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Fuel

Optimized rate expressions for soot oxidation by OH and O_2

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ABSTRACT

The two principal soot oxidizers in flames are the hydroxyl radical (OH) and molecular oxygen (O_2). Many soot oxidation rate expressions exist for these oxidizers, but they have considerable disparity and have not been sufficiently validated. To address this, twelve published experimental studies in diffusion flames, premixed flames, thermogravimetric analyzers, and flow reactors are examined. These are all the known studies that measured all of the following quantities at discrete locations: soot oxidation rate, temperature, OH concentration (if nonzero), and O_2 concentration. This yielded 160 measured soot oxidation rates spanning seven orders of magnitude. Optimized soot oxidation rate expressions for OH and O_2 are developed here by maximizing the coefficient of determination between measured and modeled oxidation rates. Oxidation of soot by OH is found to have a negligible activation energy and a collision efficiency of 0.10. The activation energy for O_2 oxidation of soot is 195 kJ/mol, which is higher than previous models. The new expressions for OH and O_2 match the measurements with a regression coefficient of 0.98, compared to 0.79 for the most widely used models. The optimized models indicate that soot oxidation in flames by OH generally dominates over that by O_2.

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1. Introduction

Soot can be destroyed in flames via oxidation by OH, O_2, O, CO_2, and H_2O [1–3] and by the reversal of soot formation reactions [4–6]. Among these, soot oxidation by OH and O_2 generally dominates soot destruction in flames [7–10] and has been the primary focus of both experimental [8–15] and numerical [4–6,16–19] studies. These oxidation reactions are generally considered to be:

$$C_{soot} + OH \rightarrow CO + products, \quad and \qquad (1)$$
$$C_{soot} + O_2 \rightarrow 2CO + products. \qquad (2)$$
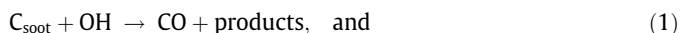
There is considerable disparity and uncertainty in the existing soot oxidation rate models for OH and O_2. Furthermore, none of the models has been systematically compared to a broad set of measurements. Thus motivated, the objective of this study is to develop optimized soot oxidation rate expressions for OH and O_2 using a broad set of published measurements.

1.1. Existing models for soot oxidation by OH

Fenimore and Jones [20] were among the first to recognize the importance of OH as a soot oxidant in flames. They considered a two-stage premixed burner where soot-laden combustion gases from the first stage were mixed with air and burned in the second stage. They reported an OH collision efficiency of η_{OH} = 0.1.

Using a similar apparatus, Neoh and co-workers [9,10] found OH to be the principal soot oxidizer, with η_{OH} = 0.13. Corrections were made for soot oxidation by O_2 using Nagle and Strickland-Constable [21]. The model of Neoh and co-workers [9,10] remains the leading OH model, and has been widely adopted [4–6,19,22].

Soot oxidation by OH has also been observed in diffusion flames, at 0.1–8.0 bar [8,11–15]. Corrections for both growth by hydrocarbons and oxidation by O_2 generally were required, which resulted in the exclusion of many conditions with negative remaining oxidation. These studies reported η_{OH} to be between 0.01 and 0.4.

1.2. Existing models for soot oxidation by O_2

The most widely used model of soot oxidation by O_2 is that of Nagle and Strickland-Constable (NSC) [21]. They measured oxidation rates of heated carbon rods at temperatures of 1000–2000 °C and O_2 partial pressures, p_{O2}, of 0.1–0.6 bar. These conditions bear little resemblance to soot oxidation in flames. Furthermore, the NSC expression is often misused, as the original expression involved a typographical error and unusual units [23]. The NSC model has been incorporated into computational fluid dynamics (CFD) models [19,22].

Another widely used model is that of Lee et al. [24], who observed soot oxidation in a propane–propylene–ethylene diffusion flame confined by a chimney. This model involves an activation energy of $E_A = 164.4$ kJ/mol and is valid for temperatures between 1300 and 1700 K and p_{O2} between 0.05 and 0.1 bar. This model was adopted by Leung et al. [17], albeit with a pre-exponential factor increased by a factor of eight.

A comparison of the O_2 soot oxidation rate predictions of NSC [21] and Lee et al. [24] is shown in Fig. 1 for typical flame conditions. The shaded regions identify the measurement ranges of these studies. The disagreement between models, up to a factor of 20 for these conditions, attests to the uncertainties in the leading soot oxidation models. Soot oxidation rate is generally predicted to increase with increasing p_{O2} or temperature. However, the NSC model [21] has a negative temperature coefficient at low p_{O2} and a decreased slope at high p_{O2}. Neither behavior has been validated for soot oxidation.

In CFD simulations, e.g., Refs. [25–27], a widely used soot oxidation model is that of Appel, Bockhorn, and Frenklach (ABF) [4–6]. ABF includes an Arrhenius form for soot oxidation by O_2 with $E_A = 31.3$ kJ/mol based on the low temperature oxidation of the phenyl radical (C_6H_5) in a shock tube [28]. The ABF soot oxidation rate by O_2 is [4]:

$$\dot{w}_{ox} = 2MW_C\,A_2\exp(-E_{A,2}/R_uT)\chi_{C\cdot}p_{O_2}/(N_AR_uT), \qquad (3)$$

where A_2 and $E_{A,2}$ are the pre-exponential factor and activation energy for Eq. (2); MW_C is molar mass of carbon; p_{O2} units are Pa; N_A is the Avogadro constant; R_u is the universal gas constant; and T is temperature. The active carbon site number density is

$$\chi_{C\cdot} = \frac{k_8[H]\chi_{C-H}}{k_{-8}[H_2] + k_9[H] + k_{10}[C_2H_2] + k_{11}[O_2]}, \qquad (4)$$

where χ_{C-H} is the steady arm-chair site number density; the k are rate coefficients, numbered according to Ref. [4]; and brackets denote concentrations.

A comparison of the ABF [4] soot oxidation rates by O_2 with those of other models requires realistic conditions including temperature, soot surface area, and concentrations of H_2, H, C_2H_2, and O_2. The measurements of flame 1 of Xu et al. [8], fueled by C_2H_2, provide these. The soot oxidation rates by O_2 predicted for this flame by ABF, assuming $\chi_{C-H} = 2.3 \times 10^{19}$ sites/m^2 [4], are

shown as a function of height above burner, z, in Fig. 2. Also shown are the predictions of two past models [21,24] and the present study (discussed below).

The models of Refs. [4,21,24] are not in good agreement for this flame. The ABF model predicts the lowest soot oxidation rates. This is most dramatic low in the flame where C_2H_2 mole fractions are as high as 0.17, reducing the active site density according to Eq. (4). Agreement with other models improves near $z = 50$ mm, where the C_2H_2 mole fraction has decreased to 0.01. The NSC [21] predictions are typically double those of Lee et al. [24] for this flame.

Although conditions in thermogravimetric analyzers (TGAs) and flow reactors are different from those in flames, they allow measurements at lower temperatures, longer residence times, and lower oxidation rates than can be achieved in conventional flames. Several studies have considered the low temperature oxidation of soot by O_2 in a TGA [29–35]. Chan et al. [29] did so at 770–1250 K, augmented with tests similar to those of Lee et al. [24] in the post-flame region, and reported $E_A = 143.5$ kJ/mol. Kalogirou and Samaras [30] observed the oxidation of diesel soot and synthetic soot in a TGA at 800–1000 K and reported $E_A = 161.2$ kJ/mol and a dependence on $p_{O2}^{0.75}$. Sharma et al. [31] observed the oxidation of diesel soot in a TGA at 800–900 K and reported $E_A = 155$ kJ/mol.

Higgins et al. [36] studied the oxidation of soot by O_2 at 1100–1400 K in a flow reactor. Soot mass was determined from soot particle mobility diameters. They reported $E_A = 164$ kJ/mol and a pre-exponential factor that varied with initial particle size by ±35%.

The activation energy for soot oxidation by O_2 is commonly compared with that obtained in coal combustion. Smith [3] reviewed the combustion of coke, char, graphite, and soot from various studies and obtained a mean activation energy of 179.1 kJ/mol. However, most coke or char particles are several orders of magnitude larger than soot primary particles. Soot primary particles, with typical diameters of 30 nm, are small enough that the diffusion of oxidants to the surface is fast and the oxidation process is kinetically controlled [9].

2. Past soot oxidation measurements

The open literature was searched for sufficiently detailed measurements of soot oxidation rates. Only conditions that reported all of these properties for mature soot were admitted: soot
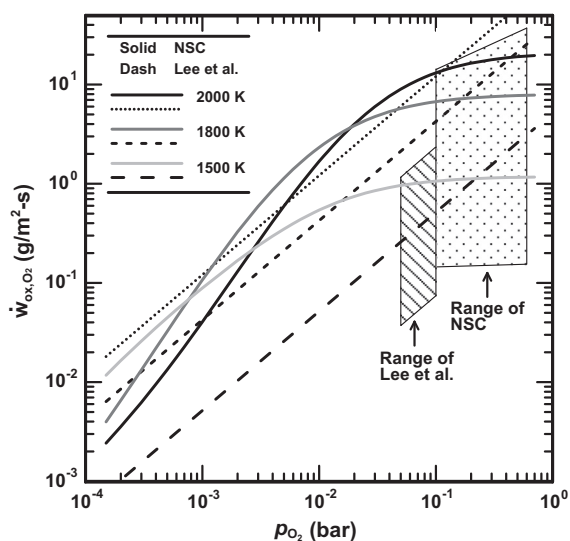

Fig. 1. Predictions of NSC [21], and Lee et al. [24] of soot oxidation rates by O_2 at various conditions. The shaded regions show the measurement ranges.
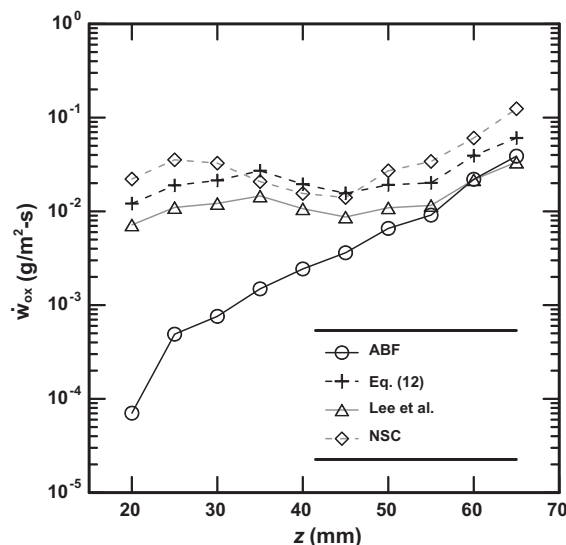

Fig. 2. Predicted soot oxidation rates by O_2 for flame 1 of Ref. [8] using the soot oxidation models of: ABF [4], see Eq. (3); Lee et al. [24]; NSC [21]; and the present model, see Eq. (12).