



# A general calorimetry framework for measurement of combustion efficiency in a suppressed turbulent line fire



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## ARTICLE INFO

### Keywords:

Calorimeter  
Carbon dioxide generation  
Extinction  
Heat release rate  
Oxygen consumption

## ABSTRACT

The present study seeks to measure suppression effects in a canonical experimental configuration, featuring the exposure of a buoyant, turbulent, methane or propane-fueled diffusion flame to a co-flowing oxidizer diluted with nitrogen gas. Species-based calorimetry measurements, using either oxygen-consumption (OC) or carbon-dioxide-generation (CDG) based methods, are derived and applied to this configuration. Traditional OC models, which cannot account for oxidizer-dilution, are found to significantly overpredict total heat release rate in the present configuration, while traditional CDG models coincidentally give accurate results. Only the present calorimetry formulation, with full accommodation for oxidizer dilution, provides accurate results for both methods. In both methane and propane flames, global combustion efficiency is found to remain close to unity over a wide range of oxidizer dilution, decreasing abruptly only at the onset of global extinction. Similar trends are noted in the net combustion yields of oxygen, carbon-dioxide, and water-vapor. Net yields of carbon-monoxide remain close to zero for both fuels, but increase slightly near the extinction limit. These measurements reveal that despite visible suppression effects in all of the present flames, until the extinction limit is reached, nearly all of the fuel continues to react and combustion products are produced in stoichiometric proportions.

## 1. Introduction

In the field of fire safety, rate of heat release is often regarded as the most important parameter available to characterize a fire hazard [1]. This parameter can be useful and often essential in deriving various other fire properties including size, rate of growth/spread, material flammability, toxic species yields, suppression effectiveness, and combustion efficiency. Despite this importance, heat release rate can be difficult and costly to measure accurately, with a limited set of feasible measurement techniques available. Of the available techniques, species-based calorimetry is widely recognized as the most appropriate. By such methods, heat-release information is derived from the rates of consumption or production of the major chemical species involved in the combustion reaction.

The importance and empirical basis for species-based calorimetry has been well established in the literature. Notable review works have summarized the seminal and developmental studies leading to the establishment of these techniques [2,3]. Species-based calorimetry has been successfully applied in numerous studies ranging from small bench-scale applications [4–10], to large full-scale experiments [11–17]. These methods also form the basis of several national and international testing

standards for the determination of material flammability [18–21]. As in the present study, previous works have also explored the application of calorimetry measurements to characterize the combustion efficiency of suppressed fires [22–26]. Other studies have devoted to the characterization of the principal sources of uncertainty in the predominant calorimetry formulations [27–31].

While species-based calorimetry methods have been widely adopted by the fire testing and research communities and successfully employed in numerous studies, most of these implementations utilize simplified formulations that rely on specific and often unstated assumptions. In particular, most existing formulations apply only to simple systems where the primary mass exchanges to/from the combustion region are limited to the supply of fuel, entrainment of ambient air, and exhaust of combustion products. Certainly, this scenario adequately describes most fires, for which existing formulations have been shown to apply very well. However, for more complex systems with additional mass exchanges, such as those involving suppression agents or sprays, the existing formulations may not be applicable. The present study, which involves a co-flowing oxidizer with variable oxygen concentration, is a prime example of such a system.

Despite the wide body of existing literature, there is a limited

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availability of general guidelines to direct the design and implementation of calorimetry measurements in complex applications. As a result, it can be difficult to confidently extend the existing formulations to novel applications that may oppose their simplifying assumptions. One recent study has attempted to establish a modified calorimetry formulation and testing protocol applicable to a unique configuration with oxidizer dilution [32]. Though it provides some progress, the methodology advocated in that work lacks generality and requires unnecessary assumptions and limitations to the testing procedure. Clearly, additional guidance is needed to support the development of more generalized calorimetry formulations.

The present work seeks to fill this need by providing a comprehensive description of the physical principles underlying species-based calorimetry, developing from these principles a general framework for the design of calorimetry measurement systems, and demonstrating the successful implementation of such a system, within a configuration comprising complex mass exchanges that are incompatible with existing formulations.

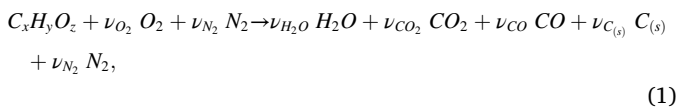
In the present configuration [33], a buoyant, turbulent diffusion flame is suppressed via diluted oxidizer stream. Species-based calorimetry techniques are developed and utilized within this configuration to assess flame-suppression response in both species yields and combustion efficiency across a range of conditions from complete combustion through total extinguishment. In addition to providing a basis for the development of the present calorimetry formulation, these measurements are useful in the pursuit of an improved understanding of suppression performance in realistic fire hazards.

## 2. Calculation

### 2.1. Combustion treatment

The foundation for species-based calorimetry is the thermodynamic concept that the heat released by a chemical reaction is directly related to the mass-rates of consumption and production of the major chemical species involved. In any species-based calorimetry application, it is necessary to first assume the combustion chemistry. The major species included in the assumed reaction determine which species must be considered in the enthalpy balance for the reaction, tracked in the mass conservation analysis that follows, and eventually measured in the calorimetry system.

Considering the combustion of a simple organic fuel in air, a global single-step reaction perspective gives



where  $\nu_k$  are the molar reaction coefficients for each species,  $k$ , involved in the reaction. In this mechanism, an arbitrary fuel compound ( $C_xH_yO_z$ ) and oxygen ( $O_2$ ) are consumed to produce primarily water-vapor ( $H_2O$ ) and carbon-dioxide ( $CO_2$ ), while carbon-monoxide ( $CO$ ) and soot ( $C(s)$ ) are included as potential products of incomplete combustion. Nitrogen ( $N_2$ ), along with any other inert species that may be present, is assumed to be globally unaffected by the reaction.

Detailed reaction kinetics are neglected in Eq. (1) via Hess's law, whereby the total enthalpy change over the course of a chemical reaction is independent of the reaction pathway. By the first law of thermodynamics, the enthalpy of reaction may then be equated to the heat of reaction, as long as the reaction occurs at constant pressure. The global perspective adopted in Eq. (1) is appropriate, so long as the primary species in the assumed mechanism indeed represent the major species present at the initial and final states of the reaction. Here, the initial state refers to an initially non-reacting fuel-oxidizer mixture and the final state

The mechanism in Eq. (1) should apply to most fire applications. For special applications in which there may be complex fuel chemistry, involvement of other reactive compounds, or any other factor leading to the net consumption or production of additional species in considerable quantities ( $H_2$ ,  $OH$ ,  $NO_x$ ,  $NH_3$ ,  $HCl$ , etc.), those species should be included in Eq. (1) and in the analysis that follows.

A significant advantage of species-based calorimetry is the well-reported observation that the heat released per-unit-mass of  $O_2$  consumed in combustion reactions is approximately constant across wide variations in fuel chemistry [34–37]. As a result, species-based calorimetry may be applied with reasonable accuracy to characterize the combustion of unknown fuel compounds. Similar observations have been reported regarding the heat released per-unit-mass of  $CO_2$  produced, leading to the establishment of two separate but similar methodologies. The former is referred to as oxygen-consumption (OC) calorimetry, and the latter as carbon-dioxide-generation (CDG) calorimetry.

While OC and CDG methods may have certain advantages and disadvantages in specific applications, their underlying formulations are similar. Based on the combustion chemistry assumed in Eq. (1), formulations for each method are given as

$$\dot{Q}_{OC} = -\Delta h_{O_2} \dot{\omega}_{O_2} + (\Delta h_{O_2} - \Delta h_{O_2, CO}) \left( \dot{\omega}_{CO} \frac{M_{O_2}}{2M_{CO}} \right) + (\Delta h_{O_2} - \Delta h_{O_2, C(s)}) \left( \dot{\omega}_{C(s)} \frac{M_{O_2}}{M_{C(s)}} \right), \quad (2a)$$

$$\dot{Q}_{CDG} = \Delta h_{CO_2} \dot{\omega}_{CO_2} + (\Delta h_{CO_2} - \Delta h_{CO_2, CO}) \left( \dot{\omega}_{CO} \frac{M_{CO_2}}{M_{CO}} \right) + (\Delta h_{CO_2} - \Delta h_{CO_2, C(s)}) \left( \dot{\omega}_{C(s)} \frac{M_{CO_2}}{M_{C(s)}} \right), \quad (2b)$$

where  $\dot{Q}$  is the combustion heat release rate,  $\dot{\omega}_k$  is the mass reaction rate of species  $k$ ,  $M_k$  is the molar mass of species  $k$ , and  $\Delta h_k$  is the mass-specific enthalpy of reaction for species  $k$ .

In particular,  $\Delta h_{O_2}$  and  $\Delta h_{CO_2}$  are the enthalpies of reaction for the assumed combustion mechanism (Eq. (1)) for complete combustion to  $CO_2$  and  $H_2O$  ( $\nu_{CO}$ ,  $\nu_{C(s)} = 0$ ), respectively per-unit-mass of  $O_2$  consumed and  $CO_2$  generated. Of the remaining terms,  $\Delta h_{O_2, CO}$  ( $\Delta h_{CO_2, CO}$ ) is the enthalpy of reaction for the oxidation of  $CO$ , given by the reaction  $CO + 0.5 O_2 \rightarrow CO_2$ , per-unit-mass of  $O_2$  ( $CO_2$ ), and  $\Delta h_{O_2, C(s)}$  ( $\Delta h_{CO_2, C(s)}$ ) is the enthalpy of reaction for the oxidation of soot, assumed to consist of pure graphitic carbon and given by the reaction  $C(s) + O_2 \rightarrow CO_2$ , per-unit-mass of  $O_2$  ( $CO_2$ ).

If the fuel chemistry is known,  $\Delta h_{O_2}$  and  $\Delta h_{CO_2}$  may be determined using Hess's law and a stoichiometrically balanced form of Eq. (1) (with  $\nu_{CO}$ ,  $\nu_{C(s)} = 0$ ), with reference standard enthalpies of formation for the applicable product and reactant species ( $\Delta \bar{h}_{f,k}^\circ$ ). This provides the most accurate (fuel-specific) determination of the enthalpy parameters, but requires prior knowledge of the fuel chemistry and its standard enthalpy of formation ( $\Delta \bar{h}_{f,C_xH_yO_z}^\circ$ ). For applications where the required fuel properties are known, general expressions for determination of  $\Delta h_{O_2}$  and  $\Delta h_{CO_2}$  as a function of fuel properties are provided in Table 1.

For applications where fuel properties are unknown,  $\Delta h_{O_2}$  and  $\Delta h_{CO_2}$  may be approximated using average reference values, also provided in Table 1. These reference values represent the mean and standard deviation statistics for a collection of fuel-specific values determined by applying the general expressions in Table 1 to a list of roughly 150 hydrocarbon compounds comprising alkanes, alkenes, alkynes, arenes, alcohols, aldehydes, ketones, and esters (see Tables 3–4.12 and 3–4.13 in Ref. [37] for the list of compounds). These reference values should only be used when fuel properties are unknown, but still expected to be well represented by this group of compounds. As shown, the standard

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