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SOOTING LIMITS OF MICROGRAVITY SPHERICAL DIFFUSION FLAMES IN OXYGEN-ENRICHED AIR AND DILUTED FUEL

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Limiting conditions for soot-particle inception were observed in microgravity spherical diffusion flames burning ethylene at 0.98 bar. Nitrogen was supplied to the ethylene and/or oxygen to obtain the broadest available range of stoichiometric mixture fraction, Z_{st} . Both normal flames (surrounded by oxidizer) and inverse flames (surrounded by fuel) were considered. Soot-free

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conditions were found to be favored at increased Z_{st} and there was no observed effect of convection direction on the sooting limits. The sooting limits follow a linear relationship between adiabatic flame temperature and Z_{st} , with Z_{st} accounting for a variation of about 700 K in the sooting-limit adiabatic flame temperature. This relationship is in qualitative agreement with a simple theory that assumes soot inception requires the local C/O atom ratio and temperature to be above threshold values, (C/O)_c and T_c, respectively. The theory indicates that different mechanisms are responsible for sooting limits at low and high Z_{st} . When inert is added to a fuel/air flame, a sooting limit is obtained when temperature becomes so low that the kinetics of soot inception are too slow to produce soot. On the other hand, a flame with a high Z_{st} has low C/O ratios far into the fuel side of the flame. For such a flame, soot-free conditions can be attained at much higher temperatures because there is sufficient oxygen on the fuel side to favor oxidation of light hydrocarbons over formation of soot precursors.

Keywords: sooting limits, spherical diffusion flames, microgravity, inverse flames, oxygen enriched air, oxygen enhanced, permanently blue flames

INTRODUCTION

Soot formation in flames is an active research area owing to its significance and complexity, as discussed in the reviews by Haynes and Wagner (1981), Glassman (1988), and Urban and Faeth (2001). The goal of this work is to advance the fundamental understanding of the limits of soot-particle inception in diffusion flames, with particular emphasis on understanding the effects of stoichiometric mixture fraction, Z_{st} , on these limits. Stoichiometric mixture fraction has been shown to have a strong influence on soot inception in strained flames (Du and Axelbaum, 1995) and it has been suggested that, with sufficiently high Z_{st} , conditions are such that it is not possible to form soot at any strain rate (Du and Axelbaum, 1995; Lin and Faeth, 1996). These so-called permanently blue flames (Lin and Faeth, 1996) are defined to involve a pairing of gaseous fuel and oxidizer (i.e., Z_{st}) for which soot cannot form in nonpremixed flames regardless of strain rate or residence time. This regime defines an absolute bound for flames at the sooting limit.

High- Z_{st} flames require oxygen mole fractions greater than 21%. Oxygen-enriched combustion is common in industry because it permits certain benefits and flexibility that are not otherwise available for practical combustors, as discussed by Baukal (1998). Furthermore, the cost of oxygen enrichment has declined to the point that oxygen-enhanced

combustion is preferable to combustion in air for many specialty applications. Interestingly, the problem of global warming by carbon dioxide has spurred an interest in the use of oxygen-enhanced combustion in the power industry. This has occurred because the Department of Energy (DOE) is considering carbon sequestration as a means of reducing the CO_2 loading from combustion processes (Klara and Srivastava, 2002). The sequestration of carbon dioxide is facilitated when the product stream has a high concentration of CO_2 because this stream can then be sequestered to underground geological formations. The DOE has estimated that this approach can curtail CO_2 emissions from power plants for over 200 years. By eliminating or reducing nitrogen from a combustion process, the concentration of CO_2 in the product stream is increased. For example, when natural gas is burned in pure oxygen (possibly diluted with CO_2), the only significant products are H₂O and CO_2 .

In this work we vary the oxygen mole fraction from 0.13 to 1 and show that oxygen-enhanced combustion has important implications for sooting limits in diffusion flames. In the past, data on fundamental sooting limits have come largely from studies of laminar premixed flames (Glassman, 1988; Harris et al., 1986; Haynes and Wagner, 1981; Markatou et al., 1993; Takahashi, 1997; Takahashi and Glassman, 1984). One reason for this is that both temperature and the carbon-to-oxygen atom ratio, C/O, are nearly constant in the soot-forming regions of premixed flames. Sooting limits in laminar premixed flames depend on fuel type, equivalence ratio, amount and type of inert, and, to a lesser extent, pressure. The limits typically are identified by the C/O (or, alternatively, the equivalence ratio or effective equivalence ratio) at which luminous yellow emission is barely perceptible. The limits are intrinsic properties of the mixtures and offer both practical value and fundamental information about soot-inception processes. When a limit occurs at a high C/O for a given flame temperature, this indicates that conditions (e.g., fuel type) are less conducive to forming soot.

Takahashi and Glassman (1984) concluded that sooting limits in premixed flames arise from a competition between fuel pyrolysis and oxidative attack. They successfully correlated the premixed-flame sooting limits for a wide range of fuels by accounting for C–C bonds and flame temperature and found that the structure of the fuel molecule was not important (see also Takahashi, 1997). Markatou et al. (1993) performed detailed kinetic calculations and used measurements of premixed-flame

sooting limits to validate the H-abstraction/ C_2H_2 -addition (HACA) mechanism of soot formation. They found that oxidation of light hydrocarbons (such as C_2H_3), rather than oxidation of polyaromatic hydrocarbons (PAHs), is the mode of oxidation that is critical to sooting limits for premixed flames. The formation of PAHs and soot can be prevented by the oxidation of these light hydrocarbons. Sooting limits in premixed flames furnish rigorous tests of the accuracy of soot-particle inception models because they involve PAH chemistry.

Until the present work, sooting limits in nonpremixed systems had been observed only in counterflow and coflow diffusion flames. Unlike those in freely propagating premixed flames, sooting limits in diffusion flames are not fundamental properties of the reactants because they depend on strain rate and flame geometry. In counterflow flames, limits have been found by varying the strain rate or by varying the inert supply at a fixed strain rate (Du and Axelbaum, 1995; Du et al., 1988, 1990, 1995; Hwang and Chung, 2001; Kang et al., 1997; Lin and Faeth, 1996; Sugiyama, 1994). In coflow diffusion flames, limits have been observed by changing flame length or by varying the inert supply (Du and Axelbaum, 1995; Kang et al., 1997). Addition of inert can decrease the flame temperature and/or fuel concentration until soot-inception chemistry is too slow for soot particles to form.

The role of temperature is different in premixed and nonpremixed flames; increased temperature suppresses soot formation in premixed flames and promotes soot formation in nonpremixed flames (Glassman, 1988; Takahasi and Glassman, 1984). In premixed flames, higher temperatures favor oxidation of light hydrocarbons over formation of soot precursors. In nonpremixed systems, light hydrocarbon oxidation typically is not considered to be an intrinsic part of soot inception because oxygen concentrations generally are low on the fuel side of a flame. Oxygen can appear on the fuel side of coflow flames if it leaks through the quenched base region (Glassman, 1988; Kaplan and Kailasanath, 2001), but here we are concerned only with oxygen that is intrinsic to the fuel side of the flame.

Despite the differences between soot inception in premixed and nonpremixed flames, C/O (which varies with position in diffusion flames) is shown here to be relevant to sooting limits in diffusion flames. Du and Axelbaum (1995) employed C/O to explain their observations of what later came to be called "permanently blue flames". The fundamental point here originates from the same reasoning as to why C/O is relevant in premixed flames. The reasoning is as follows. Consider the general stoichiometry of

$$C_n H_m + (n/2)O_2 \rightarrow n \operatorname{CO} + (m/2)H_2 \tag{1}$$

where *n* and *m* are the number of C and H atoms in the fuel molecule, respectively. When C/O is unity, there is exactly enough oxidizer to retain the carbon in the gas phase as CO, whereas at higher C/O there is insufficient oxidation to gasify the carbon and this would be expected to lead to soot formation. If the products are instead assumed to be CO and H₂O, the sooting limit can be expressed in terms of an effective equivalence ratio (Takahashi and Glassman, 1984), but herein we will consider only C/O. Owing to finite-rate chemistry and the production of H_2O and CO₂, the measured sooting limit, (C/O)_c, in premixed ethylene/air combustion is less than unity. For ethylene it occurs around $(C/O)_c = 0.6$ (Glassman, 1988; Harris et al., 1986; Haynes and Wagner, 1981; Takahashi, 1997; Takahashi and Glassman, 1984). This limiting or critical C/O was found to have only a slight dependence on the amount of N_2 in the reactants. As noted earlier, sooting limits in premixed flames result from a competition between oxidation of light hydrocarbons and formation of soot precursors (Markatou et al., 1993). This explains why simple stoichiometric considerations like those mentioned earlier are valuable in understanding sooting limits.

For nonpremixed systems it is possible to have a similar competition between oxidation and formation on the fuel side owing to the presence of oxygen-containing species such as CO₂ and H₂O. Du et al. (1990) showed that adding CO₂ to the fuel side of diffusion flames can suppress soot formation chemically. Liu et al. (2001) also found a chemically suppressive effect of CO₂ and concluded that oxidation by CO₂ was enabled by the reaction $CO_2 + H \rightarrow CO + OH$. These studies emphasized soot-particle *inception* but other studies have also found that soot-particle *oxidation* can be significant on the fuel side of a diffusion flame (Kaplan and Kailasanath, 2001; Sunderland and Faeth, 1996; Urban and Faeth, 2001).

We propose the following criteria for soot inception in nonpremixed flames: there should be a region in the flame where three quantities—C/O, temperature, and residence time—are above certain critical values. It is well known that soot does not form at low temperatures in non-premixed flames, with the threshold ranging from about 1250 to 1650 K (Dobbins, 2002; Glassman, 1988, 1998; Santoro et al., 1987; Sunderland and Faeth, 1996). This temperature will be referred to as the critical

temperature for soot inception, T_c . These studies indicate that this critical temperature is not strongly affected by pressure, fuel type, or fuel dilution with inert gas. Recently, Dobbins (2002) correlated a wide range of published soot-inception temperatures by considering the rate of increase of temperature with time, detector sensitivity, and published Arrhenius rate constants for the conversion of precursors to soot.

Soot inception also can be suppressed when residence time is short (equivalently, when the strain rate in counterflow flames is high). Soot induction times of 0.8-15 ms were reported by Tesner and Shurupov (1993) for acetylene/nitrogen mixtures at 1473 K. Strain rates for suppression of soot range from 30 to 200 s⁻¹ for common fuels (Du et al., 1988, 1990), which is consistent with induction times on the order of 10 ms.

With these assumptions, one can gain insight by considering a simple model of the global flame structure in mixture-fraction space for a reaction between a typical fuel (here C_2H_4) and O_2 , following Du and Axelbaum (1995). Mixture fraction Z is a scalar between 0 and 1 and is defined for ethylene/oxygen systems as

$$Z = [(24/7)Y_{C_2H_4} - Y_{O_2} + Y_{O_2,0}]/[(24/7)Y_{C_2H_4,O} + Y_{O_2,0}]$$
(2)

where Y denotes mass fraction and subscript 0 denotes conditions in the supply gas (Kuo, 1986; Williams, 1985). With the Burke–Schumann assumptions, $Y_{C_2H_4}$ and Y_{O_2} are linear in Z on the fuel and oxidizer side of the flame, respectively. The mass fractions of carbon atoms and oxygen atoms (Y_C and Y_O) and temperature also are linear in Z. Note that the Burke–Schumann assumptions are used only for clarity, and the essential issues are not dependent on the assumptions of the Burke–Schumann model. Equation (2) leads to the following equation for Z_{st} for ethylene/oxygen systems:

$$Z_{\rm st} = \left[1 + (24/7) Y_{\rm C_2H_4,O} / Y_{\rm O_2,0}\right]^{-1} = \left[1 + 3X_{\rm C_2H_4,O} (1/7 + 1/X_{\rm O_2,0})\right]^{-1} \quad (3)$$

where X is mole fraction.

The above model is employed in Figure 1 to explain the role of local C/O and temperature T in unstrained nonpremixed flames. Figure 1 depicts two diffusion flames, both with $Z_{st} = 0.226$ (and thus the same relationship between C/O and Z) but with dramatically different adiabatic flame temperatures, T_{ad} , owing to different amounts of inert in the flames. For the purpose of discussion, we assume here that $T_c = 1250$ K and $(C/O)_c = 1$. Consider first a flame of undiluted C_2H_4 and O_2 indicated



Figure 1. Effect of adiabatic flame temperature on regions suitable for soot formation in mixture-fraction space. The shaded region indicates the region of potential soot inception for the high-temperature flame (dotted line). Such a region does not exist for the low-temperature flame (dashed line).

by the dotted line. As shown by the shading, a broad region exists where both T > 1250 K and C/O > 1; this region is expected to form soot given sufficient residence time. Consider next the diluted flame in Figure 1, shown by the dashed line, where both ethylene and oxygen have been diluted with nitrogen such that Z_{st} is unchanged but T_{ad} has been reduced until C/O is unity precisely where the local temperature is 1250 K. Note that the C/O profiles are the same for the two flames but the structures of the flames vis-à-vis temperature and C/O are very different. In fact, the diluted flame (dashed line) characterizes a flame at the sooting limit because the region where both C/O and temperature are above their critical values is infinitely thin. In other words, throughout this flame either the kinetics of soot inception are too slow (since T < 1250 K) or the oxygen content is sufficiently high that the carbon is tied up in the gas phase (C/O < 1). Despite considerable simplifications, these concepts are helpful in interpreting the experimental results that follow. Of course, the underlying assumption for using C/O as an indicator of sooting limits in nonpremixed systems is that one need not differentiate between the various species containing oxygen and carbon. The justification for such an assumption will be discussed in the results section.

Burner-stabilized spherical microgravity flames are employed in this work for two main reasons. First, this configuration offers unrestricted control over convection direction. Second, in steady state these flames are strain-free and thus can yield intrinsic sooting limits in diffusion flames, similar to the way past work in premixed flames has provided intrinsic values of C/O associated with soot-inception limits.

The emphasis of this work is not soot growth or soot oxidation but rather soot-particle inception, which is far less dependent on convection direction because it involves only gas-phase chemistry. Nevertheless, the role of convection direction will be considered in this work and as noted earlier is one motivation for the present choice of spherical geometry. Convection direction affects soot growth and oxidation because soot kinetics are relatively slow, and soot particles typically follow the flow field. For inverse flames, where oxidizer flows toward fuel, soot particles are formed near the flame sheet and grow as they are transported into richer regions. The rapid falloff in temperature and the high activation energy of soot chemistry confines particle inception to regions near the flame sheet, as has been observed in counterflow flames whose convection direction at the flame sheet is toward the fuel (Kennedy, 1987). When instead the direction of convection is from fuel to oxidizer, soot particles that form are transported into leaner conditions where soot oxidation can occur. This resembles what happens along the centerline of a normal coflow flame where soot particles form and are convected through the flame tip into the oxidizer. Kang et al. (1997) and Hwang and Chung (2001) used the terms soot formation flame and soot formation-oxidation flame to differentiate between the two convection directions.

EXPERIMENTAL

The present experiments were conducted in microgravity in the NASA Glenn 2.2-s drop tower. The experimental apparatus is described in detail by Sunderland et al. (2003). As before, the burner is a 6.4-mm-diameter

porous stainless-steel sphere. All tests were conducted in quiescent ambient gas at 295 K and 0.98 bar (with an estimated uncertainty of ± 0.005 bar), and ignition was performed in microgravity following 2 s of flow in normal gravity.

The present tests employed three gases: ethylene, nitrogen, and oxygen. Purity of ethylene was 99.9% while that of nitrogen and oxygen was 99.999%. Gas mixtures were prepared by partial-pressure mixing and had an estimated composition uncertainty of ± 0.001 mole fraction. Burner flow rates were established prior to ignition using the mass flowmeter calibration in conjunction with gas-correction factors K_i (0.6, 1, and 1 for C₂H₄, O₂, and N₂, respectively) and the following relationship:

Indicated/Actual flow rate =
$$1/K_{\text{mix}} = \sum_{i=1}^{2} X_i/K_i$$
 (4)

The flow rates were verified with a soap bubble meter. Uncertainties in the flow rates are estimated at $\pm 10\%$. Burner flow rates were selected such that all flames involved a steady-state ethylene consumption rate of 1.51 mg/s assuming complete combustion, which indicates a heat release rate of 71 W for all flames (based on a lower heating value of ethylene of 47,158 J/g).

The flames were imaged using a color CCD camera with a 16-mm manual-iris lens at f 1.4–4. Spatial resolution was 0.3 mm. Experiments have confirmed that the onset of visible yellow emissions is an effective means of determining soot-inception limits in hydrocarbon flames (Du et al., 1988; Haynes and Wagner, 1981), and normal-gravity flame testing has confirmed that the present video system is nearly as sensitive as the naked eye to the presence of soot in flames. Sooting limit conditions were defined as conditions for which yellow luminosity was visible at the drop end but for which a small reduction in $X_{C_2H_{4,0}}$ or $X_{O_{2,0}}$ yielded flames devoid of yellow.

Flame diameter d_f and sphericity (both at drop termination) were measured based on the contours of peak blue emission in the video record. Flame diameter was determined by averaging the longest chord through each flame and its perpendicular chord. Sphericity was defined as the ratio of the minimum to maximum distance from the burner center to the blue flame sheet. Test-to-test repeatability of d_f and sphericity was about $\pm 2\%$. Total radiative emission was measured with a thermopile radiometer but is reported only qualitatively here. Adiabatic flame temperatures were calculated using Chemical Equilibrium with Applications (CEA; McBride and Gordon, 1996), neglecting radiation and transient conduction losses to the burner. Uncertainties in $Z_{\rm st}$ and $T_{\rm ad}$ arise from uncertainties in gas compositions and are estimated at ± 0.001 and ± 5 K, respectively.

Residence time is characterized here by the time required for a parcel of gas to convect from the burner surface to the flame sheet. Spherical flames with short residence times (ca. 10 ms or less) encounter hydrodynamic suppression of soot akin to that observed in counterflow flames. Flames with long residence times (ca. 0.5 s or more) are unlikely to reach steady conditions within 2.2 s and have large radiative losses. To evaluate these concerns we introduce here a characteristic residence time, $t_{\rm res}$, defined as the mass of gas contained between the flame and the burner surface divided by the burner mass flow rate. It is assumed that the flame is a stationary sphere of diameter $d_{\rm f}$. The gas within the flame is assumed to have the same molecular weight as the burner effluent and an average temperature of $(T_{ad} + 295 \text{ K})/2$. With this definition, t_{res} is biased toward low values for expanding flames, owing to gas accumulation (as with fuelvapor accumulation in droplet studies). Despite these simplifications, $t_{\rm res}$ is estimated to agree within $\pm 30\%$ of the actual convection time for the present flames and is adequate for the interpretations that follow.

RESULTS AND DISCUSSION

The general behavior of the present flames resembles that described by Sunderland et al. (2003), although here only flames near sooting limits are considered. The diameters and total radiative emissions increased throughout the 2.2-s drops for all flames, and when yellow emission was observed its intensity decreased with time. Exchanging N₂ from the ambient gas to the burner effluent at constant $T_{\rm ad}$ decreased the flame size, sphericity (owing to flow nonuniformity generated by the porous burner), and the characteristic time to reach steady state and increased the peak brightness.

Four representative flames at or near their sooting limits are shown in Figure 2. These flames represent both convection toward oxidizer (normal flames) and convection toward fuel (inverse flames). The flames of Figures 2b and 2d are considered here to be at the experimental sooting limits since a small reduction in reactant concentration yields blue



Figure 2. Images of representative flames below the sooting limits (a and c) and at the sooting limits (b and d) for convection toward oxidizer (a and b) and convection toward fuel (c and d). Flames (b) and (d) correspond to flames 5 and 17, respectively, in Table 1. Images were taken just before drop termination. (See Color Plate 1 at the end of this issue).

conditions. Note that soot, when present, appears inside the flame sheet for normal flames and outside for inverse flames.

Seventeen sooting limits have been identified as summarized in Table 1. Both normal and inverse flames are represented in Table 1, and a wide range of reactant mole fractions, $Z_{\rm st}$, and $T_{\rm ad}$ were obtained at the sooting limits. The variation in burner effluent mass flow rate, $m_{\rm b}$, is required to match ethylene consumption rates for all flames. Also tabulated are measured $d_{\rm f}$ and calculated $t_{\rm res}$. Adiabatic flame temperature is used in this work as a surrogate for measured peak temperature owing to the prohibitive number of tests required for thermocouple measurements of peak temperature (Sunderland et al., 2003). The implications of

295K and	d 0.98 bar							
Flame	Environment	$X_{\mathrm{C_2H_4,0}}$	$X_{O_2,0}$	$Z_{ m st}$	$T_{ m ad}, { m K}$	$m_{ m b}, { m mg/s}$	$d_{ m f}, { m mm}$	$t_{ m res},{ m s}$
1	Oxidizer	1	0.22 ± 0.02	0.065 ± 0.004	2390 ± 63	1.51	28.8 ± 2.7	2.06 ± 0.62
2	Oxidizer	0.6	0.21 ± 0.01	0.102 ± 0.004	2326 ± 44	2.52	30 ± 1	1.44 ± 0.17
3	Oxidizer	0.31	0.21 ± 0.01	0.18 ± 0.007	2226 ± 43	4.87	33 ± 1.7	1.03 ± 0.21
4	Oxidizer	0.25	0.23 ± 0.02	0.225 ± 0.011	2238 ± 56	6.03	33.4 ± 2.8	0.86 ± 0.243
5	Oxidizer	0.18	0.28	0.333	2306	8.38	29.9	0.429
9	Oxidizer	0.17	0.29	0.353	2308	8.87	29.3	0.383
7	Oxidizer	0.11	0.5	0.586	2381	13.7	22.5	0.107
8	Oxidizer	0.11	0.8	0.685	2528	13.7	16.4	0.038
9	Oxidizer	0.15	1	0.661	2740	10.1	11.6	0.015
10	Fuel	1	0.13	0.041	1847	35.4	17.5	0.024
11	Fuel	0.8	0.13	0.051	1835	35.4	20.3	0.039
12	Fuel	0.6	0.13	0.066	1814	35.4	21.8	0.049
13	Fuel	0.21	0.25	0.277	2274	18.7	29.6	0.196
14	Fuel	0.19	0.3	0.336	2370	15.7	28.3	0.197
15	Fuel	0.15	0.5	0.509	2539	9.69	27.5	0.283
16	Fuel	0.12	0.8	0.666	2578	6.3	25.9	0.374
17	Fuel	0.13	1	0.692	2670	5.17	25	0.406

Table 1. Sooting limit conditions for burner-stabilized spherical nonpremixed flames in microgravity. Ambient temperature and pressure are

radiative heat loss (i.e., nonadiabatic flames) on the conclusions will be addressed.

The sooting limits for flames 1–4 are specified by ranges, rather than specific values, because for these flames it was difficult to determine whether the yellow luminosity was from soot that was being produced at the drop end or instead was from soot formed early on but trapped by thermophoresis inside the flame sheet. Flames 5–17 did not suffer from this ambiguity; they were distinctly yellow at the drop end and for these flames a decrease in fuel or oxygen mole fraction of just 0.01 produced blue flames at drop end.

As Figure 2 reveals, the flames were not perfectly round. The present flames had an average sphericity (defined earlier) of 0.77. The lowest sphericities (0.50–0.65) were for flames 10–13 and no other flames had sphericities below 0.75. For reference, the flames of Figure 2 have sphericities of 0.84–0.87. Imperfect sphericities are not expected to affect the present sooting limits because an increase of 0.01 reactant mole fraction above each sooting limit flame yielded a flame at drop termination that had soot along its entire perimeter.

The sooting limits of Table 1 are presented in Figure 3 in a plot of O_2 mole fraction in the oxidizer versus C_2H_4 mole fraction in the fuel. Included here are the 17 sooting limits of Table 1. Error bars are included for flames 1-4 owing to the ambiguities described earlier. The present spherical flames allow a boundary to be identified between conditions where soot cannot form in unstrained, long-residence-time flames (also called permanently blue flames) and conditions where soot can form given sufficient residence time. Such a boundary cannot be identified conclusively in normal-gravity studies owing to the unavailability of unstrained one-dimensional flows with long residence times. This boundary is identified by the solid curve, determined from a correlation that will be explained. The dashed curves are T_{ad} isotherms, determined with the equilibrium code CEA. As expected, there is a monotonic relationship at the sooting limits between $X_{O_2,0}$ and $X_{C_2H_4,0}$. Neglecting flames 1–4 (see discussion to follow) we find that, within experimental uncertainties, convection direction does not have an impact on the sooting limits.

Figure 3 also includes sooting limits measured in normal-gravity counterflow C_2H_4 flames in three previous studies. Du and Axelbaum (1995) considered flames using 11-mm gas jets separated by 8 mm at various strain rates. Lin and Faeth (1996) used a similar burner and



Figure 3. Sooting limits plotted as oxygen mole fraction versus ethylene mole fraction in the supply gases for the present flames and for published normal-gravity flames.

similar strain rates. For both studies, the flames with measured strain rates of 70 s^{-1} are included here. Hwang and Chung (2001) considered C_2H_4 flames in a counterflow apparatus with 14.2-mm fuel and oxidizer jets separated by 14.2 mm and a fixed global strain rate of 27 s^{-1} . The data of Du and Axelbaum (1995), Lin and Faeth (1996), and Hwang and Chung (2001) all fall on the sooting side of the boundary curve identified in the present microgravity measurements. This is attributed to the strained conditions of the counterflow flames. Hwang and Chungs (2001) data have their greatest deviation into the sooting region at high $X_{O_2,0}$, probably because these flames have higher velocities in the soot-inception region than do the other counterflow flames shown.

SOOTING LIMITS OF SPHERICAL DIFFUSION FLAMES

Further insight can be gained by plotting the present sooting limit data in terms of T_{ad} versus Z_{st} , as motivated by the following simplified model. Recall in Figure 1 that (C/O)_c and T_c were used to identify where soot can and cannot form in unstrained nonpremixed flames. In other words, if (C/O)_c occurs at the same location as T_c on the fuel side, conditions suitable for soot formation are infinitely thin, indicating a sooting limit given sufficient residence time. Employing the Burke–Schumann assumptions, Y_C , Y_O and T are linear in Z, as in Figure 1, yielding for any fuel and oxidizer

$$C/O = (4/3)Y_C/Y_O = (4/3)(Y_{C,0}/Y_{O,0})Z/(1-Z)$$
(5)

and, on the fuel side,

$$(T_{\rm ad} - T_0)/(T - T_0) = (1 - Z_{\rm st})/(1 - Z)$$
(6)

Equation (3) yields, for ethylene/oxygen systems,

$$Z_{\rm st} = (1 + 4Y_{\rm C,0}/Y_{\rm O,0})^{-1} \tag{7}$$

Combining Eqs. (5)–(7) and replacing T with T_c and C/O with (C/O)_c yields

$$(T_{\rm ad} - T_0)/(T_{\rm c} - T_0) = 1 + Z_{\rm st}[3({\rm C/O})_{\rm c} - 1]$$
 (8)

Under the assumption that T_c and $(C/O)_c$ are constants, Eq. (8) predicts a linear relationship between Z_{st} and T_{ad} at the sooting limits. For example, inserting $T_0 = 300$ K, $T_c = 1250$ K, and $(C/O)_c = 1$ yields

$$T_{\rm ad} \ (K) = 1900 Z_{\rm st} + 1250 \tag{9}$$

This linear relationship is illustrated in Figure 4. This plot shows two flames, one at low and the other at high Z_{st} , where each are at their respective sooting limits (i.e., where C/O = 1 coincides with T = 1250 K). The T_{ad} of these two flames are on the line described by Eq. (9), as shown in the figure. Figure 4 predicts the observed trends that sooting-limit flames will have a dramatically higher T_{ad} at high Z_{st} . Of course, this analysis assumes that the critical temperature is a true limiting condition, which is true only for the conditions at which this temperature was



Figure 4. Effect of Z_{st} on sooting limits in the Burke–Schumann approximation.

determined (Dobbins, 2002). Nonetheless, the simplicity of the model and, as will be shown, its consistency with the experiments suggest that the concepts are valid.

Motivated by this analysis, the data in Figure 3 are plotted in Figure 5 in terms of Z_{st} versus T_{ad} , again defining a region of permanently blue conditions. Here again, error bars are included for flames 1–4. Flames 1–4 have the longest t_{res} of the present flames (see Table 1), all in excess of 0.5 s, indicating that these flames cannot reach steady conditions in 2.2 s. Such conditions also are associated with large gas-phase radiative losses, leading to a large reduction of actual peak temperature below T_{ad} . This is confirmed by past measurements (Sunderland et al., 2003), which found that a flame similar to flame 1 had a peak temperature that was reduced 970 K from its T_{ad} , whereas flames with shorter t_{res} had much smaller reductions. Owing to their long residence times, flames 1–4 are excluded from the data correlation in Figure 5.



Figure 5. Sooting limits plotted as adiabatic flame temperature versus stoichiometric mixture fraction for the present flames and for published normal-gravity flames. The ordinate symbol v_{N_2} is associated with the stoichiometry of $C_2H_4 + 3O_2 + v_{N_2}N_2 \rightarrow \text{products}$, and corresponds to T_{ad} as shown.

Figure 5 allows the data to be correlated with a least-squares fit, yielding

$$T_{\rm ad} \ (K) = 1198 \, Z_{\rm st} + 1838 \tag{10}$$

as shown. This correlation also is included as the solid curve in Figure 3, where the mapping from the axes of Figure 5 to those of Figure 3 was done using CEA. A comparison of this correlation and Eq. (8) reveals measured soot formation thresholds of $T_c = 1838$ K and $(C/O)_c = 0.59$. Given the approximations of the theory and recognizing that the predicted T_c assumes adiabatic flames, there is remarkable agreement between these values and previous directly measured values of T_c in

diffusion flames and $(C/O)_c$ in premixed flames. T_c has been measured in diffusion flames by many investigators and has been found to have values in the range 1250–1650 K (Dobbins, 2002; Glassman, 1988, 1998; Santoro et al., 1987; Sunderland and Faeth, 1996). In premixed flames the measured $(C/O)_c$ is about 0.6 for ethylene (Glassman, 1988; Harris et al., 1986; Haynes and Wagner, 1981; Takahashi, 1997; Takahashi and Glassman, 1984). The slope of the line fit in Figure 5 reveals the profound effect of Z_{st} on sooting limits, accounting for a variation in T_{ad} at the sooting limits of about 700 K.

Figure 5 shows that convection direction has no measurable effect on the sooting limits of the present flames. The development of Eq. (8) and Figures 1 and 4 was possible with no allowance for hydrodynamics other than requiring sufficient residence time. Although soot formation can be suppressed by decreasing residence time (or increasing strain rate), the present flames have residence times that are longer than those of past counterflow flames. This is supported by the $t_{\rm res}$ values in Table 1, where only flame 9 approaches the soot-inception time range reported by Tesner and Shurupov (1993). Incidentally, this short time could explain why flame 9 resides above the line fit in Figure 5, just as do the normal-gravity sooting limit flames.

The normal-gravity sooting limit flames in Figure 3 also are included in Figure 5. Once again, conditions identified as sooting limits in normalgravity tests yield yellow flames in the spherical configuration. This is attributed to the intrusion of strain in the normal-gravity tests. We note that the closest agreement between the data of Hwang and Chung (2001) and the present sooting limits is near $Z_{st} = 0.46$ (Figure 5). For this value of Z_{st} , soot inception occurs near the stagnation plane of the counterflow flame and residence times are their longest.

Figure 4 indicates that different mechanisms are responsible for sooting limits at low and high Z_{st} . The adiabatic flame temperature for the low Z_{st} sooting-limit flame in Figure 4 is close to T_c . Thus, when inert is added to a fuel/air flame, a sooting limit is obtained when temperature becomes so low that the kinetics of soot inception are too slow to produce soot. On the other hand, the flame with high Z_{st} has low C/O far into the fuel side of the flame. For this flame, soot-free conditions can be attained at much higher temperatures because there is sufficient oxygen on the fuel side of the flame to favor oxidation of light hydrocarbons over formation of soot precursors. C/O is higher farther into the fuel-rich region, but there the temperature is too low for soot inception to occur. For C/O to be an appropriate indicator of soot inception requires that the speciation of the carbon and oxygen is of secondary importance. In other words, there is a quasi equilibrium for those species that are important to the soot-inception pathway. We have already noted that CO_2 has been shown to chemically suppress soot inception, and so it is reasonable to expect that the kinetics for CO_2 /precursor chemistry is sufficiently fast. For example, $CO_2 + H \rightarrow CO + OH$ produces hydroxyl radicals that can attack the small hydrocarbons, like C_2H_3 , that are important to soot inception. Furthermore, the thermodynamics of $C_2H_3 + CO_2 \rightarrow C_2H_3O + CO$ strongly favors the forward reaction. Since the residence times in the present flames are long, the quasi-equilibrium assumption appears to be valid, thus making C/O an effective parameter for characterizing soot inception.

The present flames are limited by the 2.2-s test times and, while heat release rate was held constant, the flames had different sizes and residence times. The flames can be affected by transient size, imperfect sphericity, burner heating, radiation, and thermophoresis. For flames with characteristic residence times below 0.5 s, effects of transient flame development, including that due to reactant accumulation (King, 1996; Tse et al., 2001) and gas-phase radiation (Atreya and Agrawal, 1998; Tse et al., 2001), are expected to be small. For the other four flames, these effects could be significant. These limitations are not expected to impact the major conclusions of this work.

CONCLUSIONS

Sooting limits were studied in spherical microgravity diffusion flames reacting ethylene and oxygen at various levels of dilution. Unlike past measurements of limits in normal gravity, the present configuration involves unstrained flames and allows independent variation of Z_{st} and convection direction. The major conclusions are as follows:

1. Increased Z_{st} favored soot-free conditions, accounting for an increase of about 700 K in the sooting limit T_{ad} . An increase in Z_{st} at fixed T_{ad} led to a reduction in C/O in the high-temperature zone on the fuel side. We propose that this favors permanently blue conditions as a result of competition between oxidation of light hydrocarbons and formation of soot precursors similar to the competition that exists in premixed flames.

- 2. Sooting limits for the present flames were successfully correlated as a linear relationship between Z_{st} and T_{ad} . This relationship is predicted by the Burke–Schumann approximation and the hypothesis that soot inception requires local conditions where both temperature and C/O are above their critical values.
- 3. Convection direction had no systematic effect on the observed sooting limits. This is consistent with the preceding hypothesis.
- 4. Previous sooting limits from normal-gravity counterflow tests were found to correspond to conditions that were yellow in the spherical configuration. This is attributed to the intrusion of strain in the counterflow arrangement.
- 5 Different mechanisms are responsible for sooting limits at low and high Z_{st} . In the standard fuel/air flame (low Z_{st}), a limit is attained by reducing the temperature until the kinetics of soot inception are too slow to produce soot. On the other hand, at high Z_{st} the limit is attained because the amount of oxygen on the fuel side of the flame is sufficient to tie up the carbon in the gas phase and prevent soot formation. Farther into the fuel-rich region, where the amount of oxygen is reduced, the temperature is too low for soot to form.

REFERENCES

- Atreya, A. and Agrawal, S. (1998) Effect of radiative heat loss on diffusion flames in quiescent microgravity atmosphere. *Combust. Flame*, **115**, 372.
- Baukal, C.E. (1998) Oxygen-Enhanced Combustion, Baukal, C.E. (Ed.). CRC Press, Boca Raton, FL, pp. 1–45.
- Dobbins, R.A. (2002) Soot inception temperature and the carbonization rate of precursor particles. *Combust. Flame*, 130, 204.
- Du, D.X., Axelbaum, R.L., and Law, C.K. (1988) Experiments on the Sooting Limits of Aerodynamically-Strained Diffusion Flames, Proc. Combust. Instit., 22, 387.
- Du, D.X., Axelbaum, R.L., and Law, C.K. (1990) The Influence of Carbon Dioxide and Oxygen as Additives on Soot Formation in Diffusion Flames, *Proc. Combust. Instit.*, 23, 1501.
- Du, D.X., Axelbaum, R.L., and Law, C.K. (1995) Soot formation in strained diffusion flames with gaseous additives. *Combust. Flame*, **102**, 11.
- Du, J. and Axelbaum, R.L. (1995) The effect of flame structure on soot-particle inception in diffusion flames. *Combust. Flame*, 100, 367.
- Glassman, I. (1988) Soot Formation in Combustion Processes, Proc. Combust. Instit., 22, 295.

- Glassman, I. (1998) Sooting Laminar Diffusion Flames: Effect of Dilution, Additives, Pressure, and Microgravity, *Proc. Combust. Instit.*, **27**, 1589.
- Harris, M.M., King, G.B., and Laurendeau, N.M. (1986) Influence of temperature and hydroxyl concentration on incipient soot formation in premixed flames. *Combust. Flame*, 64, 99.
- Haynes, B.S. and Wagner, H.Gg. (1981) Soot formation. Prog. Energy Combust. Sci., 7, 229.
- Hwang, J.Y. and Chung, S.H. (2001) Growth of soot particles in counterflow diffusion flames of ethylene. *Combust. Flame*, **125**, 752.
- Kang, K.T., Hwang, J.Y., Chung, S.H., and Lee, W. (1997) Soot zone structure and sooting limit in diffusion flames: Comparison of counterflow and co-flow flames. *Combust. Flame*, **109**, 266.
- Kaplan, C.R. and Kailasanath, K. (2001) Flow-field effects on soot formation in normal and inverse methane-air diffusion flames. *Combust. Flame*, **124**, 275.
- Kennedy, I.M. (1987) The evolution of a soot aerosol in a counterflow diffusion flame. *Combust. Flame*, **68**, 1.
- King, M.K. (1996) An Unsteady-State Analysis of Porous Sphere and Droplet Fuel Combustion under Microgravity Conditions, *Proc. Combust. Instit.*, 26, 1227.
- Klara, S.M. and Srivastava, R.D. (2002) U.S. DOE integrated collaborative technology development program for CO₂ separation and capture. *Environ. Prog.*, **21**(4), 247.
- Kuo, K.K. (1986) Principles of Combustion, Wiley, New York, p. 35.
- Lin, K.-C. and Faeth, G.M. (1996) Effects of hydrodynamics on soot formation in laminar opposed-jet diffusion flames. J. Propul. Power, 12, 691.
- Liu, F., Guo, H., Smallwood, G.J., and Gülder, Ö.L. (2001) The chemical effects of carbon dioxide as an additive in an ethylene diffusion flame: Implications for soot and NO_x formation. *Combust. Flame*, **125**, 778.
- Markatou, P., Wang, H., and Frenklach, M. (1993) A computational study of sooting limits in laminar premixed flames of ethane, ethylene, and acetylene. *Combust. Flame*, 93, 467.
- McBride, B.J. and Gordon, S. (1996) Computer Program for Calculation of Complex Chemical Equilibrium Compositions and Applications. NASA RP-1311-P2, Cleveland, OH.
- Santoro, R.J., Yeh, T.T., Horvath, J.J., and Semerjian, H.G. (1987) The transport and growth of soot particles in laminar diffusion flames. *Combust. Sci. Technol.*, 53, 89.
- Sugiyama, G. (1994) Nonluminous Diffusion Flame of Diluted Acetylene in Oxygen-Enriched Air, Proc. Combust. Instit., 25, 601.
- Sunderland, P.B. and Faeth, G.M. (1996) Soot formation in hydrocarbon air laminar jet diffusion flames. *Combust. Flame*, **105**, 132.

- Sunderland, P.B., Axelbaum, R.L., Urban, D.L., Chao, B.H., and Liu, S. (2003) Effects of structure and hydrodynamics on the sooting behavior of spherical microgravity diffusion flames. *Combust. Flame*, **132**, 25.
- Takahashi, F. (1997) Sooting correlations for premixed combustion. In Dryer, F.L. and Sawyer, R.F. (Eds.). *Physical and Chemical Aspects of Combustion:* A Tribute to Irvin Glassman, Gordon and Breach, Amsterdam, pp. 161–187.
- Takahashi, F. and Glassman, I. (1984) Sooting correlations for premixed flames. *Combust. Sci. Technol.*, **37**, 1.
- Tesner, P.A. and Shurupov, S.V. (1993) Soot formation from acetylene-benzene mixture. *Combust. Sci. Technol.*, 92, 71.
- Tse, S.D., Zhu, D., Sung, C.-J., Ju, Y., and Law, C.K. (2001) Microgravity burner-generated spherical diffusion flames: Experiment and computation. *Combust. Flame* **125**, 1265.
- Urban, D.L. and Faeth, G.M. (2001) Soot Research in Combustion Science: Introduction and Review of Current Work. 39th AIAA Meeting, January 8–11, Reno, NV, AIAA 2001–0332.
- Williams, F.A. (1985) Combustion Theory, Benjamin/Cummings, Menlo Park, CA, p. 75.