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Critical Size for the Particle Burn-out of Solid Carbon and/or Boron as the High-Energy-Density Fuel

(Revised)

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1. Introduction

The high-energy-density fuels have attracted particular interests, because of their high gravimetric and/or volumetric heating values, so that extensive research has been conducted, especially for boron [1, 2], besides those utilized in practice. Nonetheless, it is a matter of regret that little has been examined for size effects on their particle burn-out. Indeed, much of the understanding has been based on the quasi-steady analysis of Spalding [3], indicating that burn-out time reduces with decreasing particle size through the d^2-law. Even in R&D of technology-sensitive devices, such as air-breathing rockets [4] and high performance solid-propellants [5], little has been made in selecting appropriate size of the high-energy-density fuels. Furthermore, too much credit has been given to nano-sized particles [5, 6], without any scientific bases for the ignition and/or burn-out.

Here, it is intended to demonstrate an existence of the critical size for the particle burn-out, being exposed directly to oxidizers at high temperatures under which oxide vaporization can be facilitated, with the solid carbon taken as an example. The solid carbon has been chosen because its combustion behavior has been clarified [7, 8], compared to others, by virtue of extensive research for coal/char combustion. An extension for the boron combustion is also conducted.

2. Formulation

The problem of interest is the combustion of a spherical carbon particle (temperature T and radius r) in a quiescent environment (T_∞ and oxidizer mass-fractions $Y_{O,\infty}$, $Y_{P,\infty}$, and $Y_{A,\infty}$ for O_2, CO_2, and H_2O, respectively). Particle temperature is assumed spatially uniform but temporally varying, because of its high thermal conductivity λ, compared to that of gaseous oxidizers [9].

The temporal variations of the particle temperature and size are [10]:

$$\frac{C}{3}R^2\frac{d\tilde{T}}{d\tilde{t}}=\left(\frac{d\tilde{T}}{d\tilde{r}}\right)_s-\tilde{m}(1-C)\left(\tilde{T}_s-\tilde{T}_0\right)+R\left(Q_{s,O}A_{s,O,0}\,\tilde{Y}_{O,s}+Q_{s,P}A_{s,P,0}\tilde{Y}_{P,s}\right.$$

$$\left.+Q_{s,A}A_{s,A,0}\,\tilde{Y}_{A,s}\right)-\frac{\varepsilon R}{Bo}\left(\tilde{T}_s^{\,4}-\tilde{T}_\infty^{\,4}\right), \qquad (1)$$

$$\frac{dR^2}{d\tilde{t}}=-2\tilde{m}\,. \qquad (2)$$

Because of the brief nature of this communication, we shall adhere almost completely to the model definition and nomenclature of Ref. [10]. Only new symbols will be defined. Here, the nondimensional time is defined as $\tilde{t}=\left(\rho_\infty D_\infty t\right)/\left(\rho_C r_{s,0}^2\right)$. Note that whether liquid HC [11] or solid C [10] under an atmospheric pressure, a particle less than 100 μm is too small to support a gas-phase envelop-flame even at elevated temperatures because the characteristic diffusion time, scaled with $r_{s,0}^{\;2}/D_\infty$, becomes too small compared to the characteristic chemical reaction time.

As reported [10], a particle first experiences rapid heating, which is followed by a gradual heating around T_∞. After that, activation of the surface reaction raises the particle temperature further, with exhibiting the d^2-law profile in size history. It is also observed that below the critical particle size, the surface reaction ceases to be activated.

3. Analytical Results

Temperature histories with and without activation of the surface reaction tracks each other at temperatures close to T_∞, until the activation for the former. This is quite similar to that for the spontaneous ignition for gaseous reactive mixtures, studied in the 1930s, so that by conducting the asymptotics with $T_s = T_\infty[1+\epsilon\theta+O(\epsilon^2)]$ and $\epsilon = T_\infty / Ta_{s,O}$, Eq. (1) yields

$$\frac{d\theta}{d\tau} = e^{\theta} - \alpha\theta, \tag{3}$$

where $\tau = t\,\Delta$ and

$$\frac{1}{\Delta} = \frac{2r_{s,0}R}{12B_{s,O}Y_{O,\infty}} \frac{\rho_C}{\rho_\infty} \frac{W_O c_p T_\infty}{W_C q_{s,O}} \frac{C}{1+(C-1)\dfrac{c_p T_\infty}{q_{s,O}}\left(1-\dfrac{T_0}{T_\infty}\right)} \frac{T_\infty}{Ta_{s,O}} \exp\left(\frac{Ta_{s,O}}{T_\infty}\right), \tag{4}$$

with the heat loss parameter

$$\alpha = \frac{12}{(2r_{s,0}R)^2} \frac{1}{\Delta} \frac{\rho_\infty}{\rho_C} D_\infty \left(\frac{\tilde{m}}{\beta} + \frac{2r_{s,0}R}{\rho_\infty D_\infty c_p} 2\varepsilon\sigma_{SB}T_\infty^3 \right) \frac{1}{C}. \tag{5}$$

Equation (3) is well-known one, as explained in textbooks [12, 13]. The critical condition for the "thermal explosion" is also known as $\alpha < e$. Then, we have

$$\left(2r_s\right) > \frac{\left(\tilde{m}/\beta\right)}{\dfrac{eB_{\mathrm{s,O}}Y_{\mathrm{O},\infty}}{D_\infty}\dfrac{W_{\mathrm{C}}q_{\mathrm{s,O}}}{W_{\mathrm{O}}c_pT_\infty}\left\{1+\left(C-1\right)\dfrac{c_pT_\infty}{q_{\mathrm{s,O}}}\left(1-\dfrac{T_0}{T_\infty}\right)\right\}\dfrac{Ta_{\mathrm{s,O}}}{T_\infty}\exp\left(-\dfrac{Ta_{\mathrm{s,O}}}{T_\infty}\right)-\dfrac{2\varepsilon\sigma_{\mathrm{SB}}T_\infty^3}{\rho_\infty D_\infty c_p}}, \tag{6}$$

which confirms the existence of critical size, below which particles are quenched, due to heat-loss, not recognized in the previous studies, especially in the solid combustion. If we further ignore the second term in the denominator and introduce a formula, $(D_\infty/D_0)=(T_\infty/T_0)^{1.75}/(P_\infty/P_0)$, we have a comprehensive parameter, $(2r_{\mathrm{s}})Y_{\mathrm{O},\infty}(P_\infty/P_0)$, which only depends on T_∞.

4. Experimental Comparisons

Although experimental conditions are quite different [14-17], results locate in the upper region separated by the Arrhenius plot of the comprehensive parameter, as shown in Fig. 1. Here, use has been made of the surface kinetic parameters of the artificial graphite reported [18], as well as other physicochemical parameters. Note here that 10^0 in the ordinate corresponds to $2r_{\mathrm{s}}$=1 μm when $Y_{\mathrm{O},\infty}$=1 and P_∞/P_0=1.

The present criterion is also anticipated to apply to boron combustion at the moment just after the removal of oxide layer on a particle as its temperature rises. Figure 2 shows a similar plot for the boron (crystalline) particles. Although sources [2, 19-26] are different, results in general locate in the upper region. Use has been made of $E_{\mathrm{s,O}}$=320 kJ/mol, reported [27], and $B_{\mathrm{s,O}}=6\times10^8$ m/s, evaluated from the observed cut-off temperature [23] for the deactivation, through the condition for vanishing denominator in Eq. (6). The dotted line passes through the point, reported to be non-ignition [21]. Although fair agreement is demonstrated, a further study is required to confirm the boundary.

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Figure Captions

Fig. 1 Arrhenius plot of the comprehensive parameter $(2r_s)Y_{O,\infty}(P_\infty/P_0)$ with respect to the critical condition for the particle burn-out of solid carbon. Data points are experimental [14-17]; an open symbol designates the burn-out, while a symbol (×) the quenching. A solid curve is the critical condition for the comprehensive parameter; dashed curves are those by use of Eq. (6).

Fig. 2 Arrhenius plot of $(2r_s)Y_{O,\infty}(P_\infty/P_0)$ for the particle burn-out of boron (crystalline). Data points are experimental [2, 19-26]. Notation is the same as that in Fig. 1.

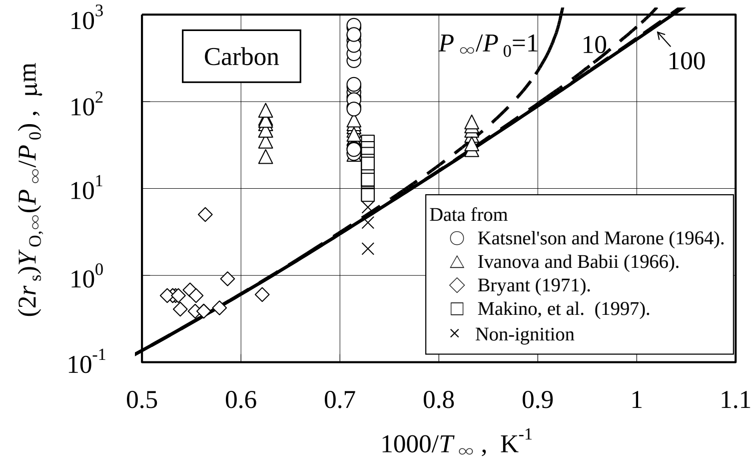
Carbon
P_∞/P_0=1
10
100
Data from
Katsnel'son and Marone (1964).
Ivanova and Babii (1966).
Bryant (1971).
Makino, et al. (1997).
Non-ignition
$(2r_s)Y_{O,\infty}(P_\infty/P_0)$, μm
10^3
10^2
10^1
10^0
10^{-1}
0.5
0.6
0.7
0.8
0.9
1
1.1
$1000/T_\infty$, K^{-1}

Fig. 1

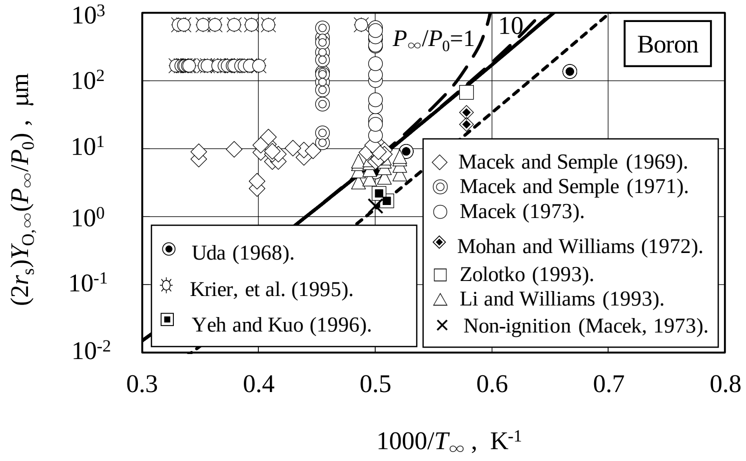
Boron
P_∞/P_0=1
10
Macek and Semple (1969).
Macek and Semple (1971).
Macek (1973).
Mohan and Williams (1972).
Zolotko (1993).
Li and Williams (1993).
Non-ignition (Macek, 1973).
Uda (1968).
Krier, et al. (1995).
Yeh and Kuo (1996).
$(2r_s)Y_{O,\infty}(P_\infty/P_0)$, μm
10^3
10^2
10^1
10^0
10^{-1}
10^{-2}
0.3
0.4
0.5
0.6
0.7
0.8
$1000/T_\infty$, K^{-1}

Fig. 2