



## Full Length Article

# Lower heating value of jet fuel from hydrocarbon class concentration data and thermo-chemical reference data: An uncertainty quantification

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## ARTICLE INFO

## Keywords:

Lower heating value  
Sustainable alternative fuel  
GC × GC  
Thermo-chemical reference data

## 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 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.

## 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 gage 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, in principle can be higher or lower than conventional fuels. At present, all

SAF blend components, covered by ASTM D7566 specifications have LHVs that are >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 [1]. 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 [2,3]. The total number of species in a gaseous fuel, including N<sub>2</sub> and CO<sub>2</sub>, 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.

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<https://doi.org/10.1016/j.fuel.2021.122542>

Received 12 June 2021; Received in revised form 27 October 2021; Accepted 7 November 2021

Available online 18 November 2021

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**Abbreviations / Nomenclature**

GC-MS	Gas chromatography, coupled with a mass spectroscopy
GC × GC-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 <sub>bomb</sub>	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 <sub>f</sub>	Heat of formation
σ	Uncertainty or standard deviation

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 [4]. 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 (GC × GC-FID) has been used in the past [5,6]. However, all previous methods with GC × GC-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 GC × GC-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 [5–7]. For example, <1 ml of sample is required for GC × GC-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 GC × GC-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<sub>bomb</sub>, the measured quantity in ASTM D4809) to net heat of combustion at constant pressure is clearly defined in ASTM D4809 and reproduced here as Eq. (1), the reference enthalpy for the H<sub>2</sub>O and CO<sub>2</sub> products is not entirely clear which could lead to differences

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

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

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

between research labs or industries who may not all be referring to

ASTM D4809. For hydrocarbons, it turns out that (HHV-LHV) = 2.444 MJ/(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 GC × GC-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 [7], 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 [5,6]. Thorough reviews of the literature on the topic are provided by Vozka and Kilaz [8] and by Gautam et al. [9]. 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. [10] 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. [11] 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. [12] and Wang et al. [13] used Fourier transform infrared spectra to correlate with fuel specification properties. Striebig et al. [14] correlated fast (5 min) 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<sup>2</sup> 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 GC × GC-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 [15] 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 [14] and ASTM D4809 [16] 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 the LHV range of conventional jet fuels: 42.9–43.3 MJ/kg [15] and is significantly broader than the range covered by at least one prior work [17] 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 [13,16].

### 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 [18]. As with any data gathering endeavor, this process included evaluation of the reported NIST data. Working together with NIST, all

**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 [15]. 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	12,344	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)	10,301	170.18	2.16	10.1 / 86.1 / 3.7 / 0.1 / 0.0	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.)	12,756	166.00	2.16	0.8 / 96.3 / 2.8 / 0.0 / 0.0	43.90
Gevo	11,498	178.45	2.16	0.0 / 99.6 / 0.1 / 0.0 / 0.3	43.93
A-1	10,264	151.79	2.01	26.1 / 37.5 / 22.9 / 13.6 / 0.0	43.24
C-2	12,223	173.00	2.00	5.2 / 77.5 / 0.1 / 17.1 / 0.2	43.39
C-6	10,279	166.84	1.99	7.5 / 8.9 / 83.1 / 0.5 / 0.0	43.30
C-3	12,341	179.55	1.97	9.2 / 45.2 / 31.7 / 13.6 / 0.0	43.30
C-7	12,925	169.77	1.97	3.3 / 29.5 / 62.3 / 4.9 / 0.0	43.30
A-2	10,325	158.96	1.94	20.0 / 29.7 / 31.8 / 18.5 / 0.0	43.06
C-5	12,345	135.41	1.92	17.7 / 51.6 / 0.1 / 30.7 / 0.0	43.01
A-3	10,289	166.29	1.89	13.4 / 18.9 / 47.4 / 20.4 / 0.0	42.88
JP-5	10,376	169.00	1.89	13.7 / 18.6 / 47.3 / 20.4 / 0.0	43.00
C-8	12,923	160.39	1.86	13.7 / 21.0 / 38.0 / 27.3 / 0.0	42.90

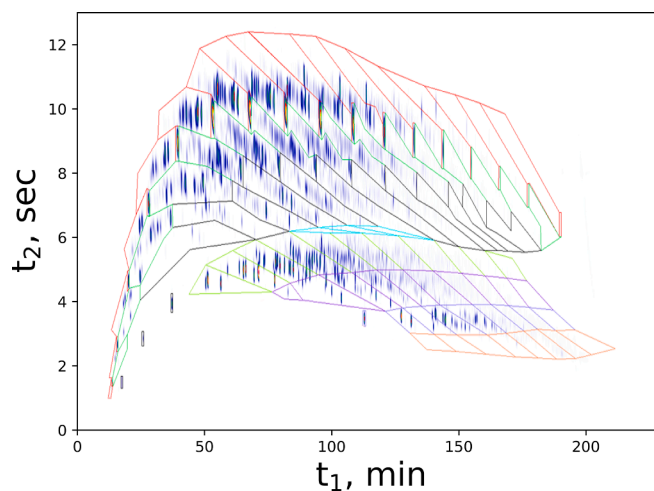
inconsistencies found were resolved before incorporation into our internal database. The NIST database is built from a variety of measurements and analysis methods, resulting in a precision that is an order of magnitude smaller than ASTM D4809 in many cases. The class species concentration data was provided by L. Shafer and has been used previously [7].

The LHV data was provided by T. Edwards [16] and is also available through the Federal Aviation Administration National Alternative Jet Fuels Test Database [19]. 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 GC × GC configuration, the details of which are described by Striebich et al. [20], 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 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 Fig. 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.

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. [5] and by Berrier et al. [6]. 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.



**Fig. 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.

**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	1231	36	0.03
cyc-C12	3232	38	0.01
C9 aromatics	8	6	0.75

In contrast, the fundamental approach is narrower in scope. To rigorously apply the physical model for LHV [3] 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  $0.15 \pm 0.15$  kJ/kg, based on the measurements of Lundberg [21], which is less than 1% of the reproducibility of ASTM D4809. Lundberg investigated a range of mixture fractions of 27 different binary solutions of hydrocarbons in the jet fuel distillation range. 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 [2]. 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 graphic representation of the relationship between real fuel and the database is provided in Fig. 2 where P is a uniform distribution of all possible isomers, M is the uniform distribution of the isomers in the database, and F is the real distribution of the fuel, that could have any shape. While the total population, P could be statistically represented by the model population or the fuel population, this graphic shows that the model and fuel population are related to each other by their respective relationship to the total population. A graphic representation of the simulation methodology is provided in Fig. 3. For each element of the simulation and each hydrocarbon class within that element, a random isomer is selected from the database and decorated with its associated property which is sampled from a normal distribution about its mean reported value. This property is then weighted by the mass fraction of the whole hydrocarbon class, where the mass fraction is sampled from a normal distribution about the GC  $\times$  GC-FID measurement [22]. Upon summing over all hydrocarbon classes, one element of the Monte Carlo simulation is completed. In total, these Monte Carlo simulations were comprised of 10,000 such elements, which has been shown previously [7] to be sufficiently large to achieve sampling convergence.

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

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

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

approach, and is exact as written but for the neglect of  $\Delta H_{mix}$ , 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. When that distribution is used to execute a weighted

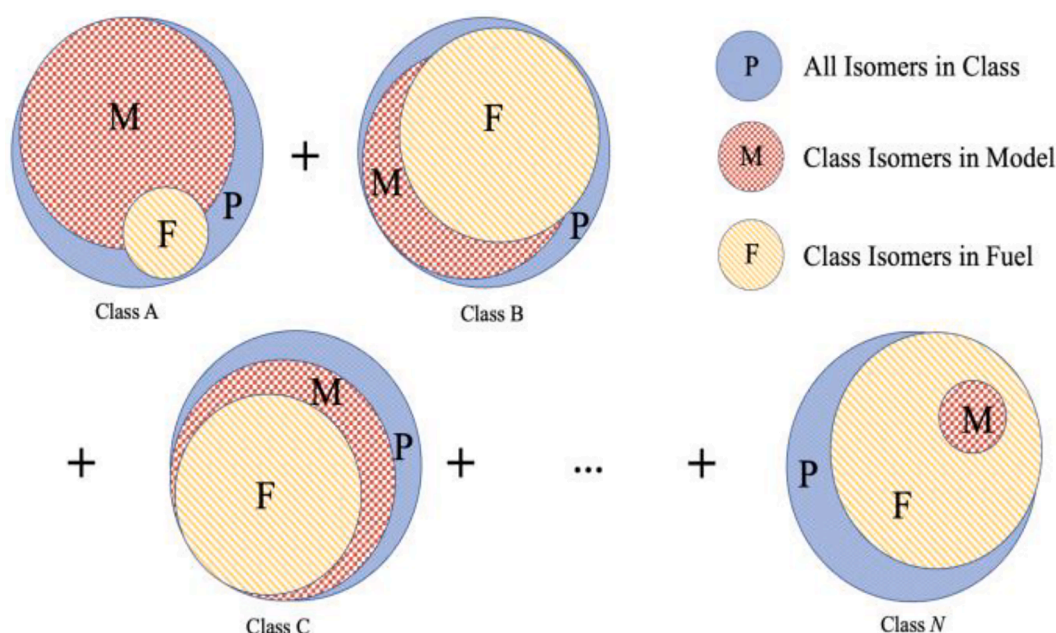


Fig. 2. Graphic representation of fuel to database relationship.

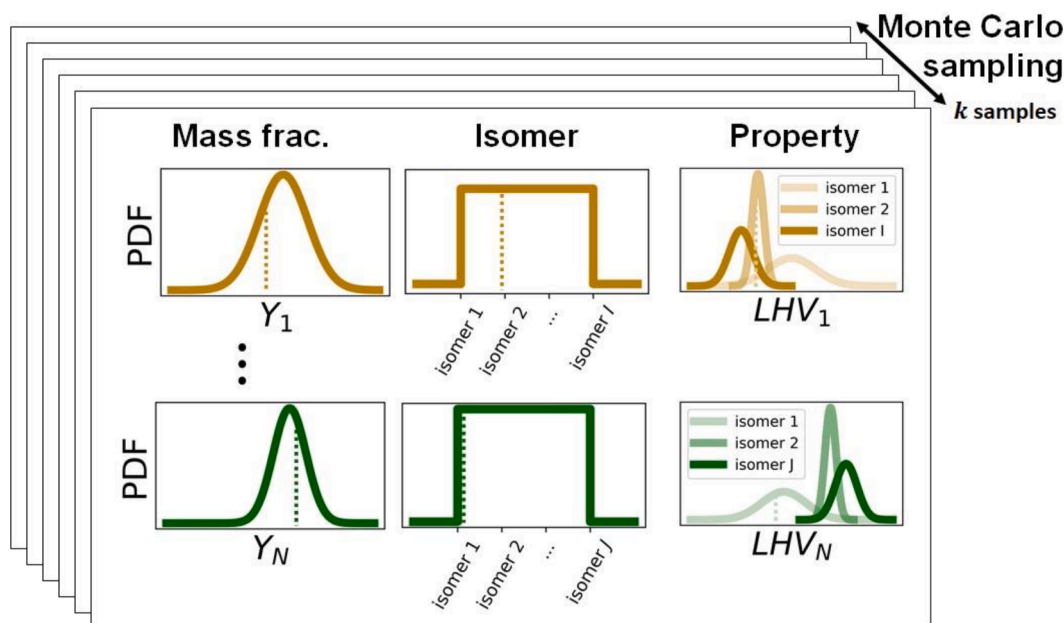


Fig. 3. Graphic representation of the simulation sampling methodology.

sum of the heats of formation of each molecule in that class, the average heat of formation ( $\Delta\bar{H}_{fj(l)}$ ) for class,  $j$  results. 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 Eq. (4), where  $X_j$  and  $Y_j$  are the number of carbon and hydrogen atoms in class  $j$ , respectively.

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

The total differential of  $HHV_{fuel}$  as expressed through Eqs. (2)–(4)

produces seven terms (not nine because  $X_j$  and  $Y_j$  are constant), and the differential elements such as  $(d HHV_{fuel})$ ,  $(d c_j)$ , etc. can be replaced by any (consistent) metric of change or uncertainty – 95 percentiles were used for this work - to derive an expression for the uncertainty in the higher heating value, by quadrature addition. The two terms relating to the uncertainty in the heats of formation of gaseous carbon dioxide and liquid water have been neglected in this work since those quantities are very well known compared to the heats of formation of most hydrocarbons. That leaves five terms. Three of these terms relate to the uncertainty in the hydrocarbon class concentration measurements and

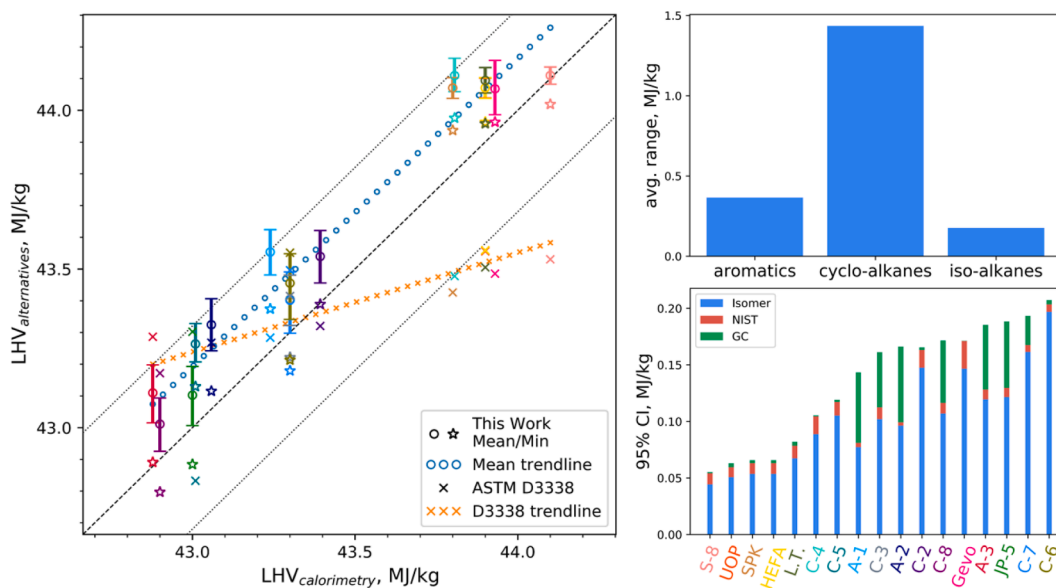


Fig. 4. (Left) Unity plot comparing three methods of LHV determination. The black dotted lines correspond to the reproducibility (95 percentile) of ASTM D4809 test method. The colored circles represent the mean value of the fundamental approach and the colored stars represent the minimum determined LHV 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 arising from the reported uncertainties of the thermo-chemical reference data. Green bars represent the contribution arising from the GC  $\times$  GC-FID concentration measurement. (Upper Right) Range of LHV values, averaged across carbon number for each category, arguing for its eventual inclusion as an acceptable method for LHV determination in the ASTM D7566 (and D1655) fuel specifications.

their sum is designated as A in Eq. (5). Since the sum over all mole fractions must always be exactly one, that is placed as a constraint. In principle, term A could be evaluated by quadrature addition of each component uncertainty, but we chose to use Monte Carlo analyses for convenience. Term B as defined in Eq. (6) accounts for the uncertainties associated with the data pulled from the NIST database, and it too could be evaluated analytically. Since the population distribution of isomers in class, j which is designated by  $c_{ij}$  in Eq. (3) is unknown, it has been approximated by a uniform distribution which is designated by  $\bar{c}_{ij}$  in Eq. (6). Term C as defined in Eq. (7) accounts for the uncertainties arising from the unknown population distribution of isomers within each hydrocarbon class. Evaluation of term C must be accomplished via Monte Carlo analyses. The  $\sigma$  in Eq. (7) notionally represents the 95 percentile confidence interval of the modeled isomer population distribution for each hydrocarbon class. These three terms, A, B and C are captured for each simulation and their resulting values are shown in the lower right of Fig. 4.

$$A = \sum_j \sigma c_j^* X_j^* \Delta H_{f,CO2(g)} + 0.5^* \sum_j \sigma c_j^* Y_j^* \Delta H_{f,H2O(l)} + \sum_j \sigma c_j^* \Delta \bar{H}_{f,j(l)} \quad | \quad 1 = \sum_j c_j \quad (5)$$

$$B = \sum_j c_j^* \sum_i \bar{c}_{ij}^* \sigma \Delta H_{f,i,j(l)} \quad (6)$$

$$C = \sum_j c_j^* \sum_i \sigma c_{ij}^* \Delta H_{f,i,j(l)} \quad | \quad 1 = \sum_i c_{ij} \quad (7)$$

## 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. While the population distribution of synthesized isomers is unknown for most samples, farnesane by Amyris (ASTM D7566.A3) is primarily a single isomer, synthesized through a biological mechanism and alcohol-to-jet fuel by GEVO (ASTM D7566.A5) is primarily two isomers, made from isobutanol. 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, heat of formation needed to be determined experimentally. By incorporating *ab initio* calculations, as has been done recently [23,24], 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 mean that would result by sampling from a Boltzmann population distribution. 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 Fig. 4, a comparison is made between this work and two other methods; ASTM D4809 (calorimetry-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  $R^2 = 0.39$ ),

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 Gibbs 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 Fig. 4. 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 inter-laboratory 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 [15] 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 Fig. 4 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

**Table 3**  
Statistic of alternative LHV methods

	This Work	ASTM D3338
Mean Error (ME)	0.179	-0.073
Mean Absolute Error (MAE)	0.179	0.285
Mean Square Error (MSE)	0.039	0.099
Coefficient of Determination ( $R^2$ )	0.765	0.398
Slope	0.971	0.314

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 Fig. 4, 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 Fig. 5. On the left side, LHV is plotted as a function of H/C, highlighting 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.

### 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% of the LHV data, calculated as described above, is plotted in Fig. 6 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 Fig. 6, 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 Fig. 7, 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 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 [15]. 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 GC × GC-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

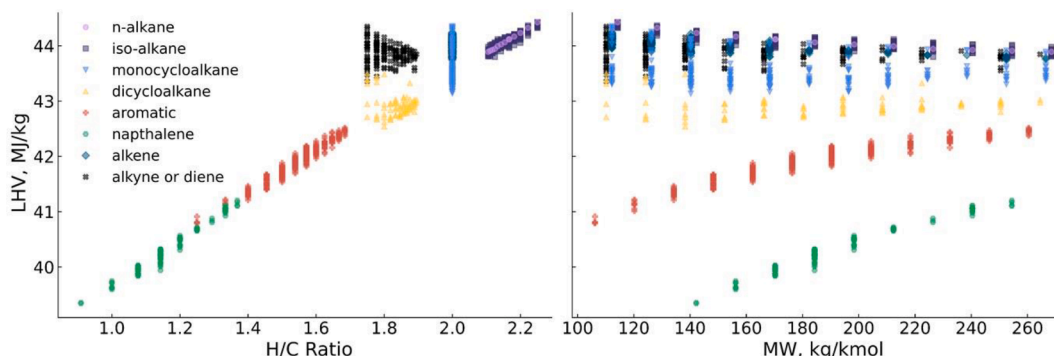


Fig. 5. Heat of combustion variation within hydrocarbon classes.

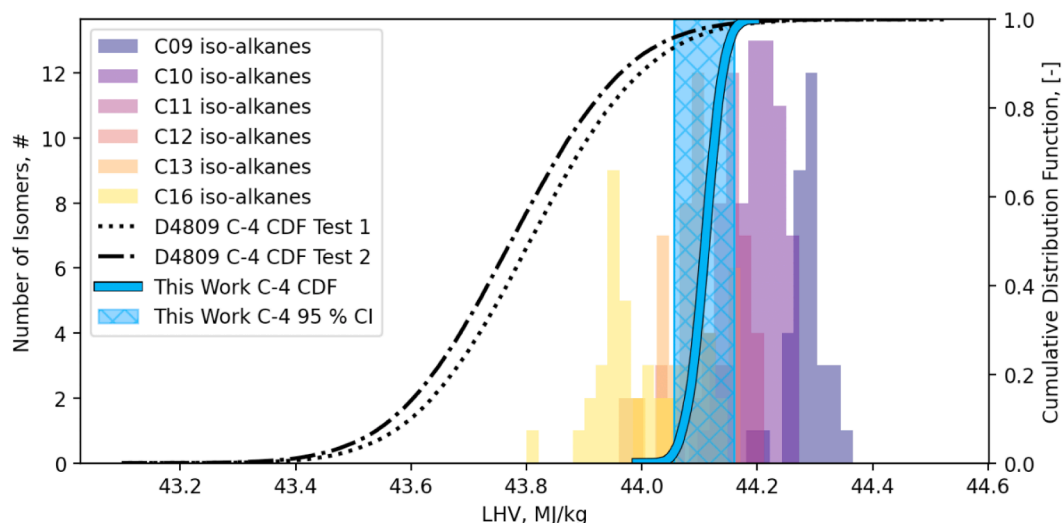


Fig. 6. The histograms from the six major hydrocarbon classes are compared, left vertical axis. The (imagined) cumulative distribution function for two ASTM D4809 measurements (dotted and dash-dot line) and this work's Monte Carlo simulation (black outlined teal line) are compared, vertical right axis. The 95% confidence interval for the simulation of this work are bounded by the teal hashed and filled region, vertical right axis.

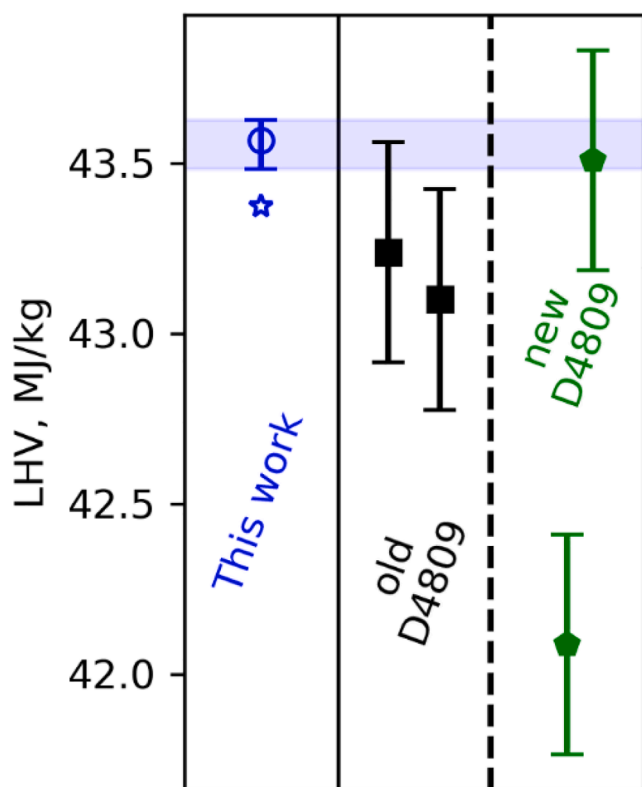


Fig. 7. Comparison of LHVs from ASTM D4809 testing and determinations from this work. All error bars represent the 95% confidence interval for reported method. Initial ASTM D4809 data, black squares or 'old D4809', is compared to recently tested measurement results, green pentagons or 'new D4809', and this work, an open blue circle.

between these two bounding assumptions is 0.13 MJ/kg.

#### CRediT authorship contribution statement

**Randall C. 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 C. Bell:** Data curation, Validation, Investigation, Visualization, Writing – review & editing. **John Feldhausen:** Data curation, Software, Validation, Investigation, Visualization, Writing – review & editing. **Joshua S. Heyne:** Conceptualization, Funding acquisition, Writing – review & editing.

#### Declaration of Competing Interest

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

#### Acknowledgements

This research was funded by the U.S. Federal Aviation Administration Office of Environment and Energy through ASCENT, the FAA Center of Excellence for Alternative Jet Fuels and the Environment, project 065a through FAA Award Number 13-C-AJFE-UD-026 under the supervision of Dr. Anna Oldani. Any opinions, findings, conclusions or recommendations expressed in this material are those of the authors and do not necessarily reflect the views of the FAA.

#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.fuel.2021.122542>.

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1. Report No.	2. Government Accession No.	3. Recipient's Catalog No.	
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7. Author(s)		8. Performing Organization Report No.	
9. Performing Organization Name and Address		10. Work Unit No. (TRAIS)	
		11. Contract or Grant No.	
12. Sponsoring Agency Name and Address		13. Type of Report and Period Covered	
		14. Sponsoring Agency Code	
15. Supplementary Notes			
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17. Key Words		18. Distribution Statement	
19. Security Classif. (of this report) <b>Unclassified</b>	20. Security Classif. (of this page) <b>Unclassified</b>	21. No. of Pages	22. Price