

Lower Heating Value of Jet Fuel from Hydrocarbon Class Concentration Data and Thermo-Chemical Reference Data: An Uncertainty Quantification

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Highlights

- A detailed LHV determination method with uncertainty quantification is reported
- Determinations leverage a fundamental approach with GCxGC-FID measured class concentrations
- Uncertainty quantifications consider isomeric, GC, and heats of formation variance
- All 17 determinations from this work agree with ASTM D4809 measurements
- The ASTM D3338 estimation method agrees poorly with ASTM D4809 for alternative fuels

Abstract

A detailed assessment is presented on the calculation and uncertainty of the lower heating value (net heat of combustion) of conventional and sustainable aviation fuels, from hydrocarbon class concentration measurements, reference molecular heats of formation, and the uncertainties of these reference heats of formation. Calculations using this paper's method and estimations using ASTM D3338 are reported for 17 fuels of diverse compositions and

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compared against reported ASTM D4809 measurements. All the calculations made by this method and the reported ASTM D4809 measurements agree (i.e., within 95% confidence intervals). The 95% confidence interval of the lower heating value of fuel candidates that are comprised entirely of normal- and iso-alkanes is less than 0.1 MJ/kg by the method described here, while high cyclo-alkane content leads to 95% confidence bands that approach 0.2 MJ/kg. Taking a possible bias into account, the accuracy and precision of the method described in this work could be as high as 0.23 MJ/kg for some samples.

Keywords

Lower Heating Value, Sustainable Alternative Fuel, GCxGC, Thermo-chemical Reference Data

Abbreviations / Nomenclature

GC-MS	=	Gas chromatography, coupled with a mass spectroscopy
GCxGC-FID	=	Gas chromatography with two columns and a flame ionization detector
HHV	=	Higher heating value, or gross heat of combustion, MJ/kg at 25 °C and 1 atm
LHV	=	Lower heating value, or net heat of combustion, MJ/kg at 25 °C and 1 atm
Q_{bomb}	=	Heat of combustion at constant volume
MAE	=	Mean absolute error
ME	=	Mean error
MSE	=	Mean square error
MW	=	Molecular weight
NIST	=	National Institutes of Standards and Technology
H/C	=	Hydrogen to carbon ratio (mole basis)
H	=	Mass fraction of hydrogen
S	=	Mass fraction of sulfur
ΔH_f	=	Heat of formation
σ	=	Uncertainty or standard deviation

1. Introduction

The net heat of combustion, which is often called the lower heating value (LHV), is important to fuel consumers and suppliers because it is the source of energy which is ultimately converted to usable power. Engine manufacturers and their customers rely on determined LHV to gauge engine performance and thermal efficiency, which are quality assurance measurements done at the product level prior to shipping an engine for installation into an aircraft or a power generation platform. Observations made by the correspondence author during his 20-year tenure working combustor design for industry imply terms/requirements around the performance margins measured by these new-engine tests may be written into sales contracts. During the product development phase of a gas turbine engine, accurate LHV is necessary to establish performance margins for the engine model and to optimally interpret/assess test data pertaining to other engine-level requirements as well. Once in service though, as of today, the LHV of fuel that is consumed by an engine used for air transportation (unlike power generation platforms) is generally known only to be within the range specified by ASTM D1655 (for example), which is, “greater than or equal to 42.8 MJ/kg”.

The LHV of sustainable aviation fuel (SAF) blend components can be higher or lower than conventional fuels. At present, all SAF blend components, covered by ASTM D7566 specifications have LHVs that are greater than 42.8 MJ/kg and 1-2% higher than conventional fuels because they are composed almost entirely of saturated hydrocarbons. In contrast, conventional fuels may contain up to 25%v aromatics. Higher LHVs offer the potential for lower fuel consumption rates and the ability to potentially impact other emissions and environmental outcomes of aviation kerosene combustion. Through investigations with these alternative aviation fuel blend components, inconsistencies, particularly with the ASTM D3338 estimation method, motivated an alternative determination approach. At present, SAF prescreening aims to predict key properties with minimal fuel volumes, making accurate and precise predictive determinations critical to the decarbonization of aviation.

For ground-based applications of gas turbine engines, the LHV of fuel that is to be consumed is frequently measured by the consumer because it is required input to engine control software, as advanced in part by the correspondence author. Sometimes it is determined from a continuous recording calorimeter (e.g., ASTM D1826 – 94), and sometimes it is determined periodically from species concentration measurement via gas chromatography [1,2]. The total number of species in a gaseous fuel, including N₂ and CO₂, is typically ~10, and it is a straightforward application of Hess’s Law to construct LHV of the fuel from its components’ concentrations and a small library of thermo-chemical data. Heavier fuels such as propane, butane, gasoline, kerosene, diesel, etc. have more molecular

components, increasing ~factorially with average carbon number, which makes it progressively more difficult to derive LHV from composition data and a reference library of thermo-chemical data of pure molecules.

For fuel within the jet fuel volatility range, the range and concentration of molecules present is bounded by a flash point (38 °C) and T10 (205 °C) on the light end. On the heavy end, the freeze point (-40 or -47 °C) and endpoint of distillation (300 °C) limit the heavy species. There are thousands of molecules possible between the light and heavy ends of the range. Accurate measurement of every molecular concentration is not practical. However, a fundamental approach for LHV determination is still possible. The use of multidimensional gas chromatography with flame ionization detection (GCxGC-FID) has been used in the past [3,4]. However, all previous methods with GCxGC-FID have used correlative methods, instead of the fundamental approach described in this work, which is based on Hess' Law.

A physically based modeling approach utilizing GCxGC-FID data is attractive because such a method would require minimal sample and labor, while yielding a diverse array of additional property determinations or predictions [3–5]. For example, <1 ml of sample is required for GCxGC-FID compared to 1-2 ml combined for ASTM methods D4809 for HHV, D2622 for S, and D5291 for H. However, recent experience with a commercial lab suggests a total volume of 50 ml is requested for just the calorimetry measurement; perhaps, 50 mL is closer to the industry standard. One concern with a physically based modeling approach, leveraging GCxGC-FID experimentation has been, until now, a thorough assessment of the accuracy and precision of its property determinations. For reference, the stated reproducibility, 95% confidence interval, for LHV determined by the method described in ASTM D4809 is 0.324 MJ/kg, which is less than 0.1% of the LHV.

While the conversion from gross heat of combustion at constant volume (Q_{bomb} , the measured quantity in ASTM D4809) to net heat of combustion at constant pressure is clearly defined in ASTM D4809 and reproduced here as Equation 1, the reference enthalpy for the H₂O and CO₂ products is not entirely clear which could lead to differences

$$HHV = Q_{bomb} + 0.006145 * H_{\%m} \quad \&$$

$$LHV = Q_{bomb} - 0.2122 * H_{\%m} \quad \therefore$$

$$HHV - LHV = 0.218345 * H_{\%m} \quad (1)$$

between research labs or industries who may not all be referring to ASTM D4809. For hydrocarbons, it turns out that $(\text{HHV}-\text{LHV}) = 2.444 \text{ MJ}/(\text{kg-of-water})$, which corresponds to the heat of vaporization of water at 25 °C. In this work, HHV is calculated from the heats of formation of the products and reactants in their respective ground states at 25 °C and 1 atmosphere, and the mass percent hydrogen is determined from GCxGC-FID measurements to determine LHV. A comparison between different methods to determine hydrogen content is out of scope for this work.

Relative to the work previously reported [5], the current methodology differs in several ways. The reference state is now liquid at 25 °C for water and for all reactant molecules. The database has grown as a result of this work to include now 1077 molecules within the jet fuel range and another 2047 molecules that are unlikely to be present in jet fuel but may be present in samples that have yet to be tailored into potential alternative jet fuel. The uncertainties in concentration measurements and database heats of formation are now propagated through the calculations and contribute to the reported uncertainty of the determined LHV.

Related research by other teams is introduced in this paragraph. Two previous works will be revisited later to help underscore the differences between the fundamental approach described here and the correlation methods [3,4]. Thorough reviews of the literature on the topic are provided by Vozka and Kilaz [6] and by Gautam et al. [7]. In contrast to the fundamental approach described in this work, all these methods use correlation to train a statistical model which, theoretically could be used to predict the LHV of fuel samples that are not part of the training dataset. These correlation methods are good for interpolations, as similar variants of them are used in many ASTM methods (e.g., ASTM D3338 and D2887). Caswell et al. [8] used proton NMR to derive an average structure of eluted fractions from liquid chromatography, which then serve as the basis functions for correlation to middle distillate fuel properties. Johnson et al. [9] used partial least squares regression of 45 fuel samples to evaluate the correlation between near-infrared, Raman, and GC-MS data and fuel specification properties. Fodor et al. [10] and Wang et al. [11] used Fourier transform infrared spectra to correlate with fuel specification properties. Striebich et al. [12] correlated fast (5 minutes) GC data with fuel volatility and freeze point properties. While the correlation approaches show good agreement with measured fuel properties as reported, the agreement of predictions for fuel compositions that are outside the range of the training data is unknown.

Perhaps more importantly, the physical uncertainty of correlation methods remains unclear. Confidence intervals and R^2 values are only one type of uncertainty imparted on the prediction of a regression model, and the inclusion of even those unknowns in uncertainty quantification can be lacking. Statistical and correlative methods that train data

directly to observations need many more observations than physically based models. For example, the method and number of independent variables described later in this paper would need a minimum of 100 observations to determine coefficients for each class considered while reserving many additional observations for testing. Approximately two to three times that number of observations (200-300 total observations) would be needed to bound upper and lower limits for each of the coefficients. In stark contrast, physically based models require no training data, and all compared results can be viewed as untrained test data. The typical ‘80-20’ rule for training (80% of data is used for training) and testing (20% of data is used for evaluation of the method) data does not hold for physically based models. Here a physically based LHV calculation from GCxGC-FID data and reference thermo-chemical data is applied to a diverse array of aviation turbine fuels and blend components leveraging a large heat of formation database, with comprehensive uncertainty quantification.

2. Materials

A total of 17 samples were utilized in this study for the evaluation of LHV determinations; four petroleum-derived jet fuels, six neat SAFs, and six hydrocarbon mixtures that were defined under the National Jet Fuels Combustion Program [13] to have some properties outside of jet fuel specification (ASTM D1655). Relevant information on these fuels is displayed in Table 1. These samples were chosen due to the availability of existing multidimensional gas chromatography [12] and ASTM D4809 [14] data. The samples span a wide range of physical and chemical properties. For example, the LHV range of these samples is 42.9 - 44.1 MJ/kg, which is somewhat broader than LHV range of conventional jet fuels: 42.9-43.3 MJ/kg [13] and is significantly broader than range covered by at least one prior work [15] which utilized a correlation approach instead of a fundamental approach. Many of the samples reported here have been studied extensively, and those results are reported in other publications as well [11,14].

3. Data

Two types of data are required to determine LHV by the fundamental approach, species concentration data and reference heats of formation data. Reference heat of formation data (including uncertainties) for 1077 molecules that are within the jet fuel volatility range has been mined from the NIST Standard Reference 203: TRC Web Thermo Tables [16]. As with any data gathering endeavor, this process included evaluation of the reported NIST data. Working

Table 1. Fuel sample composition. Sample numbers are identical to those assigned by the Air Force Research Laboratory upon receipt. Many of the names match those designated by the National Jet Fuel Combustion Program [13]. The names starting with 'A-' indicate that it was one of the conventional fuels selected to represent the range of operational experience. The names starting with 'C-' indicate that it was a solvent blend crafted to probe the impact of specific fuel properties on combustion figures of merit.

Sample name	POSF	Molecular weight, kg/kmol	H/C	Composition, mass% (n/iso/cyclo/aro/alkene)	LHV, MJ/kg (ASTM D4809)
Syntroleum FT-SPK (S-8)	5018	167.52	2.17	24.2 / 75.2 / 0.6 / 0. / 0.0	44.10
C-4	12344	162.17	2.17	0.2 / 98.9 / 0.4 / 0.4 / 0.0	43.81
Sasol FT-SPK (SPK)	7629	153.15	2.17	0.3 / 91.3 / 5.2 / 0.6 / 2.7	43.80
UOP HEFA-SPK (UOP)	10301	170.18	2.16	10.1 / 86.1 / 3.7 / 0.1 / 0.	43.90
Dynamic HEFA-SPK (HEFA)	7272	175.89	2.16	9.5 / 88.4 / 2.0 / 0.0 / 0.0	43.90
Lanzatech ETJ (L.T.)	12756	166.00	2.16	0.8 / 96.3 / 2.8 / 0.0 / 0.0	43.90
Gevo	11498	178.45	2.16	0.0 / 99.6 / 0.1 / 0.0 / 0.3	44.00
A-1	10264	151.79	2.01	26.1 / 37.5 / 22.9 / 13.6 / 0.0	43.24
C-2	12223	173.00	2.00	5.2 / 77.5 / 0.1 / 17.1 / 0.2	43.39
C-6	10279	166.84	1.99	7.5 / 8.9 / 83.1 / 0.5 / 0.0	43.30
C-3	12341	179.55	1.97	9.2 / 45.2 / 31.7 / 13.6 / 0.0	43.30
C-7	12925	169.77	1.97	3.3 / 29.5 / 62.3 / 4.9 / 0.0	43.30
A-2	10325	158.96	1.94	20.0 / 29.7 / 31.8 / 18.5 / 0.0	43.06
C-5	12345	135.41	1.92	17.7 / 51.6 / 0.1 / 30.7 / 0.0	43.01
A-3	10289	166.29	1.89	13.4 / 18.9 / 47.4 / 20.4 / 0.0	42.88
JP-5	10376	169.00	1.89	13.7 / 18.6 / 47.3 / 20.4 / 0.0	43.00
C-8	12923	160.39	1.86	13.7 / 21.0 / 38.0 / 27.3 / 0.0	42.90

together with NIST, all inconsistencies found were resolved before incorporation into our internal database. The NIST database is built from a variety of measurements and analysis methods, resulting in a precision that is an order of magnitude smaller than ASTM D4809 in many cases. The class species concentration data was provided by L. Shafer and has been used previously [5].

The LHV data was provided by T. Edwards [14] and is also available through the Federal Aviation Administration National Alternative Jet Fuels Test Database [17]. That online database was also mined for input data required by ASTM D3338. None of this data is required to make an LHV determination via the fundamental approach, and was used in this work strictly for validation of the model.

4. Methodology

The concentration of 73 different classes of hydrocarbons, ranging from 7 to 20 (n) carbon atoms and $(2n+2)$ to $(2n-12)$ hydrogen atoms, are determined by integrating the signal from an FID detector which is positioned at the back end of the second column in a GCxGC configuration, the details of which are described by Striebich et al. [18], over a stenciled boundary of elution times corresponding to the time spent in the first and second columns, respectively. The conversion of integrated FID signal to concentration units is aided by leveraging calibration mixtures of molecules covering the range of the 73 classes of hydrocarbons that are of interest. An exemplar stencil in time/time-space marking the boundaries of each hydrocarbon class is provided in Figure 1. The total number of isomers of the ten most common hydrocarbon classes within the jet fuel range is presented in Table 2, along with the total number of isomers in each class with liquid-phase heat of formation values included in the database.

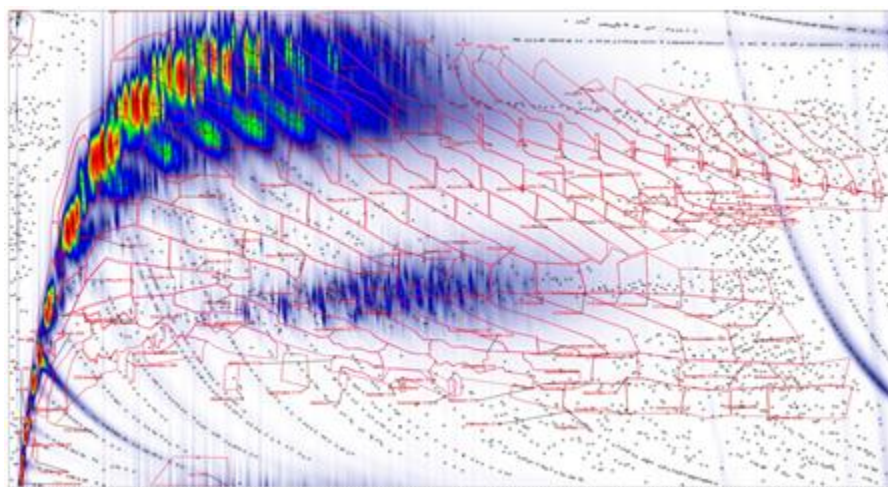


Figure 1. Definition of hydrocarbon classes. Species classes with a relatively high concentration show up as orange spots, and the corresponding bins that subtend each are of particular interest—figure provided by L. Shafer [5].

Table 2. Representative sample coverage of isomer populations. 60% of the average fuel composition is represented.

Class	Isomer Population (N)	Samples in Database (n)	n/N
iso-C9	34	34	1.00
iso-C10	74	71	0.86
iso-C11	158	42	0.27
iso-C12	354	48	0.14
iso-C13	801	38	0.05
iso-C14	1857	30	0.02
iso-C15	4346	30	0.01
cyc-C11	> 48	36	< 0.75
cyc-C12	> 100	38	< 0.38
C9 aromatics	8	6	0.75

Once the class concentration data is available, it can be used to calculate or estimate other properties of interest via physical models, such as the fundamental approach taken in this work, or regression models such as the approach taken by Shi et al. [3] and by Berrier et al. [4]. Properties that are physically determined by molecular bonds and atomic characteristics can be accurately determined by physical models, while properties that are heavily influenced by inter-molecular interactions in the condensed phase, typically are harder to determine accurately from first principles. Clear examples of the former include molecular weight, H/C ratio, and heat of combustion. Clear examples of the latter include viscosity and freeze point. While the utility of a regression model linking molecular weight, H/C ratio or LHV to some other data is unclear, recent innovations in regression software have made it easy to select any property as a dependent variable.

In contrast, the fundamental approach is narrower in scope. To rigorously apply the physical model for LHV [2] it is necessary to know the concentration and standard heat of formation of each constituent in the fuel and some quantification of the error associated with any assumptions or approximations related to the inter-molecular interactions. For LHV of liquid fuels, the contribution from inter-molecular interactions, called heat of mixing or heat of solution in most physical chemistry textbooks, is 0.15 ± 0.15 kJ/kg, based on the measurements of Lundberg [19].

Lundberg investigated a range of mixture fractions of 27 different binary solutions of hydrocarbons in the jet fuel distillation range, which is less than 0.1% of the reproducibility of ASTM D4809. The lack of detailed knowledge of every species' concentration and their corresponding heats of formation prevents direct application of a physical model for liquid fuels the same way that it is applied routinely to gaseous fuels [1]. That said, the same model structure can be used with class species concentration measurements, and some informed guess at the heat of formation corresponding to each class. This fundamental approach is advanced in this work. Later, we describe how to make an informed approximation of the heat of formation corresponding to each class. In contrast to the fundamental approach, correlation methods, if coupled with physically based regression equation constraints, and if decorated with a copious dataset, may provide some insight into the LHV mean for some or all hydrocarbon classes as compared to the ranges used for the fundamental approach.

In this work, the heat of formation of each class of hydrocarbons is determined by performing a Monte Carlo analysis where the mole fraction of a random member of the database class is set equal to one and all others in that class are assigned the value of zero. This process is repeated for each of the hydrocarbon classes, giving 73 sets of isomeric mass fractions that each sum to one. A visual representation of this process is provided in Figure 2, by which the model population with a uniform distribution is related to the fuel population with an unknown distribution. Each of the modeled classes is weighted by the GCxGC-FID, measured mass concentration [20], to define one element of the Monte Carlo simulation. In total, 10,000 random samples were created for the simulation, which has been shown previously [5] to be sufficiently large to achieve sampling convergence.

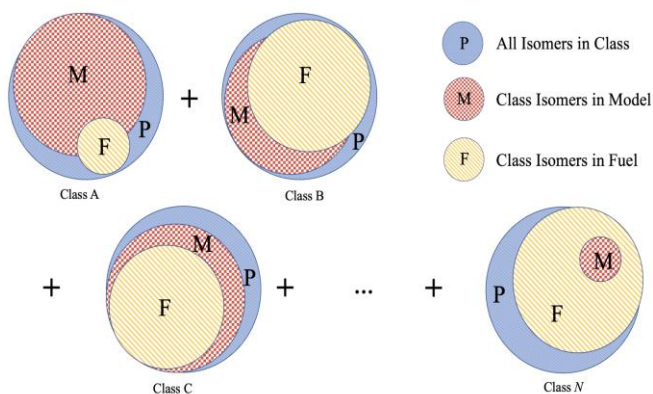


Figure 2: Visual representation of fuel composition

The higher heating value (HHV) of fuel with an empirical formula represented as C_xH_y is given by Equation 2, where $\Delta H_{f,m}$ is the standard heat of formation of material, m. Equation 3 is the cornerstone of the fundamental

$$HHV_{fuel} = X * \Delta H_{f,CO2(g)} + \frac{Y}{2} * \Delta H_{f,H2O(l)} - \Delta H_{f,fuel(l)} \quad (2)$$

$$\Delta H_{f,fuel(l)} = \sum_j c_j * \sum_i c_{i,j} * \Delta H_{f,i,j(l)} \quad (3)$$

approach, and is exact as written but for the neglect of ΔH_{mix} , which is negligibly small. The second sum in this expression is what distinguishes this approach for liquid fuels from its conventional usage for gaseous fuels, for which no such term is required. The first coefficient, c_j is the measured concentration of hydrocarbon class, j. The second coefficient $c_{i,j}$ represents the unknown population distribution of all molecules that belong to class j. The values of X and Y in the empirical formula of the fuel are also determined by the measured concentrations of each hydrocarbon class, as shown in Equation 4, where X_j and Y_j are the number of carbon and hydrogen atoms in class j, respectively.

$$X = \sum_j c_j * X_j \quad \text{and} \quad Y = \sum_j c_j * Y_j \quad (4)$$

For reasons that will become clear, the uncertainties affiliated with this fundamental approach for HHV of liquid fuel are broken into three terms as given by Equations 5-7. Term A as defined in Equation 5 accounts for the uncertainty arising from the GCxGC-FID measurements of hydrocarbon class concentrations. Term B as defined in Equation 6 accounts for the uncertainties associated with the data pulled from the NIST database. Term C as defined in Equation 7 accounts for the uncertainties arising from the unknown population distribution of isomers within each

$$A = \sum_j \sigma c_j * X_j * \Delta H_{f,CO2(g)} + 0.5 * \sum_j \sigma c_j * Y_j * \Delta H_{f,H2O(l)} + \sum_j \sigma c_j * \overline{\Delta H_{f,j(l)}} \mid 1 = \sum_j c_j \quad (4)$$

$$B = \sum_j c_j * \sum_i \overline{c_{i,j}} * \sigma \Delta H_{f,i,j(l)} \quad (5)$$

$$C = \sum_j c_j * \sum_i \sigma c_{i,j} * \Delta H_{f,i,j(l)} \mid 1 = \sum_i c_{i,j} \quad (6)$$

hydrocarbon class. The σ in Equations 4 [21] and 5 represents reproducibility of measurements, and it represents model uncertainty in Equation 6. To estimate a representative heat of formation for each hydrocarbon class in term A, an arithmetic average was taken over the population of isomers contained within the database for each class. To estimate the average isomeric concentration in term B, an arithmetic average was taken over the 10,000 elements contained within the simulation. The calculated values of terms A and B are thus invariant to the simulation. To estimate term C, the results of the simulation must be analyzed, as well as the underlying assumptions about the isomeric population distributions, and how closely the modeled distributions match the corresponding distributions that may be present in the real fuel.

5. Results and Discussion

The uncertainty of determinations made by the fundamental approach involves three principal components: 1) the measurement error associated with the concentration of each class of hydrocarbon, 2) the error associated with the heats of formation of individual molecules as determined by NIST, and 3) the uncertainty of the population distribution of isomers that each belong to the same class of hydrocarbon. The uncertainty resulting from the unknown isomer population distribution has two sub-components: a) the confidence interval associated with the potential difference between the population mean and fuel sample and b) the confidence interval associated with the potential difference between the population mean and modeled mean. However, the second piece to this is much smaller than the first because the number of components in each modeled class is high (or a high fraction of the total population), while the number of components within a given class in the real fuel could be as few as one.

Naturally occurring isomer population distributions, developed over geological timescales of exposure to high temperature and pressure, may be determined by minimization of the Gibbs free energy of the system, or at least influenced by it more than chemicals manufactured in a chemical plant by any of several potential synthetic pathways. That said, the population distribution of synthesized isomers is also expected to be skewed toward lower heats of formation, with rare exceptions. Farnesane by Amyris (ASTM D7566.A3) is one such exception, as it is a single isomer, synthesized through a biological mechanism. The database used to create our model of the full population is also expected to be biased toward isomers that are more readily produced and purified because, until recently, all methods used to make the heat of formation determinations required at least some volume of the real molecule. By

incorporating *ab initio* calculations, as has been done recently, any isomer can be included in the model's database regardless of whether it is produced naturally (in an appreciable fraction) or by any known synthetic pathway.

Unbiased sampling from the database produces an unweighted mean of the database, which will be higher than the real value of petroleum-derived fuels and many synthetic fuels as well. Correcting for this bias is not well-defined and is left for future work. In this work, the quantification of the sources of uncertainty in the fundamental approach reveals that the largest contribution to uncertainty is in the range of heats of formation within each hydrocarbon class. In the left half of Figure 3, a comparison is made between this work and two other methods; ASTM D4809 (calorimetry-

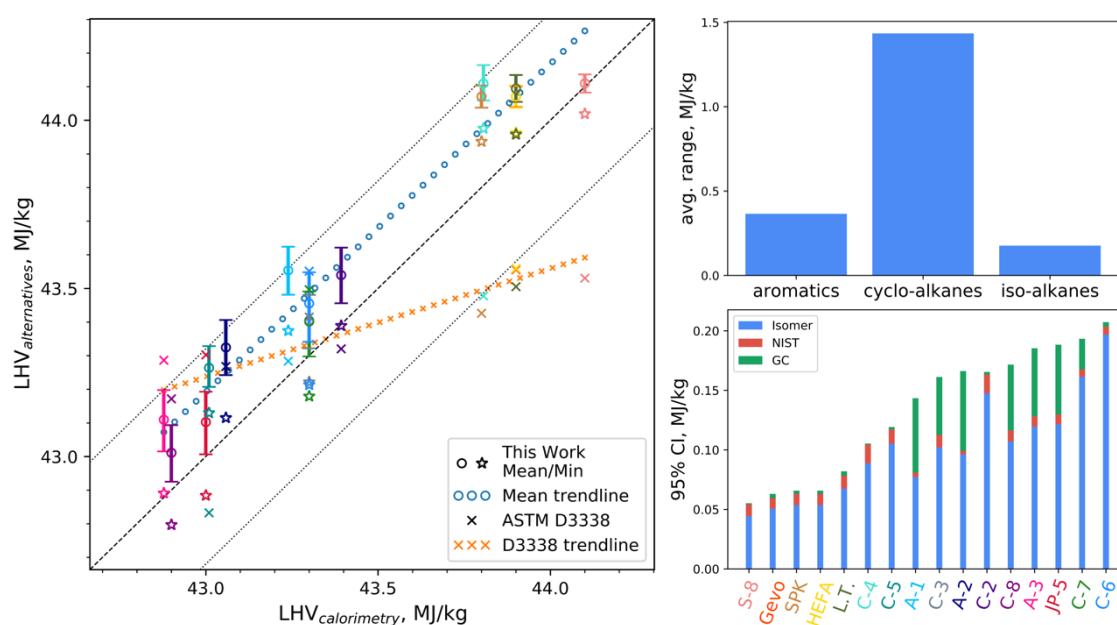


Figure 3: (Left) Unity plot comparing three methods of LHV determination. The black dotted lines correspond to the reproducibility (95 percentile) of ASTM D4809 test method. The colored circles represent the mean value of the fundamental approach and the colored stars represent the minimum determined LHV given the measured composition and the NIST database value corresponding to the most stable isomer in each class. The colored x's represent estimations made via the ASTM D3338 method. The vertical lines through each circle correspond to the 95 percentiles. Each color represents to a different fuel sample, which are named in the lower right of the figure. (Lower Right) Components of uncertainty in this work. Blue bars represent the contribution originating from the unknown population distribution of isomers within each class. Red bars represent the contribution arising from the reported uncertainties of the thermo-chemical reference data. Green bars represent the contribution arising from the GCxGC-FID concentration measurement. (Upper Right) Range of LHV values, averaged across carbon number for each category.

based method) and ASTM D3338, which is a correlation-based estimation referenced in the ASTM D7566 fuel specification. Statistics comparing the fundamental approach with the ASTM D3338 estimation are provided in Table 3. Relative to method ASTM D3338, the fundamental approach has a lower mean absolute error (0.18 compared to 0.29) and a tighter correlation with calorimetry measurements ($R^2=0.77$ compared to $R^2=0.39$), arguing for its eventual inclusion as an acceptable method for LHV determination in the ASTM D7566 (and D1655) fuel specifications.

Table 3. Statistic of alternative LHV methods

	This Work	ASTM D3338
ME	0.179	-0.077
MAE	0.179	0.289
MSE	0.04	0.103
R^2	0.766	0.389
Slope	0.9584*	0.3083

*One is perfect agreement.

The mean of all seventeen LHV determinations by the fundamental approach is within the 95 percentile band around the ASTM D4809 measurements. On average, the values determined in this work are 0.18 MJ/kg higher than those measured by the ASTM D4809 standard test method. Some of this offset is caused by the working assumption to use unbiased (uniform) sampling instead of sampling that attempts to represent a population in thermodynamic equilibrium (i.e., biasing the distribution sampling with Gibb energy). To provide a lower bound on the determinations, an extra calculation was made using the lowest energy isomer in each class to represent the whole class. These results are shown using the star symbols on the left side of Figure 3. A mean offset of 0.06 MJ/kg relative to ASTM D4809 persists even in this bounding extreme, but this number is within the reported “net bias (0.089 MJ/kg) of ASTM D4809 as determined by the statistical examination of interlaboratory test results.” Trace impurities, e.g. oxygenated species, particularly in the conventional fuels (A-1, A-2, A-3 and JP-5) are not considered in this fundamental approach, which may lead to some overestimation of LHV. That said, A-1 is a carefully selected (best-case petroleum) fuel [13] with low sulfur content, low total acid number and low existent gum that is expected to have the lowest hetero-atom content

of any of the petroleum-derived samples considered in this study. Therefore, the decision to neglect corrections for trace impurities does not explain the relatively high difference between ASTM D4809 and the fundamental approach for this sample.

The 95 percentile bars shown on the left side of Figure 3 are sorted from lowest to highest and re-displayed in the bar chart in the lower right of the figure, which also serves as the legend for the colors displayed in the unity plot on the left. As is quite evident from the bar chart, most of the uncertainty in the LHV determinations made here originate with the unknown isomer population distributions. The uncertainties in molecular heats of formation add approximately 0.01 MJ/kg to the uncertainty in our determination. The uncertainty from the measured class concentration reproducibility (labeled GC) varies significantly from sample to sample for two reasons. The percent uncertainty of the concentration measurement for a given class scales inversely with concentration so samples that are comprised of many classes will not be characterized as well as samples that are comprised of few classes. Also, samples with a more even distribution of constituents across the range of possible LHV's (range of hydrocarbon types) will not be characterized as well as those that are comprised almost entirely of constituents with nearly the same LHV (e.g. C-4 is 99% iso-alkanes). The main reason for the observed differences in the uncertainty ascribed to isomeric population distribution uncertainty is that some hydrocarbon classes have a greater range of heat of formation (which maps directly with the range of HHV and LHV) across their population than others. This can be seen by the bar chart in the upper right of Figure 3, where the class average range is shown for three common categories of species in jet fuel. The LHV of samples with a relatively high concentration of cyclo-alkanes will be determined less precisely than others, while those with a relatively high concentration of normal-alkanes (range=0) will be determined more precisely than others.

A more detailed representation of class-wise variation in LHV is shown in Figure 4. On the left side, LHV is plotted as a function of H/C revealing the not-so-surprising results that LHV trends higher as proportionately more water is produced by the reaction, and some general observations about the LHV of different categories of hydrocarbons. Neither alkynes or dienes are normally present in jet fuels, but they do help to focus attention on the importance of hydrocarbon type on both LHV and the range of LHV by carbon number. Generally, small normal- or iso-alkanes have the highest LHV while aromatic compounds have the lowest LHV due to their low H/C and the special stability (aromaticity) of these compounds. On the right side, LHV is plotted as a function of molecular weight to highlight the variation in LHV from category to category and within each category as carbon number varies.

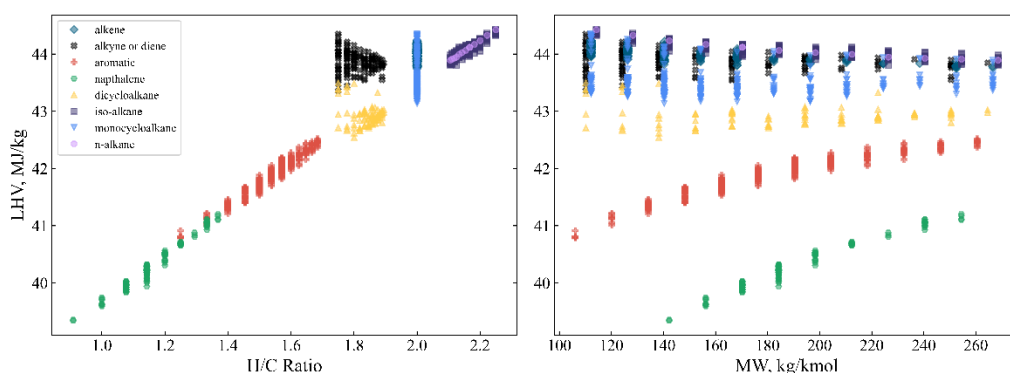


Figure 5: Heat of combustion variation within hydrocarbon classes

5.1 Near-misses between this work and ASTM D4809

From this work, two determinations, A-1 and C-4, are found in the tails of the ASTM D4809 probability distributions. In the case of C-4, the simple composition of the mixture illustrates how and why disagreements between the determinations of this work and ASTM D4809 can arise. C-4 is composed of almost 99% iso-alkanes, with only 6 iso-alkane classes represented by >97%. The LHV data, calculated as described above, is plotted in Figure 5 along with cumulative distributions functions for the ASTM D4809 measurements (imagined) and the Monte Carlo simulations of this work, with LHV histograms of molecules in six hydrocarbon classes in the background. The histograms reported here are the conglomeration of all molecules in the database that meet the criteria in the legend, i.e. C9 to C16 iso-alkanes. The vast majority (>97%) of the C-4 sample is composed of the reported hydrocarbon groups in Figure 5, with 42% alone composed of C12 iso-alkanes. Unsurprisingly, the C12 iso-alkane LHV grouping is also near the expectation value for the bulk mixture. The tails of the ASTM D4809 confidence intervals marginally overlap the 95% confidence interval range of this work and the C12 iso-alkane distribution. Meaning, it is highly unlikely that the actual LHV for this fuel is below the confidence interval reported for this work, unless the NIST database is incorrect or missing the most stable isomers of each class, which is highly unlikely.

For the other near-miss, two samples of A-1 from the same container were given different labels and sent to a commercial laboratory for ASTM D4809 testing. These new D4809 results for A-1 (42.1 and 43.5 MJ/kg) are compared in Figure 6, along with the initial ASTM D4809 (reported earlier) results and the determination from this work for A-1. The newly measured D4809 data points are not within the reported repeatability of measurement. While neither of the recent LHV measurements should be trusted because they do not agree with each other, they are reported

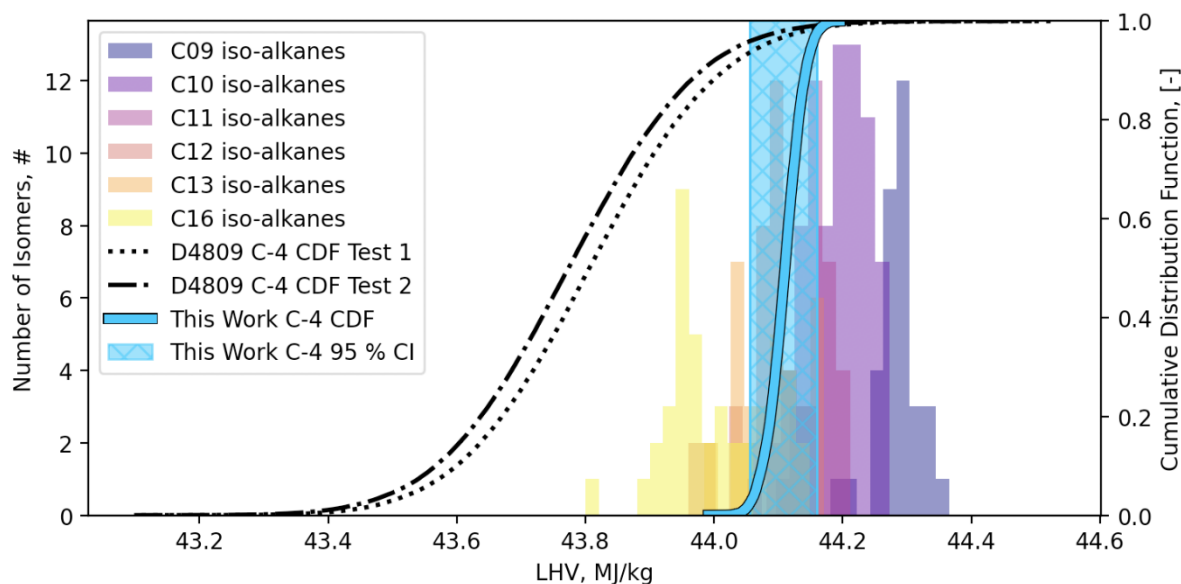


Figure 5: The histograms from the six major hydrocarbon classes are compared, left vertical axis. The (imagined) cumulative distribution function for two ASTM D4809 measurements (dotted and dash-dot line) and this work's Monte Carlo simulation (black outlined teal line) are compared, vertical right axis. The 95% confidence interval for the simulation of this work are bounded by the teal hashed and filled region, vertical right axis.

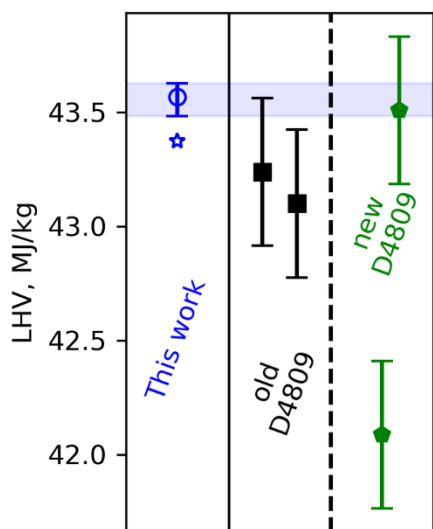


Figure 6: Comparison of LHVs from ASTM D4809 testing and determinations from this work. All error bars represent the 95% confidence interval for reported method. Initial ASTM D4809 data, black squares or 'old D4809', is compared to recently tested measurement results, green pentagons or 'new D4809', and this work, an open blue circle.

here to illustrate another source of uncertainty with all fuel property data from a customer's perspective. Namely, not all technicians follow the procedures as expected or maintain the equipment as expected, but the customer usually has no way of knowing when this has happened.

These two near-miss examples are consistent with experience in the National Jet Fuels Combustion Program [13]. There, several conventional fuels were tested multiple times with inconsistent results, while another fuel composed of very few hydrocarbon classes was reported with a non-physical LHV. Combined, these near-miss observations reinforce the desire to have more properties determined by diverse experimental and numerical methods (such as GCxGC-FID chromatograms, IR absorption spectra, or NMR spectra), regardless of approach, because the stakeholders-in-aggregate benefit from the additional checks and balances.

6. Conclusion

The lower heating value of jet fuel and sustainable alternative fuel candidates can be determined from hydrocarbon class concentration data and thermo-chemical reference data with high precision and accuracy. While the seventeen samples reported here is less than previous studies, all determinations reported here are made in the absence of any training data. Using the standard 80/20 rule for training and test data, a correlation method would require at least 85 samples overall to support seventeen predictions. The 95% confidence interval of the lower heating value of fuel candidates that are comprised entirely of normal- and iso-alkanes is less than 0.1 MJ/kg, while high cyclo-alkane content leads to 95% confidence bands that approach 0.2 MJ/kg. However, the accuracy of LHV determinations made by the fundamental approach depends on how well the population distribution of isomers in each hydrocarbon class is represented. In this work, we have assumed first that the distributions are uniform (no Boltzmann-type weighting) which is likely to bias the result toward higher LHV and, to gage the possible magnitude of this bias, a set of simulations was run using the lowest LHV isomer in each class to represent the whole class. On average, the difference between these two bounding assumptions is 0.13 MJ/kg.

CRediT authorship contribution statement

Randall Boehm: Conceptualization, Methodology, Supervision, Investigation, Writing – Original draft, Writing – Review & Editing. **Zhibin Yang:** Conceptualization, Methodology, Software, Validation, Formal analysis,

Investigation, Writing - Review & Editing, Visualization. **David Bell:** Data curation, Validation, Investigation, Visualization, Writing - Review and Editing. **John Feldhausen:** Data curation, Software, Validation, Investigation, Visualization, Writing - Review and Editing, **Joshua Heyne:** Conceptualization, Funding Acquisition, Writing - Review & Editing.

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References

- [1] Zhang J. Calculation of Natural Gas Calorific Value with the Agilent 990 PRO Micro GC System n.d. <https://www.agilent.com/cs/library/applications/application-natural-gas-calorific-value-990-pro-micro-gc-5994-1374en-agilent.pdf> (accessed April 23, 2021).
- [2] Stufkens JS, Bogaard HJ. Rapid Method for the Determination of the Composition of Natural Gas by Gas Chromatography. *Anal Chem* 1975;47:383–6. <https://doi.org/10.1021/ac60353a060>.
- [3] Shi X, Li H, Song Z, Zhang X, Liu G. Quantitative composition-property relationship of aviation hydrocarbon fuel based on comprehensive two-dimensional gas chromatography with mass spectrometry and flame ionization detector. *Fuel* 2017;200:395–406. <https://doi.org/10.1016/J.FUEL.2017.03.073>.
- [4] Berrier KL, Freye CE, Billingsley MC, Synovec RE. Predictive Modeling of Aerospace Fuel Properties Using Comprehensive Two-Dimensional Gas Chromatography with Time-Of-Flight Mass Spectrometry and Partial Least Squares Analysis. *Energy and Fuels* 2020;34:4084–94. <https://doi.org/10.1021/acs.energyfuels.9b04108>.
- [5] Yang Z, Kosir S, Stachler R, Shafer L, Anderson C, Heyne JS. A GC \times GC Tier α combustor operability prescreening method for sustainable aviation fuel candidates . *Fuel* 2021;292:120345. <https://doi.org/10.1016/j.fuel.2021.120345>.

- [6] Vozka P, Kilaz G. A review of aviation turbine fuel chemical composition-property relations. *Fuel* 2020;268:117391. <https://doi.org/10.1016/j.fuel.2020.117391>.
- [7] Gautam K, Jin X, Hansen M. Review of spectrometric techniques for the characterization of crude oil and petroleum products. *Appl Spectrosc Rev* 1998;33:427–43. <https://doi.org/10.1080/05704929808002061>.
- [8] Caswell KA, Glass TE, Swann M, Dorn HC. Rapid Prediction of Various Physical Properties for Middle Distillate Fuels Utilizing Directly Coupled Liquid Chromatography/1H Nuclear Magnetic Resonance. *Anal Chem* 1989;61:206–11. <https://doi.org/10.1021/ac00178a004>.
- [9] Johnson KJ, Morris RE, Rose-Pehrsson SL. Evaluating the predictive powers of spectroscopy and chromatography for fuel quality assessment. *Energy and Fuels* 2006;20:727–33. <https://doi.org/10.1021/ef050347t>.
- [10] Fodor GE, Mason RA, Hutzler SA. Estimation of Middle Distillate Fuel Properties by FT-IR. *Appl Spectrosc* 1999;53:1292–8. <https://doi.org/10.1366/0003702991945542>.
- [11] Wang Y, Ding Y, Wei W, Cao Y, Davidson DF, Hanson RK. On estimating physical and chemical properties of hydrocarbon fuels using mid-infrared FTIR spectra and regularized linear models. *Fuel* 2019;255:115715. <https://doi.org/10.1016/j.fuel.2019.115715>.
- [12] Striebich RC, Motsinger MA, Rauch ME, Zabarnick S, Dewitt M. Estimation of select specification tests for aviation turbine fuels using fast gas chromatography (GC). *Energy and Fuels* 2005;19:2445–54. <https://doi.org/10.1021/ef050136o>.
- [13] Colket M, Heyne J. Fuel Effects on Operability of Aircraft Gas Turbine Combustors. submitted. AIAA, Progress in Astronautics and Aeronautics; 2021.
- [14] Edwards T. Reference Jet Fuels for Combustion Testing. AIAA SciTech Forum - 55th AIAA Aerosp. Sci. Meet., Grapevine, TX: American Institute of Aeronautics and Astronautics Inc.; 2017, p. 1–58. <https://doi.org/10.2514/6.2017-0146>.
- [15] Kehimkar B, Hoggard JC, Marney LC, Billingsley MC, Fraga CG, Bruno TJ, et al. Correlation of rocket propulsion fuel properties with chemical composition using comprehensive two-dimensional gas chromatography with time-of-flight mass spectrometry followed by partial least squares regression analysis. *J Chromatogr A* 2014;1327:132–40. <https://doi.org/10.1016/j.chroma.2013.12.060>.
- [16] Kroenlein K, Muzny C, Kazakov A, Diky V, Chirico R, Magee J. NIST Standard Reference 203: TRC Web

Thermo Tables (WTT) 2012:1.

[17] Home | AJF:TD | U of I n.d. <https://altjetfuels.illinois.edu/> (accessed June 5, 2021).

[18] Striebich RC, Shafer LM, Adams RK, West ZJ, DeWitt MJ, Zabarnick S. Hydrocarbon group-type analysis of petroleum-derived and synthetic fuels using two-dimensional gas chromatography. *Energy and Fuels* 2014;28:5696–706. <https://doi.org/10.1021/ef500813x>.

[19] Lundberg GW. Thermodynamics of Solutions XI. Heats of Mixing of Hydrocarbons. *J Chem Eng Data* 1964;9:193–8.

[20] Flora G, Kosir S, Behnke L, Stachler R, Heyne J, Zabarnick S, et al. Properties calculator and optimization for drop-in alternative jet fuel blends. AIAA Scitech 2019 Forum, American Institute of Aeronautics and Astronautics Inc, AIAA; 2019. <https://doi.org/10.2514/6.2019-2368>.

[21] Johnson K, Loegel T, Metz A, Wrzesinski P, Shafer L, Striebich R, et al. Method for Detailed Hydrocarbon Analysis of Middle Distillate Fuels by Two-Dimensional Gas Chromatography. NAVAIR Public Release 2020-361: 2020.