THE MORPHOLOGY OF CHROMIUM AND LIF MEASUREMENT OF ATOMIC ARSENIC IN LAMINAR DIFFUSION FLAMES

Youngbin Yoon
Department of Aerospace Engineering
Seoul National University
Seoul, KOREA

ABSTRACT

The morphology and size distribution of chromium oxides and the concentration measurement of atomic arsenic have been studied in laminar diffusion flames. Nitrogen was added to vary flame temperatures in hydrogen flames. Ethene flames were used in order to investigate the potential for interaction between the soot aerosol that is formed in these flames and the chromium aerosol. Two sources of chromium compounds were introduced: chromium nitrate and chromium hexacarbonyl. A detailed investigation of the morphology was carried out by scanning electron microscopy (SEM). The amounts of Cr(VI) and total Cr were determined by a spectrophotometric method and by X-ray fluorescence spectrometry, respectively. Also, LIF was used for the measurement of atomic arsenic, which was excited at 197.2 nm and was detected at 249.6 nm.

Results showed that the morphology of the particles varied with the flame temperature and with the chromium source. The particles were characterized by porous structures, cenospheres and agglomerated dense particles when chromium nitrate solution was added to the flames. At low to moderate temperatures, porous sintered cenospheric structures were formed, in some cases with a blow hole. At higher temperatures, an agglomerated cluster which was composed of loosely sintered submicron particles was observed. It was also found that the emission of Cr(VI) from the undiluted H_2 flame was more than 10 times larger than in the 50% H_2 / 50% N_2 flame on a mass basis. Single point LIF measurement of atomic arsenic indicated that arsenic exist only in the low temperature, fuel rich region.

INTRODUCTION

The disposal of hazardous waste has been a major issue as the amount of waste has increased. Thermal treatment systems, such as incineration, can be useful methods for the disposal of toxic chemicals. However, pollutant emissions, such as toxic gas, fly ash and bottom ash [1], from combustion processes are of great concern. Toxic metal aerosols emitted as a result of the incineration process are composed of micron and submicron particles [2] which can stay airborne for long periods of time and penetrate deep within the lung, causing mutagenic and carcinogenic effects [3].

Chromium, identified as a carcinogenic metal [4], has been widely used in alloys, refractories and dyes. The toxicity of chromium depends on the valence of the metal; the hexavalent form of chromium (Cr[VI]) is known to be highly carcinogenic, whereas the trivalent form of chromium (Cr[III]) is non-carcinogenic and an essential nutrient for humans [4,5]. Almost all the hexavalent chromium in the environment comes from human activities. It may be derived from incineration, producing the oxidized form of Cr(VI). In this hexavalent

oxidation state, chromium is relatively stable in air and pure water although it is reduced to the trivalent state over a long time period. Arsenic is also known as a carcinogenic metal, which usually appears as arsenite (As_2O_3) and arsenate(As_2O_5). Consequently, it is very important that incinerators be designed to minimize the generation of the toxic metal emissions [6,7].

Investigators have developed various methods to determine the speciation of chromium and its compounds that were obtained from incinerators [8-9]. Scanning Electron Microscopy (SEM) of the nickel oxide particles revealed a cenospheric structure composed of thin-walled hollow spheres having single blow holes on their surfaces [10]. These hollow particles are a common feature of many fly-ashes and they apparently result from H_2O, CO_2 and SO_2 evolution during rapid heating which causes bubble nucleation and growth of the liquid particles [11]. Cenosphere formation is dependent upon chemistry, swelling characteristics and combustion conditions [12].

The formation of submicron particles has been investigated by many researchers [13-14]. High concentrations of inorganic submicron particles with a bimodal size distribution were found in an evaporation-oxidation furnace in the study of Bolsaitis et al.[13]; they suggested that submicron particles were due to either homogeneous or heterogeneous nucleation. However, there is little information available on the size distribution and the emissions of hexavalent chromium from flames with varying flame temperature, residence time, concentration of soot etc. In this study, laminar diffusion flames of hydrogen and ethene have been used to provide a well-controlled model of non-premixed combustion. The hydrogen flame has been used to examine the effect of temperature on the formation of chromium compounds by adding nitrogen gas to the flame. The amount of soot produced from the ethene flame was varied in order to investigate interaction of soot with chromium particles. In addition, LIF technique was adopted to measure the concentration of atomic arsenic in the hydrogen flame. A fundamental understanding of the fate of chromium and arsenic in these flames will facilitate the development of reduction technologies and predictive capabilities for the toxic metal emissions from incinerators.

EXPERIMENTAL METHODS

Apparatus

The coflow, laminar, diffusion flame system is shown in Fig. 1. The 5 mm burner nozzle was positioned in the center of a 100 x 100 mm duct containing flow straighteners and a series of fine-mesh screens to insure air flow uniformity. Two fuels were used in this experiment : hydrogen and pure ethene. In the hydrogen flame, nitrogen was added to vary the flame temperature; the hydrogen was also used to atomize the chromium solution. The flow rate of the hydrogen was fixed at 1.3 L/min and the feed rate of chromium nitrate solution was constant as shown in Table 1. The fuel and entrained aerosol were mixed with nitrogen gas and injected at the fuel nozzle. In ethene flames, the fuel was the carrier gas and the flow rate of ethene was varied to achieve different types of sooting flames. All flow rates were controlled by calibrated sonic orifices.

Two different sources of chromium compounds were introduced: chromium nitrate and chromium hexacarbonyl. Chromium nitrate ($Cr(NO_3)_3.9H_2O$) is soluble in water and has an oxidation state of Cr(III). A 0.5 M chromium nitrate solution and a 0.5 M aqueous cacodylic acid ($(CO_3)_2As(O)OH$) solution were atomized by a Lovelace nebulizer and introduced into the flame. Chromium hexacarbonyl ($Cr(CO)_6$) was used as a source of zero oxidation state of chromium. A 13 mm diameter glass cartridge containing 0.5g of chromium hexacarbonyl was plugged with glass wool at both ends and connected to the fuel lines. Since chromium hexacarbonyl is volatile at room temperature, its vapor was carried by the fuel and then introduced directly to the flame.

Sampling

Samples of vapor and particle phases of chromium compounds emitted from the flame were obtained using a stainless steel sampling probe positioned 20 mm above the flame tip at the centerline. The 200 mm long, 22 mm outer diameter sampling probe contained a 150 mm long, 13 mm diameter inner sintered metal tube. A nitrogen dilution gas was provided to the sampling probe through the sintered metal part and mixed with the sample in order to quench reactions and the development of aerosols through the sampling lines. The sampling probe was grounded to avoid electrostatic deposition of charged chromium particles along the sampling line wall.

Figure 2 shows the chromium sampling system. The particle phase of chromium was captured on a 47 mm diameter alumina membrane filter with 20 nm pores. The sampling rate was measured with a flowmeter and was controlled to achieve an isokinetic condition. Tygon^{TM} was used in all the sampling lines to reduce the problem of electrostatic deposition. The sampling lines between the sampling probe and the filter were heated with heating tapes to prevent condensation in the lines. Thus, the temperature of the sampled gas at the filter was 105 $^{\circ}$C, which is high enough to prevent water from being condensed along the sampling lines and is low enough to avoid the conversion between Cr(VI) and Cr(III). Hence, the chromium particles were collected in a dry environment.

Sample Analysis

A spectrophotometric method was used for Cr(VI) analysis A 1.7 mL sample was mixed with 200 mL 6N H_2SO_4 and 100 mL diphenyl dicarbazide (0.5g in 100 mL acetone) and absorbance was measured at 540 nm in a quartz cuvette using a Shimadzu PC-2101A spectrophotometer. An X-ray Fluorescence (XRF) method was used to measure the total chromium with a Kevex 0700/8000 energy-dispersive XRF spectrometer; solutions were analyzed by loading 100 mL of solution onto alumina filters. Cr(III) was determined by subtracting Cr(VI) concentration from total chromium [10].

LIF Measurement of Atomic Arsenic

A Spectra Physics Quantum Ray Nd:YAG and PDL-3 dye laser were used. The 197.2nm beam used to excite arsenic was generated by mixing the fourth harmonic of the YAG laser(266nm) and the dye laser(760nm) through a BBO crystal. The dye laser was pumped by the second harmonic of the YAG(532nm). The dye laser was finely tuned so that the mixed beam was exactly at 197.2nm. The fluorescence signal was detected at 249.6nm. LIF signal was collected at a right angle with a 2-inch plano-convex fused silica lens and focused onto the side entrance slit of a 0.75m single monochromator. An R1477 Hamamatsu PMT was attached to the exit slit to receive the signal. The signal from the PMT was processed by a Stanford Research Systems Boxcar Averager for spectral analysis and the part of input laser intensity was recorded in a multi-channel CAMAC charged integrator to normalize each pulse signal.

RESULTS

One of the significant factors in the destruction of hazardous wastes and in the formation of chromium compounds is the flame temperature. The temperature could affect not only the formation of chromium species but also the morphology of chromium oxides. Thus, the adiabatic flame temperature was varied in the hydrogen flames; as the addition of nitrogen inert gas increased from 0 to 67% on a mole basis, the maximum adiabatic flame temperatures decreased from 2450 to 1873 K as shown in Table 1.

The results of Cr sample analysis showed the effect of N_2 addition to the flame and the importance of the form in which chromium was added to the flame. A porous structure was

observed in the micron sized chromium oxides particles at low temperatures (67% N_2 diluted hydrogen flame) as shown in Fig. 3. The relatively large particles in Fig. 3 were likely to be formed by the unvaporized component of each droplet as found in the study by Mulholland and Sarofim[10]. As the particles heated, swelling could occur and they may have become porous. Submicron particles can also be observed in Fig. 3. The formation of submicron particles was not likely to be due to the vaporization-condensation mechanism because the volatility of Cr_2O_3, which is the major species in this temperature range, is very low. Therefore, it is conjectured that the formation of submicron particles was due to the onset of bubble explosion.

As shown in Fig. 4, cenospheres were found at moderate temperatures (50% N_2diluted hydrogen flame). It was likely that the viscous melt in the core released NO_2 and O_2, leading to a bubble explosion inside the droplet and a blow hole. It is expected that most micron size particles were hollow spheres in this temperature range. Some hollow spheres have blow holes or cracks on their surface, which is an indication of cenosphere fragmentation. This mechanism resulted in a shower of submicron fragments. Hence, more submicron particles and shell-shape fragments may be found in Fig. 4 than in the lower temperature case of 67 % N_2 diluted flame shown in Fig. 3, where most micron particles appeared to be porous. The cenospheres were composed of many spherules that may have been formed from a melt of the nitrate as it heated in a manner similar to that described by Mulholland and Sarofim [10]. The size (or volume) distribution of the aerosol sample was bimodal with a distinct submicron mode as shown in Fig. 5(b). Samples obtained by seeding with hexacarbonyl were quite different. A shiny yellow-orange color filter was obtained from the pure hydrogen flames, which was consistent with the color of CrO_3($Cr(VI)$ oxide), whereas a dark green color was observed with the hydrogen flames diluted by N_2 gas. This color corresponded to the color of Cr_2O_3($Cr(III)$ oxide). These two chromium oxides are expected to be the major Cr compounds formed from non-chlorinated chromium waste flames.

It was found from the sample analysis that the emission of $Cr(VI)$ from the H_2 flame decreased as N_2 was added to the flame; high temperatures favored the formation of $Cr(VI)$ although this was not expected to be an equilibrium product at the low sampling temperatures above the flame. For example, $Cr(VI)$ emissions from the 100% hydrogen flame with chromium hexacarbonyl addition was 15 times larger on a mass basis than those from the 50% H_2 / 50% N_2 flame as shown in Fig. 6. Although less $Cr(VI)$ was produced in the 100% hydrogen flame using chromium nitrate, the trend was similar to that of the chromium hexacarbonyl case. These observations were consistent with the results reported by Steinsberger et al.[14]. They found that higher incinerator temperatures and longer residence times led to an increase in the ratio of $Cr(VI)$ to total chromium in the incinerator emissions. Their results indicated that improved combustion actually exacerbated the $Cr(VI)$ problem, posing something of a dilemma when hazardous wastes need to be destroyed to very low levels.

Atomic arsenic was only found in the low temperature, fuel rich side of the flame. However, with oxygen and OH radical also existing on the fuel rich side of the flame, arsenic was quickly oxidized at high temperature, even though the fuel oxygen ratio was still above the stoichiometric ratio. Higher atomic arsenic concentration was found in the diluted hydrogen flame(50% H_2 / 50% N_2) than in the pure hydrogen flame as shown in Fig. 7. The higher atomic arsenic concentration is the result of lower temperatures in the diluted flame.

CONCLUSIONS

The morphology and sampling of chromium and the LIF measurement of atomic arsenic in hydrogen and ethene flames have been performed in the present study. A nebulized solution of chromium nitrate formed micron size cenospheres, some of which exhibited blow holes that are typical of gas evolution in a viscous melt. Submicron particles were formed by shattering cenospheres. High resolution scanning electron microscopy showed that the macroscopic

cenospheres were formed from the sintering of much smaller spherules. These sub-units exhibited dimensions of about 50 nm. At low flame temperatures, the cenospheres were densely compacted with small openings. Higher temperatures favored a more loosely sintered and open structure.

All the samples were analyzed by a spectrophotometric method and X-ray fluorescence spectrometry to quantify the amounts of Cr(VI) and Cr(III), including the partitioning of Cr(VI) phases. The results of Cr sample analysis showed the emission of large amounts of Cr(VI) in a pure H_2 flame decreased as N_2 was added to the flame; the amount of Cr(VI) emitted from the 100% hydrogen flame was more than 10 times larger than that of the 50% H_2 / 50% N_2 flame on a mass basis. This shows the strong effect of the flame temperature on the nature of chromium emissions. Single point LIF measurement of atomic arsenic indicated that arsenic exist only in the low temperature, fuel rich region.

REFERENCES

[1]   Linak, W. P. and Wendt, J. O. L., Progr. Energy Combust. Sci. 19 : 145-185 (1993).

[2]   Davidson, R. L. et al., Environ. Sci. Technol. 8: 1107-1113 (1974).

[3]   Smith, R. D., Prog. Energy Combust Sci. 6: 53-119 (1980).

[4]   Health Assessment Document for Chromium, US EPA, EPA-600/8-83-014F (1983).

[5]   Environmental Health Criteria 61 for Chromium, World Health Organization, Geneva (1988).

[6]   Linak, W. P., Srivastava, R. K. and Wendt, J. O. L., Combust. Sci. Tech. 101: 7-27 (1994).

[7]   Oppelt, E. T., J. Air Poll. Control. Assoc. 37: 557-583 (1987).

[8]   Winter, R. M. and Mallepalli, R. R., Hellem, K. P., and Szydlo, S. W., Combust. Sci. Tech. 101: 45-58 (1994).

[9]   Axner, O. and Rubinsztein-Dunlop, H., Applied Optics 32: 867-883 (1993).

[10]   Mulholland, J. A. and Sarofim, A. F., Environ. Sci. Tech. 25: 268-274 (1991).

[11]   Fisher, G. L., Chang, D. P. Y. and Brummer, M., Science 192: 553-555 (1976).

[12]   Smith, R. D., Prog. Energy Combust. Sci. 6: 53-119 (1980).

[13]   Bolsaitis, P. P., McCarthy, J. F. and Mohiuddin, G., Aerosol Sci. Tech. 6: 225 -246 (1987).

[14]   Steinsberger, S. C., DeWees, W. G., Bell, A. C., Finken, R. A., Knoll, J. E., and Midgett, M. R., Fuel Processing Technol. 39; 265-276 (1994).

Table 1. Experimental Conditions of Hydrogen Flames Using Chromium Nitr

	100 % H_2	67 % H_2 / 33 % N_2	50 % H_2 / 50 % N_2	33 % H_2 / 67 % N_2
H_2 Flow Rate (L/min)	1.30	1.30	1.30	1.30
N_2 Flow Rate (L/min)	0	0.65	1.30	1.95
Air Flow Rate (L/min)	315	315	315	315
Max. Adiabatic Flame Temperature (K)	2450	2224	2032	1873
Flame Height (mm)	65	75	85	95
Feed Rate of Chromium Nitrate Solution (mg/min)	31.6	31.6	31.6	31.6
Concentration of Chromium Nitrate Solution (g/L of nano pure H_2O)	200	200	200	200
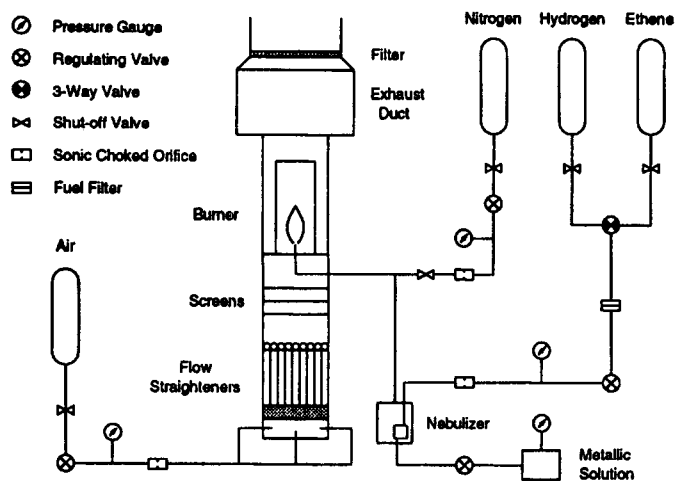
Figure 1. Schematic of Experimenl Apparatus.
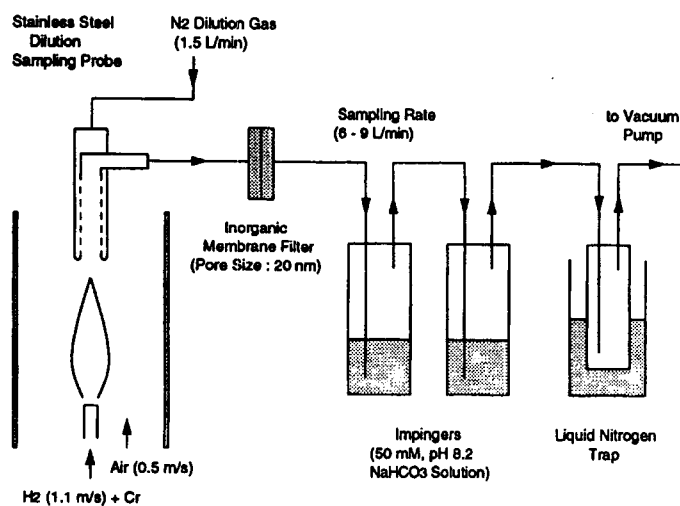
Figure 2. Schematic of Chromium Sampling System.
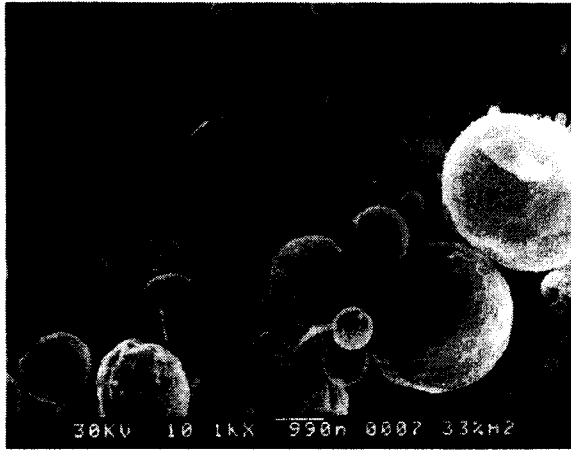
Figure 3. Scanning Electron Microscope Photograph of Chromium Oxide Particles Obtained from 33% H₂ / 67% N₂ Flame Using Chromium Nitrate. (Image of Porous Particles.)
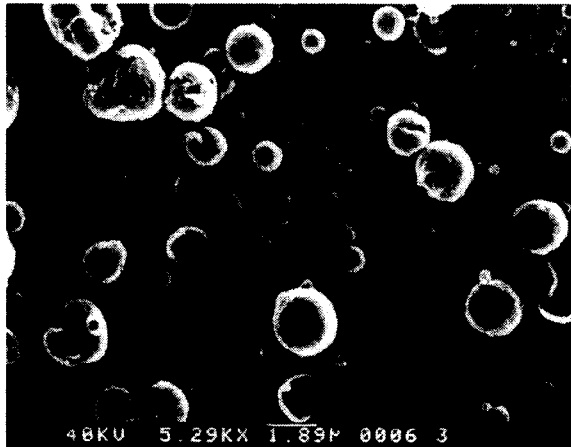

Figure 4. Scanning Electron Microscope Photograph of Chromium Oxide Particles Obtained from 50% H₂ / 50% N₂ Flame Using Chromium Nitrate. (Image of Cenospheres.)
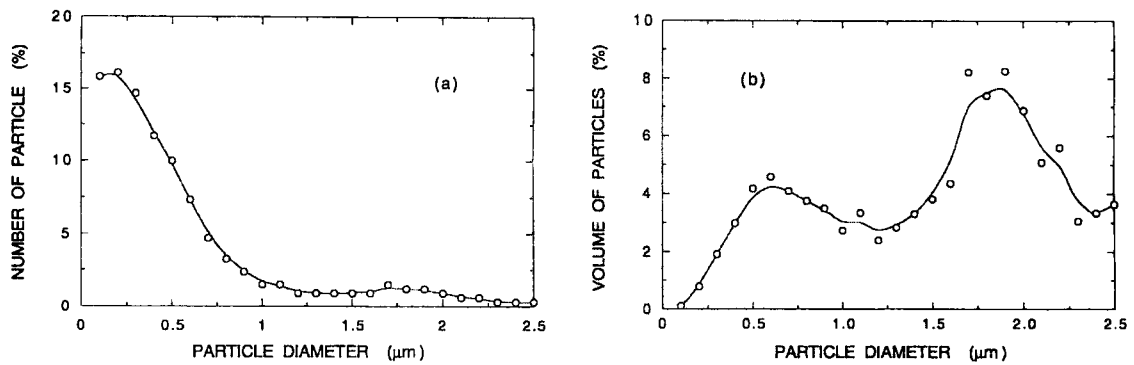

(a)

(b)

Figure 5. Particle Size Distribution of Chromium Oxide Particles
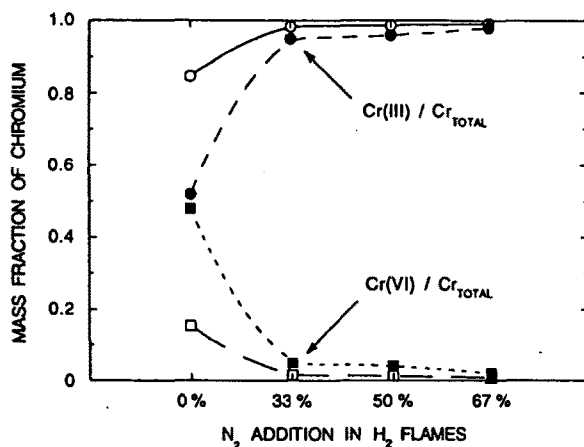(a) Number Distribution (b) Volume Distribution

-67-

Figure 6. Fractions of Total Chromium emitted as Cr(III) and Cr(VI) from Hydrogen Flames with Varying N_2 Addition: Chromium Nitrate (open symbols) and Chromium Hexacarbonyl (solid symbols).
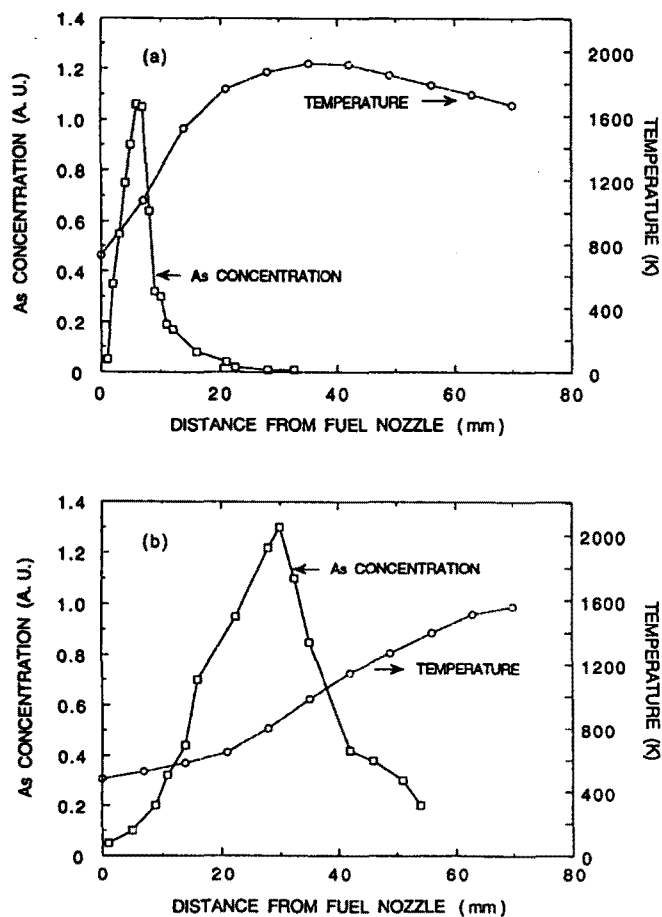

Figure 7. Centerline Profile of Atomic Arsenic Concentration and Temperature.
(a) 100% H_2 (b) 50% H_2 / 50% N_2