO$_2$ reactions: a theoretical study, J. Phys. Chem. A 115 (2011) 10218–10225.
[79] M.S. Stark, D.J. Waddington, Oxidation of propene in the gas phase, Int. J. Chem. Kinet. 27 (2) (1995) 123–151.