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Article

Comprehensive Two-Dimensional Gas Chromatography: A Universal Method for Composition-Based Prediction of Emission Characteristics of Complex Fuels

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ABSTRACT: Liquid fuels such as gasoline, kerosene, or diesel exhibit a very complex chemical composition. The transition toward a sustainable world requires the development of novel alternatives to fossil-based light and middle distillates, leading to a further increase in the composition complexity by the introduction of chemical structures absent in fossil fuels. The transfer of fundamental knowledge on molecular behavior in combustion demands in the first place a reliable analysis of the composition of such fuels, containing hundreds of molecules and chemical structures. This study presents a universal comprehensive two-dimensional gas chromatography (GCxGC) method for the complete group-type to component-by-component analysis of fossil and



alternative fuels. The emphasis was placed on the optimized separation of hydrocarbon groups in a large number of different synthetic and fossil fuels and their crude products, with simultaneous sensitive detection by mass spectrometry and flame ionization. The optimized analysis method is applicable for the full range of fossil light to middle distillates as well as various synthetic fuels. In addition to the classification and quantification of the composition in up to 20 chemical groups, the method is characterized by the fact that a component-by-component evaluation is possible. This level of detail is suitable to derive chemicophysical and combustion properties solely from the composition analysis. This is demonstrated by the prediction of the sooting behavior of 20 gasoline fuels including various types of alternative non-petroleum fractions. The sooting tendency is obtained from tabulated molecular Yield Sooting Indices (YSI). The results are successfully validated against smoke point and soot precursor species measurements from a molecular-beam mass spectrometry (MBMS) flow reactor experiment.

INTRODUCTION

The need for a transformation of the society into a sustainable world is the key challenge for combustion science. In particular, there is still a significant gap in linking the fundamental understanding of molecular properties and reaction behavior with the actual technical processes involved in combustion. Impressive progress has been made in the understanding of combustion reactions at a molecular level in experiments, reaction kinetics,^{4,5} and theory.^{6,7} No less progress was achieved in the field of developing efficient, clean combustion technologies.^{8–11} Despite these efforts, fundamental investigations are intentionally related to specific molecules and chemically well-defined substances. Liquid fuels usually consist of a very complex chemical composition with several hundred molecules and chemical structures. The mandatory conversion process toward sustainable combustion does not change this discrepancy but rather expands the complexity of technical fuels through additional chemical structures through novel alternative production pathways such as biofuels¹²⁻¹⁴ and Power-to-X,^{15–19} including solar²⁰ production routes. Starting from the chemical composition, application of the molecular knowledge enables the determination of numerous fuel properties such as density, freezing point, flash point, heat of combustion, surface

tension, and viscosity.^{21,22} As a consequence, a very detailed understanding of the composition of complex fuel mixtures becomes the crucial factor in linking molecules to combustion processes. Detailed compositional determination can be achieved by comprehensive two-dimensional gas chromatography (GCxGC), playing an important role in the analysis of petroleum-derived products, fossil fuels, and increasingly synthetic fuels and fuels from bio-based sources.^{23–31}

GCxGC is a multidimensional separation technique for the identification of volatile and semi-volatile compounds in complex mixtures. Besides fuels,^{25–27,31–35} this specialized analytical method has proven to be a very versatile and powerful tool for the detailed characterization of complex samples from the fields of flavors,³⁶ fragrances,³⁷ plastics,³⁸ pollutants,³⁹ and forensics⁴⁰ to name just a few. Nevertheless, and this is certainly related to the complexity of the GCxGC method and the

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associated data evaluation, there are a plenty of other analytical techniques for the more routine analysis of conventional gasoline, kerosene, and diesel. Typically, standardized techniques are developed exclusively for the individual fuels, i.e., gasoline, kerosene, and diesel, and are therefore often limited to these. These established techniques reach their limits when complex fuels need to be analyzed in sufficient detail to derive related physicochemical properties, especially when novel alternative components are considered. For gasoline, for example, there are a variety of methods listed for the EU in the EN228 standard to determine individual components and composition. Accurate component analysis of gasolines can be performed according to ASTM standards D5134, D6729, D6730, D6733, D7900, or D8071-all are representing GC methods. These are based on the comparison of known retention indices or reference spectra with those of the analytes. However, the large number of peaks in the chromatograms can lead to misinterpretations and additional new peaks, for example, for components from synthetic or renewable sources, are prone to errors. Here, an additional increase in separation performance while reducing analysis time could be provided by GCxGC. To date, however, the use of GCxGC methods for the detailed analysis of gasolines has not been widespread. In the field of kerosene and diesel analytics, the situation is comparable to gasoline-a large number of methods are known for determining the composition or individual groups-whereby the use of GCxGC is now part of the standard repertoire although no standardized method is yet available.^{23,} The physicochemical properties of diesel fuel in the EU are regulated in the EN590 standard and specify, for example, the total content of polycyclic aromatic hydrocarbons (PAH) and fatty acid methyl esters (FAME). For the determination of these HC-groups, several well-established methods are existing (aromatic content: EN12916 or ASTM D6591; FAME-content: EN14078 or ASTM D7371, EN14103). For jet fuels, the requirements are stated in ASTM D1655 and D7566 for fossil and synthetic fuels and their blends. Here too, various methods exist (aromatics: ASTM D6379, ASTM D1840; HC-types: ASTM D2425) and the detailed investigation of the composition of kerosene or mixtures with GCxGC is the focus of current scientific investigations. The growing interest proves how important it is to have precise knowledge of the composition, especially of synthetic fuels. Furthermore, large amounts of fuel are required to perform the abovementioned standard analyses and to determine other chemical-physical parameters. This can be problematic, especially for novel processes that are only available on a laboratory scale. The determination of the detailed composition by GCxGC—only a few milliliters are required-coupled with the possibility of simulating parameters represents a decisive option here and has already been demonstrated several times.^{22–24,41} For example, the National Jet Fuel Combustion Program (NJCFP) and the JETSCREEN project have developed a tool for pre-screening SAF candidates that can derive chemical-physical properties based on detailed composition.^{22,41,42}

The possibilities of the detected determination of the compositions of complex mixtures by GCxGC are comparable to the number of different systems described in the literature.^{23,43-47} For the quantification of hydrocarbon compounds, GCxGC coupled to a univariate flame ionization detector (FID) is an established option. Note that FID responses vary with different compound classes.⁴⁸⁻⁵⁰ Oxygenated species for example show lower FID responses in

comparison to non-oxygenated hydrocarbons. Differences can also occur within the hydrocarbon-group: aromatic species usually show stronger signals than saturated ones. However, the use of methanation before the FID detector can simplify quantification. As no structural information is gained by FIDanalysis, compound identification relies solely on the comparison of 2D retention indices between a given standard reference and the analyte. Since this makes a component-specific analysis too time-consuming, the chromatogram is often divided into different hydrocarbon patterns.^{27,34} For the analysis of conventional diesel or kerosene samples, a classification according to corresponding patterns has proven to be sufficiently accurate. However, this type of evaluation has its limits, especially when analyzing samples from synthetic sources, in which unusual species may be present compared to conventional fuels. At times, this can lead to large uncertainties and is especially challenging to distinguish between two substances showing comparable polarities and overlap in the chromatogram. In the search for new sustainable fuel sources and evaluation of new processes for fuel production, a high accuracy and the knowledge about these unusual species are of great importance. Thus, the prediction of properties based on composition depends very much on the fidelity of the analysis.^{22,41,42} The potential portfolio of substances that do not occur or only occur to a limited extent in conventional fossil fuels is growing. These species, which are difficult to distinguish from another, are mainly olefins, diolefins, and naphthenes as well as polycyclic naphthenes partially eluting with monoaromatics or cycloalkenes.^{24,25}

Multivariate detectors such as mass spectrometers have the ability to provide structural information about analytes. Timeof-flight mass spectrometry (TOF-MS) has long been the first choice for the combination with GCxGC due to the high scan rate (up to 500 spectra/s), and several studies exist for detailed fuel analysis.^{26,44} The development of high-speed scan single quadrupole mass spectrometers (qMS) has also led to an increasing role of qMS as a detector for GCxGC.⁵¹⁻⁵⁴ Nevertheless, a major drawback of GCxGC analysis by MS is that the quantification of the analytes is laborious, as individual MS response factors often have to be determined for each compound. Consequently, most GCxGC-MS methods are only semiquantitative and do not account for response differences between compounds.^{44,45} In addition, the discrimination of compound classes eluting in the same region of the chromatogram with comparable fragmentation patterns can be quite challenging (e.g., naphthenes and olefins). Thus, targeted, component-specific species identification by MS, in addition to quantification by FID, can not only improve the overall accuracy of the group analysis but can also distinguish structural isomers, at least for one species. On the one hand, this opens up additional possibilities for inferring properties from composition, e.g., the prescreening procedure for the evaluation of jet fuel candidates, 22,41 and on the other hand, it opens up new possibilities for the design of fuels with regard to their chemicalphysical properties or their sooting tendency.

In this study, we describe the development and validation of a universal GCxGC-MS/FID method for group-based to component-by-component analysis covering the entire boiling range from light to medium distillates $(25-350 \ ^{\circ}C)$ of gasoline, kerosene, and diesel including synthetic fuels and components. Optimization of the method for simultaneous characterization of the fuels using two orthogonal detectors, MS for determination of structural information and FID for quantifi-



Figure 1. Schematic overview of the two-dimensional gas chromatography system used in this study. The system consists of a split/splitless injector, an autosampler for up to 150 vials, a thermal modulator from ZOEX, a four-port splitter for detector splitting, a quadrupole mass spectrometer, and a flame ionization detector. The 1st dimension and the 2nd dimension column are located in the same GC oven.

cation, also allows compositions to be obtained with a higher level of detail. This not only proves to be an advantage over previously established methods but also reduces the error proneness that these methods can have, especially in the component analysis of gasoline and synthetic fuels. The method is validated using a validation blend of pure components and a comparison of GCxGC-derived values of a range of gasoline, kerosene, and diesel samples using complementary standard analytical methods (H-content, O-content, specific components, etc.). In addition, the detailed, component-specific analysis of 20 gasoline fuels, including fully and partly renewable fractions, is carried out and used to derive combustion emission related properties of the fuels. For this purpose, Yield Sooting Indices (YSI)⁵⁵⁻⁵⁸ are derived from tabulated single compound values to investigate the sooting tendency. The results are compared to experimental Smoke Point (SP) measurements (ASTM D1322) as well as molecular soot precursor species obtained from an established Molecular-Beam Mass Spectrometry (MBMS) flow reactor experiment on the same set of fuels.^{59–61} The successful correlation demonstrates the ability to determine the chemical composition of complex fuels in sufficient precision to derive related physicochemical and combustion properties once precise fundamental molecular models are available as for example in chemical kinetic modeling of combustion processes.^{60,62,62}

MATERIALS AND METHODS

GCxGC-Instrumentation. In order to gain a detailed understanding of the chemical compositions of all investigated fuels, a Shimadzu GC2010 Plus gas chromatograph was used. The system is equipped with a combination of a GCMS-QP2020 quadrupole mass spectrometer (Shimadzu) and a flame ionization detector (Shimadzu, GCxGC-MS/FID) allowing a simultaneous recording and quantitation of individual components of the complex fuel mixtures. In particular, a precise categorization into known molecular classes is enabled: *n*-

alkanes, iso-alkanes, cyclo-alkanes, aromatics, alkenes, alcohols, fatty acid methyl esters, and more. Additionally, the system is equipped with a ZX1 thermal loop modulator from Zoex. Theory and operational characteristics of the modulator are described elsewhere.⁶⁴ The modulation period t_m (cold pulse with liquid N₂) was set to 4.5 s followed by a hot pulse at 330 °C for 0.5 s. These settings have proven to be the best compromise for a universal analysis of different conventional and synthetic fuels within our operations. To obtain information from multiple channels of complementary data at the same time (MS and FID), the system is equipped with a 4-port flow splitter (Trajan, SilFlow GC 4 port splitter). The injection ports of the splitter were connected to the outlet of the 2D column, an auxiliary pressure controller (APC, Shimadzu), the FID-detector, and the MS-detector. Both detectors were connected by fused silica restrictors (Restek) with different lengths and internal diameters (ID) (MS: 1.0 m, ID: 0.15 mm; FID: 1.2 m, ID: 0.2 mm). The APC is operated at a constant pressure (17 kPa) in order to provide makeup gas to the splitter as the resulting flows from the column can be quite small. This configuration results in a theoretical detector splitting ratio of 1:1.6 (MS:FID), calculated using Shimadzu's Advanced Flow Technology software, and is chosen to ensure that the less sensitive detector (FID) receives the greater analyte fraction. A schematic overview of the GCxGC system is provided in Figure 1.

GCxGC-Columns and Conditions. All GCxGC analyses were carried out according to the reversed phase approach, i.e., (semi)polar 1st dimension and 2nd nonpolar dimension by combining a BPX50 (60 m length; 0.25 mm ID; 0.25 μ m film thickness, SGE) with a BPX5 (3 m length; 0.15 mm inner diameter; 0.25 μ m film thickness, SGE) column. The GC-oven program was initiated at a temperature of 28 °C, held for 0.5 min at 28 °C, and subsequently increased to 330 °C at a rate of 3.3 K/min. In addition, the pressure during the oven program was controlled at 230 kPa, held for 0.5 min, and subsequently increased to 330 kPa at a rate of 1.1 kPa/min. The APC was held constant at a pressure of 17.0 kPa over the entire GC run. 1 μ L of undiluted sample was injected by an AOC-20i + s (Shimadzu) autosampler equipped with a 10 μ L Hamilton syringe at a split ratio of 450:1 and injection temperature of 330 °C. Additional chromatographic and mass spectrometric conditions are listed in Table 1.

Table 1. GCxGC Chromatographic Conditions and Further Parameters of the Detectors Used

He (6.0)
temperature: 330 °C
He makeup flow: 30 mL/min
H ₂ -flow: 40 mL/min
air flow: 400 mL/min
ion-source temperature: 200 $^\circ C$
interface temperature: 250 °C
detector voltage: 0.8 kV
scan speed: 20000 u/s
scan range: m/z 40–400
spectral scan rate: 56 Hz

Raw-data processing of the GCxGC-MS/FID data was done using GCImage software package (Zoex, v2020r3). Quantification of each component was achieved by integrating the volume of the blobs in the 2D GCxGC-FID chromatogram.

GCxGC-MS/FID RRF Determination and Validation. Quantification was performed by using FID responses. For the calibration and normalization of the FID responses, relative response factors (RRF) for different hydrocarbon (HC) groups (n-alkane, iso-alkane, n-alkene, cyclo-alkane, mono-aromatics, cyclo-aromatics, poly-aromatics, oxygenates) and different carbon chain lengths were recorded. The selection of different hydrocarbon compounds as calibration standards is based on components that are typical representatives of different conventional and synthetic fuel-types (approximately from C5-C20). A total of three different calibration mixtures and up to four different concentration distributions of each mixture were prepared (Tables S1-S3). Each standard solution was finally measured three times. From these measurements, response factors (RF) were calculated as the average of the three individual measurements. RFs were normalized to n-hexane, which was present in all four mixtures to finally obtain relative response factor (RRF). In order to check, FID signal linearity mixtures with different concentration distributions were used (Tables S1-S3). Key figures of the GCxGC system were determined by a self-mixed validation standard (STD-Mix, Table S4). All mentioned regents, chemicals, and fuels were used as received without any further purification or treatment.

GCxGC-MS/FID Analyte Identification and Data Evaluation. High-speed scan single quadrupole mass spectrometry was used to identify individual components. The assignment of the obtained mass spectra was performed by comparison with existing commercial and inhouse created libraries (NIST MS '17) using GC Image (ZOEX) and GCMS Solution (Shimadzu) software. The allocation of different blobs was carried out either by spectrum matching-based searches with the mentioned databases or by comparing them to external standards. The similarity score threshold was set to 80 (out of 100) and the confidence of identification was further validated manually, considering the ¹D and ²D retention times.

For the quantification of the individual components and chemical groups, the normalized FID signal was used as mentioned above. From the combined results of the two detectors, further chemicophysical parameters of the investigated fuels were determined. These include the following: H/C/O-content (mass%), average molecular weight (MW), average molecular formula, each from the classification of the components into the different hydrocarbon groups resolved by C-chains, H/C-ratio, and n-/iso ratio. For some of the fuels, the YSI was determined as described below. For the determination of YSI_{Fuel}, the mole fraction of each individual component (x_i) was calculated from the mass fraction (w_i), the molecular weight of the component (MW_i), and the average molecular weight of the fuel (MW_{Fuel}). The determination of the YSI(GCxGC) from GCxGC data was then performed according to eq 1.

Reference Fuels. Optimization of the GCxGC method was performed using a wide range of different conventional and synthetic fuels (i.e., gasoline, Jet-A1, diesel, HEFA, FT, MtG). Representative chromatograms are available in the SI. Different properties of a total of

32 conventional and synthetic fuel samples were used to validate the GCxGC method. For the comparison of the simulated soot properties (YSI) to the smoke point and soot precursor species (MBMS), 20 gasolines, partly with synthetic components, were analyzed.

Smoke Point Determination and Simulation of YSI from GCxGC Data. The Yield Sooting Index (YSI) of a mixture, which is a characteristic measure for the tendency of a hydrocarbon mixture or a pure compound to produce soot in a combustion environment,^{SS-S8} could be calculated from the YSI_i of the individual components *i* present in the mixture following a simple linear mixing rule. Since the YSI is a molecular quantity, the YSI_{Fuel} for a fuel can be derived following eq 1.

$$YSI_{Fuel} = \sum_{i} (x_i \cdot YSI_i) = \sum_{i} \left(w_i \cdot \frac{MW_{Fuel}}{MW_i} \cdot YSI_i \right)$$
(1)

Here, w_i corresponds to the mass fraction of component *i*, MW_i is the molecular mass of component *i*, and MW_{Fuel} is the medium molecular mass of the fuel mixture. Consequently, the YSI can be used to calculate the sooting propensity of newly developed fuels or hydrocarbon mixtures. For this purpose, only the quantitative component-resolved composition of the fuel must be known. This can be achieved using the GCxGC-FID/MS method presented here allowing the derivation of the average molecular mass MW_{Fuel} of the fuel. The determination of the YSI(GCxGC) for the selected gasolines in this study is based on their component-by-component analysis by the method presented and considering eq 1. The mole fraction and average molecular weight were obtained from the GCxGC results and the individual YSI_i from the database established by the Pfefferle research group.⁶⁵ Measured YSI values are available in the database for about 95% of the components determined by GCxGC. The remaining 5% were linearly extrapolated from the nearest available neighbors. Another option to predict the sooting tendency of a fuel is the determination of smoke points (SP),^{65,67} which is a widely used approach. This is even specified as a parameter for certification of jet fuels. The SP is inversely proportional to the soot tendency of a fuel, i.e., the more a fuel tends to form soot, the smaller its SP. As recently postulated by the Pfefferle research group, there is a correlation between YSI and SP according to eq 2.

$$SP = \frac{30.4}{\frac{YSI(SP)}{S} - 0.427}$$
(2)

Here, DSP is the derived smoke point and S stands for the stoichiometric air requirement per mole of fuel. In the converted formula, derived YSI(SP) can thus also be calculated from measured SPs. SP measurements are available for the entire set of 20 gasolines and were used within this study for a comparison of the simulated YSI(GCxGC) and the experimentally derived YSI(SP).

Soot Precursor and MBMS Flow Reactor Experiment. Regarding the soot precursor chemistry, oxidation of gasoline fuels was investigated applying DLR's atmospheric laminar flow reactor (ALFR) equipped with a molecular-beam mass spectrometry (MBMS) system for a comprehensive, quantitative detection of combustion intermediates. A detailed description of the experimental setup^{61,69} and applied procedures for gasoline⁵⁹ can be found elsewhere. In brief, the pre-evaporated fuels are mixed with oxygen to yield slightly fuel rich conditions ($\varphi = 1.2$) fed to a laminar flow reactor in high Ar dilution (>99%). Conditions are chosen to prevent self-sustaining combustion reactions ensuring that the reaction temperature is predetermined by the reactor oven. Combustion intermediates are detected by a MBMSsystem at the reactor exit while varying the reactor temperature corresponding to non-reactive state to temperatures sufficient for complete oxidation of the fuel within the residence time (ca. 2 s) of the reactor. During this temperature range the destruction of fuel molecules, formation and depletion combustion intermediates and the formation of the combustion products CO₂ and H₂O (and some CO/H₂ due to the rich conditions) can be observed. Typically, 150-250 species within the oxidation of a technical gasoline can be detected, identified by their elemental composition (C/H/O) and quantitatively evaluated.



Figure 2. Comparison of the FID response (upper graphics) and the MS total ion chromatogram (lower graphics) of the validation mixture. Both the 1D chromatograms and the processed 2D chromatograms show that the corresponding component peaks/blobs appear approximately simultaneously in the two different detector channels. The intensities of individual peaks differ. In addition, in the 2D chromatograms, it is visible that almost the entire separation space is used and a good separation between the individual species is achieved.

The experiment was designed to provide well-resolved speciation data under controlled conditions for the validation of chemical kinetic models.⁷⁰⁻⁷² Application of technical fuels, i.e., a mixture of several hundred chemical species, represents a significant challenge to evaluation and interpretation of the obtained dataset. Precise knowledge of the fuel composition is mandatory for the usability of such datasets as a validation target for kinetic mechanism development.^{60,73} In particular, the calibration of the various fuel species is only possible, if GCxGC analysis for the fuel is available. Within the present work, species profiles of important soot precursor intermediates (m/z =78: C_6H_6 , m/z = 154: $C_{12}H_{10}$; m/z = 166: $C_{13}H_{10}$; m/z = 178: $C_{14}H_{10}$) have been recorded for 20 gasoline fuels. It is worth noting, that all of the profiles exhibit an intermediate species profile, i.e., formation and subsequent depletion, even if small amounts of the respective aromatic species may also be a fuel constituent. Quantitative evaluation was performed applying a direct calibration procedure based on reference substances." ^{4,75} The peak mole fraction of the respective species values is determined from the full species concentration profile and used for comparison with YSI.

RESULTS AND DISCUSSION

GCxGC-FID/MS with Dual Detection in Split Mode— **Method Development.** Comprehensive two-dimensional gas chromatography is a very complex technology for the separation and identification of complex mixtures. Despite the large number of publications on the subject of detailed analysis of fuels,^{24–27,41,42,75–79} each system has its own characteristics that require individual optimization. Due to the large number of parameters having a direct influence on the separation performance, method development can be very laborious. Some of the most important parameters that are used to optimize the universal GCxGC-MS/FID method presented are discussed below. For a more detailed overview, please refer to the literature.^{27,43,46,80,81} The aim was to achieve an ideal separation of the different hydrocarbon groups present in the (synthetic) fuel-classes, while maintaining the sensitivity of both detectors and the overlapping capability of the detector signals.

The modulation period has a direct influence on the separation capability of the system and can be derived from a representative 1D chromatogram. According to Murphy, we found that a modulation period of 4.5 s is needed to prevent ¹D separation and allow that each compound eluted from primary column to be sampled at least three to four times.⁸² The choice of this modulation time leads to wraparound of some peaks in some marginal cases, especially at very early or very late retention times, i.e., for relatively very light or very heavy compounds. In order to not lose any separation resolution, this is accepted here since relevance is given only for mixtures with a very broad C-atom distribution (C5-C36), e.g., FT-fuels. Note that the wraparound takes place in the empty space of the chromatogram, whereby the entire separation range can be utilized and also co-elution is prevented (see Figure S1 in the SI). Representative GCxGC-MS/FID-chromatograms of the validation matrix are shown in Figure 2.

The temperature-programming rate, which has a direct influence on the second column retention-time, was found to be ideal at rates of 3.3 K/min. The rate in combination with the before mentioned modulation period of 4.5 s is the ideal compromise for preserving the efficiency of the first-dimension separation besides the efficiency of the second dimension. Lower temperature ramp rates resulted in a loss of separation sensitivity at the aforementioned modulation time, where higher



Figure 3. (A) Plot of correlation between the FID signal and mass fraction for selected molecules of different hydrocarbon groups and C-chain lengths. The dashed line represents the linear fit through the experimentally determined values. The *y* error bar shown corresponds to one standard deviation calculated from three individual determinations. The inset shows the FID behavior for tetradecylbenzene. (B) Relative response factors (normalized to *n*-hexane) for different hydrocarbon groups as a function of the number of carbon atoms. Each value shown is the average of at least three individual measurements. For some of the points, different constitutional isomers, which can be assigned to the same group and C atom number, were used (e.g., monoaromatic C8: ethylbenzene and *p*-xylene). The RRF was then obtained by averaging all values of a specific group. The error bars correspond to one standard deviation.

temperature ramp rates resulted in narrower bands at the expense of separation. Due to the choice of the two columns with different internal diameters coupled in series the carrier gasflow and hence the linear velocity affect the separation in both columns differently.^{46,83} As already mentioned, the GCxGC was operated under pressure control conditions. To compensate for a decrease of the column flow during the oven program and for a loss in sensitivity and analysis speed, a pressure program was applied. The initial head pressure p = 230 kPa at a furnace temperature T = 30 °C was linearly increased during the GC oven program to a final pressure of 330 kPa (T = 330 °C). This pressure program was chosen to achieve a theoretical linear velocity of >30 cm/s (36.5 cm/s) for the 1st dimension column with the aim of achieving the highest possible separation performance as described by the van-Deemter-equation.⁸⁴ In iterative experiments with different pressure profiles, the above parameters have proven to be ideal for separation under the previously mentioned conditions, although the carrier gas velocity for the 2nd dimension lies well-above its theoretical optimum.⁸⁰ The pressure of the APC was held constantly at 17 kPa over the entire oven program. This pressure value proved to be ideal for a sufficient total flow to the detectors while maintaining a stable signal-to-noise ratio. The optimized GCxGC-MS/FID-method presented here leads to a successful separation of the individual components present in conventional and synthetic fuels. Thus, an analysis of a large number of different fuel samples and their raw products is possible. However, the choice of individual parameters, such as adjusting the pressure or using an additional pressure controller on the detector splitter, leads to the analyte flow arriving at the detectors varying within a measurement. This in turn means that

a normalization of the FID detector signal, which is used for quantification, must take place.

Verification of Linearity of the FID Signal and **Determination of FID Relative Response Factors.** Given the adaptations of the GCxGC-MS/FID system, the relatively high sample capacities for some of the expected substances and the flow-rate/pressure variations during one GCxGC run, a linearity test was performed as a measurement of instrument performance. This was also used to identify a possible concentration dependence of the relative response factors (RRFs). The linearity check was performed for different species in different concentration ranges depending on the experience of real samples. Toluene, methyl tert-butyl ether (MTBE), and ethyl tert-butyl ether (ETBE), for example, stand out as being particularly present in gasolines, which is why the linearity of its FID response was verified in a range of approx. 6-18 m/m% (maximum signal intensity for toluene: 3×10^8 a.u) what is at the upper limit of ordinary FID signal linearity.⁸⁵ In jet fuels or diesel in particular, individual molecules are present in significantly lower proportions. The verification of the linearity for some aromatic species like tetradecylbenzene was therefore carried out in ranges as low as 0.15-0.75 m/m% to prove that even lower concentrations can be validly quantified with the developed method. Different standards (see Tables S1-S3) for such purposes and results are presented in Figure 3 and in Figure S2 in the SI. Both figures show that the FID detector exhibits linear behavior for all hydrocarbon classes studied here and in the relevant mass ranges. For the linear regression lines, we calculated correlation coefficients R^2 between 0.987 and 0.999, which reflects the linearity very well proving that the split ratio is sufficiently large, no detector overloading occurs, and also the

flow splitter with the APC unit has no negative effect on the linearity.

In addition to determining the linearity of the FID signal, its behavior toward different hydrocarbon classes with varying carbon chain lengths is of great importance. The FID detector is usually characterized by the fact that the response is the same for hydrocarbons of different groups and chain lengths that only contain C and H atoms, and standardization can therefore be dispensed with.^{49,50} Nevertheless, a normalization of the signal is necessary for the method presented for several reasons: (1) the method also includes the determination of oxygen-containing species, which have a detector response deviating from 1; (2) by not operating the system at constant flow, the flow to the detectors change over the course of the temperature program. While the splitting ratio of the flow to the two detectors remain constant (MS:FID = 1:1.6), the total flow arriving at the detectors varies within one measurement. The fact that components with different chain lengths and thus different 1D retention times result in different signal sensitivities for identical masses can already be seen from the variation of the slopes of the linear regression lines in Figure 3A. For the determination of RRF values, three standard solutions were prepared with representatives of the relevant hydrocarbon groups over a broad C-chain distribution (Tables S1-S3), yielding RRF (normalized to *n*-hexane) values as a function of group and Cchain length. Figure 3B and Figure S3 show the RRFs obtained for n-alkanes, cyclo-alkanes, mono-aromatics, alkenes, and polyaromatics. A summary of the calculated RRF values (as a function of the HC group and the C chain length) used for the evaluation of the GCxGC-method and all further measurements of this study is given in Table S5. For some of the RRF values of certain HC groups and C-chain lengths, several constitutional isomers were used (e.g., mono-aromatics: ethylbenzene and pxylene). In this case, the group RRF corresponds to the mean value of all species of this group/chain length. Similar detector behavior was found for all HC groups (cf. Figure 3B): the lighter representatives (C5-C6) show a reduced detector signal compared to *n*-hexane, which is why their RRF value is >1; followed by an approximately constant range in which there is hardly any change in RRF for increasing the C number (~C7-C14); followed by a minimal constant increase for even heavier molecules. We assume that this phenomenon is related to our individual system configuration and that the additional He flow, which is controlled by the APC and maintains the splitting ratio, accounts for it. This probably leads to a shift of the splitting ratio between MS and FID due to the additional change of the gas pressure of the GC during the oven temperature program. Additionally, the signal offset differs for the different groups. Thus, the FID detector is in principle more sensitive for species containing aromatic moieties. In summary, the above findings indicate that individual determination of HC group RRF values is necessary for universal use of GCxGC-FID data. Hence, the determined RRF values reported here were applied for the quantification of the fuels described in this study. The linearity check of the FID has shown that linear behavior is present in the relevant concentration ranges and that the determination of one RRF per component/group is valid for all concentrations.

Validation of the Optimized Universal GCxGC-MS/FID Method. The validation of the optimized GCxGC-MS/FID method was carried out using an individualized validation standard. The exact composition is given in Table S4 and available in the SI. To determine the accuracy, reproducibility, and deviations of the method, the validation standard was measured 10 times under identical measurement conditions. In a first step, the reproducibility of the ¹D and ²D retention times for the two detectors was determined. Figure 4 gives an overview of



Figure 4. Plot of the mean value of the ¹D retention time against the mean value of the ²D retention time of the GCxGC validation standard. The mean value was obtained from 10 individual measurements under identical conditions. The *x* and *y* error bars shown correspond to the value of one standard deviation. The retention times of the MS are shown in red those of the FID in blue. The two plots on the bottom show the discrepancies between the ¹D and ²D retention times between the FID and MS signals, respectively. The black line corresponds to the correlation line.

the results obtained. The values shown correspond to the mean over the 10 individual measurements, while the x and y error bars correspond to one standard deviation. The ¹D and ²D retention times prove very good reproducibility for both detectors, respectively. The standard deviations are in the range of ± 0.02 to ± 0.16 min for the ¹D and ± 0.01 to ± 0.07 s for the ²D retention time. For the ¹D separation, this indicates a good reproducibility of the temperature accuracy as well as the column flow. The modulator also demonstrates high precision, which is evident from the only small deviation of the ²D retention time. In addition to confirm the precision of the retention times of the two detectors for itself, the superposition of the signals from the two detectors is also of great importance for precise and fast group to component accurate evaluation of samples. The correlations between the FID and MS retention times of the 1st and 2nd dimensions are shown for this purpose in Figure 4. For the 1st dimension, a high precision is observed identifiable by the small deviation from the correlation line (black origin line). The standard deviations found are correspondingly low with values between ± 0.01 and ± 0.05 min.

In contrast, a somewhat larger shift is found between the ²D-MS and ²D-FID retention times. Hence, the corresponding values exhibit a slight deviation from the correlation line. The shift is somewhat larger for substances that elute later from the

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Figure 5. Comparison of the mass ratio of the HC groups present in the validation standard measured by GCxGC-FID/MS compared to the weighedin mass ratio of the validation standard (see top left). Shown is the mean value over 10 individual measurements. A comparison of the values can be found in the table above right. The standard deviation (SD, σ) corresponds to the obtained deviation starting from the measured group masses of the 10 individual determinations. In addition, the relative deviation of the measured mean from the theoretically expected value of the standard matrix is listed. The mean value of the mass fractions over the 10 individual measurements of the individual components contained in the matrix is shown as a bar in the lower graph. The error bars shown again correspond to one standard deviation. The theoretical values are shown as black dots.

column than for those with short retention times. Components eluting with a retention time <30 min still show good FID and 2 D-MS retention time overlays. Above this, there is a shift to lower 2 D retention times for the MS detector, most likely attributable to the different pressure conditions within the detectors (atmospheric vs vacuum).

Determination of the accuracy of quantification by FID was performed by comparing the mass ratios determined by GCxGC to the actual weighed-in mass of the validation standard (STDmix). The accuracy was determined at the level of the mass concentrations of the different hydrocarbon groups as well as for the individual components. The results obtained are again based on ten measurements of the standard. Figure 5 shows the comparison between the actual values and the values obtained by GCxGC-MS/FID. For the group analysis, it can be stated that all values are close to the correlation line and a high level of accuracy can be achieved using the here presented GCxGCmethod. n- and iso-alkanes as well as n-alkenes are slightly overestimated (rel. deviation 2.1–2.8%), whereas mono-, cyclo-, and poly-aromatics tend to be slightly underestimated (rel. deviation 1.1-4.4%). The high reproducibility of the quantification is also visible from the relatively low standard deviations. Ultimately, all measured values are within three standard deviations of the real value of the STD-mix. The deviation of the GCxGC result was less than 5% relative to the known concentration.

One of the main advantages of the described method is the quantification of individual components and, therefore, the validation was also carried out with regard to the individual components. A comparison between the measured and the real mass concentrations can be taken from Figure 5. High accuracy and reproducibility of the concentrations from GCxGC can also be found for the determination of the individual components. All measured values are again within the range of three standard deviations. The experimentally observed concentrations of the individual components do not deviate from the real value by more than 10%. This is ultimately slightly higher than the deviation of the quantification of the HC groups and can probably be explained by the fact that group RRFs were applied for the individual components. Overall, the agreement between the group composition determined using GCxGC and the real composition of the STD-mix is very high. Since real samples contain significantly more components, a wide range of conventional fuels and synthetic fuels are expected to be examined using the method presented here. A validation based on some real samples follows below.

Scope of the Universal GCxGC-MS/FID-Method. As already mentioned above, the universal GCxGC method presented here stands out by covering the complete boiling range from light to medium distillates (25–350 °C). This means that not only jet fuels and diesel can be analyzed but also gasolines whose analysis by GCxGC has not been common so far. The extension of the method to the complete boiling range is

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Figure 6. Comparison of the composition of a selection of representative fossil fuels (gasoline, Jet-A1, and diesel) and synthetic fuels (methanol-togasoline (MtG), hydroprocessed esters and fatty acids (HEFA), and Fischer–Tropsch crude oil (FT-crude)). The compositions of the fuels shown were determined using the optimized GCxGC-MS/FID method presented here.



Figure 7. Qualitative and quantitative determination of the individual components of Fuel_8 as an example, which was determined by the optimized universal GCxGC-FID/MS method.

particularly important for the analysis of synthetic crude products. This is especially valuable for the targeted evaluation of synthetic fuels from novel process chains since the raw products produced always retain a more or less wide boiling range and; thus, a wide C-chain distribution (C4–C36) depending on the process and product refinements. In addition, synthetic (raw) fuels often contain components that are not found in conventional fuels or components that are regulated, thus preventing approval of the synthetic fuel. Through the targeted analysis of individual components as described here, GCxGC analysis offers a great opportunity to provide a useful basis for decision-making already at an early stage of the process with manageable effort, without (1) requiring huge quantities, (2) having to use the entire analytical laboratory, and (3) requiring time- and cost-intensive investigations. A depiction of representative conventional fuels—a gasoline, a Jet-A1, and a diesel sample—as well as synthetic fuels—a methanol-togasoline (MtG), a hydroprocessed esters and fatty acids (HEFA), and a Fischer—Tropsch fuel sample—is shown in Figure 6. These fuels are representative for the composition, the C-atom-range or the different hydrocarbon groups commonly present in samples from different sources.



Figure 8. Specific composition-related fuel properties determined by GCxGC-MS/FID compared to the results obtained for the same fuel by complementary standard methods. The fuels include gasoline, jet fuel, and diesel samples including respective alternative drop-in and non-drop-in fuels.

The selection of fuels presented here thus show not only that the method covers the complete boiling range, but also that a classification of the components into hydrocarbon groups is possible with a very high degree of detail.

For example, carbonyls or cyclic alkenes that usually do not occur in conventional fuels and that are hard to discover by conventional pattern matching can also be resolved. Furthermore, the method presented here makes it possible to determine the composition of individual fuels with component accuracy (Figure 7) and has not been described in the literature so far.^{23–27,76,78} Such a detailed determination of the composition opens up numerous additional possibilities, for example, in the prediction of additional physical quantities. On the one hand, there is the possibility to improve models for the prediction of critical properties, such as the freezing point, which was previously only possible with large errors.^{22,41,42} On the other hand, it is possible to predict important combustion properties with high accuracy (see also below). Hence, the here-presented universal GCxGC method can be used for a variety of fuels with different prerequisites. In addition to the basic requirement that the GCxGC method must ensure separation of the components in the appropriate boiling range and thus C-chain length range, accurate quantification must also be provided. Therefore, a comparison with other complementary analytical methods is used to validate the quantification of GCxGC data. An evaluation of the composition determined using GCxGC in comparison to various standardized methods such as determining the aromatic content using EN12916 or ASTM D6379, the



Figure 9. Overview of the composition (by elements and chemical class) and the predicted YSI(GCxGC) of the 20 gasolines investigated in this study.

FAME content using EN14103, or the H-content are a favorable choice. 26,27

In order to validate the quantitative results of the GCxGC-MS/FID method presented here for a wide range of fuels, we decided to compare key properties, which can be derived directly from the determined composition. A comparison of the results obtained using GCxGC for the specific indicators compared to the values for the same samples determined using complementary analytical methods is summarized in Figure 8. The 32 fuels used for the validation are representatives from the group of gasoline, jet fuels, and diesel including respective alternative drop-in and non-drop-in fuels. One of the selected indicators is the H-content of the fuels. This parameter was chosen because it is very sensitive to incorrect quantification/classification of the blobs into the different hydrocarbon groups. Furthermore, there are several established methods with which the H-content can be determined. In the three cases considered, GCxGC provides very good agreement with the chosen reference methods' NMR (ASTM D4808), calculated from detailed PiONA measurements (ASTM D6730) and by elemental analysis (ASTM D5291). Across methods, the standard deviation for all determined H-content values is below $\pm 0.2\%$. Please note that not all samples were analyzed using the whole set of comparative methods shown. An analogous correlation can be observed for the determination of O content from GCxGC data compared to O content from PiONA analysis (ASTM D6730) or values determined by elemental analysis (DIN51732). Again, a small distance of the shown points from the origin line can be observed. Since the GCxGC method presented here can also be used for the determination of individual components, high accuracy is proven by a comparison of the determined mass fractions of ethanol and toluene. Here, the reference toluene and ethanol values were determined according to ASTM D8071. The high agreement of the GCxGC results with established methods is also found for the determination of the FAME content (reference method

EN14078) and polyaromatics (reference method EN12916), two parameters important for characterization of diesel.

In summary, the universal GCxGC-FID/MS method presented here provides quantitative data with a very high accuracy for a wide variety of conventional and synthetic fuels. In addition to the already established HC-group-type quantification, reliable component-specific data can also be obtained. The detailed data can be used, for example, to predict sooting tendencies and to optimize models for the prediction of additional physical-chemical properties of the fuel.

Sooting Tendencies from Detailed Composition Analysis of Gasolines: Correlation (D)SP vs. YSI. The above described universal GCxGC method was further applied to determine the detailed composition of 20 gasolines. Figure 9 summarizes the simplified elemental and group composition of the comprehensive fuel selection. The fuels are primarily specification compliant drop-in fuels (EN228) containing a variable amount of synthetic blending components including FT-products and MtG-products as well as different classes of oxygenates such as ethanol, butanol, MTBE, and ETBE. The selection contains 10 standard-compliant, 5 near drop-in fuels that violate the current specification in some limited properties (e.g., max oxygen content) but are nevertheless applicable in modern SI engines as well as 5 fuels for special application and synthetic fuel blends. Within the chemical composition, a broad variation through the major hydrocarbon classes are represented, i.e., linear n-alkanes, branched iso-alkanes, unsaturated alkenes, cyclic naphthenes, aromatics, and oxygenates. The cyclic naphthenes and aromatics are primarily present as monocyclic six-membered rings, i.e., substituted cyclohexanes or benzenes. A limited number of fuels additionally contain very small fractions of bicyclic compounds such as decalins or naphthalenes. In total, the full variability of currently discussed conventional alternative drop-in gasoline fuels is covered herein.

Based on this composition analysis, the YSI is calculated according to eq 1 for each of the fuels. Results are summarized in



Figure 10. Comparison of the simulated YSI(GCxGC) and SP(GCxGC) obtained from GCxGC data against the experimental SP or values derived from the experimental data (YSI(SP)).

Figure 9. The individual YSI_i for each fuel constituent are taken form tabulated literature values determined in the Pfefferle research group.⁶⁵ Literature YSI_i values are available in the database for about 95% of the components determined by GCxGC while the remainder is estimated from linear extrapolation form the nearest available neighbors. The fuel's simulated YSI (YSI(GCxGC)) are in the range of 40 to 130 and thus covers the full range of slightly to heavy sooting fuels. In order to validate the resulting indices, smoke points (SP) have been determined for all fuels according to ASTM D1322. Based on the SP measurements, YSI of the fuel can be determined using the correlation of Zhu et al.⁶⁸ The resulting correlation of YSI gained from GCxGC and from SP measurements is presented in Figure 10. Excellent correlation is found for the YSI obtained by both methods.

For comparison, the complementary calculation of the respective derived smoke point (SP(GCxGC)) based on the YSI(GCxGC) is compared to the measured values in Figure 10, applying the same correlation equation (eq 2).⁶⁸ Since high smoke points correspond to low sooting fuels, this plot highlights the good correlation especially for the low sooting fuels. The excellent correlation proves the predictive resolution of the GCxGC composition analysis for the full range of gasoline fuels. A reliable ranking of the sooting tendencies, i.e., the YSI can directly be obtained from the chromatographic measurements.

Simulated YSI as the Indicator for Sooting Tendency: Soot Precursor Chemistry. For further evaluation of the prediction capabilities of the simulated YSI(GCxGC) based on the GCxGC, composition analysis to the soot precursor chemistry with oxidation of the gasolines is examined. For this purpose, the reaction intermediates occurring with combustion of the fuels were directly monitored by MBMS at DLR's atmospheric laminar flow reactor (ALFR).⁶¹ A detailed discussion of the combustion chemistry and a comparison to real engine emissions for a subset of the fuels presented herein is provided by Zinsmeister et al.^{59,86} These studies highlight the direct impact of the composition of complex fuels to the combustion chemistry and subsequently on the particulate emissions. Figure 11 and Figure S4 therefore compare the simulated YSI(GCxGC) to the peak mole fraction of key soot precursors intermediates obtained form ALFR for the 20 gasolines. The selected soot precursor intermediates are following the established soot formation pathways^{87,88} from the first aromatic ring formation, i.e., benzene (C_6H_6) followed by hydrocarbon addition toward larger PAH structures forming the multiple core species acenaphthene/biphenyl $(C_{12}H_{10})$ and fluorene $(C_{13}H_{10})$ to the three-fused benzene ring PAH anthracene/phenanthrene ($C_{14}H_{10}$). Consequently, the general peak mole fractions of those soot precursors decrease systematically with increasing molecular size.

For the single core aromatic benzene (C_6H_6) , only an unsystematic rough correlation to the YSI(GCxGC) can be stated. This is in accordance with previous investigations proving the high sensitivity of benzene to individual fuel constituents that may lead to increased or decreased benzene formation based on fuel specific reaction pathways. 59,62,71 Benzene and substituted benzenes are constituents of some fuels. This enables reaction pathways that are not directly leading to molecular growth of larger soot precursor molecules. Note that benzene is formed above the initial level for all fuels. The resulting intermediate peak mole fraction is two orders of magnitude higher compared to the other molecules shown. Consequently, a noticeable fraction of the formed benzene is not contributing to the PAH growth pathways. For this reason, the reaction intermediate benzene is not necessarily a good indicator for sooting tendency of a fuel.



Figure 11. Simulated YSI(GCxGC) vs relevant soot precursor species benzene (C_6H_6), acenaphthene/biphenyl ($C_{12}H_{10}$), fluorene ($C_{13}H_{10}$), and anthracene/phenanthrene ($C_{14}H_{10}$) measured at DLR's atmospheric laminar flow reactor.

Correlation quality is increasing with the size of the respective soot precursor species, i.e., $C_6H_6 < C_{12}H_{10} < C_{13}H_{10}$ until approaching the detection limitations for C₁₄H₁₀ due to its low concentrations. A clear relation of the larger intermediate soot precursor species to the YSI(GCxGC) is obvious. Since numerous previous investigations have proven the capability of predicting the soot formation tendency from the soot precursor chemistry as well as for the YSI, this relation can be expected. Nevertheless, it underlines the capability and precision of the presented GCxGC method for very complex fuel compositions. Identification and classification of chemical compounds as well as the quantitative evaluation is sufficient for resolving the individual combustion chemistry, e.g., soot formation potential of the fuel. Reliable predictions of the soot formation potential can be obtained solely from the composition analysis and tabulated literature values for the individual constitutional chemical compounds.

SUMMARY AND CONCLUSIONS

Multidimensional gas chromatography is a powerful technique for investigating the detailed composition of chemically complex fuels with a minimal amount of sample. In this study, we presented a two-dimensional GCxGC method for universal application to alternative and conventional fuels ranging from light gasoline to kerosene to diesel. This includes even nonrefined petroleum products and a comprehensive set of alternative fuels, fuel blends, and additives. Validation was performed using multicomponent calibration blends and real fuels. The method combines excellent reproducibility with sufficient absolute precision, i.e., uncertainties below 5% at the chemical group level and below 10% for individual compounds. Sufficient reproducibility with many standard analytical methods has been demonstrated, including hydrogen content or polyaromatics. Identification and quantification of several hundred chemical compounds from up to 20 chemical groups and their respective carbon numbers are provided. This level of detailed compositional analysis allows the derivation of chemicophysical and combustion properties of a given fuel sample. In particular, its ability to resolve non-standard compounds provides access to rapid evaluation, development, and optimization of novel alternative fuels for all sectors.

The predictive power was demonstrated for the sooting behavior of 20 gasoline fuels. The detailed component-specific composition was used to calculate the Yield Sooting Index (YSI) as a measure of the sooting tendency of the complex fuel blend. This value, derived solely from the composition, was in excellent agreement with actual experimental values. As a follow up in complexity, the correlation of the GCxGC-based simulated YSI(GCxGC) to soot precursor intermediate species during combustion of the fuels in a laminar flow reactor was demonstrated. The consistent results underscore the ability to predict fuel properties, including combustion behavior, from this analysis once a fundamental understanding of the individual molecular constituents is available. For the development of sustainable alternative fuels, the determination of detailed composition provides the fundamental bridge from molecules to processes.

ASSOCIATED CONTENT

1 Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.2c04270.

GCxGC raw chromatograms, additional figures and table, compositions of calibration and validation mixtures, relative response factors for quantification (PDF)

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Notes

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