Surrogate fuels for the simulation of diesel engine combustion of novel biofuels

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Abstract

Recently, several promising biomass-derived fuels for diesel engines have been identified, produced, and tested. Diesel engine experiments confirmed very low soot and low nitrogen oxide emissions. With regard to further improvements of the combustion system, it is desirable to complement the diesel engine experiments with numerical simulations. To date, this is hindered by the lack of suitable chemical reaction mechanisms for these novel fuels. Therefore, a surrogate approach is presented here and applied in computational fluid dynamics simulations. Combustion and pollutant formation is simulated using the representative interactive flamelet model. Ignition, combustion, and pollutant formation are described in a consistent manner by inclusion of detailed reaction chemistry. Different mixtures of *n*-heptane, toluene, ethanol, dimethylether, ethane, and phenol are employed to describe the combustion chemistry of the biofuels. The compositions of the surrogate fuels are compiled according to hydrogen/carbon ratio, oxygen content, cetane rating, and molecular properties of the experimental fuels. Spray, injection, and evaporation properties of the experimental fuels, as obtained from spray vessel experiments, are included in the computational fluid dynamics simulations. By systematic comparison of experimental and numerical results, the surrogate methodology is validated and an improved understanding of the limitations of the current surrogates is achieved. Thus, a methodology for the fast adoption of novel fuels for simulations is proposed that can be used regardless of the availability of specific chemical reaction mechanisms.

Keywords

Diesel engine combustion, biofuels, detailed chemistry, surrogate fuels, computational fluid dynamics

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Introduction

The need of future societies for continuous mobility necessitates the search for alternatives for fossil energy sources. One attractive option is the production and use of fuels from biomass, as they have the potential to considerably reduce carbon dioxide (CO₂) emissions as well as pollutant emissions such as soot or nitrogen oxides (NO_x). The holistic development of these fuels as a combination of biomass processing and combustion technology has proven to be a research area with a high need for interdisciplinary cooperation between natural and engineering sciences. In this context, the Cluster of Excellence “Tailor-Made Fuels from Biomass” (TMFB) at Rheinisch Westfälische Technische Hochschule Aachen (RWTH) Aachen University was established in 2007 as part of the Excellence Initiative by the German Research Foundation in order to

develop new, biomass-based, synthetic fuels for mobile applications.

Several novel biofuels for diesel engine combustion were identified and produced in the TMFB framework. Compared to standard diesel fuel, these fuels have an increased oxygen content and typically lower cetane rating. Diesel engine experiments utilizing these fuels confirmed very low soot and NO_x emissions.^{1–4} As a

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drawback, increased emissions of unburned hydrocarbons (HCs) and carbon monoxide (CO), especially in the low-load operating range, have been observed.

To further improve the combustion system and assess fuel effects and emission formation mechanisms in more detail, it is desirable to complement the diesel engine experiments with numerical simulations. Here, simulations are performed using the representative interactive flamelet (RIF) model.^{5,6} In many studies concerning the modeling of compression ignition in internal combustion engines, the RIF model has been applied successfully. A general review of the model and its applications can be found in Barths et al.⁷ Different engines were investigated, ranging from small displacement volumes (300 cm³/cylinder) to marine diesel (4800 cm³/cylinder) engines.^{5,8–12} By the use of detailed chemical reaction mechanisms, the RIF model inherently accounts for low- and high-temperature auto-ignition, heat release, and pollutant formation. However, despite the focused research on reaction chemistry within the TMFB group and elsewhere,^{13–20} chemical reaction mechanisms of novel biofuels are not readily available. New fuel classes containing numerous isomers with partly very different chemical properties have to be considered. While the use of automated methods might speed up the reaction scheme generation considerably, the development of accurate mechanisms is also based on the validation against time-consuming experimental measurements and will remain complex. Even if mechanisms are developed for the presently considered fuels, future development of detailed chemical kinetics might not be able to keep up with the number of newly proposed bio-derived fuel components. The surrogate approach presented in the following tries to bridge the time between the appearance of a promising fuel candidate and the time when a detailed reaction scheme for this fuel becomes available. This approach is exemplified for 2-methyltetrahydrofuran (2-MTHF), a cellulose-derived fuel with a furanic structure, and for a blend of 70% 2-MTHF and 30% di-*n*-butylether (DnBE) by liquid volume.

This article is arranged as follows: the first section describes the combustion modeling approach employed in the current investigation. After this, the engine test bench, the investigated operating points, and the corresponding numerical setup are presented. This includes the composition of the surrogate fuels, the chemical reaction mechanism, and a comparison of the proposed surrogate to experimentally determined ignition delay times of 2-MTHF. To validate the spray setup for the engine simulations, spray vessel experiments at diesel engine-like conditions are compared to simulations, confirming the correct representation of the spray. Section “Results and discussion” contains the comparison of the numerical simulations to the engine experiments, including heat release rates (HRRs) and pollutant emissions. This is complemented by detailed

analysis of the differences in pollutant formation for the investigated fuels and load points. Finally, the conclusions and major findings from the study are summarized.

Mathematical model

Computational fluid dynamics code

The computational fluid dynamics (CFD) code used in this work is AC-FluX (formerly known as GMTEC), a flow solver based on the finite volume method²¹ that employs unstructured, mostly hexahedral meshes. AC-FluX solves the partial differential equations for continuity and momentum, an equation for the total enthalpy (including heat of formation), and two equations to account for the turbulence (*k*- ϵ model). AC-FluX is documented by Khalighi et al.²² and Ewald et al.²³

The liquid phase is modeled using the discrete droplet model (DDM), which describes the spray using a Monte Carlo method. Since the spray consists of a large number of droplets, only the behavior of a representative subset of all droplets (called parcels) is calculated in detail. The gas phase and the liquid phase are coupled through source terms in the governing equations for the gas phase. A detailed description of the spray modeling in AC-FluX can be found in Spiekermann et al.²⁴

To approximate the physical properties of the experimental fuels, toluene has been used. For the experimental fuels, the database is quite incomplete while the most relevant properties of toluene such as molecular weight (MW), heat of vaporization, critical pressure, and critical temperature are very similar. This approach is in line with the general concept of this article to provide a way to quickly integrate novel fuels into reactive CFD simulations, regardless of the lack of detailed experimental data. The approximation is validated by comparison of CFD simulations using toluene to spray vessel experiments below (section “Spray chamber”). Concerning the 2-MTHF/DnBE blend, a single-component vaporization model is used and the fuel composition is assumed uniform in the liquid phase, which is consistent with the typical modeling approach for other complex fuels. For instance, diesel fuel contains hundreds of species with a wide range of boiling temperatures, but no separation of these components is usually observed in evaporating diesel sprays. In a recent study, Hottenbach et al.²⁵ optically investigated a diesel-like spray of an iso-octane/ethanol mixture, where no separation of these components could be found.

Laminar flamelet concept

The laminar flamelet concept views a turbulent flame as an ensemble of flamelet structures attached to the instantaneous position of the flame surface, which itself

is corrugated by the turbulent flow field. The assumption of combustion occurring in thin, locally one-dimensional layers was introduced by Williams.²⁶ Flamelet equations based on the mixture fraction as independent parameter and using a scalar dissipation rate to describe the turbulent mixing process were derived by Peters.^{27,28} Reviews on the flamelet concept can be found in Peters.^{6,27–29} An asymptotic analysis of the species transport equations yields the flamelet equations for the mass fraction Y of species j as

$$\frac{\partial Y_j}{\partial t} - \frac{\chi}{2} \frac{\partial^2 Y_j}{\partial Z^2} - \frac{\dot{\omega}_j}{\rho} = 0 \quad (1)$$

where χ denotes the scalar dissipation rate, ρ is the density, and $\dot{\omega}_j$ is the chemical source term for species j , which is typically evaluated using detailed chemistry calculations. In the derivation of equation (1), unity Lewis numbers and equal diffusivities for all species are applied. The underlying model assumption is that mixing and diffusion processes are dominated by the turbulent flow field. Numerous experimental observations supporting this can be found in the literature. A more detailed discussion on the importance of molecular effects can be found in Pitsch.³⁰

RIF model

Of fundamental importance for the RIF model is the separated treatment of physical and chemical processes, which decouples time scales and spatial discretization. This allows for solving the chemistry, which is extremely nonlinear especially during ignition, with time steps much smaller than the CFD time steps. Additionally, the discretization of the flame structure in phase space is independent of the spatial discretization used in the CFD simulation, and the flame structure is accessible for detailed analysis.

In Figure 1, the schematic flow diagram shows the interaction of the CFD and the flamelet code. At every time step, the CFD code passes the scalar dissipation rate conditioned on stoichiometric mixture $\hat{\chi}_{st}$ and the mean pressure $\hat{p}$ to the flamelet code. Based on this information, a presumed shape for the dissipation rate, and the given initial and boundary conditions, the flamelet code solves equation (1) in addition to an energy equation in similar form with time steps that may be much smaller. The solution yields species profiles for every species contained in the chemical reaction mechanism. The species profiles as function of mixture fraction are convoluted with a presumed probability density function (PDF) of mixture fraction, typically taken to be a β -PDF³¹ scaled by the mean and the variance of the mixture fraction in a particular cell, to yield the mean species mass fractions for each CFD cell. This yields the three-dimensional species distribution, heat release, and temperature. The scalar dissipation rate considers the effect of turbulence on the flame chemistry regarding mixing and flame stretch.

Figure 1. Structure of the representative interactive flamelet concept.

CFD: computational fluid dynamics.

Experimental and numerical setup

Diesel engine test bench

The single-cylinder engine used for the diesel engine tests was operated at the Institute for Combustion Engines (VKA). It has a swept volume of 0.39 L and was designed for low emission levels and high fuel efficiency. A compression ratio of 15:1 was selected in order to keep the NO_x emissions low in spite of the increased charge density, following typical Euro 6 development strategies. The combustion system reaches a specific output of 80 kW/L at maximum peak firing pressures of 220 bar. A common rail system with a maximum fuel injection pressure of 2000 bar is used as injection system. To optimize the flow characteristics, one intake port was designed as a filling port and the second one as a classic swirl port. Creating charge movement was supported by seat swirl chamfers on both intake valves. The combustion chamber geometry was designed with a conventional recess shape, which was further optimized together with the nozzle geometry (eight-hole, $k_s = 1.5$) in order to maximize air utilization. The low compression ratio of 15:1, early injection and high injection pressures, as well as improved exhaust gas recirculation (EGR) cooling make very low particulate emissions possible, and as a result, the research engine meets the Euro 6 standard. Table 1 shows a summary of the parameters of the test engine used. Additional information on the single-cylinder research engine can be found in earlier publications.^{32–34}

Four load points were selected, three of which are within the New European Driving Cycle (NEDC) range for an inertia weight class of 1590 kg. The fourth load point is of interest for future downsizing concepts. Table 2 shows the respective calibration. Both fuels were analyzed with a single injection and at a constant center of combustion, which was chosen differently for the respective load points (see Table 2), whereby in each

case the start of injection (SOI) was adjusted accordingly. The tolerance for the center of combustion is $\pm 0.1^\circ$ crank angle (CA). The constant ISNO_x level was obtained by adjusting the EGR rate accordingly. The other calibration parameters such as intake manifold pressure, fuel injection pressure, and charge air temperature had been optimized in earlier studies for a realistic four-cylinder engine with a two-stage boosting device, all in compliance with the Euro 6 standard.³⁵ Some details on the engine settings, along with the indicated efficiencies resulting from the above-described strategy, are given in Table 3.

Spray chamber

Shadowgraphic investigations of the fuel spray have been conducted in a high-pressure chamber, capable of

pressures up to 150 bar and temperatures up to 1000 K. Details on the setup can be found in Jakob et al.³⁶ The chamber is equipped with the same injection system as the diesel engine described above, ensuring comparability of the results. Density gradients as well as the shadow of the solid spray core are visualized, enabling the investigation of angle, penetration, distribution, and temporal development of the liquid and gaseous spray phase.

The sprays were investigated at two different ambient conditions, the lower at a temperature of 800 K, back pressure of 50 bar, and rail pressure of 900 bar, corresponding to the engine conditions for load point 2. The higher ambient conditions are at a temperature of 900 K, back pressure of 100 bar, and rail pressure of 900 bar, corresponding to the engine conditions for load point 3. CFD calculations for these conditions have been performed and the parameters of the Kelvin–Helmholtz/Rayleigh–Taylor (KH/RT) breakup model were adjusted accordingly. The results for liquid and gaseous penetrations are compared to the measurements in Figure 2 for 2-MTHF and for the 2-MTHF/DnBE blend in Figure 3. In all cases, good agreement is shown. Thus, the approximation of the physical spray properties by toluene is confirmed and the correct representation of the spray, which is of major importance for diesel engine simulations, is validated.

Numerical setup

Computations started from intake valve closure (IVC) at -134.6° CA after top dead center (aTDC) and ended at exhaust valve opening (EVO) at 120° CA aTDC. The starting solution at IVC was initialized with pressure and temperature taken from the experiments. The internal EGR rate was assumed to be 5%. The EGR

Table 1. Single-cylinder engine configuration.

	Single-cylinder engine
Benchmark	Euro 6
Displacement (cm ³)	390
Stroke (mm)	88.3
Bore diameter (mm)	75
Compression ratio	15
Valves per cylinder	4
Maximum peak pressure (bar)	220
Fuel injection system specifications	Bosch Piezo Common Rail System
Maximum injection pressure (bar)	2000
HFR (cm ³ /30 s)	310 at 100 bar
Nozzle hole diameter (μm)	109
Number of spray holes	8
Spray cone angle (°)	153

HFR: hydraulic flow rate.

Table 2. Engine calibration.

Load point	Center of combustion (°CA after TDC)	Pressures (bar absolute)		
		Rail	Boost	Exhaust manifold
1. $n = 1500 \text{ min}^{-1}$, IMEP = 4.3 bar	6.6 at 0.2 g/kW h ISNO _x	720	1.07	1.13
2. $n = 1500 \text{ min}^{-1}$, IMEP = 6.8 bar	5.8 at 0.2 g/kW h ISNO _x	900	1.5	1.6
3. $n = 2280 \text{ min}^{-1}$, IMEP = 9.4 bar	9.2 at 0.6 g/kW h ISNO _x	1400	2.29	2.39
4. $n = 2400 \text{ min}^{-1}$, IMEP = 14.8 bar	10.8 at 0.75 g/kW h ISNO _x	1800	2.6	2.8

CA: crank angle; TDC: top dead center; IMEP: indicated mean effective pressure.

Table 3. Engine setting details.

Load point	2-MTHF				70% 2-MTHF + 30% DnBE			
	EGR (%)	Inlet O ₂ (%)	SOI (°CA aTDC)	η_i (%)	EGR (%)	Inlet O ₂ (%)	SOI (°CA aTDC)	η_i (%)
1	No ignition obtained				32.4	18.2	−17.65	41.5
2					49.5	14.3	−13.46	42.7
3	47.4	15.5	−11	45.4	43.4	16.9	−5.31	44.6
4	39.8	15.5	−6.6	44.8	36.8	16.4	−5.9	45.0

2-MTHF: 2-methyltetrahydrofuran; DnBE: di-*n*-butylether; EGR: exhaust gas recirculation; SOI: start of injection; CA: crank angle; aTDC: after top dead center.

Figure 2. Comparison of liquid (solid lines) and gaseous (dashed lines) spray penetration from experiment (red) and simulation (blue) for 2-MTHF. Left part at 50 bar, 800 K ambient; right part at 100 bar, 900 K ambient.

Figure 3. Comparison of liquid (solid lines) and gaseous (dashed lines) spray penetration from experiment (red) and simulation (blue) for the 2-MTHF/DnBE blend. Left part at 50 bar, 800 K ambient; right part at 100 bar, 900 K ambient.

composition regarding oxygen, CO, NO_x, CO₂, and water vapor content was initialized according to the experimental measurements. The velocity field was initialized with a swirl number of 1.159, according to the experiments.

The simulation used a sector grid representing 1/8th of the combustion chamber, thereby taking advantage of the axial symmetry with respect to the placement of the nozzle holes. The mesh size was 40,224 cells at TDC. A sensitivity study revealed that this was a sufficient resolution for all cases. To account for the compression of the grid cells along the cylinder axis due to the piston movement, a cell layer removal technique was applied in the cylinder region throughout the simulations. Spray parameters were set according to the spray chamber simulations in the preceding subsection. The CPU time for a complete simulation is about 36 h on a single processor. The wall temperatures were set to 440 K, based on experimental experience, and held

constant during the simulations. The combustion chemistry is discretized on 101 grid points in *Z* direction.

Reaction chemistry

Chemical reaction mechanism. A chemical reaction mechanism for a mixture of *n*-heptane, iso-octane, toluene, ethanol, dimethylether (DME), phenol, and ethane is used for the simulations. These compounds are often and widely used as surrogate compounds for petroleum fuels. Their mechanisms have been well studied and thus ensure the prediction accuracy in this study. DME is added to the palette to represent the oxygenated part of 2-MTHF. Also this component has been studied extensively and reliable chemical mechanisms are available.

A detailed chemical kinetic mechanism for DME was taken from Fischer et al.³⁷ The mechanism consists of 79 species and 351 reversible reactions and was

validated extensively over a wide range of temperatures, pressures, and equivalence ratios.^{37–39} Using a multi-stage reduction method by Pepiot-Desjardins and Pitsch,⁴⁰ the detailed mechanism was reduced to a skeletal mechanism composed of 33 species and 64 forward and reverse reactions. The reduced mechanism was combined with a consistent chemical kinetic mechanism for *n*-heptane, iso-octane, toluene, and ethanol that consists of 631 reactions among 139 chemical species. A submechanism from Hewson and Bollig,⁴¹ which accounts for thermal, prompt, and nitrous oxide contributions to NO_x formation and for NO_x reburn by HC radicals and amines, is added, leading to a total number of 910 reactions and 170 chemical species. Rate conflicts detected during the combination were always resolved in favor of the better validated mechanism.⁴² The resulting mechanism accounts for low- and high-temperature auto-ignition, heat release, and pollutant formation. Soot emissions were very low in the experiments, with filter smoke numbers (FSNs) ranging from 0 to 0.09. For the simulations, no soot model was used.

Surrogate approach. Surrogate fuels are mixtures of components with known reaction chemistry, compiled to match the behavior of a given fuel. Perhaps, the most widely known surrogate is the primary reference fuel, denoting a mixture of *n*-heptane and iso-octane that can be used to describe the knocking propensity of gasoline. Typically, surrogate fuels describe the reaction chemistry of fuels that are too complex in composition to be modeled directly, as is the case for essentially all fossil-based, liquid HC fuels. Examples for such surrogates can be found in Andrae et al.,⁴³ Dooley et al.,⁴⁴ Farrell et al.,⁴⁵ Krishnasamy et al.,⁴⁶ and Pitz et al.⁴⁷ for diesel, gasoline, and jet fuels, respectively. While in these examples good results are obtained using surrogate fuels, there are obvious limitations for simple surrogates. For example, European premium gasoline has a research octane number (RON) of 95 and a motor octane number (MON) of 85. Octane numbers (ONs) are defined such that the fuel behaves like a mixture ON-% iso-octane with *n*-heptane in a standardized engine test, with different boundary conditions for RON and MON. For diesel fuel, *n*-heptane is often used as surrogate because it has the same cetane rating. Evidently, aromaticity and hydrogen/carbon (H/C) ratio cannot be matched with such simple surrogates. However, despite this issue, these surrogates have often been shown to lead to satisfactory results.

Composition of surrogate fuel. In recent studies, the focus in the development of surrogates has shifted from representing the fuel composition as accurately as possible to a model-based matching of certain properties of the fuels.^{42,44,48} Properties matched in these studies are, for instance, H/C molar ratio (H/C), derived cetane number (DCN), threshold sooting index (TSI), and average MW. These properties are often not interesting in their own right, but representative for important aspects of combustion behavior. For instance, H/C/O ratio is important for heat release, which determines flame temperature, which is important for NO formation. This means that not the fuel composition has to be matched by the surrogate, but only the part of the fuel molecular structure that is important for a certain property of interest. This implies that the palette of components chosen for the surrogate has to allow for independently matching the different important structural groups of the real fuel. If the chosen palette of surrogate components does not allow for matching the molecular structural groups of the real fuel, then adequate substitutions will have to be made. For example, soot formation is promoted by aromatics, but also by quaternary carbon, so either one can be used to increase the sooting tendency of a fuel. In that sense, matching the structural groups is very desirable, but not essential as long as the properties are matched.

The general methodology to define the surrogate composition is sketched in Figure 4. A set of properties that have to be matched is defined as a first step. These properties are as follows: cetane number, oxygen content, H/C ratio, functional groups, and the existence of carbon-carbon double bonds in the molecules. Subsequently, a set of suitable surrogate components is chosen (see section “Chemical reaction mechanism”). The cetane number is chosen as a measure for the self-ignitability of the fuels. Cetane numbers of the individual components are taken from the literature, while the other properties can be taken directly from the fuels’ molecular structures. Oxygen content and H/C ratio reflect adiabatic flame temperature and heat of combustion. In addition, the oxygen content of a fuel has a considerable impact on stoichiometry and soot formation. The cetane ratings of the surrogates are approximated by a linear interpolation of the cetane numbers of the individual components. Different properties of the components allow to fine tune the resulting surrogate properties (compare Table 4). Here, both *n*-heptane and DME have considerable low temperature

Figure 4. Flowchart showing the steps for the definition of the surrogate composition.

H/C: hydrogen/carbon; CN: cetane number.

Table 4. Properties of experimental fuels and surrogate components.

Fuel	Cetane number	Oxygen (wt%)	H/C ratio (molar)	Functional group	C–C double bonds
2-MTHF	19.8	18.6	2.0	CH ₃	No
2-MTHF/DnBE blend	36.1	16.1	2.1	CH ₃ , ether	No
<i>n</i> -Heptane	52.5	–	2.29	CH ₃	No
DME	56	34.8	2.5	CH ₃ , ether	No
Ethanol	10	34.8	2.5	OH	No
Toluene	9	–	1.14	CH ₃	Yes
Ethane	0	–	3	CH ₃	No
Phenol	5	17.0	1.0	OH	Yes

H/C: hydrogen/carbon; 2-MTHF: 2-methyltetrahydrofuran; DnBE: di-*n*-butylether; DME: dimethylether.

Table 5. Properties of experimental fuels and fuel surrogates.

	2-MTHF	Surrogate	70% 2-MTHF + 30% DnBE	Surrogate
Compound formula (wt%)	C ₅ H ₁₀ O	26% <i>n</i> -Heptane 8% DME 30% Ethanol 6% Ethane 30% Phenol	73.5% C ₅ H ₁₀ O 26.5% C ₈ H ₁₈ O	23.5% <i>n</i> -Heptane 33% DME 13.5% Ethanol 30% Toluene
H/C ratio	2.0	2.1	2.1	2.1
Oxygen content (wt%)	18.6	18.3	16.2	16.2
Cetane number	19.8	19.8	36.1	36.1

2-MTHF: 2-methyltetrahydrofuran; DnBE: di-*n*-butylether; DME: dimethylether; H/C: hydrogen/carbon.

reactivity, contain methyl (CH₃) groups, and no C–C double bonds. DME and ethanol have a high oxygen content while their H/C ratio is rather high. Ethanol has the additional alcohol (OH) functional group. Ethane has no double bonds, low ignitability, and a methyl group, but high H/C ratio. Phenol contains oxygen and has a low H/C ratio. Toluene and phenol help to reduce the H/C ratio of the mixture, but add C–C double bonds.

For the 2-MTHF surrogate, DME, ethanol, and phenol are used to set the oxygen content. To keep the cetane number of the mixture in the desired range, the amount of DME has to be limited, despite its favorable properties regarding methyl group and C–C bonds. Finally, *n*-heptane and a small amount of ethane are used to fine tune the low temperature reactivity of the surrogate mixture. For the 2-MTHF/DnBE blend surrogate, DME and ethanol are used to match the oxygen content. Here, a higher portion of DME can be used due to the higher cetane number of the experimental fuel. Also with regard to the ether functional group, DME fits the DnBE content of the blend very well. Toluene is used to keep H/C ratio and cetane number at the desired level. A drawback of toluene is the C–C double bonds in the molecule, while the methyl group corresponds to the methyl group of the experimental fuel. *n*-Heptane is also employed, adding low temperature reactivity.

First setting oxygen content, H/C ratio, and cetane rating, and then minimizing unwanted additional properties (functional group and C–C double bonds) yield

the surrogate mixtures, as presented in Table 5. Due to the fact that the oxygen content and cetane rating of the 2-MTHF/DnBE blend are easier to match, the methodology works better for the blend surrogate. Here, more freedom is left to optimize the additional properties. However, for both surrogates, a rather high aromatic content, OH groups, and C–C double bonds are present in contrast to the experimental fuels. Here, new surrogate components, better suited to the furanic structure of 2-MTHF, are desirable.

The surrogate approach renders combustion simulations of fuels with only roughly known reaction chemistry possible. Due to the use of verified chemical reaction schemes, kinetic information is retained in the approach, and ignition, combustion, and pollutant formation can be modeled with good accuracy, as will be shown in section “Results and discussion.”

Ignition delay time validation for 2-MTHF surrogate. On the left part of Figure 5, experimental ignition delay time measurements from Brassat et al.¹³ and Heufer et al.¹⁶ for 2-MTHF at stoichiometric air–fuel mixture and 20 bar pressure are compared to zero-dimensional ignition delay time calculations for the individual surrogate components, using the FlameMaster Code.⁴⁹ It is evident that none of the individual surrogate components matches the experimental behavior. In the right part of Figure 5, results from homogeneous reactor simulations for the 2-MTHF surrogate (see Table 5) are compared to the same experiments.

Figure 5. Ignition delay time over inverse of temperature at stoichiometric conditions and 20 bar. RCM experiments from Brassat et al.¹³ (red plus symbols) and shock tube experiments from Heufer et al.¹⁶ (green crosses) for 2-MTHF. Left part: ignition delay time for surrogate components compared to 2-MTHF measurements. Right part: results from 2-MTHF surrogate (blue, dotted line). 2-MTHF: 2-methyltetrahydrofuran; DME: dimethylether; RCM: rapid compression machine.

Figure 6. Pressure traces (left scale) and HRRs (right scale) for 2-MTHF. Load points 3 (left) and 4 (right) from engine experiment (red, solid line) and simulation (blue, dashed line). CA: crank angle; HRR: heat release rate.

The calculated ignition delay times at high and intermediate temperatures (above 800 K) match the experimental results quite well. For the lower temperatures, the ignition delay times calculated from the surrogate are shorter and the slope is flatter than the slope from the rapid compression machine (RCM) experiments. However, for ignition delay times greater than 50 ms, heat losses become an increasingly relevant issue also for RCMs with creviced pistons,¹⁹ so the comparability of the RCM results at lower temperatures remains questionable. This example shows that by matching the specified fuel properties, the right balance of functional groups promoting chain branching and chain breaking was found, even if the surrogate composition does not exactly match the functional groups of the real fuel.

No ignition delay time measurements were available for the 2-MTHF/DnBE blend, limiting the assessment of the respective surrogate to the engine cases. Application of both surrogates to diesel engine simulations is discussed in the next section.

Results and discussion

Comparison of experimental and numerical results

Figure 6 compares the pressure traces and HRRs for 2-MTHF from the diesel engine experiments and the numerical results. As in the experiments and also the corresponding simulations, 2-MTHF did not ignite at the low load points 1 and 2, only the load points 3 and

Figure 7. Pressure traces (left scale) and HRRs (right scale) for the 2-MTHF/DnBE blend. Load points 1–4 (left to right, top to bottom) from engine experiment (red, solid line) and simulation (blue, dashed line). CA: crank angle; HRR: heat release rate.

4 (see Table 3) are shown. For both cases, ignition timing and peak pressure from experiment and simulation match well. The HRR following the ignition is clearly overpredicted for both cases, producing a too steep pressure gradient, compared to the rather smooth experimental pressure rise. The first stage ignition and the corresponding low-temperature heat release are slightly overestimated. This corresponds to the too fast low-temperature chemistry, observed in Figure 5.

Figure 7 compares the pressure traces and HRRs for the 2-MTHF/DnBE blend from the diesel engine experiments and the numerical results for the corresponding surrogate (see Table 5). In the experiment, 30% DnBE (by liquid volume) was blended to the 2-MTHF in order to enable stable operation in the low load points 1 and 2. Simulations using the surrogate match the ignition timings of the experiments at all load points. The prediction quality for peak pressures and burn rates is satisfying. For the lower load points 1 and 2, low-temperature heat release is distinctly overpredicted and the subsequent pressure rise is too steep, yielding too high peak pressure for load point 1. For the higher load points 3 and 4, peak HRRs are

overestimated, while ignition timing and peak pressures are matched with sufficient accuracy.

Assessment of pollutant formation

Figure 8 shows the emissions at EVO for load points 3 and 4 from operation with pure 2-MTHF from experiment and simulations. Regarding CO emissions, the simulations slightly overestimate the experimental results, while the trend is clearly reproduced. NO_x emissions are distinctly underestimated by the surrogate, and emissions of unburned HCs are strongly overestimated. The general trend is captured for NO_x as well as HC emissions.

Figure 9 depicts the emissions from operation with the 2-MTHF/DnBE blend and from the corresponding simulations. Again, CO emissions are slightly overpredicted, while the trend is reproduced across all load points. For NO_x, the trend is captured from load points 2 to 4, with slightly underpredicted values. However, for load point 1, simulated NO_x emissions are too high, inverting the experimentally observed trend. The deficiency in NO_x prediction may be attributed to the too

Figure 8. CO (left), NO_x (middle), and HC (right) emissions from experiment (red) and simulation (blue) for 2-MTHF. Load points 3 and 4.

CO: carbon monoxide; NO_x: nitrogen oxides; HC: hydrocarbon.

strong first stage heat release and overpredicted peak pressure for load point 1 (compare upper left of Figure 7), which leads to overpredicted peak temperatures and thus overestimated NO_x emissions. HC emissions are overpredicted, while the general trend of decreasing HC emissions with increasing load is reproduced.

Flame structure and fuel effects

In the following, the flamelet solution is analyzed with regard to pollutant formation pathways and the differences between the two fuels and the respective load points. As described above, the chemistry is solved in flamelet space. In the flamelet, a mixture fraction value of $Z = 0$ corresponds to pure oxidizer, while a value of $Z = 1$ corresponds to pure fuel. The mixture fraction can be seen as a normalized equivalence ratio, ranging from 0 to 1. The stoichiometric mixture fraction Z_{st} depends not only on the fuel but also on the oxygen concentration of the oxidizer and thus on the EGR rate. The individual values for Z_{st} are given in the captions of the respective figures below. The species mass

fractions for each CFD cell are obtained by the integration of a β -PDF,³¹ scaled by the mean and the variance of the mixture fraction in the cell.

Figures 10–15 show the CO mass fraction, the NO_x mass fraction (scaled by a factor of 100 to fit the axis), and the mass-weighted PDF of the mixture fraction for the whole CFD domain for the different fuels and load points. For better analysis of the graphs, only the range from $Z = 0$ to $Z = 0.1$ is shown, while computations included the whole range from 0 to 1.

The left sides of Figures 10–15 show the flamelet profiles just after the main pressure rise (compare Figures 6 and 7), while the right sides show the profiles at EVO. In Figure 10, the flamelet solution profiles for the 2-MTHF surrogate at the third load point are presented. In the left part of Figure 10, the PDF shows a range of mixture fraction from 0 to 0.1, indicating a stratified mixture, and a peak at $Z = 0$, which indicates the presence of pure, unmixed oxidizer in the cylinder. As expected, the CO mass fraction sharply rises in the rich region (right of Z_{st}). Another CO peak is observed at very lean conditions ($Z = 0.025$), indicating yet

Figure 9. CO (left), NO_x (middle), and HC (right) emissions from experiment (red) and simulation (blue) for the 2-MTHF/DnBE blend. Load points 1–4.

CO: carbon monoxide; NO_x: nitrogen oxides; HC: hydrocarbon.

Figure 10. Flamelet solution profile for 2-MTHF for load point 3. PDF (red, solid line), NO_x mass fraction (blue, dashed line), and CO mass fraction (black, dotted line). Left side: at 10° CA after TDC; right side: at 120° CA after TDC. Stoichiometric mixture fraction is $Z_{st} = 0.054$.

PDF: probability density function; NO_x: nitrogen oxides; CO: carbon monoxide.

Figure 11. Flamelet solution profile for 2-MTHF for load point 4. PDF (red, solid line), NO_x mass fraction (blue, dashed line), and CO mass fraction (black, dotted line). Left side: at 14° CA after TDC; right side: at 120° CA after TDC. Stoichiometric mixture fraction (green, dashed-dotted line) is $Z_{st} = 0.054$.

PDF: probability density function; NO_x : nitrogen oxides; CO: carbon monoxide.

Figure 12. Flamelet solution profile for 2-MTHF/DnBE blend for load point 1. PDF (red, solid line), NO_x mass fraction (blue, dashed line), and CO mass fraction (black, dotted line). Left side: at 10° CA after TDC; right side: at 120° CA after TDC. Stoichiometric mixture fraction (green, dashed-dotted line) is $Z_{st} = 0.062$.

PDF: probability density function; NO_x : nitrogen oxides; CO: carbon monoxide.

unburned lean and presumably cold mixture. Between $Z \approx 0.03$ and Z_{st} , the flamelet is fully ignited, and thus, only minor CO concentrations are left here. The NO_x mass fraction is highest close to Z_{st} , with a distinct decay toward the rich and the lean side. At the $Z = 0$ boundary condition, small mass fractions of CO and NO_x are present, reflecting the EGR in the oxidizer stream. At EVO (right part of Figure 10), the mixture has homogenized substantially, as indicated by the sharper, less distributed shape of the PDF. The NO_x profile has flattened due to diffusive and reburn effects. The majority of the engine-out CO emissions originates from very lean mixtures, as indicated by the overlap of the CO profile and the PDF between $Z = 0$ and $Z \approx 0.025$. The CO from close to stoichiometric mixture

contributes only to a negligible fraction of the total CO emissions. These observations correspond to the results of Musculus et al.,⁵⁰ where it was shown experimentally that unburned HC emissions in a low-temperature combustion diesel engine originated from very lean regions, where the reaction rates are too low to complete combustion.

In Figure 11, the flamelet solution profiles for the 2-MTHF surrogate at the fourth load point are presented. The general evolution of the CO profile is quite similar to Figure 10. The shape of the PDF indicates more mixing prior to combustion and a more homogeneous mixture at EVO. The mean of the PDF at EVO is shifted to higher values of Z , yielding less overlap of PDF and CO profile and stronger overlap of PDF and

Figure 13. Flamelet solution profile for 2-MTHF/DnBE blend for load point 2. PDF (red, solid line), NO_x mass fraction (blue, dashed line), and CO mass fraction (black, dotted line). Left side: at 5° CA after TDC; right side: at 120° CA after TDC. Stoichiometric mixture fraction (green, dashed-dotted line) is $Z_{st} = 0.054$. PDF: probability density function; NO_x : nitrogen oxides; CO: carbon monoxide.

Figure 14. Flamelet solution profile for 2-MTHF/DnBE blend for load point 3. PDF (red, solid line), NO_x mass fraction (blue, dashed line), and CO mass fraction (black, dotted line). Left side: at 8° CA after TDC; right side: at 120° CA after TDC. Stoichiometric mixture fraction (green, dashed-dotted line) is $Z_{st} = 0.058$. PDF: probability density function; NO_x : nitrogen oxides; CO: carbon monoxide.

NO_x profile. This corresponds to the trends of lower CO and higher NO_x emissions with increasing load, as observed in Figure 8. In addition, the CO mass fraction at very lean mixtures is slightly smaller while more NO_x is present in the flamelet solution, which might be explained by the higher load and thus higher combustion temperatures.

In Figures 12–15, flamelet solution profiles for the 2-MTHF/DnBE blend for load points 1–4 are presented. For the first load point (Figure 12), high peaks of CO and NO_x are present in the flamelet solution after ignition. At EVO, most of the CO is burned, but, similar to the cases before, a substantial amount of CO remains at the lean side. The PDF overlaps with this

lean CO peak, leading to the high CO emissions observed for this load (compare left part of Figure 9). The rather high NO_x mass fraction in the flamelet at EVO corresponds to the overestimated engine-out NO_x emissions (compare right part of Figure 9). The significantly different NO_x profiles from Figures 12 and 13 are attributed to the higher inlet oxygen concentration for load point 1 (compare Table 3) and also to the overestimated first-stage heat release and subsequently overpredicted peak pressure (compare upper left of Figure 7), which leads to overpredicted peak temperatures and thus overestimated NO_x emissions. For the second load point (Figure 13), the CO profile evolves very similar to load point 1. Due to the different means

Figure 15. Flamelet solution profile for 2-MTHF/DnBE blend for load point 4. PDF (red, solid line), NO_x mass fraction (blue, dashed line), and CO mass fraction (black, dotted line). Left side: at 5° CA after TDC; right side: at 120° CA after TDC. Stoichiometric mixture fraction (green, dashed-dotted line) is $Z_{st} = 0.058$. PDF: probability density function; NO_x : nitrogen oxides; CO: carbon monoxide.

of the PDF at EVO (right part of Figure 13) and the resulting smaller overlap of CO profile and PDF, the engine-out CO emissions are distinctly lower, compared to load point 1. The NO_x mass fraction in the flamelet is distinctly lower, yielding lower engine-out NO_x emissions despite the stronger overlap of NO_x profile and PDF.

In the context of Figures 14 and 15, especially the comparison to Figures 10 and 11 is of interest, as it shows the influence of the fuel on flame structure and emissions. In Figure 14, the PDF indicates less premixing prior to combustion than for the same load point with pure 2-MTHF (Figure 10). Due to stronger mixing during combustion, less CO from very lean regions is present at EVO in Figure 10. This leads to distinctly lowered engine-out emissions despite the similar PDF. The NO_x mass fraction is slightly higher, probably due to the higher inlet oxygen concentration (see Table 3). In Figure 15, the PDF again indicates less premixing prior to combustion than for the same load point with pure 2-MTHF (Figure 11). The lowered CO emissions can be attributed to more mixing during and after combustion, almost completely eliminating the lean CO at EVO. Again, the NO_x emissions are slightly higher.

In summary, the flamelet solution profiles indicate a substantial contribution of very lean regions to the CO emissions for all load points. For the 2-MTHF/DnBE blend, the mixture is less homogeneous at ignition, which leads to less overleaning and thus lower CO emissions than for operation with pure 2-MTHF. This corresponds to the difference in the cetane rating of the fuels (see Table 5). Differences in NO_x emissions are attributed mainly to load and inlet oxygen concentration. However, due to the low sooting propensity of the experimental fuels, high EGR rates can be employed, keeping NO_x emissions within Euro 6 regulation limits.¹⁻⁴

Conclusion

A surrogate approach to describe the combustion chemistry of novel biofuels in a diesel engine has been described and tested. The surrogate fuels have been compiled according to cetane number, oxygen content, H/C ratio, and molecular properties of the biofuels. Ignition delay time calculations and diesel engine simulations, both using detailed reaction chemistry of a surrogate fuel, have been compared to the respective experiments for 2-MTHF. The ignition delay time calculations confirmed the applicability of the surrogate approach. The assessment of the surrogate for a 2-MTHF/DnBE blend was limited to engine simulations, as no ignition delay time measurements were available.

For the engine simulations, good results regarding pressure traces and pollutant emissions were obtained. HRRs, however, were distinctly overestimated by the surrogates, showing the limitations of the approach. Nevertheless, the comparison to diesel engine experiments confirmed the proposed approach and the methodology to define the surrogate composition and allowed for insight into the pollutant formation processes in the engine. The increased cetane rating of the blended fuel proved to be beneficial in terms of CO emissions, minimizing over-leaned, noncombustible mixture.

Declaration of conflicting interest

The authors declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

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