AN EXPERIMENT IN COMBUSTION

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In modern chemical engineering, environmental issues contribute significantly to process design and operation. Consequently, curricular changes must be made to incorporate new approaches and examples that illustrate concepts related to the protection of the environment.

Combustion is an excellent example of applied high-temperature reaction engineering where thoughtful compromises should be made between pollutant formation and power generation. Combustion is also a widely used process, with applications ranging from space heating to automotive and air transportation, and is the major contributor to air pollution. Consequently, students can easily relate to many environmental issues associated with combustion technologies—for example, the formation of nitrogen oxides (NO_x) and soot.

While senior chemical engineering students are well aware that the oxidation of hydrocarbon fuels produces carbon dioxide and water as the major products, however, they are not familiar with the fact that hundreds of trace by-products are also routinely formed in combustion and that combustion conditions cannot simply be altered to minimize the emission of *all* pollutants. In Figure 1, the levels of thermal NO_x and hydrocarbon by-products formed in combustion are presented as a function of fuel-air equivalence ratio. Equivalence ratio, ϕ, is defined as the actual fuel/air ratio used divided by the fuel/air ratio corresponding to stoichiometric conditions:

$$\phi = \frac{(\text{fuel / air})_{\text{act}}}{(\text{fuel / air})_{\text{stoich}}}$$

Figure 1 shows that NO_x emissions formed as a consequence of the reactions of N_2 exhibit a maximum near stoichiometric conditions due to high flame temperatures and decrease rapidly at higher and lower equivalence ratios when temperatures decrease because of the presence of excess fuel and air, respectively. Lower temperatures, however, reduce reaction rates and result in the emission of unburned hydrocarbons from combustion systems. Consequently, careful compromises must be made between NO_x and hydrocarbon emissions.

When heat recovery is necessary, such as in heaters and boilers, a section of the combustion device is operated under fuel-rich conditions to promote radiative heat transfer from gases. The fuel-rich stage is then followed by a fuel-lean stage in order to fully oxidize unburned hydrocarbons. This "two-stage" combustion is widely used today to minimize both thermal NO_x and hydrocarbon emissions.[1] In addition, control technologies, such as catalytic converters, may also be required to meet emissions standards.

Among the hydrocarbons emitted from combustion processes, polyaromatic hydrocarbons (PAH) are of particular concern due to the potential mutagenicity and carcinogenicity of some of their isomers.[2] PAH are also believed to be precursors to soot, the formation of which represents a loss in combustion efficiency and is a significant environmental problem by itself. Although PAH are emitted at trace levels, on the order of parts per billion by volume (ppbv) to parts per million by volume (ppmv), they often represent the greatest health risk associated with combustion systems.[3,4] Therefore, the development of combustion technologies and/or operation strategies that will reduce these emissions, together with NO_x emissions, continues to be of significant practical interest.

Combustion devices generally operate under conditions in which the oxidizer (air) and fuel are not mixed prior to

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reaction. Consequently, diffusion flames dominate the mode of burning. At UCLA, we implemented an opposed jet burner system that mimics the diffusion flames encountered in practical combustion devices. In this system, the oxidizer and fuel move in an opposed flow configuration, whereby the combustion reaction occurs in a flat flame near the stagnation plane. Because this flow field has a central axis of symmetry, the quantitative chemical composition of the flame can be readily determined by withdrawing samples along the central longitudinal axis of the burners.

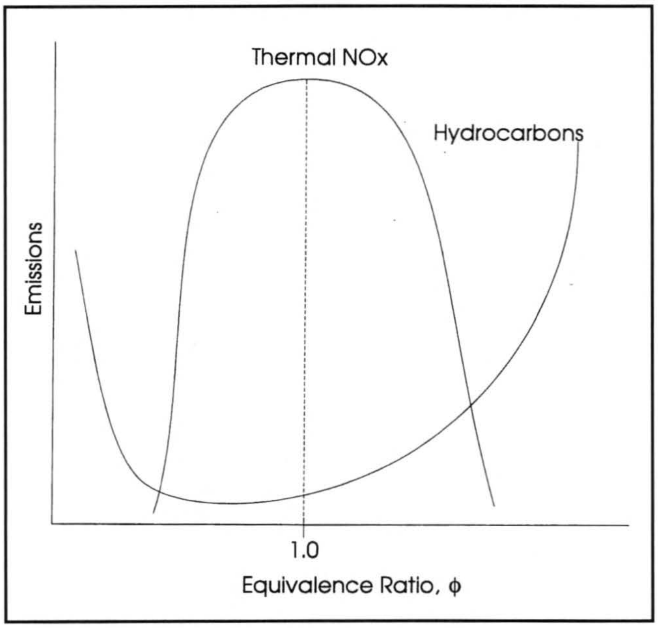

Figure 1. *The dependence of NO_x and hydrocarbon emissions on equivalence ratio.*

Prior to the experiment, students attend lectures that emphasize the effect of fluid dynamic residence time and mixing on pollutant formation within diffusion flame structures, coupled with a fluid dynamic analysis of the Navier-Stokes equations describing the flow field encountered in the opposed flow experiment. In addition to a discussion of the relevant transport phenomena, various chemical pathways, such as those involved in the formation of benzene and PAH, and in the oxidation of methane to carbon monoxide, are reviewed.[5-7] For example, students are introduced to both "even" and "odd" number carbon reaction pathways that lead to the formation of aromatics within hydrocarbon flames. The following even-number carbon pathway describes the formation of the first benzene ring at low temperatures:

$$C_2H_2 + C_2H_3 = n - C_4H_5$$
$$C_2H_2 + n - C_4H_5 = C_6H_6 + H$$

where C_2H_2 is produced as a result of a sequence of dehydrogenation reactions, such as

$$C_2H_6 + H = C_2H_5 + H_2$$
$$C_2H_5 = C_2H_4 + H$$
$$C_2H_4 + H = C_2H_3 + H_2$$
$$C_2H_3 = C_2H_2 + H$$

In the odd-number carbon reaction route, benzene has been proposed to form via

$$C_3H_3 + C_3H_3 = C_6H_5 + H$$

followed by the hydrogenation of the phenyl radical

$$C_6H_5 + CH_4 = C_6H_6 + CH_3$$

The C_3H_3 radicals are produced by the addition of a singlet methylene radical, $CH_2(s)$, to acetylene:

$$CH_2(s) + C_2H_2 = C_3H_3 + H$$

Similar pathways for the formation of PAH are also reviewed. At the end of a two-week work period, students write a final report discussing the effects of fluid dynamics, fuel structure, dilution, and other process conditions on the formation of pollutants in hydrocarbon flames. They also present their work orally in front of other groups and selected faculty.

THE EXPERIMENT

An illustration of the experimental burner system and sampling configuration is shown in Figure 2 (next page). The flame was stabilized between two opposed 1.0-inch I.D. burner ports. The flows of oxidizer and fuel gases were regulated using mass flow controllers. The oxidizer stream was introduced through the top burner port and the fuel stream was introduced through the bottom burner port. Argon diluent was used in the fuel stream to control the flame temperature. The flame was protected from ambient air by an argon shield gas. The shield gas also aided in cooling the hot combustion products. All gases were vented through the water-cooled heat exchanger that was built around the bottom burner.[8] The arm supporting the top burner was similarly water-cooled (not shown).

In the present experiment, the distance between the burner ports was 1.8 cm, the oxidizer stream was air at a flow rate of 5.8 L/min, and the fuel stream was a CH_4/Ar mix (75% by volume CH_4 and 25% by volume Ar) at a flow rate of 4.0 L/min. This corresponds to an overall equivalence ratio significantly greater than one ($\phi = 4.9$). We chose this condition to increase the emission of products of incomplete combustion from the burner system.

Visually, the flame exhibited blue, luminous yellow, and dark orange zones characteristic of a diffusion flame, with the flame being positioned on the oxidizer side of the stagnation plane, as illustrated in Figure 3 (next page). Since oxygen was the limiting reactant, methane necessarily diffused across the stagnation plane into the oxidizer side. The blue zone marked the occurrence of reactions associated with stoichiometric flames. In addition, a dark zone, located between the blue and luminous yellow zones, was noted by the students during the experiment.[9] The luminous yellow and dark orange zones indicated the presence of higher molecular weight hydrocarbons and the formation of soot particles or precursors.

Samples were withdrawn via a heated quartz microprobe having a 100 μm orifice at its tapered tip and transported through a silica-lined, stainless steel transfer line to the Hewlett-Packard (HP) 5890 II gas chromatograph (GC). Light gases were separated by Hayesep DB and Hayesep T packed GC columns and detected with a thermal conductivity detector (TCD). Heavier gases were separated by an HP-5MS capillary column and detected with an HP 5971A mass selective detector (MSD). The entire sampling system was maintained at 300°C and subambient pressure to minimize the adsorption of PAH with five rings or less. Mole fraction profiles were generated by moving the entire burner assembly relative to the fixed sampling probe. Temperature measurements were made in a similar fashion with a silica-coated 0.15 mm Pt-13%Rh/Pt thermocouple.

SAFETY

This experiment presents obvious safety concerns. High flame temperatures (1200°C) and sampling system temperatures (300°C) must be handled with extreme care. The fuel gas used is flammable, and poisonous by-products such as CO are produced. Therefore, many safety features have been incorporated into both the design and the construction of the experimental facility and student operating procedures.

Contact with the burners or the sampling line must be avoided during the course of the experiment. The surface temperatures of the burners were kept sufficiently low by both the shield gas and water cooling. The sampling line was insulated. Although the combustion products were vented through the bottom burner, an overhead fume hood was constructed on top of the experiment to increase safety. As a final safeguard, a carbon monoxide detector was installed.

With the potential hazards in mind, an experienced teaching assistant checks the oxidier and fuel flow rates before the flame is lit. In addition to the mass flow controller displays, rotameters were installed to provide further visual indication of the flow rates. The flow of both oxidizer and methane can be ceased at any time with manual shut-off valves. Students are taught the safe start-up and shutdown procedures. Gas flows must be turned on sequentially in the following order: the fuel-side Ar, the Ar shield gas, the air, and finally the methane. Following each flame sampling, the gas flows are turned off (*i.e.,* the flame is extinguished) in the reverse order.

A routine problem that has been encountered is a flaring of the flame immediately after lighting, due to an imbalance between the total flow rate and the venting flow rate. If the appropriate adjustments cannot be made quickly, students are instructed to use the manual shut-off valves to shut off the methane first, then the air, and then to set the mass flow controllers to a setpoint of zero flow rate so that a hazardous situation does not arise upon future start-up. To avoid an accident, students are instructed to immediately alert the teaching assistant (who is always present) of any equipment malfunction or unusual sight or sound. They are also trained in the correct evacuation procedure from the laboratory should this be necessary.

In spite of all these precautions, *the active presence of a knowledgable and experienced teaching assistant is im-*

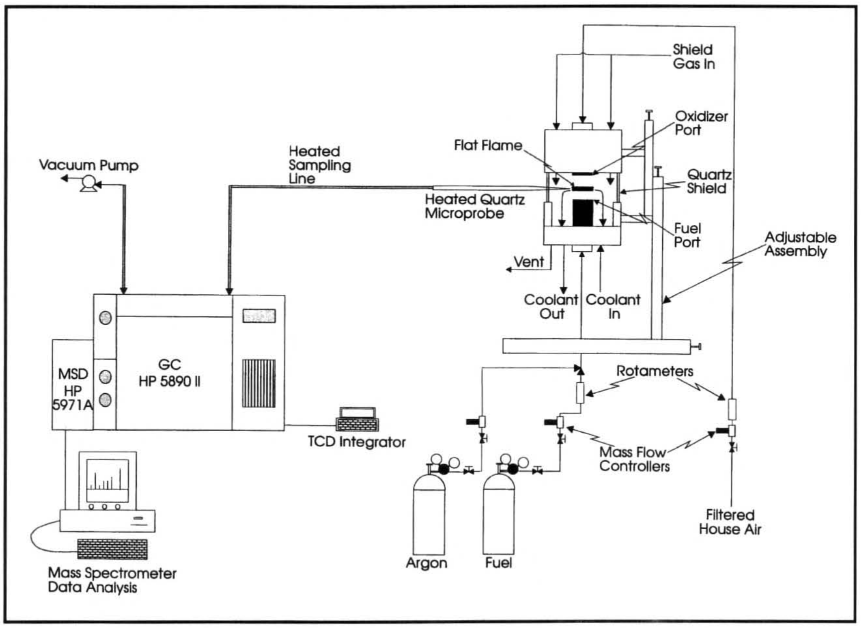

Figure 2. *Experimental set and sampling configuration.*

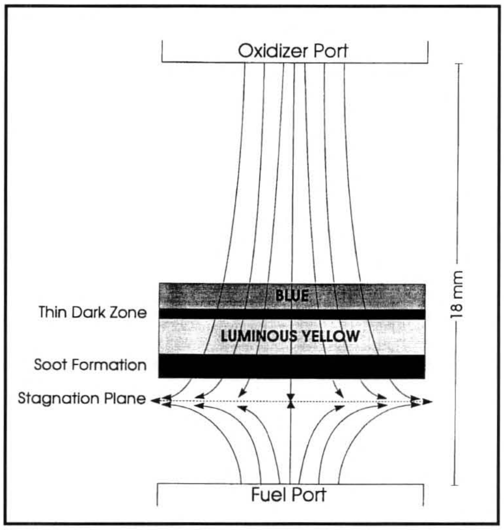

Figure 3. *Visual characteristics of an opposed flow diffusion flame.*

perative to the safe operation of this experiment.

DATA ACQUISITION AND ANALYSIS

The mole fraction profiles for a total of thirty chemical species, ranging from major components to trace aromatics and PAH, were determined in experiments that lasted from four to five hours. This represents the analysis of approximately ten samples withdrawn from the flame, which is typically adequate to discern trends in the species mole fraction profiles. Major components are defined as CH_4, Ar, O_2, N_2, CO, H_2, and H_2O and were all detected with the TCD and quantified with calibration standards.

Figure 4 shows the chemical structure and summarizes the method of quantification for each hydrocarbon product and by-product species detected in the flame. The species that were detected with the MSD, with the exception of vinylacetylene and benzene, were quantified with the ionization cross section method.[10] This method provides mole fractions that are accurate within a factor of two.[10,11] The accuracy of the mole fractions of species that were quantified using calibration standards was estimated to be ±15%.

For those species detected with the MSD, data analysis and calculations were undertaken with the aid of HP ChemStation software. Prior to the experiment, the following information was entered for each species: 1) Retention time and the masses of parent and fragmentation ions, for purposes of identification; 2) Calibration abundance or ionization cross section information, in order to determine absolute concentrations. After each MSD run, the software was used to automatically extract raw data from the ion chromatogram and to report the number of moles present of each species (n_i) detected by the MSD. Separation and detection of all species was achieved in under thirty minutes for each sample withdrawn from the flame, allowing students to quickly view their data and take corrective action if necessary before continuing.

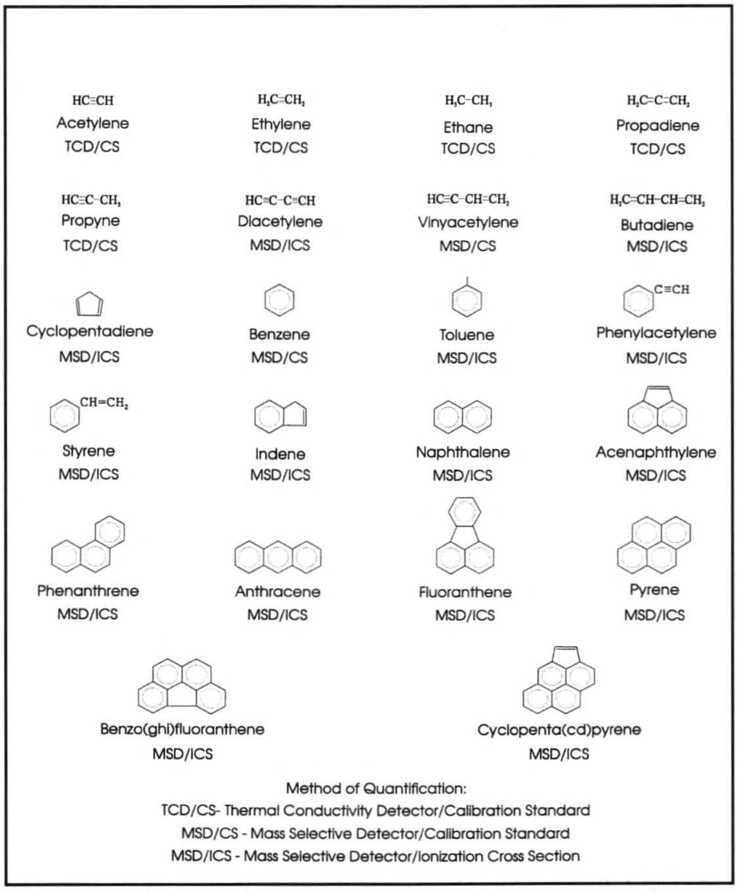

Figure 4. *Hydrocarbon species detected in an opposed flow methane-air diffusion flame.*

Using a spreadsheet program, students then converted the raw data from the TCD into n_i values. The total number of moles (n_T) injected into the GC was also determined using the ideal gas law at the sampling conditions. The consistency of the experimental data was calculated from the expression

$$\text{Consistency} = \frac{\sum_i n_i}{n_T} \text{ X } 100\%$$

Typical consistency values ranged from 95% to 105%.

Due to the sharp concentration gradients associated with certain species, additional data points may be required to define the mole fraction profiles. The need for more samples is not apparent until the raw data from both the MSD and TCD has been translated and plotted. The students may use additional lab periods during the two-week time frame to reduce the data and possibly analyze more samples, under the close direction and supervision of the teaching assistant.

The fluid dynamic strain in the flame as set up by the opposed flow field was calculated as an illustration of residence time constraints. The strain rate, K, is defined as the axial velocity gradient on the oxidizer side of the stagnation plane. Mathematically, K is defined as

$$K = -\frac{du}{dz}$$

where u is velocity and z is displacement along the axis connecting the centers of the burner ports. Since the above expression requires knowledge of the actual flow field, which was not available, the strain rate was calculated using the following expression that requires only observable quantities:[12]

$$K = \frac{-2\,u_o}{L}\left(1 + \frac{u_f}{(-u_o)}\sqrt{\frac{\rho_f}{\rho_o}}\right)$$

where L, u_o, u_f, ρ_f, and ρ_o are the distance between the burner ports, the oxidizer port outlet velocity, the fuel port outlet velocity, the fuel stream density, and the oxidizer stream density, respectively. With the assumption of plug flow (ensured by a network of screens) and using the experimental conditions given earlier, this corresponds to a computed strain rate of 34 sec^{-1} at 298 K. This is a relatively low value when compared to the extinction limit of CH_4, suggesting a high residence time within the flame, which should lead to the production of measurable quantities of PAH. The maximum mole fractions of the product species detected in the flame is presented in Figure 5.

SPECIES MOLE FRACTION PROFILES

Mole fraction profiles for the major species, together with the temperature profile, are shown in Figure 6. The temperature profile shows a maximum temperature of 1200°C at a distance of 6.5 mm from the fuel port. The flame temperature exhibited a nearly linear variation from each burner port to the point of maximum temperature, which is in good agreement with the literature.[13]

The results for the major species mole fraction profiles compare well with the work done in previous diffusion flame studies.[13,14] As can be seen in Figure 6, both CH_4 and O_2 were largely consumed at about 7 mm from the fuel port, near where the maximum flame temperature was observed. A significant, yet relatively small, amount of O_2 penetration into the fuel-rich portion of the diffusion flame was noted, however. The mole fraction of CO increased as the fuel was consumed and exhibited a peak mole fraction of 0.035 at 6 mm, followed by a decrease with increasing distance from the fuel port. Hydrogen followed the same trend as CO with a maximum mole fraction of 0.014 at 5.5 mm. The mole fractions of CO and H_2 both exhibited maxima on the fuel-side of, and near to, the point of maximum heat release (maximum flame temperature), consistent with the transition from fuel-rich to fuel-lean flame chemistry. Carbon dioxide and H_2O mole fraction profiles followed a pattern similar to CO and H_2 and exhibited maxima at about 7.0 mm from the fuel port, also close to the point of maximum flame temperature. These results are indicative of the occurrence of the highly exothermic oxidation reactions, $CO + OH = CO_2 + H$ and $H_2 + OH = H_2O + H$.

In Figure 7, the mole fraction profiles for species ranging from butadiene to PAH are presented. These species were selected to illustrate the wide range of hydrocarbon pollutants that can be formed in combustion processes. As can be seen in the figure, benzene was by far the most abundant of the aromatic species produced, with a peak concentration of about 77 ppm at 4-5mm. All hydrocarbon species exhibited a sharp decrease in concentration at 7 to 7.5 mm from the fuel port, corresponding to the transition from fuel-rich to fuel-lean flame chemistry created by the competition between gas-phase polymerization and oxidation reactions, respectively.[5-7] Some of the PAH detected, presented in order of abundance, were naphthalene, pyrene, phenanthrene, and cyclopenta(cd)pyrene. Naphthalene appeared in greater concentration than any of the other PAH, reaching a maximum level of 7.4 ppm. These results are in excellent agreement with previous studies[15] and are consistent with those in premixed flames.[11]

Future plans involve development of the capability to simultaneously measure PAH and NO_x emissions. This way, students will be able to readily observe the intimate connections that exist between flame temperature, overall equivalence ratio, dilution, and NO_x and PAH emissions.

CONCLUSIONS

The opposed jet diffusion flame provides a convenient laboratory tool to illustrate fundamental environmental chemical engineering principles associated with combustion. These experiments strengthen students' engineering knowledge and skills, concomitant with exposure to the use of sophisticated

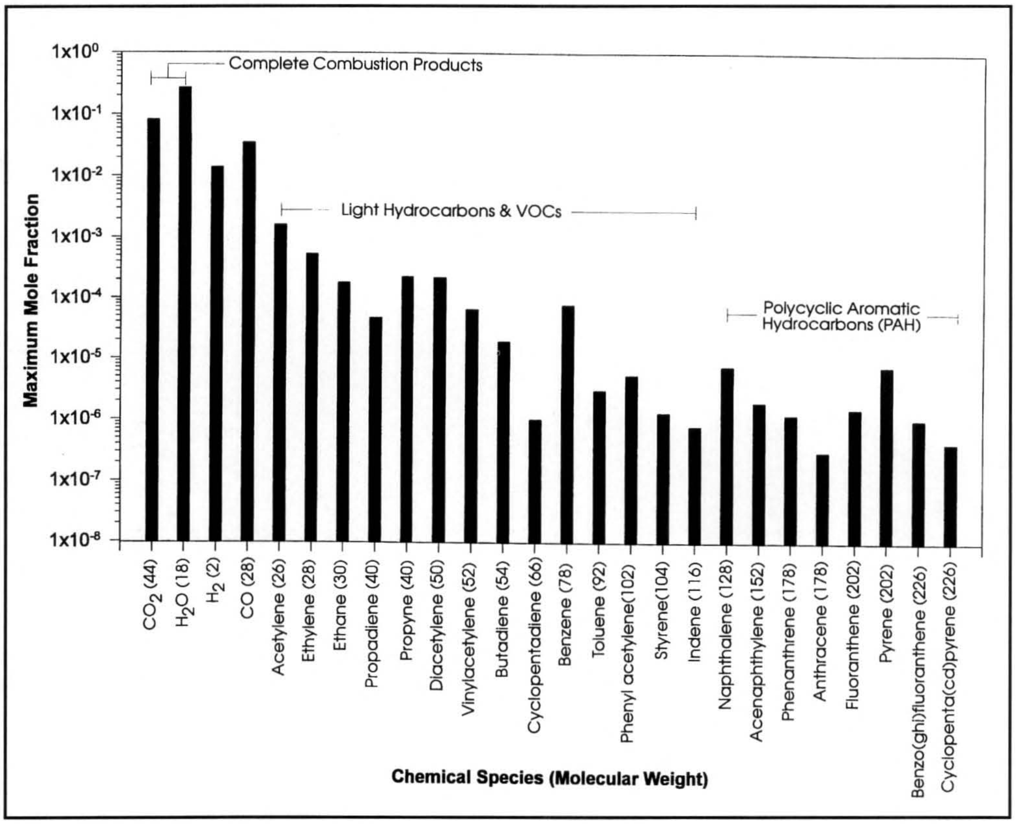

Figure 5. *Maximum mole fractions of product species detected in the experiment.*

instrumentation and the detailed chemistry innate to combustion systems. To make it a valuable and rewarding experience for students requires faculty with research interests in the area of combustion to provide in-house expertise and future generations of experienced teaching assistants who are seasoned in the associated theory and experimental and safety techniques and procedures.

We have demonstrated that a large variety of potentially toxic by-products are formed in the combustion of simple hydrocarbon fuels. Of the 26 product species detected, 12 are either explicitly or implicitly listed as "hazardous air pollutants" in the Clean Air Act Amendments of 1990.[16] The measurement of a large variety of pollutants made an impact on the undergraduates who participated in this experiment, as they were able to better appreciate the complexity and breadth of modern environmental issues.

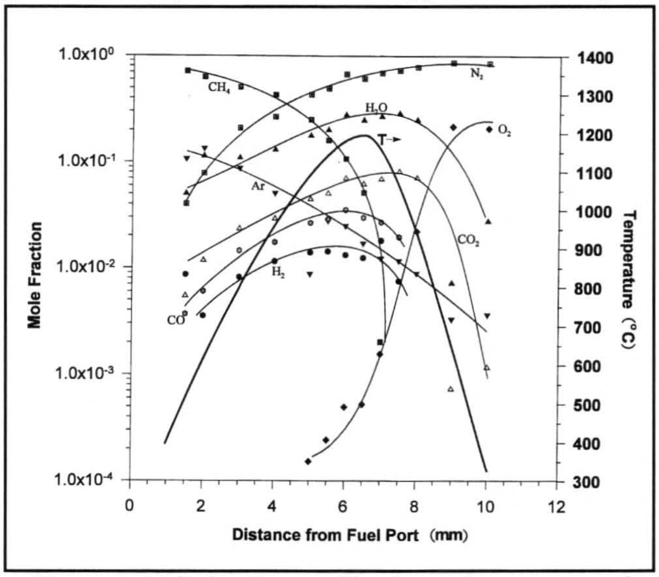

Figure 6. *Mole fraction profiles for major species and temperature profile (T).*

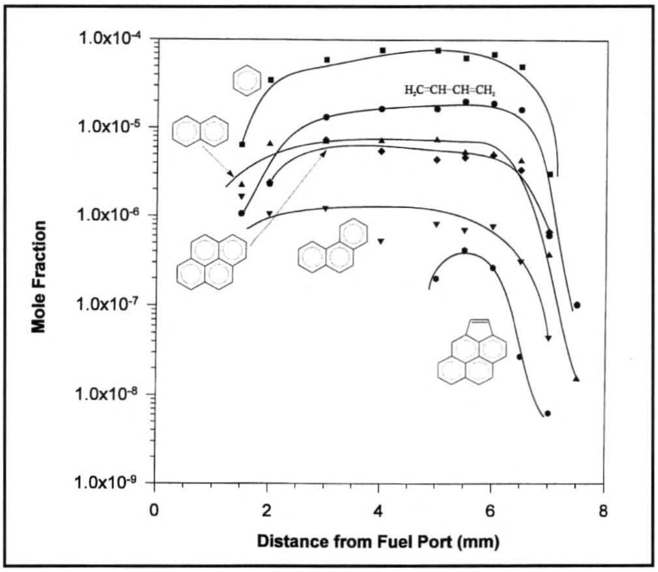

Figure 7. *Mole fraction profiles for select trace species.*

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