

### Combustion Calorimetry Applications

There are six major applications for oxygen bomb calorimeters

The industrial revolution in the 19<sup>th</sup> century caused a rapid increase in demand for energy sources. The idea of burning coal and other fuels was not new, but this was the first time when the advances of science and technology made possible the commercially viable utilization of fossil fuels. The chemical energy stored in such fuels was converted into mechanical energy and electricity, opening doors for giant factories and power stations. Coal production and consumption in the US rose tenfold between 1870 and 1900.<sup>1</sup> Of course such consumption and the market required an assessment tool to measure the fuel quality. Advances in thermodynamics in the 19<sup>th</sup> century created bomb combustion calorimetry in response to this need.

Although combustion calorimetry existed well before the 1880s, it occurred in the form of flame combustion calorimetry. In 1881 Berthelot<sup>2</sup> was first to report the combustion of a gaseous mixture in a sealed vessel. In subsequent years, together with Vieille<sup>3</sup>, the technique related to the combustion of solid and liquid samples in oxygen under pressure developed. This spawned the modern bomb combustion calorimeter that we know today.

Professor S.W. Parr at the University of Illinois developed the peroxide bomb calorimeter in 1899. At that time there were very few satisfactory commercial calorimeters available, and these were all of the oxygen bomb type that required expensive noble-metal linings as well as a source of compressed

oxygen and considerable technical experience in their operation. Professor Parr sought to construct a simple calorimeter which could be sold at low cost and which would be suitable for use by semi-skilled operators in fuel producing industries where there was a definite and growing need for data on heating values. Instead of using compressed oxygen as the oxidizing medium in his apparatus, he proposed to use sodium peroxide. This material could be obtained in powdered form and, when mixed with a fuel sample and ignited in a small calorimeter bomb, it yielded the large amount of oxygen necessary to affect the desired complete combustion. The thousands of these calorimeters placed in service during the nearly half a century of production provide ample evidence of their general acceptance.

One of the biggest problems for oxygen bomb calorimetry at that time was that the vessels required some sort of passivation to prevent corrosion and diminished accuracy related to the byproducts produced during combustion. Platinum and other noble metals were available options and this made such vessels extremely expensive. Platinum still remains the ultimate choice for fundamental thermodynamic research, however the market for fuel testing required a less costly solution. Various unsuccessful attempts were made, and little progress took place until Professor Parr discovered Irium in 1912. This alloy was 500 times cheaper than platinum at the time, but provided ample corrosion resistance. Due to that, the oxygen combustion calorimeter became an affordable commercial product.

Thermodynamic research and commercial oxygen bomb calorimetry developed along two parallel paths. The former always put precision as the ultimate goal, where the latter searched for the balance between precision, price, and usability. The premium features available only in research instruments made their way into the commercial market. One of the more notable examples is the implementation of the isoperibol method. Thermodynamic research calorimetry always used this method. The complexity of the isoperibol calculations was compensated by the simplicity of the isoperibol calorimeter hardware design,

thus minimizing deviations from the ideal calorimetric system. However such complexity of the calculations was not suitable at the time for industry, requiring highly skilled personnel to perform them and a significant amount of time for calculation per experiment. Thus commercial calorimeters remained mostly adiabatic until the development of commercially available microprocessors, where these complex calculations were performed automatically in real-time by the calorimeter. This resulted in diminished use of the adiabatic method which required complicated mechanics and systems related to temperature control.

Today, bomb combustion calorimetry related to fundamental thermodynamic studies is a mature and well developed area, and there is little active research. In contrast, commercial bomb combustion calorimetry is still thriving. Advances in the state of the art focus on increased automation, greater throughput, improved usability and information management.

Today in the 21<sup>st</sup> century, the energy demand of society keeps growing, and the applications of oxygen bomb calorimetry continue to expand. New technologies make it possible to obtain energy from non-traditional sources; however the old sources are not going away.

Today, oxygen combustion calorimetry has the following major application areas:

- Fuels and Alternative Fuels
- Waste and Refuse Disposal
- Food, Metabolic, Medical Studies
- Propellant and Explosive Testing
- Thermodynamic Research
- Educational Training

## Fuels and Alternative Fuels

The fuel industry is the main user of oxygen bomb calorimeters today. Depending on the estimate, it utilizes half or more of all manufactured oxygen bomb calorimeters. The reason for this is that calorimeters determine the maximum energy stored in the fuel - the calorific value, which is one of the major factors determining the price of the fuel. Fuels are tested by the producers, consumers, independent auditors, and government labs to ensure its quality and conformance to specifications.

The fuel industry is diverse. It includes several different types of fuel:

*-solid fossil fuels: from coal and coke to peat*

Despite these fuels not being considered “green” and having a significant impact on the environment as well as the decline of their usage in developed countries, the total consumption ( $\approx 8 \text{ Gt}$ )<sup>4</sup> of such fuels shows steady growth. This is mainly due to actively developing Asian countries. These fuels are tested using bomb combustion calorimeters, according to various standards: ISO 1928, ASTM D5865, DIN 51900, IS 1350-2, GB/T 213.

*-liquid oil, and its derivatives: gasoline, kerosene, diesel, etc.*

Liquid fuels are the primary source of energy for ground, air and ocean transportation. Many organizations do not require a calorific value determination using oxygen bomb calorimetry, but rather calculate it by using gas chromatography or by other inferential methods. ASTM D240, ASTM D4809, DIN 51900, and GB/T 384 are common combustion calorimetric standards used for testing liquid fuels.

*-alternative fuels: biomass (including. wood, liquid biofuels and waste fuels)*

Environmental protection and the search for new sources of energy have resulted in the active development of alternative fuels. The world production of liquid biofuels has increased six times, while total biomass production rose one and a half times within the first decade of the 21<sup>st</sup> century. Production has reached an approximate level of  $\approx 0.15 \text{ Gt CO}_2\text{-eq}$  for electricity generation

(including waste fuels).<sup>4</sup> Some of the applicable testing standards are: ISO 18125, GB/T 30727, and EN 14918. The study of alternative fuels is also a very active research field, with a search for methods producing fuels from new sources (for example algae biofuel<sup>5</sup>). This process is happening in universities and research organizations across the globe using oxygen bomb calorimeters as an essential instrument in this process.

### **Waste and Refuse Disposal**

Municipal solid waste is currently about 1.3 billion tons per year total for the planet, and will increase to 2.2 billion tons per year by 2025 for OECD countries.<sup>6</sup> On national and international levels, regulations are introduced to reduce the environmental impact of such materials. One approach uses part of the waste as an alternative fuel. The cement industry is a perfect example. It uses over one million tons of hazardous waste per year.<sup>7</sup> Although it can be argued that this category falls under the fuel category, the main focus of this category is rather disposal of the waste, while getting the energy as a bonus. The use of oxygen bomb calorimetry for characterization of such waste is described in the following standards: CEN/TS 16023, EN 15400, and EN 15170. Apart from calorimetry, oxygen vessels themselves are actively used for the preparation of waste samples for further analysis according to EPA Method 5050, Bomb Preparation Method for Solid Waste.

### **Food, Metabolic, Medical Studies**

Researchers have found bomb calorimetry to be of value when studying the effects of diet, not only in laboratory animals, but also humans. The gross energy (G.E.) content of a food is determined by bomb calorimetry. The digestible energy (D.E.) content of a food is the amount of energy in the food which is able to be absorbed. The metabolizable energy (M.E.) content of a food represents the amount of energy in the food which the animal actually utilizes. One such

study is that of González-Cossío, et al.<sup>8</sup> which determines a link between lactation and malnutrition. Another metabolic study was performed by Rammerstorfer et al.<sup>9</sup> at the Texas Agricultural Experiment Station to characterize physiological responses of reining horses during an exercise simulating reining horse performances.

The application of combustion calorimetry for nutrition purposes is described in the ISO 9831 standard.

Other applications of this nature involve preparing samples for analysis through the use of an oxygen bomb. Tissue and vegetative matter is broken down during the combustion process in a closed system allowing the user to analyze the resulting products. W.H. Hill<sup>10, 11</sup> performed multiple analysis of this nature.

## **Propellant and Explosive Testing**

Chemical explosives can be classified as low or high explosives. Low (or deflagrating) explosives are used primarily for propelling; they are mixtures of readily combustible substances that when ignited undergo rapid combustion.<sup>12</sup> Propellants are often materials such as gun powders, smokeless powders, or liquid fuels. Generally, propellants burn in a predicable manner at a controlled rate.

High (or detonating) explosives (e.g., TNT) are used mainly for shattering; they are unstable molecules that can undergo explosive decomposition without any external source of oxygen and in which the chemical reaction produces rapid shock waves. In an explosion, the reaction products fill a much greater volume than that occupied by the original material and exert an enormous amount of pressure.<sup>12</sup>

These types of applications are generally found in government operations and their private sector suppliers and contractors. Recently however, the automotive industry has become active in this market. Air bags are inflated with a violent

reaction of sodium azide. Other economic and passenger friendly compounds are being researched. Examples of explosive compounds are listed in the following table:

**Table UCRL-52821** <sup>13</sup>

| <b>Compound</b>                          | <b>Heat of Detonation (cal/g)</b> |
|--|-----------------------------------|
| 2,4,6-Trinitrotoluene (TNT)              | 1093 +/- 11                       |
| Pentaerythritol Tetranitrate (PETN)      | 1490 +/- 5                        |
| Cyclotetramethylene Tetranitramine (HMX) | 1334 +/- 9                        |
| Cyclotrimethylene Trinitramine (RDX)     | 1452 +/- 15                       |
| Ethylenedianine Dinitrate (EDN)          | 1163 +/- 20                       |
| Hydrazine nitrate (HN)                   | 1247 +/- 25                       |
| Hexanitrobenzene (HNB)                   | 1653 +/- 17                       |

There are various test methods which cover the testing of explosives. These include: Naval Ordnance 9375, OS 6765B, Mil-Std 286B, Mil-P- 46994, and EN ISO 1716.

Parr offers the Dynamic Pressure Recording System which monitors the pressure associated with the fast decomposition associated with propellants and explosives. More information on this application can be found in Tech Note 106.

### **Thermodynamic Research**

Although this application is rare today, with few research groups remaining active, it is still very important. There are many areas of study in this category related to bomb calorimeters:

- Standard Reaction Enthalpy
- Enthalpy Change for Isomerization
- Heats of Formation – Hess's Law

- Heats of Reaction

The standard enthalpy of combustion  $\Delta H_c^\theta$  is the heat content change which occurs when one mole of a substance is completely burned in oxygen, under standard conditions. The standard enthalpy of formation  $\Delta H_f^\theta$  is the heat content change when one mole of a compound is formed from its elements in their standard states, under standard conditions.

### **Educational Training**

Roughly 20% of combustion calorimeters go to universities and colleges solely for teaching purposes. The use of combustion calorimeters is generally focused within the realm of thermodynamics and physical chemistry. Many schools find the 6765 Semimicro / Solution Combination Calorimeter to be an attractive option as it allows for both oxygen bomb calorimetry studies as well as thermodynamic studies to be taught. Another attractive option, due to its low cost and basic components, is the 1341 Plain Jacket Calorimeter. Additionally, the 6772 Calorimetric Thermometer provides schools with the ability to interface their calorimeters directly with a PC and therefore teach data analysis to students.

Chemists, physicists, biologists, ecologists, and technicians are just some of the many occupations who use combustion calorimetry. Without a doubt combustion calorimetry will remain an important skill for the 21st century.

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