# The Chemical Structure of a 30 cm Methanol Pool Fire

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**Abstract**
This study documents a series of time-averaged gas species measurements made along the centerline of a 30 cm methanol pool fires steadily burning in a quiescent environment. All gas species measurements are obtained using a Gas Chromatograph/Mass Spectrometer System (GC/MS). Measurements were made at different heights along the centerline of the fire and repeated at least twice for each location. Gas species volume fractions were determined via the GC/MS using predetermined calibration factors. The gas species volume fractions are compared at different heights within the methanol fire.

## 1. Introduction

Use of fire modeling, such as the Fire Dynamic Simulator[1], in fire protection engineering, has increased dramatically during the last decade. The reason is the development of practical, computational fluid dynamics, fire models and the decreased cost of computational power. Today, fire protection engineers use models to design safer buildings, nuclear power plants, aircraft cabins, trains, and marine vessels to name a few types of applications. To be reliable, the models require validation, which involves an extensive collection of experimental measurements. An objective of this report is to provide data for use in fire model evaluation by the research community.

A pool fire is a basic combustion configuration of interest in model development. In liquid pool fires, the fuel surface is isothermal, flat, and horizontal, which provides well-defined boundary conditions for testing models and simplifies the investigation of fire phenomena. In moderate and large-scale pool fires, radiative heat transfer is the dominant mechanism of heat feedback to the fuel surface. Species concentrations and temperatures have a significant influence on the radiative heat transfer. A zone of interest is the fuel-rich core just above the pool surface, where gas species can absorb energy that would otherwise have been transferred to the fuel surface. Few studies in the literature have reported local chemical species measurements, which provide a deep understanding of the chemical structure of a pool fire and provide insight into significant kinetic, heat, and mass transfer processes.

The purpose of this study is to characterize the spatial distribution of stable gas-phase chemical species in a moderate-scale liquid pool fire steadily burning in a well-ventilated quiescent environment. Here, methanol is selected as the fuel. Fires established using methanol are unusual since no carbonaceous soot is present or emitted. The uniqueness of methanol fires creates a particularly useful testbed for fire models and radiation sub-models that consider emission by gaseous species - without the confounding effects of blackbody radiation from soot.

In this study, measurements are made in a 30 cm diameter methanol pool fire. This configuration is selected for study since the measurements complement the results from previous works, including analyses of the mass burning rate, the temperature and velocity

fields, radiative emission, flame height, and pulsation frequency[2-3]. Additional characterization of this fire enables a more comprehensive understanding of its detailed structure, thereby enhancing the understanding of fire physics.

## 2. Experimental Method

The experimental setup used in this work has been documented previously[3-6]. Experiments are conducted under a canopy hood surrounded by a 2.5 m x 2.5 m x 2.5 m enclosure made of a double-mesh screen wall. The walls of the enclosure are formed by a double layer of the wire-mesh screen (5 mesh/cm). The purpose of the mesh enclosure is to maintain a quiescent environment within the enclosure and minimize effects of air currents in the lab on fire behavior including air entrainment into the fire. All measurements are made once the burning conditions, specifically the mass burning rate, reach steady-state, achieved approximately 10 min after ignition.

### 2.1 Pool Burner

A circular stainless-steel pan with an inner diameter of 30 cm, a depth of 15 cm, and a wall thickness of 0.13 cm is used as the pool burner and is shown in Fig.1. The burner is placed within an overflow basin, which extends 3 cm beyond the burner wall. The burner is fitted with legs such that the burner rim is positioned 30 cm above the ground. The bottom of the burner is maintained at a constant temperature by flowing water (20 °C ± 3 °C) through a 3 cm section on the bottom of the fuel pan.

While burning, the fuel level is monitored by a camera with a zoom lens to allow visual observations, displayed on a 50 cm monitor, of the barely discernable dimple made from the fuel-level indicator on the fuel surface. The fuel level indicator is positioned near the center of the burner. To preserve a consistent mass burning rate, the fuel level is maintained 10 mm below the burner rim, following conditions used in previous studies[2-3,7-8]. Fuel to the burner is gravity fed from a reservoir positioned on a mass load cell located outside the enclosure and monitored by a data acquisition system. The fuel flow is manually adjusted using a needle valve. The expanded uncertainty with a coverage factor of 2 of the fuel level is estimated to be 0.5 mm for these experiments.

### 2.2 Gas Species Measurement

Gas-species measurements are made using an Agilent 5977E Series Gas Chromatography and Mass Spectrometry Detector System (GC/MS) fitted with a thermal conductivity detector (TCD)[†]. The GC/MS can quantify a wide range of stable reactants, intermediates, and combustion product species, whereas other instruments are exclusive to certain species. Figure 2 displays the flow diagram for gas sampling into the GC/MS. The GC is fitted with a 2 ml sampling loop maintained at 200°C. After achieving steady-state burning conditions, a vacuum pump, located downstream from the GC/MS, is initiated and gas samples are collected using a quenching probe. The quenching probe is composed of two concentric, stainless-steel tubes with an outer annular coolant flow and an inner, extracted gas-sample flow. The inner and outer tube diameters are 7.9 mm and 16 mm, respectively. To overcome the major challenge of vapors condensing in the sampling line, the sampling probe and the

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[†] Certain commercial products are identified in this report in order to specify adequately the equipment used. Such identification does not imply recommendation by the National Institute of Standards and Technology, nor does it imply that this equipment is the best available for the purpose.

sampling line leading into the GC are heated (90 °C) with circulating water and electrical heating tape (set to 140 °C), respectively.

The sample line consists of a 150 ml mixing chamber positioned upstream from the GC/MS. To reduce the time required to fill the mixing chamber, the sample line is split downstream into a 6.40 mm diameter "bypass" and a 1.7 mm diameter "sample loop" line. For the first four min of sampling, gas is collected through the "bypass" line at a rate of 3.0 L/min. After the sampling path is switched to the "sample loop" line, the flow is reduced to 0.8 L/min for 6 min until injection into the instrument. When the sampling period is completed, the two-way valve located downstream of the sample loop line is closed. The gas sample is held within the sample loop line for one min before injection, allowing the pressure to equilibrate. The pressure is monitored using a digital pressure gauge located downstream of the GC/MS.

Once injected into the GC/MS, the sample is transported by a helium carrier gas flowing into a permanent gases-dual column (Agilent CP7430) comprised of molecular sieve (M) and Porapak Q (Q) capillary columns configured in parallel and rejoined at their ends. After the columns, the flow path is divided between the TCD (3 ml/min) and the MS (1 ml/min). The TCD and MS signals are synchronized such that the respective chromatograms can be compared, facilitating identification of species elution times from the TCD.

The sample analysis time is approximately 30 min, in which the GC oven temperature is maintained at 30 °C for 10 min, then ramped at 8 °C/min for 20.25 min until a temperature of 192 °C is reached. During the sample analysis, the TCD is maintained at 300 °C with a makeup and reference flow of 12 ml/min and 27 ml/min, respectively. The MS source and quad temperatures are 250 °C and 200 °C, respectively.

Gas species are identified using the total ion chromatogram (TIC) provided from the MS and quantified from the TCD chromatogram. A typical TCD chromatogram, produced from a pool fire gas sample, is shown in Fig. 3. The TCD chromatogram figure exemplifies the connection between a peak and gas species; the area of a peak corresponds to the number of moles detected of a given species.

TCD and MS gas calibrations are conducted using commercial gas calibration standards. Vapor calibrations, using water and methanol, are conducted using the bubbler setup shown in Fig. 4. Nitrogen, acting as a carrier gas, is bubbled through the liquid of interest, which is held in an insulated pyrex flask sitting on a temperature-controlled heating plate. Varying the temperature allowed control of the liquid vapor pressure and thereby the partial pressure injected into the GC/MS. The nitrogen calibration carrier gas flow is estimated to be 30 ml/min ± 3.0 ml/min. During a liquid-vapor calibration, a thermocouple is placed at the liquid surface to measure the temperatures, which controlled the vapor pressure. Liquid calibrations are conducted once the bath temperature achieved steady-state (approximately 1 hour). The measurements are repeated and a calibration curve for mass injected versus measured GC signal is developed.

All measurements are repeated at least twice at each location along the centerline of the pool fire. The amount of a given species is directly determined from the calibration. Volume fraction measurements of species are determined by taking the amount of a species over the total amount detected from the GC/MS. Once all volume fractions of species are made at a given location, the repeated measurements are averaged together. The uncertainty of the reported volume fractions is determined from the combined uncertainty, which incorporates the variance between the repeat measurements and the uncertainty in the species calibrations.

A coverage factor of two, representing a 95 % confidence interval, is applied to the combined uncertainty. A detailed description of the uncertainty analysis for the gas species measurements is described in detail elsewhere[9-10].

## 3. Results and Discussion

Figure 5 shows sequential images of the pulsing methanol pool fire. The pulsation frequency is previously measured as 2.65 Hz[11]. The fire shape fluctuated during its pulsing cycle with uniformly curved flame sheets present at the burner rim rolling towards the fire centerline to form a long and narrow plume. The observed dynamic fire shape is consistent with previous descriptions[3,8,12].

### 3.1 Gas Species Concentrations

Table 1 and Fig. 6 display the averaged volume fraction, $\overline{X_i}$, of major and minor species concentrations made at various heights along the fire's centerline relative to the fuel surface. The species measured included the reactants, methanol ($CH_3OH$) and oxygen ($O_2$), combustion products such as water ($H_2O$) and carbon dioxide ($CO_2$), combustion intermediates such as carbon monoxide ($CO$), hydrogen ($H_2$) and methane ($CH_4$), and inert gases such as nitrogen ($N_2$) and argon ($Ar$). In some instances, species were either undetected or detected in trace amounts (less than 100 ppm). As expected, the fuel volume fractions are highest, and the oxygen volume fraction is lowest close to the fuel surface. The carbon dioxide has a maximum volume fraction approximately 10 cm above the fuel surface. Hydrogen, carbon monoxide, and water have peaks approximately 2 cm above the fuel surface. Nitrogen and argon volume fractions exhibit a similar trend, increasing with distance from the fuel surface. It is also shown that the gas sampled from the centerline at approximately 60 cm above the fuel surface nearly mimicked the composition of air, with the addition of small concentrations of water and carbon dioxide.

## 4. Conclusion and Future Works

In summary, time-averaged local measurements of gas species concentrations are made to characterize the structure of a 30 cm diameter, methanol, pool fire steadily burning in a quiescent environment. These local measurements are essential to providing insight into the complex chemical composition of this medium-scale pool fire. These data, in conjunction with previous measurements of the mass loss, total and radiative heat feedback, calorimetry, radiative emission, and the temperature and velocity fields begin to provide a comprehensive picture of the structure of the 30 cm methanol pool fire[3-5,7-9].

It is anticipated that the data will be useful for model development and validation. The experimental approach described in this work demonstrates a method for investigating chemical species concentrations within a fire. Future work will apply this same technique to investigate fires of different configurations including burner shape and size and fuel type. Once a significan amount of data from various configurations is collected, correlations between fire parameters and species concentrations will be explored.

## 5. Acknowledgments

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**Table 1.** Concentrations (%) of all species as a function of height relative to the methanol pool surface

| Position | $\bar{X}_{CH_3OH}$ | $\bar{X}_{O_2}$ | $\bar{X}_{CO_2}$ | $\bar{X}_{H_2O}$ | $\bar{X}_{CO}$ | $\bar{X}_{H_2}$ | $\bar{X}_{CH_4}$ | $\bar{X}_{N_2}$ | $\bar{X}_{Ar}$ |
|---|---|---|---|---|---|---|---|---|---|
| 1.0 cm | 24±6.0 | 1.8±0.2 | 4.6±0.6 | 17±7.6 | 6.1±0.4 | 5.6±0.4 | 0.11±0.01 | 40±2.5 | 0.5±0.1 |
| 2.0 cm | 19±9.6 | 1.6±1.0 | 4.9±0.7 | 18±8.5 | 7.0±0.9 | 6.0±0.9 | 0.13±0.02 | 42±5.9 | 0.5±0.1 |
| 4.0 cm | 8.2±3.2 | 3.4±0.9 | 5.7±0.7 | 18±8.0 | 6.1±0.8 | 4.7±0.7 | 0.10±0.01 | 53±4.2 | 0.6±0.1 |
| 6.0 cm | 4.1±1.3 | 5.1±0.5 | 5.9±0.4 | 17±6.8 | 4.5±0.4 | 3.3±0.4 | 0.07±0.01 | 59±3.3 | 0.7±0.1 |
| 10 cm | 2.2±1.3 | 8.3±0.9 | 6.1±0.4 | 15±6.8 | 2.5±0.6 | 1.8±0.5 | 0.04±0.01 | 63±3.4 | 0.7±0.1 |
| 14 cm | 0.2±0.1 | 10±0.8 | 5.2±0.4 | 12±5.2 | 1.8±0.2 | 1.1±0.1 | 0.022±0.001 | 68±2.4 | 0.8±0.1 |
| 20 cm | Trace | 14±0.4 | 3.8±0.1 | 7.1±3.3 | 0.3±0.1 | 0.2±0.1 | Trace | 74±1.9 | 0.8±0.1 |
| 30 cm | Trace | 16±0.3 | 2.6±0.1 | 4.7±1.1 | 0.1±0.1 | * | Trace | 75±1.6 | 0.9±0.1 |
| 60 cm | * | 19±0.4 | 0.9±0.1 | 1.4±0.4 | * | * | * | 77±1.5 | 0.9±0.1 |

* denotes undetected; Trace denotes species less than 100 ppm