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Standard Article



Large-eddy simulation of diesel pilot spray ignition in lean methane-air and methanol-air mixtures at different ambient temperatures

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Abstract

In dual-fuel compression-ignition engines, replacing common fuels such as methane with renewable and widely available fuels such as methanol is desirable. However, a fine-grained understanding of diesel/methanol ignition compared to diesel/methane is lacking. Here, large-eddy simulation (LES) coupled with finite rate chemistry is utilized to study diesel spray-assisted ignition of methane and methanol. A diesel surrogate fuel (n-dodecane) spray is injected into ambient methane-air or methanol-air mixtures at a fixed lean equivalence ratio ϕ_{LRF} = 0.5 at various ambient temperatures $(T_{amb} = 900, 950, 1000 \text{ K})$. The main objectives are to (1) compare the ignition characteristics of diesel/methanol with diesel/methane at different T_{amb} , (2) explore the relative importance of low-temperature chemistry (LTC) to hightemperature chemistry (HTC), and (3) identify the key differences between oxidation reactions of n-dodecane with methane or methanol. Results from homogeneous reactor calculations as well as 3 + 3 LES are reported. For both DF configurations, increasing T_{amb} leads to earlier first- and second-stage ignition. Methanol/n-dodecane mixture is observed to have a longer ignition delay time (IDT) compared to methane/n-dodecane, for example \approx three times longer IDT at T_{amb} = 950 K. While the ignition response of methane to T_{amb} is systematic and robust, the T_{amb} window for n-dodecane/methanol ignition is very narrow and for the investigated conditions, only at 950K robust ignition is observed. For methanol at T_{amb} = 1000 K, the lean ambient mixture autoignites before spray ignition while at T_{amb} = 900 K full ignition is not observed after 3 ms, although the first-stage ignition is reported. For methanol, LTC is considerably weaker than for methane and in fully igniting cases, heat release map analysis demonstrates the dominant contribution of HTC to total heat release rate for methanol. Reaction sensitivity analysis shows that stronger consumption of OH radicals by methanol compared to methane leads to the further delay in the spray ignition of n-dodecane/ methanol. Finally, a simple and novel approach is developed to estimate IDT in reacting LES using zero-dimensional IDT calculations weighted by residence time from non-reacting LES data.

Keywords

LES, dual-fuel spray, diesel, methanol, methane

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Introduction

Diesel engines have still a dominant role in large scale power production and marine engines.¹ While the technology is relatively mature and robust, the major concern is to limit its pollution contribution.¹ This concern has led to promising technologies over the past decade, including dual-fuel (DF) combustion, which feature low NOx and soot emission.² In particular, the main research focus of DF combustion has been on extending the operational range of DF compression ignition (CI) engines while gaining higher efficiency and lower emissions.^{2,3} In the context of renewable fuels, one of the common challenges is to ensure smooth and robust control over the DF ignition process for different fuel combinations and operational ranges.^{4,5}

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Ignition process in multi-fuel combustion systems is an intricate process due to the interlinked length and timescales of chemistry and mixing phenomena.⁶ Of particular importance is to acquire knowledge on the mixing process, low temperature chemistry (LTC), high temperature chemistry (HTC), and ignition delay time (IDT), which helps to develop and implement the technology in practice. Despite the recognized importance of DF combustion implementation, specifically in heavy-duty engines,^{2,7} a fine-grained understanding of the ignition phenomenon in such stratified reactivity systems, particularly for renewable fuels such as methanol, is still lacking. In the present study, threedimensional (3d) large-eddy simulations (LES) are employed to investigate mixing and ignition phenomena in DF diesel/methane and diesel/methanol cases corresponding to the Spray A baseline conditions of the engine combustion network (ECN) (https://ecn.sandia.gov). Such an LES investigation helps in understanding the intertwined physics and chemistry processes in reacting DF sprays.⁸

In a typical CI DF combustion, a low-reactivity fuel (LRF) with a relatively long IDT is the background primary fuel. The LRF is interactively burned with small amounts of a high-reactivity fuel (HRF) with a relatively shorter IDT, such as diesel. In this configuration, the liquid HRF is injected into the lean LRF/oxidizer mixture in the cylinder and IDT stratification is created. The role of HRF is to facilitate the ignition process, whereas the LRF moderates the system reactivity and delivers the main energy release.³ Recently, there has been substantial progress in the characterization of ignition mechanism in DF diesel/methane under CI engine relevant conditions. In an LES study of DF ignition in diesel-surrogate/methane under the ECN Spray A injection conditions, Kahila et al.⁶ specified the role of ambient methane on prolonging the ignition delay time by a factor of two. They explained this effect by detailed LTC and HTC analyses. In a following study,⁹ they demonstrated the impact of diesel pilot injection duration on spray overleaning and consequently, the IDT. The findings were supported by engine experiments. More recently, in the studies by Tekgül et al.¹⁰ and Kannan et al.¹¹, effects of ambient temperature on IDT with different chemical mechanisms were investigated. The present study is a continuation of these works to study the ambient methanol influence on the ignition process, as compared to methane, under various ambient temperatures.

Recently, a few experimental studies on DF combustion have been carried out with methane as the LRF,^{12–15} which mainly focus on the performance, efficiency, emissions, and combustion instability. Nonetheless, several insights have been obtained on ignition characteristics. For instance, the previous studies indicate that mixing methane with oxidizer retards both low- and high-temperature ignition stages. These findings match well with the findings in previous numerical studies.^{6,9–11,16–20} Moreover, direct numerical simulations (DNS) have provided numerical evidence on the importance of LTC and HTC in the DF ignition process.^{21,22} Using renewable fuels such as methanol in DF CI engines have been studied both experimentally^{23–26} and numerically.^{27–34} Those studies predominantly focus on the engine geometry and performance,^{23,28,30–32} fuel reactivity,^{24,27,28} combustion instability,²⁵ and emissions characteristics.^{26,27,29–31,33}

Using methanol over methane, natural gas, and gasoline as the LRF has attracted the interest of DF engines manufacturers over the past few years due to several reasons.³⁵ First, methanol is a renewable fuel, and it is widely available.⁴ Second, its high octane number can mitigate knock tendency in engines.³⁶ Third, since there is an oxygen atom in the methanol formula and it is free of aromatics, soot formation is mitigated. Fourth, methanol has a higher heat of vaporization compared to methane, natural gas, and gasoline, which leads to cooling effects during combustion and consequently, lower charge peak combustion temperature leading to smaller NOx emissions.⁴ With relevance to this study, methanol ignition is a particularly sensitive process and several challenges on the smooth ignition of methanol in the DF engines context have been reported in the literature, where for example the crucial role of intake temperature control has been acknowledged in the works by Zou et al.³¹, Wang et al.³⁷, Hu et al.³⁸ and Wang et al.³⁹ Recently, Xu et al.³⁴ investigated effects of increasing the initial ambient methanolair mixture fraction on ignition at a constant temperature of 900 K. They provided evidence that adding methanol to the ambient may delay the ignition of *n*-heptane and prolong the transition from low to high-temperature ignition. More recently, we have investigated tri-reactivity ignition of methane/hydrogen⁴⁰ and methanol/hydrogen⁴¹ at fixed temperature of 900 K by diesel spray. However, in those studies we did not thoroughly discuss the dualreactivity, that is dual-fuel case of diesel/methanol versus diesel/methane at various ambient temperatures. Here, we carry out a systematic analysis to fill the research gap with regard to the effect of ambient temperature on diesel spray assisted ignition of methane and methanol.

The overarching goal of this study is to investigate utilization of methanol, as a renewable fuel, in the DF CI context as compared to methane through spray LES, following the recent research framework developed by Kahila et al.^{6,9} This is the first study comparing n-dodecane/methanol and n-dodecane/methane DF spray ignition for different ambient temperatures using LES and finite rate chemistry. Accordingly, the main objectives of this study are to (1) understand DF ignition at different ambient temperatures when methane is replaced by methanol, (2) compare the mixing and ignition characteristics of DF spray systems including *n*-dodecane/methanol and *n*-dodecane/methane, (3) identify ignition modes and the relative importance of LTC/HTC, (4) provide a further insight into chemical reactions yielding different ignition delay times for *n*-dodecane/methane and *n*-dodecane/methanol using reactions sensitivity analysis, and (5) provide and test a simple approach to estimate spray ignition delay time

Table I. List of all abbreviations.

Abbreviation	Full name	Abbreviation	Full name
LES	Large-eddy simulations	CI	Compression ignition
DNS	Direct numerical simulations	LRF	Low-reactivity fuel
ECN	Engine combustion network	HRF	High-reactivity fuel
LTC	Low-temperature chemistry	IDT	Ignition delay time
HTC	High-temperature chemistry	DF	, Dual-fuel
TCI	Turbulence chemistry interactions	HRR	Heat release rate
DFI	Dual-fuel <i>n</i> -dodecane/methane	ILES	Implicit LES
DF2	Dual-fuel <i>n</i> -dodecane/methanol	MR	Most reactive
PISO	Pressure implicit/splitting of operator	SF	Single-fuel
ODE	Ordinary differential equation	60	Zero-dimensional
FGM	Flamelet generated manifolds	2d	Two-dimensional
PDF	Probability density function	3d	Three-dimensional
PLIF	Planar laser-induced fluorescence	RO ₂	C12H25O2
LPT	Lagrangian particle tracking	HR	Heat release

using zero-dimensional (0d) homogeneous reactor calculations and non-reacting spray LES data. We note that the main goal of this work is to study differences of diesel spray-assisted ignition of methane and methanol. However, these results do not represent the overall combustion in an engine cycle since the effect of volumetric compression is not included. Finally, a list of all abbreviations used in this work is provided in Table 1 to improve the readability of the paper.

Methodology

Case setup

The simulation configuration is based on the modified ECN Spray A baseline conditions for DF ignition.^{6,9} As in the ECN Spray A setup, liquid n-dodecane (diesel-surrogate) at T = 363 K is injected from a 90 μ m diameter nozzle at 150 MPa injection pressure into a constant volume combustion vessel. In the present configuration, the ambient gas inside the vessel is modified by adding methane (DF1) or methanol (DF2), while O₂ molar fraction of the ambient gas is kept constant at 15%. For DF conditions, the LRF (methane or methanol) is added to the mixture such that the premixed LRF/air has a constant equivalence ratio, $\phi_{LRF} = 0.5$. The other species are modified following the procedure by Kahila et al.⁶ as presented in Table 2. The ambient temperature is varied in the simulation cases herein while the ambient pressure is set to approximately 6 MPa such that ambient density is $\rho = 22.8 \text{ kg/m}^3$. The ambient gas is initially stagnant and homogeneous in terms of mixture composition. The fuel spray injection profile is obtained from an injection mass flow rate profile generator suggested by the ECN and the generator was used in our previous study as well.6

Numerical methods

Reacting LES is carried out within the OpenFOAM finite-volume framework⁴² integrated with our open-

Table 2. Ambient premixed gas initial conditions in spray LES^a.

	Spray A	DFI	DF2
Ambient conditions			
LRF		CH₄	CH₃OH
Temperature (K)	900	Varied ^b	Varied ^b
Density (kg/m^3)	22.8	22.8	22.8
O2 % (molar)	15.0	15.0	15.0
CO2 % (molar)	6.230	5.955	5.863
H2O % (molar)	3.620	3.460	3.407
N2 % (molar)	75.150	71.835	70.73
LRF % (molar)	0	3.750	5.0
ϕ_{LRF}	0	0.5	0.5

^aSimilar to the ECN Spray A, $n-C_{12}H_{26}$ is injected continuously at T = 363 K and p = 150 MPa, and the nominal nozzle diameter is 90 μ m. ^bThe ambient temperature is varied between 900, 950, and 1000 K.

source finite-rate chemistry solver.^{43,44} Modeling assumptions and discretization methods are similar to our previous LES studies.^{6,9,10} Nonetheless, assumptions and methods are briefly mentioned here. For further details, the reader is referred to the work by Kahila et al.⁶

LES formulation of the governing equations, that is continuity, momentum, species concentration, and enthalpy, with Favre-filtering is the same as those by Kahila et al.,^{6,9} and Tekgül et al.¹⁰ which are provided as:

$$\frac{\partial \bar{\rho}}{\partial t} + \frac{\partial \bar{\rho} \tilde{u}_i}{\partial x_i} = \overline{S}_{\rho},\tag{1}$$

$$\frac{\partial(\bar{\rho}\tilde{u}_i)}{\partial t} + \frac{\partial(\bar{\rho}\tilde{u}_i\tilde{u}_j)}{\partial x_j} =$$

$$\frac{\partial}{\partial t} = 0 \quad (2)$$

$$\frac{\partial x_{i}}{\partial x_{j}}(-\rho \sigma_{ij} + \rho u_{i}u_{j} - \rho u_{i}u_{j} + \tau_{ij}) + S_{u_{i}},$$

$$\frac{\partial (\bar{\rho} \widetilde{Y}_{k})}{\partial (\bar{\rho} \widetilde{Y}_{k})} = 0$$

$$\frac{\partial t}{\partial x_i} \frac{\partial x_i}{\left(\bar{\rho}\widetilde{u}_i \widetilde{Y}_k - \bar{\rho}\widetilde{u}_i \widetilde{Y}_k + \bar{\rho}\widetilde{D}\frac{\partial \widetilde{Y}_k}{\partial x_i}\right) + \overline{S}_{Y_k} + \bar{\omega}_k,$$
(3)

$$\frac{\partial(\bar{\rho}h_{t})}{\partial t} + \frac{\partial(\bar{\rho}\tilde{u}_{j}h_{t})}{\partial x_{j}} = \frac{\partial\bar{p}}{\partial t} + \frac{\partial}{\partial x_{j}} \left(\bar{\rho}\tilde{u}_{j}\tilde{h}_{s} - \bar{\rho}\tilde{u}_{j}h_{s} + \frac{\bar{\lambda}}{\bar{c}_{p}}\frac{\partial\tilde{h}_{s}}{\partial x_{j}}\right) + \bar{S}_{h} + \bar{\omega}_{h},$$
(4)

where $\overline{\rho}$, $\widetilde{u_i}$, \overline{p} , $\widetilde{Y_k}$, $\widetilde{h_s}$, $\widetilde{h_t}$, and $\overline{\tau_{ij}}$, denote filtered density, velocity, pressure, mass fraction of the species k, sensible enthalpy, total enthalpy, and viscous stress tensor, respectively. Here, tilde (\sim) and overbar (-) denote density-weighted and unweighted ensemble average. The total enthalpy is defined as the sum of sensible enthalpy and specific kinetic energy. The production rates of each species and heat release rate (HRR) are represented by $\bar{\omega}_k$ and $\bar{\omega}_h$, where $\bar{\omega}_h = \Sigma_k \Delta h_{f,k}^0 \bar{\omega}_k$, in which $\Delta h_{f,k}^0$ is the enthalpy of formation. The source terms \overline{S}_{ρ} , \overline{S}_{u_i} , \overline{S}_{Y_k} , and \overline{S}_h allow the coupling between liquid and gaseous phases with respect to mass, momentum, species, and energy. In equation (4), \overline{c}_p and $\overline{\lambda}$ represent specific heat capacity and thermal conductivity of the mixture, respectively. Unity Lewis number assumption for all species $(D = \lambda / \rho c_p)$ is considered. Also, the ideal gas law and thermal equation of state close the system of equations.

In the finite volume solver, an implicit, three timelevel, second-order scheme is used for time integration. A second-order central scheme discretization for diffusion terms along with a non-linear flux limiter for convective flux treatment⁴⁵ are utilized as in the authors' previous spray studies.^{46,47} The compressible solver utilizes the standard PISO (pressure implicit with splitting of operator) pressure-correction approach. For the injected liquid phase modeling, the Lagrangian particle tracking (LPT) method is applied using the cylindrical injection volume approach, as discussed by Gadalla et al.,48 which extends the standard disk injection model of OpenFOAM to 3d. The standard correlations of Ranz and Marshall⁴⁹ and Frossling⁵⁰ are used for modeling heat and mass transfer between the liquid and gas phases.

It is noteworthy that the utilized Implicit LES (ILES) approach has been previously demonstrated to be a reliable assumption as compared to other SGS models, c.f. Grinstein et al.,⁵¹ Grinstein and Fureby,⁵² Aspden et al.,⁵³ and it has been applied to several different problems for example in studies on free shear flows,⁵⁴ supersonic jets,⁵⁵ and sprays.^{6,9,46,47,56} Here, the same implicit LES/LPT approach as in the previous studies by the authors is used wherein extensive validation studies on reacting $^{6,9-11}$ and non-reacting 48,56 single-fuel (SF) and DF ECN Spray A are provided. Furthermore in this work, the no breakup model approach for the droplet secondary atomization is utilized with ILES following our recent model sensitivity study by Gadalla et al.48

The utilized reacting flow solver is based on the recent work by Kahila et al.⁶ In the solver, the open source library pyJac⁵⁷ is coupled with OpenFOAM

32.0 ° \mathbb{R}^2 **Figure 1.** The computational domain and mesh structure: R₃,

R3

64.0

32.0

R₂, and R₁ correspond to 125 μ m, 250 μ m, and 1 mm uniform resolution, respectively.

providing the analytical Jacobian matrix formulation required by the ordinary differential equation (ODE) system solver. The operator-splitting strategy is utilized to separate the chemical source terms $\overline{\dot{\omega}}_k$ and $\overline{\dot{\omega}}_h$ in equations (3) and (4) from the flow solution, due to the much smaller timescales associated with chemistry.⁶ Dynamic load balancing and reference cell methods, further explained by Tekgül et al.,43 are utilized to accelerate the numerical solution of the chemical reactions.

Mesh structure and sensitivity analysis

Figure 1 provides the physical dimensions and structure of the mesh in the computational domain. The mesh consists of three refinement regions similar to our previous studies, for example Kahila et al.⁶ Here, a standard mesh resolution, $125 \,\mu$ m, is used in the fine region (R_3). In addition, R_2 and R_1 have 250 μ m and 1 mm grid resolutions, respectively. Consistent with our previous LES studies,^{6,9,10} no model for turbulence chemistry interactions (TCI) is used. The approach is reliable since the present study targets the autoignition process only, which is often assumed to be less sensitive to micro-mixing issues compared to for example quasisteady flame lift-off length estimation in the Spray A context.⁵⁸ Furthermore, within the dual-fuel Spray A context by Kahila et al.,⁶ we have compared IDT results obtained by the present combustion model (nomodel) and the flamelet generated manifolds (FGM) method with a presumed probability density function (PDF) approach to include TCI effects within the manifold. The present approach provides an IDT value within 1% of the one obtained by the FGM solver. The low-temperature combustion features were noted to be very similar for both ILES no-model and FGM methods with a successful comparison to experimental CH₂O PLIF data.

For completeness, a mesh sensitivity analysis is provided in Appendix A for the DF1 case at 1000 K ambient temperature with two different grid resolutions: a very fine $62 \,\mu m$ grid and the standard fine resolution of

 $125\,\mu\text{m}^6$. In the sensitivity analysis, we consider two indicators for ignition: first, C12H25O2 species (called RO_2 hereafter) to designate the onset of the first-stage ignition, and second, temperature and hydroxyl radical (OH) to designate the onset of the second-stage ignition. Similar to the provided definitions in the remainder of this work, the first-stage ignition time (τ_1) is defined as when 20% of the maximum concentration of RO₂ within the domain is reached. The second-stage ignition time (τ_2) is also defined as the time instance when the highest gradient of maximum temperature within the domain is observed. It is found that both grid resolutions yield consistent profiles and the present grid resolution (125 μ m) clearly captures the same ignition phasing as the finer grid. Based on the grid sensitivity assessment, we assume that the present numerical results are insensitive to the chosen grid resolution and that the micro-mixing in the subgrid scales can be neglected. The mesh resolution requirements are also extensively investigated in our previous study under non-reacting conditions.⁵⁶

Chemical kinetics mechanism

A reduced chemical kinetics mechanism developed by Frassoldati et al.,59 called Polimi-reduced hereafter, is used. The mechanism has been developed for *n*-dodecane combustion under engine relevant conditions. Polimi-reduced as well as another chemical mechanism, Yao et al.⁶⁰ mechanism, were earlier validated and used for similar DF ECN Spray A studies with methane at 900 K ambient temperature by Kahila et al.⁹ We note that as the Yao mechanism does not include methanol, it is not considered in this study. According to Kahila et al.6 and Tekgül et al.,10 Polimi-reduced presents a longer IDT compared to Yao mechanism for DF ndodecane/methane. However, numerical tests carried out by the authors have shown that the relative ratio of the first- and second-stage ignition time remains approximately constant between the two mechanisms for DF n-dodecane/methane. In addition, Polimireduced mechanism has been recently validated for methanol combustion under engine relevant conditions by Karimkashi et al.⁶¹ and it is used in numerical simulations for DF n-dodecane/methanol by Karimkashi et al.⁶² This mechanism has been also compared against other mechanisms in the DF context by the authors¹⁷ and a sensitivity analysis of the chemical mechanism is provided in our previous publication under dual-fuel conditions.⁶ Finally, we note that all the modeling assumptions related to the present results are of numerical character. In particular, the considered chemical mechanism is only validated against SF experimental data for *n*-dodecane, methane, and methanol. Therefore, it should be noted that the conclusions of this work have direct relevance with the selected chemical mechanism and further validation is not currently possible due to the lack of experimental data for DF ignition.

Results and discussion

In this section, DF ignition properties of *n*-dodecane/ methane (DF1) and n-dodecane/methanol (DF2) are presented and discussed at three different ambient temperatures: 900, 950, and 1000 K. First, insight into DF1 and DF2 ignition characteristics is given using 0d homogeneous reactor simulations. Second, high-fidelity LES of *n*-dodecane spray-assisted ignition of methane and methanol at different ambient temperatures are provided along with discussions on the first- and second-stage ignition. Different ignition types are identified for DF2 compared to the robust DF1 ignition at various ambient temperatures. Next, heat release map analysis is provided to give further details on the significance of LTC versus HTC in DF1 and DF2 ignition. Moreover, a reaction sensitivity analysis on the secondstage ignition time, reveals the key reactions causing a longer IDT in DF2 compared to DF1. Finally, a simple approach based on the non-reacting LES and 0d homogeneous reactor IDT data is proposed, which can estimate the second-stage ignition (τ_2) in reacting LES spray simulations.

Insight into DF ignition properties using Od simulations

Polimi-reduced is used in constant pressure 0d homogeneous reactors using Cantera⁶³ to acquire knowledge on the ignition properties of the three fuels used in the present LES. Hereafter, IDT refers to the second-stage ignition time defined as when the highest gradient of the maximum temperature within the domain is reached. Figure 2(a) depicts premixed ambient IDT (τ^{amb}) against temperature at p = 6 MPa for SF ignition of methane and methanol as well as n-dodecane. All the SF reactors are simulated at a constant $\phi = 0.5$. The results obtained for SF ignition of methane and methanol using Polimi-reduced are compared against mechanisms developed by Petersen et al.⁶⁴ and Klippenstein et al.⁶⁵ for the respective fuels. The simulations are noted to provide consistent IDT values for methane and methanol ignition when the Polimireduced mechanism is used. According to Figure 2(a), methanol has a higher reactivity compared to methane within the entire considered temperature range. Although *n*-dodecane presents the shortest IDT, at high temperature values (≈1000 K) its reactivity is comparable with that of methanol. The last observation is relevant in terms of autoignition of the ambient methanol-air mixtures at high temperatures as it will be observed in the following 3d simulations.

In this work, the premixing ratio is defined based on the mixture fraction, ξ . Mixture fraction describes the state of mixing between fuel and oxidizer in classic nonpremixed flames. In the current DF study, it describes the mixing extent of *n*-dodecane ($\xi = 1$) and the ambient mixture ($\xi = 0$) based on the coupling functions of element mass fractions considering the weight factors in



Figure 2. 0d homogeneous reactor calculations using Polimireduced mechanism (lines): (a) IDT versus T for single-fuel methane, methanol, and *n*-dodecane ($\phi = 0.5$, p = 6 MPa), results from other chemical mechanisms are shown with symbols, (b) IDT against ξ under Spray A conditions for *n*-dodecane/methane (DF1), and (c) *n*-dodecane/methanol (DF2).

the definition provided by Bilger et al.⁶⁶ Similar to our previous studies,^{6,10,62} the adiabatic mixing line relation introduced in Mastorakos,⁶⁷ is used in 0d homogeneous ignition to emulate the mixing chemistry in the spray region. Here, a mixture of *n*-dodecane at T = 363 K and the gaseous ambient mixture at DF1 and DF2 conditions (c.f. Table 2) at three different temperatures, $T_{amb} = 900, 950$, and 1000 K are considered. At each ξ , the mixture temperature is calculated based on the inert mixing of *n*-dodecane and the ambient mixture considering their enthalpies, $h = \sum_{\alpha=1}^{N} Y_{\alpha}h_{\alpha}$, where *h*, *Y*, *N*, and α are the absolute enthalpy, mass fraction, total number of species, and species index, respectively. The procedure is further explained by Mastorakos et al.⁶⁸

Results of IDT against mixture fraction according to the described mixing line concept are presented in Figure 2(b) and (c) for DF1 and DF2, respectively. It has been previously observed in the literature that adding methane to the ambient retards ignition compared to the ECN Spray A conditions.^{6,10,17} According to Figure 2(b) and (c), adding methanol to the ambient delays IDT even further compared to methane, consistent with the observations by Karimkashi et al.⁶² For instance, IDT at the most reactive mixture fraction (the point with the shortest IDT within the considered range of mixture fraction) is observed to be longer in DF2 compared to DF1 at similar T_{amb} . The quantified values of IDT are provided in the following parts of the paper as compared to LES data. Additionally, in DF conditions, increase of T_{amb} from 900 to 1000 K may lead to (1) a shorter IDT at each mixture fraction and (2) a richer most reactive mixture fraction, ξ_{MR}^{0d} , defined as the ξ with the shortest IDT (IDT_{MR}) at each T_{amb} .

The following observations in Figure 2 motivate the temperature sweep in the present study for DF1 and DF2. At $T_{amb} = 900 \text{ K}$, $IDT_{MR}^{0d} \approx 0.3 \text{ ms}$ in DF1, while $IDT_{MR}^{0d} \approx 0.71 \text{ ms in DF2}$. Based on a previous study,⁶ in LES, n-dodecane/methane ignition is expected to occur later in time than IDT_{MR}^{0d} . Additionally, stoichiometric mixture fraction, ξ_{st} , in DF1 ignites within 2 ms for all T_{amb} considered here. However, in DF2, ignition timing of ξ_{st} at $T_{amb} = 900$ K is considerably longer than 3 ms. These observations imply that at $T_{amb} = 900 \text{ K}$, DF2 would pose a rather large IDT. Therefore, higher Tamb values are included in the LES to achieve earlier ignition in DF2. According to Figure 2(c), at higher T_{amb} , IDT_{MR}^{0d} decreases and ignition of ξ_{st} is less than 2.5 ms. However, an inflection effect is observed at lean ξ when $T_{amb} = 950$ and 1000 K: increasing ξ leads to a longer IDT up till $\xi = 0.02$ in $T_{amb} = 950$ K and $\xi = 0.05$ in $T_{amb} = 1000 \text{ K}$. This effect corresponds to the IDT of methanol approaching IDT of n-dodecane at high temperatures, c.f. Figure 2(a). When $\xi = 0$, the IDT is relatively short and the homogeneous mixture temperature is equal to T_{amb}. Adding *n*-dodecane, decreases the homogeneous mixture temperature and accordingly, IDT increases up to the inflection point. At the inflection point, the amount of *n*-dodecane in the mixture is high enough to compensate the homogeneous mixture temperature drop and IDT decreases with ξ . The explanation is consistent with similar reactivities of methanol and n-dodecane around 1000 K in Figure 2(a). The low IDT of pure methanol ($\xi = 0$) may lead to ambient autoignition, as discussed in the following LES.

We note that as long as a validated chemical mechanism for DF n-dodecane/methanol ignition at engine-relevant conditions is not developed, the validity of the observed IDT trend and the inflection effect may pose uncertainties. However, the authors have performed similar 0d tests with DF n-heptane (another common diesel surrogate) and methanol. In those simulations we used a chemical mechanism provided by Lu et al.,⁶⁹ which is validated and used for DF nheptane/methanol by Hu et al.³⁸ Similar IDT trends and the inflection effect at $T_{amb} = 1000 \text{ K}$ were observed for *n*-heptane/methanol, which support our current results. We do not show those results here for brevity. Recently, Gadalla et al.⁴¹ examined 0d ignition of DF *n*-dodecane/methanol at $T_{amb} = 1000 \text{ K}$ using several different chemical mechanisms and an inflection behavior was observed for some mechanisms closer to stoichiometric mixture fraction. On the contrary, other chemical mechanisms showed milder or no inflection behavior. However, for all the examined mechanisms,



Figure 3. *N*-dodecane surrogate spray in ambient methane (DFI) and methanol (DF2) with the marked regions of evaporation (I), LTC (II), and HTC (III). Here, *n*-dodecane, RO₂, and OH radicals are rendered for liquid evaporation and mixing, LTC, and HTC regions, respectively.

IDT around the stoichiometric mixture fraction was found to be short compared to that for *n*-dodecane/ methane at $T_{amb} = 1000 \text{ K}$, implying that DF *n*-dodecane/methanol at $T_{amb} = 1000 \text{ K}$ is prone to ambient autoignition.

DF1 and DF2 LES

Figure 3 depicts volume rendering of DF1 (n-dodecane/methane) and DF2 (n-dodecane/methanol) at $T_{amb} = 950 \, K$ slightly after the ignition event. According to Kahila et al.^{6,9} the following regions are common to SF and DF sprays: (I) liquid fuel evaporation and turbulent mixing, (II) activation of LTC, and (III) high-temperature ignition, including transition from LTC to HTC with rapidly growing ignition kernels. Consistent with Figure 2, the main difference between the two DF sprays is the slower ignition in DF2 occurring further downstream when the spray is spanning a larger volume. In addition, the presence of relatively more green color in the LTC region for diesel/methane indicates that RO₂ concentration is higher in DF1 compared to DF2. Further evidence and details on RO₂ concentration are provided in the following sections of the paper. In the following, ignition characteristics of DF1 and DF2 in LES are discussed.

Within the LTC regime, low-temperature reactions lead to the early decomposition of *n*-dodecane and intermediate radicals such as RO_2 and H_2O_2 are formed.⁷⁰ According to Westbrook,⁷¹ the dodecyl peroxy radical (RO_2) is among the first species formed after *n*-dodecane decomposition and therefore, it is considered as an appropriate marker for LTC activity and the first-stage ignition. Here, the first-stage ignition time (τ_1) is defined as the time when 20% of RO_{2, max} is reached. This specific definition for τ_1 is chosen for the sake of consistency with the definitions in other similar works.^{6,9–11,20,40,41,62} However, we note that the firststage ignition time does not vary significantly with changing RO_{2, max} threshold in the definition. On the other hand, maximum temperature (T_{max}) and OH mass fraction (OH_{max}) are good markers of HTC, that is the second-stage ignition.^{6,9} Here, the second-stage ignition time (τ_2) is defined as the time instance at which the maximum gradient of T_{max} is reached, following the ECN guidelines for IDT definition and consistent with the definitions in the aforementioned works from the literature.

Temporal evolution of the maximum RO₂ mass fraction (RO₂, max), OH_{max}, and T_{max} for DF1 and DF2 LES are presented in Figure 4. In this figure, τ_1 and τ_2 are marked, following the definitions provided earlier. We note that the absolute values of τ_1 and τ_2 for DF1 depict less than 5% variations compared to those reported by Kannan et al.¹¹ with a similar setup and using Polimi-reduced mechanism. These slight differences mainly attribute to variations in flow field evolution from one case to another.

Three observations are made according to Figure 4. First, higher ambient temperature advances the first-stage ignition and consequently, the second-stage ignition in both DF1 and DF2. A similar trend for DF1 was previously reported by Tekgül et al.¹⁰ Second, τ_1 and τ_2 are longer in DF2 compared to DF1 at similar T_{amb}. This observation was earlier reported by Karimkashi et al.⁶² Third, in DF2, RO_{2, max} reaches considerably smaller peak values compared to DF1 as consistently reported by Karimkashi et al.⁶² Such a numerical finding implies that LTC in *n*-dodecane/methanol (DF2) is weaker than that of *n*-dodecane/methane (DF1), which is further explored in the following.

The observed trend of advanced τ_1 and τ_2 with higher T_{amb} in both DF1 and DF2 was also noted for 0d results presented earlier. However, in LES, ignition starts later in time compared to 0d homogeneous reactors, mainly due to the time required for mixing in spray conditions. The effect of mixing in LES on the ignition timing compared to 0d IDT results is discussed with detail in the final section of this work. Table 3 shows IDT_{MR}^{0d} in 0d and the computed τ_2 in LES. Moreover, the ratio of IDT_{MR}^{0d} to τ^{amb} in Table 3 explains the significantly higher difference in reactivity of the pilot diesel and ambient mixture in DF1 compared to DF2, as discussed earlier in Figure 2(b) and (c). The similar ratios of τ_2^{3d}/τ_1^{3d} in DF1 and DF2 shows the consistent sequence of the first- and second-stage ignition in DF1 and DF2. In DF2 at $T_{amb} = 900 \text{ K}$, $\tau_1 = 0.52 \,\mathrm{ms}$, and τ_2 was not achieved after 3 ms, which is further discussed in the following.

Figure 5 depicts 2d cut-planes for spatial distribution of temperature at the time $1.2\tau_2$ where τ_2 depends



Figure 4. Temporal evolution of T_{max} (solid), RO₂, max (dotted), and OH_{max} (dash dotted) in DF LES with (a) methane (DF1) and (b) methanol (DF2). Here, τ_1 and τ_2 are marked with square and diamond, respectively.

Table 3. Ignition time calculations from 0d homogeneous ignition at ξ_{MR}^{0d} (IDT_{MR}^{0d}) and 3d spray LES (τ^{3d}) in millisecond. Here, τ^{amb} is the ambient premixed charge IDT, while τ_1^{3d} and τ_2^{3d} are the first-stage and second-stage ignition time in 3d simulations, respectively. Weighted IDT, IDT_{MR}^{0d,w}, is defined and used in the following sections.

	T _{amb}	ξ ^{0d} ξMR		IDT ^{0d, w} MR	$ au_2^{ m 3d}$	$IDT^{0d}_{MR}/ au^{\mathit{amb}}$	$ au_2^{ m 3d}/ au_1^{ m 3d}$
DFI	900 K	0.075	0.30	0.63	0.54	0.0032	2.58
	950 K	0.1	0.20	0.38	0.43	0.0061	3.60
	1000 K	0.13	0.15	0.27	0.31	0.0116	3.80
DF2	900 K	0.11	0.71	1.19	> 3	0.1110	$\tau_{2}^{3d}/0.57$
	950 K	0.12	0.42	0.75	1.17	0.2085	² 3.70
	1000 K	0.15	0.29	0.48	0.55	0.3932	3.35

on the fuel/temperature combination. Three ignition types are observed as annotated in the figure. First, in DF1 with all of the considered T_{amb} and in DF2 at $T_{amb} = 950 \text{ K}$, ignition starts in the vicinity of the spray cloud tip. Second, in DF2 at $T_{amb} = 900 \text{ K}$, ignition is not observed until 3 ms of the simulation time. Third, in DF2 at $T_{amb} = 1000$ K, although ignition starts at the tip of the spray cloud, the ambient mixture autoignites as well, as predicted earlier using 0d simulations. In this case, as time marches toward τ_2 , ambient temperature increases significantly, leading to an unfavorable autoignition of the ambient mixture. Existence of three different ignition types in DF2 with slightly different T_{amb} demonstrates that the appropriate T_{amb} window for a robust spray-assisted ignition is very narrow for methanol. The appropriate T_{amb} should be high enough to avoid the extremely late ignition, yet low enough to avoid autoignition of the ambient. In particular, ambient autoigntion can result to sudden rise of the in-cylinder pressure leading to knock phenomenon, for instance as reported by Wang et al.³⁹ for DF diesel/methanol. It should be noted that here, $1.2\tau_2$ is the selected time for visualization and our conclusions on the ignition types are not drawn by looking into this time instance only. In particular, in the case of normal (spray-assisted) ignition for DF1 cases and DF2 at $T_{amb} = 950$ K, our observations indicate that there is no ambient autoignition until $1.4\tau_2$. Moreover, in DF2 at $T_{amb} = 1000$ K, ambient temperature is observed to raise even before τ_2 . The interested reader is referred to the presented 2d cut-plane animations in the Supplemental Materials, which present temporal evolution of temperature and key species fields in our DF LES.

Contour-lines of ξ_{st} , 1% RO_{2,max}, and 25% H₂O_{2max} are marked in Figure 5. The ξ_{st} contour-line indicates the longer penetration length of the diesel surrogate in DF2 compared to DF1 at each respective T_{amb}, which is due to the longer IDT in DF2. For DF2, the longer spray penetration at 1.2 τ_2 leads to an extended LTC region (cool flame) for DF2 according to the displayed 1% RO_{2,max}, and 25% H₂O_{2max} contour-lines. Therefore, there is a considerably longer time for mixing and a higher extent of dilution for DF2 compared to DF1 at a given T_{amb}. Consequently, HTC in DF1 starts at the vicinity of the spray tip in rich and high temperature ignition kernels, consistent with the observations by Kahila et al.^{6,9} and Tekgül et al.¹⁰ In



Figure 5. Spatial distribution of temperature at $1.2\tau_2$, embedded with iso-lines of ξ_{st} (magenta), $1\%RO_{2,max}$ (green), and $25\%H_2O_{2,max}$ (blue) at $T_{amb} = 900$, 950, and 1000 K (top to bottom) for DFI *n*-dodecane/methane (left) and DF2 *n*-dodecane/ methanol (right). DF2 at $T_{amb} = 900$ K is shown at 3 ms. Note the robust ignition of DFI in contrast to the narrow window of sprayassisted (normal) ignition in DF2.

DF2, at $T_{amb} = 950$ and 1000 K, large ignition kernels are noted to form around the spray. In DF2 at $T_{amb} = 900$ K, although LTC is active, full ignition is not observed. The main reason for no ignition is that based on our numerical assessment, the spray overdilutes mostly to sub-stoichiometric values.

Figure 6 demonstrates scatter plots of temperature against mixture fraction for LES cases at their respective $1.2\tau_2^{3d}$. In addition, conditional means are plotted on top of each scatter data to further show detailed distribution of temperature against mixture fraction. As consistent with the above discussion, DF1 simulations with shorter IDT at the most reactive mixture fraction, here $IDT_{MR}^{0d} \leq 0.3 \text{ ms}$, ignite over a wide range of mixture fraction values between ξ_{st} and ξ_{MR}^{0d} . Also, DF2-900 K and DF2-1000 K display no ignition and ambient autoignition, respectively, implying the narrow window of ignition for methanol cases as previously mentioned. However, DF2-950 K (IDT $_{MR}^{0d} = 0.42 ms$) ignites within a narrow range around its ξ_{st} and far from $\xi_{MR}^{0d} \approx 0.1$, implying the strong leaning before ignition in this case. To provide a better insight to mixing and ignition processes, 2d cut-plane animations from our DF LES in the Supplemental Materials depict progress of temperature along with certain intermediate radicals indicative of the first- and second-stage ignition.

Heat release map analysis

Our observations in the former section indicated significant differences in the ignition process of n-dodecane/ methane (DF1) and n-dodecane/methanol (DF2) sprays at various T_{amb}. In order to quantify the significance of LTC and HTC in DF1 and DF2, heat release (HR) map analysis, used previously in the literature for example by Borghesi et al.,⁷² is provided in Figure 7. Five different ignition modes relevant to LTC and HTC are considered as explained by Kahila et al.9: early LTC, LTC, pre-HTC, HTC pre-ignition, and HTC. The selection criteria for each mode according to RO2, H2O2, and OH mass fractions and temperature are listed in Table 4. Here, heat release rate (HRR) for each ignition mode is integrated over the spray volume, defined as $\xi > 10^{-4}$. In the HR maps, time is normalized with the respective τ_2 value for each LES, except for DF2 at $T_{amb} = 900 \text{ K}$ where the simulation time, that is 3 ms, is used for normalization. In DF2, HRR is rather small at the beginning and here we show it within the normalized time period of 0.8 and 1.1 for better data visualization. Moreover, the pie charts show the percentage of total HRR from each mode within the time period from the start of each simulation till $1.1\tau_2$.

In DF1, changing T_{amb} does not significantly affect the relative dominance of the modes. In particular, in



Figure 6. Scatter plots of temperature versus mixture fraction from LES simulations at their respective $1.2\tau_2^{3d}$. For DF2-900 K, the scatter plot at 3 ms is shown with no ignition. Dashed black lines display conditional means of the scatter data.



Figure 7. Modal decomposition of the HR maps within the spray region ($\xi_{st} > 10^{-4}$) for DF1 *n*-dodecane/methane (left) and DF2 *n*-dodecane/methanol (right) at T_{amb} = 900, 950, and 1000 K (top to bottom). Pie charts represent the time-integrated contribution of each mode till 1.1 τ_2 .

all DF1 cases LTC and HTC pre-ignition modes have dominant contributions to the total HRR, that is together $\approx 40\%$ of the total HRR. While the contribution of early LTC mode is negligible, LTC and pre-HTC contributions start earlier in time compared to HTC pre-ignition and HTC. These observations are qualitatively consistent with the HR maps provided by Kahila et al.⁹ for DF1 *n*-dodecane/methane, despite using a different chemical mechanism. In DF2, different trends are observed for igniting cases. The contribution of HTC pre-ignition is much smaller than in DF1. However, contributions of pre-HTC and HTC to total HRR are dominant over the other ignition modes, \approx 70%–80% in total. The contribution of early LTC remains negligible and LTC has a small contribution to total HRR. As a numerical evidence, the presented HR maps quantify our earlier observations in this study, which already indicated the significantly weaker LTC in DF2 compared to DF1. We note that we have investigated the sensitivity of our findings with

Table 4. Criteria for HR maps ^a.

Mode	Definition
Early LTC LTC Pre-HTC HTC pre-ignition	$\begin{array}{l} (RO_2 \ge I0^{-7}) \cap (H_2O_2 < H_2O_2^{\star}) \cap (T < T^{\star}) \\ (RO_2 \ge RO_2^{\star}) \cap (H_2O_2 \ge H_2O_2^{\star}) \cap (T < T^{\star}) \\ (RO_2 < RO_2^{\star}) \cap (H_2O_2 \ge H_2O_2^{\star}) \cap (T < T^{\star}) \\ (OH < OH^{\star}) \cap (T \ge T^{\star}) \end{array}$
нтс	$(OH \ge OH^{\star}) \cap (T \ge T^{\star})$

 ${}^{a}RO_{2}^{\star} = 10^{-5}, H_{2}O_{2}^{\star} = 10^{-4}, OH^{\star} = 10^{-5}, T^{\star} = 1150 \text{ K}.$

respect to the choice of parameters in Table 4 for both fuels. Our investigations indicate slight impact of the choice of parameters on our findings.

Reaction sensitivity analysis

For completeness, we carry out a reaction sensitivity analysis in order to understand why the second-stage ignition time is longer in DF2 compared to DF1 at similar T_{amb}. In particular, the analysis aims at revealing which reactions have greater effects on the second-stage ignition time for the two DF cases (n-dodecane/ methane vs n-dodecane/methanol) considered in this study. We note that in this analysis, the most reactive mixture fraction is considered in order to study reaction sensitivity with relevance to spray ignition only, and it does not intend to study ambient autoignition. The analysis method herein is similar to the one utilized by Kahila et al.⁶ According to Kahila et al.,⁶ when comparing SF n-dodecane and DF1 n-dodecane/ methane, adding CH4 influences chemical pathways and production/consumption rates of intermediate species as well as early decomposition of n-dodecane, leading to a longer IDT in DF compared to SF ignition.

According to Yao et al.,⁶⁰ we define a sensitivity indicator, S_i , as

$$S_i = \frac{\partial \ln(\tau_2)}{\partial \ln(k_i)} = \frac{k_i \partial \tau_2}{\tau_2 \partial k_i},\tag{5}$$

wherein k_i is the rate constant for the i^{th} reaction step. By varying k_i by factor 2 and recalculation of τ_2 , equation (5) gives

$$S_i = \frac{\tau_2(2k_i) - \tau_2(k_i)}{\tau_2(k_i)}.$$
 (6)

We note that according to our tests, using different k_i values ranging between 1.1 to 2.0 does not lead to significant differences and our reaction sensitivity results are independent of the chosen small perturbation value. In equation (6), negative S_i indicates a decreasing influence (promoting effect) while positive S_i denotes an increasing effect on τ_2 (inhibiting effect).

The relevant reactions of Polimi-reduced mechanism which have larger $|S_i|$ in SF and DF ignition are listed in Table 5. The ignition process of SF *n*-dodecane is discussed in the literature^{6,73} and summarized herein. Decomposition of *n*-dodecane is initiated through R946

R272	$CH_3OH + OH \Rightarrow CH_2OH + H_2O$
R948	$NC_{12}H_{26} + OH \Rightarrow H_2O + NC_{12}H_{25}$
R512	$NC_{12} - OOQOOH \Rightarrow NC_{12} - QOOH + O_2$
R513	$NC_{12} - OOQOOH \Rightarrow NC_{12} - OQOOH + OH$
R569	$CH_4 + OH \Rightarrow CH_3 + H_2O$
R508	$NC_{12} - QOOH \Rightarrow HO_2 + I.2NC_{10}H_{20}$
R503	$NC_{12} - QOOH + O_2 \Rightarrow NC_{12} - OOQOOH$
R950	$HO_2 + NC_{12}H_{26} \Rightarrow H_2O_2 + NC_{12}H_{25}$
R474	$NC_{12}H_{25} + O_2 \Rightarrow HO_2 + I.2NC_{10}H_{20}$
R505	$NC_{12}H_{25} - OO \Rightarrow NC_{12} - QOOH$
R514	$NC_{12} - OQOOH \Rightarrow CH_2O + CH_3CO$
	+0.8NC10H20+0.25NC4H8+OH
RI3	$2OH(+M) \Leftrightarrow H_2O_2(+M)$
R517	$NC_{12} - OQOOH \Rightarrow 0.84C_2H_5 + CH_3CHO$
	+0.16CH ₃ COCH ₂ + 0.84CO + NC ₇ H ₁₄ + OH
R960	$CH_{3}O + NC_{12}H_{26} \Rightarrow CH_{3}OH + NC_{12}H_{25}$
R507	$NC_{12} - QOOH \Rightarrow NC_5H_{10} + NC_7H_{14}O + OH$
R946	$NC_{12}H_{26} + O_2 \Rightarrow HO_2 + NC_{12}H_{25}$
R502	$NC_{12}H_{25} + O_2 \Rightarrow NC_{12}H_{25} - OO$

followed by the LTC-relevant reactions R502 and R474, in low temperature (LT) and negative temperature coefficient (NTC) regions leading to the production of RO₂ and HO₂ short-lived intermediate species, respectively. In the LT region, RO₂ formation leads to the sequence of reactions R505, R503, R513, and R517, which further decompose n-dodecane and produce sufficient OH for the start of HTC. At the onset of the second-stage ignition, chain carrying reactions like R948 consume the produced OH and feed further NC₁₂H₂₅ radicals to the aforementioned reactions for further decomposition. In the NTC region, R474 and R508 generate HO₂. Thereafter, HO₂ radicals combine and form the metastable species H2O2 which slows down the ignition process along with reverse reactions of R503 (R512) and R502 that decrease the concentration level of RO₂; that is a reduced overall reactivity.

In the considered DF cases, all of the abovementioned reactions are still among the top sensitive ones according to their $|S_i|$. Figure 8 demonstrates results of the analysis for DF2 and DF1 at $T_{amb} = 900$, 950, and 1000 K at their respective ξ_{MR}^{0d} (reported in the following in Table 3). The simulations are conducted using the 0d homogeneous reactor model in Cantera at the conditions reported earlier for 0d simulations. In Figure 8, only the 15 most sensitive reactions in all case studies are shown. We note that non-integer coefficients appearing in certain reactions in Table 3 are tuned coefficients provided in Polimi-reduced mechanism.

According to Figure 8, variation of temperature at the corresponding ξ_{MR}^{0d} does not significantly influence S_i in DF1 and DF2. Furthermore, switching between methane and methanol remarkably affects S_i only for R272, R948, R569, and R950. In particular, R272 and R569 are inhibiting reactions (positive S_i) in DF2 and DF1 and they correspond to the decomposition of methanol and methane, respectively. These two



Figure 8. Reaction sensitivity analysis for DF2 and DF1 ignition at T_{amb} = 900, 950, and 1000 K at their respective ξ_{MR}^{0d} . Note the extreme sensitivity of R272 in DF2 versus R569 in DF1, which explains the stronger delay of IDT in DF2 compared to DF1.

reactions consume the available OH required for the ignition of *n*-dodecane; hence, further IDT delay in both cases compared to SF *n*-dodecane ignition. On the other hand, R948 and R950 have promoting roles (negative S_i and they are dominant in DF2 compared to DF1. As mentioned earlier, these two reactions lead to the decomposition of n-dodecane during the secondstage ignition. When comparing DF1 and DF2, the inhibiting role of R272 in the ignition process of DF2 is found to be superior with respect to all other reactions, which explains the longer IDT in methanol DF2 compared to methane DF1. Yet, the promoting effects of R948 ($S_i \approx -0.37$) and R950 ($S_i \approx -0.1$) cannot compete with the superior inhibiting effect of R272 $(S_i \approx 0.9)$ in DF2. For DF1, however, the inhibiting effect of R569 ($S_i \approx 0.15$) delays SF IDT with a weaker impact compared to R272 ($S_i \approx 0.9$) in DF2.

The acquired knowledge from reaction sensitivity analysis along with the 3d spray results provide insight into the reason of the observed narrow ignition window in DF2. From the reaction sensitivity analysis we know that R272 in DF2 dramatically prolongs ignition of *n*-dodecane spray compared to that in DF1. This prolongation leads to further dilution before ignition in DF2 cases compared to DF1 cases. The over-dilution itself leads to further delay of the spray ignition, which typically starts from richer pockets on the tip of the spray. Accordingly, in *n*-dodecane/methanol cases, different ignition behaviors are observed depending on the ambient temperature: at lower T_{amb} (900 K), dilution dominates and no spray ignition is observed while at $T_{amb} = 950 \text{ K}$, reactions dominate and spray ignition initiates. However, at higher T_{amb} (1000 K) ambient reactions dominate, leading to ambient autoignition before spray ignition initiates.

Mixing and residence time analysis

Considering the high computational cost of LES with finite rate chemistry, for example in DF2 with longer IDT leading to longer spray penetration, it would be beneficial to predict the DF spray ignition delay time based on 0d homogeneous reactor calculations and computationally less expensive non-reacting LES. Here, we outline a simple approach for such a purpose as follows. It is discussed by Kahila et al.⁶ and shown in Table 3 of the current study that the calculated IDT from 0d homogeneous reactor calculations is typically two to three times shorter than the ignition time in LES spray simulations. This difference mainly corresponds to the mixing time in spray simulations. The idea here is to estimate the mixing time using non-reacting 3d spray simulations and contribute it to 0d IDT to provide a better estimation of the spray ignition timing.

For estimating mixing time, a residence time, τ_{res} , is defined based on the fluid travel time along the spray axis (z), similar to the analysis by Kahila et al.⁴⁷ Here, we envision that a fluid element travels from the nozzle along the axial direction of the spray. For estimation of τ_{res} , (1) we repeat LES cases in non-reacting mode, (2)



Figure 9. Calculated residence time along the mixture fraction using non-reacting LES for DF1-900 K case. Along the spray axial direction (z), the fluid element evaporates after injection $(0 < z < z_1)$ and then, leans out during the mixing phase $(z_1 < z < Z)$. It is assumed that there is no reaction onset in the evaporation phase.

we construct mean velocity $\langle u(z) \rangle$ and mean mixture fraction $\langle \xi(z) \rangle$ profiles along the spray axis, and (3) we calculate residence time as $\tau_{res}(\xi) = \int_0^{z^*} dz/\langle u(z) \rangle$, in which integration limits are respectively the nozzle location (z = 0) and $0 \leq z^* \leq Z$, wherein Z is an arbitrary length selected far away from the nozzle along the spray axis such that $\xi(Z) \approx 0$. Figure 9 depicts an example of the calculated τ_{res} in the mixture fraction space for DF1-900 K. The ascending left branch of the profile specifies evaporation within the liquid length, while the descending branch indicates leaning due to mixing.

We estimate ignition time in 3d spray simulations by weighting the 0d IDT data, c.f. Figure 2, with τ_{res} . The weighted IDT (IDT^{0d, w}) is therefore defined as

$$IDT^{0d,w}(\xi) = \frac{\int_{z_1}^{z^*} IDT^{0d}(z) \ \tau_{res}(z) \ dz}{\int_{z_1}^{z^*} \tau_{res}(z) \ dz}.$$
 (7)

Here, we neglect the evaporation phase and we only integrate along the descending branch of the profile in Figure 9, in which z_1 and Z are annotated. The lower limit of the integrals is z_1 while the upper limit is the respective z at each ξ along the descending branch; that is $z_1 \leq z^* \leq Z$. As a remark, the spray evaporation phase is essentially non-reacting and hence the integration is started from the liquid length at $z = z_1$.

Figure 10(a) displays weighted and unweighted IDT profiles against mixture fraction for DF1-900K. It is observed that the most reactive IDT is further delayed and shifted toward leaner mixture fractions. Figure 10(b) and (c) compare the most reactive weighted IDTs $(IDT_{MR}^{0d,w})$ against τ_2^{3d} and IDT_{MR}^{0d} for DF1 and DF2 cases, respectively. Moreover, the corresponding $IDT_{MR}^{0d,w}$ values are reported in Table 3. It is observed that $IDT_{MR}^{0d,w}$ provides better estimations of τ_2^{3d} compared to IDT_{MR}^{0d} for all of the considered cases. For all DF1 cases as well as DF2-1000 K, the estimation is relatively accurate. However for DF2-900 and 950K, despite the improvement compared to IDT_{MR}^{0d} , $IDT_{MR}^{0d,w}$ underpredicts τ_2^{3d} . This underprediction is mainly due to the atypically long IDT^{0d}_{MR} in these cases which leads to the continuous leaning at the spray tip before ignition. In particular, in the weighted IDT approach, it is assumed that the followed fluid element leans out until reaching a mixture fraction with its respective IDT shorter than the mixing timescale. Since mixing is a continuously evolving process, if IDT within the entire range of mixture fraction is rather long, the weighting approach may fail because the fluid element can lean out significantly before it can ignite. Under such a scenario, the weighting approach underpredicts τ_2^{3d} . For the six considered cases in this work, it is observed that the longer the IDT_{MR}^{0d} , the less accurate the prediction of the weighted IDT approach. Moreover, we note that weighted IDT approach does not take into account the radical formation process before ignition in 3d spray simulations. Accordingly, the main reason for no ignition in DF2-900 K after 3 ms can be related to its longer IDT_{MR}^{0d} and $IDT_{MR}^{0d,w}$ compared to other cases, which leads to over-leaning of the spray tip before ignition.

In summary, we note that the proposed weighted IDT concept provides a simple correction to the DF1 cases with reasonably good IDT prediction. However, the concept was shown to be less accurate, although improved, for the more sensitive DF2 case.



Figure 10. (a) Unweighted and weighted IDT from 0d data for DF1-900 K case. Comparison of the most reactive 0d IDT (IDT_{MR}^{0d}) and weighted IDT ($IDT_{MR}^{0d,w}$) against 3d spray IDT (τ_2^{3d}) for (b) methane DF1 cases, and (c) methanol DF2 cases.

Conclusions

Ignition characteristics of diesel surrogate (*n*-dodecane) injection into hot and lean ($\phi_{LRF} = 0.5$) ambient mixture of methane/air and methanol/air under the ECN Spray A relevant conditions are investigated using 0d homogeneous reactor simulations and 3d LES with finite-rate chemistry. The main scope is to understand effects of (1) replacing methane with methanol in the ambient and (2) ambient temperature (T_{amb}) variation on dual-fuel (DF) ignition. Variation of T_{amb} and ambient fuel is shown to change combustion characteristics from non-igniting spray to ambient autoignition. The main findings of the study are highlighted in the following.

- 1. Replacing methane with methanol in the ambient lean mixture of DF sprays leads to inhibited ignition almost by a factor of two. Moreover, higher T_{amb} shortens both the first- and second-stage ignition time. Compared to DF *n*-dodecane/methane spray, ignition of DF *n*-dodecane/methanol initiates further downstream when the spray is spanning a larger volume. The more diffusive ignition of methanol compared to methane is due to the further delay of the DF spray ignition with methanol compared to methane.
- 2. With methanol, different ignition types are observed for different T_{amb} . At $T_{amb} = 900$ K, IDT is considerably long (more than 3 ms). At $T_{amb} = 1000$ K, ambient autoignites after initial ignition of the spray, which is unfavorable and may promote knock in CI engines.
- 3. With methanol, the T_{amb} window for robust ignition is found to be very narrow, being concentrated around 950 K. This is important due to cycle-to-cycle variations in engines, which may fluctuate the ambient temperature from one to another cycle. The narrow ignition window of methanol may lead to misfire or ambient autoignition leading to knock.
- 4. Weighting 0d IDT data using residence time from non-reacting LES is shown to offer a correction factor for estimation of spray IDT with substantially lower computational expenses compared to 3d reacting spray LES. Although the concept is more reliable for methane DF cases, it provides improvements even for more sensitive methanol DF cases. The method is proposed as a diagnostic tool to assess spray ignition delay time.
- Heat release maps indicate the small contribution of LTC in ignition for methanol cases compared to methane cases. LTC becomes weaker with methanol and an extended LTC region is observed, mainly due to the longer IDT.
- 6. According to the reaction sensitivity analysis, R272 (CH₃OH + OH \Rightarrow CH₂OH + H₂O) in DF methanol and R569 (CH₄ + OH \Rightarrow CH₃ + H₂O) in DF methane consume the available OH required for

the ignition of *n*-dodecane and hence, they are considered to be the main sources of longer IDT in DF cases compared to SF. However, the inhibiting effect of R272 in DF2 appears stronger than that of R569 in DF1, which explains the further prolongation of ignition time in DF2 compared to DF1.

Considering the reported limitations in robust ignition of methanol in DF conditions in this work, our recent research results suggest that adding H₂ to methanol/air ambient may favorably impact ignition.⁶² In our recently published studies, tri-reactivity ignition of methane/hydrogen and methanol/hydrogen by a diesel spray at a fixed ambient temperature (900 K for methane/hydrogen and 950K for methanol/hydrogen) are investigated.^{40,41} As a closing remark, we note that the conclusions of this study are dependent on the selected chemical mechanism for DF mixtures of ndodecane/methane and n-dodecane/methanol. Due to the lack of experimental data for validation of the utilized chemical mechanism under the considered conditions, the presented conclusions need to be further assessed using experimental engine tests, in specific for *n*-dodecane/methanol DF combustion.

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Appendix A: Mesh details and sensitivity analysis

The computational geometry, mesh structure, and mesh sensitivity analysis of the studied LES are presented here. The volume of the computational domain is the same as the experimental combustion vessel for the ECN Spray A. The computational domain and the sizes (in mm) are displayed in Figure A1. The standard mesh (the upper half) – which is used for the studied LES – is compared to a finer mesh (the bottom half) – which is used for the sensitivity test. The only difference between the two meshes is the higher resolution in the spray envelope region of the finer mesh. Four regions are marked, which specify resolutions: R1: 1000, R2: 250, R3: 125, and R4: $62.5 \,\mu$ m.

The finer mesh is used in an LES test for validation of our results in one of the studied cases, DF1-1000 K. The result of this sensitivity test is presented in Figure A2, which shows temporal evolution of the maximum temperature (T_{max}), OH and RO₂ mass fractions computed with the finer mesh (symbols) and the standard mesh (lines). It is observed that the standard mesh results match well with those of the finer mesh. The major difference is observed for RO₂ after its peak value, which relates to LTC. However, according to this result, the first- and second-stage ignition time (τ_1 and τ_2) are not influenced by the mesh resolution.



Figure A1. The computational domain of the studied LES (sizes in mm). The standard mesh used for the LES studies (top) is shown against the finer mesh used for the sensitivity analysis. Mixture fraction fields in the two different mesh at τ_2 for DFI at T_{amb} = 1000 K are shown (the magenta colored field).



Figure A2. Temporal evolution of temperature and intermediate species in DF1-1000 K, using the standard mesh (lines) and the finer mesh (symbols).