

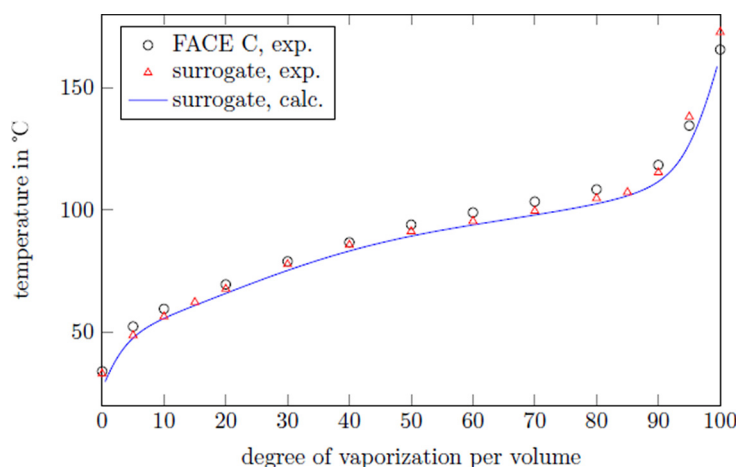


Full Length Article

Surrogate generation and evaluation of gasolines

Tobias Grubinger^a, Georg Lenk^b, Nikolai Schubert^b, Thomas Wallek^{a,*}^a Institute of Chemical Engineering and Environmental Technology, NAWI Graz, Graz University of Technology, Graz, Austria^b OMV Refining & Marketing GmbH, Vienna, Austria

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ABSTRACT

Fuel surrogates are substitute mixtures that are developed to reproduce real fuels' physical and chemical properties. These mixtures are created with a small number of components, considering their application in various types of simulations and for bench tests. In the present paper, new gasoline surrogates are proposed by extending and applying an algorithm which was previously developed and successfully used to create diesel surrogates. The five target properties chosen for surrogate optimization include the true boiling point curve (TBP), the research octane number (RON), the liquid density, the carbon-to-hydrogen (C/H) ratio and the oxygenate content. The algorithm is applied to three target fuels, comprising two reference fuels from the FACE working group and one typical oxygenated gasoline that is commercially available in Europe. The proposed surrogates consist of six chemical components which are also represented in reaction kinetics for fuel combustion. An experimental comparison of the boiling point curves, densities and RONs among the surrogates and their respective target fuels provided evidence that the proposed surrogates excellently reproduce the real fuels' properties.

1. Fuel characterization by surrogates

Combustion engines have been improved over decades. In order to

continue this successful trend, modern engine development processes include combustion and emissions simulations, which have grown increasingly important in recent years. These simulation results serve as

* Corresponding author.

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Nomenclature

$A_{1,i} + A_{2,i}$	differential areas of the true boiling point (TBP) curve
C_i	number of carbon atoms of component i
CH	mass-based carbon-to-hydrogen ratio in the objective function
$F(w_i)$	objective function for surrogate optimization
H_i	number of hydrogen atoms of component i
M_i	molar mass of component i
RON_{mix}	research octane number of the mixture
RON_i	pure component research octane number of component i
ρ_{mix}	mixture density at 15 °C
ρ_i	liquid density of component i at 15 °C
v_i	volume fraction of component i
$v_{NBP,i}$	molar volume of component i at the normal boiling point
VO	volume fraction of oxygenates in the objective function
w_i	mass fraction of component i
w_C, w_H, w_O	mass fractions of carbon, hydrogen and oxygen, respectively
x	degree of vaporization by volume
$x_{l,i}$	lower degree of vaporization of component i
$x_{u,i}$	upper degree of vaporization of component i

Abbreviations

AAD	absolute average deviation
AKI	anti-knock-index

BRON	blending research octane number
CAS	chemical abstracts service
CFD	computational fluid dynamics
CFR	cooperative fuel research
C/H	carbon-to-hydrogen ratio
CSA	component selection algorithm
EtOH	ethanol
FBP	final boiling point
GDI	gasoline direct injection
HHV	higher heating value
IBP	initial boiling point
ID	ignition delay
LC ₅₀	lethal concentration measure
LHV	lower heating value
MON	motor octane number
NBP	normal boiling point
PIONA	<i>n</i> -paraffins, <i>iso</i> -paraffins, <i>olefins</i> , <i>naphthenes</i> , and <i>aromatics</i>
PRF	primary reference fuel
RON	research octane number
RVP	Reid vapor pressure
SA	simulated annealing
SD	simulated distillation
TBP	true boiling point curve
TEL	<i>tetra</i> -ethyl lead

the basis for meeting the increasingly strict requirements concerning pollutants and CO₂ emissions. Since modern gasolines tend to contain oxygenates (e.g., alcohols or ethers) as additives, partly for the same reason, their impact on a fuel's combustion behavior is of great interest to engine developers. However, a detailed simulation of combustion reactions, considering all components occurring in real fuels, is not feasible, due to the immense computational efforts required, partly limited reaction mechanisms, and limited availability of physical property data for many of these chemical components [1,2]. It should nevertheless be noted that there has been substantial progress on optimizing simulation techniques over the last decade, in particular concerning the handling of large kinetic mechanisms based on advances in applied mathematics and algorithm design [3].

As an alternative, surrogates, that consist of only a few chemical components, can efficiently be used for simulations and be applied on test stands for related experimental investigations.

As surrogates are designed, the chemical compositions of such surrogates are chosen in such a way as to mimic selected key properties of the respective target fuels. Some of these key properties, like the distillation characteristics, densities, or octane ratings are specified by relevant standards [4,5], while others which are of high importance for engine developers, are not standardized, particularly the heating value, the C/H ratio, or the viscosity. Modeling a wide variety of fuel properties is becoming steadily more difficult. For one thing, there is a general lack of suitable components for the surrogate. Furthermore, the inclusion of too many components in the surrogate may lead to mathematical conflicts among the selected target properties, since every component contributes one variable to the target function of the optimization algorithm. Hence, an acceptable compromise needs to be found by choosing the most appropriate set of target properties. Once target properties have been chosen, an algorithm is designed to optimize the composition of fuel constituents by varying this composition in such a way that an objective function, accounting for deviations between given and calculated fuel properties that depend on composition, is minimized.

Over the past two decades, various approaches have been taken to

generate and optimize surrogates for gasolines.

Using a database of nine components, containing *n*-alkanes, *iso*-alkanes and aromatics as well as ethanol to cover the distillation range of gasoline, Greenfield [6] proposed to make surrogates comprising seven to eight components. In his work he used the distillation characteristics as the only fitted target property, which was based on an ASTM D86 [7] distillation curve model [8].

Mehl et al. [9] described the chemical properties of a real non-oxygenated fuel under different operating conditions by reproducing the ignition delay times and flame speeds with a surrogate of four components. However, a significant reduction in the applied reaction mechanism was necessary.

Focusing on auto-ignition modeling in engines, Pera et al. [10] proposed a three-component surrogate, using the C/H ratio, O/C ratio, molecular mass, RON and compound motor octane number (MON) as target properties to optimize the surrogate composition. The components were selected from among six components with well-known chemical kinetics. In addition to the target properties, the gasoline density, lower heating value (LHV) and distribution of molecular groups could be closely reproduced by the resulting surrogate.

Samimi Abianeh et al. [11] proposed using an iterative methodology to generate surrogates which was based on an analysis of a batch distillation and required the same number of surrogate components as the number of available points on the distillation curve. The methodology was applied to generate two three-component surrogates for gasoline. To perform combustion modeling of gasoline direct injection (GDI) engines, the latter approach was further developed [12] to create a seven-component surrogate, which successfully reproduced properties of non-oxygenated research grade gasoline RD387, supplied by Chevron-Phillips, in terms of its C/H ratio, RON, MON, LHV, density, molecular structures and distillation characteristics. The proposed algorithm distinguishes between primary targets (C/H ratio, RON, MON, density, LHV and distillation curve) which are consistently predictable without an investment of high computational effort, and a secondary target (i.e., the ignition delay), which requires considerably more computation effort due to the application of kinetic mechanisms.

By using combustion simulations simultaneously while optimizing an objective function, Ahmed et al. [13] formulated surrogates containing six components to meet RON, C/H ratio, density, molecular structures and distillation characteristics of selected FACE [14] gasolines. In this context, the RON was calculated by correlating it with the ignition delay time and the distillation characteristics using the simulation tool REFPROP [15]. While most of the target properties were reproduced properly, the distillation curves were reproduced with only limited accuracy.

Targeting numerical modeling of spray evaporation in GDI engines, Su et al. [16] developed a six-component surrogate using an inverse batch distillation model, which was applied to estimate droplet evaporation rates comparable to those of fuel sprays. While the distillation curve of the surrogate was in good agreement with that of the real fuel, the predicted RON (which was not chosen as a target property) showed considerable deviations, implying that the proposed surrogate would be of limited usability when describing ignition characteristics.

Focusing on chemical kinetic modeling, Sarathy et al. [17] proposed surrogates with seven and eight components using an objective function containing RON, MON, the PIONA matrix (*n*-paraffins, *iso*-paraffins, olefins, naphthenes and aromatics), C/H ratio, average molecular weight, density and distillation characteristics. While RON and MON were estimated by applying a linear mixing model, the distillation curves were calculated using the simulation tool REFPROP [15]. Although most of the target properties could be reproduced satisfactorily, the distillation curves of the surrogates showed significant deviations from those of the real fuels.

Recently, Zhang et al. [18] proposed a six-component gasoline surrogate using an objective function comprising the Reid vapor pressure (RVP), the higher heating value (HHV), density, viscosity, and the lethal LC₅₀ concentration. Furthermore, two additives from a comprehensive list were added to the surrogate to match the properties more precisely.

In this paper, an algorithm which was previously developed and successfully used for the generation of diesel surrogates [2,19] is extended and applied to optimizing gasoline surrogates. It is structured as follows: First, criteria for selection of surrogate components are developed. Second, the choice of the target properties is discussed, including an explanation of the modeling approaches used for both target properties and derived properties. Finally, surrogates for three different target fuels are proposed and verified by experimental results. Conclusions are drawn that indicate how the algorithm can be further developed.

2. Algorithm for surrogate optimization

2.1. Selection of components

A database with potential component candidates for gasoline was established to allow for component selection for each target fuel. This database comprises 40 typical components that are found in gasoline, including ethanol as a representative oxygenate (see [Supplementary Material \(Table 1\)](#)). However, the number of components actually used for optimization was further reduced, based on the following considerations:

First, the final boiling point (FBP) of gasoline is limited to 210 °C in EU standards and to 225 °C in U.S. standards, while its initial boiling point (IBP) can be lower than 0 °C. At least this span should be covered by the provided components to reproduce a distillation curve completely.

Second, the number of component candidates was further reduced as they lack physical property data required for the algorithm. In particular, critical data, acentric factors, Antoine saturation pressure parameters and research octane numbers for components with a boiling point close to the FBP were lacking for certain components.

Third, in view of the application of surrogates for combustion

simulations, the available components needed to be part of a suitable multi-component mechanism for reaction kinetics. Only few mechanisms cover more than five components as a result of increasing complexity [20], which further restricted the number of database components. By taking a simplified approach, it is possible to ensure a chemically acceptable representation while covering significantly more components. Ra and Reitz [1] demonstrated this with their reduced mechanism containing 43 components. With regard to the applied component selection algorithm (CSA), a comprehensive mechanism is desirable. For this reason, it was decided to only use components which were also considered by the Ra and Reitz reaction kinetics mechanism. However, an evaluation of the proposed surrogates regarding the combustion simulations using this mechanism does not fall within the scope of this paper.

Finally, taking the above arguments into account, the 18 database components shown in [Table 1](#) remained and were used as component pool for surrogate optimization in this work.

2.2. Selection of target properties

With regard to surrogate formulation, the significant gasoline properties include the distillation characteristics (boiling curve), density, octane rating, molecular structures distribution and oxygenate content.

Distillation characteristics are undeniably key properties which have been modeled in many comparable works [11–13,6,16,21,22]. Their major impact on fuel vaporization and spray combustion behavior [12,16] makes it necessary to reproduce the distillation characteristic for efficient engine development through computational fluid dynamics (CFD) simulations. Describing the boiling behavior of fuels can be achieved by applying different standardized analytical methods. Distillation analysis, according to ASTM D86 (equivalent to EN ISO 3405), is a popular method and predominantly used for gasoline. The separation process is carried out in a simple distillation flask, which makes this method rapidly available. However, this leads to a limited separation of the mixture [23]. Hence, the approach used to describe the distillation characteristics of real fuels requires the use of analytical methods which offer more accurate separation, in order to obtain distillation data which reflect the actual boiling points of the included components. This can be accomplished by carrying out a true boiling point (TBP) or simulated distillation (SD) analysis. Both methods differ only marginally from each other [23]. While TBP curves can be related to both distilled volume or mass, an SD curve is always related to the evaporated mass, and a D86 curve is always related to the evaporated volume.

The density of European gasoline is specified in EN 228, ranging from 720 kg/m³ to 775 kg/m³ at 15 °C. Its effect on viscosity and spray formulation makes it an important property that is considered in this work.

Another crucial property of gasoline is its ignition quality, which is determined through an experimental investigation of a fuel's knock propensity in cooperative fuel research (CFR) engines. A CFR engine is operated under different standardized conditions to obtain either the research octane number (RON) or the motor octane number (MON). Both RON and MON are considered within the EU gasoline standard EN

Table 1
Pool of basic components used for surrogate optimization in this work.

Substance group	Components
<i>n</i> -alkanes	butane, pentane, hexane, heptane
<i>iso</i> -alkanes	pentane, octane
alkenes	1-pentene, 1-hexene
cycloalkanes	cyclohexane, methylcyclohexane, <i>cis</i> -decalin, <i>trans</i> -decalin
aromatics	benzene, toluene, tetralin, <i>m</i> -xylene, pentylbenzene
oxygenates	ethanol

228, while RON is the most widely used octane rating worldwide [13]. Therefore, in this work, RON was chosen as a chemical target property to account for combustion quality. Several studies [13,9,24,25] have been conducted to determine the octane rating of a surrogate by running simulations of ignition delay (ID) times, referring to correlations between ID and RON. Clearly, this procedure leads to a significantly higher investment of computational effort than is required with equation-based predictions, particularly considering the high number of optimizations caused by CSA. Although this procedure has less informative value compared to other simulative methods, RON was predicted in this work by applying a simple mixing rule, as explained later.

To reflect the distribution of molecular structures in a generic way, the C/H ratio was considered as another essential target property, which is underpinned by the findings of various studies [13,12,9,21,10,22,26]. It is recommended to take the C/H ratio into account due to its close relation with other properties like the heating value and density [10]. Mehl et al. [9] pointed out its effect on flame propagation and temperature, and Ahmed et al. [13] mentioned the C/H ratio as one decisive factor that could be used to reproduce combustion characteristics of real gasoline. It should nevertheless be noted that, on a molecular level, there can be substantial differences in the reaction kinetics between substances of the same C/H ratio, as has been shown in ignition delay time experiments for *n*-octane and 2,5-dimethylhexane, for example [27].

Finally, since the maximum oxygenate content of gasoline is specified in the EU [4] and U.S. [5] standards, it is reasonable to add the content of oxygenates as an additional target property. Oxygenates have become promising blend components due to their positive influence on combustion behavior (i.e., they reduce knocking and emissions [28–35]). When produced from biomass, oxygenates can also help reduce overall greenhouse gas emissions, allowing combustion engines to display lower CO₂ emission profiles.

Reliable viscosity data for gasolines are rarely available because, at a typical viscosity measurement temperature of 20 °C, its lighter components will already have begun to vaporize. Furthermore, as mentioned earlier, viscosity is not specified in the EU and U.S. standards, which also contributes to the fact that viscosity has rarely been chosen as a target property in similar studies. In contrast, the lower heating value (LHV) has been chosen more often as a target property. The LHV is normally predicted by the elemental composition of the surrogate, which is, in case of hydrocarbons, strongly affected by the C/H ratio. This could result in mathematical conflicts when both the C/H ratio and LHV are simultaneously chosen as target properties. Consequently, in this paper, neither the viscosity nor the LHV were considered for optimization.

In conclusion, the five target properties chosen for surrogate optimization in this work include the true boiling point curve (TBP), liquid density, research octane number (RON), carbon-to-hydrogen (C/H) ratio and oxygenate content. A limiting aspect of this choice is that these properties merely represent bulk characteristics rather than detailed molecular information. Consequently, restrictions on the distinctness of molecular characteristics are to be expected, in particular concerning differences in the reaction kinetics of the substances involved.

2.3. Modeling the chosen target properties

TBP Curve The TBP distillation curve was modeled by applying the stepwise approximation method presented by Reiter et al. [2]. This curve fitting approach is illustrated in Fig. 3 of their work. It is applicable using a mass-based or volume-based degree of vaporization, which is generally expressed as x . However, TBP or SD distillation data are usually available for middle distillates like diesel and kerosene but only rarely for gasoline. Although SD data can be gained for gasoline according to ASTM D3710, gasoline distillation data are primarily measured according to ASTM D86. A conversion of available D86 data

to TBP curves was performed in advance using a method published by Daubert [36] because, as mentioned earlier, a D86 distillation curve is not suitable for the above mentioned fitting approach. Because a D86 curve is strictly volume-based, the TBP data obtained with this method are volume-based as well. Consequently, the difference between the upper degree of vaporization, $x_{u,i}$, and lower degree of vaporization, $x_{l,i}$ of a component i is equal to its volume fraction, v_i . Taking into consideration the fact that the algorithm is based on mass fractions, w_i , a mathematical correlation is needed that takes the temperature dependency of v_i into account. This was implemented by the following equation, providing the molar volume at the normal boiling point, $v_{NBP,i}$, and the molar mass, M_i , for each component i :

$$v_i = \frac{w_i \cdot v_{NBP,i} \cdot \frac{1}{M_i}}{\sum_{i=1}^n w_i \cdot v_{NBP,i} \cdot \frac{1}{M_i}} \quad (1)$$

In order to provide an algebraic function for the algorithm, the TBP data were approximated by a least-squares fit based on a sixth-degree polynomial function, $TBP(x)$, where x represents the degree of vaporization by volume. **Liquid density** The mixture density at 15 °C was calculated by applying the following ideal mixing model, which was also used by Reiter et al. [2]:

$$\rho_{mix} = \left(\sum_{i=1}^n \frac{w_i}{\rho_i} \right)^{-1} \quad (2)$$

where w_i represents the mass fraction of component i and ρ_i its liquid density at 15 °C. With eq (2), Reiter et al. obtained an excellent agreement between their experimental data and data for diesel fuel. The linear mixing rule was also successfully applied to predict the density of gasoline in several other works [13,18,37]. **C/H ratio** The mixture C/H ratio was calculated based on its atomic mass according to the following equation, where w_i represents the mass fraction and C_i and H_i the numbers of carbon and hydrogen atoms of component i , respectively:

$$C/H = \frac{\sum_{i=1}^n w_i \cdot C_i}{\sum_{i=1}^n w_i \cdot H_i} \quad (3)$$

As the molecular structures of the considered components are known, eq (3) can be applied directly. **Research octane number (RON)** Interactions between components and their intermediates, which occur during the oxidation process, make it difficult to predict the octane numbers of mixtures precisely [10]. Ghosh et al. [38] developed a non-linear model for the computation of mixture octane numbers, which can be used to consider interactions between molecular groups and predict the MONs and RONs of mixtures with a standard error of about 1. However, the model's crucial parameters were not published in detail, which limits its application.

The most generic way to describe mixture octane numbers is by forming a linear combination of pure component octane numbers, RON_i , weighted either by volume fractions, mass fractions, or molar fractions. Despite their simplicity, recent studies have obtained satisfactory results by using volume-based linear mixing models to predict the cetane number of diesel [2,19] and kerosene [37] surrogates, which is why a linear approach using volume fractions, v_i , was also used in this work to predict RONs of a mixture:

$$RON_{mix} = \sum_{i=1}^n v_i \cdot RON_i \quad (4)$$

Apart from potential inaccuracies caused by the linear mixing rule, inaccuracies in pure component octane numbers, RON_i , are a particularly common source of errors. A comprehensive collection of RON_i ,

published in 1958, is provided by ASTM STP225, including 384 pure components [39]. Although more recent sources for RON_i are available, these can differ significantly for some components, as illustrated in Table 2. Furthermore, RON measurements of aromatics tend to be less accurate, which is caused by their combustion peculiarities as well as their generally high octane numbers [39].

A pure component RON greater than 100 can commonly be obtained by previously blending a primary reference fuel (PRF) with a RON of 60 at a ratio of 80:20 by volume with the pure component, whereas an octane rating is obtained by extrapolation of experimental data. The octane number resulting from this procedure is called the blending research octane number (BRON). Furthermore, a BRON represents a hypothetical value and is, therefore, not suitable for the prediction of RONs for mixtures [39]. As an alternative, octane numbers higher than 100 can be specified through the amount (milliliter) of *tetra*-ethyl lead (TEL) added to one U.S. gallon of pure *iso*-octane, whereby TEL acts as an octane booster. The desired RON can then be obtained from the added amount of TEL with the help of correlations [23]. Both procedures must be viewed as makeshift methods.

Due to unavailability of reliable octane ratings for components with boiling temperatures close to the FBP of usual gasolines, in this work, RON_i were estimated for *n*-pentylbenzene, *c*-decalin, *t*-decalin, *n*-hexylbenzene and tetralin. The method used for estimation was that proposed by Albahri [40]. Its absolute average deviation (AAD)¹ is stated as four for the prediction of research octane numbers (RONs). To provide a better overview, the pure component research octane numbers which were actually used are compiled in Table 2 of the Supplementary Material [39–44].

2.4. Modeling the derived properties

In addition to the fuel properties used in the target function, the following models were used to estimate derived fuel properties which were not considered in the target function for optimization. *D86 Curve* Since the TBP data used for fitting were generated by converting the measured D86 data, a comparison between the measured D86 curves of the real fuels and calculated D86 curves of the surrogates was necessary to ensure an appropriate validation of distillation characteristics. The model used for D86 calculation is based on a batch distillation model, originally developed by Greenfield et al. [8] and further refined by Reiter et al. [2] by considering heat conduction as well as radiation, while neglecting the solubility of air in the fuel. *Lower heating value (LHV)* The LHV in MJ/kg was calculated according to the approximation proposed by Boie [45], whereby only the mass fractions of carbon, w_C , hydrogen, w_H , and on a small scale also oxygen, w_O , were considered as relevant, as the gasoline surrogates only consist of hydrocarbons and oxygenates:

$$LHV = 34835 \cdot w_C + 93870 \cdot w_H + \dots - 10800 \cdot w_O. \quad (5)$$

It is thus apparent from eq (5) that the LHV is strongly affected by the C/H ratio, as mentioned earlier.

2.5. Determining the surrogate composition

The algorithm used for surrogate formulation is based on one published in a previous work by Reiter et al., who developed their approach for crude oil, fossil diesel, biodiesel and mixtures thereof [46,2,19]. The same TBP-curve fitting approach was used by Wu et al. [37] for the development of kerosene surrogates. The algorithm was implemented as a proprietary Fortran 2003 program, using the Simulated Annealing Method [47] in a Fortran implementation by Goffe et al. [48,49] to solve the optimization task.

¹ AAD = $\frac{1}{n} \sum_{i=1}^n |x_i - \bar{x}_i|$ where x_i stands for the experimental value and \bar{x}_i for the related calculated value when considering a number of n pairs of values.

Table 2

A selection of pure component research octane numbers (RONs) from various sources, to illustrate considerable scattering of literature values. The RONs actually used for optimization are compiled in Table 2 of the Supplementary Material.

Component	RON_i			
<i>n</i> -octane	−18 [39]	−19 [40]	0 [41]	−15 [38]
toluene	105.8 [23]	124 [39]	112 [41]	118 [38]
ethylbenzene	100.8 [23]	124 [39]	107 [41]	
propylbenzene	101.5 [23]	127 [39]	129 [41]	
<i>m</i> -xylene	104 [23]	145 [39]	124 [41]	
ethanol	125 [23]	109 [42]	108 [38]	

In the present paper, the following objective function for surrogate optimization was used:

$$F(w_i) = \left(\frac{\sum_{i=1}^n (A_{1,i} + A_{2,i})}{TBP_{ref}} \right)^2 + \left(\frac{\rho_{calc} - \rho_{exp}}{\rho_{ref}} \right)^2 + \left(\frac{RON_{calc} - RON_{exp}}{RON_{ref}} \right)^2 + \left(\frac{CH_{calc} - CH_{exp}}{CH_{ref}} \right)^2 + \left(\frac{VO_{calc} - VO_{exp}}{VO_{ref}} \right)^2 \quad (6)$$

This function includes the differential areas $A_{1,i} + A_{2,i}$ with regard to the true boiling point (TBP) curve, the liquid density at 15 °C, the research octane number (RON), the mass-based carbon-to-hydrogen (C/H) ratio and, when necessary, the volume fraction of oxygenates (VO). The denominators of this function act as weighting factors. The surrogate composition in terms of mass fractions, w_i , of the selected components is obtained by numerical minimization of eq (6) by applying the simulated annealing (SA) method [47,48].

Component selection is conducted by using an F-to-remove component selection algorithm (CSA). Starting with the components listed in Table 1, every single component is removed successively while optimizations are performed for the remaining components. Subsequently, the absent component which leads to the highest value of the objective function, is eliminated permanently during the remaining reduction process. This process is repeated until the desired number of surrogate components has been reached. It is obvious that considering a higher number of potential components, n_{comp} , will quickly result in a large number of optimizations, n_{opt} , as illustrated in Fig. 1. To ensure that a global minimum was found, every optimization was conducted several times, after varying initial starting values.

Concerning the desired number of surrogate components, recent studies [12,13,16,18] mostly use more than five components in order to achieve good agreements; particularly with an increasing number of target properties and a wider distillation range, this appears to be necessary. On the other hand, it is desirable to achieve a satisfactory fit of the target properties, while using as few components as possible. Eventually, using fewer components leads to a lower investment of mathematical effort in combustion simulations, depending on the mechanism used. Finally, the sample generation process needed to experimentally validate the developed surrogate becomes cheaper and less prone to errors, because pure hydrocarbons can be very expensive and often contain traces of other substances. Greenfield [6] indicates that fewer than ten components are sufficient to represent a complete distillation curve. Furthermore, Ra and Reitz [1] mention that previous studies described physical and chemical properties of gasoline with up to ten components.

For the reasons mentioned, all resulting fits that were computed

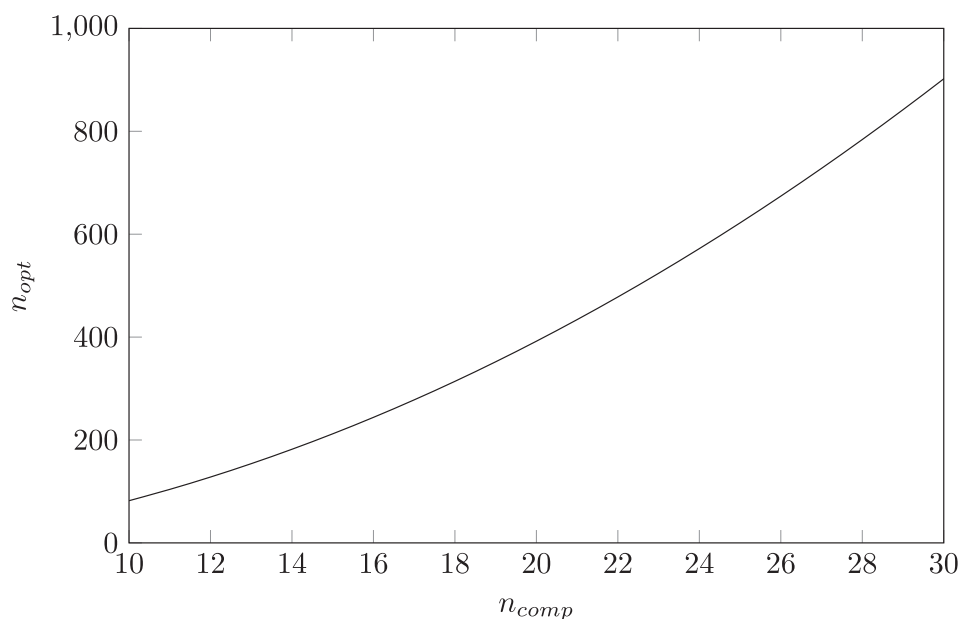


Fig. 1. Number of conducted optimizations, n_{opt} , in relation to the number of components provided to the CSA, n_{comp} .

with the F-to-remove procedure and comprised up to ten components were compared. In particular, six surrogates with five to ten components were then evaluated in detail for each target fuel. These evaluation results showed shortcomings of the surrogates in the region of the final boiling point, which can be explained by the fact that relatively few components in the component database have boiling points that are high enough to reproduce the FBP of gasoline. This deficiency could be overcome by the manual replacement of the component with the highest boiling point remaining by one of the previously removed components, which had an even higher boiling point, indicating that a combination of the component reduction algorithm with an inclusion procedure may give better results than the one-way reduction procedure used up until now. This could serve as a starting point for further improvement of the component selection algorithm.

3. Target fuels and resulting surrogates

Two non-oxygenated reference gasolines developed by the FACE working group [14] and one oxygenated gasoline from OMV Refining & Marketing GmbH with an ethanol content of 4.9 vol-% were chosen as target fuels. The latter represents a typical Eurosuper (E5) fuel, which is commercially available in Europe. The main characteristics of these fuels are summarized in Table 3. In addition, the distillation data according to ASTM D86 were available for these three target fuels, displayed later in Figs. 5–7.

The choice of these target fuels reflects some of the variety in the gasoline properties, as FACE C does not meet the density requirements of the European standard EN 228, and both FACE C and FACE H fuels are rated below the required RON of 91, specified in EN 228 for regular-grade gasoline. In the U.S., antiknock performance of gasoline is specified by the anti-knock-index (AKI), which is determined as mean value of RON and MON. Though it is not mandatory, the AKI of U.S. gasoline ranges from 85 to 94.

Using the component selection process described above and the component pool of Table 1, six surrogates with five to ten components were calculated for each target fuel. While the residuals for RON, density and C/H ratio turned out to be negligibly small for all surrogates, their average TBP-curve deviation ranged between 7.9 °C and 13.2 °C. Although TBP residuals basically decrease with an increasing number of components due to the stepwise approximation, it could not automatically be anticipated that the D86 residuals would behave

similarly. Consequently, the developed surrogates were examined more closely by comparing their calculated D86 distillation curves to experimental D86 data for the real fuels. As illustrated in Fig. 2, contrary to expectations, the D86 validation revealed a better performance for surrogates containing only six components.

Fig. 2 shows that all three target fuels were described best with six components. This result is remarkable because one would actually expect that, as more components are included, the TBP residuals would decrease due to the stepwise adjustment applied. However, this behavior can be attributed to the limited number of available component candidates in combination with the relatively flat shapes of the gasoline boiling curves in general, compared to those of middle distillates [19]. This conclusion was drawn from comparative surrogate optimizations carried out using an extended component database. This optimization used components regardless of whether they belonged to a reaction mechanism to cover a broader boiling range.

Since the differences among the residuals in terms of RON, density and C/H ratio were practically negligible, the D86 deviation was used as the deciding factor to choose the best surrogate for each fuel. Table 4 provides the calculated compositions of the ultimately proposed surrogates.

To perform a final validation of the algorithm and calculated D86 data, the three surrogates listed in Table 4 were investigated experimentally. The purities of the chemicals, which were purchased by Sigma-Aldrich, Carl Roth and Linde Gas GmbH, are listed in the Supplementary Material, Table 3. To prevent the evaporation of volatile

Table 3

Properties of target fuels along with EU (EN 228) and U.S. (ASTM D4814) standard specifications. FACE C and FACE H are research fuels, The OMV fuel, oxygenated with ethanol (EtOH), represents a typical Eurosuper (E5) fuel, which is commercially available in Europe.

Property	FACE C	FACE H	OMV + EtOH	EN 228	ASTM D4814
IBP (D86) [°C]	33.9	33.6	36.4	unspecified	unspecified
FBP (D86) [°C]	165.6	208.9	176.5	210	225
Density at 15 °C [kg/m ³]	691	759	750	720–775	unspecified
RON	84.3	86.9	96.5	91/95/98	(AKI 85–94)
C/H ratio	5.47	6.98	6.25	unspecified	unspecified
LHV [MJ/kg]	44.79	43.32	41.4	unspecified	unspecified

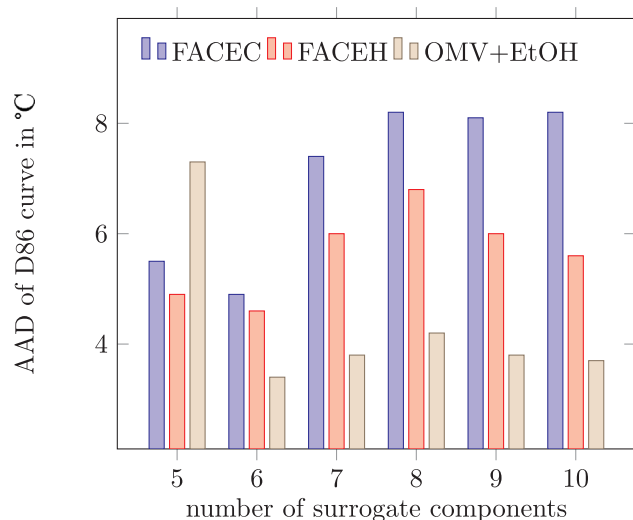


Fig. 2. Absolute average deviations (AAD) between target fuels and calculated surrogate distillation curves according to ASTM D86, depending on the number of surrogate components.

Table 4

Resulting compositions of the proposed surrogates in mass%. These components were chosen by the CSA based on the provided component pool of Table 1.

Component	FACE C	FACE H	OMV + EtOH
<i>n</i> -butane	3.86		
<i>iso</i> -pentane	12.99		27.08
1-pentene		11.20	
<i>n</i> -hexane	18.68	19.97	
ethanol			5.26
cyclohexane			18.01
<i>iso</i> -octane	51.50	16.05	10.72
toluene		9.99	
<i>m</i> -xylene	9.35	31.19	30.08
<i>t</i> -decalin	3.63		8.83
<i>n</i> -pentylbenzene		11.60	

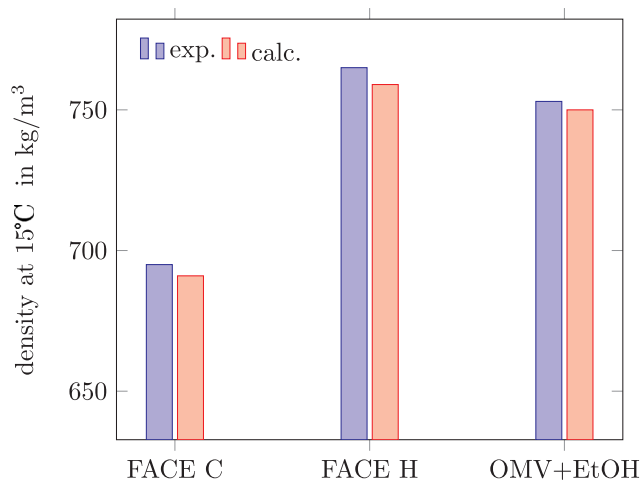


Fig. 3. Density at 15 °C of surrogates, both experimental and calculated.

components, and in particular, *n*-butane, the components were cooled to -5 °C before sample preparation. Measurements comprised the distillation behavior according to EN ISO 3405 (the European equivalent to ASTM D86), the RON according to EN ISO 5164 and the liquid density at 15 °C according to EN ISO 12185 and were conducted by the Institut für Mineralölprodukte und Umweltanalytik ZT-GesmbH (Institute for Petroleum Products and Environmental Analysis),

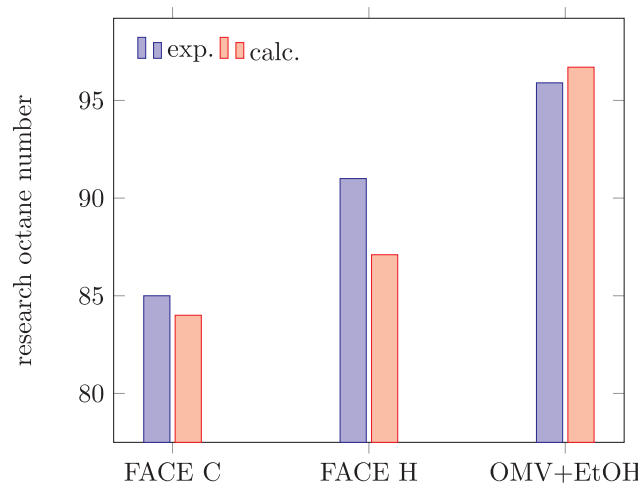


Fig. 4. Research octane numbers of surrogates, both experimental and calculated.

Schwechat.

As portrayed in Fig. 3, the deviations in density are insignificant, while Fig. 4 shows a notable deviation for FACE H in terms of RON. This could be partly due to the fact that the pure component RON of toluene was set to 112 (according to Demirbas et al. [41]), which seems to be too low compared to the values given in other sources (see Table 2).

Figs. 5–7 show the experimental D86 data for surrogates and corresponding fuels together with the calculated D86 data of the surrogates. In the area close to FBP, it can be observed that the calculated D86 data for surrogates are lower than the experimental values. This is also true regarding the IPB of FACE H. However, it is altogether remarkable that the distillation ranges of these gasolines can be reproduced with little deviation, ranging from 4.9 °C for FACE C to 3.4 °C for OMV + EtOH, by only six components and that, at the same time, other properties are also well-matched. This is also striking considering the use of a conversion method with an average error of 4.6 °C for TBP data generation from D86 data and the fact that higher uncertainties in the range of initial and final boiling points have been reported when a D86 analysis method is applied [23].

Although Greenfield [6] mentions that non-ideal effects can be neglected if the ethanol content is below 5 vol-%, the distillation curve of OMV + EtOH shows a significant point of inflection at about 45% degree of vaporization, which can be potentially attributed to the non-ideal behavior of ethanol, the content of which is 4.9 vol-% and corresponds exactly with that of the target fuel. In order to test this hypothesis, further tests with mixtures of FACE C and FACE H with an increasing fraction of ethanol were conducted, showing increasing deviations in terms of AAD; for example, an ethanol content of 10 vol-% resulted in AAD of up to 10 °C for D86 data.

In Fig. 8, the predicted lower heating values (LHV) of the surrogates are compared with experimental data for the target fuels. Although the LHV was not chosen as a fitting criterion in the objective function, the calculated values agree closely with the experimental data. The deviations are insignificant and range from 1.4% for OMV + EtOH to 2.5% for FACE H.

4. Conclusion

In this paper, an algorithm originally proposed by Reiter et al. [2] for diesel surrogates was applied to generate gasoline surrogates. For this purpose, the algorithm was extended by a conversion from D86 to TBP distillation curves, and the RON and the C/H ratio were added as fitting criteria, while the TBP curve and the density at 15 °C were properties that were adopted from the proposed algorithm. On the basis of 18 components, reflecting a set suitable for a multi-component

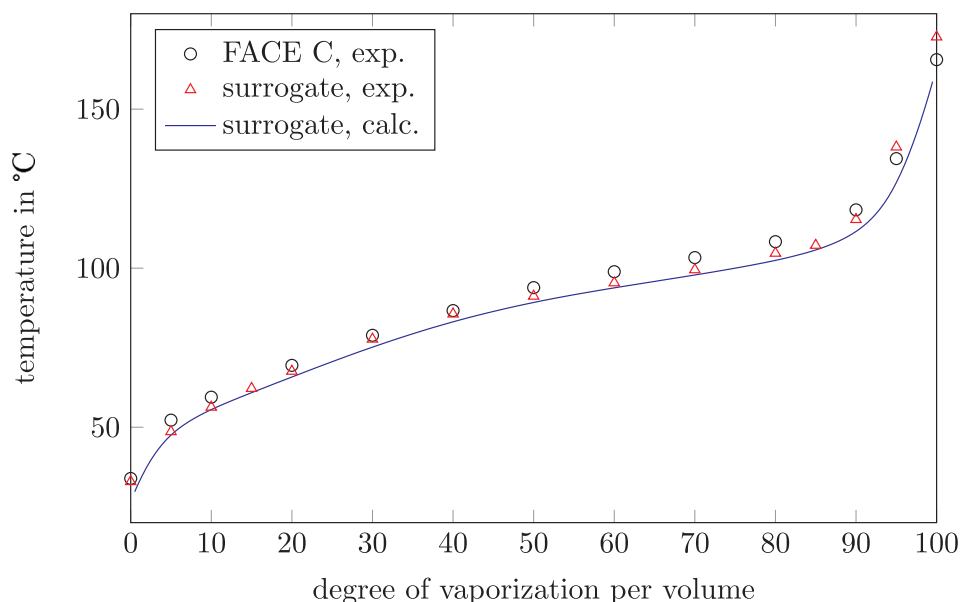


Fig. 5. Experimental (exp.) and calculated (calc.) distillation characteristics according to ASTM D86 for fuel FACE C and its proposed surrogate from Table 4.

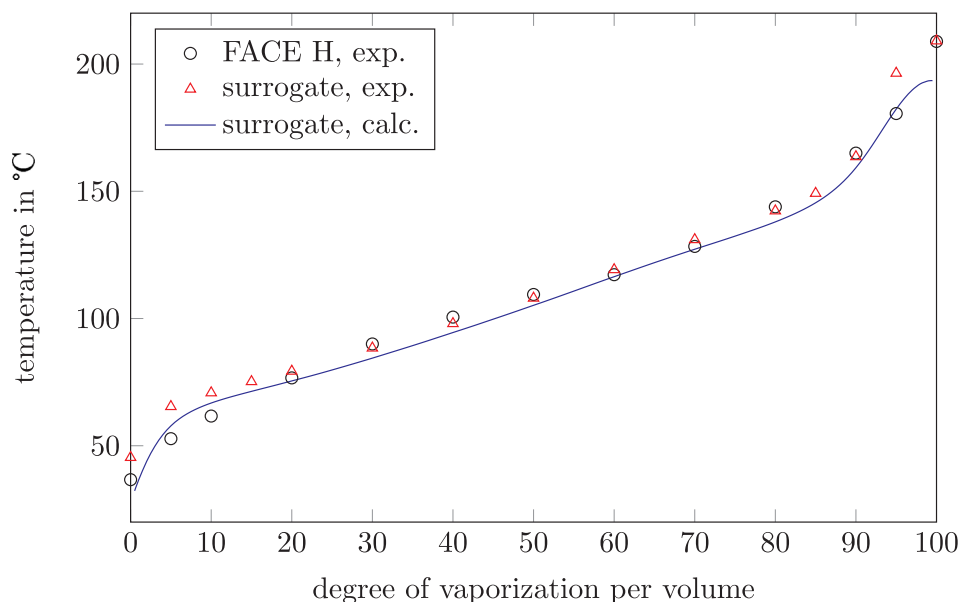


Fig. 6. Experimental (exp.) and calculated (calc.) distillation characteristics according to ASTM D86 for fuel FACE H and its proposed surrogate from Table 4.

mechanism for reaction kinetics, an F-to-remove algorithm was used to identify the most suitable component set for each target fuel.

It was demonstrated that the applied algorithm can be used to characterize gasoline in a proper manner with surrogates comprising six components, even if the conversion of ASTM D86 data is used for TBP data generation whenever the results of a TBP analysis are not available. The developed surrogates can be utilized for engine development while performing CFD calculations and can be further evaluated in combustion simulations using the reduced mechanism proposed by Ra and Reitz [1].

In the course of optimization, it is entirely possible that hydrocarbon species will be identified that have not yet been studied in single component experiments (e.g., ignition, chemical kinetics, flame speeds, etc.). Hence, as a side-benefit, this work could help identify current needs in the combustion community in order to set new priorities for hydrocarbon research.

Although an experimental evaluation has provided results that

broadly confirm the predicted surrogate properties, our findings indicate that the prediction of RON can be inaccurate because of the linear mixing model, on the one hand, and unreliable pure component data, on the other hand. These inaccuracies are particularly pronounced when considering components with higher RON (e.g., aromatics). Thus, it can be assumed that the development of more accurate models to predict the RON of mixtures, together with reliable pure component data, will lead to further improvements.

Shortcomings of the surrogates regarding the final boiling point, which could be overcome by the manual replacement of the component with the highest boiling point remaining by one of the previously removed components, showed that applying the component reduction algorithm and carrying out an inclusion procedure could help further develop the component selection algorithm itself.

Finally, a long-term goal for further development could be the inclusion of more application-oriented optimization criteria (e.g., ignition properties), by combining the surrogate algorithm with a reaction

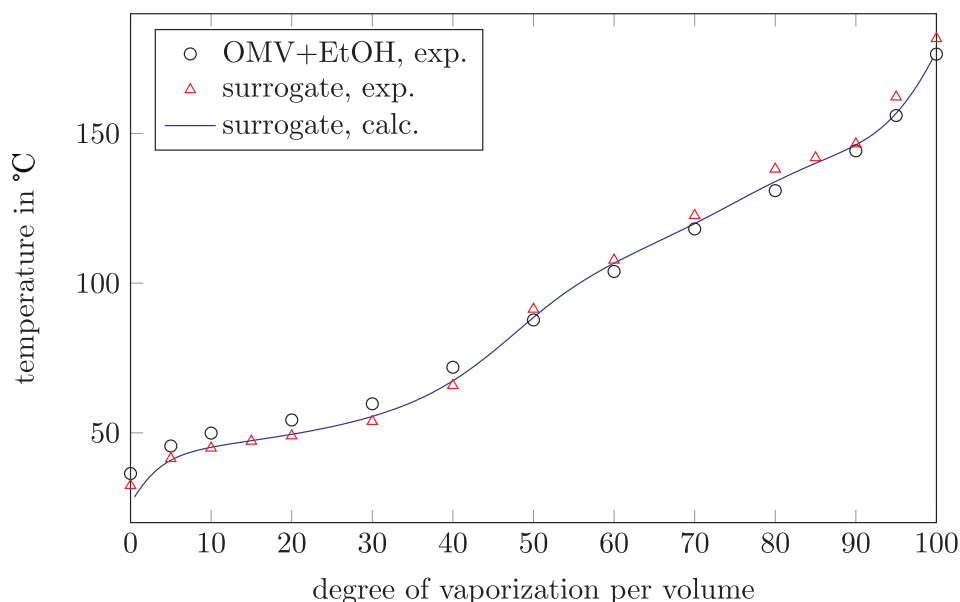


Fig. 7. Experimental (exp.) and calculated (calc.) distillation characteristics according to ASTM D86 for fuel OMV + EtOH and its proposed surrogate from Table 4.

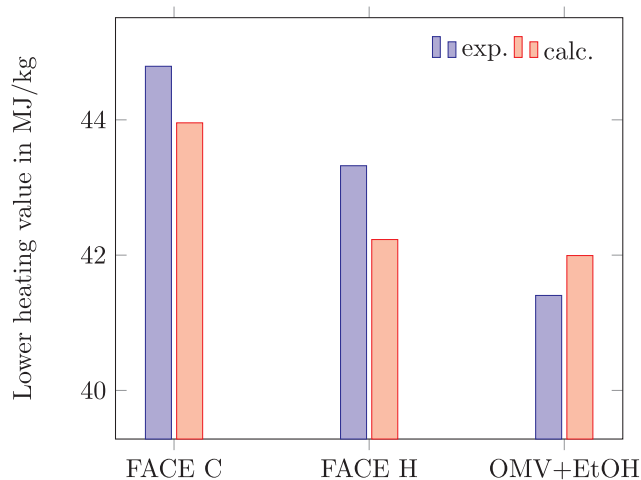


Fig. 8. Experimental (exp.) LHV of target fuels, and calculated (calc.) LHV of the surrogates.

kinetics calculation based on comprehensive multi-component reaction mechanisms. This step could overcome the currently limited consideration of molecular properties for optimization and further improve the surrogates' applicability for combustion and emissions simulations.

CRediT authorship contribution statement

Tobias Grubinger: Methodology, Software, Investigation. **Georg Lenk:** Writing - review & editing. **Nikolai Schubert:** Writing - review & editing. **Thomas Wallek:** Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <https://doi.org/10.1016/j.fuel.2020.118642>.

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