

CRC Report No. AV-29-20

**A REVIEW OF CURRENT
EXPERIMENTAL AND CORRELATION
METHODS TO DETERMINE THE
CALORIFIC ENERGY CONTENT OF
LIQUID FUELS**

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Coordinating Research Council Project AV-29-20

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EXECUTIVE SUMMARY

Aviation fuel energy density by mass or volume, also known as heat of combustion or specific energy, can be measured directly by complex calorimeters requiring skilled operators, or, more simply by using estimation methods based on standard specification parameters and correlations, the latter coming with caveats regarding reliability. Each technique has strengths and weaknesses. Energy density is a basic requirement in all aviation fuel specifications and has a direct pro rata impact on engine and aircraft fuel consumption so is a critical parameter for support of engine and aircraft performance measurement and flight range/load carrying capacity.

There is increasing focus on accurate energy density measurement supporting engine/aircraft performance improvement, monitoring, load optimisation, CO₂ reduction combined with market changes to increase use of synthetic blends. These developments are challenging the established relationship between fuel composition and energy density.

Direct determination and estimation methods have been around for many years but a detailed and critical examination with respect to relevance to current fuels and the latest specification tests and equipment is now warranted.

Responding to this requirement in 2020 the CRC issued a Statement of Work: “A Review of Current Experimental and Correlation Methods to Determine the Calorific Energy Content of Liquid Fuels” designated as CRC Project No. AV-29-20 to commission a study of both estimation and determined methods. This study was designed as a two-phase programme:

- Phase 1 – Literature review of calorific instruments, methods, and correlations.
- Phase 2 – Experimental study.

The CRC subsequently funded Phase I which has supported the preparation of this report.

Starting with the fundamental principles that underpin current methods for determination by calorimeter or estimation by correlation with other parameters and a literature review to offer historic perspective, the report then provides a critical assessment of the state-of-the-art for over a dozen current standard test methods and details over 30 calorimeters. The report also provides a forward-looking insight into the latest technology and techniques that may provide future developments in the measurement or calculation of this important parameter. Additionally, a comprehensive survey of data producers and users has been undertaken to analyse current practices and equipment together with capturing industry requirements for data quality and applications.

In addition to very specific findings for individual methods some major findings common to all methodologies include:

- There is a high degree of commonality across the different national test methods reviewed in this study (ASTM (US), EI (UK), DIN (Germany), Russian and Chinese).
- With particular relevance to EI and ASTM methods, which are the primary focus of the review, the following observations have been made.
 - Basic methodology can be traced back to studies (industry and academic based) carried out in the 1950-70s.
 - Since this time, other test methods which have significant impact on calculated (estimated) heat of combustion methods have been updated which could impact results.
 - Calorimetry equipment has developed in the areas of critical measurement and automation. Current standard test methods do not recognise these developments.

- No formal inter-laboratory survey (ILS), round robin, or extensive cross method (calculated versus determined) comparisons have been carried in the last 20 years.
- There are only limited data sets where determined and estimated (calculated) values are available for the same samples to allow comparison of accuracy. The data that are available shows estimation methods may not always provide reliable results which confirms the caveats that most methods include.
- Changes in conventional jet fuel composition and the increasing prevalence of synthetic fuels challenge the validity of estimation methods. Similarly, potential radical changes in composition for development of a high-octane unleaded AVGAS will challenge estimation methods even further and potentially also impact determination methods where a pure hydrocarbon is assumed.
- The user survey provides an insight into the methods being used, that methods generally met requirements but again highlighted key areas requiring improvement. This view complements the main report and provides useful information to guide further work to ensure it meets industry needs.

In summary, the report demonstrates the standard test methods for determination and estimation require updating to reflect current test methodology and equipment. Precision for determination test methods requires re-assessment and may well be improved with modern equipment. This review failed to find any viable alternative to the basic principle of calorimeter-based measurement systems for assured, accurate, aviation fuel energy content determination.

This report is Phase I of a two phase programme and is provided to guide efforts in Phase II where further method development including experimental work is planned. Some key recommendations include:

- Determination methods require updating to reflect current calorimeter technology. The availability of both normal and high precision methods should be retained.
- Estimation methods need re-assessment of their ongoing validity. Correlations need to be updated (if possible) to account for the changes in fuel property measurement methods and property relationships particularly regarding current and future synthetic blends. The requirement to assess accuracy for the fuel types to which the methods are being applied should be a mandatory.
- Assessment of precision and accuracy of both determined and estimation methods is overdue, but should be carried out following any significant updates brought about by the completion of the CRC Phase II study
- A review of R&D work aimed at predicting many fuel properties from basic laboratory tests and more advanced analytical techniques has provided new insights into both future possibilities and challenges to develop more reliable estimation methods. This work should be reviewed and applied to any update of estimation methods.

Future experimental and method development work needs to be in cooperation with the key stakeholders and in particular the relevant sub-committees that have responsibility for these methods namely, D0.05 and SC-B-10 for ASTM and Energy Institute (IP) methods, respectively.

Given the depth and breadth of these findings and the complexity of the subject in general, discussion with industry members is recommended to understand and agree what future work should be carried out and relative priority of these options. Therefore, it is proposed that following the issue of this report a symposium or workshop is arranged to review and agree future actions including any CRC funded Phase II experimental work.

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1 INTRODUCTION

1.1 GENERAL

Currently measurement of aviation fuel energy density by mass or volume (also known as heat of combustion or specific energy) has to be carried out using complex calorimeter equipment. Strict laboratory conditions and skilled staff are required to achieve good accuracy within the precision of the method being used. Consequently, estimation methods are often adopted. Estimation methods use standard specification test results to provide a means of calculating heat of combustion for a defined scope of fuel types based on correlations. Whilst precision statements based on work during correlation development may appear good, all these methods have caveats that accuracy may well be much worse. Further, actual accuracy can vary for current conventional fuels and is more uncertain for synthetic blends where composition may be outside that used at the time of method development. In addition, the original datasets used to create the correlations may be limited or insufficiently varied to cover modern fuel production.

There is increasing focus on the need for accurate energy density measurement due to the emphasis on engine and aircraft performance, load optimisation, CO₂ monitoring/trading and possibly market changes to promote increased use of synthetic blends. Further, the established (conventional fuel) relationship between standard specification properties, particularly fuel density, and energy density may not always apply. This challenge is likely to become more relevant in future years with increased use of synthetic blends within current blend limits, and even more so if there are moves towards 100% synthetic fuels. The testing of engines and aircraft during development and approval requires accurate energy density determination as this property is critical to performance calculations. Therefore, the availability of accurate energy density data has significant benefits to many users across the aviation industry.

In summary, there is an increasing need for accurate, rapid, and cost-effective data on fuels that are changing in compositional scope.

Energy density measurement and estimation methods have been around for many years but a detailed and critical examination with respect to relevance to current fuels has been neglected. Further, no in-depth review of the latest test equipment has been carried out to assess opportunities for improvement. The CRC and MoD studies which covered all test methods recognised that methods for determined and estimated values warranted further examination (see 2.4). Even a cursory review of ASTM D4809 shows that equipment meeting that specifications requirement still cites the Parr 1261 but this unit was rendered obsolete around 15 years ago and other manufacturers also supply similar systems that warrant review. Examples of modern laboratory bench top units which supersede the Parr 1261 and its contemporaries are in wide use but have not been rigorously evaluated as regards their application within D4809 based on evidence gathered to date.

Therefore, against these changing industry requirements the relevance and applicability of current methods require in-depth review. Further, with advances in equipment, analytical techniques of all kinds and availability of greater computing power it is timely to consider whether new methodology is available to better meet industry needs.

Responding to this requirement in June 2020 the CRC issued a Statement of Work: “A Review of Current Experimental and Correlation Methods to Determine the Calorific Energy Content of Liquid Fuels” designated as CRC Project No. AV-29-20 [ref. 1] to commission a study of both estimation and determined methods. This study is designed as a two-phase programme:

- Phase 1 – Literature review of calorific instruments, methods, and correlations.
- Phase 2 – Experimental study.

The following review and report has been prepared by CLFC Ltd to cover Phase 1 – Literature review of calorific instruments, methods, and correlations, following a successful technical proposal [ref. 2].

1.2 REPORT METHODOLOGY

This report has been compiled based on a critical review of standard test methodology, both by determination and estimation (calculation), equipment, and associated test methods. The aim has been to understand the state-of-the-art, impact on the final results and all pertinent information and data. Further dialogue with key individuals and companies has been undertaken. The scope of literature searches and discussion have covered both historic data that support current test methodology and equipment together with looking forward to the latest technology and techniques. Such innovation could provide future developments in the measurement or calculation of this important parameter.

The report starts by reviewing the fundamentals of the various test methods such that the reader can understand and interpret the review that follows. Data have been collected and collated from many sources including:

- National/International standard test methods.
- Review of available research reports cited in these methods.
- Academic papers on relevant subjects.
- Literature search and dialogue with equipment manufacturers.
- Dialogue with the relevant working groups in ASTM and Energy Institute.
- Discussions with workers on Research and Development (R&D) programmes including those developing new analytical techniques to define fuel composition and computational modelling to predict fuel properties.

Additionally, a survey has been undertaken to capture and analyse current practices and equipment actually in use. Further, the survey examined industry requirements for data quality versus application. This has been carried out in two phases, firstly as part of the CRC study and secondly as part of the 2021 ASTM PTP (JF2103) survey. The results of the survey are reported in section 10 and should be read in conjunction with the relevant sections of the main report.

Following a critical review of the current state of the art and industry practice, the report reviews emerging technologies. These include fuel analytical and computational techniques that could support future developments in heat of combustion calculation as well as searching for any disruptive developments in heat of combustion calorimetry.

The report then includes an overall discussion, conclusions, and recommendations with particular reference to potential activities in Phase II of the project.

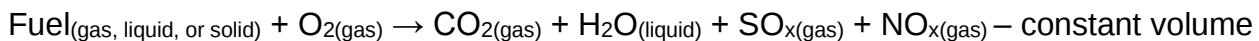
2 BACKGROUND, DEFINITIONS AND TERMINOLOGY

2.1 HEAT OF COMBUSTION DEFINITIONS

The definitions of gross and net heat of combustion are common across all industry methods since they represent fundamental properties and are defined as follows:

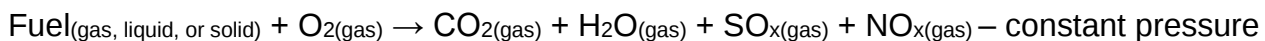
2.1.1 GROSS HEAT OF COMBUSTION

This is the amount of energy released when a unit mass of fuel is burned in oxygen in a constant volume enclosure, with the products being gaseous, other than water that is condensed to the liquid state. The fuel can be either gas, liquid or solid, and contain the elements carbon, hydrogen, nitrogen, oxygen, and sulphur. The products of combustion, in oxygen, are gaseous carbon dioxide, nitrogen oxides, sulphur dioxide, and liquid water. Commonly, as defined within the method the energy released is defined at the standard temperature of the test – typically 25°C.



2.1.2 NET HEAT OF COMBUSTION

This is the amount of energy released when a unit mass of fuel is burned at constant pressure, with all the products, including water, being gaseous. The fuel can be either gas, liquid or solid, and contain the elements carbon, hydrogen, oxygen, nitrogen, and sulphur. The products of combustion, in oxygen, are carbon dioxide, nitrogen oxides, sulphur dioxide, and water, all in the gaseous state. By definition, the combustion takes place at a constant pressure of 101.325 kPa (1 atm), and again 25 °C is the initial temperature of the fuel and the oxygen, and the final temperature of the products of combustion.



Note that some documents use the term lower heat value or simply heat of combustion which is equivalent to Net Heat of Combustion.

2.1.3 GROSS VS NET HEAT OF COMBUSTION

Gross Heat of Combustion is the value obtained directly from a determination within a bomb calorimeter of fixed volume. Under normal gas turbine combustion conditions to a first approximation the pressure is constant within the combustion zone, and products are exhausted in gaseous form. Therefore, the Net Heat of Combustion more closely relates to these conditions. Net Heat of Combustion is therefore calculated from the gross value and reported. Note that engine performance calculations will be based on Net Heat of Combustion (as defined above and within standard test methods) as reference units but will have corrections specific to particular scenarios. This applies to both reciprocating and gas turbine engines.

In this report the term gross and/or net “heat of combustion” has been adopted for general use.

2.1.4 SPECIFIC ENERGY

Energy Institute (IP) test methods and Defence Standard fuel specifications use the term Specific Energy. Strictly speaking this should be defined as Net Specific Energy. Net Specific Energy is equivalent to Net Heat of Combustion. ASTM and other international methods generally cite gross and/or Net heat of combustion with Net typically quoted by default and featured in specifications.

2.1.5 ENERGY DENSITY

In more academic work the terms energy density per unit mass or per unit volume are often cited. Energy density per unit mass is taken as equivalent to Net Heat of Combustion. Energy per unit volume is calculated using the density of the fuel.

2.1.6 ENERGY EQUIVALENT

All bomb calorimetry systems have at their core a unit (usually a bucket containing stirred water and the bomb) which captures the heat released. The heat capacity of this system is expressed as the “energy equivalent” or sometimes “water equivalent” as the energy in joules (or other heat units) required to raise the system 1°C. Using this value multiplied by the temperature rise therefore gives the total heat released.

2.1.7 UNITS

Most methods are now in SI units. In SI heat of combustion has the units J/kg, but for practical use a multiple is more convenient. The MJ/kg is therefore most widely used for the representation of heats of combustion of petroleum fuels.

For older methods and data which may use other units the following conversion factors are defined as:

- 1 cal (International Table calorie) = 4.1868 J
- 1 Btu (British thermal unit) = 1055.06 J (rounded to 2 decimal places for practical purposes)
- 1 cal (I.T.)/g = 0.0041868 MJ/kg
- 1 Btu/lb = 0.002326 MJ/kg
- 1 atm = 0.101325 MPa

2.1.8 DETERMINATION AND ESTIMATION METHODOLOGY

There are fundamentally two distinct methods of producing heat of combustion data.

1. Carrying out a direct measurement of heat released under controlled conditions. Results obtained by such experimental procedures will be referred to in this document as **“determined values”**
2. Predicting or estimating a heat of combustion from other fuel parameters based on established correlations. These methodologies can be referred to as “estimated”, “calculated” or “predicted” values. This report will adopt the most widely accepted (based on specification test titles) and most accurate terminology of **“estimated values”**.

2.2 HEAT OF COMBUSTION REQUIREMENTS WITHIN FUEL SPECIFICATIONS.

All aviation fuel specifications require the net heat of combustion to be measured and meet minimum requirements with a range of test methods being offered. Most specifications allow the use of both determined and estimated values citing methods defined by organisations most closely allied to the fuel specification.

Table 1 below provides an overview of major international aviation fuel specifications and associated requirements.

2.3 STANDARD HEAT OF COMBUSTION TEST METHODOLOGY

Table 2 provides an overview of all widely recognised bomb calorimeter determination methods and Table 3 provides an overview of all widely recognised estimation methods. Both these latter Tables cover all methods as cited in internationally recognised specifications listed in

Table 1 and include some obsolete/historical methods for completeness [ref. 3- 15]. The following sections examine in detail the calorimeter determined value test methodology and associated equipment and then the estimation (calculation) methods.

Grade or Type	Fuel Specification	ASTM				IP		Others				Notes
		D3338 &/or D3338M	D4529	D4809	D240	IP12	IP381	GOST 11065	GOST 21261	GB/T 384	BG/T 2429	
Jet A/A-1 - AVTUR	91-091	X		X		X						Measurement method by agreement
	91-087	X		X		X						Measurement method by agreement
	JP-8	X	X	X		X						
	ASTM D1655	X	X	X		X						
	ASTM D7566	X	X	X								
	GOST 10227 TS-1/RT							X	X			
	GB6537 No 3									X	X	
	GOST R52050	X	X	X		X	X					
High Flash - AVCAT	91-086	X		X		X	X					Measurement method by agreement
	JP-5	X	X	X								
Wide-Cut AVTAG	91-088	X		X		X						Measurement method by agreement
	D6615	X	X	X								
	JP-4	X	X	X								
	GOST 10227-86 T2							X	X			
Jet C-1	ASTM D7223	X	X	X								
Evaluation Process	ASTM D4054			X								Estimation methods require validation
AVGAS	D910	X	X	X								
	D7547 (Unleaded Avgas)	X	X	X								
	D6227	X	X	X								
	D7719			X								
	D7690			X								
	Def Stan 91-090	X		X		X						
	Russia GOST 1012-72								X			
	China GB 1787—2018									X		
Notes												
Quoted Method		X										
Referee Method												
Estimation Method												
Determination Method												

Table 1: Fuel Specifications and Associated Heat of Combustion Requirements.

Test Method Measurement	Date	W=Withdrawn C=Current	Summary	Modes of Operation AD= Adiabatic. IS=Isothermal IP=Isoperibol O=Other	Repeatability MJ/kg net	Reproducibility MJ/kg net	Stated Bias MJ/kg	Key supporting methods
IP12	1993	C	Bomb Calorimetry	IS, AD	0.276	0.773	None	Hydrogen Sulphur
D240	2019	C	Bomb Calorimetry	IS, AD	0.13	0.40	None	Hydrogen Sulphur
D4809	2018	C	Bomb Calorimetry - High Precision	IP, AD	All Fuels = 0.096 Non-volatile = 0.099 Volatile = 0.091	All Fuels = 0.342 Non-volatile = 0.234 Volatile = 0.450	0.089	Hydrogen Sulphur
D2382	1988	W	Bomb Calorimetry - High Precision (Historic Interest)	IP, AD	Jet fuel = 0.051 Avgas = 0.072	Jet fuel = 0.130 Avgas = 0.279	None	Hydrogen Sulphur
GB/T 384	1981	C	Bomb Calorimetry (partial translation only)	???	0.126	??	??	Hydrogen Sulphur
GOST 21261	1991	C	Bomb Calorimetry	IS, AD	0.130	0.445	None	Hydrogen Sulphur

Table 2: Standard Test Methods – Determination by Bomb Calorimeter.

Test Method Estimate	Date	W=Withdrawn C=Current	Summary	Repeatability MJ/kg net	Reproducibility MJ/kg net	Stated Bias MJ/kg	Input Parameters
D3338	2020	C	Estimation Reference to: D1405 D4529	0.021	0.046	None	Density, Aromatics, Distillation
D4529	2017	C	Estimation (with ASTM D611) Uses a single equation	0.012	0.035	None	Aniline Point API Gravity or Density
D1405/1405M	Obs	W	Precursor to ASTM D4529 Uses 4 equations for different fuel groups	0.012	0.035	None	Aniline Point API Gravity or Density
IP355	Obs	W	Estimation	0.05	0.06	None	Density, Hydrogen and Sulphur
IP 381	1997	C	Estimation (ISO 2977)	0.012	0.035	None	Aniline Point API Gravity or Density
GB/T 2429	1988	C	Aniline Gravity			None	Aniline Point API Gravity or Density
GOST 11065	1990	C	Aniline Gravity	0.012	0.035	None	Aniline Point API Gravity or Density

Table 3: Standard Test Methods – Estimation Methods.

Note all methods provide means of correction for the presence of sulphur if required.

2.4 PREVIOUS RELEVANT FUEL SPECIFICATION REQUIREMENT STUDIES

The CRC commissioned a study to review the suitability of aviation fuel test methodology primarily focussed on ASTM standards [ref. 16] and their ongoing relevance [ref. 17] which was issued in 2018. This was very comprehensive and covered all test methods. However, due to the wide scope it was unable to go into great depth on heat of combustion methods. The study raised some key concerns and issues for both determined and estimated methods. These have been recognised as part of the thinking behind the current review and examined in greater detail.

Such issues are still valid and have been incorporated into this study including but not limited to:

- Concerns with estimated method due to the number of assumptions on which the defined relationships between specification parameters and heat of combustion rely.
- Concerns over the use of estimation methods versus general changes in conventional fuel composition over time and increasing use of novel blends which could have composition outside the limits prevalent at the time these methods were developed.
- The fact that aniline gravity-based methods are based on relationship that were developed in the 50's and 60's.
- In the discussion section the review notes the relevance and application of estimated (quick and easy) versus determined (slow and costly), each having a place in the list of acceptable methods.

Similar to the CRC study the UK Ministry of Defence (MoD) commissioned a comprehensive review of Defence Standard aviation fuel specification methods. This survey [ref. 18] reviewed the history, origins and development of test specification requirements, their applicability and relevance, and future developments. Originally published in 1997 and updated in 2008 this document again covered all fuel specification requirements. The review raised some key points on estimated and determined heat of combustion requirements and test methods that remain relevant today. A summary of the findings of this study are provided in Annex I.

Numerous industry studies and surveys of aviation fuels have been undertaken. While not addressing heat of combustion methodology per se they have at least reported some limited results. The numbers of samples and scopes of these studies have varied considerably. They do, however, provide at least a starting point to compare estimated versus determined values when calorimeter determined values and the required specification parameters have been reported for the same samples. This has been examined in Section 7.

2.5 THE COMBUSTION PROCESS

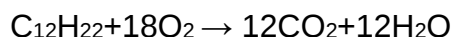
Whilst an in-depth discussion of the thermochemical and thermophysical processes of combustion are outside the scope of this report it is worth summarising the key steps in the process. This is important to place the discussion on bomb calorimetry and estimation method discussions in context.

The key steps starting with a liquid fuel are:

1. Energy input to evaporate the hydrocarbon liquid phase to a gas phase.
2. Energy input to break (cause dissociation) of all the chemical bonds for example C-C, C=C, C-H. The energy to break these bonds will vary according to the position of the bond within the molecule and the type of molecule, for example, normal, isomerised or cyclic paraffins, olefins, single or multi-ring aromatics and derivatives thereof. Molecules containing sulphur and other heteroatoms will also undergo dissociation if present in the fuel.
3. Activation energy required to start the reaction and the heat released from the (complete) oxidation of the C, H and S to form CO₂, H₂O and SO_x, respectively.

4. Heat released by the condensation of products (water) if this occurs.

The typical combustion reaction for a jet fuel can be approximately represented by the following equation where $C_{12}H_{22}$ is the simplified jet fuel composition representation most commonly cited:



In bomb calorimetry oxygen is typically used at high pressure, 30 atmospheres, to ensure complete combustion. This can change the reaction route and final products compared to a typical combustion system and therefore must be corrected.

Any trace Sulphur will be converted to sulphuric acid due to water also being formed in the process versus in typical combustion systems where the exhaust would be SO_x . For example, the equation below shows the formation of SO_3 which would normally exit the engine exhaust as such but within the calorimeter a further reaction occurs to form sulphuric acid.



Any trace Nitrogen can under certain high temperature conditions form oxides collectively referred to as NO_x , comprising mainly NO but also NO_2 and N_2O . Again, the assumption is that these would exit the engine exhaust as such but under calorimeter conditions would form nitric acid, and like the sulphuric acid require correction. The levels of such compounds in jet fuel is expected to be negligible. NO_x may also be formed from the residual air trapped in the bomb prior to pressurisation with oxygen, again providing a source of NO_x but again at low levels. The formation of NO_x is very complex but the simplified reaction is shown below with the subsequent formation of nitric acid.



Within an internal combustion engine only NO_x and SO_x tend to be formed due to the different conditions and thus this variation in reactions must be accounted for as described below.

It is relevant to note that step 4, condensation of gaseous water, may or may not occur and therefore must be accounted for in the correction from gross to net values.

These steps give the overall heat released (chemical energy) by the fuel which is in essence the heat release from the combustion of free radical C, H and S less the energy needed to get to that point. The heat released from the formation of CO_2 , H_2O and SO_x (step 3) is well established as is the energy to break individual bonds prior to this (step 2). However, the complex composition of aviation fuels is such that it is been thus far impossible to calculate the overall energy required for step 2 for a given fuel (see section 7.3 for more detail examination). Therefore, to determine the heat of combustion there are only two possible methods:

- **Direct Determination (Measurement) Using Bomb Calorimetry** by combusting fuel within a calorimeter system under controlled conditions.
- **Estimation (by Calculation)** based on broad fuel compositional data to account for the different molecules in terms of type, molecular weight, volatility, and relative concentration.

These two primary approaches as currently in use are the subject of this review. Later the review addresses the latest developments in analytical and computing techniques that may offer the capability to improve on estimation methods (see section 11).

2.6 FUEL COMPOSITION IMPACT ON HEAT OF COMBUSTION MEASUREMENT.

The overall heat of combustion of a given fuel is summation (assuming ideal behaviour) of the physical and chemical properties of all the constituent components to go through the steps defined above from fuel to CO₂, H₂O and oxides of any trace impurities (if present). For calorimeter measurements, these processes are performed for all the components and their contribution measured as a total heat released despite there being many hundreds or thousands of identifiable components. The one caveat is that the scope of the very detailed test methodology and procedures and calibration must be proven for the range of fuels to be measured. This is particularly relevant for fuels which contain heteroatomics in significant quantities, which may change the required calculations and corrections for the formation of water, etc. This therefore applies to potential composition changes, for example, as being currently assessed in the development of high-octane unleaded AVGAS.

The challenge for estimated (calculated) values, based on broad compositional data, is to account for this complex mixture and assumed overall compositional data that is built into the correlations versus the variations within these broad groups. These assumptions will be based on the scope of fuels used in the original correlations and the validity of this is discussed in section 7.3.

3 OVERALL IMPACT OF HEAT OF COMBUSTION

3.1 RELEVANCE OF HEAT OF COMBUSTION TO ENGINE AND AIRCRAFT OPERATION

Fuel heat of combustion is of fundamental importance in aviation. Prior to the review of determination and estimation methods to quantify this property, an insight into its relevance is provided below. As will be seen, with growing pressure on the industry to manage CO₂ emissions, heat of combustion has a key role to play in many areas including in support of engine and airframe development, testing, certification and production testing, and in service, aircraft fuel loading optimisation.

At a basic level net heat of combustion testing or calculation is required to ensure that a fuel has sufficient energy content to meet minimum specification requirements, 42.8 MJ/kg net for Jet A/A-1 or 43.5 MJ/kg net for AVGAS 100LL. This will ensure that that an aircraft will have sufficient stored energy for the planned flight. Also, this parameter has a direct impact on engine fuel flow/consumption. The chemical energy released which can be used in the combustion systems depends on the actual operating conditions. For consistency of units and the closest representation of this net heat of combustion is used (see definitions 2.1). This can be estimated based on correlations with other parameters or measured by bomb calorimetry. Estimated values are always based on correlations which give a net value directly whereas, as explained in section 2.1, due to the unrepresentative conditions in the bomb, this gives a gross value and must be corrected to the net value.

Gas turbines and reciprocating engines convert chemical (heat of combustion chemical energy) energy to rotational power (shaft horsepower) and/or thrust, i.e. mechanical energy. The efficiency of conversion is wholly dependent on the engine design and operating conditions. The required power will be demanded, and the engine will adjust fuel flow to provide it. The flow is not actually volume or mass but energy. Mass or volume flow will be a function of energy content by mass or volume. These latter two terms are related by density.

For example, this was noted in the Air New Zealand flight test of a Hydrotreated Esters and Fatty Acids (HEFA)¹ based blend [ref. 19]. When changing from a typical Jet A/A-1 to the HEFA blend with a fixed overall engine pressure ratio (EPR) as a measure of thrust of 1.4, a 1.07 percent lower mass fuel flow that was observed on the engine run of the HEFA jet fuel blend. This was consistent with the 1.08 percent higher energy density per unit mass of the HEFA fuel blend which was determined experimentally.

It is important to note that for aviation turbine engines, changes in fuel consumption on different fuels is not a change in engine efficiency. Fuel consumption changes due to fuel properties and the efficiency of chemical to mechanical energy does not actually change, only the required mass or volume flow to achieve the required energy flow. However, overall aircraft efficiency can be affected as discussed in section 3 .

Aviation piston engines represent a more complex case as fuel flow may also be used to control cooling and detonation under certain flight conditions. However, whilst the calculations and indeed actual values are different the same principle applies. Like turbine engines, for a given fuel octane / engine combination, energy content remains influential to flight range or conversely the required fuel load for a given flight.

¹ Referred to in the report as Bio-SPK which was subsequently formally named HEFA within ASTM D7566 specification.

In any type of engine if the fuel energy density is significantly reduced from design assumption values fuel delivery and control systems may reach maximum flow capacity before full rated power is reached and may in the long run cause increase fuel system wear.

Therefore, with more granularity than just ensuring minimum requirements are met this property will have impact or can be used to optimise operations in several ways. Further, since achieving accurate values by measurement are costly there is a balance between measured and estimated that is changing such that more accurate data at the airport, for example, could pay dividends.

Some examples of where heat of combustion has a direct impact and where better or more convenient methods would yield benefits include:

- **Aircraft Loading** is calculated based on volume and/or mass loading to meet the requirements of the planned flight. However, the aircraft actually needs an “energy load” to meet the range required with some safety margin. Calculations of fuel loading therefore use estimations of the actual fuel load that will be consumed. This is often based on fuel density as this is the only information readily available with an assumed or estimated energy value. Significant uncertainty has to be recognised and therefore additional load for safety margin will be applied. It has been shown that optimising fuel load could save at least 1-2% fuel consumption and therefore CO₂ reduction. Since fuel load could be optimised, increased loading of cargo and/or passengers could be taken on or range extended. In either case the carrier has the potential to improve fuel loading and therefore reduce environmental impact and reduce fuel costs. Currently fuel represents roughly between 30% to 50% or more of direct carrier operating costs. This optimisation, and hence saving, could only be achieved by having accurate energy density at time of fuel loading since almost all fuel supply systems are fungible and it is critical to measure the actual fuel being loaded.
- **Synthetic Fuel Blends**, which will be increasingly used to mitigate CO₂ footprint, tend to have different density and energy density (by mass and volume) compared to typical conventional fuels. Further, the relationship between density and energy density is different. Therefore, aircraft loading calculations will be sub-optimal and carriers may be unable to use the potential of these fuels based on different energy content. Data presented during approval of synthetic blends have shown that blends approaching the maximum of 50% synthetic often have atypical density towards the 775 kg/m³ lower limit - see ref. 19 as a prime example. More interestingly, the energy density can be around 1% greater per unit mass but 2% less per unit volume. It has been shown that use of such high energy per unit mass could provide up to 1% reduced fuel consumption by lowering the required fuel (mass) loading. Again, this difference could only be exploited if the density and energy density were known accurately at the time of fuel loading. In summary, a means of accurately measuring heat of combustion in the field would facilitate further loading optimisation to exploit the specific properties of synthetic blends than is possible at present.
- **Fuel Purchase** practise is to purchase by volume, yet, the aircraft loading calculations are by mass (actually energy is needed but estimated as stated above). Whilst this system works well it has been shown that significant margins need to be built in to compensate for lack of accuracy. This means excess fuel is both being purchased and carried with penalty. Apart from only purchasing the fuel required, the ability to know energy content could create a new purchasing paradigm where the carriers purchase energy somewhat as per electricity and gas. This ability becomes even more relevant with synthetic blends. Not only would the purchaser be more able to load the energy required but also deal with the different properties of fuel manufacturing and supply cost. For example, synthetic blends may have 1% more energy per unit mass and so less mass is required, purchasing by volume will require about 2% more and so attract a price premium due to the higher volume

purchased – on top of the premium due to specialist manufacture. Therefore, optimising purchasing either to only buy the fuel required and/or purchasing by energy could provide commercial benefits to the manufacturer and carrier.

- **Aircraft Performance Monitoring** is often carried out to ensure the engine and aircraft meet fuel consumption contractual requirements and record trends for system health monitoring. Again, accurate energy density as delivered would reduce errors due to estimated values. Currently it is very difficult (if not impossible) to get fuel density/energy density data during commercial operations across many airports. Individual aircraft consumption, if known accurately, could be used for flight profile optimisation, for CO₂ reduction and monitoring of operations, for example.
- **During Aircraft/Engine Development, Certification and Production Pass-Off Testing** the ability to know energy density accurately is essential for accurately calculating engine performance and efficiency (often called specific fuel consumption). Fuel consumption is measured and then corrected to a datum value such as fuel specification minimum of 42.8 MJ/kg. Again, actual measured values provide better assurance of accuracy but incur a cost and logistic penalty compared to estimated values.

3.2 HEAT OF COMBUSTION IMPACT ON AIRCRAFT LOADING – ILLUSTRATIVE EXAMPLE

As an illustrative example of the impact of fuel heat of combustion and density on aircraft loading, range, payload, and CO₂ emissions data provided in a study carried out by Blakey et al. [ref. 20] has been extracted and summarised below².

Ref. 20 “Fuel effects on range versus payload for modern jet aircraft” modelled 3 types of aircraft ranging from a small business jet (Gulfstream G500) through short haul Boeing 737 (737-300-CFM563B1) and long haul 747 (747-200B-RB211-S24D4) using a range of techniques and using some basic assumptions on a range of hydrocarbon and other fuels. Thus, the impact of changing fuel properties can be seen.

The basic relationship between fuel density and heat of combustion used is shown in Figure 1. This is similar to that shown later in this report – see Figure 9.

Based on this relationship (for the purposes of this analysis other properties were assumed to be acceptable) the impact of different fuels on range and payload characteristics were calculated. These show that within the range of allowable Jet A/A-1 fuel density and predicted lower combustion value (LCV)³ range and/or payload can be impacted at the extremes. Figure 2 and Figure 3 show examples of model output showing the potential difference between maximum, minimum and typical density fuels with their associated heat of combustion per unit mass (referred to as LCV in that reference). Note that the typical values are based on the 20-year average Jet A-1 in the UK.

It is notable that with increased use of SPKs towards maximum 50/50 blend ratio (approx. 760 kg/m³ and 42.7 MJ/kg) range performance will be different compared to typical fuels of 800 kg/m³ and 43.2 MJ/kg. Therefore, knowing the exact heat of combustion will be useful for the extreme fuels and/or where the assumed (conventional fuel) general relationship between density and heat of combustion may not apply. Further, even estimated values based on density combined with other properties as reviewed later may give sub-optimal calculations due to compositions outside scope.

² The Figures and Tables in this section are based on data provided in ref. 20.

³ Same as net heat of combustion.

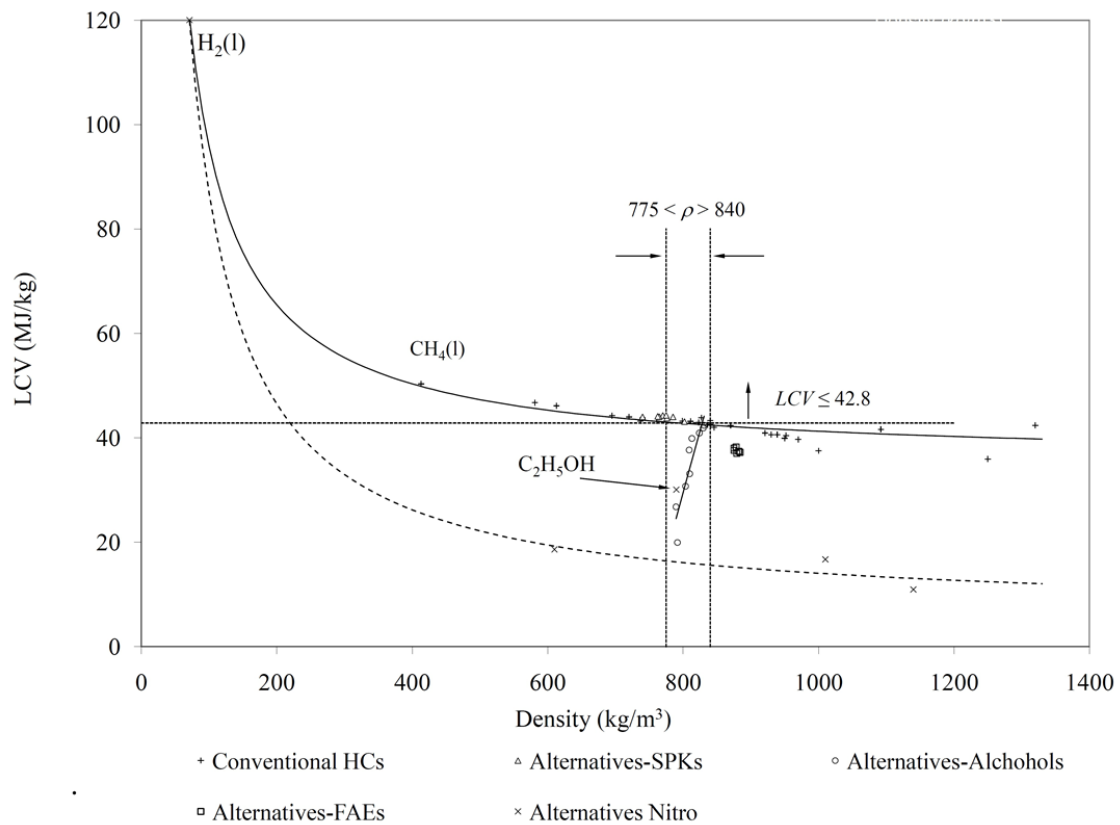


Figure 1: Relationship between LCV and density (at 15°C) for a range of liquid fuels showing limits of Jet A-1 specification [ref. 20].

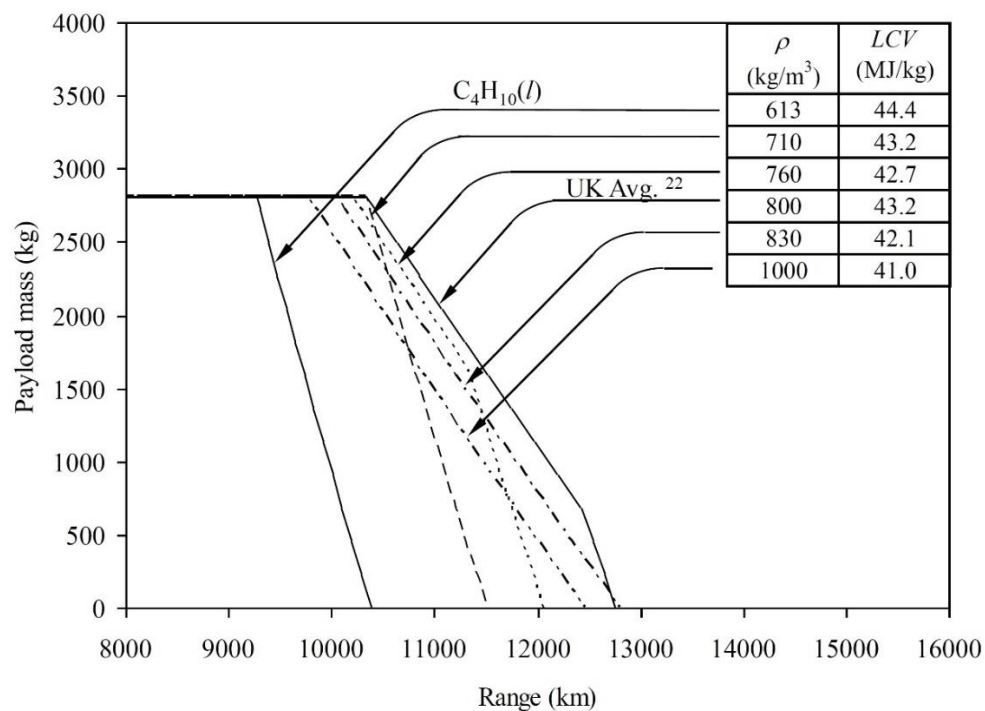


Figure 2: Changes to the range performance of Gulfstream G550 due to alterations to the Hydrocarbon fuel used for flight [ref. 20].

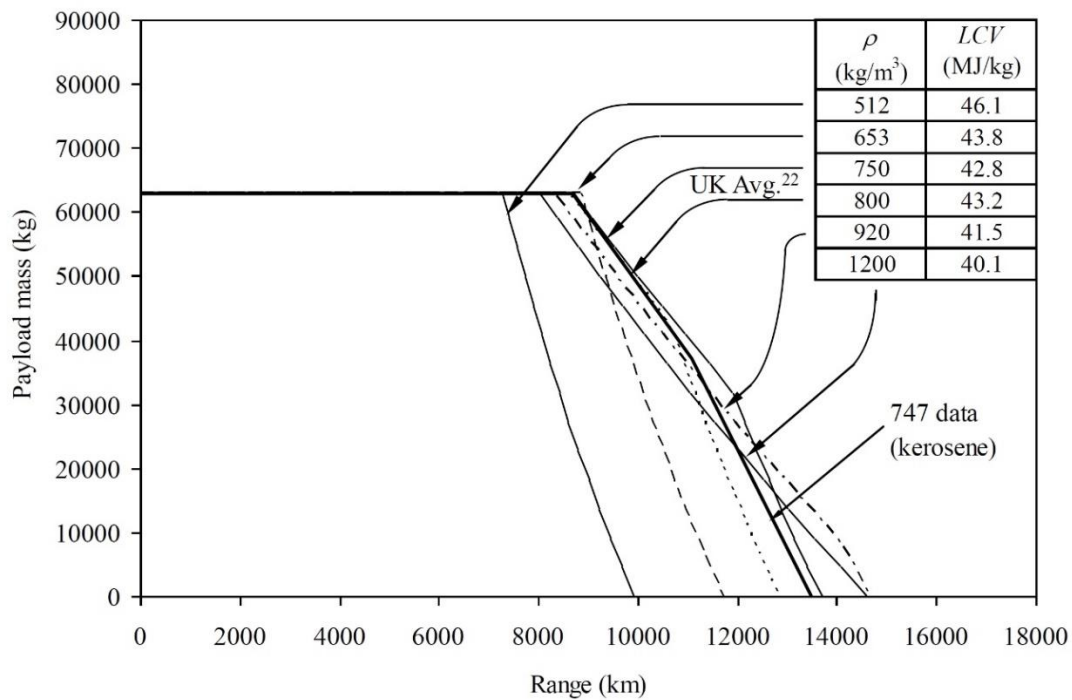


Figure 3: Changes to the range performance of Boeing 747-200B- RB211-S24D4 due to alterations to the Hydrocarbon fuel used for flight [ref. 20].

Perhaps more interesting are the data extracted from [ref. 20] which have been combined into Table 4. In this Table the range payload analysis for each aircraft shows that different fuels would be needed for optimised flights with zero or maximum load and of course by inference any point in between these loading extremes an optimised fuel could be calculated. Also, of interest is the potential specific fuel consumption (sfc) and overall fuel consumption reduction by mass of around 2.5% and CO₂ saving of around 3% for the calculated flight with an optimised load of maximum SPK content blend. The data for FAME have also been included to show the significant increase in fuel consumption for an oxygenated fuel by mass (shown as -15% and -17.4% in reduction and therefore an increase for both aircraft types) and a similarly a -12.6% reduction (therefore overall increase) in CO₂ due to the fuel's poor energy content.

In summary, these data generally illustrate that density and heat of combustion have a significant impact on aircraft loading and fuel consumption. Further, knowing the density and heat of combustion to a high degree of accuracy and confidence would allow aircraft loading to be more accurately optimised providing fuel consumption and CO₂ reduction benefits. This knowledge would be increasingly relevant where fuels are at the extremes of the allowable range and this is very true of most SPK based blends and future blends which may diverge from the established norm, particularly where 100% synthetic blends are being considered.

	LCV (MJ/kg)	Density (kg/m ³)	Fuel Mass for 8000km (kg)	sfc mg/Ns	Fuel tank usage (m ³ /m ³)	Fuel tank usage (kg/kg)	Fuel reduction (kg/kg)	Energy reduction (MJ/MJ)	CO ₂ reduction (kg/kg)
Gulfstream G550									
Typical Conventional Jet Fuel (UK avge for 20 yrs)	43.3	800	12685	18.16	68%	70%	N/A	N/A	N/A
Range payload analysis									
Max. range (Max. payload)	44.4	613	12719	17.69	89%	70%	-0.30%	-2.94%	3.32%
Max. range (No payload)	43.2	710	13061	18.18	79%	72%	-3.00%	-2.84%	-1.19%
Alternative Fuels									
SPK at spec limit	44.3	775	12362	17.73	68%	68%	2.50%	0.18%	3.01%
FAME	37.4	868.6	14890	21	73%	82%	-17.40%	-1.51%	-12.61%
Boeing 747									
Conventional									
Typical Conventional Jet Fuel (UK avge for 20 yrs)	43.2	800	123614	17.511	75%	77%	N/A	N/A	N/A
Range payload analysis									
Max. range (Max. payload)	43.3	797.6	121942	17.471	74%	76%	0.20%	1.12%	1.40%
Max. range (No payload)	41.3	956.1	129979	18.317	66%	81%	-4.60%	-0.52%	-8.29%
Alternative Fuels									
SPK at spec limit	44.3	775	120464	17.076	75%	75%	2.50%	0.07%	3.01%
FAME	37.4	868.6	145168	20.227	81%	91%	-15.50%	-1.67%	-12.66%

Table 4: Fuel consumption analysis for 747 and Gulfstream G550 flying an 8,000km flight [ref. 20].

4 DETERMINATION METHODS - FUNDAMENTALS

4.1 BOMB CALORIMETERY BASIC PRINCIPLES

Calorimetry is defined as the process of measuring the amount of heat released or absorbed during a chemical reaction. For combustion this is determined by burning a sample of known weight (or mass) in an oxygen-bomb calorimeter under carefully controlled conditions. The temperature increase is measured accurately before, during and after ignition. The heat of combustion is calculated from the temperature rise after heat loss/gain corrections of the system with known heat capacity. Bomb calorimeters can operate on the principle of isothermal, isoperibol or adiabatic (see section 4.3.2 for detailed description of these modes).

The sections below provide a broad overview of the required equipment and procedures to support the review and discussion which follows. Detailed procedures are provided in the standard test methods and equipment manuals.

4.2 BOMB CALORIMETER GENERAL ARRANGEMENT

Methods to determine the heat of combustion of liquid fuels by bomb calorimeter may vary in terms of detail but have many common attributes and features. The following provides a summary of the principles of operation common to all methods before a critique and discussion of the more detailed nuances of different methods is provided.

The main components of a bomb calorimeter system comprise:

- A pressure vessel (bomb) with a screw cap with two arms to support a crucible containing the fuel sample.
- Arms that are electrically insulated: a standard length of firing wire is mounted between these arms such that an electrical current can pass to ignite the sample.
- A means of controlling the current to the firing wire in a consistent manner.
- A crucible (sometimes referred to as a cup) containing a known mass of fuel.
- A bomb which sits within a metal bucket totally immersed in a known amount of water which is stirred to ensure temperature equilibrium.
- A bucket which is in turn contained within a chamber surrounded by a jacket which may have insulation (simplest arrangement) or more complex provision for circulating water and temperature control.
- Very accurate temperature measurement of the bucket system and jacket.
- A thermostatic control of the outer water jacket and/or insulation, the exact arrangement of which is dependent on the mode of operation.

Figure 4 illustrates a typical oxygen bomb loaded into the water filled bucket and calorimeter jacket. Figure 5 (courtesy of Parr) shows the pictorial arrangement of a 1341 calorimeter. This again shows the oxygen bomb within the calorimeter bucket surrounded by, in this case, a relatively simple insulated jacket. The view is simplified to allow the inner workings to be seen clearly. In more complex isothermal, adiabatic or isoperibol units (see 4.3.2) the outer jacket as shown in Figure 4 would comprise a double walled system filled with temperature controlled circulating water. The optional seal tape (for volatile fuels) and firing cotton are also shown. Firing cotton is normally used with tape but for non-volatile samples, tape (or other vapour suppression methods) is not required. If firing cotton is not used the firing wire is extended to dip into the sample. Accurate bucket and water jacket temperature measurement allows system to achieve the required temperature monitoring and control. Figure 6 (courtesy of Parr) shows a typical modern semi or fully automated calorimeter with the lidded enclosure for the calorimeter system and keyboard and display for control.

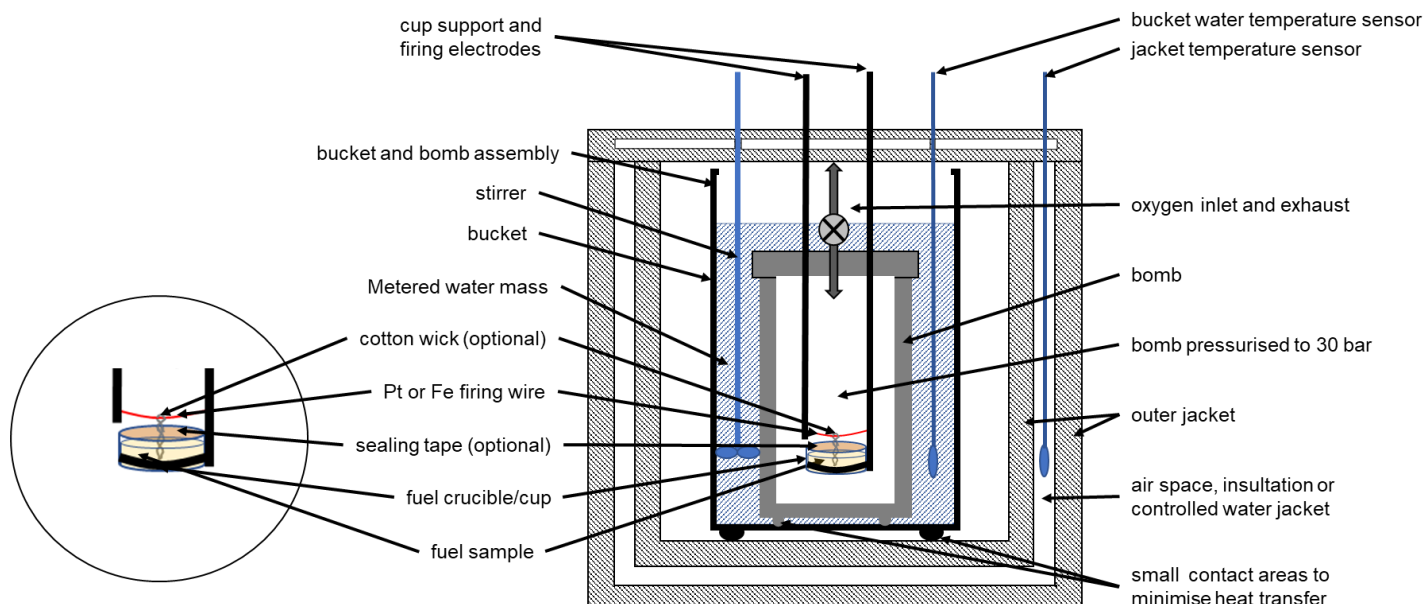


Figure 4: Typical Cross Section of Calorimeter, Water Bucket and Oxygen Bomb Assembly

Parts for the 1341 Calorimeter

Key No.	Part No.	Description
1	A50MEB	Motor Assembly with Pulley, 115V 60 Hz
	A50MEE	Motor Assembly with Pulley, 230V 50/60 Hz
2	36M4	Motor Pulley
3	37M2	Stirrer Drive Belt
4	37C2	Stirrer Pulley
5	A27A	Stirrer Bearing Assembly
6	A468E	Ignition Wire
7	A30A3	Stirrer Shaft with Impeller
8	A391DD	Oval Bucket
9	A1100DD	Calorimeter Jacket with Cover
10	1108	Oxygen Combustion Vessel
11	182VBAD	Male Connector
12	1168E2	Thermistor

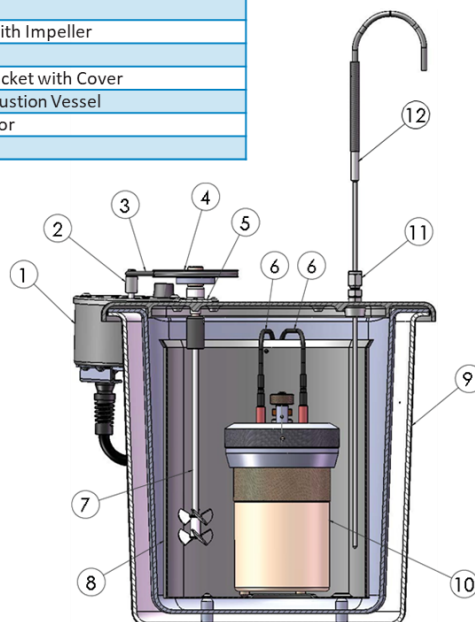


Figure 5: Cross Section of an Air Jacketed Calorimeter [Parr]



Figure 6: Typical Modern Automated Calorimeter and Oxygen Bomb (not to scale) [Parr]

4.3 TYPICAL TEST PROCEDURE

4.3.1 OVERVIEW OF BASIC ROUTINE

Prior to any fuel measurements the system comprising bucket, water, and bomb (all of which are in temperature equilibrium throughout the test) is first calibrated. This is usually achieved by firing a known mass of benzoic acid⁴ (industry reference), or liquid reference materials for specific testing, under conditions as near identical to the planned fuel measurements as possible. This provides an accurate measure of the thermal capacity of the system or energy equivalent in joules per degree Celsius (J/°C). With this information the heat released by the fuel sample (after corrections) can be calculated from the temperature difference before and after firing. The heat gain/losses are accounted for both during calibration and measurements but how this is carried varies with the equipment and mode of operation. This is discussed in more detailed in Section 4.3.2.

Fuel is loaded into a crucible and accurately weighed and then loaded into the bomb supporting arm. A quantity of water is added to the bomb to collect any acids formed for later analysis. The bomb is then sealed and pressurised with high purity oxygen, normally to 30 atmospheres. This is then loaded into the bucket and inserted into the jacket and the jacket lid closed.

The method of ignition is always based on passing a regulated current through a platinum or other metal wire. Methods may require the firing wire to be arranged to be dipped directly into the fuel or alternatively the addition of a cotton thread tied to the wire and dipped into the fuel. The use of cotton or not varies between methods.

⁴ Reference values for certified benzoic acid are provided in air and vacuum.

Additional provisions are required for volatile samples where losses may occur due to evaporation. These include:

- The use of self-adhesive tape over the crucible top but details can vary slightly – see Figure 7.
- Gelatin capsules into which the fuel is sealed. This then ignites releasing the fuel.
- Glass capsules (phials) into which the fuel is sealed. These collapse under the pressure of oxygen and thus release the fuel ready for combustion.
- In the case of GOST calorimetry method [ref. 8] the method describes how to make a plastic pouch into which the fuel is heat sealed. Again, the pouch ignites releasing the fuel.

Clearly for all these methods the weight and heat of combustion of the sealing devices must be known and subtracted at the calculation stage (except for glass phials). Further, most methods make provision to use 2,2,4 trimethyl pentane reference fluid to ensure precision is achieved where volatility is an issue and more complex operator technique is necessary. However, criteria where volatilisation minimisation are required (usually related to flash point) vary between methods.

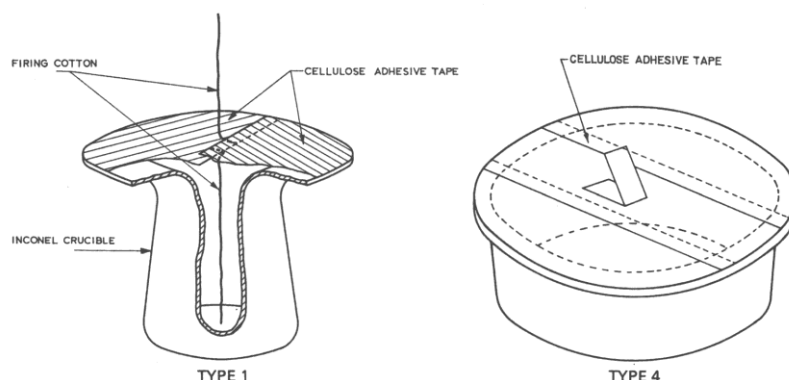


Figure 7: Examples of Tape Sealed Cup or Crucible [BS 2000 : Part 12 : 1993 – IP12/79].

After loading the whole system is allowed to reach equilibrium by monitoring the bucket water temperature and when ready the sample is ignited by a current through the firing wire. Temperature rise in the bucket (and jacket) is monitored until again a new equilibrium or constant drift is reached. Start temperature must be consistent and is normally 25°C and the temperature rise is normally 3°C.

Following test, the bomb is opened and rinsed, and the acid is titrated to measure acid content.

4.3.2 ALTERNATIVE MODES OF OPERATION

In simple terms the heat released when a known amount of fuel is combusted is:

$$\text{Energy Released} = \text{Energy Equivalent of the Calorimeter Bucket} \times \text{Temperature Rise}$$

Knowing the true temperature rise is critical, as is any heat lost or gained which would affect this value. Therefore controlling, monitoring, and correcting for any heat loss/gain to or from the inner calorimeter bucket is necessary to achieve accurate results. This allows the temperature rise to be calculated for the theoretical zero loss/gain case.

Bomb calorimeters operate in several different modes as regards controlling or minimising and monitoring heat flow between the inner bucket assembly and the outer jacket with associated correction calculations. Since the complete test may take several minutes and the bucket temperature will change after firing this is a complex problem that must be accounted for.

Operating modes to deal with this are defined within the various test methods along with the associated mathematical treatment of the raw measurements.

They can be broadly defined as:

- **Uncontrolled or Plain Insulated Jacket:** Where there is no active control of the jacket (sometimes referred to as free or variable). Note that this is the least accurate method.
- **Isothermal:** Here the outer jacket (again usually with water circulation) is kept at a constant temperature, related to the bucket start temperature, such that whilst heat loss/gain can occur it is predictable and can be compensated for.
- **Adiabatic:** The outer jacket (usually with water circulation) is controlled to be precisely the same temperature as the bucket and therefore (in theory) prevent any heat loss or gain. The ability to exactly match the inner to outer and rapidly follow during the moments following firing is both challenging and critical.
- **Isoperibol:** Is a more complex version of isothermal where the outer jacket is kept at constant temperature, which is usually set above the end temperature, but a more complex microprocessor control system monitors the outer jacket and bucket and corrects for heat loss/gain in real time. Many calorimeters can operate in isoperibol mode divided into further sub-modes of operation. For example:
 - Equilibrium mode where the reaction and heat flow are allowed to go to completion following a test and reach equilibrium.
 - Dynamic mode where the equipment interpolates the end of the test.

Notes on modes of operation:

1. Current test methods generally quote acceptable modes of operation, but other modes are not excluded (see Section 2.3). Relative merits of each mode are discussed below.
2. Some modes are specific to individual manufacturers, e.g., Parr “continuously compensated mode” exists but this mode and other modes/details are not specifically defined within any current test methods under review.
3. Some equipment manufacturers cite specific proprietary modes of operation which may be special versions of the standard modes and/or use proprietary terminology.

In Adiabatic modes where it is assumed, for an ideal system, that no heat is gained or lost because the outer jacket follows the inner assembly exactly, no correction is required. However, the calorimeter must be left for sufficient time in the initial period before test to ensure no temperature drift (within limits) and again post-test for this to be achieved. Thus, extrapolating back to the point of firing the actual temperature before and after will be correct. This also requires perfectly accurate jacket water temperature control with rapid response times.

Whilst details of specific calorimeters and procedures may vary, in general, all are dependent on the mode of operation and initial conditions. For the bomb/bucket/water assembly the heat loss or gain is as follows:

- **Adiabatic:** Retains all the heat of the process: $T_{\text{bucket}} = T_{\text{jacket}}$
- **Isoperibol:** Absorbs heat from the combustion process and jacket: $T_{\text{bucket}} < T_{\text{jacket}}$
- **Static/Isothermal:** Absorbs heat from the combustion process and loses or gains heat to the environment (static) jacket: $T_{\text{bucket}} \neq T_{\text{jacket}}$

Mode specific corrections either during or post-test are therefore required to ensure the theoretical temperature rise of the calorimeter bucket with no loss or gain is calculated (except for adiabatic mode where no loss/gain is assumed). The different modes of operation and associated test

methods define these requirements and how to process the data. This is required since heat loss/gain cannot be eliminated. Furthermore, since the temperature rise in the bucket is not instantaneous, calculations are required to determine the theoretical temperature rise that would have occurred in an ideal system (no heat transfer and instantaneous rise from start to finish) as illustrated in Figure 8.

Such corrections may be by manual calculation as defined in the method, see refs. [4, 5] for typical examples. The fundamentals behind these calculations are discussed below.

A typical firing sequence is shown in Figure 8 illustrating the pre-firing equilibrium (initial period), the rapid temperature rise immediately following the firing (main period) and the post firing equilibrium (final period).

While different methods are used to calculate what the initial and final temperature would have been under ideal conditions, close examination of many methods shows that they all have a similar fundamental basis. An example of manual calculation is that provided in ASTM D4089, section 11 [5]. These equations feature the US based National Bureau of Standards (NBS) monograph No 7 [ref. 21] which is the basis for corrections used in D4809 and many other methods. The NBS monograph is itself based on fundamental research of this and other reference works at that time. In essence this determines what the initial and final temperatures would have been at the point where the temperature rise reaches 63% of the total rise - which will be the corrected delta to be used. This concept is also examined by Santos et al [ref. 22]. The fundamental principles behind the 63% point are discussed below.

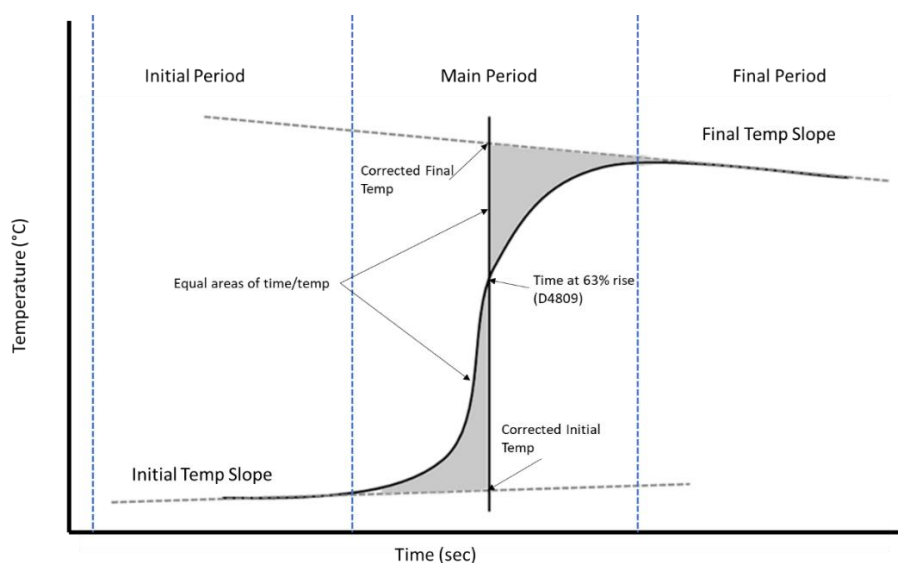


Figure 8: Example Calorimeter Time/Temperature Profile and Temperature Correction.

Figure 8 provides an example time/temperature profile for isothermal and isoperibol methods. The pre-firing and post-firing temperature must be allowed to reach a constant rate of rise or fall to ensure equilibrium is reached and is accounted for. Normally isoperibol instruments perform this procedure under microprocessor control in real time. Since total heat loss/gain is a function of time and temperature difference, all manual or microprocessor correction methods in effect seek to ensure the shaded area shown in Figure 8 before and after firing are equal and therefore net

zero. For manual methods this give rise to the calculation of the delta at the 63% temperature rise point.

With increasing automation these calculations and corrections are built into the processor control and whilst some parameters can be adjusted, access to actual calculations may not be possible for the user and maybe proprietary.

Much of the early work on calorimetry was supported by API Project 44 [ref. 23] which measured and catalogued the thermodynamic and engineering properties of 650 hydrocarbons deemed to be of “industrial importance”. This dataset served as a reference for such properties as heat of combustion, density, volatility, and aniline point. These data formed the basis of developing the methodology for both determined and estimated values which generally remain applicable to this day despite the different methods of implementation.

For ultimate accuracy of temperature delta, corrections for other sources of heat input/output to the system must be accounted for, such as:

- self-heating of the temperature probes due to the small current flow.
- heating due to viscous loss from stirring.
- heat soak into and out from the stirrers and probes, etc.

This is normally achieved by making calibration and sample firings identical, to ensure that each effect is cancelled out.

4.3.3 CALORIMETER CALCULATIONS

4.3.3.1 GROSS HEAT OF COMBUSTION

Heat released (under conditions of temperature and constant volume) is calculated by multiplying the energy equivalent of the bucket assembly by the (corrected for heat loss/gain) temperature rise, divided by the mass of fuel. However, in practice additional corrections for heat release must also be made:

- Under normal combustion conditions nitrogen would be converted to oxides as would sulphur. However, due to the high-pressure oxygen, any nitrogen left in the bomb during filling or from the fuel will be converted into nitric acid and any sulphur will form sulphuric acid. Both these reactions produce heat that would not normally be produced so must be subtracted. The titration is made and a correction, assuming that all the acid is nitric acid, is subtracted from the overall heat release (amount of acid times heat released per unit mass). Equally, if the fuel contains sulphur this must also be subtracted by the same mathematical method.
- If firing cotton has been used this must be subtracted.
- If a combustible firing wire (e.g., iron) has been used this must be subtracted (except for platinum which does not burn).
- If any sealing system such as sealing tape is used, the energy released from this must be subtracted.

4.3.3.2 NET HEAT OF COMBUSTION

Net heat of combustion is the figure normally quoted in fuel specifications and more closely relates to typical real-world combustion conditions. To convert gross heat of combustion (heat release under constant volume and high-pressure oxygen with water in the condensed phase) to net corrections must be made. These compensate for:

- The difference between constant volume (bomb conditions) and constant pressure to account for the work done by expansion (function of pressure and volume).
- Water being in gaseous rather than condensed form, representing a significant energy change and requiring knowledge of the fuel hydrogen content for adjustment.

Both IP12 and D240 allow the use of a simplified correction if hydrogen content is not known. However, it should be noted that this equation does not assume a fixed hydrogen content but mathematically assumes an amount based on net calorific value. This simplified correction is likely to be unreliable for synthetic blends and any fuels with significant levels of oxygenates etc. such as current and/or future piston engine formulations.

The fundamentals of gross to net correction were established by many workers during the development of calorimetry. This is best described and codified in the NBS monograph [ref. 21] which brought all these developing concepts into one clear document and is therefore often cited. This in turn references National Advisory Committee for Aeronautics (NACA) Technical Note No. 996 [ref. 24] which defines the basis for the equations used in all standard bomb calorimetry test methods to correct from gross to net. The combined equation as seen in most methods corrects for the work done due to expansion at constant pressure as opposed to constant volume in the bomb (function of pressure and volume) of the gas expansion, the difference between water as a gas or liquid, and water evaporation/condensation.

These basic equations are found in ASTM methods D240, D2382 and D4809, IP 12 and are generally used in all the methods under review albeit in slightly different forms. This is fundamental chemistry and physics and ultimately traceable to the NBS monograph in most cases. D240, D2382 and D4809 also cite ASTM Research Report D02-1346 [ref. 25] which is in fact a direct reference to the NACA Technical Note No. 996 [ref. 24].

For all methods samples are weighed in air (as opposed to in vacuum) so this must be considered when using the final values if ultimate accuracy is required. For instance, by definition, density is based on mass which is in vacuum so converting between volume and mass calculations use in-vacuum values. If energy flow calculations are being made, heat of combustion values must be made consistent with density. Some specify that mass of fuel is in air (e.g., D4809) but others do not. Note that the benzoic acid standard will have declared heat of combustion in either air or vacuum and therefore the value consistent with sample weighing method must be used. For example, typical certified benzoic acids are typically 26454 kJ/kg in air or 26434 kJ/kg in vacuum, the difference being 0.076% and therefore a potential source of error in high accuracy measurements if not used correctly. Similarly, other reference materials often quote their energy content per unit mass in vacuum and this must be accounted for to maximise accuracy.

4.3.4 TYPICAL CALCULATION

The following provides an example of how all the data from sample preparation, firing sequence and temperature measurement to post-test analysis is used to calculate the gross heat of combustion.

Calculation of Gross Heat of Combustion at Test Temperature

- $$Q_g (\text{gross, } t^{\circ}\text{C}) = (\Delta t \times W - C_1 - C_2 - C_3 - C_4) / 1000 \times M$$

Calculation of Gross Heat of Combustion at 25°C

- $$Q_g (\text{gross, } 25^{\circ}\text{C}) = Q_g (\text{gross, } t^{\circ}\text{C}) + A(t - 25)$$

Calculation of net heat of combustion from gross value

- $$Q_n (\text{net, } 25^{\circ}\text{C}) = Q_g (\text{gross, } 25^{\circ}\text{C}) - 0.2122 \times H$$

Where:

Q_g (gross, $t^{\circ}\text{C}$) = gross heat of combustion at constant volume and final temperature of the experiment, MJ/kg,

Q_g (gross, 25°C) = gross heat of combustion at constant volume, MJ/kg at 25°C

Q_n (net, 25°C) = net heat of combustion at constant pressure, MJ/kg at 25°C

A = correction factor, MJ/kg $^{\circ}\text{C}$ to correct from final temperature of combustion to 25°C

Δt = corrected temperature rise, $^{\circ}\text{C}$, (correction dependent on operating mode of calorimeter)

W = energy equivalent of calorimeter, J/ $^{\circ}\text{C}$

C_1 = correction for the heat of formation of the HNO_3 , J

C_2 = correction for the heat of formation of sulfuric acid, J

C_3 = correction for the heat of combustion of pressure- sensitive tape, gel or ampoule, J (if used)

C_4 = correction for heat of combustion of firing wire, J (if not platinum)

M = mass of sample, g,

t = final temperature of combustion, $^{\circ}\text{C}$

H = hydrogen content, mass %.

4.3.5 ANALYSIS OF ERROR SOURCES.

The stated precision of a method includes all intrinsic errors summated to give an overall measure for calorimetry and provide a means of measuring laboratory and/or operator performance. The prime sources of error at the point of analysis which can be impacted by operator skill and laboratory environment include but are not limited to: accuracy of sample weighing (particularly when using volatility suppression), bucket weighing, generally handling of the sample and loading procedure, control of calorimeter and its immediate environs, and post-test handling and titration. There are also factors external to the method and possibly outside the control of the operator. Most importantly is the impact of precision of input data used in the calculations including hydrogen and sulphur content which may be determined by various methods and may or may not be generated in the same laboratory.

An analysis of all the factors and their impact is not possible within the scope of this report but will be all rolled up into the precision of the method⁵. However, some key sources of error and their

⁵ Assuming the precision reflects current practice which may not be the case as discussed elsewhere in detail.

overall impact on precision can be estimated and these are to some extent outside the control of the operator. The following analysis reviews the impact of three such factors: Calorimeter overall errors (as stated by manufacturers) which will impact the gross value; impact of precision of sulphur levels to correct for sulphur in the fuel; and precision of hydrogen content used in the gross to net correction. Sulphur error has been calculated at 0.30% m/m as this is the maximum allowed in D1655 / Def Stan 91-091 jet fuels and the calculation shows the impact of assuming zero.

Taking a jet fuel with properties:

Gross HOC	46.00	MJ/kg
Hydrogen	13.60	%
Sulphur (% m/m)	0.30	%
Net HOC	43.11	MJ/kg

These external errors and the errors of the calorimeter are shown in Table 5 with errors expressed as MJ/kg in gross or net values. For each relevant case, this error is expressed as a percentage of the stated reproducibility of ASTM D4809 (shaded boxes). This shows the contribution for the maximum expected error of each as defined as the reproducibility of the measurement used. The examples of 0.1% and 0.2% are used for the calorimeter errors based on typical manufacturers' stated values.

4.3.6 ANALYSIS TIME AND OPERATOR TIME.

A key question on carrying out calorimetry, apart from the cost of facilities and equipment, is the turnaround time and operator involvement time. This question arises in its own right as a laboratory planning issue and may be part of the decision regarding using determined versus estimated methods. Cycle time and operator involvement is very dependent on many factors so only general indications can be provided in this study. These are summarised in Table 6.

	Hydrogen Content precision		H2 Content Impact Max. Error Gross to Net		Max Error %age of Reproducibility	Sulphur Error (Jet A/A-1)	Max Error %age of Reproducibility	Calorimeter (0.1% Error)	Max Error %age of Reproducibility	Calorimeter (0.2% Error)	Max Error %age of Reproducibility	ASTM D4809 - Net (all Fuels)		
	%	%	MJ/kg		%	%	%	MJ/kg	%	MJ/kg	%	MJ/kg	MJ/kg	MJ/kg
Hydrogen Content Method	Repeatability	Reproducibility	Repeatability	Reproducibility		0.3% error		---		---		Repeatability	Reproducibility	Bias
D1018: Lamp Method	0.110	0.180	0.023	0.038	11.7	0.000	0.0	0.046	14.2	0.092	28.4	0.096	0.324	0.089
D3701: Low Res. NMR	0.090	0.110	0.019	0.023	7.1	0.000	0.0					0.096	0.324	0.089
D7171: Low Res. Pulsed NMR	0.140	0.270	0.030	0.057	17.6	0.000	0.0					0.096	0.324	0.089

Table 5: Examination of Calorimetry External Error Sources.

Process Stage	Time and Operator Involvement
Pre-Test Preparation: Weighing and loading of fuel into cup, inserting into bomb and loading into the bucket	2-5 minutes This is a wholly manual operation though data transfer between balance and calorimeter may be automatic.
Calorimeter Firing: This may be from full manual (unusual), semi-automated requiring operator monitoring to fully automated.	Typical cycle time for complete process is between 5 – 25 minutes dependent on equipment type and mode of operation. Often there is a balance between precision and speed. Fully automated systems need 1-2 minutes of operator time. Less automated systems may need constant attention – up to 25 minutes.
Post Test Analysis: Removing bomb and analysing washings etc.	4-5 minutes. This may be a wholly manual operation. Auto-titrators may be used which are slower but need less operator time.
Calculations.	May be instant for fully automated systems having entered all the required data. Manual calculation may take 2-5 minutes.

Table 6: Summary of Calorimetry Cycle and Operator Timings.

5 DETERMINATION (EXPERIMENTAL MEASUREMENT) METHODS - STATE OF THE ART

5.1 SUMMARY OF CURRENT TEST METHODS

The following is a review and critique of current standard determination methods commonly cited in key aviation fuel specifications.

Table 1 provides a summary of all the leading specifications within the scope of this study and the standard methods quoted for both determined and estimated net heat of combustion. The sub-set of determined heat of combustion methods is then summarised in Table 2 with the following paragraphs offering an overview of some general findings as a preamble to examining each individual method in turn. The review is based on the following research protocol:

- Review of the test methods in detail.
- Review of research reports and cited documents within each respective method (where available).
- Discussion with the relevant sub-committees that have responsibility for these methods namely, D0.05 and SC-B-10 for ASTM and Energy Institute (IP) methods, respectively.

All determination methods are based on the same basic principle of a bomb calorimeter combusting a known mass of sample and determining the heat released. Heat loss/gain control systems and calculations vary but a study of these equations leads to the conclusion that they are all mathematically equivalent. The same can be said for correction from gross to net values, and the correction for the presence of sulphur, etc.

Further, guidance on how to manage volatile samples may vary, but in practice they all have the same objective, to minimise losses by evaporation prior to the firing. The main risk is incomplete combustion of fuel resting on the inner surface of the bomb or surface of the water introduced to collect acids. A comparison of how good each volatile fuel handling method works cannot be determined from available data, but it is clear that precision when using these methods can be worse.

It is important to note that whether explicitly stated in the scope section or implied by general terms such as “hydrocarbon fuels ranging from/to...” for example, these methods have been specifically designed to be used on typical distillate fuels. Even more specifically the high precision of ASTM D4809 is limited to aviation turbine fuels only. This raises the following two issues given the range of fuels which were in use at the time the test methods were created:

- What is the impact on precision for fuels outside the existing range at time of development, for example alternative and sustainable synthetic blendstocks and, in the future, possible moves outside the current specification or even fully synthetic fuels.
- For potential future high octane unleaded aviation gasoline grades, possible changes in composition and the presence on heteroatomic species to modify performance, for example organometallics, oxygenated or amine octane boosters, etc.

Therefore, current developments in aviation fuels are pushing the boundaries of what was consider normal for these test methods and the impact requires evaluation and validation.

To ascertain the provenance of the methods and calculations used, many research reports which are cited in the methods have been collated and reviewed. As discussed elsewhere it is apparent that all methods in some way can be traced back to the NBS monograph produced in 1960 [ref.

21] and data on pure hydrocarbons from work preceding and in the same period such as API project 44 [ref. 23].

Further, all methods calibrate on the same standard material, benzoic acid, which again can be seen as the industry reference based on early work. One observation is that benzoic acid is a very stable solid with known heat content and easy to handle. Since it is solid, whilst other conditions within the bomb system (starting temperature and overall temperature rise for example) can be matched to the actual firings to ensure a valid calibration, this does not really challenge the fuel sample handling process. The calibration therefore does not cover the whole chain of potential errors (systematic or random). Whilst 2,2,4 trimethyl pentane is used as an overcheck this is only applied to volatile samples. Extending quality assurance of the whole process by the firing of a liquid sample with traceable heat of combustion value should be assessed. So, for lower volatility samples a certified pure compound which is a close analogue of the fuel under test should be used as a control, examples being dodecane, hexadecane or similar. Use of these liquid reference materials with traceable (reference) values would also allow assessment of any bias.

Some general findings regarding the methods include:

- The level of industry review and how up to date the methods are, varies considerably.
- Methods vary in terms of control and measurement requirements which provide a range of precision.
- Good precision comes at a cost of skilled staff, time, equipment, and dedicated test area. Therefore, there is a balance between ease of use and cost versus the required precision for a particular application of the resulting data.
- All methods use data from other analysis, for example hydrogen content, sulphur content and these methods must also be maintained.
- Equipment and instrumentation have dramatically changed, mostly for the better, in terms of temperature measurement and processor-controlled calorimeters, data logging, automation and calculations (see section 6). It is clear that all written methods do not necessarily reflect these updates and some only to varying degrees.
- No real innovative (disruptive technology) systems or techniques were identified in this study, the methods representing an evolution from the historic systems. Aside from some innovative features such as dry systems and one unit that used a laser ignition system, all equipment reviewed operated on fundamentally the same principle. (Also see section 11.1).

It must be recognised that none of the determined test methods are easy, convenient, or cheap. Consequently there is a preference for estimated methods if data precision requirements are met.

One final observation that warrants reiteration is that in general methods provide gross and/or net values in air (not corrected to buoyancy) as this seems to be the industry standard. Care must be taken to correctly account for this when:

- Using reference fluids or benzoic acid that may have data based on mass in vacuum.
- Performing critical calculations involving calculating heat flow balance based on fuel mass or volume flow such that in air or in vacuum data are used consistently. For instance, strictly speaking density is in vacuum.

The following individual method reviews are based on a detailed examination of the method, cited references (where available) and discussion with the relevant ASTM and IP sub-committees. In particular, as a key part of the brief for this report the provenance and/or traceability of equations used and stated precision is examined.

On examining the technical detail within some test methods it has been identified that a number overseen by different standardisation committees are expected to be technically identical, when for example inferred by multiple authority designations or stated as “joint methods”. In all cases these have the same core principles and methodology but may be out of sync in absolute terms of detailed text and/or date of last revision. This observation is worthy of addressing, ideally in parallel with a wider review and modernisation of the methods to allow rationalisation and re-synchronisation.

The following sections review:

ASTM	ASTM D240 - 19 ASTM D4089 -18 ASTM D2382- 88 WITHDRAWN (included for historic reference)
ENERGY INSTITUTE (IP METHODS)	IP12/79 (2001). BS 2000:PART 12: 1993
INTERNATIONAL METHODS	RUSSIA: GOST 21261 – 1991 CHINA: GB/T 384 – 1981

5.2 ASTM

5.2.1 ASTM D240 - 19

This method uses a bomb calorimeter with either isothermal or adiabatic calorimeter jackets. Water jacket in adiabatic mode (following the temperature of the calorimeter bucket) or isothermal mode (constant jacket temperature) is allowed. A double walled jacket is allowed if the room is held at +/- 1°C which is therefore considered isothermal.

Uses benzoic acid to calibrate the equipment and 2,2,4 trimethyl pentane as an overcheck with volatile fuels.

The method allows the use of mercury in glass thermometers or platinum resistance thermometers with Wheatstone bridge and galvanometer. Mercury in glass thermometry is virtually obsolete technology. Whilst platinum resistance sensor technology is still relevant the use of Wheatstone bridge/galvanometers has largely been replaced with electronic instrumentation that is more accurate and easier to use / less operator sensitive. For temperature measurement much better, convenient and less operator sensitive instrumentation is available than specified.

Parr Instruments is referenced as sole source of supply, but specific equipment / model numbers are not mentioned.

The method does not specifically stipulate that the use of experienced operators is required to achieve stated precision, but this is known to be the case.

The method also has a procedure for determining the level of sulphur (for correction) by titration of the bomb washings. The widespread availability of much better methods of determining sulphur level in the fuel under test has rendered this procedure unnecessary.

The use of modern instruments and particularly temperature measurement systems would potentially have a beneficial impact on precision. In fact the removal of allowance to use mercury in glass thermometers would probably improve overall precision. Further, many calorimeters use the isoperibol methods (with variations) which deliver results of higher precision and are generally

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quicker and convenient, but the isoperibol method is not recognised in D240 (similarly to IP12). Most equipment can be operated in adiabatic and/or isothermal mode so could comply with D240 but may compromise precision and/or speed.

Section 4 describes the traceability of the equations used to correct test temperature and for gross to net heat of combustion conversion. The use of a simplified equation for gross to net heat when Hydrogen content is not known is also similar to IP12 where this is allowed.

As regards traceability of precision, ASTM Research Report D02-38 [ref.26] is cited as the substantiation of the precision statements. In summary a cross laboratory study was carried out comprising 4 fuels: aviation gasoline grade 100/130, JP-4, kerosine (of undefined specification) and n-hexadecane. 14 labs. took part and included adiabatic, isothermal, and double walled plain jacket. The results from three of the laboratories and several other results were excluded as outliers. Plain jacket calorimeters were included in the statistics but not allowed in the method. This dataset is considered somewhat limited by today's statistical criteria. Further, calorimeter technology has changed significantly since 1966 rendering these data in effect obsolete.

Discussion with members of ASTM Subcommittee D02.05 indicated that no ILS or similar assessment of precision has taken place in the last 20 years. Therefore the most recent data on precision is based on the historical Research Reports cited within the method.

In summary, while this method has been recently reviewed and probably meets the original precision stated, the method would benefit from adoption of modern instrumentation, procedures, and equipment. Whilst precision may be improved and should be assessed if an update is carried out, this method serves to complement ASTM D4089 and is still applicable where lower precision is adequate with cost and convenience benefits. Therefore, efforts to improve the method should not be carried out that compromise cost and ease of use. If higher precision is required ASTM D4809 is available.

5.2.2 ASTM D4089 -18

This method uses a bomb calorimeter. Water jacket in adiabatic mode or isoperibol mode is allowed.

The high levels of control required by the method seek to ensure the defined high precision is achieved in practice. These include:

- Stringent requirements for the number, scatter, and period of time for energy equivalent determinations with a relative standard deviation (RSD) of 0.1% or less over a specified number of days, regular re-assessment every 2-3 days and, averaging of results over the last 6 tests.
- Test room requirements.
- Temperature measurement requirements (see section 6.2.3).
- Weighing equipment requirements (see section 6.3).

The high precision definition is provided in the scope in addition to standard precision statements towards the end of the method. This includes that the permissible difference between duplicate determinations is in the order of 0.2% but wider for volatile samples. Further, each critical individual measurement, e.g., mass or temperature should be kept below 0.04%. (See also analysis of errors in 4.3.5.)

Uses benzoic acid to calibrate the equipment and 2,2,4 trimethyl pentane as an overcheck with volatile fuels.

This method does not mention the requirement for skilled or experienced operators but in the author's experience this is essential to meet the stated precision requirements on a routine basis for such a complex and operator sensitive procedure.

The method allows the use of mercury in glass thermometers or platinum resistance thermometers with "associated instrumentation". Temperature measurement should be capable of recording to a resolution of 0.0001°C and a repeatability such that precision requirements of water equivalent are met. However, it is considered that mercury in glass thermometry is now obsolete technology and if removed from the method, precision could be improved further.

Specific Parr equipment (for example calorimeter, bomb) is cited as meeting the requirements of this method. However, many of the items specified are long obsolete and therefore certainly not available new and/or if still in use, may not be in fully serviceable condition. Other equipment manufacturers claim to produce equipment that meets this specification, see section 6, but this appears to not have been formally reviewed by the relevant test method sub-committee.

The use of automated calorimeter control, temperature recording, and data processing is recognised and allowable, reflecting the capabilities of instruments available contemporaneous to the method development.

Section 4 describes the traceability of the equations used to correct test temperature and gross to net heat of combustion values as per ASTM D240. The use of a simplified equation for gross to net heat is not allowed where Hydrogen content is unknown in contrast to D240.

It is clear that in many respects this method and ASTM D240 are significantly out of step with what can be supplied and is indeed in use.

Stated precision of this method is based on an interlaboratory study and reported in Research Report D02-1229 [ref.27]. Key points of this study taken from the report are:

- The test matrix included 16 laboratories and 12 fuel samples.
- There was a range of volatilities since precision was calculated and subsequently defined in ASTM D4809 within 3 classes: I. all fuels, II. Non-volatile fuels and III. volatile fuels⁶.
- Fuels included the following samples: 3 of Jet A, 2 of Jet A-1, 2 of JP-4 and 1 of each of JP-5, JP-7, AVGAS 100LL, Diesel, 2,2,4 Trimethylpentane.
- Several laboratories and samples were rejected based on statistical indication of outliers and some sample test results were missing. This led to a significant reduction in the sample set actually used to determine precision.
- Statistical analysis of bias was also carried out by inter laboratory comparison.
- Calorimeters were all Parr Adiabatic calorimeters (mostly model 1241) apart from one laboratory which used the same model as the other laboratories but in isothermal mode.

Some key observations regarding the ongoing validity of using these data and associated precision include:

- Only one manufacturer's calorimeter was used but many alternatives exist today and are in use that may meet these requirements.
- The equipment used is now generally obsolete.

⁶ Neither the research report or ASTM D4809 explicitly define the demarcation between volatile and non-volatile fuels. This is important as the demarcation where such measures are required is essential to ensure consistent operations between laboratories.

- All laboratories except one used adiabatic mode whilst many calorimeters now operate in isoperibol mode which is a special version of isothermal.
- Lack of definition of the criteria for use of precision for volatile versus non-volatile fuels.
- The method only requires one determination to be carried out but best practice would be to carry out at least two firings and ensure they are within acceptable limits.
- No requirement is stated for skilled/experienced staff as was required within ASTM D2382 (see below). Whilst accredited laboratories will have appropriate training procedures in place the complexity of this procedure perhaps warrants a specific comment associated with the precision statement.

Discussion with some members of ASTM sub- committee D02.05 raised some key points:

- There is debate about the different Hydrogen determinations methods including D7171, D3701, D5291 and D3343, not least because of their applicability and lack of availability across the industry.
- There is recognition that reference to obsolete calorimeters requires addressing.

Discussion with members of ASTM Subcommittee D02.05 also indicated that no ILS or similar assessment of precision has taken place in the last 20 years. Therefore, the most recent data on precision is based on the historical Research Reports cited within the method.

In summary, whilst the method is still used and with skilled operators may achieve the stated precision, significant changes in calorimetry have occurred since the inception of this method. This means that the basis for the stated precision cannot be considered relevant (in fact today's equipment may be better) and the equipment listed as recognised by ASTM appears obsolete. This means that users may meet the spirit of ASTM D4809 but not the letter of the procedure.

5.2.3 ASTM D2382- 88 WITHDRAWN (INCLUDED FOR HISTORIC REFERENCE)

ASTM D2382 has now been withdrawn and replaced by ASTM D4809, the latter largely being a development from both D240 for the fundamental method and D2382 to achieve higher precision on a day-to-day basis. ASTM D2382 had a higher precision than D4809 but this was not always achievable in practice, an observation confirmed in a UK MoD review [18]. Further, major changes in equipment, automation and temperature measurement technology had occurred which needed to be incorporated. The re-worked and updated method was so different to D2382 that it was issued as a new method D4809. A new precision statement based on testing was also defined within D4809 (see section 5.2.2.).

ASTM D2382 cites research report D02-1236 as the basis for the precision but this report appears not to be available despite extensive enquiries.

Discussion with members of ASTM Subcommittee D02.05 indicated that no ILS or similar assessment of precision has taken place in the last 20 years. Therefore, the most up to date data on precision is based on the historical Research Reports cited within the method.

The UK MoD review [18] also noted that the main reason to withdraw ASTM D2382 in preference to ASTM D4809 is that the precision of the former was not achievable in practice on a regular basis.

5.3 ENERGY INSTITUTE (IP METHODS)

5.3.1 IP12/79 (2001). BS 2000:PART 12: 1993

IP 12 features a bomb calorimeter with either isothermal or adiabatic calorimeter jackets. Benzoic acid is used to calibrate the equipment and 2,2,4 trimethyl pentane as an overcheck with volatile

fuels. The method has not been updated since 1979. Precision was established in 1971 from an ILS.

A testing requirement is the availability of experienced operators to achieve stated precision. This is probably in part due to the use of mercury in glass thermometers where skill is required to accurately read scales by eye. Such technology is now obsolete and much better, convenient and less operator sensitive instrumentation is available. However, skilled and experienced operators are still required for the handling of samples.

The method has a procedure for determining the level of sulphur (for correction) by titration of the bomb washings. The widespread availability of much better methods of determining sulphur level in the fuel under test has also rendered this procedure unnecessary.

Since this method was developed, and subject to ILS to define the precision, better bomb calorimeter instruments have become available as has been observed for all the ASTM methods.

Discussion with members of Energy Institute Subcommittee SC-B-10 overseeing IP 12 indicated that no ILS or similar assessment of precision has taken place in the last 20 years, again matching ASTM experience. There is reference to an ILS carried out in 1971 but this cannot be located at the Energy Institute.

The use of modern instruments and particularly temperature measurement systems probably would have a positive impact on precision. Further, many calorimeters use the isoperibol methods (with variations) which would further benefit data quality and are generally quicker and more convenient. However, in its current form, IP 12 does not recognise the isoperibol approach. Most equipment can be operated in adiabatic and/or isothermal mode so could comply with IP12 but with likely associated compromise of precision and/or speed versus isoperibol.

Lastly, whilst IP12 may seem similar to ASTM D240 there are significant differences, and a review of equivalence / update would be helpful.

In summary, this method is out of date in many areas and therefore requires either a significant update and re-assessment of precision or withdrawal. Discussion with key members of the SC-B-10 has led to the conclusion that they generally concur with the above findings. Indeed, the committee review of IP 12 was in part the motivation behind the current CRC project.

5.4 INTERNATIONAL METHODS

5.4.1 RUSSIA: GOST 21261 – 1991

Note: A translation of this method from Russian to English was obtained by the author but the accuracy of this cannot be guaranteed.

This method follows the general principles of IP and ASTM methods. Some notable differences include:

- The method defined bomb calorimeters of types V-08, V-09, V-08MA, V-08MB with an isothermal or adiabatic water shell in accordance with TU 25-11.1426 and other calorimeters that provide determination results within the permissible discrepancies (see section 6 included a detailed review of equipment used in Russia).
- The method allows for use mercury in glass or platinum resistance thermometers.
- Calorimeter water equivalents (effective heat capacity) are only required to be carried out every quarter, or if the room changes by 5°C or if changes to the equipment has occurred. The method requires the effective heat capacity to be determined with an error of less than 0.1% so in parity with D4809.

- The (unique) method of preparing volatile samples, defined as those with flash points below 38°C, features use of polymer “ampoules” which appear to be small bags rather than a rigid shape so perhaps “ampoule” is a poor translation. The chilled sample is introduced and the ampoule sealed using heat which is an interesting alternative. See [ref. 8]
- The fuel sample weight is determined in vacuum.
- Heat loss/gain corrections are different to account for the fact that determinations are carried out in isothermal or adiabatic mode.
- The true temperature rise appears to be calculated from temperature gradients and stated at reading number 4 within the rapid rise phase which is somewhat different to the typical IP/ASTM methodology. It is impossible to calculate the difference this would make without carrying out back-to-back tests.
- The method uses different calculations to correct for gross to net:
 - The formula is slightly different and requires the water content of the fuel to be determined as well as the hydrogen content so that the total water produced is calculated.
 - There is a further correction factor from gross to net.
 - The method uses an empirical formula to estimate hydrogen content based on the gross determined value.
- It is not possible to (reverse) calculate the difference the above correction factors would make to a result without carrying out actual tests.
- The method requires duplicate results with a difference not to exceed 130 kJ/kg.

The test method provides traceability to the original author(s) and their affiliation and states the date of 1991. It notes subsequent updates but does not cite any traceable reports or data to support the original development and precision.

5.4.2 CHINA: GB/T 384 – 1981.

Note: A full translation of this document was not available. Some comments were kindly provided by the Chinese team at BP via Alisdair Clark (ref. 28).

Key points regarding this specification include:

- This is clearly a bomb calorimeter method.
- It appears that true temperature rise is calculated from temperature gradients and stated at reading number 4 within the rapid rise phase in a similar fashion to the Russian test method.

There are 3 options in the specification:

1. Test 1 calorific value method:
 - a. Accuracy: The difference between the two results of repeated determination of the calorific value of the sample should not exceed 30 Cal / g.
 - b. Final report: The arithmetic mean value of the two results of repeated determination is taken as the experimental result.
2. Test 2 and 3 calorific value method.
 - a. Both tests 2 and 3, total calorific value method and net heating value method, have the same requirements:
 - b. Calculations are accurate to 1 Cal/g, and then rounded to the nearest whole number with finally accuracy to 10 Cal/g.
 - c. Repeatability is same as Test 1. However, if the result is over 30 Cal/g, 3 determinations are required and the arithmetic mean value of the two measurement results within the allowable range is taken as the test result; If the difference between

the results of the third determination and the results of the first two times is within the allowable range, then take the arithmetic mean value of all three measurements is the test result.”

No traceable reports or data to support the test method and/or precision is available based on the level of translation available.

6 CURRENT CALORIMETRY MEASUREMENT EQUIPMENT

6.1 SUMMARY OF EQUIPMENT AVAILABLE FOR CALORIMETRY

Table 7 provides a summary of all the equipment manufacturers identified by a comprehensive literature search of internet sites and downloaded information. This Table provides information available for manufacturers across the globe including those familiar to ASTM and EI groups but also the less familiar from countries including Russia and China. Some key notes and caveats should be observed when considering the following review of information and data available on calorimeter equipment. These include:

1. Only models relevant to aviation fuel measurement are cited.
2. Data is based on review of vendors literature and websites with additional data on Russian equipment.
3. Terminology and basis of precision statements vary in terms of derivation and should be taken as an indication of precision for comparison only.
4. Main calorimeter unit type, model number and key operating parameters are listed. Details of various options regarding bombs and ancillaries are not listed for brevity.
5. Some Chinese calorimeters may appear on several supplier's websites which are seemingly identical but have different names/model numbers.

In the analysis of calorimeter equipment identified, variability between different models can be summarised by the following key attributes relevant to this study:

- **Mode(s) of Operation** primarily outer jacket control/monitoring and heat flow correction.
- **Temperature Measurement:** Temperature measurement methods and resolution.
- **Precision:** This includes of both the calorimeter water equivalent and precision of sample results.
- **Calorimeter Test Method Compliance:** Compliance with national/international specifications.
- **Analytical Balance Requirements:** As defined by weighing requirements for both samples and calorimeter water bucket filling.

Other attributes that may be important to users but figure less importantly to the above include:

- **Range** of samples and energy content.
- **General Arrangement** of equipment and ancillaries.
- **Degree of Automation:** Level of automation of each stage of the process from weighing samples, through loading the bomb, pressurising, and accurately filling the bucket for example. This can result in equipment that varies from totally hands on to minor manual intervention once the bomb is inserted.
- **Time of Analysis:** Where many samples need to be analysed then time of cycle is important. Manufacturers may offer a range of units with the aim to increase speed and automation but sometimes at the expense of precision.

Additionally, a very useful survey of Russian equipment (dated May 2011) is provided in [ref. 29] and

Table 8 is an extract from this report which specifically catalogues Russian equipment used in Russian and provides a comparison with imported equipment including Parr, LECO, and IKA. Note this is an update by the author of a similar review carried out in 1998.

Report [ref. 29] also states that about 40% of calorimeters are INPK RET manufactured versus 30% Etalon (Kazakhstan) and the remaining 30% divided between IKA, Leco and Parr.

						Stated Compliance from Vendor Literature							
Manufacturer	Model	Description	Modes of operation	Stated Precision	Temp. Res (°C)	IP12	D240	D4809	D2382	GB/T 384	GOST21261	Other	Comments
Parr	6400	Automatic Isoperibol	Isoberibol	0.10%	0.0001		X	X				DIN 51900	Chinese and Russian pattern Approval
	6200	Isoperibol	Isoberibol	0.05-0.1%	0.0001		X	X				DIN 51900	Chinese and Russian pattern Approval
	6100	Compensated	Compensated	0.1-0.2%	0.0001								
	6050	Compensated (PC control)	Compensated	0.20%	0.0001								
	1341	Plain Jacket	Insulated Jacket	0.30%	0.002								
	1241	Manual/Auto calorimeter - Obsolete	Adiabatic/Isoperibol				X		X				Cited in ASTM D2382 - Obsolete
	1261	Manual/Auto calorimeter - Obsolete	Isoberibol				X	X					Cited in ASTM D4809 - Obsolete
IKA	C200	Entry level Semi automated calorimeter	Isoberibol/dynamic	0.1% RSD	0.0001		X	X			X	DIN 51900	
	C6000	Automatic calorimeter	Isoberibol/Adiabatic	0.05-0.15% RSD	0.0001		X	X				DIN 51900	
	C7000	High speed dry system	Double Dry system	0.2% RSD	0.0001								Does not use water – has unique double dry system
DDS	CAL 3K-AP	Automatic Dry system	Dynamic/Isothermal/Adiabatic	<0.01% RSD	0.000001			X				DIN 51900	Several variants of the Calorimeter
	CAL2K	Manual calorimeter	Isothermal (static Jacket)	0.1% RSD	0.00001			X				DIN 51900	Obsolete replaced by CAL 3K

Table 7: Equipment Manufacturers – Summary of Information.

						Stated Compliance From Vendor Literature							
Manufacturer	Model	Description	Modes of operation	Stated Precision	Temp. Res (°C)	IP12	D240	D4809	D2382	GB/T 384	GOST21261	Other	Comments
LECO	AC500	Semi-automatic calorimeter	Isoberibol	≤ 0.05%	0.0001		X	X					
MRC labs.	CALO-11-V2		Isothermal	0.0001	0.0001		X	X		X			
	CALO-3		Isoberibol	≤ 0.15%	0.0001		X						
	CALO-6		Isothermal	≤ 0.15%	0.0001		X						
	CALO-(11/13/15)	Models vary time of analysis	Isoberibol	<0.01% RSD	0.0001		X						
	CALO-40		Isothermal?										
CKIC	5E-C5500	Semi-automatic Calorimeter	Isoberibol	0.05%RSD (benzoic)	0.0001			X					
	5E-C5808/-c5808J	Automatic Calorimeter	Isoberibol/Adiabatic	0.05%RSD (benzoic)	0.0001			X					Unique laser ignition option
	5E-5508	Automatic Benchtop	Isoberibol	0.05%RSD (benzoic)	0.0001			X					
	5E-AC/PL	Semi-automatic Vertical	Isoberibol	0.05%RSD (benzoic)	0.0001			X					
Sundy	SDAC6000	Fully Automatic Calorimeter	Isoberibol	0.05%RSD (benzoic)	0.0001		X	X					
	SDACM3100	Bomb Calorimeter	Isoberibol	≤ 0.15%	0.0001		X	X					
	SDACM4000	Bomb Calorimeter - Vertical	Isoberibol	≤ 0.15% RSD	0.0001		X	X					
	SDC712	Bomb Calorimeter	Isoberibol	≤ 0.1%	0.0001		X	X					
	SDC715	Bomb Calorimeter	Isoberibol	≤ 0.1%	0.0001		X	X					

Table 7: Equipment Manufacturers – Summary of Information (continued).

						Stated Compliance From Vendor Literature							
Manufacturer	Model	Description	Modes of operation	Stated Precision	Temp. Res (°C)	IP12	D240	D4809	D2382	GB/T 384	GOST21261	Other	Comments
INPK RET	Tantal TA-5	Bomb Calorimeter	Free/Variable Temperature	See Table 8	0.00001						X		
	ABK-1	Bomb Calorimeter	Adiabatic		0.0001						X		
	ABK-1V	Bomb Calorimeter	Free/Variable Temperature		0.00001						X		
RTI	BKS-2x	Bomb Calorimeter	Heat Conducting Type		0.0001						X		Unique heat flow system
Etalon	V-08MA NM	Bomb Calorimeter	Isothermal		0.0001						X		
	V-08MA K	Bomb Calorimeter	Isothermal		0.0001						X		
U-Therm	XRY-1C	Automated Calorimeter	Isothermal?	<0.01% RSD	0.0001		X			X			
	PT-XRY-1A+	Partially Automated Calorimeter	Isothermal?	≤0.2%	0.001		X			X			
	PT-HK-384	Fully Automated Calorimeter	Isothermal?	≤0.2%	0.001		X						
Koehler	K88900/88990	Bomb Type Calorimeter	Isothermal/Adiabatic/Isoperibol	0.1% RSD	0.0001		X	X				DIN51900	

Table 7: Equipment Manufacturers – Summary of Information (continued).

Company	Type (model)	Year of Russian Approval	Heat of combustion measurement range, kJ	Normalized relative measurement error, %		Calorimeter experiment time, min	Bomb volume, cm ³
				energy equivalent	specific heat of combustion		
	Tantal TA-5	2006	5–40	0.1	–	23	330 ± 30
INPK RET	ABK-1	2002, 2007	13–40	0.1	–	23	325 ± 30
	ABK-1V	2010	8–40	–	0.1	14	330 ± 30
RTI	BKS-2x	2006	5–11	–	0.2	15	157
	V-08MA NM	2003, 2008	10–40	0.1	–	20	325 ± 15
Etalon	V-08MA K	2008	10–40	0.1	–	20	325 ± 15
	1261 (obsolete)	2000	14–35	–	0.2	9	340 ± 15
Parr	1266	2002	14–35	–	0.2	12	340 ± 15
	6200	2005	15–34	–	0.2	13	340 ± 15
	C200	2006	15–40	–	0.2	17	260 (C5010)
	C2000 up to 2008	2003	13–40	–	0.2	22	260 (C5010)
	C2000 since 2008	2008	13–40	–	0.1	22	260 (C5010)
	C4000 (obsolete)	2003	12–35	–	0.2	16–20	305
IKA	C5000 up to 2008	2003	13–40	–	0.2	22	365
	C5000 I since 2008	2008				22	
	C5000 A since 2008		13–40	–	0.1	14–18	260 (C5010)
	AC-350 (obsolete)	1997, 2004	14–35	–	0.2	20	360
Leco	AC-500	2004, 2009	14–35	–	0.2	20	360
	AC-600	2009	14–35	–	0.2	9*	200

* For the Delta T mode.

Table 8: Review of Equipment Used in Russian [ref. 29].

6.2 CALORIMETER OPERATION

6.2.1 MODES OF OPERATION

Current calorimeter units in production tend to operate on a range of modes and some machines can operate in more than one mode. Isothermal and Isoperibol predominate as the available modes. As noted elsewhere isoperibol control, monitoring and compensation in real time is a special version of isothermal operation and increasingly popular. This is probably because keeping an outer jacket at a constant temperature is easier to achieve than adiabatic where the outer jacket must quickly and accurately follow the inner bucket temperature. Monitoring and Isoberibol temperature compensation is commonly done by built in processors that avoid the need for complex calculations. Plain jacket (insulation only) instruments, whilst being cost effective and easy to use,

do not generally meet precision requirements even for ASTM D240 although units of this type were included in the precision study.

Some less common equipment features were noted. For example, the IKA 7000 does not require water (referred to as a double dry system), RTI, BKS-2x is quoted as having a “heat flow” system and the CKIC Model 5E-C5808/-c5808J has a unique laser-based ignition system.

IKA, members of the German DIN committee, (see Acknowledgements 17) offered the following observations regarding use of calorimetry in industry today:

Most methods allow both adiabatic and isoperibol methodology with the two approaches having their own pros and cons:

- **Adiabatic** control is technically more of a challenge, but if carried out correctly, it can be as precise and as quick as isoperibol. The benefit is that the temperature rise measured requires no correction and is based on the equilibrium temperature before and after. Thus avoiding complex calculations and assumptions.
- **Isoperibol** is somewhat simpler to implement but requires complex controls, monitoring and calculations. These calculations are often embedded in the equipment and therefore less easy to access or audit. Isoperibol can be very quick in dynamic mode but there can be a balance between speed and precision.

Much of the world tends to default to isoperibol but in Germany the preference is adiabatic mode – mostly due to historic legacy.

6.2.2 REFERENCE STANDARDS AND OTHER PROCEDURAL IMPROVEMENTS

During this study, looking across a range of methods and best practice several areas of potential improvement for high precision methods have been identified.

- While benzoic acid is the industry calibration reference, the liquid reference control checks on volatile samples (see 4.3) should be extended to replicate non-volatile liquid samples using certified analogues to jet fuel such as dodecane or hexadecane.
- Adopting the DIN 51900 procedure to do at least duplicate tests should be required for high accuracy requirements.

6.2.3 TEMPERATURE MEASUREMENT

The use of mercury in glass thermometers (MIG) has all but stopped due to difficulty/ required operator skill, increased use of automation and the elimination of mercury for health and safety reasons. Further, very specialist MIG thermometers with careful calibrations can in trained hands achieve at best approximately 0.002°C (or 0.001°C for Beckman differential thermometer) discrimination but this cannot compete with modern instrumentation which can typically achieve 0.0001°C resolution over the 2-3°C rise encountered in a typical test.

Temperature measurement technology is not always clearly stated in equipment literature. Most measurement sensors are copper or more commonly platinum resistance, thermistor, or quartz crystal sensors with associated reading systems. Such instrumentation is key for system automation and even more critically to the increasing use of isoperibol systems which require real time monitoring and correction.

As part of meeting a given test method's precision, the temperature measurement system must be capable of achieving a high degree of discrimination over small temperature changes, which is actually more important than absolute accuracy. This is often specified within the test methods which cite required overall precision but also specify temperature measurement precision, or strictly

speaking, resolution or temperature difference requirements. For example, requirements for temperature measurement of ASTM D240 and D4809 and equivalent test methods are as shown in Table 9.

Test Method	Resolution		
	MIG Thermometer	Differential Thermometer	Platinum Resistance
ASTM D240	0.002°C	0.001°C	0.0001Ω (0.0001°C)
ASTM D4809	0.002°C		0.0001°C
Most other specifications specify 0.0001°C or better.			

Table 9: Standard Test Method Temperature Measurement Requirements.

As can be seen from Table 9, the equipment specifications detailed earlier all claim to comply with ASTM test methods and meet these temperature measurement requirements.

6.2.4 PRECISION

Precision quoted in manufacturers' literature has been summarised for comparison earlier in Table 7 and

Table 8. Note that the way that these figures are defined varies and often only refers to firing with benzoic acid and/or energy equivalence of the system. Many of the equipment manufacturers state that their equipment meets the requirements of major specifications and it must therefore be assumed that precision requirements are met. This might be examined and/or verified as Phase 2 of the CRC study.

6.2.5 COMPLIANCE WITH NATIONAL/INTERNATIONAL TEST METHODOLOGY

As can be seen from this review many manufacturers state that their equipment meets national/international test method requirements. This must be taken to mean that the equipment meets all critical precision requirements with regard to temperature measurements and ultimate precision of the final results.

Although, it may be considered a minor detail it should be highlighted that some equipment (assuming it does meet the precision) does not appear to comply with the detailed requirements of equipment and operating modes. It could be said that these meet the spirit of the test methods if not the letter.

Test methods do not usually state a specific manufacturer or equipment model numbers. However, examination of the test methods in Table 2 reveals the following findings:

ASTM methods describe equipment details and requirements such as temperature measurement systems, bomb and bucket and reference specific manufacturers/models that have been shown to comply.

This approach satisfies ASTM antitrust requirements which do not allow definition of specific commercial equipment but does require some control to maintain technical integrity without excluding other suppliers. For instance, ASTM D4809 states:

“... Calorimeter Jacket, Parr No. 1261 or equivalent), available from Parr Instrument Co. meet the specification requirements” and similarly for the “oxygen bomb Parr No 1108 or equivalent”. But adds, “if you are aware of alternative suppliers, please provide this information to ASTM International Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend”.

As noted elsewhere in this report the Parr equipment listed (based on discussions with Parr and ASTM sub-committee D02.05) is now obsolete. Further, both D240 and D4809 allow the use of MIG thermometers despite their inferior resolution and obsolescence.

Conversely, since IP12 is very out of date compared to other methods, no equipment manufacturers cite compliance with the standard.

ASTM D240 only cites Parr as a potential supplier but does not specify model numbers.

In a similar way GOST 21261 ref. [8] states “Liquid bomb calorimeters of types V-08, V-09, V-08MA, V-08MB with an isothermal water shell in accordance with TU 25-11.1426 and other calorimeters that provide determination results within the permissible discrepancies specified in Sec. 6” (i.e. Sec. 6 is precision requirements).

From [ref. 29], summarised in

Table 8 it can be seen that approved units (which it is assumed would be considered acceptable for GOST 21261) are a mixture of national and imported equipment and therefore come under the “other calorimeters” allowance.

GOST 21261 precision is very similar to ASTM D240 and all the instruments listed in [ref. 29] would therefore be expected to meet precision of ASTM D240 and indeed may meet D4809 requirements. However, the precision stated for the instruments is only one element in the overall analysis and therefore it cannot be assumed that overall precision is the same level. In fact it is likely to be higher than the instrument errors alone.

In summary, taking the review of test methods and equipment together clearly demonstrates that there is somewhat of a disjoint between many methods and the actual equipment now available.

6.3 ANALYTICAL BALANCE REQUIREMENT.

Accurate weighing the benzoic acid calibration charge, sample and firing wire/cotton together with any system used for volatile samples, is critical to method precision and accuracy. Also, controlling the weight of the calorimeter bucket and water to within close limits is required to ensure a consistent water/energy equivalent.

Analytical balances are general laboratory items and specific makes/models have not been identified as part of this study. However, equipment requirements as demanded by the test methods are cited for completeness. Standard test methods generally do not specify a particular type of balances except for ASTM D4809 that defines the requirement for a “semi-micro analytical balance” for samples and a “heavy duty analytical balance” for the bucket.

For all methods, the balance requirement is in effect defined by the level of discrimination required. This does vary between methods and is summarised in Table 10.

Test Method Measurement	Sample weight specification	Water Measurement Specification
IP12	weigh to 0.1mg	within 0.5g
D240	weigh to 0.1mg	± 0.5g
D4809	weigh to 0.01mg	± 0.05g
D2382	weigh to 0.01mg	± 0.05g
GB/T 384	weigh to 0.2mg	within 1 gm
GOST 21261	weigh to 0.2mg	----

Table 10: Standard Test Method Sample and Calorimeter Bucket Weight Requirements.

6.4 AUTOMATION OF CALORIMETERS

Calorimeters range from fully manual, which are often used in research and teaching environments where the fundamentals can be observed and understood, to fully automated machines that do all the sequencing, control, monitoring, and calculations for high throughput laboratories.

However, a fully automated calorimeter where the sample is simply injected and then left to do a firing, analysis, and report does not and could not exist. Based on discussions with two major calorimeter manufacturers⁷, the main stumbling block to a fuel injection-based system is the need for extremely accurate sample weight. Even the best sample loops used in chromatography systems, for example, cannot dispense or measure a sample to the required accuracy (see Table 10). Therefore, whilst it is possible to fully automate the actual calorimeter sequencing of pre/firing/post process, loading the system beforehand and unloading afterwards essentially remains a manual task requiring a skilled laboratory operator. The handling of volatile samples requires more skill and dexterity than non-volatile samples and the need for vapour suppression measures and corrections makes the task more difficult and prone to errors. This is clearly reflected in the lower precision for volatile samples cited in ASTM D4809.

A summary of cycle times and operator intervention times are provided in section 6.4.

Key actions that require careful and skilled operations can be summarised as at least the following:

- Work in a clean and reproducible manner with the correct and controlled laboratory environment.
- Weigh the crucible, sample, and tape etc. correctly on a semimicro balance to 0.01 mg (ASTM 4809).
- Handle benzoic acid (NIST) to make pellets correctly.
- Use the correct amount of sample in combination with combustion aid to measure in the linearity range of a calorimeter.
- Use the combustion aids correctly for volatile samples, for example, tape or capsules which require skilled and careful handling.
- Ensure the calorimeter is in good working order, well maintained and calibrated.
- Check visually the proper combustion result (fully combusted or are there any residues).
- Be able to interpret results to ensure consistency and reliability.

Table 11 provides an overview of the levels of calorimeter automation available in the market today.

⁷ Input from Parr and IKA is gratefully acknowledged.

Based on industry experience with other emerging semi or fully automated equipment, control of software and hardware versions could be an issue that needs to be considered in any future test methodology and cited equipment.

Process Step	Process Description	Manual	Potential Automation in automated calorimeters	Benefits
Sample Weight	Weighing Cup Cup Plus Fuel Volatile Fuel Measures	Manual operation and manipulation	Actual Cup loading and tape, etc. cannot be automated. Electronic Transfer of data available.	Electronic transfer removes transcription errors
Bomb Loading	Inserting Cup Placing firing wire, and/or thread. Adding water.	Manual operation and manipulation	Cannot be automated	
Bomb Pressurisation	Fill to 30 atm	Manually operated valve to regulate pressure and flow.	Can be automated from semi to fully automated	Slow and consistent bomb pressurisation
Bomb Insertion.	Lower bomb into water bucket. Insert bucket in calorimeter.	Manual operation and manipulation	Can be automated. Ultimately the bomb can be fixed within the calorimeter with easy sealing/filling system.	Reduces operator time and more consistent process
Bucket water temp. and weight	Ensure correct mass of water and correct temp.	Manual water dispenser and/or balance	Automation by filling in situ possible. Ultimately the bomb can be fixed within the calorimeter with easy sealing system.	Reduces operator time and more consistent process
Pre Firing Seq.	Monitor and record temp.	Use of MIG thermometers - manual only	Read out and/or automatic data logging available	Reduces operator time. Removes operator reading errors. Increased precision and resolution. More consistent sequencing. Enables auto sequencing and calculation.
Firing	Initiate firing based on criteria	Use of MIG thermometers - manual only	Read out and/or automatic data logging available. Automatic firing init. based on processor control.	Reduces operator time. Removes operator reading errors. Increased precision and resolution. More consistent sequencing. Enables auto sequencing and calculation.
Post Firing	Monitor and record temp.	use of MIG thermometers - manual only	Read out and/or automatic data logging available. Automatic routine completion based on processor control.	Reduces operator time. Removes operator reading errors. Increased precision and resolution. More consistent sequencing. Enables auto sequencing and calculation.
Post-test bomb analysis	Check for complete combustion. Rinse and analyse	Manual operation and manipulation	Cannot be automated as regards bomb rinsing but auto titrator could be used	Still manual operation but auto titrator reduces operator intervention.
Correct for true temp. Delta	Isothermal or Isoperibol corrections	Manual Calculation as per test method	Input and/or acquisition of required data to calorimeter. Calculation by embedded software (essential for isoperibol)	Temperature correction is complex. Automatic calculation reduces potential errors. Data logging/recording improves traceability and process quality control.
Corrections	Corrections for wire, thread, tape etc	Manual Calculation as per test method	Input of required data to calorimeter still manual. Calculation by embedded software.	Inputs still required by operator but automatic calculations reduces potential error and reduces operator time. Data logging/recording improves traceability and process quality control.
Gross to Net	See text	Manual Calculation as per test method	Calculation by embedded software.	Automatic calculations reduce potential error and reduces operator time. Data logging/recording improves traceability and process quality control.

Table 11: Calorimeter Automation Levels Summary.

7 ESTIMATION METHODS - BASIC PRINCIPLES.

7.1 GENERAL PRINCIPLES OF ESTIMATION METHODS

The overall heat released by a given fuel on combustion depends on its chemical composition and physical state. Whilst obtaining the detailed composition is complex it is possible to estimate the heat of combustion from broad inspection/specification test data when fuels are in a well-defined class in terms of physical, chemical and performance properties.

For hydrocarbon fuels [see Note 1], the key factors that impact the overall heat of combustion include:

- **Density**, where there is a trend of increasing heat of combustion per unit mass as the density decreases. This also means that the energy density per unit volume falls as the density reduces (see section 3).
- **Volatility**, as defined by distillation range, which gives an insight into molecular weight distribution.
- **Aromatic content**, as determined by direct measurement or inferred by hydrogen content or aniline point [see Note 2]. This is relevant since the energy density of aromatic molecules is quite different to paraffinic molecules due to different Carbon-Hydrogen (C-H) bond strengths and lower Hydrogen (H) content. Measures of aromatic type and concentration versus paraffinic are therefore a broad indicator of relative heat of combustion. The specific influence of olefins tends to be ignored as they only present in limited amounts in aviation fuel.
- **Sulphur content**, which is included to capture the formation of sulphur dioxide.

Note 1: *The presence of oxygenates such as alcohols and ethers, together with other species such as amines, can significantly influence fuel energy content rendering many correlation methods ineffective.*

Note 2: *The aniline point is the lowest temperature at which aniline and a sample of fuel (usually in equal proportions) are completely miscible, and which serves as an indication of the type and level of aromatic hydrocarbons present in the fuel often referred to as “aromaticity”. Generally, the lower the aniline point the higher the aromatics level. However, the aniline point also varies with the type of aromatics, so the relationship is not simple.*

Estimation methods which make use of these general relationships (correlations) are defined earlier in Table 3.

Each of the above parameters has an impact, so most methods use a combination of factors. However, all are based on multivariate correlations from limited sample databases where the relevant properties are correlated with determined values. This is significantly different to a scientific examination of molecular types present and their relative heats of combustion. Current estimation methods are therefore based more on experimental data and correlations than on any understanding of the relative energy released by the molecules present (except in very broad classes) which, at the time of development, was too complex.

Historically, aniline gravity was a common method to estimate heat of combustion and featured in many fuel specifications. It relies on the principle that the two main factors influencing calorific value are density (expressed as API gravity in older test methods) and aromatics level. Density is a standard laboratory test and use of aniline point was prevalent to determine the aromaticity of a range of refined petroleum products. Therefore, since density and aniline point data were readily available, aniline gravity was a convenient method to use. However, use of aniline has raised

significant health and safety concern in recent years and this estimation had declined in favour of other correlations.

The above observation may change with recent introduction of a new method, ISO 21493 – 19 [ref. 30, 31]. This uses para-anisaldehyde as a substitute for aniline to help address health safety and environmental safety concerns. This method purports to be able to be carried out by the same method and using the same automated apparatus as used for aniline point. An equation is also provided that allows results to be converted to aniline point. This may support a resurgence in the use of aniline gravity estimations, but only after the para-anisaldehyde approach has been verified for correlation use.

Section 8 reviews the state of the art of current estimation methods.

At the extremes of the spectrum of fuel composition understanding, heat of combustion can be determined (within limits) for a fuel by actual combustion without any real knowledge of its hydrocarbon make up. At the other (theoretical) extreme, a fuel could be fully analysed and the heat of combustion of each component could be summated to give a total value. Current estimation methods try to do the latter but by overly broad categorisation of molecular types present and their concentration inferred from other properties. With the advent of improved analytical techniques and computational power it could be envisioned that a much more detailed composition, molecule data library and computational models could “dissect” a fuel to such granularity that the heat of combustion could be estimated by summation more accurately. This concept is discussed in section 11.2.

7.2 ANALYSIS TIME AND OPERATOR TIME.

Compared to carrying out specific analysis to determine calorific value, estimation by calculation takes much less time and operator resources. Manual calculation using equations or look up tables is a matter of seconds for an experienced operator and is ideal for computer automation in production laboratories. In addition, the input data required are typically available and carried out for other purposes which reduces cost. As such, calculation/estimation methods are very prevalent in Industry and may even be built into Laboratory Information System software (LIMS). If this were not true and determinations required specifically and solely for heat of combustion calculations, the benefits of this approach would be eroded.

7.3 REVIEW OF LIMITATIONS AND CHALLENGES TO DEVELOP ESTIMATION METHODS.

Examining the principles on which estimation values can be derived shows that general relationships do exist and therefore compositional data will provide a level of prediction. However, assuring accuracy (as opposed to precision) is the key issue, particularly when a wide range of compositions which, whilst meeting specification, may well be outside the original scope of the correlation database. This could be the case for example, due to changes in conventional fuel production or use of new synthetic blend components at increasing levels which although acceptable as jet fuel blend components may be outside the compositional scope of the original correlation database. The opportunity to improve these methods by using advanced analytical techniques is seen as an opportunity but again challenges of complexity may limit usefulness.

The following paragraphs provide a review of known correlations that to some degree allow estimations but also some key property characteristics that may limit accuracy. These are provided to put the following examination of current and future methods in context. As a nominal target, and for comparison with the data presented below, it is worth noting that ASTM D4809 (the most precise and accurate calorimetry method used for jet fuel) has a precision stated as 0.8% for a typical jet and a bias of 0.2%.

7.3.1 RELATIONSHIP WITH DENSITY AND VOLATILITY.

The general relationship of heat of combustion, also expressed as energy density per unit mass and per unit volume, is well established for the pure hydrocarbons and fuels ranging of from methane to heavy diesel fuels, etc.

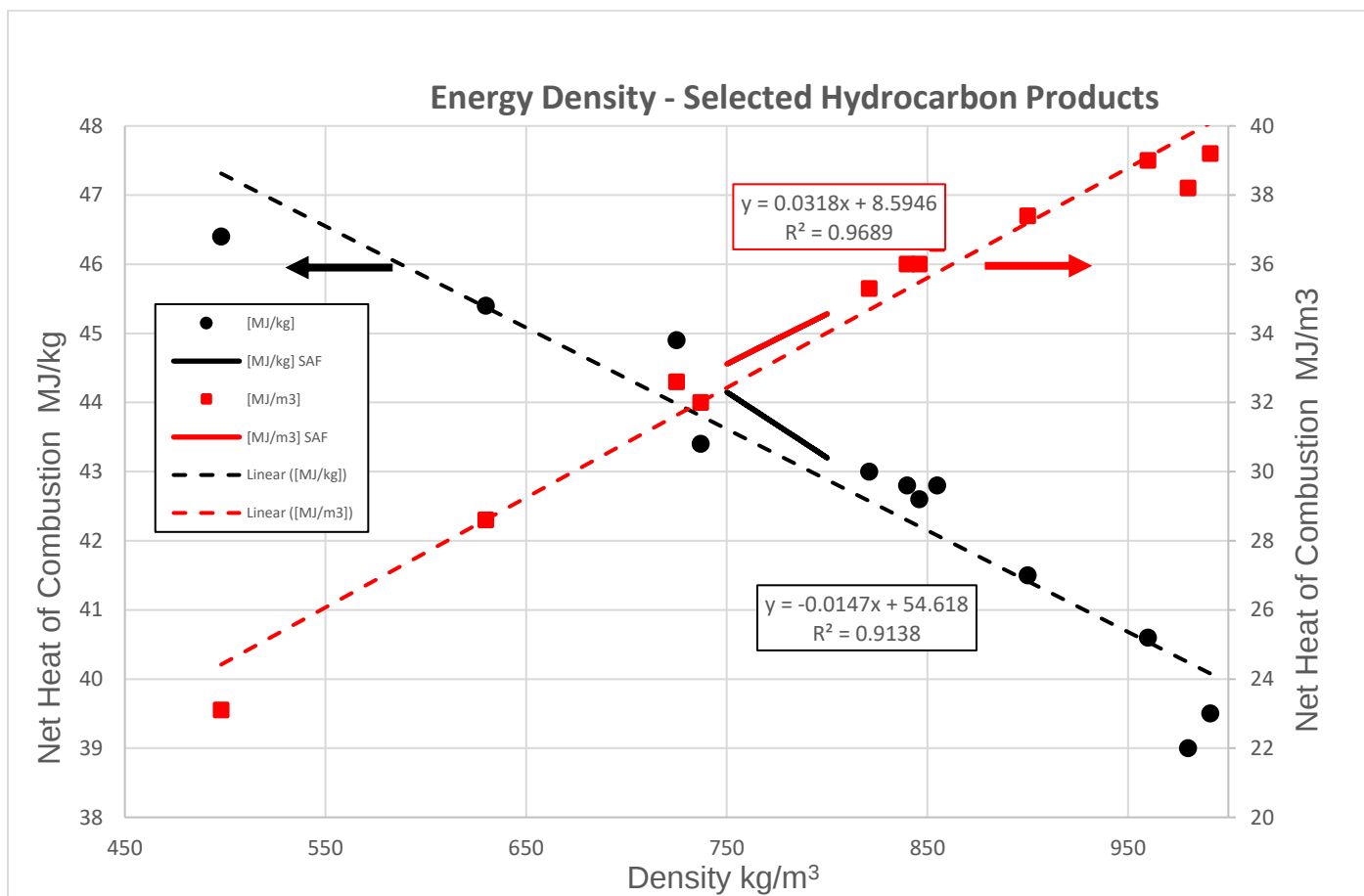


Figure 9: Relationship Between Density and Energy Density.

Figure 9 shows the general relationship between density, which also broadly correlates with volatility, for a range of pure hydrocarbons and fuel products from reference data [ref. 32]. This covers from butane through naphtha, kerosene to heavy gas oil (980 kg/m³) and the relationship is shown by the dotted lines. Whilst this relationship is clear, the reality is that within the range of jet fuel this relationship is only good for a very broad estimation and can with care be used as such but is prone to errors due to fuel compositional variability. The two solid lines show the values for a range of hypothetical blends of a typical Synthetic Paraffinic Kerosene (SPK) (often marketed as Sustainable Aviation Fuel (SAF)) taken from several reports from 0% to 100% v/v blend ratio, data being provided in Table 12 as calculated by the author. These values do not sit on the general line and the slope is also slightly different so illustrating the limitations of this parameter. Note this graph and the associated data are provided for illustration purposes since the exact details of how data were derived or their ultimate accuracy are not known.

These data also support the discussion regarding the impact of fuel density and heat of combustion relationships, which will change with increased use of current (up to 50%) or even higher blend ratios of SAF in the future and their impact on aircraft fuel loading calculations. Results correlate well with the finding discussed in section 3 (ANZ test). Note that the 50/50 blend is highlighted to show the increase in energy per unit mass of approximately 1.1% but reduction

per unit volume of approximately 2.1% which again correlates well with the ANZ test findings reported.

In the above the effect on energy density as SPK blend levels increase is mainly due to the reduction in aromatics present in the conventional component of the blend. This relationship in energy density for aromatics compared to alkanes is discussed further in the next section.

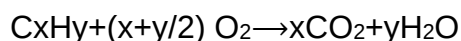
		Density	HOC (MJ/kg)	HOC (MJ/lt)	HOC (MJ/kg) % change vs Typical	HOC (MJ/L) % change vs typical
Typical Jet A/A-1		800	43.20	34.56	0.0	0.0
Typical SPK		750	44.15	33.11	2.2	-4.2
Blend Data						
Jet (%)	SPK (%)					
100	0	800	43.20	34.56	0.0	0.0
90	10	795	43.30	34.42	0.2	-0.4
80	20	790	43.39	34.28	0.4	-0.8
70	30	785	43.49	34.14	0.7	-1.2
60	40	780	43.58	33.99	0.9	-1.6
50	50	775	43.68	33.85	1.1	-2.1
40	60	770	43.77	33.70	1.3	-2.5
30	70	765	43.87	33.56	1.5	-2.9
20	80	760	43.96	33.41	1.8	-3.3
10	90	755	44.06	33.26	2.0	-3.8
0	100	750	44.15	33.11	2.2	-4.2

Table 12: Hypothetical SPK Blends and Associated Heat of Combustion.

7.3.2 IMPACT OF ALKANE ISOMERS

Since alkanes make up the major proportion of most jet fuels the following section focusses on this class of molecules and the principle of variability between isomers.

It is well established that branched alkanes (iso-alkanes) are generally more stable than the straight-chain (n-alkanes) with the same number of carbon atoms. That means iso-alkanes have higher values of enthalpy of formation (ΔH°_f) compared to n-alkanes with the same number of carbon atoms. During the combustion reaction with oxygen, all alkanes produce CO_2 and H_2O regardless of whether they are n- iso or indeed cyclo-alkanes:



The heat of combustion (note in this context heat and enthalpy are equivalent) is given by:

$$\Delta H^\circ_c = x(\Delta H^\circ_f \text{CO}_2) + y(\Delta H^\circ_f \text{H}_2\text{O}) - (\Delta H^\circ_f \text{C}_x\text{H}_y)$$

Thus, the heat of combustion is larger if the heat of formation of initial alkane molecule is lower (less stable). Thus, it would be expected that n-alkanes would have higher heat of combustion compared to their equivalent carbon number iso-alkanes [ref. 34].

Figure 10 shows that all iso (branched) alkanes do indeed have higher heat of formation than their normal (straight chain) counterparts and thus will have lower heat of combustion [ref. 35]. It is also worth note the considerable, in terms of accurate overall heat of combustion from compositional data, variability for each respective carbon number. This overall trend of lower heat of combustion for branched alkanes vs their normal equivalents is also shown in the data in Table 13 above.

7.3.3 RELATIONSHIP WITH AROMATICS

Many methods use aromatics content (or aromatics to paraffinic ratio) as a factor to predict heat of combustion, usually combined with density, e.g., aniline gravity. As noted in section 7.1, fuel aromatic concentration may be input directly or by inference from hydrogen content or by aniline point which implies a general level of aromaticity.

Table 13 shows the heat of combustion of a range of alkanes (paraffinic) and aromatic compounds to illustrate the relative heat of combustion values in terms of energy per unit mass and per unit volume. These are taken mainly from [ref. 33].

These data show the difference in energy density per unit mass, being significantly higher for typical alkanes (paraffinic) compared to the example aromatics compounds. But conversely the aromatics have relatively higher energy per unit volume due to their higher density.

Thus, an overall measure of aromatic content (ratio to alkanes) will broadly correlate with heat of combustion, and this is the principle on which estimation methods/correlations are based. These example compounds only cover a very small selection of what could be present in fuels. Should, say, high octane unleaded AVGAS development seek to include ethanol, ethyl tertiary butyl ether (ETBE) or methyl aniline, the heat of combustion would be radically different to hydrocarbons boiling in the same range. For example, ETBE boils at 69 - 71 °C but has a 19% lower net calorific value compared to n-hexane.

Hydrocarbon			
Formula	N – Alkanes (N-Paraffins)	MJ/kg	MJ/L
CH ₄	Methane	50.01	6.90
C ₂ H ₆	Ethane	47.79	—
C ₃ H ₈	Propane	46.36	25.30
C ₄ H ₁₀	Butane	45.75	—
C ₅ H ₁₂	Pentane	45.36	28.39
C ₆ H ₁₄	Hexane	44.75	29.30
C ₇ H ₁₆	Heptane	44.57	30.48
C ₈ H ₁₈	Octane	44.43	—
C ₉ H ₂₀	Nonane	44.31	31.82
C ₁₀ H ₂₂	Decane	44.24	33.29
C ₁₁ H ₂₄	Undecane	44.19	32.70
C ₁₂ H ₂₆	Dodecane	44.15	33.11
	Iso – Alkanes (Iso-Paraffins)		
C ₄ H ₁₀	Isobutane	45.61	—
C ₅ H ₁₂	Isopentane	45.24	27.87
C ₆ H ₁₄	2-Methylpentane	44.68	29.18
C ₆ H ₁₄	2,3-Dimethylbutane	44.66	29.56
C ₇ H ₁₆	2,3-Dimethylpentane	44.50	30.92
C ₈ H ₁₈	2,2,4-Trimethylpentane	44.31	30.49
	Naphthenes (cyclo- alkanes)		
C ₅ H ₁₂	Cyclopentane	44.64	33.52
C ₆ H ₁₂	Methylcyclopentane	44.64	33.43
C ₆ H ₁₄	Cyclohexane	43.45	33.85
C ₇ H ₁₄	Methylcyclohexane	43.38	33.40
	Aromatics		
C ₆ H ₆	Benzene	40.17	35.10
C ₇ H ₈	Toluene	40.59	35.19
C ₈ H ₁₀	o-Xylene	40.96	36.05
C ₈ H ₁₀	m-Xylene	40.96	35.23
C ₈ H ₁₀	p-Xylene	40.80	35.13
C ₈ H ₁₀	Ethylbenzene	40.94	35.45
C ₉ H ₁₂	1,2,4-Trimethylbenzene	40.98	35.90
C ₉ H ₁₂	n-Propylbenzene	41.19	35.51
C ₉ H ₁₂	Cumene (isopropylbenzene)	41.22	35.53

Table 13: Range of Hydrocarbon Reference Heat of Combustion Data [ref. 33].

Note 1: Data has been collated from several sources and may not be consistent.

Note 2: Data is presented for illustration purposes only as accuracy cannot be guaranteed.

Note 3: This table contains compounds that are within the range of gasolines and jet fuels but some of the lower C number compounds would not be found in either fuel types.

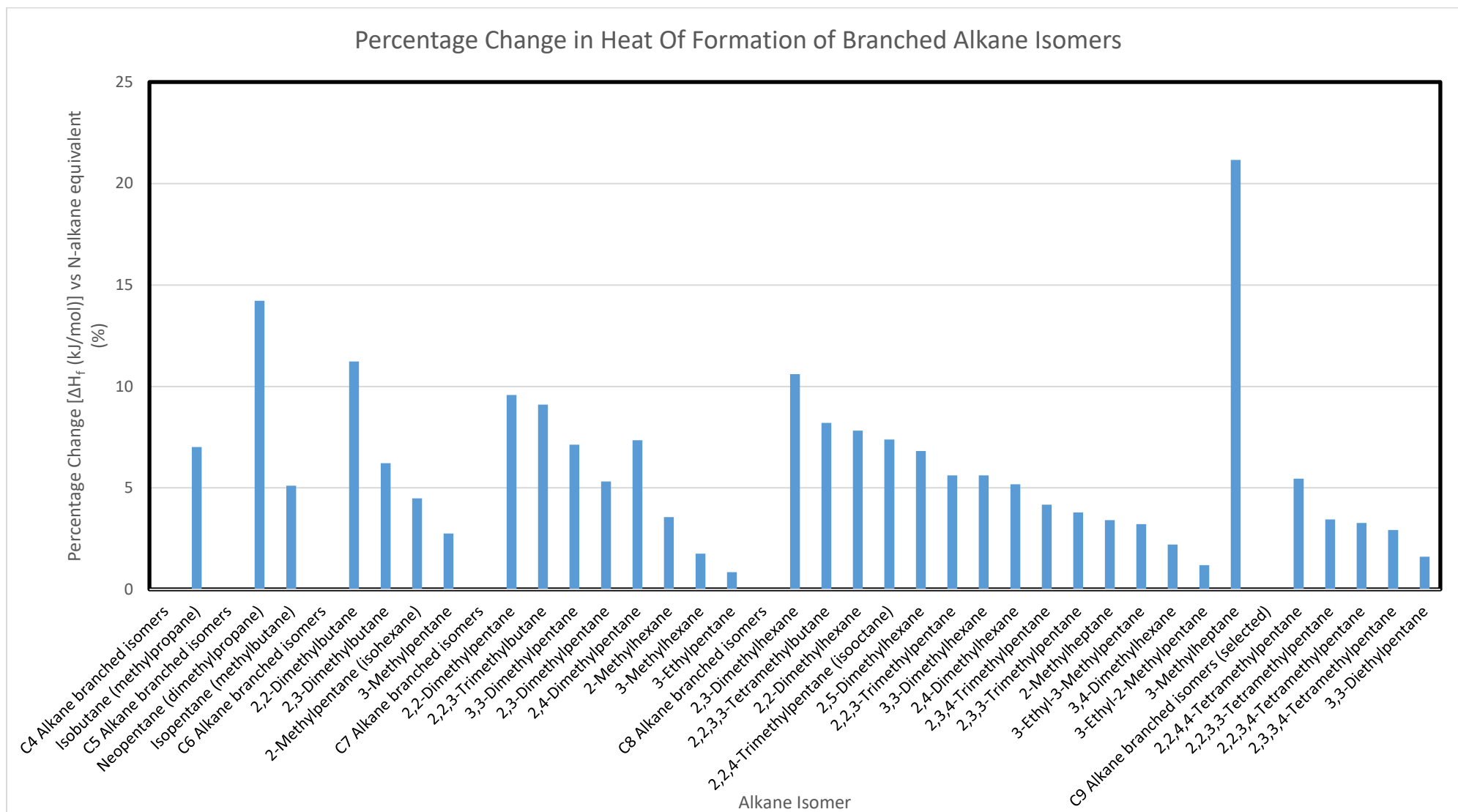


Figure 10: Comparison of Iso Alkane Isomer Heat of Formation [ref. 35].

An estimation method based on boiling distribution alone would not identify this fundamental difference and, for instance, would need to factor in the type and levels of these components. Table 13 also illustrates that even within two classes of hydrocarbon compounds, alkanes and aromatics, there is some variability. As such estimates again will have limitations to accuracy if just the percentage aromatics is used versus a more granular approach.

Heats of combustion of select hydrocarbons and Impact of C-H Bonds				
Cycloalkane	CH ₂ Units	ΔH^{25°	ΔH^{25°	Ring Strain
(CH ₂) _n	n	kJ/mole	per CH ₂ Unit	kJ/mole
Cyclopropane	n = 3	1968.54	656.04	115.92
Cyclobutane	n = 4	2580.06	645.12	110.88
Cyclopentane	n = 5	3114.3	622.86	27.3
Cyclohexane	n = 6	3704.82	617.4	0
Cycloheptane	n = 7	4348.68	621.18	26.46
Cyclooctane	n = 8	4981.2	622.44	40.32
Cyclononane	n = 9	5607	622.86	49.14
Cyclodecane	n = 10	6220.2	622.02	46.2
CH ₃ (CH ₂) _m CH ₃	m = large	—	617.4	0

Table 14: Examples Cycloparaffin Heat of Combustion Data [ref. 36].

These differences reflect subtle structural variations, including the different C-H bond energies (that need to be broken) and steric crowding of neighbouring groups and is shown numerically in Table 14. In small-ring cyclic compounds ring strain can be a major contributor to thermodynamic stability and chemical reactivity. Cyclo-alkanes can be a major component of jet fuel and cyclo isomer C-H bonds also experience angle and eclipsing strain which again affects their heat of combustion and analysis of the C-H bond energy changes. See [ref. 36].

Therefore, simple measures of overall alkane content will have limited reliability when the variation in isomer mix is unknown and this is further exacerbated by synthetic blends where the isomer mix may be very atypical or skewed compared to the conventional fuels that were used to create the correlations.

7.3.4 AROMATICS COMPOSITION IMPACT

The above sections show that bond energies and therefore molecule stability have a significant impact on heat of combustion for paraffinic molecules that represent the bulk of most jet fuels (75-92%). The same applies to aromatics (8-25%). Table 15 shows the significant difference in the typical bond length and energies for the benzene C-C bond versus typical paraffin C-C bond. The C-H bond energies for typical jet fuel aromatic compounds are even more complex than the paraffinic part. Most compounds labelled as “aromatics” by standard jet fuel specification methods will have straight chains or cyclo paraffinic rings attached and these can vary in relative size and position on the aromatic ring. Add to this the possibility of multiple aromatic rings makes deriving the overall bond energies and therefore heat of formation and/or heat of combustion highly

complex and beyond the scope of this study. These effects demonstrate that any method that seeks to predict heat for combustion by identification of aromatic type will be challenging and require a high degree of capability to identify specific molecules and their concentration.

Bond Type	Bond Length (pm)	Bond Energy (kJ mol ⁻¹)
C-C	154	356
C=C	133	636
benzene	139	518

Table 15: Typical Carbon - Carbon Bond Energies.

7.3.5 SUMMARY

The concept of being able to calculate with sufficient accuracy the heat of combustion for a well-defined class of fuels has the benefit of very little need for extra resource, effort, or equipment. However, all current methods come with caveats regarding the scope of fuels over which they can be relied, and this is primarily based on the range of fuels used on the correlations.

An analysis of the principles involved carried out in this section shows that heat of combustion will broadly correlate with the parameter inputs commonly used in existing estimation methods and therefore represent a rational approach. However, analysis of factors that will impact on actual heat of combustion values such as isomer type show that composition variability within a broad class of molecules, e.g., simple aromatic/paraffinic ratio can significantly limit the reliability of such methods.

This limitation highlights the need for the caveats that estimation methods generally state, namely that precision (based on the input data) is defined but actual accuracy (i.e., possibility of errors) can be far greater than the often good precision may suggest. It also shows that fuels with unusual composition either from conventional sources, or perhaps more likely from synthetic blends that skew away from the typical (or base correlation) ratios, may well give erroneous results.

The analysis also shows that improving current methods by more detailed analysis and reference to library values for each individual compound will be challenging. Workers in the area of predicting novel blends recognise this issue, confirming the findings of the present study. This is discussed in more detail in section 11.

At the start of this section, it was stated that, as a nominal target and for comparison with the data presented below it is worth noting that ASTM D4809 (the most precise and accurate calorimetry method used for jet fuel) has a precision stated as 0.8% for a typical jet and a bias of 0.2%. Therefore, for any estimation (calculation) method based on compositional data to compete with calorimetry, particularly when ultimate accuracy is required, will be challenging. That is not to say that there is no room for improvement with current methodology.

8 ESTIMATION METHODS – STATE OF THE ART

8.1 SUMMARY OF ESTIMATION METHODS IN USE

Table 1 provided earlier offers a summary of all the leading fuel specifications within the scope of this study and the standard test methods quoted for both determined and estimated (calculated) net heat of combustion. Based on this all the estimated heat of combustion methods featured in these major specifications are summarised in Table 3 and the current review is based on the following approach:

- Review of the test methods.
- Review of Research Reports and cited documents within each respective method. These are discussed in detail where the reports have been made available⁸.
- Discussion with the relevant sub-committees that have responsibility for these methods which are D0.05 and SC-B-10 for ASTM and Energy Institute (IP) methods, respectively.

Table 3 shows the principal inputs for the various methods. As discussed earlier, the methods all rely purely on empirical correlations based on experimental information that was produced or available at the time and quite often from limited data sets. Whilst it is known that in general the parameters used will relate to overall heat of combustion, no real in-depth science is involved, just multivariate analysis. This is an important point when considering alternative methodologies that are opening up with the advent of improved analytical techniques and computing power. This is discussed later in section 11.2.

8.2 ESTIMATION METHODS – SCOPE AND CAVEATS

It should be noted that as a rule all these methods have some critical caveats in their application which is variously defined within the test methods. These are illustrated in the following examples as extracts from ASTM D3338/D3338M – 20 [9] (also referred to as D3338 in this report for brevity) which are typical of most similar methods:

- **Significance and Use.** *This test method is intended for use as a guide in cases where an experimental determination of heat of combustion is not available and cannot be made conveniently, and where an estimate is considered satisfactory. It is not intended as a substitute for experimental measurements of heat of combustion.*
- **Scope.** *“The estimation of the net heat of combustion of a hydrocarbon fuel is justifiable only when the fuel belongs to a well-defined class for which a relation between heat of combustion and aromatic and sulfur contents, density, and distillation range of the fuel has been derived from accurate experimental measurements on representative samples of that class. Even in this case, the possibility that the estimates may be in error by large amounts for individual fuels should be recognized. The fuels used to establish the correlation presented in this method are defined as follows...”*
- **Precision:** *“The repeatability and reproducibility stated above is based on the summation of the repeatability and reproducibility of the test methods used in the calculations. It does not include the effect of the scatter of the original data about the regression line, described by Eq. 1 and Eq. 2. Therefore, the possibility that individual estimates may be in error in excess of the above precision should be recognized.”*
- **NOTE 5** *“Therefore, the possibility that individual estimates may be in error in excess of the above precision should be recognized.”*

⁸ Many of these reports are either not available or not relevant given the changes that have taken place over the years. Therefore, only relevant and available supporting reports are discussed.

The data and information reviewed in this report suggests that the above caveats and limitations will apply equally to any such methods whether it is explicitly stated or otherwise, particularly with ongoing changes in fuel composition. The magnitude of potential errors cannot be assessed within the scope of this report but warrant further examination.

The precision statements often only account for the variability by statistical treatment of the input data precision and therefore the variability due to the quality of the regression equation may in effect be ignored. This is at least a scientifically questionable approach which serves to highlight the importance of the warning statements made regarding errors in excess of the precision. This could lead to the situation where several workers analyse a fuel and get very similar results, but importantly, these could be grossly inaccurate by the same amount if the relationship has not been established as required. This emphasises the need to establish that the estimation method is valid for the fuel samples being analysed by comparison with determined values.

Further many test methods may use different language, but these limitations are essentially the same. Interestingly another common statement is that:

“These methods should only be used where actual determinations are not possible.”

Interestingly the methods necessitate that a relationship between accurate determined values and estimated values has been established. This could be interpreted in two ways:

1. The fuels that the method can be used on are limited to those classes listed within the specification.
2. The relationship for *“a well-defined class for which a relation between heat of combustion and aromatic and sulfur contents, density, and distillation range of the fuel has been derived”* suggests that this needs to be established by the user for their specific situation.

If it is the former, then any fuel meeting the specifications listed can be analysed. If it is the latter, then the relationship needs to be established against determined values. Indeed, confirmation that the equation applies to the fuels in question would increase confidence in the results. But the method does not give any indication of the process to follow in the event that a diligent laboratory undertakes a study of estimated versus determined values and a relationship does exist but is not the same as the standard equation(s) defined.

These requirements combined, if taken to the letter of the test method, severely limit its usefulness and applicability by a somewhat binary approach. In other words, the class of fuels for which the method can be applied must comply with the equations defined. Procedures to deal with the scenario where a class of fuels have a clear correlation which is not the same as the standard equations would be useful. This would allow both the letter of the test method to be met and increase precision.

For example, the World Fuels Survey reported in CRC 647 [ref. 37] offers a relatively rare example where specification data to provide an estimate by ASTM D 3338 and determined values by ASTM D4809 were available for a significant set of fuels. The report noted⁹ that *“ASTM D 3338 yields higher values of heat content when compared to ASTM D 4809. The average difference between the two methods is 76 Btu/lb (0.177 MJ/kg), with a maximum difference of 248 Btu/lb (0.577 MJ/kg) and a minimum difference of 14 Btu/lb (0.033 MJ/kg)”*. The Report provided tabulated data which have been taken and used to calculate a best fit line comparing determined and estimated values. This is shown in Figure 11 with values and correlation (blue) and the ideal (one to one) line as solid black. Combined with the findings of CRC Report 647 this clearly demonstrates that the

⁹ Values were only quoted in BTU/lb in the original report. MJ/kg values have been added by the author to allow comparison in current preferred units.

relationship for these fuels is relatively good fit. Whilst the slope looks correct a bias is present with D3338 typically +0.2 MJ/kg (+0.5%) higher. If the assumption is made that the D4809 results are correct, then this overall bias does not compare well against the stated repeatability and reproducibility of 0.021 MJ/kg, and 0.046 MJ/kg respectively. Further it should also be noted that some individual fuels gave significantly different results, particularly at the lower end. Note that this is a limited dataset and is provided to illustrate issues under discussion. A far more comprehensive study of data produced by consistent and traceable methods and with sufficient scope of fuel types/composition etc. would be required to fully assess the limitations of the methods under review.

This example confirms the need for the caveats commonly used in such methods.

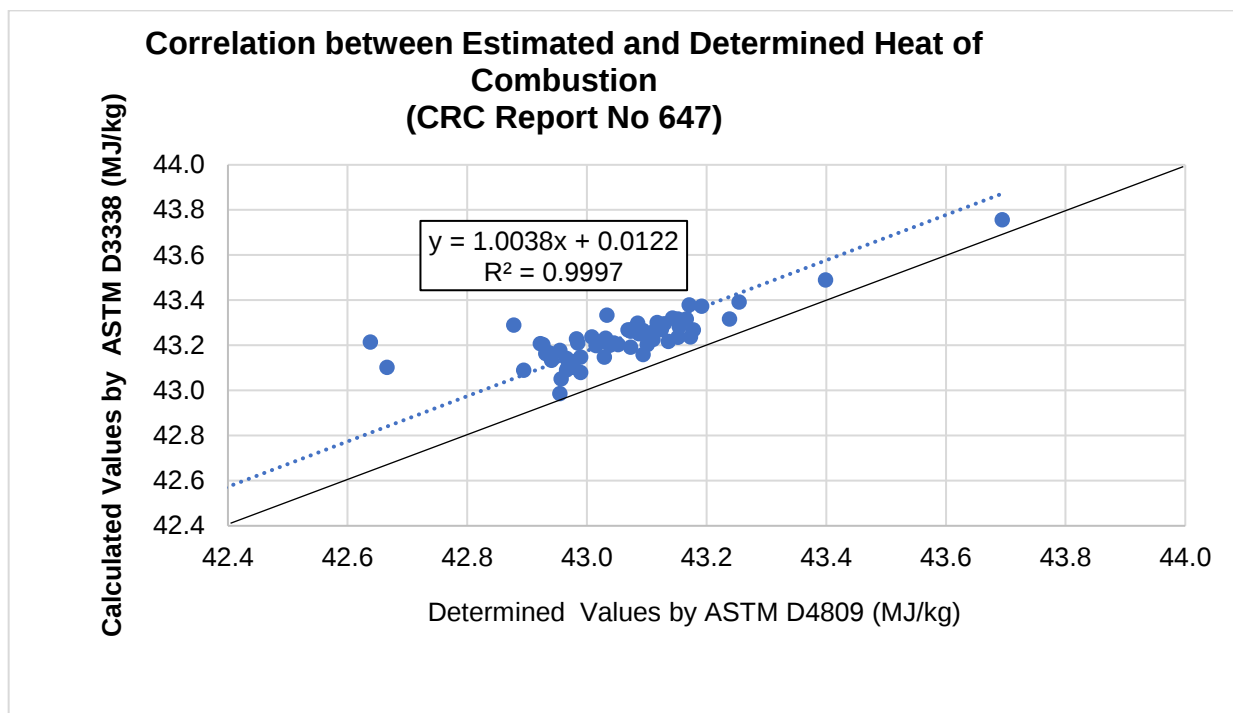


Figure 11: Correlation of World Survey Data on Estimated and Determined HOC Values [ref. 37].

Additionally none of the methods provide a bias statement, despite there being well established determination (bomb) methods. For these methods, the difference between precision (scatter within multiple results) versus accuracy (scatter around the true result) may be vastly different as noted earlier for good technical reasons. Hence the caveats and limitations.

From the author's extensive experience in aviation fuel calorimetry it is commonplace to see estimated methods being used without first establishing that the relationship applies at a given location by carrying out measured values. Indeed, it was recently noted by the US Air Force [ref. 38] in the analysis of fuels for the National Jet Fuels Combustion Program that estimated heat of combustion data produced specifically for the study was excluded. This was on the basis that use of the methods for synthetic blends had not yet been validated showing a diligent approach.

A further important observation is that classes of fuels for which these methods can be applied (sometimes with specific equations for specific classes) are explicitly stated in the scope section. Wording and detail may vary but all, in essence, have these limitations which are primarily based on the range of fuels which were used to create the equations.

A study of the various aniline gravity methods highlights that these have so many commonalities it is difficult to specifically identify from where base data originates.

Like determined values, but even more so for estimated methods, this raises the following issues given the range of fuels which were used to develop the empirical correlation and considered representative at the time:

- What is the impact on precision (and accuracy) for standard hydrocarbon fuels outside the existing set used to develop the correlation, for example current changes in fuel composition by including synthetic blends? This is particularly relevant for some synthetic blendstocks with atypical isomer and carbon number distribution.
- Specifically for high octane unleaded aviation gasoline development, the potential presence on heteroatomic species to enhance performance, for example oxygen or amine containing octane boosters.

Therefore, current developments in aviation fuels are pushing the boundaries of what was considered normal for these test methods and the impact requires consideration. Importantly, two studies carried out by Russian workers examining the GOST aniline gravity method (see section 8.5.1) identified weakness in the method when fuel composition fell outside a very limited envelope. As noted in section 8.5.1, these problems could equally apply to EI, ASTM and Chinese aniline gravity based methods since the detail may be different but the basic principle remains the same, namely reliance on the aniline point being an accurate measure of aromaticity which in turn directly relates to heat of combustion. Evidence throughout this study shows that whilst a general relationship may exist it is far from assured.

Considering further the changes for the two main groups of fuels included in the scope of this study:

Jet A/A-1

With the advent of new synthetic manufacturing processes as defined in ASTM D7566 and trends in refining for conventional fuels, it is likely that the overall scope and variability of population of fuel composition has, and will, continue to change despite fuels meeting the requirements of ASTM D1655 / Def Stan 91-091. Since most correlation methods were defined some time ago, their ongoing relevance must be challenged particularly with increasing use of synthetic fuel blends where properties may be moving towards the limit of traditional knowledge, or perhaps more commonly, unusual combinations of properties and isomer mixes can occur. Although not directly related, but offered to illustrate the issue, there has been much debate regarding the impact of synthetic blends on the relationship (shift) between density and dielectric constant in regard to fuel quantity metering systems.

In terms of reviewing the relevance of estimation methods it is notable that many of the synthetic fuel blends now sit near certain specification margins (for example low density, low aromatics, flatter distillations). Further, conventional refining has moved further away from straight-run production towards hydrotreatment and hydrocracking up-grading options to meet market demand. This itself may challenge the validity of the assumptions built into the correlations, particularly regarding relationships between parameters, on which the historical estimation methods were created.

AVGAS / Jet B

Similar to Jet A / A-1, estimation methods may be applied to AVGAS, ASTM D910 / Def Stan 91-090 and wide-cut Jet B (AVTAG) ASTM D6615. The most significant compositional change for AVGAS occurred in the 1970's with replacement of Grade 80 and Grade 100/130 with the universal product 100LL. This transition tended to increase AVGAS aromatic content in some locations to meet octane requirement while using a lower concentration of TEL-B additive. As a low volume

product compared to turbine fuel, the primary concern for AVGAS is inclusion of sufficient representative data in the development of the correlation used in estimation methods. Jet B tends to be a specialist product in the current market with extremely limited supply. However, this fuel should not be ignored as it remains an emergency product for Military use or very low temperature (Arctic) operations.

Looking to the future, a major industry program (The Piston Aviation Fuels Initiative) is underway to develop a high-octane unleaded AVGAS as a replacement for 100LL [ref. 39]. This is technically challenging with no drop-in solution. As such, a range of options are being investigated, some featuring oxygenates, aromatic amines and metals. These are outside current correlations and will need specific understanding or sole reliance on experimental calorimeter methods.

Similar to the review of determination methods, various estimation method groups are expected to be technically identical, when for example indicated by multiple authority designations or stated as “joint methods”. In all cases these have the same core principles and methodology but may be overseen by different standardisation committees and out of sync in absolute terms of detailed text and/or date of last revision. This observation is worthy of addressing, ideally in parallel with a wider review and modernisation of the methods to allow rationalisation and re-synchronisation

The following sections review:

ASTM	D3338/D3338M – 20 D4529 - 17 ASTM D1405/M - 08 WITHDRAWN (included for historic reference)
ENERGY INSTITUTE (IP METHODS)	IP 381 - 97 IP355 – WITHDRAWN (included for historic reference)
INTERNATIONAL METHODS	RUSSIAN METHODS - GOST 11065 1990 CHINESE METHODS - GB/T 2429 1988

8.3 ASTM

8.3.1 D3338/D3338M – 20

Method Summary

D3338 estimates the net heat of combustion based on correlations with other specification parameters: Aromatics, API Gravity and Distillation. Fuel sulphur content may be ignored or applied if required.

Scope

The test method covers estimation of the net heat of combustion (megajoules per kilogram or [Btu per pound]) of aviation gasolines and aircraft turbine and jet engine fuels in the range from 40.19 MJ/kg to 44.73 MJ/kg (17 280 Btu/lb to 19 230 Btu/lb) and is applicable to liquid hydrocarbon fuels that conform to the specifications for aviation gasolines or aircraft turbine and jet engine fuels of grades Jet A, Jet A-1, Jet B, JP-4, JP-5, JP-7, and JP-8.

The fuels used to establish the correlation presented in this method are defined as follows:

Fuels (references circa 1952-1963):

- Aviation gasoline—Grades 100/130 and 115/145.

- Kerosines, alkylates, and special Wright Air Development Centre (WADC) fuels.
- Pure hydrocarbons—paraffins, naphthenes, and aromatics fuels for which data were reported by the Coordinating Research Council.

The property ranges used in this correlation were as follows:

- Aromatics—from 0 % by mass to 100 % by mass
- API Gravity—from [25.7° to 81.2°API]
- Volatility—from [160 °F to 540 °F], average boiling point

Note that the designation D3338/3338M signifies that the method covers calculations in inch pounds (3338) and SI units (3338M).

Caveats.

Are as described in section 8.2.

Methodology

This method provides a means of estimating (calculating) the heat of combustion based on an empirical correlation (originally in inch-pound units) based on:

- API gravity
- Aromatic content
- Average volatility of the fuel, where average volatility is defined as the average temperature of the T10, T50 and T90 points from a D86 distillation.
- A correction for sulphur content is also provided.

Supporting Data.

The primary source reference for the work that defined this correlation is contained in reference Research Report D02-1183 dated Jan. 1985 (ref. 40). Note that the D02 report is dated 1985 but the actual work is dated 1973.

The empirical equations for the estimated net heat of combustion, sulphur-free basis, were derived by stepwise linear regression methods using data from 241 fuels, most of which conform to specifications for aviation gasolines and aircraft turbine or jet engine fuels (169 samples), but some pure compounds were also included (72 samples). The report uses data from several sources including CRC Report LD-132 [ref. 41] and the work of Jessop and Rossini referenced elsewhere in this report. The analysis of data also includes examination of several equations. Further, a comparison of results with estimated values by ASM D1405 is used to justify the final method/equation to show that this method has the same precision.

The report concludes that equation “C” (the one as used in ASTM D3338) gives the stated precision for all the fuels within the scope defined above. It should be noted that, at that time, D1405 was the method for estimation by aniline gravity and required the use of several equations dependent on fuel type and which has now been superseded by ASTM D4529.

Thus D3338/3338M was offered as firstly a simpler method, having only one equation, and secondly avoiding the use of aniline point with related health and safety concerns.

Discussion with members of ASTM Subcommittee D02.05 indicated that no ILS or similar assessment of precision has taken place in the last 20 years. Therefore, the most up to date data on precision is based on the 1985 (1973) Research Report cited within the method.

Discussion

The method states that “the experimental data on heat of combustion from which the Test Method D3338 correlation was devised was obtained by a precision method similar to Test Method D4809”. However, the reasoning is unclear given the fuel range cited pre-date D4809 by several decades. Further, the original data (ref. 40) only states that “heat of combustion was available for 241 fuels” but does not define how these values were obtained. It is not clear if these were determined or estimated values.

This method refers to the fact that net heat of combustion can also be estimated in inch-pound units by Test Method D1405 or in SI units by Test Method D4529 (see below). Test Method D1405 requires calculation of one of four equations dependent on the fuel type with a precision equivalent to that of the cited method. Test Method D4529 also requires calculation of a single equation for all aviation fuels with a similar precision caveat. Unlike Test Method D1405 and D4529, Test Method D3338/D3338M does not require the use of aniline point.

The specification test inputs and associated methods have undergone significant development and change since these methods (correlations) were originally derived. Not only have the cited methods been updated, but new methods have also been adopted for general specification testing. This may cause the accuracy/precision of the method to drift. Whilst it is expected that where different methods have been introduced these would be equivalent, that may not always be the case and needs re-assessment or validation.

Further, Section 4 which defines the calculation, is inconsistent in that some input parameters are by specifically defined methods, e.g., volatility but others such as density are not. This inconsistency is further compounded by the fact that test methods for all parameters (assuming these are the ones used in the original correlation) are cited in Section 2 of the referenced document.

Discussion with various members of ASTM sub- committee D02.05 raised some key points. Namely that this method is being subject to monitoring and update efforts in reaction to industry requirements. In particular, the committee are seeking to incorporate new test methods. For example, allowance of the latest aromatics methods including ASTM D8267 (GCVUV) is currently under review. See section 11.2. Further, an ILS is being considered pending availability of funding.

8.3.2 D4529 - 17

This method is cited as equivalent to Energy Institute method IP381-97.

Method Summary

The method defines the sulphur free estimation of net heat of combustion based on established correlations using aniline point temperature by defined method ASTM D611 and density. Correction for sulphur content is also provided. Calculation is by use of equation or look-up table.

Scope

The test method is stated as purely empirical, and it is applicable only to liquid hydrocarbon fuels derived by normal refining processes from conventional crude oil which conform to the requirements of specifications for aviation gasolines or aircraft turbine and jet engine fuels of limited boiling ranges and compositions.

These are defined by the following specifications:

Fuel	Specification
Aviation gasoline: fuels: Grades 80, UL82, UL87, 90, 91, UL91, 94, UL94, 100/100LL/100VLL	Specification D910 Specification D6227 Specification D7547 Specification D7592
Aviation turbine fuels:	Specification D6615
Jet B, JP-4	MIL-DTL-5624
JP-5	MIL-DTL-5624
JP-8	MIL-DTL-83133
Jet A, Jet A-1	Specification D1655 Specification D7223 Specification D7566

The method cross references to ASTM D1405 (see below) which is also aniline gravity but uses four different equations and has equivalent precision. ASTM D3338 is also cited.

Caveats.

The general caveats stated are as per other estimation methods but some more specifically for this type of method. For example, the estimation of the net heat of combustion of a hydrocarbon fuel from its aniline point temperature and density is justifiable only when the fuel belongs to a well-defined class. The relationship between these quantities has to be derived from accurate experimental measurements on representative samples of that class but “well defined class” is not itself defined and open to interpretation.

Methodology

D4529 uses an empirically derived quadratic equation for the net heat of combustion of a sulphur-free fuel. The method was derived by least squares analysis from accurate measurements on fuels, most of which conformed to specifications defined in the scope, chosen to cover a range of property values. Some fuels not meeting specifications were chosen to extend the range of density and aniline-point temperature above and below the specification limits to avoid end effects. The sulphur correction was found by a simultaneous least-squares regression analysis of sulphur-containing fuels among those tested.

The general relationship between net heat of combustion and the aniline gravity equation is well established across the industry and has been used widely in other estimation methods. It relies on the principle that the two main factors influencing this property are density (expressed as API gravity in older test methods) and aromatics levels. The use of aniline point is a means to characterise the aromaticity of a range of petroleum products and historically has been used to measure this property for many classes of refined product. Therefore, since density and aniline point would be part of standard laboratory analysis, use of an aniline gravity correlation was a convenient method to use. In the case of D4529 aniline point by ASTM D611 is specifically defined.

The main reference to support the method is cited as ASTBA No 201 [ref. 42] and work by Armstrong et al. [ref. 43 and 44]. These date back to the 1960's and 1970's in most cases.

The precision is stated is based on the conversion of data in Test Method D1405 (see section 8.3.3) to SI units and the calculations using this test method.

Again, cross reference to other similar estimation methods is included.

Discussion with members of ASTM Subcommittee D02.05 indicated that no ILS or similar assessment of precision has taken place in the last 20 years. Therefore, the most up to date data on precision is based on the cross reference to ASTM D1405.

Discussion

The key issue specific to this method is the need for aniline point determination and associated health and safety issues. This has all but rendered D4529 – 17 unusable in most laboratories.

8.3.3 ASTM D1405/M - 08 WITHDRAWN (INCLUDED FOR HISTORIC REFERENCE)

This method was issued in 2008 and re-approved 2013 but then withdrawn.

The method is again based on the aniline gravity correlation. However, the way the data were handled meant that different classes of fuels had their own equations leading to four calculations covering:

- Aviation Gasolines
- JP-4 (wide cut types)
- JP-5 (high flash point)
- Kerosine types including Jet A/A-1.

It is claimed that ASTM D4529 achieves the same precision but with a single equation.

This method also references ASTBA No 201 [ref. 42] and work by Armstrong et al. [ref. 43 and 44]. These date back to the 1960's and 1970's in most cases.

Discussion with members of ASTM Subcommittee D02.05 indicated that no ILS or similar assessment of precision has taken place in the last 20 years. Therefore, the most up to date data on precision is based on the Research Reports cited within the method.

8.4 ENERGY INSTITUTE (IP METHODS)

8.4.1 IP 381 - 97

This method is also designated BS 2000: Part 381 and ISO 3648:1994. The method is also cited as equivalent to ASTM D4529-94 (1994 version) but note D4529 is now on version -17 (2017).

Method Summary

IP 381 defines the sulphur free estimation of net heat of combustion based on established correlations using aniline point temperature by defined method ASTM D611 and density. Correction for sulphur content is also provided. Calculation is by use of equation or look up table.

Scope

This test method is stated as purely empirical, and it is applicable only to liquid hydrocarbon fuels derived by normal refining processes from conventional crude oil which conform to the requirements of specifications for aviation gasolines or aircraft turbine and jet engine fuels of limited boiling ranges and compositions as defined within the following specifications:

Aviation gasolines: Grades 100/130, 100LL and 115/145
Aviation turbine fuels - kerosine types: Jet A/A-1, AVTUR and JP-8
Aviation turbine fuels – high flash: JP-5 and AVCAT
Aviation turbine fuels – wide cut: Jet B, JP-4 and AVTAG.

Caveats.

The general caveats stated are as per other estimation methods but some more specifically for this type of method:

“the estimation of the net heat of combustion of a hydrocarbon fuel from its aniline point temperature and density is justifiable only when the fuel belongs to a well-defined class for which a relationship between these quantities has been derived from accurate experimental measurements on representative samples of that class”.

The interpretation of this statement is that it is more specific than other methods and seems to require determinations on the actual fuel supplies being analysed.

Methodology

IP 381 uses an empirically derived quadratic equation for the net heat of combustion of a sulphur-free fuel and was derived by the method of least squares from accurate measurements on fuels, most of which conformed to specifications for fuels defined in the scope, chosen to cover a range of values of properties. Some fuels not meeting specifications were chosen to extend the range of densities and aniline-point temperatures above and below the specification limits to avoid end effects. The sulphur correction was found by a simultaneous least-squares regression analysis of sulphur-containing fuels among those tested. The original reference report is not available to ascertain where the data came from or indeed if it is the same data set as used in ASTM D4529.

In general, the principal details of this method are equivalent to those of ASTM D4529 (see section 8.3.2) and in particular the general relationship between net heat of combustion and the aniline gravity equation which is well established across the industry. Importantly the equation and look up table are numerically equivalent. Some key differences between this method and D4529 include:

- The specified fuel types are different and, in some respects, less well defined and in some cases out of date for aviation gasolines.
- Less background data and information are provided on how the methods was derived and the provenance of the equation.
- In this method aniline point by IP2/98 (BS 2000: Part 2: 1998, ISO 2977:1997) is specifically defined and it possible that this and the ASTM cited method for aniline point are not exact equivalents.

These variations may be due to the different version of D4529 with which it is stated as equivalent compared to the current version.

As regards traceability of the method and precision, IP 381 states that it is based on statistical examination of interlaboratory test results when using data from ISO 2977 (aniline point) ISO 3675 (density by hydrometer) and ISO 4260 (sulphur content). This suggests that the precision is based purely on the combined precision of the inputs of aniline point, density, and sulphur level. It can be inferred that no allowance for errors in the correlation are accounted for – which as commented elsewhere seems scientifically questionable. It is also worth noting that methods for measuring these parameters have changed significantly and therefore render the precision statement potentially out of date.

Discussion with members of Energy Institute SC-B-10 indicated that no ILS or similar assessment of precision has taken place in the last 20 years. Therefore, the most up to date data on precision is based on the references cited within the method.

Discussion

The key issue specific to this method is the need for aniline point determination and the health and safety issues associated with that method. This has all but stopped and therefore rendered the method and D4529 – 17 practically unusable.

As noted above a new method, ISO 21493 – 19 has been developed to carry out aniline point assessment and is now issued [ref. 30] featuring para-anisaldehyde to address health and safety concerns. This method could be adopted with the same manual or automated apparatus as used for aniline point. An equation is also provided that allows results to be converted to aniline point.

Availability of ISO 21493-19 may lead to a resurgence in the use of aniline gravity estimation methods if deemed technically appropriate.

8.4.2 IP355 – WITHDRAWN (INCLUDED FOR HISTORIC REFERENCE)

IP 355/01 was also designated as BS 2000-355:2001 and ISO 15911:2000.

This method relied on using the correlation of hydrogen content and density to estimate heat of combustion of sulphur-free fuel, with an additional calculation to correct for any sulphur present. Hydrogen was specified to be measured using IP 338/98 jointed at that time with ASTM D3701-01.

The usual caveats for estimation methods equally apply to this method.

In principle IP 355 is similar to those that use aromatics content, measured as aromatics or aniline point only in this case the hydrogen was measured directly by IP 338. Hydrogen content is again used as an indication of aromaticity in that the H/C ratio for aromatics is different to that of alkanes. The method IP 338 was based on nuclear magnetic resonance spectrometer (NMR) and specifically the Oxford Instruments Newport Analyser. This instrument was relatively easy and quick to use and gave good precision.

IP 355 was withdrawn due to lack of use, which was, in turn, due to lack of availability of hydrogen data by IP 388. IP 388 was at the time offered as a good method to measure aromaticity and therefore eliminate the need for total aromatics, naphthalenes and smoke point¹⁰. Its use as a measure of hydrogen for calculation of heat of combustion was not its primary role. However, industry experience did not support the method as a suitable control for these critical combustion related parameters, and of aromatics levels for elastomer compatibility, leading to redundancy. A good summary of the history of Hydrogen as a specification parameter and its ultimate demise except for some US military specifications is provided in the MoD Spec review [ref. 18].

Discussion with members of ASTM Subcommittee D02.05 indicated that no D3701 ILS or similar assessment of precision has taken place in the last 20 years. Therefore, the most up to date statement of precision is based on the Research Reports cited within the method.

The test method does not cite any traceable reports or data that support the methodology or precision. However, the method does cite the range of fuels used to create the correlation:

- AVTUR, Jet A, Def Stan 91-91, ASTM D1655.
- Jet A-1, ASTM D1655.
- AVCAT/FSII, Def Stan 91-86.
- AVTUR/FSII, Def Stan 91-87.
- JP-4, JP-5, JP-5 ST, JP-8 ST, MIL-T-5624.

¹⁰ Based on the authors experience at that time.

- Covering the following ranges of properties:
 - Mass fraction hydrogen: 13.00% - 14.14% (m/m)
 - Mass fraction of sulphur: 0.01% – 0.33% (m/m)
 - Density at 15°C 789.0 kg/m³ – 830.5 kg/m³

In summary, heat of combustion estimation by IP 355 offered a relatively convenient method with reasonable precision. However, without the associated NMR, the method lost its relevance and was therefore withdrawn. If hydrogen content by other methods became more commonplace this method, or an updated version, could become useful again.

8.5 INTERNATIONAL METHODS

8.5.1 RUSSIAN METHODS - GOST 11065 1990

Note: A translation of this method from Russian to English was obtained by the author but the accuracy of this cannot be guaranteed.

This is a version of aniline gravity calculation. The scope is defined as “This standard applies to all jet fuels with a mass fraction of sulphur up to 0.25% and provides a calculation method for determining the lowest specific calorific value.” The method provides net (lower) heat of combustion. The scope appears to allow this method to be used on a wider range of fuels than ASTM/IP equivalent methods.

Test methods for inputting the aniline point and density are defined by GOST methods.

The equation has been developed by Russian workers and is in a different form to western methods. Comparison of results by this method, IP/ASTM aniline gravity and determined values would be required to fully assess how these methods correlate. It is notable that fuels up to 0.25% sulphur are allowed but there is no requirement to input sulphur into the calculations.

The method does state that “The standard includes the international standard ISO 3648-79 (See section 8.4.1) in terms of the accuracy of the method”. It is not clear what that actually means and may be an inaccurate translation since strictly speaking no such methods state an accuracy. This most likely refers to the precision being equivalent.

As per other such estimation methods this is cited as a substitute for bomb determined values, in this case by GOST 21261-75.

The test method provides traceability to the original author(s) and their affiliation and states the date of 1990. It notes subsequent updates. This method does not cite any traceable reports or data to support the test method and precision but as noted above refers to ISO 3648-79 precision.

A study issued in 1985 [ref. 45] compared results calculated from this method to determined values by GOST 21261-75. This found that results were substantially in error (greater than the allowed 145 kJ/kg) from the determined values in many cases. This was attributed the fact that the formula was based on straight run fuels only with relatively low naphthenes and aromatics. The report also contends that aniline point can only be taken as “an extremely (really) approximate characterisation of composition and therefore cannot be used widely for the calculation of heat of combustion”. Lastly, the report shows that estimated values by ASTM D3338 are far more reliable and recommends the use of the ASTM D3338 formula¹¹. However, it appears that this recommendation was not adopted at least up to the most current version of GOST 11065 [ref. 15].

¹¹

Another similar study [ref. 46] also concluded that aniline gravity was liable to gross errors. Interestingly, this paper showed formulae to calculate net heat of combustion based on density, sulphur, aromatics and (unusually) viscosity. This showed superior correlation with determined values, again by GOST 21261. The report presents several formulae applicable to different fuel classes related to viscosity range.

Note that although GOST 11065 does not use the same formula, the method is based on aniline gravity and therefore other methods based on this principle could suffer the same errors due to compositional variance.

8.5.2 CHINESE METHODS - GB/T 2429 1988

Note: A full translation of this document was not available. Some comments were kindly provided by the Chinese team at BP via Alisdair Clark (ref. 28).

This is a version of aniline gravity calculation as described in IP/ASTM reviews above. The method covers the use of both API and density to give results in MJ/kg.

Within the Chinese version can clearly be seen the equivalent four equations used in ASTM D1405M. Further, the equation for sulphur correction is also the same as used in ASTM D1405M.

Precision statements equivalent to those in ASTM D1405M can also be seen.

No traceable reports or data to support the test method and/or precision are available based on the limited translation available.

9 DETERMINATION VERSUS ESTIMATION COMPARISON.

9.1 OVERVIEW OF DIFFERENCES

The findings of this report show that measurement of calorific value (energy density by mass or volume) currently has to be carried out using complex calorimetry equipment under strict laboratory conditions and by skilled staff if accurate results are sought (accepting test methods require updating). Whilst the actual firing sequence and corrections/calculations can be automated by varying degrees, the pre-test loading and post-test unloading, and subsequent analysis remains a skilled, manual operation. Further, no viable alternative to calorimetry methods to determine heat of combustion has been identified.

Laboratory calorimetry analysis therefore represents a significant burden in terms of investment and resources and will only be used when the reliability and accuracy that these systems deliver is essential. Consequently, estimation methods are often used as an attractive alternative. The report notes that such methods, using standard specification test results and correlations, are convenient and low-cost. However, while good precision is achievable, data presented in this report have demonstrated that there is a significant risk of poor accuracy for current fuels outside the original data set, or potentially scattered from the correlation curve, such as, synthetic blends. It has also been noted that the precision of these methods is based on data that are out of date, and, trends in conventional fuels and synthetics may well render the accuracy less reliable. Lastly estimated methods always come with caveats regarding potential errors in results but it is debatable whether these are fully understood or given due regard.

Both types of method do have a place in the appropriate environment providing their relative strengths and weaknesses are full understood. A high-level summary of these is provided in Table 16.

Method	Strengths	Weakness	Comments
Bomb Calorimeter	Provides absolute value. Several methods available.	Very expensive and time consuming. Requires skilled operators and dedicated facility.	Rarely used except for analysis during engine or aircraft development testing or certification. Lower accuracy methods not adequate for critical applications.
Estimation Methods	Estimate value from existing specification measurements. Several methods available.	Precision comes with caveats (see test methods). Accuracy requires development from sample source. Additional specification test equipment needed to provide data.	These methods are adequate to demonstrate specification compliance vs min. limits (note that current fuels tend to be rarely near specification limit) However, significant caveats on accuracy are required and with increasing divergence from conventional fuel blends the risk of inaccuracy increase.

Table 16: Overview Comparison of Existing Determined and Estimated Methods.

9.2 DISCUSSION

Much of the above comparison means that there is understandably a preference to use established estimations methods wherever possible.

It is clear from this review that determined values are required for critical applications where the impact of errors will have significant consequences, e.g., engine performance measurements during development, certification, and production pass-off. Further, there is increasing need for accurate energy density measurement due to the emphasis on aircraft performance, load optimisation, CO₂ monitoring/trading and potential changes to purchasing systems, and, where the increased use of synthetic blends may mean that the established relationship between standards specification properties, particularly density and energy density, do not apply (see section 3). Further, the use of determined values is becoming more critical where the potential fuel composition envelope is being challenged by the increased use of synthetic alternative fuel blends and pressure to move to increase blend ratios or even towards 100% synthetic fuels unless or until existing/new estimation methods are developed.

Conversely, estimation methods provide a relatively quick and low-cost method of estimating net heat of combustion. For a given class or source of fuel, calorific value has a relationship with density which is why this parameter features strongly in all estimation methods. Other variables which may be used to refine the correlation procedure include volatility, molecular weight (aniline point indicates both aromaticity and molecular weight), total aromatic content or hydrogen content. The presence of sulphur is corrected for in all estimations. As such these methods use readily available data at the point where the fuel has been analysed for specification compliance either at refinery or downstream. Therefore estimating values involves little extra effort although the identified need for method updates must be noted. However, it is also clear that accurately determined values for a given supply should ideally be carried out before adopting the use of estimation methods, as per the estimation test method caveats, but the author is not aware how often that actually happens.

Comparing the precision of these methods against direct measurement values can give the impression that estimation methods are superior. This is a misconception. The actual precision of estimates (repeatability/reproducibility) is based purely upon the combined precision of the actual measurements used. Note that the potential uncertainty of the correlation equation is not always included in the precision statements. The actual precision and indeed accuracy of these methods may be significantly less reliable than the precision statements imply although these methods do provide caveats to that effect.

For instance, all estimation methods contain a caveat regarding the limitation of such methods to well defined classes of fuels (for which the method has been shown to apply) and warnings regarding the potential for gross errors (see individual methods). This is particularly relevant to the emerging synthetic blends which were not tested during the development of these estimated methods and such blends may have combinations of specification parameters which are outside the norm. In addition, such methods cannot be applied where novel chemical blending components might be under evaluation, for example in high octane unleaded AVGAS development, as these would be outside the original correlation data set with risk of significant error.

The study has demonstrated that the fundamentals of both calorimetry and estimation methods date back to the 1950-70s and these fundamental principles still apply but how these are implemented is facing the challenges in today's world noted in this review. Further, it is notable that no ILS type exercise has been carried out in the last 20 years based on conversations with the relevant sub-committees. Whilst this means standard test methods for both types of methodology are out of date, the impact on the reliability of the estimation methods is likely to be greater due to potential changes to the input data methods and fuel composition.

The report has also identified the potential for improvements in existing determination methods by increased use of advanced equipment for improved precision and automation to reduce laboratory burden. Further, there are possibilities for improved estimation methods but no “off the shelf” methodology that could be applied in the production laboratory environment exists yet. The cost and benefits of applying advanced analytical and computational techniques in such applications needs detailed assessment. Lastly, trending in analytical techniques for key inputs for these methods have been reviewed, including changes in aniline point determination and the use of improved composition methods e.g., GCVUV. Their full impact is yet to be fully evaluated.

9.3 SUMMARY

Each methodology (determined and estimated) has a role to play in the right circumstance and developments in each approach may well tip the balance in terms of which is most appropriate in a given circumstance, accepting the findings of this report that updates of this methods will be of benefit.

Estimation methods are acceptable as a low cost means to show specification compliance where significant margin from specification limit is available and for a well-established class of fuels e.g., at a stable and consistent refinery output where the relationship has been established. For more challenging and critical circumstances, determined values are required and for that calorimetry remains the only viable methodology.

10 CRC USER SURVEY

10.1 SURVEY OVERVIEW

This review has focused on currently available heat of combustion methods, their technical background, precision, and accuracy and how up to date they are compared to modern equipment and associated analysis requirements. The review also compares the relative merits of determination versus estimation methods.

Given the understanding of what is available to the industry, it was deemed valuable to gain insight from heat of combustion data producers and users as to what methods are actually being used and for what purpose, and some feedback on how well these methods meet current requirements.

To this end the CRC launched an internet-based survey open to all users who wished to participate and the link was also included in the 2021 ASTM PTP survey.

Note 1: The survey was carried out ensuring all individual responses remained confidential.

Note 2: By nature of the survey request circulation the data are inevitably biased towards users of ASTM and EI (IP) methodology but this reflects the focus of this study. The lack of responses citing the use of Russian and/or Chinese methods and equipment does not necessarily reflect what the world-wide statistics would be if a wider survey was carried out.

The complete list of questions is provided in Annex II – CRC and ASTM Survey question list.

In summary the list of questions were a mix of single-choice, multi-choice, and open text inputs to examine the following broad areas:

- The type of organisation, prime activity and whether they produce, use or both produce and use, heat of combustion data.
- The determination and calculation methods used including: test methods, equipment, details of procedures and other test methods used in calculations/corrections etc.
- Throughput of samples and calorimetry equipment calibration frequency etc.
- Questions regarding ease of use, adequacy, and specific comments on these methods from a data producers' perspective.
- Perspectives from data users regarding sources of data, uses and adequacy.

A total of 73 responses were received but note that not all questions were necessarily answered by each respondent.

The following paragraphs provide a summary of the findings which should be read in conjunction with the relevant sections of the main report.

10.2 SUMMARY OF FINDINGS

10.2.1 ORGANISATIONAL INFORMATION

Figure 12 to Figure 15 show a breakdown of the responses in terms of the type of organisation and their primary function. This provides a context to the subsequent responses regarding the statistics and details of methods used.

It can be seen that almost 75% of responses is represented by independent laboratories, commercial operators, and refinery laboratories. The predominant functions were independent testing for third parties and laboratories directly linked to refineries. Figure 12 and Figure 13 show that there are a range of other organisational types and functions within the data set so providing

some insight into the less frequent producers and users as well as the more regular (high throughput) users.

Figure 14 shows by far the predominant application of data was cited as fuel evaluation and approval. In this context this means standard (routine) specification testing for process control and product quality assurance with only a small number of responses for R&D and other applications as might be expected for the evaluation of new fuels and fuel blends.

From within the same data set Figure 15 shows that around half the responses were from organisations that both produce and use the data so was for their own use and those that either produced data for others or users that obtained data from an independent source were nearly equal.

Overall, this shows that the survey provides a good cross section of data producers and users and therefore reflects industry current practice and requirements within the scope of the survey group.

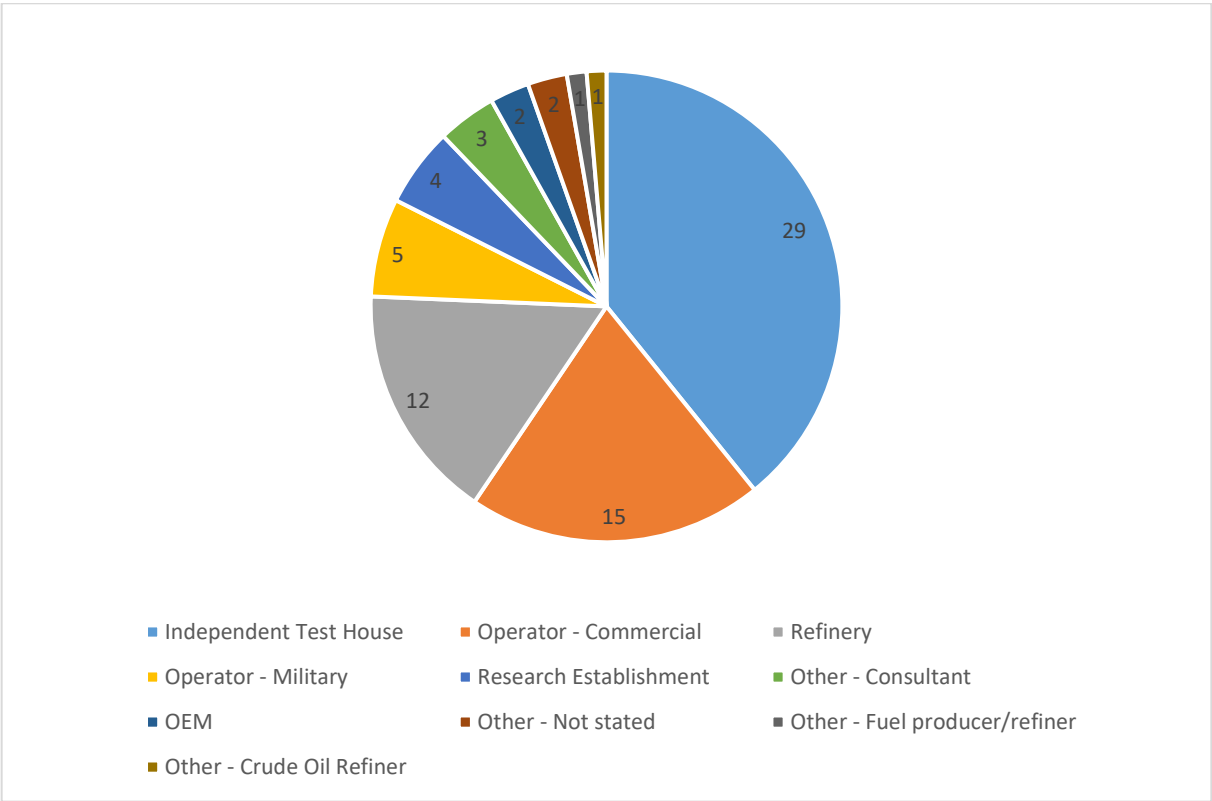


Figure 12: Survey Response Organisational Type.

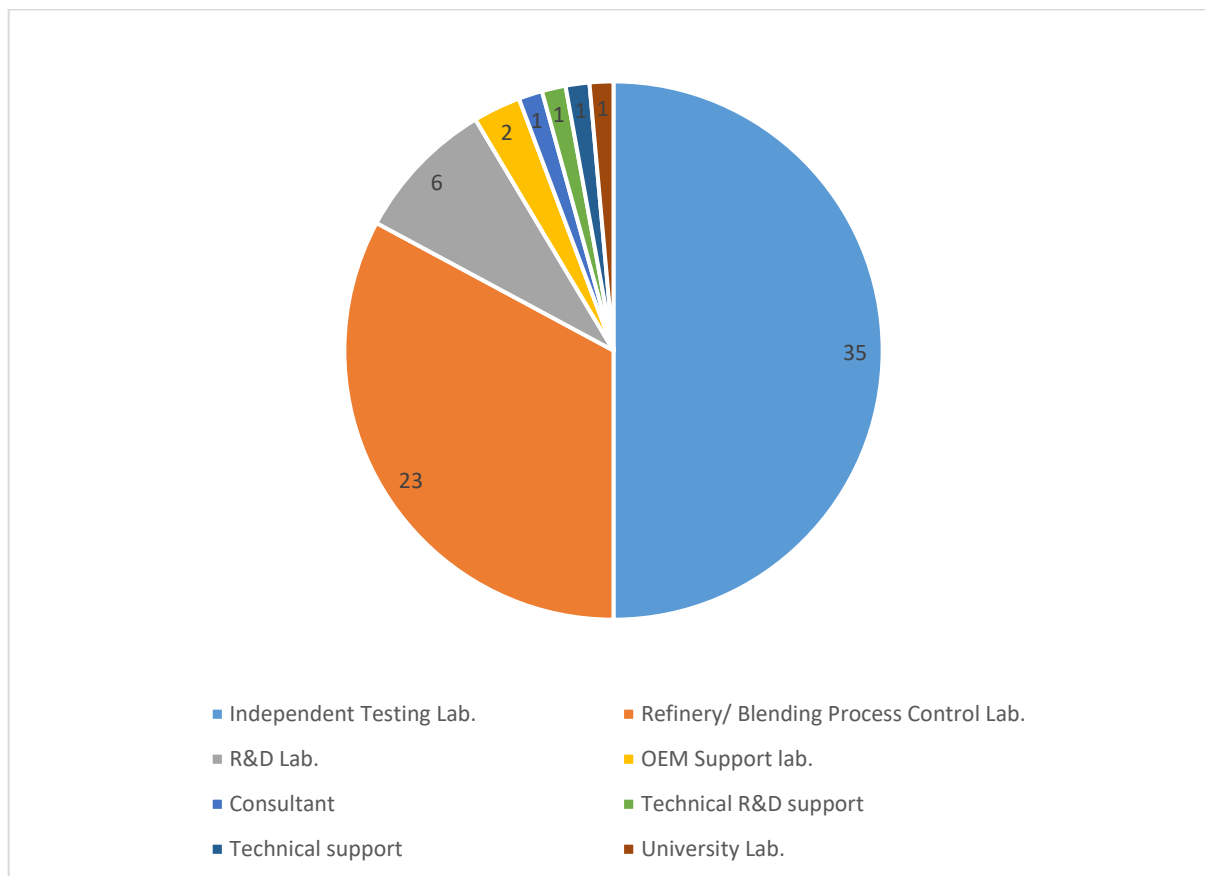


Figure 13: Primary Organisation Function.

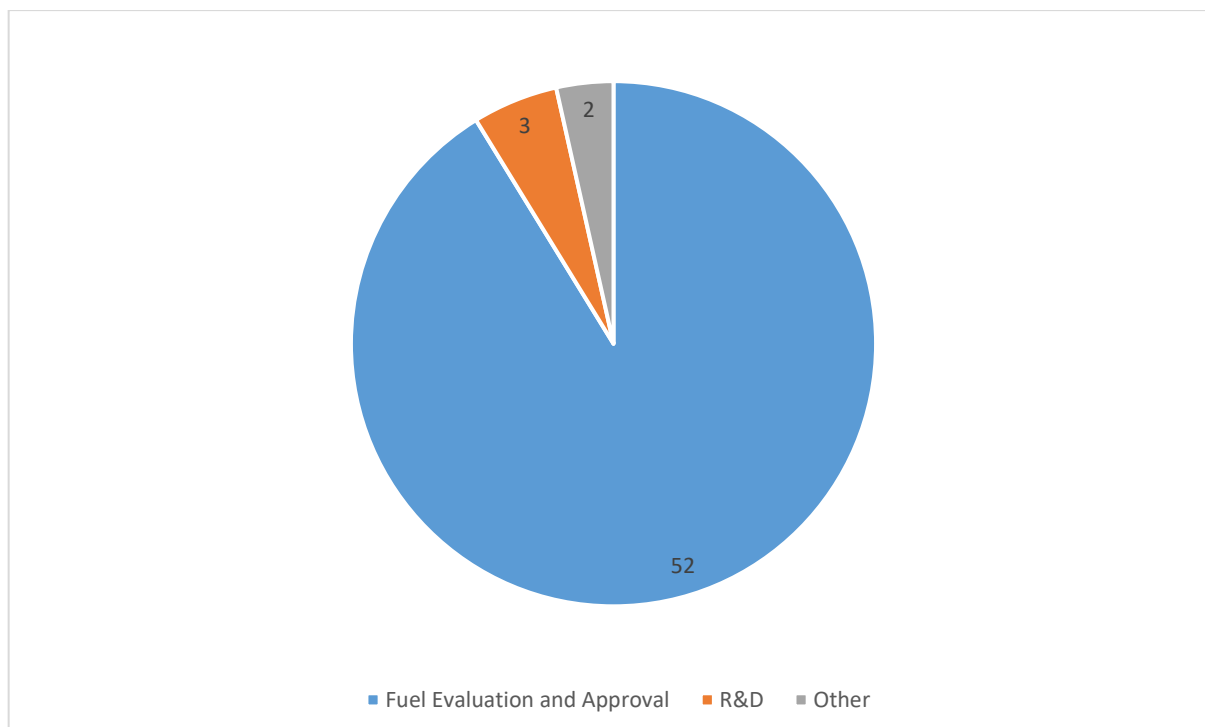


Figure 14: Data Application.

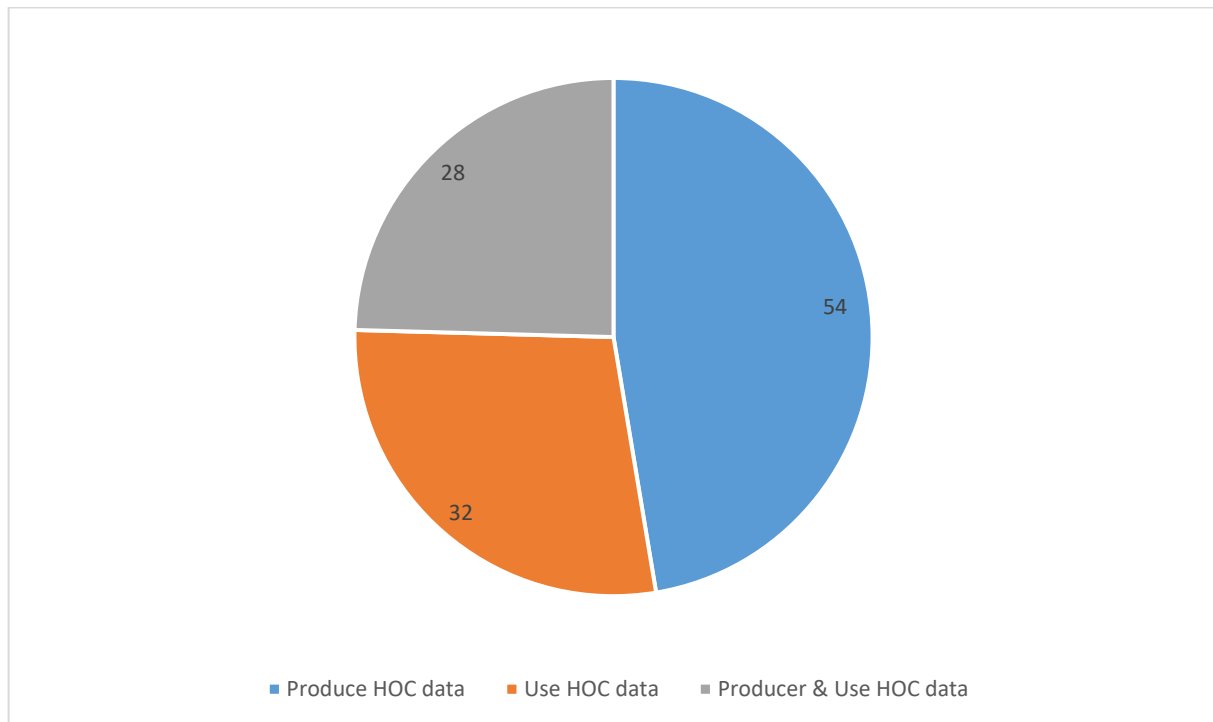


Figure 15: Data User, Producer or Both.

10.2.2 DETERMINATION AND ESTIMATION USAGE RATES

Figure 16 and Figure 17 show, respectively, the number of determined and estimated values carried out per month.

Analysis of these data shows that:

- Most organisations carry out up to 20 analyses per month but several respondents show a much higher throughput.
- Up to 5 analyses per month was the most common for both estimation and determinations.
- The data shows that, as expected, based on the convenience and ease of use of estimations, the overall number of estimations would be significantly higher than determinations.

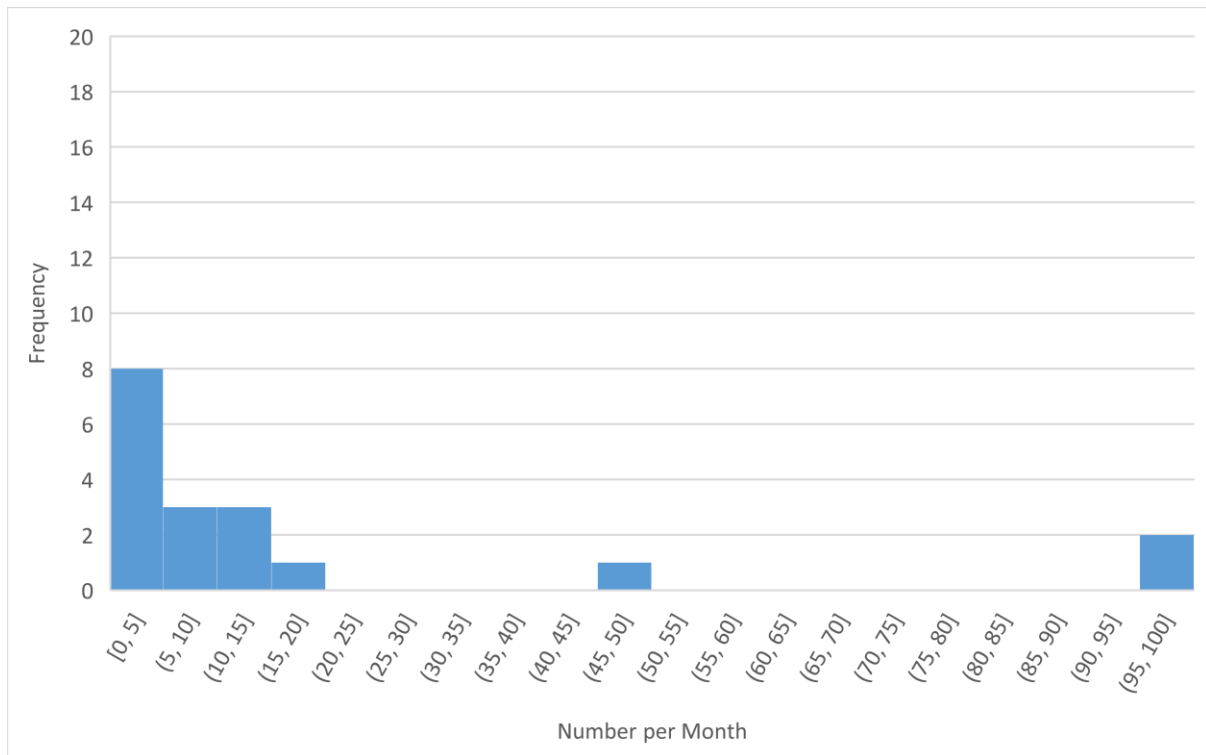


Figure 16: HOC Determinations (Calorimeter Determination) Frequency.

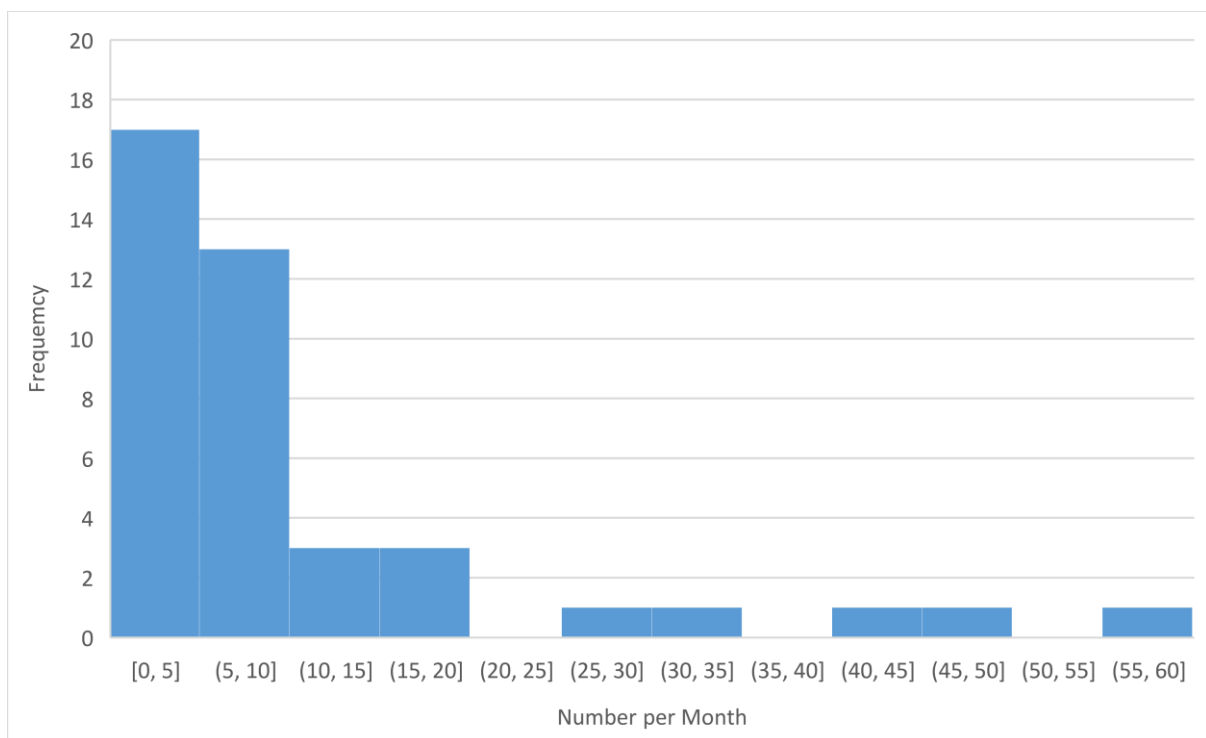


Figure 17: HOC Estimation (Calculation) Frequency.

10.2.3 DETERMINATION (CALORIMETER) DATA

Responses to questions on test methods used are summarised in Figure 18 (methods) and Figure 19 (calorimeter mode). This clearly shows ASTM D240 is the most widely used calorimetry method with D4809 (assumed for more critical applications) a close second. Responses also showed that a significant number of organisations use multiple methods and, in most cases, these were D240 paired with D4809. Slightly over half the responses reported using isoperibol mode, with isothermal and adiabatic representing almost equal proportions of the remainder.

Calorimeter type reported included a range of (current) models from manufacturers including (in no particular order) Parr, IKA, LECO and Koehler. A range of the critical temperature measurement technologies was reported but almost all were electronic instruments (assumed mostly to be integral to calorimeter) with only one reporting using mercury in glass thermometers.

One response noted specifically that the method(s) being used did not reflect current equipment. As was observed earlier no method requires specific equipment but may cite equipment options which, in the author's opinion, may not be sufficient detail for instrument critical measurements. Further, ASTM D240 and D4809 do cite specific equipment as recognised to meet requirements but these are now obsolete models. Therefore, users are meeting standard test method requirements but improved equipment definition and/or guidance is still needed.

Frequency of calorimeter calibration is shown in Figure 20 and generally reflects the throughput level of each organisation. As expected, benzoic acid was the prime calibration standard with some use of 2,2,4-Trimethylpentane where volatile samples were being analysed.

Many responses showed that volatile samples were not handled and when they were tape (7 users) was the predominant method of volatile loss suppression with only one using gel capsules and one using glass phials.

As regards ease of use and general comments about the methods and equipment 16% of responses reported problems and difficulties of various sorts. Of particular note were the needs for careful and rapid handling of volatile samples and difficulties/inconsistency with gel capsules. However, the responses show that users believed they were generally able to achieve the stated precision.

Table 17 shows a breakdown of the methods used for providing hydrogen and sulphur contents in descending order of popularity. As discussed earlier, hydrogen content is critical for correction from gross to net values so the best method possible should be encouraged but this may have to be balanced against availability of equipment. Several users recognise that at the allowable levels of sulphur in jet fuel correction is not required particularly given that most fuels have levels well below maximum¹² (see 4.3.5).

In summary, this section of the survey shows that generally users are able to comply with test methods in use and achieve the stated precision but do have some difficulties mainly with volatile samples. ASTM D240 and D4809 are most widely reported calorimetry methods being used but this might be attributed to the bias of the responses from the recipients of the CRC and ASTM based survey request.

One key finding is that the equipment being used is modern technology which is not reflected in the standard test methods. This does not mean that users are not complying with the test methods, but the test methods require updating to improve control and/or guidance on equipment to align with current calorimeter technology and user practice. The survey also gives useful insight into the test methods being used for input data on sulphur levels and hydrogen. Reported difficulties with volatile samples supports the requirement to separate the precision of such samples from non-volatile samples.

Overall the survey provides an understanding of current procedures and practices versus requirements and guidance should these test methods be subject to update and/or revision.

¹² This is legitimate for jet fuels with current sulphur levels but needs re-assessing for future fuels and if test methods improve precision to the point where sulphur correction becomes significant. In any case this should be defined in local procedures.

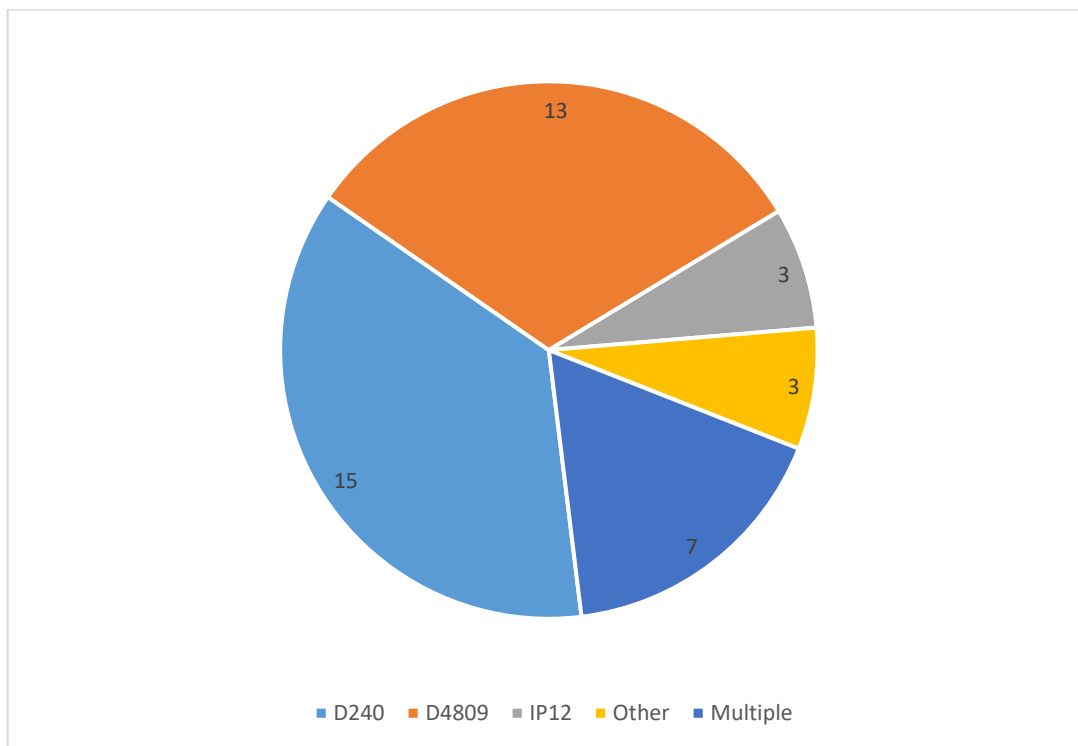


Figure 18: Determination Method In Use.

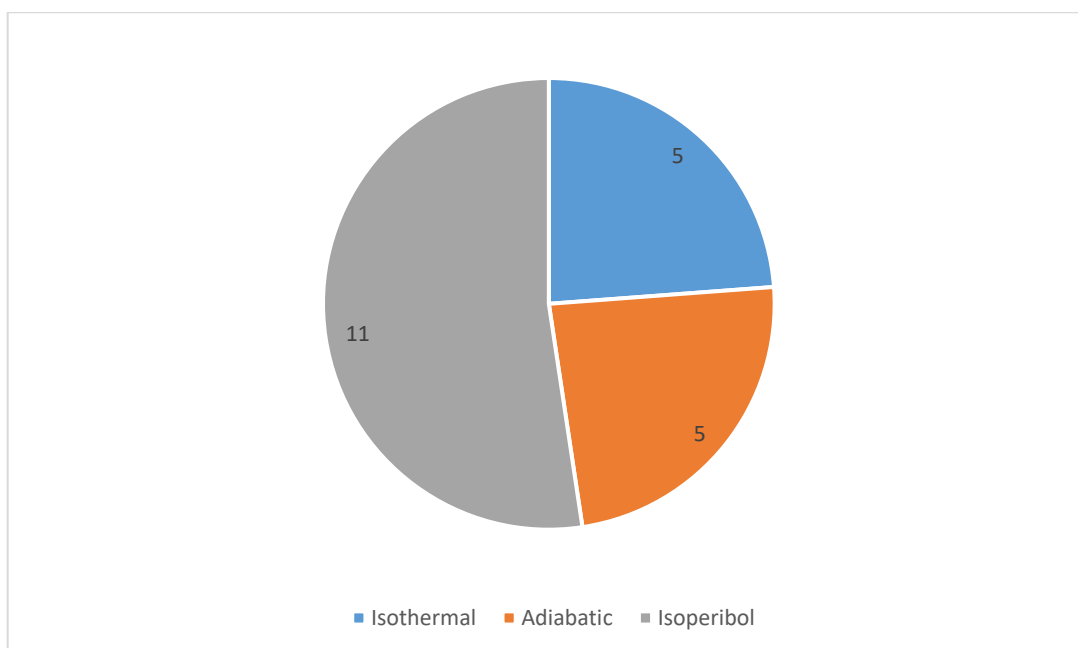


Figure 19: Calorimeter Operating Mode.

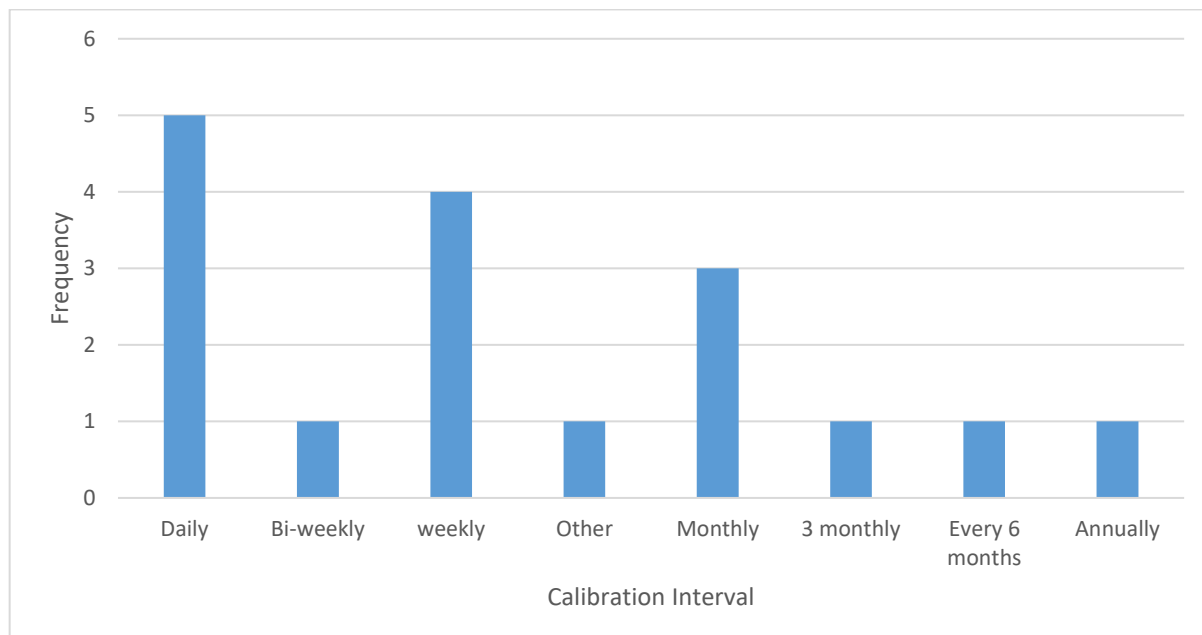


Figure 20: Frequency of Calorimeter Calibration.

Hydrogen	No
D5291	4
D3343	4
D7171	4
Calculation	1
D1018	1
D3343 or send for NMR analysis	1
D3701	1
Modified ASTM D5291 / Inhouse method	1
none	1
Use average values to correct for % hydrogen for formation of water	1
Total	19

Sulphur Content	No
D4294	6
D4294, D5453	4
D2622	3
IP 336	2
D2622, D5453	1
D2622, D7039, D4294	1
D4294, D2622, D5453	1
D7039	1
D7039 / D4294 / D5453	1
ISO14596, ASTM D2622, ISO 20884	1
none	1
Not used because aviation fuels normally contain <0.1% sulfur	1
Total	23

Table 17: Test Methods for Hydrogen and Sulphur Content.

10.2.4 ESTIMATION (CALCULATION) DATA.

Analysis of responses on procedures used to estimate fuel heat of combustion is provided in Figure 21 and Table 18. This shows that by a significant margin D3338 (84%) is the most widely used with the remainder predominantly D4529 (12%). Again this may be biased towards ASTM standards due to the scope of response organisations. Interestingly, most of those reporting using D4529 also reported using D3338.

The low use of D4529 compared to that of D3338 is most probably due to the health and safety issues with aniline point that is required for the former method. Table 18 provides a breakdown of the methods used for inputting data to the calculations. Methods are shown in descending order of occurrence quoted with ASTM and IP equivalent methods combined together. However, no organisation who stated they use D4529 (aniline gravity) reported using ASTM D611 or equivalent aniline point methods which seems to be anomaly in the survey. Other methods of generating input data were cited as various calculation methods including DIN 51603-1.

The balance between methods may well change with the introduction of the aniline substitute method. Interestingly there were responses from R&D workers using advanced GCxGC methods which are discussed later in this report.

All respondents reported that precision was sufficient for their purposes. 6 out of 48 responses confirmed that determined values were available for validation use.

In summary, this part of the survey provides valuable insight into the usage levels for the alternative estimation methods and also the methods used to provide the input data. The low use of D4529 is expected but the complete absence of responses citing use of D611 (aniline point) which is an essential input is anomaly. Again, these data give guidance to any subsequent work in terms of technical issues to be addressed and priority versus industry requirements and levels of usage.

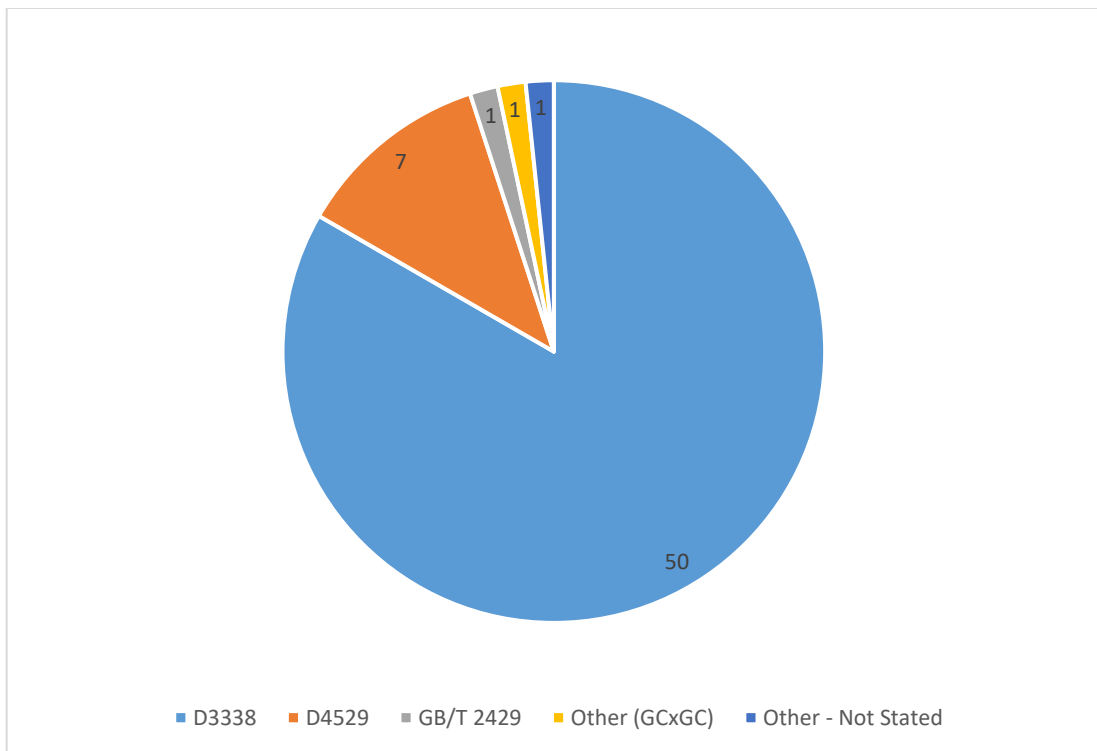


Figure 21: Estimation (Calculation) Method Used.

Analysis Type	ASTM (IP)	No
Aromatics	D1319 (156)	18
Aromatics	D6379	10
Aromatics (Gasoline)	D5580	1
Density	D4052 (365)	22
Density	D1298	3
Distillation	D86 (123)	24
Distillation (Sim)	D2887	3
Sulphur	D4294	14
Sulphur	D5453	5
Sulphur	D2622	3
Trace Nitrogen	D4629	1

Table 18: Test Methods Used for Calculation.

10.2.5 DATA USER RESPONSES.

The methods cited as being used by data users is provided in Figure 22. This relative usage generally reflects the data production methodology. These data are based on number of responses to the question “what method is used?” and is therefore not necessarily the number of samples analysis (throughput) in a given period for each method which would require a more complex survey. Also, many of the respondents will be both producers and users.

Again, D3338 is the most popular for general use. D4809 is a close second, which probably reflects that data users responding to this question had more critical requirements. The other methods figure in the lower use categories with a significant proportion using multiple methods (from multiple sources?). It is notable that D4529 is a significant number yet only a few data producer claim to use this method.

To the question “do these methods meet your requirements?” generally the answer was yes, 82% for determination methods and 89% for estimations (see Table 19). And, in an open question regarding suitability of the current methodology some key comments were received. These provided good insight into the understanding of the methods capabilities and limitations:

- Recognition by several respondents of the limitations of estimation methods and relevance of methods that were developed many years ago to current fuel supplies and particularly to synthetic blends where composition is outside scope. Some responses cited that bomb method must be run on new fuel blends.
- Recognised the need for revised methodology and correlations for new jet fuels and particularly new AVGAS components.
- Reduced uncertainty (i.e. improved precision and accuracy) for all methods would be desirable where data are critical. Also, as expected, reduced operator time and skill for methods would be useful.
- The need to update many of the methods (determined and estimated) is required to reflect current best practice. This includes validating changes to other methods used in support or the prime calorimetry and estimation methods. Particularly relevant for ASTM D4809 and all estimation methods.

This again provides useful insight into what data users currently use and their requirements.

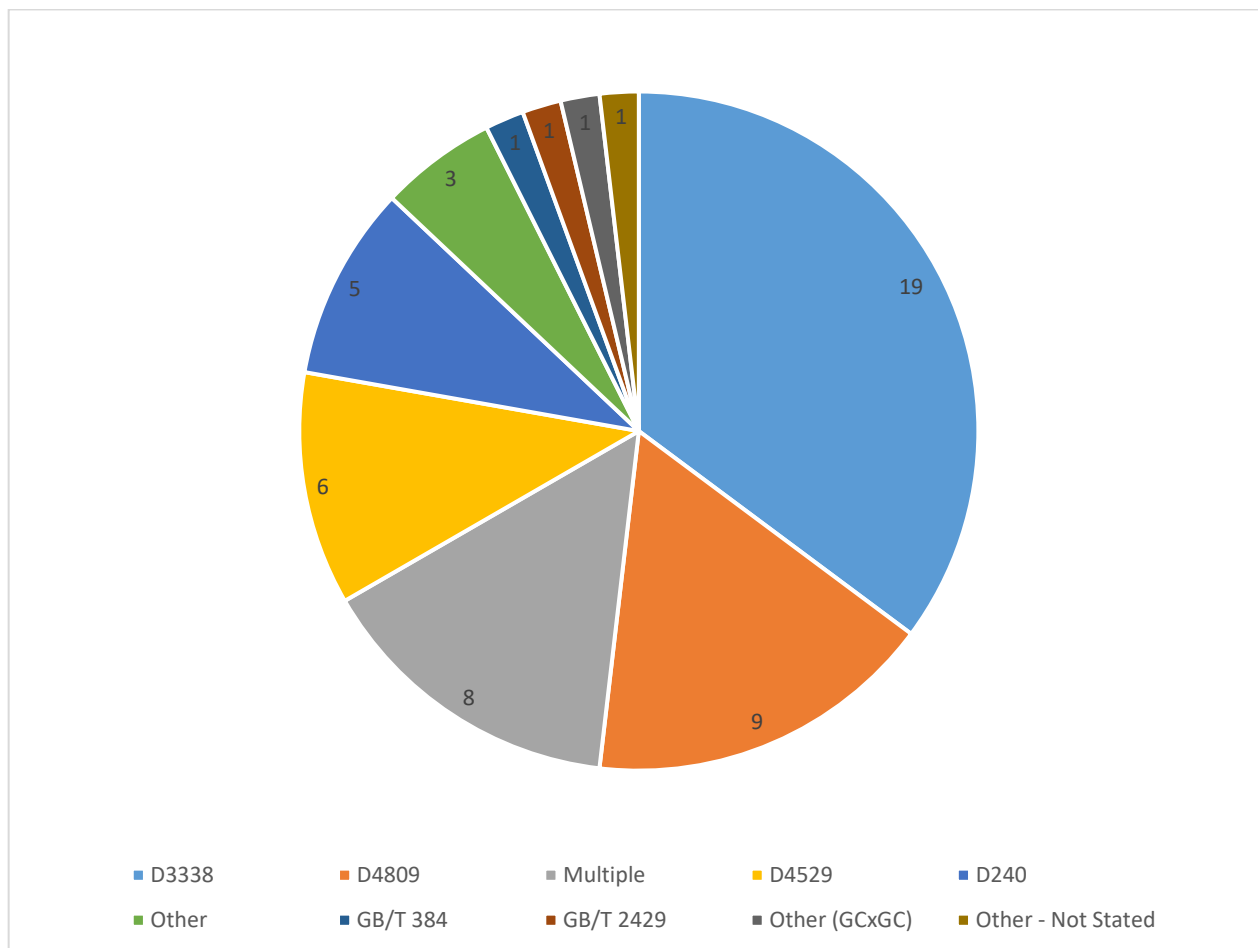


Figure 22: Data User Response – Methods Used (Determined and/or Estimated).

Does Method Meet Requirements?	HOC Determination (%)	HOC Estimation (%)
Yes	82	89
No	18	11

Table 19: Data Users – Does Method Meet Requirements.

10.2.6 USER SURVEY SUMMARY

This survey has focussed on the use of calorimetry and estimation methods primarily within the ASTM method user community. It has shown that low and higher precision calorimetry with a range of operating modes and several estimation methods are in common use, each with a role in specific applications. Throughput varies from very infrequent to many samples a month and a range of applications, so the survey provides a good sample of what current industry practice in a range of laboratory environments. These findings are a useful guide to technical requirements and priorities for future method development.

Generally, calorimetry methods meet current requirements and precision stated can usually be achieved but that does not necessarily mean the improvements are not required or could be used to benefit. However, difficulties with handling volatile samples and the fact that equipment cited in calorimetry methods is not up to date are important observations reinforcing the main reports finding.

By far ASTM D3338 is the most widely used estimation method but ASTM D4529 is still in use. As noted elsewhere, the development of an aniline point equivalent may well change this balance but the use of this new method needs assessment.

The survey also gives insight into the methods adopted for sulphur and hydrogen input for gross to net calculations, and the input of data for estimations. This provides guidance should or when these methods are updated.

11 ALTERNATIVE AND FUTURE METHODOLOGIES

11.1 DETERMINATION METHODS (CALORIMETRY)

The current extensive review of academic literature, standard test methodology and equipment manufacturers information has failed to identify any viable alternative to the fundamental bomb calorimetry measurement system.

Innovations in calorimetry over the years have been based on improved temperature measurement and control of both the calorimeter bucket and jacket, improved automation in both monitoring/control and calculation of corrected values, etc., (see section 6.4). Automatic pressurising of the bomb and water bucket filling, for example, and direct linking of balances to the calorimeter also remove operator input and thus improve precision and reliability. Improved temperature measurement and control and microprocessor capability has facilitated the use of Isoberibol modes which would not be feasible for manually operated calorimeters. Isoperibol modes bring ability to improve precision over other methods (and therefore accuracy if correctly calibrated) whilst balancing against speed of analysis.

There is ongoing research on understanding the thermodynamics and calorimeter systems and thereby improve precision accuracy and speed and examples include [ref. 22 and 47]. However, a further detailed examination of this area is a specialist subject in itself, probably more relevant to equipment manufacturers, and therefore outside the scope of this report.

Recommendations to improve calorimetry methodology is discussed elsewhere in the report but this is based on existing techniques and equipment.

In summary, no alternative to the bomb calorimetry method of directly determining calorific value was identified during this study.

11.2 ESTIMATION METHODS

11.2.1 ESTIMATION METHOD CHALLENGES

Even at the extremes of the spectrum of fuel composition, heat of combustion can be determined (within limits) of a fuel by actual combustion without any real knowledge of its hydrocarbon make up¹³. At the other (theoretical) extreme, a fuel could be fully analysed and the heat of combustion of each component could be summated to give a total value. The concept of fuel compositional granularity versus ability to predict heat of combustion reliability (or indeed any other property) is illustrated in Figure 23.

Current standard estimation methods seek to predict the heat of combustion from composition but by broad categorisation of molecular types present and their concentration. As discussed, the main compositional factors used in the various methods include density and/or distillation to give an overall measure of molecular weight, and aromatics to paraffinic (alkane) ratio by aromatics direct measurement, hydrogen content or inference by aniline point.

With the advent of improved analytical techniques and computational power it could be envisioned that a much more detailed composition linked to a molecule data library and computational models could “dissect” a fuel to such granularity that the heat of combustion could be estimated more accurately. There is a significant body of work now available where R&D efforts have been focussing on predicting a whole range of fuel properties and performance from laboratory-based measurements of basic specification type tests and new analytical techniques. Allied to this is, with the increasing computational power, is the application of sophisticated modelling programs,

¹³ With the proviso that recent developments in AVGAS that have significant levels of non-hydrocarbons are found to still give correct results using standard bomb calorimetry methods.

machine learning and genetic algorithms, for example, which can deal with the complex data produced by the detailed analysis such as 2DGC. Much of the work discussed below was aimed at the prediction of a range critical fuel properties for the purpose of evaluating new blendstocks and fuel compositions rather than developing an everyday specification type procedure. None the less with some varying levels of adaptation these techniques may offer improved heat of combustion estimation methods.

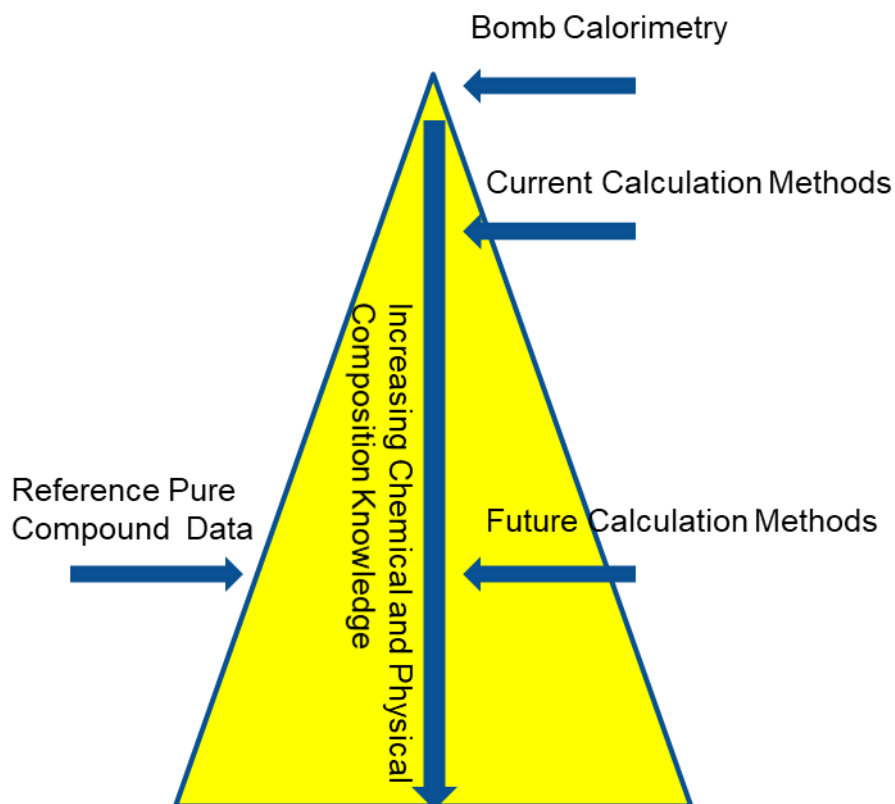


Figure 23: Concept of Methods of Increasing Compositional Granularity.

There follows a review of the latest R&D work that may offer the opportunity for improved heat of combustion estimation methods. It must be recognised that at this stage these analytical and computational techniques are being used in a research environment and for the characterisation of novel rather than conventional fuels. However, if there are any developments that may lead to improved estimation methods this is most likely to come from this type of R&D activity and be developed specifically for everyday use. It is for this reason the following programmes have been included. Even if this work does not provide any new methods, this information and the review of the impact of fuel composition reported in section 7 will provide better insight into the possibilities and challenges of either developing current methods further or indeed creating new methods.

Lastly, it is notable that the VUV method discussed below is being developed as a specification test method and therefore is closer to being used on a regular basis compared to say, GCxGC (also known as 2DGC), which is becoming more common but still not standardised. The review is based on a mixture of literature surveys and discussions with key workers in the field.

11.2.2 JOSHUA HEYNE ET AL (UNIVERSITY OF DAYTON, DEPT. OF MECHANICAL AND AEROSPACE ENGINEERING)

A virtual meeting was held with Joshua of the University of Dayton, Dept. of Mechanical and Aerospace Engineering (UDRI) and members of his team to discuss how their current work on Tier α pre-screening of novel fuel blends could contribute to this study. A presentation was provided to

support the discussion [ref. 48] and shortly after the meeting a paper published in Fuel (Elsevier) [ref. 49] was also provided.

Some key points relevant to this study which came out of the discussion and review of the provided references are:

Analysis by GCxGC can yield fuel or blendstock composition at a very high level of granularity to provide concentration (mass fraction) of types of iso, n, cyclo paraffins and classes of single and multi-ring aromatics, and, for each type allocate a carbon number. Using databases for pure compounds e.g., NIST can provide heat of combustion related data for these compounds and therefore “integrate” all these individual compounds to provide an overall estimated heat of combustion (note that the study covers prediction of many other properties in addition to heat of combustion).

The scheme used is illustrated in Figure 24 which is an extract from ref. [49]

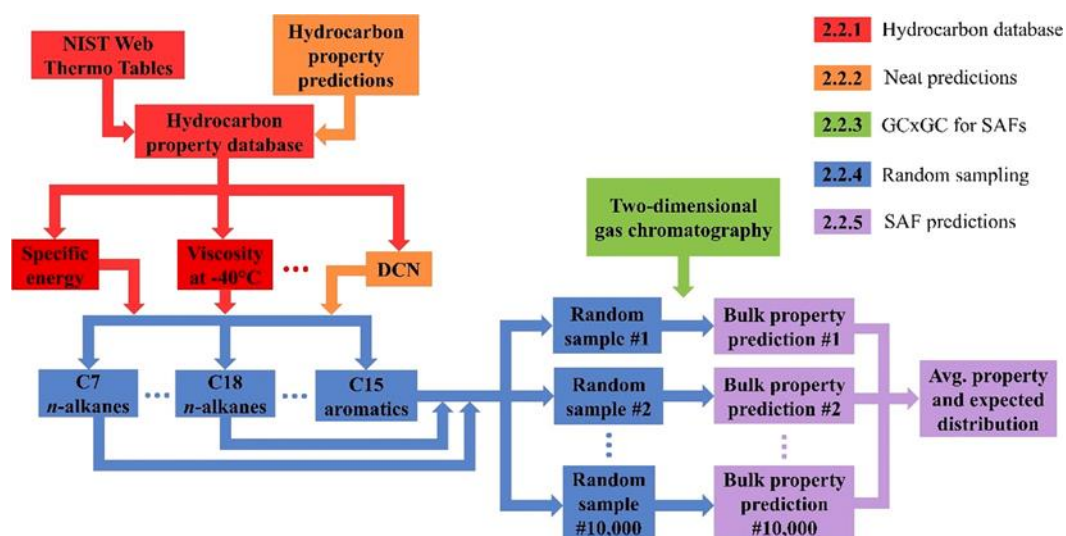


Figure 24: Flow chart of the methodology used in Study [ref. 49].

The predicted values were compared with available measured values from other programmes [ref. 50] but notes some uncertainty for ASTM D4809 results [ref. 51]. [Ref. 49] cites a mean absolute error of 0.17 MJ/kg (i.e. 0.4%) between predicted and measured values by ASTM D4809. However, the report also notes that values for Syntroleum FT-SPK (POSF 5018) varied from 43.9 MJ/kg to 44.3 MJ/kg within the 13 determinations suggesting that in this instance ASTM D4809 can produce larger uncertainty than the method precision would suggest i.e. 0.324 MJ/kg.

Ref. [49] indicates that the repeatability of GCxGC is good and accuracy is reasonably good (referring to all property predictions) but most of the uncertainty is due to the current inability of GCxGC to differentiate between isomers of the same class of molecule and carbon number. Since these can have significantly different properties this remains a limitation and is subject to further work. This confirms the findings of the theoretical examination in section 7.

During further discussions Joshua offered an insight into the latest work on specifically prediction heat of combustion. This was provided in an email but may subsequently be issued in a formal paper [ref. 52]. This further work has addressed developing the prediction based on GCxGG data by expanding the number of fuels in the database and including D3338 data.

Figure 25 and Figure 26 (reproduced with permission from the email).

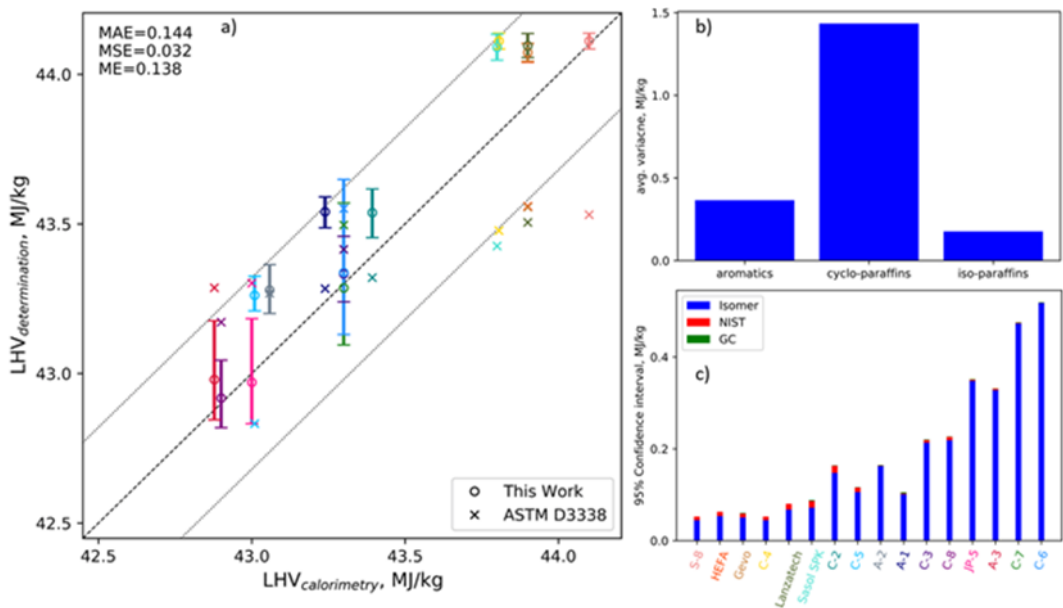


Figure 25: Comparison of UDRI and D3338 derived LHV versus Calorimetry LHV.

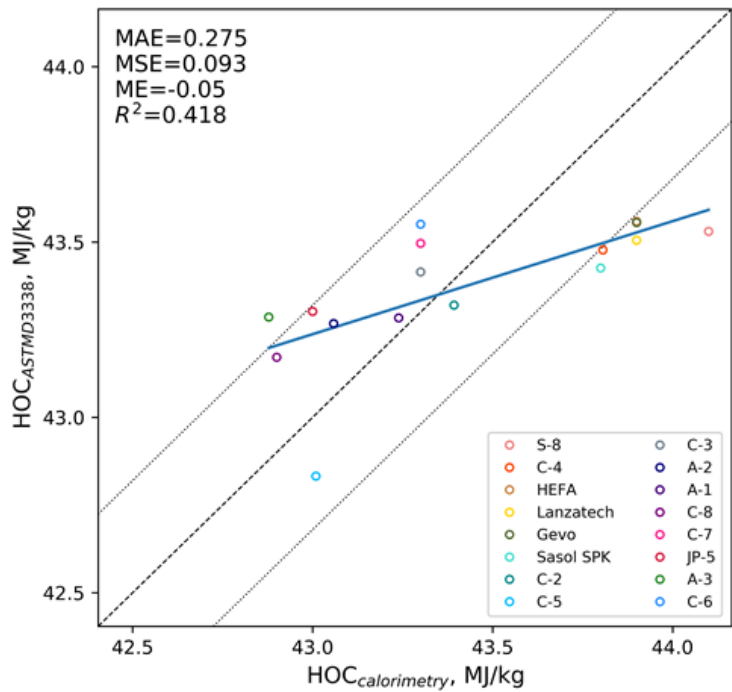


Figure 26: Comparison of D3338 derived LHV versus Calorimetry LHV.

Figure 25: A comparison of the UDRI method (circles) and D3338 (X) versus D4809 measured values. D3338 does not do well when it comes to capturing the slope of the relationship of net heat

of combustion (referred to as LHV in the figures) predictions versus actual measurement. An additional chart (Figure 26) shows just D3338 with its specific statistics.

In these discussions Joshua stated that: the overwhelming uncertainty of our (UDRI) method stems from the identification or lack thereof in the currently reported values. These are represented in the 'isomer' (blue) fraction of the confidence interval subplot. The uncertainty from NIST in the determination is very small (red). The repeatability of the GC (green) is additionally very small. Further work will include incorporating the VUV spectral identification into our predictions soon (which has the potential to dramatically reduce our uncertainty). Already, our uncertainties/repeatability is smaller than the D4809 reproducibility, dotted lines.

The observation in the UDRI work that D3338 does not capture the slope of heat of combustion change compared to measured values shown in Figure 25 is also reflected, albeit to a lesser extent in Figure 11 from the world survey data.

11.2.3 JET FUEL PROPERTIES STUDY AFRL-RQ-WP-2020-0017 – REF [51]

This review, referenced by Heyne et al [ref. 49] and issued in 2020 covers many fuel properties and their correlation but importantly includes heat of combustion and its relationship to other properties such as Hydrogen content by ASTM established NMR based methods, namely ASTM D3702 and D7171 [ref. 16] and hydrogen content from GCxGC data. The review also included some CRC 647 World Survey fuel data [ref. 37]. There is good correlation between hydrogen content for these NMR methods and GCxGC but a bias was noted for the world survey data.

The data shows (as expected) a general correlation between hydrogen content by all methods and heat of combustion but importantly includes some alternative fuels so adds to previous work which was prior to these being available. These again show a degree of correlation consistent with the other fuels.

Lastly, the report notes that it remains to be shown if ASTM D3343 (estimation of H content) and ASTM D3338 (estimation of heat of combustion) are applicable to alternative fuels.

11.2.4 JETSCREEN PROJECT.

JETSCREEN is a multi-partner European Union Horizon 2020 research and innovation programme. Somewhat similar to the UDRI work the programme had the objectives of predicting critical fuel properties from laboratory-based measurements see [ref. 53]. This is to:

- Streamline the alternative aviation fuel approval process.
- Assess the compatibility of fuel composition/properties with respect to the fuel system and the combustion system.
- Quantify the added value of alternative fuels.
- Optimize fuel formulation in order to attain the full environmental potential of synthetic and conventional fuels.

Again, it is not specifically focussed on prediction of heat of combustion but has developed a set of methods and tools to be included in a web base platform that allows the prediction of fuel properties based on advanced analytical and computational techniques (see Figure 27) for an overview.

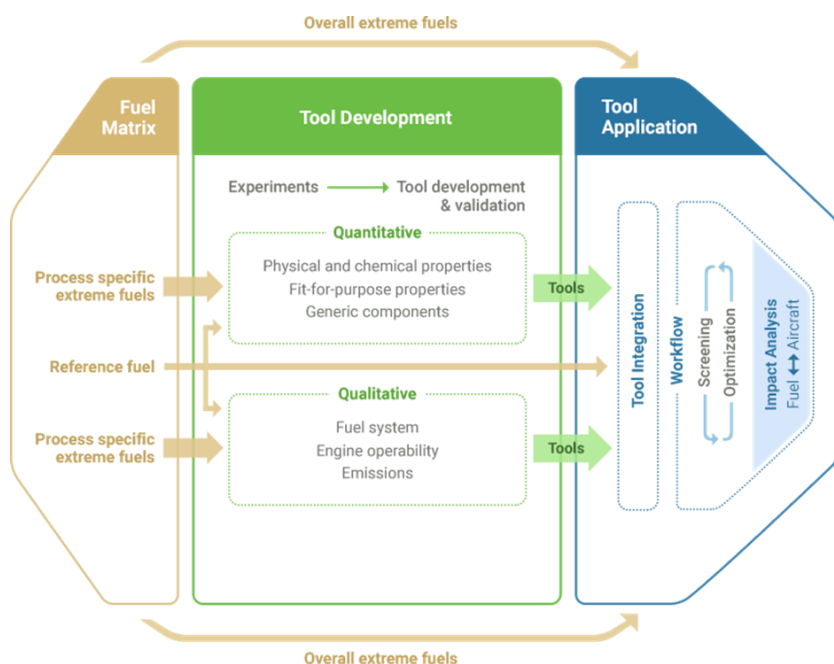


Figure 27: JETSCREEN Project Overview [ref. 53].

The programme included selection, analysis, and property prediction for 31 fuels with a wide range of specification properties which were both drop-in and non-drop-in. Analysis for input to the predictive models included:

- **GCxGC, IR absorption, and/or NMR** to provides indicative target values and direction towards D4054 evaluation.
- **DCN, Density, Distillation Curve, Viscosity, Surface Tension, Thermal Stability** for systematic de-risking for preparing ASTM D4054 based on low-cost measurements and accurate predictions.

Low and high-fidelity prediction model methodology included chemical and physical models (algorithms) as well as various forms of machine learning.

Discussions with Simon Blakey and Bastian Rauch of the JETSCREEN consortium showed that these methods and tools could be more focussed on predicting heat of combustion. This is based on experience gained to date of being able to predict a range of physical and performance properties with some confidence purely based on laboratory compositional analysis. Work looking specifically at heat of combustion is ongoing. Data provided by JETSCREEN¹⁴ demonstrated algorithms as work in progress but also based on the large database of chemicals and number of molecules identified by GCxGC, the complexity for the task should not be underestimated.

Clearly this approach and the platform being created would have the potential with specific development to be able to estimate heat of combustion from more easily measured values.

11.2.5 PREDICTIVE MODELLING OF AEROSPACE FUEL PROPERTIES - SYNOVEC ET AL.

Work by Synovec et al. issued a paper in 2020 which reported the development of a method to predict fuel properties using 2D gas chromatography linked to time-of-flight spectrometry (GCxGC-TOFMS) and correlating to determined values by partial least squares (PLS) fit analysis [ref. 54].

GCxGC-TOFMS provided a detailed breakdown of composition of a range of fuels provided by Air Force Research Laboratory (AFRL, Edwards AFB, CA and Wright-Patterson AFB, OH). The 74

¹⁴ A presentation was kindly provided to the author but this has as yet not been published in a form that could be cited.
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fuels comprised 49 rocket- grade kerosene formulations, 17 jet fuels with 4 from alternative sources, 2 specialty aerospace fuels, and 2 commercial hydrocarbon products, e.g., Jet-A, JP-5, JP-8, RP-1, and RP-2. Analysis included a comparison of predicted and the actual measured values for a range of properties, importantly including net heat of combustion.

Net heat of combustion was determined in duplicate or triplicate according to ASTM D4809 (Model 6200 calorimeter, Parr Instruments). Interestingly, for the current study determination of replicate analysis allowed some examination of repeatability for the AFRL samples. The report states that “relative standard deviation (RSD) was <0.5% for all samples and <0.1% for all but four. Compared to D4809 precision statement the difference in successive results is expected to exceed 0.096 MJ/kg for no more than 1 in 20 samples. For the 58 fuels analysed at Edwards AFB, CA, the largest discrepancy in successive results was 0.074 MJ/ kg, and the average discrepancy was 0.022 MJ/kg”.

The PLS modelling for heat of combustion was carried out and (after exclusion of 8 outliers) showed NRMSECV of 41.3 Btu/lbm but noted the method precision (repeatability) for ASTM D4809 is 0.096 MJ/kg (~40 Btu/lbm); thus, the model quality is reasonable. Further, interpretation of the data indicated that, as expected, alkanes correlate more positively with heat of combustion by mass, when compared to cycloalkanes and aromatics based on the PLS modelling. Some samples with atypical composition did not model as well as the core fuel sample set. To paraphrase the findings of the report, this method of predicting heat of combustion gives generally good results but is not 100% reliable when fuel composition falls outside certain parameters.

11.2.6 VUV ANALYTICS METHOD

There is growing industry interest in the Standard Test Method for Detailed Hydrocarbon Analysis by High Resolution Gas Chromatography with Vacuum Ultraviolet Absorption Spectroscopy (GC-VUV). This method is still under development and is therefore designated ASTM DXXXX – see ref. [55].

This analysis uses gas chromatography and vacuum ultraviolet absorption spectroscopy detection (GC-VUV) for the determination of individual compounds and compound classes by percent mass or percent volume. Individual compounds are spectrally verified and speciated. Compounds that are not spectrally verified and speciated are identified by carbon number, based on retention index, and by class type, based on spectral response. The resulting verified hydrocarbon analysis therefore identifies classifies and reports 100% of the spectral responses.

This method has the potential to analyse fuel composition quickly and conveniently to a high degree of granularity and therefore, if joined to either a component property database and/or a suitable algorithm would possibly provide an estimated heat of combustion value.

Since this method will potentially become a specification test for aromatics and other species, the data may be widely available in laboratories offering convenience of use.

11.2.7 ACADEMIC STUDIES

A tentative search on databases such Elsevier (www.elsevier.com) identified many academic studies on the prediction of hydrocarbon properties from detailed chemical analysis and library reference data to build up the total heat of combustion (and other properties) from the constituent components.

Examples include [ref. 56, 57, 58, 59, 60] but many more similar reference exist and this is a very interesting and active area of research. Reviewing these documents and many other similar reports shows some common threads with respect to heat of combustion prediction:

- A range on analytical techniques, or combinations thereof have been used to analyse the hydrocarbon mixtures including but not limited to: GCxGC (2DGC), FTIR, NIR, NMR, Raman Spectroscopy, etc.
- A range of computational methods including those discussed above, machine learning, genetic algorithms, neural networks, etc.
- Available library reference physical data for pure compounds also created some limitations.
- In most case some success was achieved but, again in most cases, the methods were not totally reliable in that certain samples would give erroneous results.
- These studies show that, specifically for heat of combustion, very detailed chemical composition is needed as bond strengths can vary significantly within what could appear to be very similar isomers. The more complex the molecule, e.g., cyclo paraffins versus simpler iso and n paraffins and even more complex aromatics, the more complex and difficult the process. The complexity of cycloparaffins was examined in detail in the work reported in ref. [60].
- All these types of analysis and computational routines are too esoteric to be applied to the everyday laboratory requiring predicted values. Further, it is debatable that in everyday use these methods would provide any benefit over current estimation or determined methods.

In summary, whilst these methods could provide useful capability in the R&D environment, none offer an alternative to current methodologies at the present time. However, as analytical techniques develop from R&D to routine capability, with the associated increased availability of computing power, these regimes may offer easier to use systems in the future.

Although of academic interest a study report in Process [ref. 61] reports a method for predicting aniline point from other properties including density and average boiling point. Seven existing and one new algorithm developed by complex computational maths were assessed with varying degrees of success. This paper demonstrates that improvements in computational methods could reap benefits on existing analytical techniques or be more powerful with advanced analytical data.

11.2.8 USE OF HYDROGEN CONTENT

As noted in section 8 methods using hydrogen with other parameters generally have fallen out of use and in some cases, methods have been withdrawn. Hydrogen is an alternative measure that indicates the aromaticity of a fuel, and this combined with other parameters that give an overall indication of molecular weight (carbon) can give good correlations to heat of combustion. It is the lack of a convenient method of determining hydrogen content that has reduced their use. Therefore, if new methods become more commonplace that can measure hydrogen directly or indirectly, derived by, e.g., GCxGC or GC-VUV, this method of estimation may again become viable.

11.2.9 IMPACT OF FUEL COMPOSITION ON RELIABILITY OF ESTIMATION METHODS

A full and detailed examination of the impact of fuel composition on heat of combustion is provided in Section 7.3 but findings from work cited on fuel analysis surveys and property prediction R&D confirms isomeric identification is needed if reliable predictions are to be possible. This shows that any future method that attempts to provide predictions from composition is a significant challenge due to isomer variations. So any “bottom up” compositional model must have sufficient granularity to detect and measure these isomers in enough detail to enable reliable calculations. It is clear from the research work reviewed above some progress has been made but there is more to be done. Further, these methods have not been stress tested on some of the emerging synthetic blendstocks that have very narrow ranges of carbon number and isomer type.

The challenge for a viable method for everyday reliable prediction based on compositional data is the conflict between needing very complex analysis versus the need for low cost and convenience. However, one benefit of this study is that although no new methods may be developed for everyday use, improvements in predictive methodology in R&D and pre-screening could be useful. Further, the insight this review has provided may assist in the development of existing methods and provide better guidance as their scope, applicability and caveats.

11.3 ADVANCED METHODS SUMMARY.

The concept of analysing a fuel's composition with greater granularity and relating that to heat of combustion by use of physio-chemical library data for individual compounds has been examined. Detailed analysis, which can more readily be carried out by, say, 2DGC or GCVUV, offers the opportunity to have much better compositional data for a given fuel. This, allied to modern computational techniques such as machine learning and genetic algorithms, offers the potential for better prediction methods. However, these potential strategies come with caveats. Work thus far has shown that due to the complexity of fuel composition they are not by any means fool proof and can only be used within the confines of the learning data but even then, may be unreliable for certain fuel compositional ranges. Further, the whole concept of having a convenient method of calculating heat of combustion from already available fuel property data would exclude the more esoteric test methodologies from use in an everyday fuel quality assurance or production laboratory environment. These methods may have a role to play in the right environment and warrant further examination in any work where data from such methods and determined values are available from the same fuel samples.

The challenge for a viable method for everyday prediction based on compositional data is the conflict between needing very complex analysis versus cost and convenience. However, one benefit of this study is that improvements in predictive methodology in R&D and pre-screening could be useful and the insight this review has provided may assist in the development of existing methods.

12 SUMMARY DISCUSSION

Determination of aviation fuel heat of combustion is required for a range of requirements from simply ensuring product meets specifications (quality assurance) to providing data for critical engine/aircraft performance and aircraft loading calculations, etc. In these roles there is varying requirements for precision and accuracy. Therefore, a choice can be made to use estimated values based on correlations with other related fuel properties or to use direct measurement using calorimetry. Both methodologies have a role to play.

Test methods provide final quoted values as net heat of combustion which is the industry standard and relates most closely to the heat released during combustion within an internal combustion engine. Values directly determined by calorimeter are corrected to net values by use of equations that correct for the specific conditions within the bomb (high pressure oxygen and constant volume) to more normal pressures and constant pressure as well as the condensation of water. In the case of calculated estimations, correlations to net heat of combustion are based on relationship, between key fuel compositional factors including density, distillation, and aromatics expressed as actual aromatics content, hydrogen content or aniline point.

Determination by bomb calorimetry provides a much higher level of precision and accuracy but requires much more operator effort and skill, investment in equipment and facilities, particularly if the highest precision is to be achieved. Even fully automated systems which control, monitor and finally carry out the required calculations still require skilled operators to load and unload the calorimeter and no viable fully automated system has been identified in this study. The key problem for a truly “black box” system where fuel is injected and analysed fully automatically is the need for extremely accurate measurement of a small mass of fuel.

Many calorimeter manufacturers produce a range of calorimeters and associated systems which vary in terms of operation and level of automation and most critically temperature measurement and control capability. Many claim to meet the requirements of national/international test methodologies but data to support this are not readily available. However, they all follow the common principle of operation where a known weight of fuel is combusted in a high-pressure oxygen bomb and the resultant heat release is measured by temperature rise of the inner assembly for which the heat capacity is known, allowing the (gross) heat released to be calculated. Methods of either preventing heat loss/gain from this inner assembly, or, correcting for heat loss/gain vary but all attempt to ensure that the (uncorrected or corrected) temperature rise is the true value. Further corrections are required to ensure the final net heat of combustion quoted (as a reference value) most closely relates to the combustion in internal combustion engines.

The review has identified several modes of operation for calorimeters. The industry has in generally moved from isothermal and adiabatic towards isoperibol, as well as using more readily available precise and cost-effective electronic sensor-based temperature measurement systems. Both adiabatic and isoperibol can, with care and right equipment, yield very accurate results. Adiabatic mode puts more emphasis on the calorimeter equipment control but requires no temperature correction whereas isoperibol systems require less control but does require careful temperature monitoring and post-test complex temperature correction which is carried out by the equipment processor.

Estimation methods have convenience and ease of use as they generally use data which are already available so requires only limited effort to calculate heat of combustion values. However, standard heat of combustion estimation test methods include caveats that results may be in error above the level that a user may have inferred from the precision under certain circumstances and so reliability and accuracy may be compromised. The precision of these methods is based on the precision of the input data but not necessarily the quality or reliability of the correlation – hence the caveats regard potential for errors. Therefore, such methods should not be used where high

accuracy is required. One observation that comes from this review is that in the case of heat of combustion estimation methods (and indeed any such prediction methods) the difference between precision (which is always defined) and accuracy and/or bias (which is not generally defined) may vary significantly more than would be expected for most measurement methods where reference materials and values are available. Comparisons of the practicality of the alternative approaches are summarised in Table 16, Section 9.

The report notes that the reliability of estimation methods relies on the fuels being analysed falling within a “well-defined class”, which is not always clear, but mainly is defined by the set of fuels on which the correlations were based. With changes in conventional refining techniques since these methods were originally developed (1950s-1970s), and particularly the advent of new synthetic fuels blends, these correlations are being challenged. Indeed, data presented in this review demonstrates that the estimate of heat of combustion may not as accurate as the method precision statements suggest.

Procedures for both estimation and determination methods are defined within national or international test methods which have been reviewed. Since these procedures are critical to achieving reliable results, these have been carefully and critically examined in this review. Some key findings common to all methodologies include:

- There is a degree of commonality across the different national test methods reviewed in this study (ASTM (US), EI (UK), DIN (Germany), Russian and Chinese).
- With particular relevance to EI and ASTM methods which are the primary focus of the review the following observations have been made.
 - Basic methodology can be traced back to studies (industry and academic based) carried out in the 1950-70s.
 - Since that time other test methods which have significant impact on estimated heat of combustion methods have been updated and, in some cases, new methods introduced which could influence results.
 - Calorimetry equipment has developed in the areas of critical temperature control and automation, and importantly, modes of operation. Current standard test methods do not recognise these developments and in some cases, methods cite equipment that has been obsolete for many years.
- No substantial ILS, round robin, or cross method (estimated versus determined) comparisons have been carried in the last 20 years by the industry committees that oversee these methods.
- There are only limited data where estimated and determined values are available for the same samples as part of other studies. What limited data are available from sources reviewed in the report shows that estimation methods may not provide results which are as reliable as their precision statements suggest. However, all estimation methods do highlight this within the caveats which give warnings regarding erroneous results.
- Changes in jet fuel composition and the increasing prevalence of synthetic fuels is challenging the validity of estimation methods. The situation is similar for AVGAS where even more radical changes are being evaluated for in efforts to develop a high-octane unleaded composition where the fuel may no longer be purely hydrocarbons but contain some significant levels of heteroatomic blend components.

In summary, standard test methods for estimation and determination require updating to reflect current associated test methodology and equipment. Precision for determined test methods require re-assessment and may well be improved with modern equipment. Estimation methods also need assessment of precision and correlations need to be developed (if possible) to account for the changes in fuel property and property relationships of emerging synthetic blends.

This review has failed to find any promising alternative to the basic principle of calorimeter-based measurement systems, which it must be said have been developed to a very high level of sophistication and automation. It is clear that one of the primary barriers to a “black box” where fuel is injected, and heat of combustion directly measured, is the need for extremely high accuracy fuel mass measurement which is not possible at this time.

The report has shown one interesting change in that aniline gravity estimation, which was widely used, fell out of favour due to the health and safety concerns with using aniline. There is now a method which provides aniline point equivalent using much safer chemicals which may support a resurgence of this method but again, would require estimation test method update and re-assessment of precision/accuracy.

A survey on the use of calorimetry and estimations methods primarily within the ASTM method user community showed low and higher precision calorimetry using a range of operating modes and several estimation methods are in common use. Throughput varies from very infrequent to many samples a month and a range of applications so providing a good sample of what current industry practice.

Generally, calorimetry methods meet current requirements and precision could usually be achieved. However, difficulties with handling volatile samples and equipment cited in calorimetry methods not being up to date are important findings reinforcing observations in the main report.

ASTM D3338 is by far the most widely applied estimation method but ASTM D4529 is still in use. As noted elsewhere, the development of an aniline point equivalent may well change this balance but the use of this new method needs assessment.

The survey also showed a range of methods being used for sulphur and hydrogen input for gross to net estimations, and, the input of data for estimations.

Overall, the survey shows that many of the standard test methods reviewed in this study are in regular use and generally meeting requirements but specific areas requiring improvement have been identified. The survey therefore provides additional guidance should or when these methods are updated.

The concept of improved estimation methodology based on the most recent developments in analytical techniques has been examined. Advanced analysis by, for example, 2DGC and GCVUV, allows the composition of fuels to be defined with much greater granularity than previously possible by broad categorisation using hydrogen content, aromatics or aniline point used in traditional methods. Combining these data with standard library data for pure chemical compounds and modern computational capability offers the potential for improved prediction of heat of combustion by summation of the heat of combustion of the individual components based on molecular species and their concentration. The schemes reviewed show promise but have yet to be optimised for this specific purpose as they have been generally applied to the prediction and evaluation of new fuel blend properties. Further, it has been noted that many methods cannot always distinguish between isomers of molecules which may have quite different heat of combustion values. This field is very much work in progress and would require further development to be optimised for the purpose of calculating net heat of combustion. The analytical equipment required is generally cutting edge and therefore unlikely to be widely available in fuel quality assurance potentially limiting applicability to everyday fuel testing. The nearest recent development is the GCVUV method which shows some promise and could be widely available in the future. However, examination of this work and a review of the impact of fuel composition provides improved insight into both the challenges and potential for improved estimation methods.

13 CONCLUSIONS

Aviation fuel heat of combustion data are required for a range of applications from basic specification compliance testing, through evaluation of new fuel blends to accurate measurement in support of engine/aircraft performance assessment.

Heat of combustion has a direct and pro rata impact on engine fuel consumption per unit mass or volume and so accurate values are required for performance assessment and/or optimising aircraft fuel loading calculations. This is particularly relevant where estimation methods are currently used that could be rendered inaccurate for modern fuels with novel compositions.

Heat of combustion can be determined by calorimetry which, in its simplest form, burns a known mass of fuel in a bomb usually surrounded by water in a bucket. Temperature rise of the calibrated system can be used to calculate the heat released. This is then corrected from bomb conditions (gross) to a value more related to use (net).

Calorimetry equipment has improved significantly over the years in terms of temperature measurement technology and control as well as microprocessor control of sequencing pre, firing and post firing control and monitoring. This increased automation has reduced operator input during the calorimeter sequence but still requires skilled operators to prepare and load the calorimeter and carry out post-test analysis.

The main operating modes include isothermal, adiabatic and isoperibol which all have advantages and challenges. Each seeks to ensure either heat loss/gain to the inner system is eliminated or corrected for. Isoperibol would not be possible without automation.

The study highlighted that the use of benzoic acid as a standard calibration material has significant benefits. However, the use of powder/pellets does not challenge the operator in the same way as handling liquid fuels and indeed firing conditions are not exactly the same. For volatile samples the use of TMP is recommended as an overcheck. The author suggests for improved precision assurance liquid samples similar to jet fuel (non-volatile) should also be required to ensure liquid handling procedures are optimised.

From experience and as reported in the survey, misfiring can occur with even the most diligent operators. Again, for the highest precision it is recommended that the average of multiple firings be used to calculate the final result.

No disruptive technology was identified for carrying out determinations i.e. replacement for calorimeters. The main barrier to a “black box system” system where fuel would be injected and automatically analysed was the need for extremely accurate fuel sample mass determination.

Heat of combustion can also be estimated (calculated) from correlations based on other fuel properties. Such estimation methods are being challenged by changes in fuel composition. A review of the impact of various fuel compositional factors shows that some improvements may be made but ability to analyse fuels with sufficient detail (particularly isomeric variations) remains a challenge.

The challenge presented by the variability in heat of combustion between isomers with the same carbon number has been demonstrated on both a theoretical and practical level in this study.

A comprehensive review of both determination and estimation methods has shown that both types of procedure have their strengths and weaknesses. Primarily, determination methods (calorimetry) results are more reliable (accurate), but the methods are complex and require specialised equipment and skilled operators. Estimation methods are quick and convenient, using input data to correlations from tests that have to be carried out anyway so minimal extra effort, but results can be

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unreliable (inaccurate) for fuels that are outside the scope of the base correlation data despite having seemingly good precision.

The fundamental principles of both types of method were established in the 1950-60s. Whilst methods have been revised since then significant changes in several areas identified in this report show that an update would be timely. Briefly these include:

- Major improvements and updates in calorimetry equipment that is not reflected in the test methods. Also, isoperibol operating mode has been developed and is now by far the most popular over isothermal and adiabatic (withing the survey group).
- Ancillary test methods used to input to the determinations and/or estimations have significantly changed and need assessment.
- Composition of conventional jet fuels have changed over the years and with the advent of synthetic blends there is evidence to show that validity of estimation methods needs re-assessment. This is particularly relevant for novel blends that have atypical isomer mix and the move toward 100% synthetics.
- Proposed new formulations for high octane unleaded Avgas which contain new heteroatoms would render current estimation and perhaps determination methods inaccurate.
- The need for more accurate and reliable data is emerging as high-performance engine and aircraft design are required to meet operator demands and environmental impact reduction.
- The issue of joint and or equivalent methods needs addressing during any future method development or updates.
- No ILSs have been carried on any of the examined methods within the last 20 years.

The study also noted that a new method for producing an aniline point equivalent has been standardised to help address health and safety issues. This may trigger a resurgence of the aniline gravity estimation methodology (ASTM D4529 or equivalent). This needs assessment and will most likely have the same reliability and, therefore caveats, as existing methods.

Discussions with the respective ASTM and IP sub-committees confirmed in principle that the methods under review warrant assessment and update and that the findings of this report will help guide that effort.

Overall the findings of this report show that with the changes in fuel composition, equipment and test methods a significant overhaul and update of both determination and estimation methods is warranted. This study seeks to provide guidance as to what specific areas need addressing and to some extent how.

A CRC and ASTM survey was also undertaken as part of the project. This has shown that a range of determination and estimation methods are in regular use for a range of applications and generally meet requirements, but areas of improvement were identified which were broadly the same as those identified within the main state of the art review.

The survey data provides a useful insight into industry practice in terms of method usage and application which should be used to guide and prioritise future method development.

As the survey covered mainly stakeholders connected to CRC and ASTM there was a bias towards ASTM and IP methods, these being the primary focus of interest. A review of responses showed a good range of users with respect to methodology used, application of data, frequency of tests etc to provide a good overview of industry practice.

Some key conclusions from the survey include:

- Most determinations are carried out by ASTM D240 or ASTM D4809.
- The vast majority of estimated values used ASTM D3338. Whilst some use of ASTM D4529 was reported this was not common. The low use of D4529 is believed to be due to the health and safety issues of the required aniline point test.
- In general the use of estimated values were much higher than determined reflecting the convenience of this methodology.
- Test methods generally met requirements and stated precision could be achieved but some problems were reported for calorimetry including difficulty handling volatile samples and observation that equipment cited in these test methods was obsolete.
- A range of ancillary test methods were cited as input to the prime determination and estimation methods which again gives insight into what is being used.

To add further value a literature search and discussions with R&D members of the aviation community were undertaken. These highlighted efforts to improve predictive capability of novel fuel blends by determining detailed composition, e.g., GCxGC and then computing total heat of combustion from library data of each compound and/or machine learning. Such techniques show some promise but do have limitations, specifically:

- Current inability to resolve all isomer composition.
- Complexity of equipment and data handling that would, at present, exclude them from everyday use in busy production laboratories.

The insight these advanced methods provide could help understand the challenges of developing current or new estimation methods and build an understanding of their strengths and weaknesses.

The use of GCVUV was identified to potentially provide a balance of improved compositional analysis with convenience.

14 RECOMMENDATIONS

14.1 GENERAL

This report covers Phase I of the CRC two Phase programme investigating aviation fuel heat of combustion: Phase 1 – Literature review of calorific instruments, methods and correlations. The report has highlighted numerous areas of interest that warrant attention, such as modernisation of determination methods and verification/adaption of estimation methods for current refining and synthetic fuel composition.

It is recommended that given the depth and breadth of these findings, and the complexity of the subject in general, discussion is required with stakeholders to understand, and agree what future work should be carried out and relative priority. In particular the relevant sub-committees that have responsibility for the methods, namely, D0.05 and SC-B-10 for ASTM and Energy Institute (IP) methods respectively, should be engaged.

As a proposal, following the issue of this report a symposium might be arranged to review and agree future actions including any CRC funded Phase II experimental work, or as part of the Phase II activity. This could be on-line or timed to coincide with an annual CRC or other aviation industry meeting.

Note that the report has highlighted the issue of joint or technically equivalent methods which applies across all ASTM and EI methods reviewed. This aspect for either the methods in their current form or following any significant updates is outside the scope of this study and is therefore deferred to the relevant sub-committees that have responsibility for the methods namely, D0.05 and SC-B-10 for ASTM and Energy Institute (IP) methods, respectively.

Some specific areas that future work should address includes but is not limited to:

14.2 DETERMINED (CALORIMETRY) HEAT OF COMBUSTION

- Updating standard test methods to reflect current equipment, temperature measurement systems and modes of operation. This could include elimination of the use of mercury in glass thermometers which would inevitably benefit ultimate method precision and safety.
- Provide guidance on recognised calorimetry equipment, and, how to validate the use of calorimeters not cited in the test methods, and, provide controls of equipment version and particularly control of software versions.
- Consider recommended improvements to high precision methodology including:
 - Use of liquid standards as a secondary or calibration check for non-volatile as well as volatile samples.
 - Requirement to carry out firings in duplicate or even triplicate and have criteria for acceptability and quote an average.
 - Specify calibration intervals.
 - Consider, given the complexity of sample handling and equipment operation, citing the requirement for skilled and experienced operators.
- Review the adequacy of current test methods for sulphur and more critically hydrogen content, etc.
- Update test methodology to reflect above improvements.
- Carry out a comprehensive ILS programme following completion of the agreed test method(s) improvements to re-assess precision and accuracy.
- Assess and define methodology accordingly to account for formulations with significant levels of non-hydrocarbons such as AVGAS.

14.3 ESTIMATED HEAT OF COMBUSTION

- Review current and near-term compositional changes of fuels e.g., Avgas and synthetic blends and future 100% SAF, and their potential impact on estimated value accuracy (reliability).
- If considered value added by industry users, assess the validity of using the new aniline substitute method(s) to allow aniline gravity calculations to be used with improved health and safety.
- Carry out a cross correlation between estimated methods and the revised high precision determination methods to assess estimated value precision and accuracy. This should include conventional fuels and novel blendstocks that specially challenge typical fuel composition e.g., narrow boiling range, unusual isomer composition and/or 100% synthetic fuels and proposed high octane unleaded AVGAS formulations featuring non-standard components.
- In addition to re-wording the estimated method caveats to provide improved guidance, consider having a requirement to establish that the estimated methods being used are validated for the specific scope of fuels being analysed at a particular location. This would be by the use of validation by comparison with determined values. The requirement for either validation of existing correlations and/or creation of specific correlations could be achieved by either:
 - Having the requirement to evaluate this aspect within ASTM D4054 and include the requirement for estimated and determined values on a range of blends that cover the entire scope of blendstocks and final blends to define a specific correlation.
 - Having the same requirements but require this to be carried out as part of the estimation method by the end user at the point of manufacture and blending.
- Review the potential for improved estimate methodology using advanced analytical techniques and library data, recognising that this may only be appropriate in specific circumstances and not for “everyday” use. This will also support understanding of the limitations of current estimation methods.
- Based on the above consider creating updated correlations and revising calculations used in standard test methodology.
- Carry out a comprehensive ILS programme following completion of the agreed test method improvements to re-assess precision and accuracy.

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ANNEX I: SUMMARY OF FINDINGS - MOD SPECIFICATION REVIEW (REF. 18)

Modern aviation fuel specifications have always had a requirement for a minimum specific energy.

Technical developments in methodology have provided an increasing number of means by which specific energy is determined or estimated.

Actual measurement of specific energy is complex, expensive and requires skilled operators if accurate results are to be obtained. Calorimeters are also expensive to purchase and maintain.

Measurement methods were originally low precision, e.g., IP12 / ASTM D240 by bomb calorimeter. A higher precision bomb calorimeter method (ASTM D2382) was later developed but has been dropped from the UK specification for practical reasons. (The quoted precision of ASTM D2382 could not be achieved on a regular basis.) The intermediate precision bomb calorimeter method ASTM D4809 was introduced in 1988 and is now considered the best balance between accuracy, precision and practicality.

Estimation methods tend to be preferred by virtue of their low cost and often only involve calculations based on measurements already made as part of specification certification requirements.

The most popular estimation method was once aniline gravity product (ASTM D1405 or D 4529) due to speed, low cost and adequate precision. However, this method has been phased out because of the health hazards associated with aniline.

The advent of hydrogen content by NMR spawned new estimation methods using hydrogen (and other parameters) and provided a high degree of precision. For example IP 355, which uses hydrogen and sulphur contents and density, was introduced into Defence Standard 91-91 as an accepted estimation method in 1994.

Comparing the precision of estimated methods against direct measurement values can give the impression that estimation methods are superior. This is, however, a common misconception. The precision of estimates (repeatability/reproducibility) is based purely upon the combined precision of the actual measurements used. The actual accuracy of these methods is, however, less reliable than that of direct measurement. All estimation methods contain a caveat regarding the limitation of such methods to well defined classes of fuels (for which the method has been shown to apply) and warnings regarding the potential for gross errors (see individual methods).

Specific energy (enthalpy of combustion) of the fuel controls the amount of energy available from combustion per unit mass of fuel. Engine control systems are designed to provide a given thrust for a specific pilot throttle position. Sufficient fuel is metered into the engine to provide this thrust (typically controlled by engine speed or pressure ratio) automatically compensating for variations in density and specific energy. The engine is developed and tested to show that a minimum guaranteed thrust and fuel consumption can be achieved on fuel of the minimum specific energy likely to be used. The minimum value used is commonly 42.8 MJ/kg which is almost universally specified as the minimum specific energy in international fuel specifications (exceptions include AVCAT (high flash types)). Testing is actually carried out on typical fuel (43.1 - 43.3 MJ/kg in the UK currently) and engine performance corrected to the 42.8 MJ/kg datum. Whilst engines are able to compensate for specific energy variations this does result in variations of fuel consumption. As a general rule, fuel loads are calculated using fuel density and density/specific energy relationships (see the section on Density in the chapter on Pumpability). This method is sufficiently accurate except in special circumstances, where the more expensive methods of determining specific energy may be employed.

One possible change to current practice is the concept of purchasing fuel by energy content. This has been considered by one aircraft operator as advantageous to the operator by paying for actual 'energy' and allowing fuel uplift estimations to be more accurate. To operate such a system would require an accurate on-line, real time calorimetry system. No system is currently capable of providing this with sufficient accuracy. If such a system did become commercially available it is believed that purchase by energy content would be given serious consideration.

ANNEX II – CRC AND ASTM SURVEY QUESTION LIST

Survey Question List

Question List
Please indicate your organisation type from the list
Please indicate your organisation type if you selected "Other"
PRIMARY role of Department / Laboratory
Do you produce HOC data?
Do you use HOC data?
What is the PRIMARY purpose for producing or using HOC data? (also see below to add more detail)
Additional Comments
Do you carry out bomb determined HOC?
On average how many determinations do you carry out per month?
What test method do you use?
What make of calorimeter do you use?
What model and component part model numbers do you use?
What mode of operation do you use?
What type of temperature measurement system is used?
Do you use benzoic acid as primary reference
If Yes, how often?
Do you use 2,2,4 trimethylpentane for verification for volatile samples?
If Yes, how often?
Do you use any other reference standards or verification procedures?
Please explain these additional verification procedures
Do you use pressure sensitive tape?
If sometimes under what circumstances?
Do you use gelatin capsules?
If sometimes under what circumstances?
Do you use glass ampoules?
If sometimes under what circumstances
Do you use other methods of preventing loss of volatile samples - if so what?
What method do you use to determine Hydrogen content?
What method do you use to determine Sulphur content?
Please list other analysis/methods used to support heat of combustion analysis and in particular correction from gross to net values.
What ancillary equipment or special measures do you take?
Do you find the current method difficult to use?

If yes what problems exist?
As a data provider do these methods meet accuracy and precision requirements and if no please specify what your requirements are.
Additional comments
Do you carry out HOC estimation estimations?
On average how many determinations do you carry out per month?
Which method do you use?
What methods do you use for input data?
Do you find the current method difficult to use?
If yes what problems exist
As a data provider do these methods meet accuracy and precision requirements and if no please specify what your requirements are?
Do you have determined (bomb) HOC data for the class of samples you analyse? (if yes please give further information in Additional Comments)
Please explain any additional procedures and/or measures taken to increase precision
Additional Comments
Do you use HOC data?
What test method is used to produce data?
What is the primary purpose for producing or using HOC data? (also see below to add more detail)
Please specify what level of accuracy/precision you require
If applicable: Do current determination methods meet your requirements?
If applicable: Do current estimation methods meet your requirements?
Please specify any improvements in determination methods you require
Please specify any improvements in estimation methods you require
Additional Comments
Please provide any comments, issues or recommendations for the development of determined HOC methods
Please provide any comments, issues or recommendations for the development of experimental methods for HOC determination
Any other comments

Notes.