INTRODUCTION

The problem of deposit formation on cold surfaces is important in a number of combustion systems and is of special interest in the Otto-cycle engine, where octane requirement is significantly increased above that for a clean engine by the formation of deposits on combustion chamber walls. Past work on this problem supplies information on the effects of fuel, lubricant, and engine variables on the formation of deposits. Elemental analysis and other limited information on deposit composition are also available; however, very little information is available on the chemical species that reach the surface from the flame to cause these deposits.

Techniques for direct sampling from a low-pressure flame into a mass spectrometer are providing a wealth of new information on the chemical species found in the flame zone. In the course of flame zone studies, it was observed that some stoichiometric flames formed deposits on the surface of the flat flame burner used. The physical nature and elemental composition of these deposits were similar to those found on the cold walls of a spark ignition gasoline engine. Flame temperatures in these studies were comparable to those in engines, but the pressure, 2.67 kPa, is much lower.

Scaling considerations (Fristrom and Westenberg, 1965) indicate that for second-order reactions and flames of the same unburned gas velocity $V_0$, distance $z$ should scale inversely with pressure $P$. Therefore, similar mole fraction and temperature profiles are expected when plotted as $z/P$. Also, since the diffusion
coefficient $D_{i, \text{mix}}$ is inversely proportional to pressure, the mass flux fraction $G_i$ of species $i$ as defined in Eq. 1 for one dimensional flat flames of different pressures should be independent of pressure at constant $z/P$.

$$G_i = \frac{P X_i M_i}{R T \rho V_0} \left[ V - \frac{D_{i, \text{mix}}}{X_i} \frac{dx_i}{dz} \right] \quad \text{(Eq. 1)}$$

In Eq. 1, $X_i$ is the mole fraction of species $i$, $M_i$ is the molecular weight of species $i$, $T$ is temperature, $R$ is the ideal gas constant, $\rho$ is mass density, and $V$ is the bulk gas velocity defined in Eq. 2 with $V_0$ being the inlet value.

$$V = \frac{\rho V RT}{P X_i M_i} \quad \text{(Eq. 2)}$$

Since the absolute convective and diffusional fluxes are expected to be proportional to pressure, the mass deposition rate is also expected to be proportional to pressure if the process is diffusion controlled. However, as a fraction of the total mass flux from the burner, the mass deposition is expected to be independent of pressure. It is therefore believed that the results discussed in this paper are relevant to the chemistry of deposit formation in practical equipment.

EXPERIMENTAL

The molecular beam mass spectrometer apparatus (Figure 1) used for collection of deposits and analysis of the flame structure has been described in detail elsewhere (Bittner and Howard, 1981; Bittner, 1981). The burner was constructed from a 1.25 cm thick by 7.1 cm diameter copper plate, drilled with 1 mm diameter holes in a close-packed hexagonal array with a 14.5% void area. Since the sampling probe orifice diameter was 0.7 mm the mole fraction profiles within several millimeters of the surface may be distorted and the gradients measured may not be those present in the absence of the probe. The solid deposit was removed from the burner surface after one to three hours of flame operation by careful scraping with a scalpel and stored in glass and teflon.

Deposits were collected and detailed gas composition profiles were measured for two benzene flames, (1) a stoichiometric (fuel equivalence ratio, $\phi = 1.0$) flame (8.2 mol % C$_6$H$_6$ - 61.8 mol % O$_2$ - 30.0 mol % Ar) and (2) a nearly sooting $\phi = 1.8$ flame (13.5 mol % C$_6$H$_6$ - 56.5 mol % O$_2$ - 30.0 mol % Ar). For both flames the