Estimation of Rate of Heat Release by Means of Oxygen Consumption Measurements

Intuitively, the rate of heat release from an unwanted fire is a major indication of the threat of the fire to life and property. This is indeed true, and a reliable measurement of a fire's heat release rate was a goal of fire researchers at NBS and other fire laboratories at least as early as the 1960s. Historically, heat release measurements of burning materials were based on the temperature rise of ambient air as it passed over the burning object. Because the fraction of heat released by radiant emission varies with the type of material being burned, and because not all the radiant energy contributes to temperature rise of the air, there were large errors in the measurements. Attempts to account for the heat that was not captured by the air required siting numerous thermal sensors about the fire to intercept and detect the additional heat. This approach proved to be tedious, expensive, and susceptible to large errors, particularly when the burning "object" was large, such as a full-sized room filled with flammable furnishings and surface finishes.

A novel alternative technique for determining heat release rate was developed at NBS during the 1970s. It had distinct advantages over the customary approach, but its widespread acceptance was hampered by uneasiness in the fire science community concerning potential errors if the technique were used in less-than-ideal circumstances. In 1980 Clayton Huggett, a fire scientist at NBS, published the seminal paper [1] that convinced the fire science community that the new technique was scientifically sound and sufficiently accurate for fire research and testing. The technique is now used worldwide and forms the basis for several national and international standards.

The underlying principle of the new heat release rate technique was "discovered" in the early 1970s. Faced with the challenge of measuring the heat release of combustible wall linings during full-scale room fire tests, William Parker, Huggett's colleague at NBS, investigated an alternative approach based on a simple fact of physics: in addition to the release of heat, the combustion process consumes oxygen. As part of his work on the ASTM E 84 tunnel test, Parker [2] explored the possibility of using a measurement of the reduction of oxygen in fire exhaust gases as an indicator of the amount of heat released by the burning test specimens. Indeed, for well-defined materials with known chemical composition, heat release and oxygen consumption can both be calculated from thermodynamic data. The problem with applying this approach to fires is that in most cases the chemical compositions of modern materials/composites/mixes that are likely to be involved in real fires are not known. In the process of examining data for complete combustion (combustion under stoichiometric or excess air conditions) of the polymeric materials with which he was working, Parker found that, although the heat released per unit mass of material consumed (i.e., the specific heat of combustion), varied greatly, the amount of heat released per unit volume of oxygen consumed was fairly constant, i.e., within 15 % of the value for methane, 16.4 MJ/m^3 of oxygen consumed.

This fortunate circumstance—that the heat release rate per unit volume of oxygen consumed is approximately the same for a range of materials used to construct buildings and furnishings—meant that the heat release rate of materials commonly found in fires could be estimated by capturing all of the products of combustion in an exhaust hood and measuring the flow rate of oxygen in that exhaust flow. The technique was dubbed *oxygen consumption calorimetry,* notwithstanding the absence of any actual calorimetric (heat) measurements.

Later in the decade, Huggett [1] performed a detailed analysis of the critical assumption of constant proportionality of oxygen consumption to heat release. Parker's assumption was based on enthalpy calculations for the complete combustion of chemical compounds to carbon dioxide, water, and other fully oxidized compounds. Indeed, a literature review by Huggett revealed that Parker's findings were actually a rediscovery and extension of the work of W. M. Thornton [3], published in 1917, which found that the heat released per unit amount of oxygen consumed during the complete combustion of a large number of organic gases and liquids was fairly constant. Nevertheless, since in real fires and fire experiments the oxygen supply is sometimes limited, incomplete combustion and partially oxidized products can be produced. Huggett's paper examined in detail the assumption of constant heat release per amount of oxygen consumed under real fire conditions and assessed its effect on the accuracy of heat release rate determinations for fires.

Instead of expressing results on a unit volume basis, as Parker did, Huggett expressed results in the more convenient and less ambiguous unit mass of oxygen

consumed. Huggett began by presenting values for the heat of combustion and heat of combustion per gram of oxygen consumed for typical organic liquid and gas fuels, assuming the products are CO_2, H_2O (g), HF, HCl, Br_2, SO_2, and N_2. Notwithstanding large variations in the molar heat of combustion (up to a factor of 4) for this group of fuels, the heats of combustion per unit mass of oxygen consumed fell within ± 3 % of their average value of 12.72 kJ/g. Huggett explained that this near constancy was not surprising because the energetic processes are the result of breaking either carbon-carbon or carbon-hydrogen bonds, and these have similar bond strengths.

An examination of the same data for typical synthetic polymers, some of which Parker did not consider, produced similar results; for this class of materials the heats of combustion per unit mass of oxygen consumed fell within ± 4 % of their average value of 13.03 kJ/g. Fuels of natural origin (e.g., cellulose, cotton, newsprint, corrugated box, wood, etc.), which are likely to be found in large quantities in building fires, have heats of combustion per unit of oxygen consumed that range within ± 5.3 % of their average of 13.21 kJ/g.

The results presented so far assumed complete combustion. Huggett explored the effects of incomplete combustion on the assumption of constant heat release per unit mass of oxygen consumed. He did this by making several conservative, but realistic, assumptions concerning incompleteness of combustion for a range of materials likely to be found in a structural fire. For example, carbon monoxide often is present in a fire's combustion products, but usually at a very low level, and rarely exceeds 10 % of the carbon dioxide concentration produced by the fire. Huggett then calculated the heat of combustion per unit mass of oxygen consumed for the burning of cellulose in limited air, such that the carbon monoxide concentration was about 10 % of the carbon dioxide concentration. The result was 13.37 kJ/g of O_2, compared with 13.59 kJ/g for the excess air case. The difference was very small and, if necessary, could be corrected for if the carbon monoxide concentration was measured.

Another consideration was that cellulosic fuels tend to form a carbonaceous char that can affect the heat release rate. By examining a hypothetical reaction that forces production of pure carbon, Huggett demonstrated that the effect was small: 13.91 kJ/g of O_2 when pure carbon was produced vs. 13.59 kJ/g when the reaction took place in excess air.

Other partial oxidation reactions can occur and affect the heat release rate. Huggett argued that although their details are unknown, the effects could be assessed via representative examples; the actual material in the example was not important since only the chemical bonds that were rearranged by the reaction significantly affected the results. He considered partial oxidation of propylene, polyacrylonitrile (which produces hydrogen cyanide under some combustion conditions), and poly-tetrafluoroethylene and argued that under worst-case conditions the heats of combustion per unit mass of oxygen consumed range from 10.76 kJ/g to 13.91 kJ/g; thus such substances, if present in small quantities, would not introduce a significant error in heat release based on oxygen consumption. All these scenarios were considered limiting cases; the effect in real fires usually would be less than that presupposed in the analyses. In situations where large quantities of incomplete combustion products were produced, corrections could be made if these products were measured.

Huggett concluded that the assumption of constant heat release rate per unit mass of oxygen consumed would be sufficiently accurate for most fire and fire-test applications. For fires burning conventional organic fuels, Huggett recommended the constant 13.1 kJ/g, which should produce heat release rate results accurate to ± 5 % or better. Ever since its publication, this value has been the accepted value for oxygen-consumption calorimetry when burning conventional materials.

Huggett examined other factors that influence the overall accuracy of oxygen consumption calorimetry. For example, dilution by products of combustion in the exhaust flow, where the oxygen concentration measurement is made, is a source of error because the number of moles of products is not the same as the number of moles of oxygen consumed. This dilution factor is a function of the fuel's stoichiometry and can be taken into account if the stoichiometry is known. In general, however, this is not the case and the dilution factor must be estimated. Through analysis of limiting cases, Huggett reasoned that if an appropriate dilution factor were not available, then assuming a value of 1.6 would lead to an error of less than 6 % in the amount of oxygen consumed.

This watershed paper by Huggett was published just as the rate of heat release was beginning to be recognized as the central property affecting fire growth [4]. The novel new technique was rapidly incorporated by Babrauskas and Twilley [5] in their invention of the Cone Calorimeter, a bench-scale device now used worldwide for heat release rate measurements. It also became the technique used in fire calorimeters of larger (room) size at NIST and at most fire laboratories throughout the world. The oxygen-consumption technique forms the basis for several national (ASTM [6], NFPA [7]) and international (ISO [7]) standards.

Clayton Huggett graduated from the University of Wisconsin and received his Ph.D. in chemistry from the University of Minnesota. During World War II he and his colleagues at Minnesota developed the fuel for the U.S. Navy's first air-to-air missile. Subsequently he

worked on rocket propellants with Amcel Propulsion and on the fire safety program for the Apollo rockets while at the Arthur B. Sloan Foundation, with ties to the Atlantic Research Corporation. A patent issued to him for *habitable but combustion discouraging atmospheres* still is used today. Clayton joined the Center for Building Technology at NBS in 1970 and began his research in flammability of apparel. In addition to heat release rate measurements and applications, he studied flame spread on floor coverings in corridors and the flammability of electrical insulating materials. He retired from NBS in 1985 while in the position of Deputy Director of the Center for Fire Research.

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