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## A second-generation phi meter for global equivalence ratio and gas species concentration measurements

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**Abstract:** This work presents a second-generation phi meter capable of making simultaneous real-time measurements of the global equivalence ratio and combustion product concentrations (i.e., water vapor, carbon dioxide, and oxygen). The fuels initially examined are methane, propane, and propene. Fuel is mixed with predetermined air concentrations to create a broad spectrum of fuel-air ratios. The global equivalence ratio of a sampled mixture is measured by the phi meter via lean combustion. Water vapor concentrations are made using a thermoelectric cooler and supplemental drying unit placed between a high-temperature mass flow controller and ambient temperature mass flow meter. The difference between the flow units provides the water vapor concentration measurement. Carbon dioxide and oxygen concentration measurements are made using IR and paramagnetic sensors, respectively. The ability to measure combustion product concentrations provides additional insight into the sampled gas, specifically, carbon to hydrogen ratio calculations and total mass balance. The measured and calculated global equivalence ratios for all gas mixtures are observed to be in fair agreement. The calculated values and estimated water vapor concentration measurements are consistent within the experimental uncertainty. The uncertainty of the calculated carbon to hydrogen ratio of incoming gas mixtures is within the parent fuels' ratio, thus validating the instrument's ability to measure gas species concentrations of the combustion products.

**Keywords:** *Gas extractive sampling, Lean combustion, Mass balance, Phi meter, Equivalence ratio*

### 1. Introduction

Ventilation can have a significant impact on the dynamics of an enclosure fire. The availability of oxygen within an enclosure is known to affect the generation of gas species, particularly CO, which can increase the threat posed by fire. Ventilation can be defined from the equivalence ratio within a compartment, either on a global or local scale. In a compartment of known volume, the global equivalence ratio is defined by the total mass of air entering and the total mass of fuel occupying said compartment. The local equivalence ratio is defined similarly, but only by the mass of air and fuel within a portion of the total volume of the compartment. In relation to each other, the global equivalence ratio of a given volume is equal to sum of the local equivalence ratios throughout said volume. Further discussion on the global equivalence ratio concept is provided in Refs. [1, 2].

There have been several techniques used to measure the equivalence ratio from combustion processes. Applications of molecular spectroscopy, such as laser induced fluorescence (LIF) and laser induced breakdown spectroscopy (LIBS), are shown to measure the equivalence ratio using a non-extractive technique [3–7] and require extensive corrections to address low signal to noise

ratios. Gas chromatography with mass selectivity detectors can provide time-averaged equivalence ratio using an extractive sampling approach [8–11]. For real-time applications, a phi meter, originally proposed by Babrauskas et al. [12], has been utilized for several applications [13] to make in-situ global equivalence ratio measurements.

The purpose of this study is to examine a second generation phi meter capable of measuring the global equivalence ratio simultaneously with the total mass in the system, via O<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O concentration measurements. A series of combustion experiments are performed to demonstrate the capability of the enhanced phi meter. Methane, propane, and propene are selected as the fuels of interest. Predetermined ratios of fuel and air spanning from fuel-rich to fuel-lean conditions are examined.

## 2. Methods and Experimental Approach

Figure 1 presents a schematic of the second-generation phi meter. Extracted gas samples are driven through the phi meter by a vacuum pump positioned at the end of the sample line. Upon extraction, gas samples are fed into the phi meter’s reactor component enclosed in a high-temperature tubular furnace. The reactor component includes quartz tubing packed with a combustion catalyst, heated to approximately 900 °C. In this work, platinum-coated silica beads (Sigma-Aldrich/Millipore Sigma 520691<sup>1</sup>) are selected based on their high performance in previous phi meter designs [14].

Excess oxygen is introduced to the extracted gas sample at the inlet of the phi meter via an inner tube within the quartz tubing. The addition of oxygen to the incoming gas mixture, combined with the presence of a high-temperature combustion catalysts, allows for a lean combustion with a reactor exhaust exclusively comprised of O<sub>2</sub>, CO<sub>2</sub>, H<sub>2</sub>O, and N<sub>2</sub>. Upon exiting the reactor, the exhaust flow is fed through a high-temperature mass flow controller (Alicat MCRW-5SLPM-D-HT/5M). The high-temperature mass flow controller regulates the total mass flow moving through the reactor, which is preset for each experiment. The high-temperature mass flow controller is heated using a 24 VDC heating element maintained at approximately 90 °C. The elevated temperature of the high-temperature mass flow controller prevents water vapor from the reactor’s exhaust condensing, thus allowing the controller to account for the vapor mass in the sample line.

A thermoelectric cooler, condensate reservoir, and supplemental drying unit that incorporates Nafion™ tubing are sequentially positioned behind the high-temperature mass flow controller for the purpose of scrubbing water from the sample line. Once dried, the sample gas flows through a mass flow meter where the mass flow of the dried gas is measured. A portion of the mass flow meter’s output is sampled into a Servoflex 5200 MiniMP Gas Analyzer, equipped with paramagnetic and infrared sensors calibrated to measure O<sub>2</sub> and CO<sub>2</sub> volume fractions.

The global equivalence ratio,  $\phi_G$ , can be calculated by the phi meter’s O<sub>2</sub> and CO<sub>2</sub> volume fraction,  $X_{O_2,A}$  and  $X_{CO_2,A}$ , and mass flow meter volumetric flow,  $\dot{V}_{MFM}$ , measurements in the equation below:

$$\phi_G = 1 + \left( \frac{1 - X_{O_2,Ent}}{X_{O_2,Ent}(1 - X_{O_2,A} - X_{CO_2,A})} \right) \left( \frac{\dot{V}_{O_2,Ex}}{\dot{V}_{MFM}} - X_{O_2,A} \right) \quad (1)$$

<sup>1</sup> Certain commercial products are identified in this report to specify adequately the equipment used. Such identification does not imply a recommendation by the National Institute of Standards and Technology, nor does it imply that this equipment is the best available for the purpose.

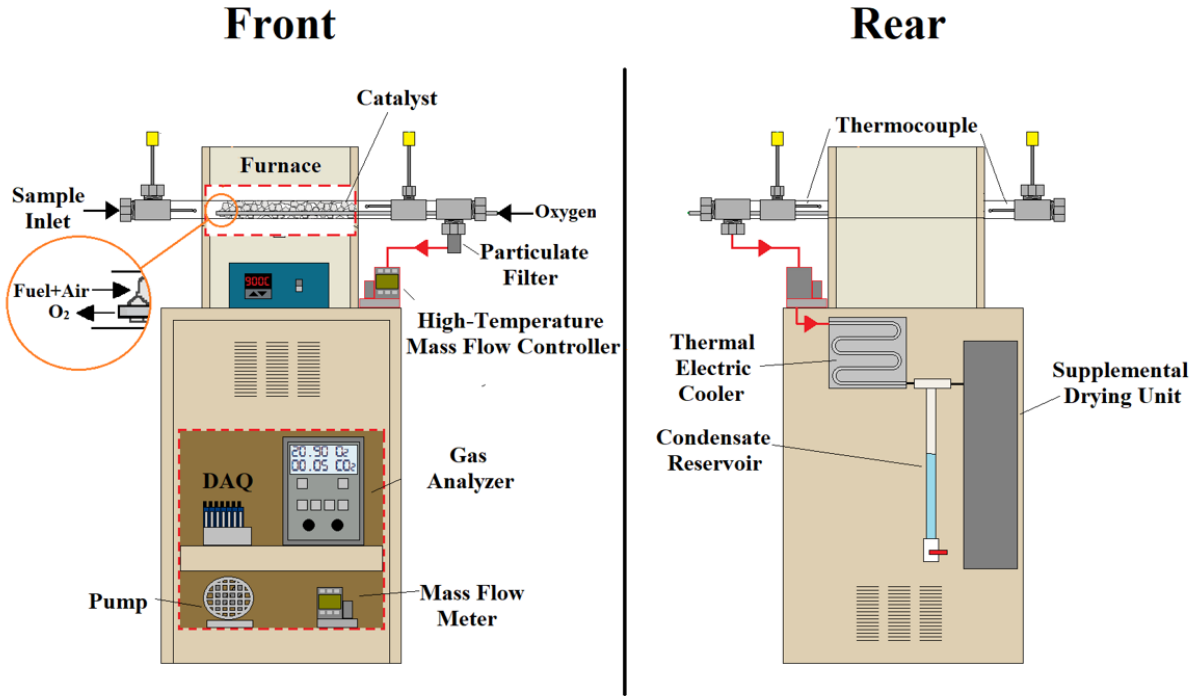


Figure 1: Schematic of the second-generation phi meter

where  $X_{O_2,Ent}$  is the volume fraction of oxygen in the air (approx. 20.95%) and  $\dot{V}_{O_2,Ex}$  is the volumetric flows of the excess oxygen, respectively. A full dry basis derivation of Eq. 1 is documented in Ref. [12].

The portion of water vapor in the exhaust flow from the reactor,  $\dot{V}_{H_2O}$ , is measured from the difference between the volumetric flow readings at the high-temperature mass flow controller,  $\dot{V}_{HTMFC}$ , and mass flow meter.

$$\dot{V}_{H_2O} = \dot{V}_{HTMFC} - \dot{V}_{MFM} \quad (2)$$

This calculation assumes that the thermoelectric cooler, condensate reservoir, and supplemental drying unit are completely drying the reactor's exhaust and that no condensate is within the sample line at the mass flow meter.

As a way to verify the accuracy of the experimental design, the carbon to hydrogen ratio is calculated from the  $CO_2$  and  $H_2O$  volume fractions,  $X_{CO_2}$  and  $X_{H_2O}$ , determined at the high-temperature mass flow controller. This calculation is represented in Eq. 3 shown below:

$$\frac{C}{H} = \frac{x_i X_{CO_2}}{y_i X_{H_2O}} \quad (3)$$

Here the C/H ratio is determined from the  $CO_2$  and  $H_2O$  at the high-temperature mass flow controller, since all fuel entering the phi meter is combusted. The number of carbon and hydrogen atoms in the molecule are represented by  $x_i$  and  $y_i$ , respectively. The carbon to hydrogen ratio of the fuel molecules examined in this work are reported in Table 1 and shown in Fig 4.

Table 1: List of carbon to hydrogen (C/H) ratio of fuels

Fuel	Methane	Propane	Propene
C/H	1/4	3/8	1/2

Incoming gas mixtures comprised of fuel and air are controlled via the phi meter inlet flow. The inlet to the phi meter is partitioned such that fuel flow maintained by an external mass flow controller mixed with ambient air are sampled into the phi meter. The incoming air flow is measured by an additional mass flow meter. The fuel-air ratio of the incoming mixture is determined from controlled fuel flow and measured air flow, which is determined by the difference between the total mass flow set by the high-temperature mass flow controller and the mass flow of the fuel.

A mass balance evaluation is applied to provide a more in-depth verification method. The total mass flow present at the inlet of phi meter,  $\dot{m}_{in}$ , which includes the mass of incoming fuel,  $\dot{m}_{Fuel}$ , air,  $\dot{m}_{Air}$  and excess oxygen,  $\dot{m}_{O_2,Ex}$ , is compared to the total mass flow at the high-temperature mass flow controller,  $\dot{m}_{HTMFC}$ , comprised of the mass of remaining oxygen,  $\dot{m}_{O_2,HTMFC}$ , carbon dioxide,  $\dot{m}_{CO_2,HTMFC}$ , water vapor,  $\dot{m}_{H_2O,HTMFC}$ , and nitrogen,  $\dot{m}_{N_2,HTMFC}$ . Assuming no mass losses between the flow units, the mass flow of nitrogen is determined from the difference between the total mass flow measured at the mass flow meter,  $\dot{m}_{MFM}$ , and the mass flow of  $O_2$  and  $CO_2$ . The mass flow of  $O_2$  and  $CO_2$  is calculated from the product of the gas analyzer  $O_2$  and  $CO_2$  volume fraction measurements and the total mass flow meter reading, as shown in Eq. 7.

$$\dot{m}_{in} = \dot{m}_{HTMFC} \quad (4)$$

$$\dot{m}_{Fuel} + \dot{m}_{Air} + \dot{m}_{O_2,Ex} = \dot{m}_{O_2,HTMFC} + \dot{m}_{CO_2,HTMFC} + \dot{m}_{H_2O,HTMFC} + \dot{m}_{N_2,HTMFC} \quad (5)$$

where

$$\dot{m}_{N_2,HTMFC} = \dot{m}_{MFM} - \dot{m}_{O_2,HTMFC} - \dot{m}_{CO_2,HTMFC} \quad (6)$$

or

$$\dot{m}_{N_2,HTMFC} = \dot{m}_{MFM}(1 - X_{O_2} - X_{CO_2}) \quad (7)$$

All measurements are collected and monitored by a data acquisition system. Data samples are recorded at 1 Hz for a 1 minute period. All experimental conditions are repeated at least twice. An extensive uncertainty analysis of all measurements is provided in Ref. [15]. Measurement uncertainties are estimated using the law of propagation of uncertainty which combines the Type A and B evaluation of uncertainty. For most measurements, the Type B evaluation of uncertainty is the dominant error. Unless otherwise stated, the uncertainty of the measurements are expressed assuming a 95% confidence level.

### 3. Results and Discussion

Figure 2 shows the comparison between global equivalence ratio measurements determined from Eq. 1 and the predetermined fuel-air mixtures at the inlet. The dotted line represents equivalency between the calculated and measured values. Since the composition of the sampled flow is consistent, the local and global equivalence ratios are equivalent. The measured  $\phi_G$  for all fuel and

fuel-air ratios are shown to be in agreement with the monitored incoming gas mixtures. The consistency between the phi meter measurements and estimated incoming equivalence ratio suggest that the incoming fuel is completely combusted within the reactor under the given configuration (i.e., reactor setup and high-temperature mass flow controller and furnace temperature settings). The indication that all incoming fuel is combusted within the phi meter suggest that the calculated water vapor flow is half the product of the number of hydrogen atoms in the incoming fuel,  $y$  and the volumetric flow of the fuel,  $\dot{V}_{\text{Fuel}}$ , as represented below:

$$\dot{V}_{\text{H}_2\text{O,HTMFC}} = \frac{y}{2} \dot{V}_{\text{Fuel}} \quad (8)$$

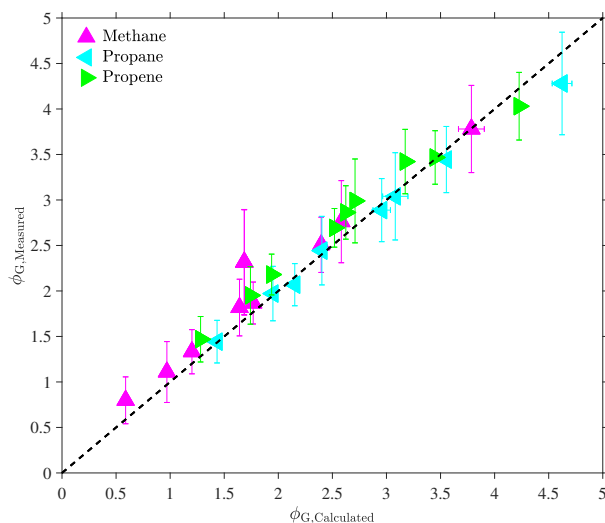


Figure 2: Measured global equivalence ratio via Eq. 1 as a function of the global equivalence ratio estimated from predetermined fuel-air mixtures. The dotted line represents the equivalency between the calculated and measured values.

The comparison between the measured and calculated water vapor flow using Eq. 2 and 8, respectively, is presented in Fig 3. The water vapor flow measurements determined from the difference in flow readings are observed to match the calculated water vapor flows within the experimental uncertainty, indicated by the dotted line where the calculated and measured values are equivalent. In the cases of propane, a discrepancy between the calculated and measured flow appears to increase when water vapor concentration is greater than 15 %. The deviation between the calculated and measured water vapor flows at high concentrations may be attributed to the inadequate performance of the thermoelectric cooler or supplemental drying unit. An increase in the flow's residence time in the thermoelectric cooler and supplemental dryer or a decrease in the thermoelectric coolers operating temperature, may reduce the discrepancy between the measured and calculated values.

The estimated carbon to hydrogen ratio from the parent fuel, indicated by the dotted line, and the calculated ratio determined from the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  measurements are plotted as a function of the measured  $\phi_G$  and shown in Fig. 4. For all measurements, the experimental uncertainty of the calculated C/H is within parent fuels' ratios. In several instances, the theoretical and calculated values are nearly matching, verifying the accuracy of the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  concentration measurements. The agreement of the theoretical and measured carbon to hydrogen ratios demonstrates the

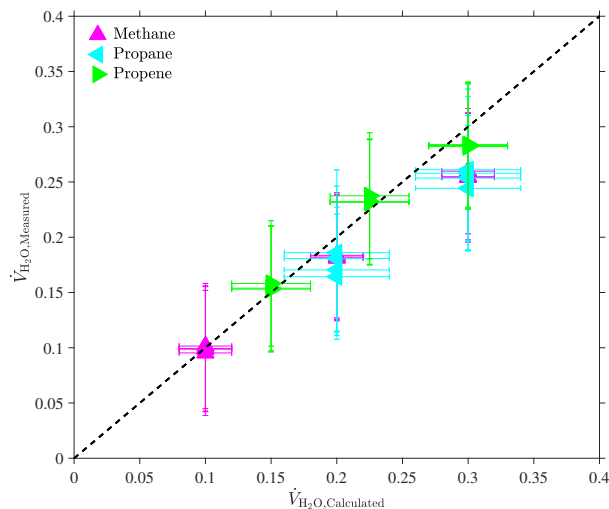


Figure 3: Volumetric flow of water vapor via Eq. 2 as a function of the anticipated volumetric flow of water vapor estimated from Eq. 8. The dotted line represents the equivalency between the calculated and measured values.

enhanced phi meter's potential for investigating combustion processes by measuring the C/H ratio without any knowledge of the parent fuel.

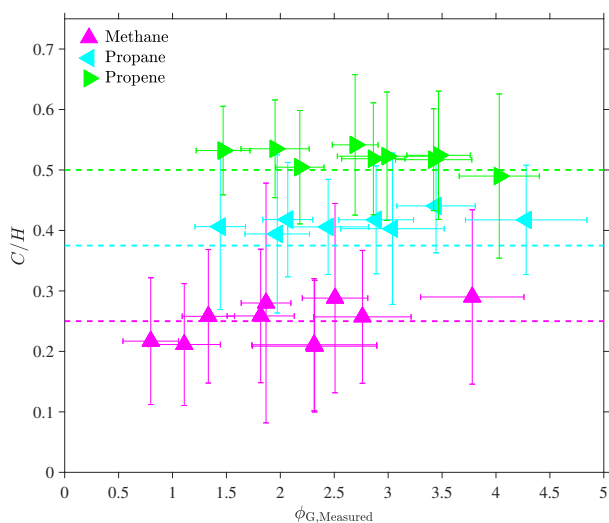


Figure 4: Carbon to hydrogen ratio calculated from the  $\text{CO}_2$  and  $\text{H}_2\text{O}$  species measurements compared to the theoretical values (dotted lines) as a function of the measured global equivalence ratio.

Figure 5 shows the ratio between the total mass calculated at the high temperature mass flow controller and measured at the inlet of the phi meter as a function of the measured  $\phi_G$ . Unity is represented by a dotted line. For each measurement, unity falls within the experimental uncertainty of each mass ratio. In some cases, the calculated mass ratios are near unity, which indicate minimal mass loss within the sample line. The agreement between masses for varying equivalence ratios and fuels further supports the validity of the  $\text{O}_2$ ,  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{N}_2$  concentration measurements and more importantly the design of the phi meter.

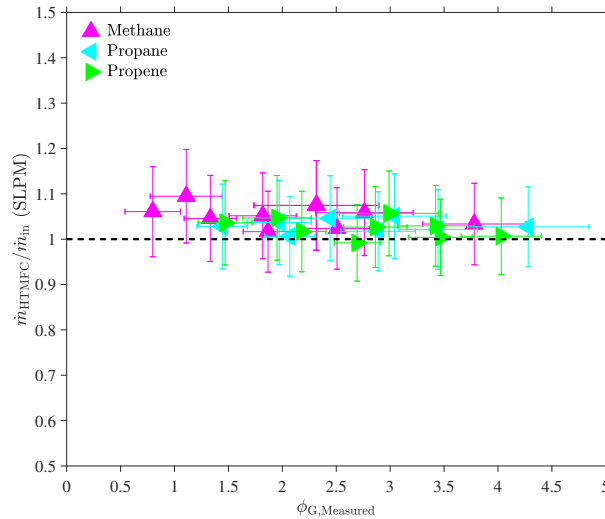


Figure 5: The ratio of the mass flow rate at the high temperature mass flow controller to the inlet of the phi meter calculated via Eqs.4-6 as a function of the measured global equivalence ratio. The dotted line represents the equivalency between the calculated and measured values.

#### 4. Conclusions

This study demonstrates the capabilities of a second-generation phi meter. Global equivalence ratios, water vapor concentrations, carbon to hydrogen ratios, and total mass flow are measured and compared to calculated values. Comparisons between the measured and calculated values are observed to be in fair agreement with the calculated values, within experimental uncertainty. The enhanced phi meter's capability to measure the global equivalence ratio simultaneously with  $O_2$ ,  $CO_2$ , and  $H_2O$  has significant potential for investigating combustion processes. For example, before entering the phi meter a portion of an extracted gas sample can be partitioned into an additional gas analyzer capable of measuring  $O_2$ ,  $CO_2$ , and  $CO$ . From a combination of the additional gas analyzer and phi meter measurements, in-situ gas species concentrations measurements and the local equivalence ratio can be determined without any knowledge of the parent fuel. Future work will focus on demonstrating this approach in large-scale applications.

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