Karimkashi, Shervin; Kahila, Heikki; Kaario, Ossi; Larmi, Martti; Vuorinen, Ville

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*Published in:*
International Journal of Hydrogen Energy

*DOI:*
10.1016/j.ijhydene.2019.12.033

E-pub ahead of print: 03/01/2020

*Document Version*
Publisher's PDF, also known as Version of record

*Please cite the original version:*
Numerical study on tri-fuel combustion: Ignition properties of hydrogen-enriched methane-diesel and methanol-diesel mixtures

Shervin Karimkashi*, Heikki Kahila, Ossi Kaario, Martti Larmi, Ville Vuorinen

Aalto University, Department of Mechanical Engineering, School of Engineering, Otakaari 4, 02150, Espoo, Finland

Article info

Article history:
Received 26 July 2019
Received in revised form 18 November 2019
Accepted 5 December 2019
Available online xxx

Keywords:
Dual-fuel ignition
Tri-fuel ignition
Diesel
Hydrogen
Methane
Methanol

Abstract

Simultaneous and interactive combustion of three fuels with differing reactivities is investigated by numerical simulations. In the present study, conventional dual-fuel (DF) ignition phenomena, relevant to DF compression ignition (CI) engines, are extended and explored in tri-fuel (TF) context. In the present TF setup, a low reactivity fuel (LRF), methane or methanol, is perfectly mixed with hydrogen and air to form the primary fuel blend at the lean equivalence ratio of 0.5. Further, such primary fuel blends are ignited by a high-reactivity fuel (HRF), here n-dodecane under conditions similar to HRF spray assisted ignition. Here, ignition is relevant to the HRF containing parts of the tri-fuel mixtures, while flame propagation is assumed to occur in the premixed LRF/H₂ containing end gas regions. The role of hydrogen as TF mixture reactivity modulator is explored. Mixing is characterized by n-dodecane mixture fraction \( x \), and molar ratio \( x = \frac{X_{H_2}}{X_{H_2} + X_{LRF}} \). When \( x < 0.6 \), minor changes are observed for the first- and second-stage ignition delay time (IDT) of tri-fuel compared to dual-fuel blends (\( x = 0 \)). For methane, when \( x > 0.6 \), first- and second-stage IDT increase by factor 1.4—2. For methanol, a respective decrease by factor 1.2—2 is reported. Such contrasting trends for the two LRFs are explained by reaction sensitivity analysis, indicating the importance of OH radical production/consumption in the ignition process. Observations on LRF/H₂ end gas laminar flame speed (\( S_l \)) indicate that \( S_l \) increases with \( x \) due to the highly diffusive features of H₂. For methane, \( S_l \) increase with \( x \) is more significant than for methanol.

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Introduction

The global requirement to shift towards carbon-neutral energy production in the stationary and transportation systems has led to development of various decarbonization strategies and using renewable energy resources [3]. While the technologies to achieve carbon-neutral systems are still under development, the next generation internal combustion engines (ICE) are designed to achieve efficient combustion of less polluting fuels or their blends with other fuels. With relevance...
to the present study, it is of particular importance to understand ignition properties of fuel blend combinations for both emerging and existing fuels in the market.

Dual-fuel (DF) compression ignition (CI) engines have been studied extensively over the past decade. An example of a relatively recent DF CI engine is the reactivity-controlled compression ignition (RCCI) technique [2]. The main idea in such DF techniques is to use a blend of a high-reactivity fuel (HRF), such as diesel, and a low-reactivity fuel (LRF), e.g. methane/methanol/gasoline, to ignite and burn the mixture interactively. In such DF CI engines, HRF at low temperature is injected to the high-temperature ambient of premixed LRF/air. Therefore, the HRF facilitates ignition process of the LRF/air blend which delivers the main energy release. The past DF studies include diesel (or its surrogates) combined with e.g. gasoline [3,4], natural gas and methane (CH4) [5–7], methanol (CH3OH) [8–11], and ethanol (C2H5OH) [12–14]. Despite their low amounts of NOx and soot particulates compared to single fuel (SF) diesel CI engines [15,16], high levels of carbon-containing emissions, such as CO and CH4, still pose a challenge. The unburned hydrocarbons are mainly resulting from incomplete combustion due to unsuccessful ignition or relatively slow turbulent flame propagation within the charge [2].

Hydrogen (H2) is a carbon-free energy carrier with well-known decarburizing features and it can potentially mitigate carbon-containing emissions in CI engines. Although commercial production of hydrogen is currently dependent mainly on natural gas steam reforming [17] and coal partial oxidation [18], it is on the pathway towards clean production through biomass- and solar-based production methods [19]. These methods include e.g. biohydrogen production, renewable electrolysis, photoelectrochemical solar water splitting, and solar high temperature thermochemical cycles [20]. Decarburizing features of hydrogen, depletion of fossil fuels and on the other hand, abundant availability of hydrogen are encouragements to consider utilization of hydrogen in CI engines. However, as hydrogen features considerably lower flammability limits compared to typical LRFs (such as natural gas) [21], its usage in CI engine context requires special attention. On the other hand, for the range of temperatures and pressures encountered in CI engines, it is challenging to autoignite hydrogen within the desired millisecond timescale [22], which hinders its use as a pure ignition provider. Despite the mentioned challenges, hydrogen blends with other commercial fuels present remarkable advantages. For example, hydrogen enriched natural gas can be produced from coal or biomass gasification and it features higher reactivity compared to natural gas without hydrogen [23,24]. Higher reactivity and higher diffusivity of hydrogen may e.g. increase the flame speed, which could reduce unburned hydrocarbon emissions.

In the spark ignition (SI) engines context, extensive efforts are devoted to investigation of hydrogen addition effects on gasoline [25,26], natural gas [27–31] or methane [25,28,32–34] combustion, where higher efficiency and reduced emissions, depending on the engine specifications, are reported. Several zero-dimensional (0d), one-dimensional (1d), and experimental studies have scrutinized characteristics of ignition and laminar flame speed (S) for DF blends, e.g. methane/hydrogen [35–38], and natural gas/hydrogen [38–40]. Despite the relatively long history of the studies on H2 addition in SI engines context, the idea behind its application in CI engines is quite recent, and relates to the addition of H2 in DF CI engines, called tri-fuel (TF) CI engines. For example, recently, Bhattacharya and Basu [41], have shown the benefits of adding H2 and CH4 to dimethyl ether (DME) in reducing NO formation.

The recent investigations on TF CI engines, whether experimentally [42–48] or numerically [49–51], mainly concentrate on its influence on improving engine performance and efficiency and decreasing carbon emissions footprint by enabling a better consumption of the primary fuel-air charge. On the other hand, compared to blends of hydrogen and light hydrocarbon LRFs (such as natural gas and gasoline), considerably fewer works have studied interactive hydrogen/HRF combustion. These scarce works investigate ignition characteristics of hydrogen addition to SF n-dodecane-air [22], n-heptane-air [52–54], and iso-octane-air [55] and present some common conclusions. For example, Aggarwal et al. [22] and Jain et al. [55] show that below ≈ 80 % by volume hydrogen in the blend does not have a significant influence on ignition. However, hydrogen in higher amounts delays ignition of n-dodecane (or n-heptane) at lower temperatures (e.g. T = 700–900 K), while it may advance ignition at higher temperatures. The main reason for delay in ignition at lower temperature conditions was noticed to be consumption of OH through H2 + OH ↔ H + H2O due to presence of H2 [22,55]. It is of high interest to increase utilization of hydrogen in CI engines which requires better understanding of its ignition features.

While there is abundant literature on simultaneous combustion of diesel (and its surrogates) with LRF such as methane and methanol, which span from 0d models [56,57] to three-dimensional spray investigations [58,59], the literature review indicates that there is still an evident gap to understand ignition properties and flame characteristics of H2 addition to various combinations of DF blends. Accordingly, this work concerns variations of ignition properties with adding H2 to two different DF combinations, n-dodecane/methane, and n-dodecane/methanol. Use of n-dodecane as a diesel surrogate is considered due to its highly similar thermochemical properties with diesel fuel [60]. Here, similar to our past DF studies [58,59], thermophysical conditions and mixture states are chosen to follow the Engine Combustion Network (ECN) Spray A target case on diesel spray combustion [61]. The target conditions are modified in steps towards various TF combinations. Ignition characteristics of TF blends are investigated by homogeneous reactor computations. Moreover, laminar flame speed characteristics are studied with sweeps of hydrogen in methane/H2 and methanol/H2 blends using 1d freely-propagating premixed laminar flames.

With relevance to the presented literature review, main objectives of this study are to 1) introduce TF concept in CI engine context, 2) validate a chemical kinetics mechanism for ignition and laminar flame speed of n-dodecane, methane, methanol, and hydrogen SF as well as for their DF blends, where experimental data is available, and 3) study effects of H2 addition on the first- and second-stage ignition properties in homogeneous TF blends of n-dodecane/methane/H2 and n-dodecane/methanol/H2 through 0d numerical simulations.
Numerical methods

Chemical mechanism validation

In the present study, ignition and laminar flame properties of n-dodecane blended with either methane/H₂ or methanol/H₂ are investigated with Cantera software [62] using a reduced chemical kinetics mechanism, which is originally developed for combustion of n-dodecane-air, by Frassoldati et al. [63], called ‘Polimi reduced’ mechanism hereafter. Polimi reduced, which is selected among different mechanisms tested under engine-relevant conditions, contains 96 species and 993 reaction steps and its validation process is presented here. It should be mentioned that neither a chemical mechanism nor any experimental data on ignition and flame properties of TF H₂/methane/n-dodecane and H₂/methanol/n-dodecane have been provided in the literature. Therefore, here, the validation process of Polimi reduced is limited to available SF or DF blends at constant volume homogeneous reactor conditions.

For brevity, here, we refer to previous validations made for Polimi reduced in the literature as much as possible, and only those required validations that do not appear in the literature are presented. For SF ignition delay time (IDT) and SI validations, we refer to Ref. [58] for methane, Ref. [66] for methanol, and Ref. [63] for n-dodecane. For hydrogen SF ignition, Fig. 1(a) and for methane/H₂ DF blend ignition, Fig. 1(b) compare the numerical results using Cantera with experiments in Refs. [64, 65], where consistency between the present and reference results is observed.

Laminar flame speed validations under various equivalence ratio (φ) and pressures for methane-air in Fig. 2(a), for H₂-air in Fig. 2(b) and (c), and for methane/H₂-air DF blends in Fig. 3 demonstrate reliability of Polimi reduced mechanism under the tested conditions. Experiments shown in Fig. 3 include experimental data from Refs. [35, 39, 67, 68], as marked in the figure. We note that the multi-component transport model in Cantera has been used for all laminar flame calculations in this study. Here, x defines molar ratio of H₂ added to LRF,

\[ x = \frac{X_{H_2}}{X_{H_2} + X_{LRF}} \]  

where LRF refers to methane or methanol. The molar ratio x is also the main parameter of interest in the present study.

It should be mentioned that the authors have not found any experimental data on IDT and SI for methanol/H₂ DF blends or any TF blends studied in this work to be used in the mechanism validation process. As such, we rely on the SF validation results and apply the Polimi reduced mechanism in TF conditions. However, as mechanism sensitivity assessment, IDT calculations with Polimi reduced mechanism against the detailed version of the mechanism called Polimi detailed with 451 species and 17848 reaction steps is provided in Fig. 4 for selected TF conditions from the results section of the present study. Here, mixture fraction, ξ, is used to describe the mixing extent of n-dodecane (ξ = 1) and the DF blend of LRF/H₂/air (ξ = 0) based on the definition by Bilger et al. [80], which will be further explained in the following section. It is observed that Polimi reduced and Polimi detailed provide similar IDT trends with varying x in both n-dodecane/methane/H₂ and n-dodecane/methanol/H₂ TF blends.

Remarks on SF IDT

Fig. 5(a) demonstrates IDT calculations against temperature for SF combustion of H₂, methane, and methanol with the equivalence ratio φ = 0.5 under 60 bar pressure. Two different chemical kinetics mechanisms have been used for each set of calculations; Polimi reduced and another mechanism, namely, Petersen mechanism [81] for H₂-air and methane-air, and Klippenstein mechanism [82] for methanol-air. Petersen mechanism has been already validated in the literature for SF H₂-air and methane-air under high pressure conditions [38] and Klippenstein mechanism is a modified version of the mechanism by Juan et al. [83] for ignition of SF methanol-air at high pressures. It is observed that Polimi reduced performs well in calculation of IDT within the wide range of considered temperature for these fuels.
According to Fig. 5(a), within the range of initial temperature encountered in engine relevant conditions, e.g. 700–900 K, all of these fuels present a rather long IDT in comparison to the diesel surrogate n-dodecane, c.f. Fig. 5(b). For example at 60 bar and 900 K, IDT values of SF H₂ and methane exceed 100 ms. For H₂, as consistent with the literature (e.g. Ref. [38]) there is a sudden decrease in IDT around 1400 K. Among methanol, methane and hydrogen, for typical compression temperatures \( T < 1000 \) K, methanol has the shortest IDT. However, the associated time scales are still typically higher than the desired millisecond time scales in the CI engine context. Therefore, in order to enable ignition of such LRFs in CI engines, DF concept has been introduced where HRF (typically diesel) with a shorter IDT facilitates the ignition process.

Fig. 5(b) shows temperature dependence of n-dodecane IDT at 60 bar and \( \phi = 0.5 \), resembling the well-known negative coefficient temperature (NTC) behavior. The considerably shorter (less than 1 ms) IDT of n-dodecane (as a diesel surrogate) within the discussed temperature range (700–900 K) facilitates the ignition process in a DF CI engine. It is worth noting that n-dodecane IDT features three different ranges; low temperature (LT), NTC, and high temperature (HT) regions as displayed in Fig. 5(b). These regions are important for better understanding of the ignition process in a DF or TF system and they will be further discussed in the results section of the present study.

**Remarks on SF and DF end gas flame speed**

As mentioned earlier, ‘end gas’ refers to a blend of LRF/H₂ with particular relevance to flame propagation after TF ignition. According to recent studies [58,59,84], flame initiation starts in the periphery of HRF spray towards the LRF primary fuel.

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Fig. 2 – \( S_f \) against equivalence ratio for a) \( \text{CH}_4 \)-air at \( T_\text{in} = 300 \) K, b) \( \text{H}_2 \)-air at \( T_\text{in} = 300 \) K, and c) \( \text{H}_2 \)-air at \( T_\text{in} = 365 \) K; using Polimi reduced mechanism under different initial pressures compared to experiments. Symbols in (a): square [69], diamond [70], circle [71], star [72], triangle [73] - Symbols in (b): square [74], diamond [75], circle [76], star [77], triangle [68], cross [78] - Symbols in (c): square [78] - the data are summarized in Ref. [79].
Thereby, for $S_l$ and flame temperature calculations, we only consider flame propagation in the end gas and concentrate on the effect of adding $\text{H}_2$ to either methane or methanol without $\text{n-dodecane}$. It is worth noting that the influence of $\text{n-dodecane}$ on methane/air laminar flame speed is considered in our previous investigations [85].

Fig. 6 presents $S_l$ against $\phi$ for SF $\text{H}_2$ compared to methane and methanol under 1 bar at 363 K (a), and 60 bar at 800 K (b) initial pressure and temperature. Although it is well known that $\text{H}_2$ has a considerably higher $S_l$ compared to methane and methanol, this effect is less strong at lean conditions encountered in CI engines (c.f. Fig. 6(c) for $\phi = 0.5$–0.7 at 60 bar). It should be mentioned that at these high pressure and temperature conditions, steady flame fronts might not exist, for example c.f. [86], and here, reported $S_l$ values are considered as numerical estimates. The main observations from Fig. 6 are that 1) hydrogen has the highest flame speed among the three fuels at both pressures and 2) at $\phi = 0.5$–0.7 and $p = 60$ bar, the flame speed of hydrogen is by factor 2 larger than for the two other fuels.

Fig. 7 shows $S_l$ against $\phi$ by adding $\text{H}_2$ to methane (a) and methanol (b) at 60 bar and 800 K. Also, Fig. 8 depicts effects of adding $\text{H}_2$ (a) on the ratio of $S_l$ (a) and adiabatic flame temperature $T_F$ (b) to their reference SF methane-air and methanol-air at initial conditions of $\phi = 0.5$, $p = 60$ bar and $T_{in} = 800$ K. According to Fig. 7, with adding $\text{H}_2$, until $\phi = 0.8$, $S_l$ trends are similar to SF LRF/air ($x = 0$) even though hydrogen addition increases $S_l$. At lean conditions $\phi = 0.5$, according to Fig. 8, effect of $\text{H}_2$ addition on $S_l$ is more dominant for methane than for methanol. For methane, at $x = 0.8$, $S_l$ decreases.
Sl becomes more than two times larger than that of SF, whereas for methanol this increase is less pronounced. Also, flame temperature increase due to H2 addition at \( \phi = 0.5 \) is relatively small in both cases. These observations are consistent with the results in Ref. [38], where for methane at lean and high pressure conditions, H2 is shown to have a limited influence on Sl and TF increase.

The main observation from the discussion above is that methane/hydrogen blends pose a high flame speed with increasing x while in methanol/hydrogen blends flame speed is comparable to that of pure methanol. We note that the high flame speed of hydrogen results largely from its high diffusivity. Hence, the flame speed and IDT are not necessarily correlated for the present tri-fuel blends. Here, the main

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Fig. 5 – Single-fuel IDT calculations using Polimi reduced (solid line) at 60 bar under different initial temperatures and \( \phi = 0.5 \) for a) H2-air, CH4-air, and CH3OH-air in comparison with Petersen mechanism [81] for H2-air, and CH4-air (dotted), and Klippenstein mechanism [82] for CH3OH-air (dotted), b) n-dodecane-air.

Fig. 6 – Single-fuel Sl calculations using Polimi reduced mechanism against equivalence ratio for H2-air, CH4-air, and CH3OH-air at a) 1 bar and \( T_{in} = 363 \) K, b) 60 bar and \( T_{in} = 800 \) K, and c) lean 60 bar and \( T_{in} = 800 \) K.

Fig. 7 – Sl against equivalence ratio at \( T_{in} = 800 \) K and \( p = 60 \) bar for different blends of a) CH4/H2, and b) CH3OH/H2.
interest is on understanding TF ignition, which forms the
focus of the remainder of this study.

Numerical setup

In a previous study, Kahila et al. [58,59] investigated DF n-
dodecane/methane ignition characteristics by means of large-
eddy simulation (LES) in engine-relevant conditions corre-
sponding to the ECN Spray A target case. Here, the same
thermodynamical conditions are followed and the focus is
extended to TF chemistry in order to include H2 in the blend.
In order to achieve adiabatic mixing line relation [87] between
the fuel-air ratio and temperature, it is needed to define two
characteristic gas streams leading to the homogeneous
reactor. The schematic picture in Fig. 9 shows the constant
volume 0d homogeneous reactor and the two presumed
streams according to their enthalpies, which is calculated based on the inert mixing of the
gaseous blend (air + CH4 or CH3OH before mixing with n-dodecane). We
note that at each x, H2 is added to the gaseous blend stream while phi_gas is always kept constant at 0.5. Second, phi_t is the equivalence ratio in the TF blend, where H2 and LRF are considered inert and not consuming O2. For instance, phi_t indicates equivalence ratio for n-dodecane when there is no
H2 in the homogeneous TF blend in the reactor before ignition. It should be noted that stoichiometric mixture fraction when
x = 0, phi_t, is 0.031 for methane case and 0.030 for methanol
case, which are used as reference values in the following
section.

For n-dodecane ignition, it is a common practice to identify
temperature chemistry (HTC) is distinguished
considered inert and not consuming O2. For instance,
that maximum gradient of temperature with respect to time,
through the second-stage IDT,
indicates equivalence ratio for n-dodecane when there is no
H2 in the homogeneous TF blend in the reactor before ignition.
maximum gradient of temperature with respect to time,
through the second-stage IDT, 10, which is defined as the time
that 20% of maximum C12H25OO (called RO2 hereafter) is produced [59]. On the other
hand, high temperature chemistry (HTC) is distinguished
through the second-stage IDT, 10, which is defined as the time
that maximum gradient of temperature with respect to time,
(\frac{dT}{dt})_{max}, is achieved. All of the following computations are
carried out by Cantera software.

An enthalpy-based progress variable (c\textsubscript{\text{H2-o}}) is defined to
determine contribution of the HRF within the HRF/LRF-air DF
blends without H2 addition (x = 0) in the 0d homogeneous
reactor in terms of enthalpy,

\begin{equation}
\frac{c_{\text{H2-o}}}{c_{\text{H2-o,new}}} = \frac{h_{\text{H2}}}{h_{\text{H2,new}}} = \frac{Y_{\text{H2,o}}}{Y_{\text{H2,new}}} \leq 0.5
\end{equation}

where h and Y denote enthalpy and mass fraction of HRF (n-
dodecane here), and LRF (whether methane or methanol).

Two equivalence ratio definitions are considered. First, phi_gas is defined in the gaseous blend stream for the blend of air, H2 and either CH4 or CH3OH before mixing with n-dodecane. We
note that at each x, phi_gas is always kept constant at 0.5. Second, phi_t indicates equivalence ratio in the TF blend, where H2 and LRF are considered inert and not consuming O2. For instance, phi_t indicates equivalence ratio for n-dodecane when there is no
H2 in the homogeneous TF blend in the reactor before ignition. It should be noted that stoichiometric mixture fraction when
x = 0, phi_t, is 0.031 for methane case and 0.030 for methanol
case, which are used as reference values in the following
section.

For n-dodecane ignition, it is a common practice to identify
temperature chemistry (HTC) using the first-stage IDT, 10, defined here based on the time that 20% of maximum C12H25OO (called RO2 hereafter) is produced [59]. On the other
hand, high temperature chemistry (HTC) is distinguished
through the second-stage IDT, 10, which is defined as the time
that maximum gradient of temperature with respect to time,
(\frac{dT}{dt})_{max}, is achieved. All of the following computations are
carried out by Cantera software.

An enthalpy-based progress variable (c_{\text{H2-o}}) is defined to
determine contribution of the HRF within the HRF/LRF-air DF

![Fig. 8 Ratio of DF to SF for a) S1 and b) T_f at \( \phi = 0.5 \) for CH4/H2, and CH3OH/H2 with \( T_{in} = 800 \) K and \( p = 60 \) bar. Note the almost unity y-axis scale in (b).](image)

Fig. 9 – Schematic representation of the presumed streams
and the constant volume 0d reactor.
Numerical results

The role of H₂ in TF ignition

N-dodecane/methane/H₂ blends

Fig. 10(a) displays the second-stage IDT \( (\tau_2) \) changes in a TF n-dodecane/methane/H₂ system against \( \xi \) with varying H₂ concentration. As mentioned in the numerical setup section, varying \( \xi \) changes n-dodecane mass fraction while \( \phi_{\text{gas}} \) (methane/H₂-air) is kept constant at 0.5. In the top x-axis, \( \phi_{\text{ndd}}=0 \) represents equivalence ratio for n-dodecane in the blend (assuming inert methane and H₂) when \( \tau = 0 \). We note that at higher values of \( x \), \( \phi_{\text{ndd}} \) varies slightly, and when \( x \) is constant, it is a function of \( \tau \). Here, \( \phi_{\text{ndd}}>0 \) is only provided as an additional information on n-dodecane concentration in the blend. Also, Table 1 provides examples of changes in fuels and air initial mole fractions (X) at two selected \( \xi \) when \( x \) varies in n-dodecane/methane/H₂ blends.

Fig. 10(a) demonstrates that H₂ concentration has an inhibiting effect on \( \tau_2 \) at the operational range of \( \xi \), i.e. within lean to the most reactive mixture fraction (\( \xi_{\text{MR}} \)) defined as the \( \xi \) with the shortest \( \tau_2 \) for each blend with constant \( x \). The prolonged second-stage IDT with higher H₂ concentration is marginal until \( x = 0.5 \), after which more distinct differences are noted. Moreover, it was earlier mentioned that adding H₂ increases \( \Delta T \) in methane/H₂ blends due to the high diffusivity of hydrogen. These findings are consistent with the literature for TF CI engine experiments and computational models, e.g. c.f. [44,51], where retard of IDT and shorter combustion duration by adding H₂ were reported.

In Fig. 10(b), first, effects of H₂ addition on the first- (\( \tau_1 \)) and second-stage IDT (\( \tau_2 \)) at \( \xi_{\text{MR}} \) for each blend at constant \( x \) compared to the DF case (\( x = 0 \)) are displayed. For the blends marked by 1–V in the figure, \( \xi_{\text{MR}} \) is respectively 0.07, 0.075, 0.08, 0.085, and 0.095. This figure shows that H₂ addition delays both \( \tau_1 \) and \( \tau_2 \) at \( \xi_{\text{MR}} \); i.e. both \( \tau_1^{\text{MR}} / \tau_1^{\text{DF}} \) and \( \tau_2^{\text{MR}} / \tau_2^{\text{DF}} \) increase. Second, according to Fig. 10(b), along the entire range of \( x \), \( \tau_2^{\text{MR}} / \tau_1^{\text{MR}} \approx 1.7 \pm 0.1 \), i.e. the ratio of \( \tau_2^{\text{MR}} \) to \( \tau_1^{\text{MR}} \) at each \( x \) remains almost constant, which indicates that the observed inhibiting effect on \( \tau_2 \) with adding H₂ is directly corresponding to the prolonged \( \tau_1 \). This finding is an important aspect when considering the general sensitivity of LTC in chemical mechanisms. The mechanism used for TF studies should be able to cover LTC features as well as possible.

In order to gain a better insight into the ignition process of a TF problem, Fig. 11 shows time evolution of temperature (a), and mass fractions for some important radicals and intermediate species (b) at a representative value of \( \xi = 0.05 \) (\( = 1.5 \xi_{\text{DF}} \)), for two extremes, \( x = 0 \) and \( x = 1 \). It is worth reminding that in general, the considered species, HO₂, H₂O₂, and OH play pivotal roles in the ignition process, and RO₂ is an important intermediate radical in decomposition of n-dodecane and it can be used to distinguish the first-stage IDT, e.g. c.f. [58]. Also, it should be noted that in this figure, mass fractions are scaled with the factors displayed in the figure labels in order to achieve a better visual presentation.

In Fig. 11(a), temperature profiles reveal the effect of H₂ addition on \( \tau_1 \) and \( \tau_2 \). It is observed that H₂ addition retards the first-stage IDT and consequently, the second-stage IDT, being inline with Fig. 10. Moreover, H₂ addition weakens the moderate first temperature rise, corresponding to the first-stage ignition. However, the products temperature after the second-stage ignition is higher with the increased H₂ content.

Fig. 10 – Ignition properties of different blends of n-dodecane/methane/H₂ (\( p = 60 \) bar, \( T_{\text{in,gas}} = 900 \) K, \( T_{\text{in,pilot}} = 363 \) K, \( \phi_{\text{gas}} = 0.5 \)): a) second-stage IDT against \( \xi \) (n-dodecane mass fraction) while \( \phi_{\text{gas}} = 0.5 \), and b) ratio of the second-to first-stage IDT at \( \xi_{\text{MR}} \).

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</tbody>
</table>
While Fig. 11(a) resembles a two-stage ignition feature at all \( x \) values, the chemical kinetics associated with these two stages is depicted in Fig. 11(b) by considering the time evolution of important intermediate species. Within the first time interval \((0 \leq t \leq t_1)\), the earlier peak of \( \text{HO}_2 \) forms, and this peak is directly related to the first-stage IDT. The low temperature first-stage ignition is also distinguishable through the peak value of \( \text{RO}_2 \) mass fraction. Over the second time interval \((t_1 \leq t \leq t_2)\), the earlier peak of \( \text{HO}_2 \) drops gradually and \( \text{HO}_2 \) converts to \( \text{H}_2\text{O}_2 \) having slow chemistry \([90]\). Eventually, when the later peak of \( \text{HO}_2 \) and peak of \( \text{H}_2\text{O}_2 \) are reached, both concentrations decrease drastically and form \( \text{OH} \) radicals, initiating HTC and being the onset of the second-stage IDT. According to Fig. 11, when \( \text{H}_2 \) is added to the system, both \( \text{RO}_2 \) peak and the earlier peak of \( \text{HO}_2 \) have smaller values, with delayed formation. Moreover, the peak magnitude of \( \text{H}_2\text{O}_2 \) and the second peak of \( \text{HO}_2 \) and \( \text{RO}_2 \) are accordingly, the peak of \( \text{OH} \) become larger in magnitude and present a significant delay.

The aforementioned observations in Fig. 11(a) and (b) imply that effects of \( n\)-dodecane concentration on the ignition process in \( n\)-dodecane/methane/\( \text{H}_2 \) TF blends are to 1) delay the first- and second-stage IDT, 2) decrease relative concentrations of intermediate species during LTC, 3) increase the \( \text{OH} \) concentration during HTC and accordingly, increase the products temperature. Consistently, Masouleh et al. [85] and Khalila et al. [58, 59] have shown that adding LRF (methane) has a large impact on the first-stage ignition throughout oxidation paths.

**N-dodecane/methanol/\( \text{H}_2 \) blends**

Fig. 12(a) depicts the second-stage IDT \((t_2)\) effects against \( \xi \) in a TF \( n\)-dodecane/methanol/\( \text{H}_2 \) system with varying \( \text{H}_2 \) concentrations. As mentioned earlier, varying \( \xi \) changes \( n\)-dodecane mass fraction while \( \phi_{\text{gas}} \) is kept constant at 0.5. Also, Table 2 lists fuels and air initial mole fractions at selected \( \xi \) and \( x \) for specific \( n\)-dodecane/methanol/\( \text{H}_2 \) blends.

According to Fig. 12(a), in contrast to what was observed before for \( n\)-dodecane/methane/\( \text{H}_2 \) TF blends, \( \text{H}_2 \) addition reduces \( t_2 \) in \( n\)-dodecane/methanol/\( \text{H}_2 \) TF blends. Therefore, the more \( \text{H}_2 \) is added to the system, the shorter the second-stage IDT - as consistently reported in Ref. [91]. Additionally, Fig. 12(b) displays that by feeding more \( \text{H}_2 \) to the system, the most reactive first- and second-stage IDT, \( t_{1\text{MR}} \) and \( t_{2\text{MR}} \), both decrease. Also, \( t_{2\text{MR}}/t_{1\text{MR}} \approx 1.6 \pm 0.05 \), i.e. the ratio remains almost constant for all values of \( x \), similar to what was observed earlier for \( n\)-dodecane/methane/\( \text{H}_2 \) TF system. For the blends marked by I-IV in the figure, \( t_{1\text{MR}} = 0.1 \), while for the blend marked by V, \( t_{1\text{MR}} = 0.095 \).

Similar to the analysis in the previous section, Fig. 13 presents temporal evolution of temperature (a), and important intermediate radicals mass fractions (b) at \( \xi = 0.05 \) \((= 1.5 \xi_{\text{st}})\) for the two extremes of \( x = 0 \) and \( x = 1 \). Here, mass fractions are scaled with the same factors used in Fig. 11 as also mentioned in the figure labels. The most important observation from this figure is that in the DF system of \( n\)-dodecane/methanol \((x = 0)\), there is no evident first-stage ignition. The phenomenon becomes distinguishable only at high concentrations of \( \text{H}_2 \) (here, \( x = 1 \)). More specifically, when \( x = 0 \) (no \( \text{H}_2 \)), there is neither moderate temperature rise nor \( \text{HO}_2 \) and \( \text{RO}_2 \) peaks observable prior to the main ignition.

Abundance of the first-stage ignition in the methanol case at \( \xi = 0.05 \) indicates that the influence of \( n\)-dodecane on the ignition potential is lower than in the corresponding methane case. In terms of initial enthalpy ratios (c.f. Eq. (3)), \( c_{x=0} = 0.118 \) and 0.5217 for methanol and methane DF cases at \( \xi = 0.05 \), respectively. Hence, in terms of enthalpy, initial ignition features of \( n\)-dodecane/methanol blend at \( \xi = 0.05 \) are closer to the pure methanol, compared to the methane case wherein initial ignition characteristics of \( n\)-dodecane/methane blend at \( \xi = 0.05 \) are strongly influenced by \( n\)-dodecane.

According to our previous three-dimensional spray LES mixing studies [58, 59], the first-stage ignition takes place where \( \xi > 2\xi_{\text{st}} \). Hence, it is worth to investigate the first-stage ignition features at higher \( \xi \) values. Increasing \( n\)-dodecane ratio to achieve \( \xi = 0.075 \) \((= 2.5\xi_{\text{st}})\) yields again a clear two-stage ignition behavior, especially when high \( \text{H}_2 \) concentration \((x > 0.5)\) is present, as illustrated in Fig. 14. This can be clearly noted from the moderate temperature rise as well as peaking \( \text{HO}_2 \) and \( \text{RO}_2 \) mass fractions. Accordingly, the second-
stage IDT becomes shorter. Also, we note that at \( \xi = 0.075 \), initial enthalpy ratios increase to \( c_j x = 0 = 0.2629 \) from 0.118 at \( x = 0.05 \).

In Fig. 13(b) and Fig. 14(b), it was observed that for the DF n-dodecane/methanol (\( x = 0 \)) case, \( H_2O_2 \) is produced in considerably large amounts (e.g. as compared to when \( x = 1 \)). It is known that \( H_2O_2 \) is a metastable radical in low and intermediate temperatures and it is an important factor for the longer second-stage IDT observed when \( x = 0 \) compared to \( x = 1 \). These aspects will be further investigated in the following reaction sensitivity analysis.

### Reaction sensitivity analysis

In order to elaborate on the inhibiting (n-dodecane/methane) and promoting (n-dodecane/methanol) effects of adding \( H_2 \) on \( r_2 \) in the TF case studies, reaction sensitivity analysis is performed. The sensitivity indicator, \( S_i \), is defined as

\[
S_i = \frac{\partial \ln (r_2)}{\partial \ln (k_i)} = \frac{r_2 \partial k_i}{k_i \partial r_2}
\]

(4)

where \( k_i \) is the rate constant for the \( i^{th} \) reaction step. To obtain the sensitivity indicator for each reaction, \( k_i \) is varied by factor 2 and \( r_2 \) is recalculated. Therefore, Eq. (4) yields

\[
S_i = \frac{r_2 (2k_i) - r_2 (k_i)}{r_2 (k_i)}
\]

(5)

### Table 2

Initial mole fractions (\( X \)) in the 0d reactor at different selected \( \xi \) and \( x \) values for n-dodecane/methanol/H\(_2\) blends.

<table>
<thead>
<tr>
<th>( \xi )</th>
<th>( x )</th>
<th>( X_{n\text{dd}} )</th>
<th>( X_{\text{methanol}} )</th>
<th>( X_{O_2} )</th>
<th>( X_{N_2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05, ( x = 0 )</td>
<td>0.0089</td>
<td>0.0649</td>
<td>0</td>
<td>0.1946</td>
<td>0.7316</td>
</tr>
<tr>
<td>0.05, ( x = 0.5 )</td>
<td>0.0085</td>
<td>0.0471</td>
<td>0.0471</td>
<td>0.1885</td>
<td>0.7087</td>
</tr>
<tr>
<td>0.05, ( x = 1.0 )</td>
<td>0.0074</td>
<td>0.1723</td>
<td>0.1723</td>
<td>0.6479</td>
<td></td>
</tr>
<tr>
<td>0.075, ( x = 0 )</td>
<td>0.0137</td>
<td>0.0646</td>
<td>0</td>
<td>0.1937</td>
<td>0.7281</td>
</tr>
<tr>
<td>0.075, ( x = 0.5 )</td>
<td>0.0130</td>
<td>0.0469</td>
<td>0.0469</td>
<td>0.1876</td>
<td>0.7055</td>
</tr>
<tr>
<td>0.075, ( x = 1.0 )</td>
<td>0.0114</td>
<td>0.1716</td>
<td>0.1716</td>
<td>0.6453</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 12 – Ignition properties of different blends of n-dodecane/methanol/H\(_2\) (\( p = 60 \) bar, \( T_{in,\text{gas}} = 900 \) K, \( T_{in,\text{pilot}} = 363 \) K, \( \phi_{\text{gas}} = 0.5 \)): a) second-stage IDT against \( \xi \) (n-dodecane mass fraction) while \( \phi_{\text{gas}} = 0.5 \), and b) ratio of the second-to first-stage IDT at \( \xi_{MR} \).

Fig. 13 – Temporal evolution of a) temperature for \( x = 0 \), 0.5, and 1, and b) intermediate radicals mass fraction for \( x = 0 \) (solid) and \( x = 1 \) (dotted), in n-dodecane/methanol/H\(_2\) blends at \( \xi = 0.05 \approx 1.5 \xi_{cr} \) (\( c_{x=0}=0.1880 \)). Mass fractions are scaled with the factors noted in labels.
In Eq. (5), negative $S_i$ indicates decreasing effects on $\tau_2$ (promoting effect) and positive $S_i$ denotes increasing effects on $\tau_2$ (inhibiting effect). In the following, we present known aspects of n-dodecane ignition pathways followed by reaction sensitivity analyses for TF cases.

N-dodecane ignition pathways

Prior to presenting the sensitivity analysis, a short review on reaction pathways of ignition process for SF n-dodecane-air is provided. As mentioned earlier in Fig. 5(b), three different regions of LT, NTC, and HT exist for n-dodecane combustion and accordingly, ignition constitutes three different reaction pathways. Considering the range of initial temperature considered in this study, n-dodecane ignition mainly takes place in the NTC region and partially in the LT region. In general, n-dodecane decomposition initiates through

\[
\text{NC}_{12}\text{H}_{26} + O_2 \rightarrow \text{HO}_2 + \text{NC}_{12}\text{H}_{25} \ldots \quad \text{(R946)}.
\]

According to e.g. Ref. [22], depending on the temperature, ignition chemistry follows primarily either of the two reactions corresponding to the first-stage IDT,

\[
\text{NC}_{12}\text{H}_{25} + O_2 \rightarrow \text{NC}_{12}\text{H}_{25} - \text{OO} \ldots \quad \text{(R502)},
\]

\[
\text{NC}_{12}\text{H}_{25} + O_2 \rightarrow \text{HO}_2 + 1.2\text{NC}_{12}\text{H}_{20} \ldots \quad \text{(R474)}.
\]

Reaction R502 is dominant in the LT region, leading to formation of RO$_2$. Instead, R474 is prominent in the NTC region, leading to HO$_2$ formation.

In the LT region, RO$_2$ leads to the following sequence of reactions which further decompose n-dodecane and produce adequate OH for start of the second-stage ignition

\[
\text{NC}_{12}\text{H}_{25} - \text{OO} \rightarrow \text{NC}_{12} - \text{QOOH} \ldots \quad \text{(R505)},
\]

\[
\text{NC}_{12} - \text{QOOH} + O_2 \rightarrow \text{NC}_{12} - \text{OOQOOH} \ldots \quad \text{(R503)},
\]

\[
\text{NC}_{12} - \text{OOQOOH} \rightarrow \text{NC}_{12} - \text{QOOH} + \text{OH} \ldots \quad \text{(R513)},
\]

\[
\text{NC}_{12} - \text{QOOH} \rightarrow 0.84\text{C}_2\text{H}_5 + \text{CH}_3\text{CHO} + 0.16\text{CH}_3\text{COCH}_3 + 0.84\text{CO} + \text{NC}_{12}\text{H}_{14} + \text{OH} \ldots \quad \text{(R517)}.
\]

In the above chain of reactions, R517 is representative of several similar reactions related to decomposition of NC$_{12}$ - QOOH and leading to formation of OH. Also, it is worth noting that non-integer coefficients appearing in R517 and similar reactions are tuned coefficients in Polimi reduced mechanism. Finally, the constructed OH radicals react with n-dodecane over the second-stage ignition process through the chain carrying reaction

\[
\text{NC}_{12}\text{H}_{26} + \text{HO}_2 \rightarrow \text{HO}_2 + \text{NC}_{12}\text{H}_{25} \ldots \quad \text{(R948)},
\]

which also produces more NC$_{12}$H$_{25}$ to feed R502 and start over the mentioned reaction chain.

In the NTC region, besides R474, the following reaction is dominant and generates more HO$_2$

\[
\text{NC}_{12} - \text{QOOH} \rightarrow \text{HO}_2 + 1.2\text{NC}_{12}\text{H}_{20} \ldots \quad \text{(R508)}.
\]

Then, high concentrations of HO$_2$ radicals combine to form H$_2$O$_2$ through

\[
2\text{HO}_2 \leftrightarrow \text{H}_2\text{O}_2 + \text{O}_2 \ldots \quad \text{(R12)}.
\]

H$_2$O$_2$ is a metastable species in low temperatures [92] and slows down the ignition process along with the following inhibiting reactions which are the reverse reactions of R503 and R502

\[
\text{NC}_{12} - \text{OOQOOH} \rightarrow \text{NC}_{12} - \text{QOOH} + \text{O}_2 \ldots \quad \text{(R512)},
\]

\[
\text{NC}_{12}\text{H}_{25} - \text{OO} \rightarrow \text{NC}_{12}\text{H}_{25} + \text{O}_2 \ldots \quad \text{(R504)}.
\]

These reactions reduce the concentration of RO$_2$ radicals which are required to drive the chain R505-R517 (responsible for the first-stage ignition) and consequently, lead to a reduced overall reactivity.

This review highlighted main reasons for relatively very short IDT for SF n-dodecane combustion as well as the important role of intermediate radicals such as OH and H$_2$O$_2$ in the ignition mechanism. In the following, we shift our focus to the main effects of adding methane, methanol and H$_2$ on the ignition mechanism of n-dodecane within the TF context.
Despite the considerable promoting effects of R950 and R948 with presence of H$_2$ (c.f. Fig. 15), the effect of R266 is prominent in inhibiting $r_2$ at higher H$_2$ ratios. However, this type of promoting reactions are able to oppose the less important inhibiting effect of R266 at lower H$_2$ values, e.g. at $x = 0.5$. For instance, insignificant effects from H$_2$ addition on $r_2$ was observed even at high values of H$_2$ up to $x = 0.6$ in Fig. 10.

As this sensitivity analysis is related to the second-stage ignition only, it reveals that the main reason for increased $r_2$ with $x$ is higher consumption of OH radicals by H$_2$. However, as another reason for increased $r_2$, it was also discussed earlier through Fig. 11 that when H$_2$ is added, the longer first-stage IDT as well as lower peaks of temperature and relevant intermediate species in the first-stage ignition can directly delay the second-stage IDT.

N-dodecane/methanol/H$_2$

A similar analysis has been performed for ignition process of n-dodecane/methanol/H$_2$ at $x = 0.075$ (consistent with the choice in Fig. 14) with three different x values, $x = 0$, $x = 0.5$, and $x = 1$. The value $x = 0.05$ is consistent with the choice in Fig. 11. Reactions listed in Fig. 15 are mainly related to fuel decomposition or chain branching and chain terminating reactions for intermediate radicals. Most of these reactions are in common with those already highlighted in the literature. For example, reactions in common with SF (n-dodecane-air) and DF (n-dodecane/methane-air) study by Kahila et al. [58] using Polimi reduced mechanism are marked in the figure with '*' and ']', respectively.

According to Fig. 15, at different levels of H$_2$ in the system ($x$), S$_i$ does not change significantly for most of the listed reactions. However, there are two exceptions, i.e. the competing reactions are R266 and R569:

\[
H + H_2O \rightleftharpoons H_2 + OH \quad (R266),
\]

\[
CH_4 + OH \rightleftharpoons CH_3 + H_2O \quad \ldots \quad (R569).
\]

It is observed from the sensitivity analysis that both R266 and R569 have inhibiting effects on $r_2$ and delay $r_2$ compared to SF n-dodecane-air. When $x = 0$, R266 has a negligible influence. However, as H$_2$ increases, R266 dominates (consistent with the observations in Refs. [22,55]) while R569 becomes less important. The relative dominance of R266 at $x = 1$ is much stronger than that of R569 at $x = 0$, leading to a stronger inhibiting effect at $x = 1$ with pure H$_2$; hence, a longer second-stage IDT.

Evidently, when more H$_2$ is added to the system, high consumption rate of OH, e.g. by backward R266 at $x = 1$, cannot be compensated by OH production from e.g. n-dodecane decomposition reactions with promoting effects on IDT, such as

\[
HO_2 + NC_{12}H_{26} \rightleftharpoons H_2O_2 + NC_{12}H_{25} \quad (R950)
\]

and

\[
NC_{12}H_{26} + OH \rightleftharpoons H_2O + NC_{12}H_{25} \quad (R948).
\]

Despite the considerable promoting effects of R948 and R950 with presence of H$_2$ (c.f. Fig. 15), the effect of R266 is prominent in inhibiting $r_2$ at higher H$_2$ ratios. However, this type of promoting reactions are able to oppose the less important inhibiting effect of R266 at lower H$_2$ values, e.g. at $x = 0.5$. For instance, insignificant effects from H$_2$ addition on $r_2$ was observed even at high values of H$_2$ up to $x = 0.6$ in Fig. 10.

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N-dodecane/methane/H$_2$

A similar analysis has been performed for ignition process of n-dodecane/methane/H$_2$ at $x = 0.05$ and 1.0 when $x = 0.05$ with three different $x$ values, $x = 0$, $x = 0.5$, and $x = 1$. The value $x = 0.05$ is consistent with the choice in Fig. 11. Reactions listed in Fig. 15 are mainly related to fuel decomposition or chain branching and chain terminating reactions for intermediate radicals. Most of these reactions are in common with those already highlighted in the literature. For example, reactions in common with SF (n-dodecane-air) and DF (n-dodecane/methane-air) study by Kahila et al. [58] using Polimi reduced mechanism are marked in the figure with '*' and ']', respectively.

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\[
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\]

\[
CH_4 + OH \rightleftharpoons CH_3 + H_2O \quad \ldots \quad (R569).
\]

It is observed from the sensitivity analysis that both R266 and R569 have inhibiting effects on $r_2$ and delay $r_2$ compared to SF n-dodecane-air. When $x = 0$, R266 has a negligible influence. However, as H$_2$ increases, R266 dominates (consistent with the observations in Refs. [22,55]) while R569 becomes less important. The relative dominance of R266 at $x = 1$ is much stronger than that of R569 at $x = 0$, leading to a stronger inhibiting effect at $x = 1$ with pure H$_2$; hence, a longer second-stage IDT.

Evidently, when more H$_2$ is added to the system, high consumption rate of OH, e.g. by backward R266 at $x = 1$, cannot be compensated by OH production from e.g. n-dodecane decomposition reactions with promoting effects on IDT, such as

\[
HO_2 + NC_{12}H_{26} \rightleftharpoons H_2O_2 + NC_{12}H_{25} \quad (R950)
\]

and

\[
NC_{12}H_{26} + OH \rightleftharpoons H_2O + NC_{12}H_{25} \quad (R948).
\]
\( \tau_2 \) (oppose the dominant promoting effect), such as R948, R950, R960, and
\[
\text{CH}_3\text{O} + \text{NC}_{12}\text{H}_{26} \rightarrow \text{CH}_3\text{OH} + \text{NC}_{12}\text{H}_{26} \quad \text{(R960)},
\]
which display their effects on small changes in \( \tau_2 \) at lower added \( \text{H}_2 \) values up to \( x = 0.6 \).

As mentioned earlier, this sensitivity analysis elaborates on the main reason for shorter \( \tau_2 \) with varying \( x \), which can be related to higher consumption rate of \( \text{OH} \) with methanol compared to \( \text{H}_2 \). However, it was also discussed earlier through Figs. 13 and 14 that \( \text{H}_2 \) addition reinforces the first-stage ignition, and also, reduces the considerable formation of metastable \( \text{H}_2\text{O}_2 \) at \( x = 0 \). This effect is also a significant reason for advance of the second-stage IDT with more \( \text{H}_2 \) in the TF n-dodecane/methanol/\( \text{H}_2 \) system.

Discussion on the TF ignition results

The presented results in sections The role of \( \text{H}_2 \) in TF ignition and Reaction sensitivity analysis highlight the features of homogeneous ignition of HRF, LRF, and \( \text{H}_2 \) with different mixing ratios. Regarding practical combustion applications, the most important finding is the inverse response of methane to hydrogen addition compared with methanol. While hydrogen prolongs the IDT values for methane, they are reduced in case of methanol. In both cases, the influence of hydrogen addition on IDT is noted to be non-linear. Similarly, it is noted that hydrogen addition influences both low- and high-temperature chemistry throughout the ignition timescale (\( t < \tau_2 \)). Such an inverse response of chemical kinetics to hydrogen addition can be explained by considering individual reactions, where the chosen LRF, \( \text{H}_2 \), n-dodecane and intermediate species such as \( \text{OH} \) and \( \text{H}_2\text{O}_2 \) interact with each other. However, concerning practical applications, the fuel-air mixture needs relatively high concentrations of hydrogen to show a practical influence on ignition characteristics.

The above-mentioned aspects become relevant for e.g. compression ignition ICE, where ignition timing is crucial and only little cyclic variations are allowed. Modern combustion engines may need to be able to utilize multiple fuels, which requires a detailed understanding of ignition characteristics changes in each case. As shown here, such changes may not be intuitive.

Conclusions

Effects of \( \text{H}_2 \) concentration variations on ignition characteristics in n-dodecane/LRF/\( \text{H}_2 \) TF blends were studied numerically using Polimi reduced mechanism. Here, LRF refers to methane or methanol. The Polimi reduced mechanism was validated against available SF and DF data in literature and its sensitivity was assessed against the Polimi detailed mechanism for TF blends. The first- and second-stage ignition were investigated using the 0d homogeneous reactor concept. Considering the main findings of this study, the following points are highlighted.

1. Low and intermediate \( \text{H}_2 \) concentrations in TF n-dodecane/ LRF/\( \text{H}_2 \) systems, for \( x \) values up to \( \sim 0.6-0.7 \), do not have significant effects on the first- and second-stage IDT compared to DF n-dodecane/LRF blends.
2. High amounts of \( \text{H}_2 \) in n-dodecane/methane/\( \text{H}_2 \) blends (\( x > 0.6-0.7 \)) retard ignition (\( \sim 1.5 \) times longer IDT at \( x = 0.8 \) compared to \( x = 0 \)) and shorten combustion duration due to higher flame speed (\( \sim 2 \) times higher laminar flame speed at \( x = 0.8 \) compared to \( x = 0 \)).
3. High amounts of \( \text{H}_2 \) in n-dodecane/methanol/\( \text{H}_2 \) blends (\( x > 0.6-0.7 \)) advance ignition (\( \sim 1.5 \) times shorter IDT at \( x = 0.8 \) compared to \( x = 0 \)) and do not significantly influence laminar flame speed and temperature.
4. Increasing \( \text{H}_2 \) in TF blends, does not influence the second- to first-stage IDT ratio at the most reactive mixture fraction. In particular, \( \tau_2^\text{MR}/\tau_2^\text{DF} \approx 1.7+0.1 \) for methane case, and \( \tau_2^\text{MR}/\tau_2^\text{DF} \approx 1.6+0.05 \) for methanol case at all \( x \) values. This indicates the direct influence of LTC on HTC.
5. For n-dodecane/methane, ignition is shown to pose a two-stage behavior when \( \xi \approx 1.5 \). For n-dodecane/methanol,
however, a single-stage ignition behavior is observed when \( \xi = 1.5 \xi_d \), while at \( \xi > 2.5 \xi_d \), a two-stage ignition behavior is recovered.

6 Opposite IDT effects of H₂ addition in n-dodecane/methane (retarded IDT) compared to n-dodecane/methanol (advanced IDT) TF blends were found to be related to two factors. First, in methane (methanol) case, the more H₂ is added, the weaker (stronger) the first-stage ignition becomes. A stronger first-stage ignition leads to a shorter second-stage IDT and vice versa. Second, the reaction sensitivity analysis indicates the significant role of OH consumption by H₂ in competition with methane and methanol in TF methane and methanol blends, respectively. Based on the reaction sensitivity analysis, H₂ is more (less) active in consumption of OH compared to methane (methanol); hence, retarding (advancing) the second-stage IDT.

Acknowledgments

The present study has been financially supported by the Academy of Finland (grant numbers 318024 and 297248).

References


