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COMMENT AND REPLY

Comment on Sooting Correlations for Premixed Flames

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by

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In a study of 21 fuels, Takahashi and Glassman (1984) find that the sooting tendency of a premixed flame depends on the flame temperature, the number of carbon atoms in the fuel molecule and the C/H ratio of the fuel. They find that the structure of the fuel molecule has no significant effect on the sooting tendency. (Takahashi and Glassman use the term structure in reference to any aspect of the fuel structure not included in the number of carbon atoms per molecule and in the C/H ratio, such as isomerism or aromaticity.) We question the validity of this last conclusion.

In Takahashi and Glassman's experiment critical equivalence ratios are measured using a Bunsen-type burner in which the flame temperature is controlled by adding varying amounts of nitrogen to the fuel–oxygen premix. The results of this experiment are summarized in a plot of the critical effective equivalence ratios for each fuel (ψ_c) vs. adiabatic flame temperature. This is Figure 4 of their paper. In this plot Takahashi and Glassman point out the similar sooting tendencies of three pairs of isomers (2-methylpropane and butane, 2-methylpropene and 1-butene, and cyclohexane and 1-hexene). Their conclusion that no structural effect is evident among the sooting tendencies of branched and straight chain aliphatics and alicyclics rests on these three cases.

In Figure 8 of their paper Takahashi and Glassman plot the critical equivalence ratios (ψ_c) of their fuels against the number of C—C bonds in the fuel molecule. (The number of C—C bonds is determined by counting a double bond as two and a triple bond as three.) The temperature dependency of ψ_c is removed by interpolating or extrapolating each ψ_c to a common adiabatic flame temperature of 2200 K. In this plot Takahashi and Glassman observe that "surprisingly, all data, even those for the aromatics, lie on a single curve." This observation leads them to extend their previous conclusion about the unimportance of fuel structure to all hydrocarbons (including *aromatics*). It also leads them to suggest that the number of C—C bonds successfully combines the carbon number and C/H ratio effects on sooting tendency, making it the sole factor (other than flame temperature) on which the sooting tendency (in a premixed flame) depends.

The first point we would make is that compared to the number of C—C bonds effect, the temperature effect on the sooting tendency is weak. This can be seen in comparing plots of ψ_c at a fixed temperature vs. number of C—C bonds and of ψ_c for fuel-air flames (temperature not fixed) vs. number of C—C bonds. This is Figure 1 of our comment. In this plot the open symbols represent the fixed temperature case (these data are from Figure 8 of Takahashi and Glassman, 1984) and the solid symbols represent the varying temperature case (these data are from Table I of Takahashi and Glassman, 1984). The vertical distances between the open and solid points represent the effect of temperature differences (400 K in the case of ethane and 200 K in the case of 1-methylnaphthalene).

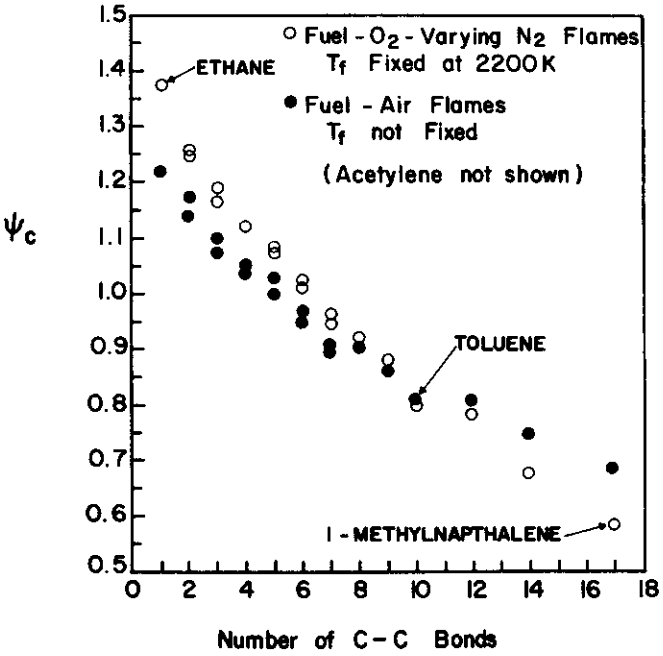

FIGURE 1 Critical equivalence ratio (ψ_c) vs. number of C—C bonds. The open symbols represent fuel-O_2-N_2 flames at a fixed adiabatic flame temperature of 2200 K. The solid symbols represent fuel-air flames. These data are from Takahashi and Glassman (1984).

In reality Figure 1 overestimates the temperature effect. Harris *et al.* (1985) and Olson and Madronich (1985) point out that nitrogen directly affects the sooting tendency of a premixed flame through dilution of the hydroxyl radical (*i.e.*, increasing $[N_2]$ at a fixed temperature decreases ψ_c).

Considering Figure 1, the open symbols to the left of toluene represent lower nitrogen content flames than do the solid symbols. These open symbols will shift downward if, at constant temperature, the nitrogen contents of their flames could be made the same as those of the fuel-air flames. The open symbols to the right of toluene represent higher nitrogen content flames then do the solid symbols. These open symbols would shift upward when, at constant temperatures the nitrogen contents of their flames are made the same as those of the fuel-air flames. This shifting will be in proportion to the distance from toluene.

Thus, as the fuel-air flames of Figure 1 show, the number of C—C bonds appears to be a useful parameter in determining the sooting tendency even if the flame temperature is not held constant. In view of this fact, we are led to wonder if Takahashi and Glassman's number of C—C bonds correlation could be used to obtain useful information from previous, more extensive measurements of critical equivalence ratios for which no temperature information is available. One such study is that of Olson and Pickens (1984). In their paper they report the critical equivalence ratios of 55 fuels in premixed fuel-air flames. Their burner differs greatly from that of Takahashi and Glassman so it is not surprising that their measured values of ψ_c are different.

The data of Olson and Pickens are plotted in Figure 2 of this comment. Their data which correspond to fuels also studied by Takahashi and Glassman are indicated by the symbol "+". Concentrating only on these points, one again sees, as noted by Takahashi and Glassman, that the sooting tendencies of all the fuels are scattered about a single curve (although the scatter is greater). However, the balance of the data in Figure 2 does not follow the trend established by this curve. In particular, a distinct difference develops at larger values of the number of C—C bonds between the critical equivalence ratios of the aliphatic and the aromatic fuels. This difference suggest that there might be an aliphatic-aromatic structural dependence in the sooting tendencies of fuels.

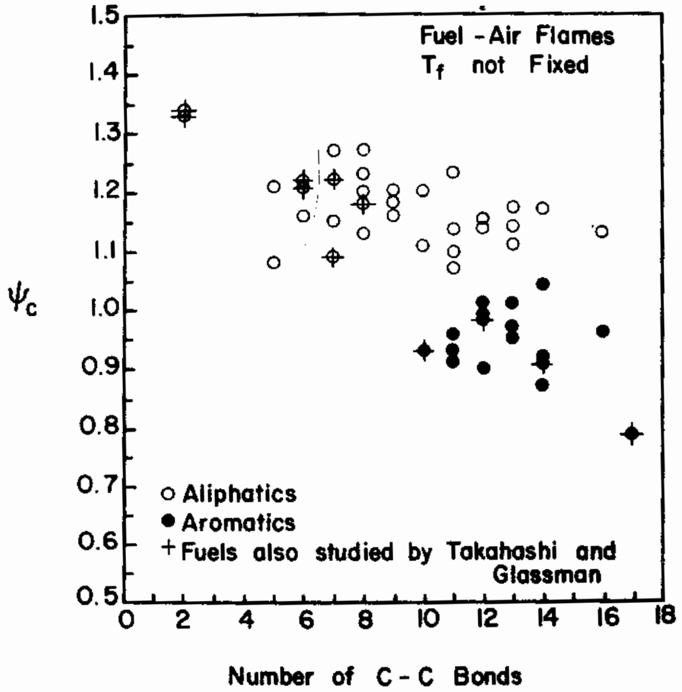

FIGURE 2 Critical equivalence ratio (ψ_c) vs. number of C—C bonds for fuel-air flames. These data are from Olson and Pickens (1984).

It is problematic for Takahashi and Glassman to conclude that there is no difference between aliphatic and aromatic fuels when there is no overlap, in terms of the number of C—C bonds, of these two structure types among the fuels they tested. More experimentation with a greater variety of fuels is needed before judgements about the importance of fuel structure can be made.

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Authors' Reply

Ramer *et al.*'s criticism (1987) on our paper (Takahashi and Glassman, 1984) is welcome since it has given us an opportunity to clarify further the physical insight of the number of C—C bond correlations, leading to more general correlating expressions (Takahashi, 1987). Unfortunately, their comment also includes some misleading statements.

First, we wish to respond in a qualitative sense. Although there is a weak temperature dependence with respect to the critical sooting equivalence ratio, it is important to account for this dependence, or else acetylene would appear to have a lesser tendency to soot than ethylene or ethane. Only when the three C_2 compounds are compared at the same temperature does one obtain the result ψ_c,ethane > ψ_c,ethylene > ψ_c,acetylene, which is consistent with what is known about their rich oxidation steps. Unfortunately the word "surprisingly" should have been omitted from the statement "... surprisingly, all data, even those for aromatics, lie on a single curve" as we developed greater understanding of the mechanism of soot formation in premixed flames immediately after publication of our paper. It is now apparent to use that in premixed flames, soot formation occurs in the post-flame zone where the parent fuel molecule no longer exists, only its rich oxidation products, which are not different in character from those of aliphatic fuels. This concept is supported by the results of Harris and Weiner (1984), who found that toluene addition to an aliphatic fuel showed no effect on soot formation other than that which would result from the increased number of carbon atoms in the fuel.

Now, in more detail, of course, the relatively weak temperature dependence of the sooting limit under premixed conditions has long been known (Hayes and Wagner, 1981), and we did measure the temperature effect systematically for 21 pure fuels (Takahashi and Glassman, 1984) and several mixtures (Takahashi *et al.*, 1984). As Hayes and Wagner (1981) also summarized, by quoting previous results (Millikan, 1962; Millikan and Foss, 1962; Flossdorf and Wagner, 1967), dilution of the combustible mixture at a constant temperature does not have a marked effect on the sooting limit of a particular fuel. Millikan and Foss (1962) measured a critical C/O = 0.71 ($\phi_c = 2.13$, $\psi_c = 1.42$) at 1800 K in the ethylene/oxygen flame, and a value of C/O = 0.60 ($\phi_c = 1.80$, $\psi_c = 1.20$) was found (Millikan, 1962) for the ethylene/air flame at the same temperature. The decrease in the critical value was only about 15 percent, while the nitrogen concentration varied from 0 to 70 percent. This decrease appears to be even smaller at higher temperatures, *e.g.*, estimated as about 7 percent at 2200 K, due to larger temperature dependence of the air flame, as is seen in a replot of these data (Figure 1 in Harris *et al.*, 1986). In our experiment, the nitrogen concentration was varied over a range of 33 percent (from 39 to 72 percent), at most, for ethane and, for the rest of fuels, less than 20 percent, down to a minimum of 4 percent for 1-methylnaphthalene. Consequently, the nitrogen variation over our experimental range would produce roughly a 3 percent difference in the sooting limit, at most for ethane. For most fuels it must be practically negligible, among the order of experimental uncertainties, *i.e.*, typically ±2–3 percent, and at most ±5 percent (Takahashi and Glassman, 1984). Therefore, the variation in the sooting limit by varying the nitrogen content in our experiment can be regarded practically only affecting the flame temperature. Thus, their comment that our results overestimate the temperature effect because of the nitrogen dilution and the subsequent argument on Figure 1 (Ramer *et al.*, 1987) are misleading.

Based on these considerations, they proceeded to apply the number of C—C bond correlations to the fuel/air flame data, in which the flame temperature was uncontrolled. It should be noted, as well, that the flame conditions are quite different for different types of burner systems (Takahashi and Glassman, 1987). Particularly for flat-flame burners, fuel properties may not correctly reflect upon the sooting limit data since the flame temperature depends largely on the gas mixture velocity. One of the authors (Takahashi, 1987) has recently examined the data obtained by various investigators and experimental systems including Bunsen-type burners, flat-flame burners, and well-stirred reactors. In the extension of the concept of the number of C—C bonds that reflects both the fuel pyrolysis rate and the soot precursors oxidation rate, more general expressions of the sooting correlation indices have been formulated including weighting factors for adjusting the effects of these two competing rates. As a result, all data were successfully correlated with these indices, showing no peculiar deviation of the data points for large aliphatics seen in the number of C—C bond plots, smoothly connecting the data points of non-aromatics and aromatics.

It should be emphasized, however, that what is important is the basic concept of the number of C—C bonds we proposed (Takahashi and Glassman, 1984) as a combined index indicating both effects of the fuel pyrolysis and precursors oxidation rates, which has been embraced in the more general expressions. Thus we believe that the number of C—C bonds is the simplest and most useful sooting correlation index, readily known from the number of carbon and hydrogen atoms of the fuel, even though the correlation coefficient is slightly lower than the optimum value obtainable and the discrimination between large aliphatics and aromatics is relatively weak. For the applications which need higher accuracy in estimating the sooting tendency, perhaps the optimum correlation proposed (Takahashi, 1987) including empirical coefficients should be used.

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