

# Combustion of Solid Refuse

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## ABSTRACT

Chemical and physical processes involved in the combustion of solid refuse are examined and formulated with main emphasis on the time required for incineration. Quantitative predictions of pyrolysis and burning times of refuse pieces are presented, and equations are developed which show how burning time is affected by temperature, pressure, oxygen mole fraction, specimen size and shape, and relative velocity between the solids and the ambient gas.

## INTRODUCTION

The combustion of solid refuse involves heat and mass transfer, pyrolysis of both solid and gaseous material, and both gas-phase and heterogeneous chemical reactions. With regard to incinerator design, the most important property of the overall combustion reaction is probably the rate, since this quantity dictates the size of the combustion chamber. Knowledge of other details of the combustion reaction is also necessary for designing the sophisticated incinerators demanded by current requirements. The following analysis considers the essential details of the combustion of refuse, and develops some understanding of the overall rate by generating predicted values of the times required for heating and burning under given sets of conditions. The effects of temperature,

pressure, specimen size and shape, oxygen mole fraction, and ambient velocity are discussed.

The refuse is assumed to be converted to gaseous combustion products and an inert solid residue in a series of steps including drying, pyrolysis, and combustion. Drying is assumed to occur before pyrolysis and combustion, and the time required for drying is not considered in the following. Furthermore, pyrolysis and combustion are treated as independent processes, even though the combustion of pyrolyzing solids has been shown to be influenced by the pyrolysis process[5]. Consideration of this particular effect is not justified here, since other, perhaps more important, aspects of refuse combustion (e.g., the effect of a wide variety of materials) are not treated in such detail, owing to the lack of information about them.

## NOMENCLATURE

- A = frequency factor, g-moles/sq cm-sec
- Bi = Biot number,  $hr_0/\lambda_s$
- d = thickness of flat plate and diameter of sphere, cm
- D = coefficient of diffusion of oxygen in ambient gas, sq cm/sec
- E = activation energy, kcal/g-mole
- f = mole fraction of oxygen in ambient gas
- F = moles of solid material burned per mole of oxygen reacting

$Fo$  = Fourier number,  $t/r_0^2$   
 $h$  = coefficient of heat transfer from ambient gas to surface of refuse specimen, cal/sq cm-sec-deg C  
 $k$  = reaction rate constant, g-moles/sq cm-sec  
 $k_p$  = pyrolysis rate constant, 1/sec  
 $k_f$  = mass transfer coefficient for oxygen flow to burning surface, g-moles/sq cm-sec  
 $K$  = ratio of burning time of solid sphere to the square of the initial sphere diameter, sec/sq cm  
 $K_1$  = a constant, cm-sec/g-mole  
 $K_2$  = a dimensionless function of  $U$   
 $K_3$  = the stoichiometric ratio of the moles of oxygen required to burn unit volume of solid material, g-moles/cc  
 $K_4$  = a constant for combustion in air, sq cm-sec<sup>1/2</sup>/g-mole  
 $K_5$  = a constant for the carbon-oxygen reaction, sec/cm  
 $K_6$  = a constant for the carbon-oxygen reaction, sec/cm  
 $L$  = length of flat plate of refuse specimen, cm  
 $m$  = order of the temperature dependence of the relative velocity between solids and ambient gas  
 $M$  = molecular weight, g/g-mole  
 $n$  = order of the pressure dependence of the relative velocity between solids and ambient gas  
 $\dot{N}$  = oxygen flux reaching burning surface, g-moles/sq cm-sec  
 $Nu$  = Nusselt number for heat transfer from ambient gas to surface of refuse specimen,  $hL/\lambda_g$  for flat plates, and  $hd_0/\lambda_g$  for spheres  
 $P$  = absolute pressure, atm  
 $Pr$  = Prandtl number of ambient gas: ratio of kinematic viscosity to thermal diffusivity  
 $r$  = half-thickness of a flat-plate, refuse specimen, or radius of spherical specimen, at any time during burnout, cm  
 $\dot{r}$  = specific reaction rate, g-moles/sq cm-sec  
 $R$  = ideal gas constant, 82.05 cc-atm/g-mole-deg K  
 $\dot{R}_s$  = specific burning rate, grams solid material/sq cm-sec  
 $Re$  = Reynolds number for flow of ambient gas past refuse specimen:  $VL/\nu$  for flat plates and  $Vd/\nu$  for spheres  
 $Re_0$  = initial STP value of  $Re$ ,  $V_0d_0/\nu_0$   
 $Sc$  = Schmidt number of ambient gas: ratio of kinematic viscosity to thermal diffusivity  
 $t$  = time, sec  
 $t_b$  = burning time, sec  
 $t_h$  = heating time, sec  
 $T$  = absolute temperature, deg K

$U$  = a dimensionless, temperature-dependent function of  $Re_0$   
 $V$  = relative velocity between refuse pieces and ambient gas, cm/sec  
 $x$  = distance from center of spherical specimens, and perpendicular distance from midplane of flat plates, cm  
 $y$  = integration variable  
 $z$  = integration variable  
 $\alpha$  = thermal diffusivity of solid refuse, sq cm/sec  
 $\eta$  = steric factor for oxygen adsorption on carbon  
 $\theta$  = fraction of active sites on carbon surface occupied by adsorbed oxygen  
 $\lambda$  = thermal conductivity, cal/cm-deg C-sec  
 $\nu$  = kinematic viscosity of ambient gas, sq cm/sec  
 $\rho$  = density of solid material, g/cc

#### Subscripts

1 = adsorption  
 2 = desorption  
 a = in ambient gas (when on f); adsorption-controlled burning (when on  $t_b$ )  
 c = carbon  
 c.c. = chemically controlled burning  
 d = desorption-controlled burning  
 m.t. = mass-transfer controlled burning  
 o = initial value (when on r, d, Re); at 1-atm and 0 deg C (when on D, P, Re, T, V,  $\nu$ ); oxygen (when on M)  
 p = pyrolysis  
 s = at solid surface (when on f); solid material (when on M,  $\lambda$ ,  $\rho$ )

## PYROLYSIS

### GENERAL DESCRIPTION

Pyrolysis of carbonaceous materials, even those as simple in structure and composition as cellulose, includes many individual reactions, some of which are endothermic, bond-breaking, or cracking reactions, and others of which are exothermic, bond-forming reactions. In general, the cracking reactions occur as an early stage of pyrolysis and convert the original material into a new, sometimes plastic structure. These reactions generate gaseous products with a composition that varies from mainly  $CO_2$  and  $H_2O$  at first, to mainly hydrocarbons (tar, light oil, and fixed gases) in the later stages of pyrolysis. The bond-forming reactions are accompanied by solidification of plastic material to form char with the evolution of volatiles that become progressively hydrogen-rich as pyrolysis is carried to higher temperatures. The overall pyrolysis reaction is generally endothermic.

The extent of pyrolysis of a given material depends upon the temperature to which the material is heated and the time spent at that temperature. It is now generally believed that pyrolysis is fast enough to keep up with the heating process, unless the rate of temperature rise is faster than some critical value which is probably around  $10^4$  deg C/sec<sup>6</sup>. Consequently, no time lag should exist between heating and pyrolysis in incinerators where the heating rate is probably less than 100 C/sec, and a piece of refuse may be regarded as having been pyrolyzed at a given temperature as soon as it has reached that temperature.

Pyrolysis is an activated process; therefore, the temperature dependence of the rate of pyrolysis may be expressed in terms of an activation energy in the standard form

$$k_p = A_p \exp(-E_p/RT) \quad (1)$$

where  $k_p$  is the pyrolysis rate constant,  $A_p$  is the frequency factor,  $E_p$  is the activation energy for pyrolysis,  $R$  is ideal gas constant, and  $T$  is the absolute temperature. However, the "pyrolysis" process observed in practice includes not only pyrolysis as described in the foregoing, but also the processes of heat transfer from the surroundings to the decomposing material and mass transfer of the pyrolysis products both out of the solid specimen and into the surroundings. The rate of the overall process is the rate of practical interest.

Some disagreement exists among different investigators about the rate-controlling step of the overall pyrolysis process. For example, Pitt [9] and van Krevelen [16] support the proposition that the rate of pyrolysis of bituminous coal is controlled by the decomposition of the material, whereas Berkowitz [1] argues that the rate is controlled by diffusion of volatiles to the surface of the particle. Such disagreement probably results from differences in experimental conditions. The overall pyrolysis rate is known to depend upon properties of the system, such as particle size, heating rate, upper temperature attained, and the type of material, but to account for variations in these quantities between different experiments is very difficult. Until sufficient data are available, prediction of the pyrolysis rate for a given material, under a given set of conditions, requires judgment based on qualitative knowledge of the relative rates of the individual processes [4]. In general, if particle size is small enough, or if heating rate is slow enough so that significant pressure and temperature gradients are not established within the solid material, then the overall rate of pyrolysis is

simply the rate of decomposition of the material; otherwise, the processes of heat and mass transfer influence the rate.

#### TIME REQUIRED FOR PYROLYSIS

In order to estimate the time required for the overall pyrolysis process, it is assumed that the overall rate is equal to the rate of heating, thus implying that both the pyrolysis reaction and the flow of pyrolysis products out of and away from the particles are infinitely fast. This assumption is based on the knowledge described in the foregoing that pyrolysis at a given temperature occurs instantaneously when the material reaches that temperature, and on the fact that most materials in refuse, such as paper, garbage, and wood, should heat internally at a slow enough rate, and should provide a low enough resistance to gas flow through their structure, so that the escape of volatiles out of the particle should not significantly influence the overall pyrolysis rate.

The pieces of refuse are assumed to be plunged suddenly into a hot combustion chamber, maintained at a certain temperature which, for purposes of discussion, is assumed to be 1300 C (2375 F). The times required for the surface temperature, the center temperature, and the space-mean temperature of the pieces to rise by 95 percent of the initial temperature difference between the refuse and the combustion chamber are calculated. These times serve as a measure of pyrolysis time. Heat transfer by radiation and by direct contact with hot particles already in the chamber is neglected.

The calculations are described in Appendix A. The pyrolysis (heating) times are given in Figs. 1 and 2 as a function of particle size and relative velocity between the pieces and the surroundings. Two different shapes, thin slabs and spheres, are considered, but space-mean temperatures are given for slabs only. With regard to heating times, these two shapes should bracket the particle shapes found in practice.

The particle-size dependence of the pyrolysis time is very significant. Within the range of conditions studied here, the time varies approximately with the square of the dimension of the specimen for both spheres and flat plates. For example, if the ambient velocity is 1 fps, the heating time for the center of a sphere drops from about 3 to about 0.5 min. as the diameter is reduced from 3/8 to 1/8 in.

The effect of ambient velocity is also significant. Relative velocities between the specimens and the surroundings of up to 100 fps are considered, even though such large values may be difficult to achieve in practice. The curves labeled  $2\lambda_s/hd_0 = 0$  repre-

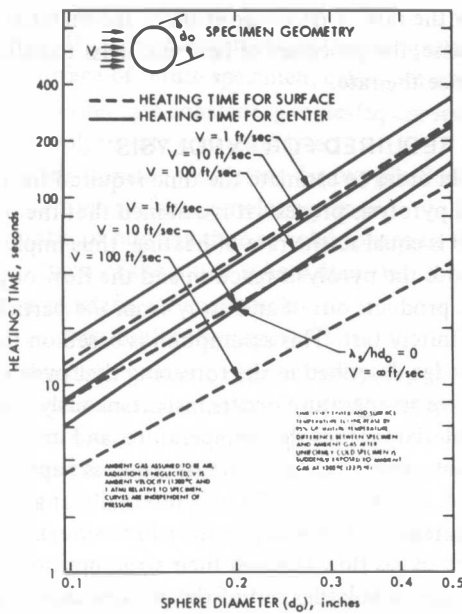


FIG. 1 HEATING TIMES OF SPHERES: APPROXIMATE PYROLYSIS TIMES

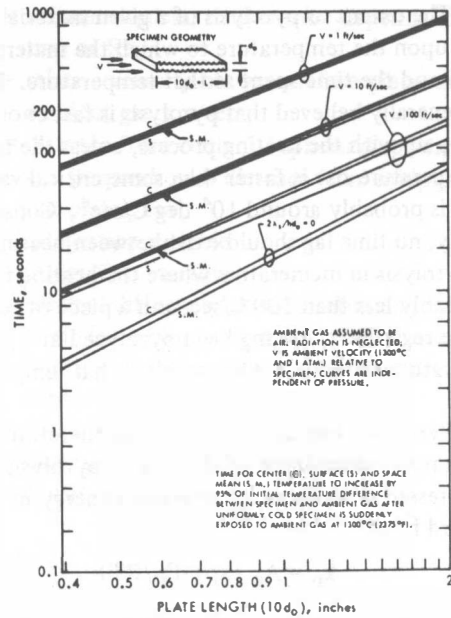


FIG. 2 HEATING TIMES OF FLAT PLATES: APPROXIMATE PYROLYSIS TIMES

sent an infinitely large surface heat-transfer coefficient, which is equivalent to an infinitely large velocity of the ambient gas relative to that of the particle. Under such conditions, the surface of the specimen attains the temperature of the combustion chamber immediately upon entering the chamber, and the rate of heating is determined solely by the properties of the specimen.

## COMBUSTION

### GENERAL DESCRIPTION

Although incineration of solid refuse includes both gas-phase and heterogeneous combustion, only heterogeneous combustion is considered here, since we are mainly interested in the time required for burning, and heterogeneous combustion is, by far, the slower of the two processes. The material experiencing heterogeneous combustion includes both solid residues of pyrolyzed material and non-pyrolyzing pieces.

Ignition of the solid pieces of refuse requires that certain conditions of temperature and oxygen concentration be satisfied at the solid surfaces. If we visualize, for the purpose of discussion, a well-mixed combustion chamber containing a certain concentration of oxygen, then the oxygen concentration at the surface of an unignited pyrolyzing particle is less than that in the ambient gas, owing to the outward flow of

volatiles from the surface. If pyrolysis (i.e., heating) is fast enough, ignition may be delayed, even though the surface may be very hot, until the surface flux of volatiles drops below a certain critical value which depends heavily upon particle size [5]. At the other extreme, nonpyrolyzing particles, such as tin cans and nails, can ignite as soon as the surface attains a critical temperature, which is probably inversely related to the oxygen concentration in the combustion chamber. For present purposes, we shall define the burning time of a piece of refuse as the time between ignition and complete conversion to gaseous combustion products and an inert solid residue (ash), and we shall assume this time to be independent of the details of the ignition process.

Heterogeneous combustion of refuse consists of the physical processes of heat and mass transfer and the chemical process of reaction between the solid material and the gaseous surroundings. The physical processes are largely independent of the type of material being burned and may be formulated, even though the chemistry of the combustion of some of the materials in refuse is unknown. An exception to this statement is the case, such as the combustion of some metals, where the products of combustion condense on the reacting surface, thus forcing the oxygen to diffuse through an oxide shell. In such cases, knowledge of the properties of the oxide layer must be known, in order to calculate burning times.

The chemistry of heterogeneous combustion depends upon the material being burned. One or more reactions may be involved, and parallel or sequential steps, or both may occur. A large portion of the solid material encountered in incineration is mainly carbon, whose reaction with oxygen is relatively well understood. Conversely, the chemistry of metal combustion is not clear; for simplicity, the reaction is often assumed to be first-order in oxygen concentration [7].

The chemistry of the combustion of carbon with oxygen has been shown to agree well with a mechanism involving two steps in series [3]. The first step is adsorption of oxygen on the carbon surface; the second step is desorption of oxides of carbon. Adsorption is first-order, and desorption is zero-order with respect to oxygen concentration. The activation energy of adsorption depends upon surface coverage and is generally low. At low surface coverage (rapid desorption), the adsorption activation energy corresponds to a temperature dependence similar to that of heat and mass transfer [3]. Conversely, the activation energy of desorption is large, so that the temperature dependence of desorption is very strong. The rates of these two steps are given in the following.

Adsorption rate:

$$\dot{r}_1 = k_1 f_s (1 - \theta) \quad (2)$$

Desorption rate:

$$\dot{r}_2 = k_2 \theta \quad (3)$$

where  $\dot{r}_1$  and  $\dot{r}_2$  are the specific rates of adsorption and desorption (g-moles carbon equivalent/sq cm-sec),  $k_1$  and  $k_2$  are the rate constants for adsorption and desorption,  $f_s$  is the mole fraction of oxygen at the solid surface, and  $\theta$  is the fraction of the active sites on the carbon surface that is occupied by adsorbed oxygen.

At low temperatures, less than about 750 C (1400 F) for the case of chemically controlled combustion in air, the rate of the combined chemical steps of the carbon-oxygen reaction is completely controlled by the rate of desorption. At high temperatures, greater than about 1150 C (2100 F) for the case of chemically controlled combustion in air, the rate is controlled by adsorption. In the transition region, both steps influence the rate. This behavior is illustrated in Fig. 3, which gives results obtained by fitting the data to Tu, Davis, and Hottel [15] with the mechanism described in the foregoing. The transition region between adsorption and desorption con-

trol is seen to depend upon the concentration of oxygen at the solid surface, which, in turn, depends not only upon the oxygen concentration in the ambient gas, but also upon the rate of mass transfer between the ambient gas and the burning surface.

The rate of transport of oxygen to the burning surface of a carbon specimen is given as follows:

Mass transfer rate:

$$\dot{N} = k_f (f_a - f_s) \quad (4)$$

where  $k_f$  is the mass transfer coefficient,  $f_a$  is the mole fraction of oxygen in the ambient gas, and  $\dot{N}$  is the molar flux of oxygen reaching the surface. A similar equation could be written describing convective heat transfer from the specimens; however, consideration of heat transfer is avoided in the present analysis by assuming that the solids and ambient gas are at the same temperature during burning.

Thus, the rate of carbon combustion is described in terms of three sequential steps. Since the rates of these steps are all equal at steady state, an equation for the rate of the overall process is obtained from equations (2), (3), and (4), by eliminating both the surface coverage and the partial pressure of oxygen at the reacting surface. The overall burning rate,  $\dot{R}_s$ , is expressed in terms of the ambient oxygen partial pressure and the chemical and physical rate constants as follows:

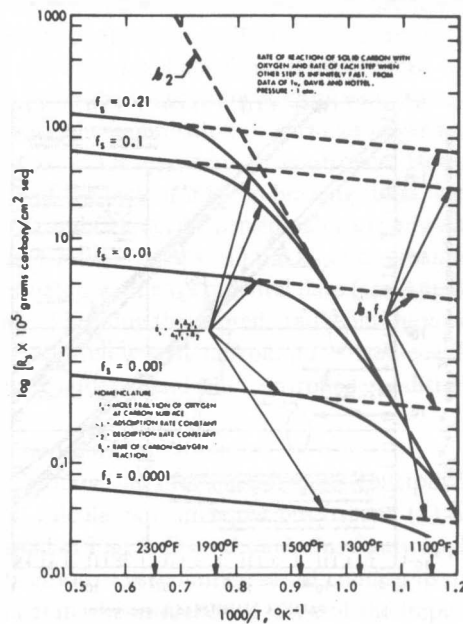


FIG. 3 KINETICS OF CARBON-OXYGEN REACTION

Overall burning rate:

$$\dot{R}_s = \frac{1}{2 \left[ \frac{1}{k_f f_a} + \frac{1}{k_1 f_a} + \frac{1}{k_2} \right] + \sqrt{\left[ \frac{1}{2} \left[ \frac{1}{k_f f_a} + \frac{1}{k_1 f_a} - \frac{1}{k_2} \right] \right]^2 + \frac{1}{k_1 k_2 f_a}}} \quad (5)$$

The burning rate described by equation (5) is studied best by considering specific, limiting conditions. Since the rate of the overall process is no faster than the rate of the slowest step, the rate-controlling step, under a given set of conditions, is identified by comparing the rate of the three individual steps. Information for such a comparison is given in Fig. 4. Mass transfer becomes more important as a rate limiting step as particle size increases; for a given set of conditions, there is a critical particle size above which mass transfer completely controls the rate. For example, if we consider the combustion of carbon spheres in air at 1527 C (2780 F) with a relative velocity of 3.5 cm/sec (0.11 fps) between the sphere and air, then the burning rate is limited by mass transfer, if the sphere diameter is larger than about 3/8 in. Under the same conditions, the rate is adsorption controlled, if the particle size is less than about 0.01 in.

Most of the residues from refuse pyrolysis are probably porous. Under conditions where mass transfer is much faster than the chemical reaction, a non-zero concentration of oxygen exists at the outer surface of a specimen, and oxygen may diffuse into and burn out the pores. The rate of pore combustion increases as the concentration of oxygen at the surface

increases, but the reaction on the superficial surface, plus the reaction in pores, can never exceed the rate of transport of oxygen to the specimen. In general, the importance of combustion in pores decreases as temperature increases, as total pressure increases, as particle size increases, and as the relative velocity between the specimen and the surroundings decreases.

## BURNING TIMES OF SOLID SPECIMENS

### Technique of Analysis.

The technique, used for studying the time required to burn pieces of refuse with air, is to consider simplified, limiting cases. Basically, two categories of cases are considered: combustion of any solid material under such conditions that the rate is completely mass-transfer controlled, and combustion of carbon specimens under conditions where both chemical and mass transfer phenomena limit the burning rate.

### Burning Time of Any Solid Material with the Burning Rate Controlled by Mass Transfer.

The case of mass-transfer controlled burning rate is realized when the solid pieces are so reactive that the chemical rate exerts negligible resistance to burning. Mass transfer through the gaseous surroundings of the solids is assumed to be the rate-limiting physical process, thus neglecting possible contributions from accumulated oxide on the burning surface. The results are valid, under conditions of mass-transfer control, whether the material is porous or nonporous, and for material of any composition, provided the stoichiometry is accounted for properly.

The following equations, derived in Appendix B, give the mass-transfer controlled burning time  $(t_b)_{m.t.}$  of spheres of diameter,  $d_o$ , and slabs of thickness,  $d_o$ , and length,  $L$ , as functions of known properties of the system.

Sphere; mass-transfer control:

$$(t_b)_{m.t.} = [K_1 K_2 K_3 (T_o/T)^{1/2} (1/f_a)] d_o^2 \quad (6)$$

where  $K_1$  is a constant,  $K_2$  is a dimensionless function of the relative velocity between the specimen and the ambient gas,  $K_3$  is a function of the combustion stoichiometry, and  $T_o$  is 273 K.

Flat plate; mass-transfer control:

$$(t_b)_{m.t.} = [K_3 K_4 (T_o/T)^{1/4} (L/v_o)^{1/2} (1/f_a)] d_o \quad (7)$$

where  $K_4$  is a constant for combustion in air, and

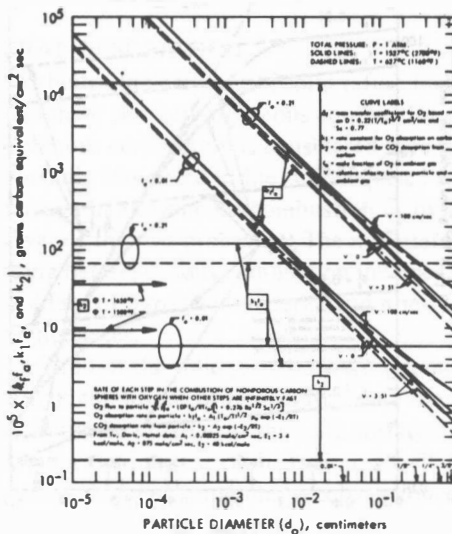


FIG. 4 IDENTIFICATION OF RATE-CONTROLLING STEP IN CARBON COMBUSTION

$V_o$  is the relative velocity (at STP) between the specimen and the ambient gas.

#### Burning Time of Solid Carbon Under Various Conditions of Rate Control.

The equations given in the following, derived in Appendix B, give the burning times of carbon specimens in air. When the burning rate is completely controlled by the adsorption of oxygen on the carbon surface, the burning time is:

Carbon sphere or flat plate; adsorption control:

$$(t_b)_a = K_5 (P_o/P) (1/f_a) [1/(T_o/T)^{1/2} \exp(-E_1/RT)] d_o \quad (8)$$

where  $K_5$  is a constant,  $P$  is absolute pressure ( $P_o = 1$  atm), and  $E_1$  is the activation energy of oxygen adsorption on carbon.

If desorption controls the burning rate, the burning time is:

Carbon sphere or flat plate; desorption control:

$$(t_b)_d = K_6 [1/\exp(-E_2/RT)] d_o \quad (9)$$

where  $K_6$  is a constant, and  $E_2$  is the activation energy of the desorption of combustion products (assumed to be  $CO_2$ ) from the carbon surface.

When the burning rate is controlled jointly by adsorption and mass transfer (i.e., desorption infinitely fast); the burning time is found to be:

Carbon sphere or flat plate; joint adsorption and mass-transfer control:

$$t_b = (t_b)_{m.t.} + (t_b)_a \quad (10)$$

When adsorption is infinitely rapid relative to the rates of desorption and mass transfer, the burning time is not given by the sum of the burning times predicted for complete desorption control and complete mass-transfer control as might be expected in view of the form of equation (10). The case of infinitely rapid adsorption differs from that of infinitely rapid desorption, because desorption, unlike adsorption, is not coupled with mass transfer, since it is independent of the concentration of oxygen at the solid surface. Thus, when adsorption is infinitely fast, the burning time is given by

Carbon sphere or flat plate; desorption and mass-transfer control:

$$t_b = (t_b)_{m.t.} \text{ or } (t_b)_d$$

where  $(t_b)_{m.t.}$ , from equations (6) and (7), is used if mass transfer is slower than desorption, and  $(t_b)_d$ , equation (9), is used if desorption is slower than mass transfer.

#### Test of Equations with Experimental Data.

Few data exist for testing the foregoing equations. In the case of mass-transfer controlled burning, Essenhigh [2] finds that existing data on the burning times of coal and carbon particles are correlated by an equation of the form  $t_b = K d_o^2$ , which is similar in form to equation (6). These data cover the size range 0.05 to 0.4 cm, but pertinent information, such as temperature and ambient velocity, is missing. Nevertheless, Essenhigh's estimated values of  $K$  range from 330 to 2125 sec/sq cm for the different data.

The expression for  $K$  obtained from equation (6) is

$$K = K_1 K_2 K_3 (T_o/T)^{1/2} (1/f_a)$$

Values of  $K$  predicted from this expression are very similar to the larger values in Essenhigh's summary. For example, if the particles are assumed to be burning in air, with natural convection creating an ambient velocity of 1 fps past the particle, and if the particle surface is assumed to be at 1400 C (2550 F), then  $K$  in equation (6) is found to be 2100 and 2640 sec/sq cm for 0.05 and 0.4 cm particles, respectively. In order to predict  $K$  values near the lower limit of the experimental data, either ambient velocity or temperature (or both), would have to be much higher than the foregoing values. Nevertheless, the agreement appears to be good enough to allow equation (6) to be used with considerable confidence; and, by inference, equation (7) should also be useful for the case of flat-plates.

Data on burning times of carbon particles under chemically controlled conditions appear to be limited to particle sizes less than about 0.005 or 0.01 cm, the reason being that, under the conditions of most experiments, the combustion of particles larger than about 0.01 cm is mass transfer controlled. However, in spite of the lack of data on burning times, equations (8) and (9) receive considerable experimental backing for two reasons: 1) the kinetics parameters are evaluated with experimental data (see Appendix B); and 2) burning times predicted from these equations agree well with data from pulverized-coal flames operating under chemically controlled conditions.

#### Calculated Burning Times.

Burning times for mass-transfer controlled conditions, calculated from equations (6) and (7), are presented in Fig. 5. Even though this figure applies specifically to a very limited set of conditions, it does demonstrate the influence of some of the important variables and shows the range of burning times to be expected.

## CONCLUSIONS

The following, somewhat qualitative, conclusions are based on the predictions generated in this discussion and may be useful in incinerator design.

### TIME REQUIRED IN THE COMBUSTION CHAMBER

Assuming that dry refuse particles are injected into a hot combustion chamber, the time required for pyrolysis is approximately the time required for heating, and the time required for combustion is the time required to burn the solid pieces of both nonpyrolyzing materials and residues of pyrolyzing materials. The minimum time required for combustion is the burning time under conditions of completely mass-transfer controlled burning. Assuming that pieces of refuse exhibit geometries ranging from spheres to flat plates and dimensions ranging from tiny particles up to about 1/2-in. for chunks and about 2 x 2 x 0.2-in. for flat pieces, and that conditions in the combustion chamber give approximately mass-transfer controlled burning, then the predicted heating and burning times are each about 5 min. for the largest pieces, thus requiring a residence time in the combustion chamber of about 10 min. Since the total time required for the smallest pieces approaches zero, a burner design, which permits prolonged residence times for large pieces, appears to be highly desirable.

### SPECIMEN SIZE

Specimen size, and therefore comminution, has a striking effect on residence time, since heating time is approximately proportional to the square of specimen size, and burning time is proportional to either the first or second power of size, depending upon the shape of the specimen and the relative rates of mass transfer and the chemical reactions. However, comminution is much more important for chunks than for flat pieces, since the thickness of a flat specimen is much more important than its lateral dimension in determining heating and burning times, and the thickness of flat pieces tends to remain constant during comminution until the lateral dimension approaches the thickness. Although this statement becomes less valid as the ambient velocity relative to the solids increases, it is probably approximately true for most all practical burner designs owing to the difficulty of attaining large relative velocities. Therefore, the answer to the economic question of how far to carry comminution of the refuse is probably almost independent of the flat pieces.

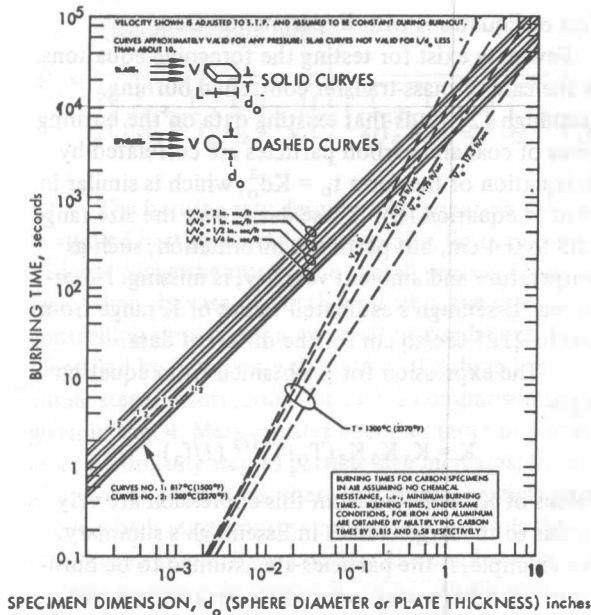


FIG. 5 BURNING TIMES OF SOLID SPECIMENS

The times, shown in Fig. 5, are minimum values, since chemical resistance is neglected. The effect of chemical resistance can be accounted for in the case of carbon combustion. For example, the combustion of a 2-in. x 2-in. x 0.1-in. carbon plate in air at a temperature of 817 C (1500 F), and an air velocity of 1 fps (at STP, is controlled jointly by desorption and mass transfer. Therefore, according to the earlier discussion, the burning time is the larger of the two values predicted by assuming a) complete desorption control, and b) complete mass-transfer control. The times predicted by equations (7) (mass-transfer control) and (9) (desorption control) are 1450 and 2000 sec, respectively. Hence, the burning time is 2000 sec, which is about 3.4 percent larger than that predicted by Fig. 5.

A second example is the combustion of a 0.1-in. carbon sphere in air at 1-atm and 1300 C (2370 F) with no ambient velocity past the particle. In this case, the burning rate is controlled jointly by adsorption and mass transfer; therefore, the burning time is given by equation (10). The separate contributions to burning time by adsorption and mass transfer are found to be 171 sec [from equation (8)] and 210 sec [from equation (6)], respectively. Therefore, the burning time is 381 sec, which is 81 percent larger than that given by Fig. 5.

In the case of materials of unknown combustion characteristics, the effect of chemical resistance cannot be accounted for, and the burning times obtained from mass transfer considerations serve as limiting values.



## TEMPERATURE

In general, increasing the temperature decreases the time required in the combustion chamber, but the effect is relatively small if the chamber is hot enough in the first place, so that the burning rate is mass-transfer controlled. At lower temperatures, where the rate is controlled by chemical reactions, temperature may be exceedingly important. In extreme cases, where the temperature is low enough that desorption is rate-controlling, a twofold decrease in the burning time of carbonaceous specimens can be achieved with roughly a 40 C (70 F) increase in temperature. Conversely, if combustion is mass-transfer controlled, the same rise in temperature reduces the burning time by only about 1 percent.

The temperature region at which transition from strong to weak temperature dependence occurs depends upon the conditions of the system. For example, in the case of carbonaceous materials burning in air at a pressure of 1-atm, transition for 0.25-in-dia spheres and 0.1-in-thick plates occurs near 900 C (1650 F) and 875 C (1600 F), respectively. Under the same conditions, transition for 0.1-in-dia-spheres and 0.05-in-thick plates occurs near 950 C (1750 F) and 910 C (1675 F), respectively. Owing to the dependence of mass-transfer upon particle size, rate control can shift from mass-transfer to chemical during burnout of a specimen.

## PRESSURE

If burning rate is mass-transfer controlled, both the heating time and the burning time are approximately independent of pressure. Under conditions where chemical reactions influence the burning rate, the effect of pressure depends upon the order of the combustion reaction with respect to oxygen. Burning times of carbonaceous specimens range from being inversely proportional to pressure (adsorption control) to being independent of pressure (desorption control). Other materials, such as metals, are also expected to be sensitive to pressure, if burning is not fast enough to be mass-transfer controlled.

## VELOCITY

A high velocity of the ambient gas relative to the solids is always desirable with regard to decreasing heating time, and is also desirable with regard to decreasing burning time, unless burning rate is chemically controlled. Since the flow rate of gas through the combustion chamber is fixed for a given feed rate of refuse, and since the relative motion between the solids and the gas is enhanced by changes in the magnitude and the direction of the ambient velocity, the

implication is that burners, which generate turbulence and swirl, are desirable.

## OXYGEN MOLE FRACTION

Since increasing the excess air in the combustion chamber lowers the temperature and increases the mole fraction of oxygen, and since temperature and oxygen mole fraction have opposite effects on burning rate, knowledge of the effect of oxygen mole fraction is necessary in selecting the ratio of air to refuse.

Burning time is inversely proportional to the mole fraction of oxygen in the ambient gas, unless the burning rate is influenced significantly by chemical reactions that are not first-order in oxygen. For example, the rate of the desorption step in the carbon-oxygen reaction is independent of oxygen concentration; therefore, the burning time of carbon specimens is independent of oxygen mole fraction if the burning rate is desorption controlled. However, completely desorption-controlled burning is probably of limited importance, owing to the low temperatures at which it occurs.

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## APPENDIX A

### HEATING TIMES OF SOLID SPECIMENS

#### INTRODUCTION

The heating of dry pieces of solid refuse in an incinerator is a problem in unsteady state heat transfer which is complicated by both endothermic and exothermic pyrolysis reactions. The time required for heating is estimated in the following analysis by considering simplified, but still meaningful, conditions.

Energy absorption and liberation within the pieces of refuse is neglected. The error introduced by this simplification is decreased by the fact that the endothermic reactions, which are more energetic than the exothermic reactions, occur at a temperature which is low in comparison with that of the ambient gas, so that heat transfer to the energy-absorbing zone within a specimen tends to be rapid.

The pieces of refuse are assumed to be suddenly plunged into a hot chamber whose temperature remains constant. This is, in effect, assuming well-mixed, steady conditions in the heating chamber.

Heat transfer by radiation and by particle-particle contact is neglected. The error thus introduced depends on the design of the incinerator. Furthermore, the particles are assumed to be either thin, flat slabs or spheres, the heating times of which should bracket the times for the actual shapes.

The heating time is defined as the time required for the temperature of a specimen to rise by 95 percent of the initial temperature difference between the specimen and the surroundings. Each of the following criteria of hotness is employed: surface, center, and in the case of flat plates, space-mean temperatures.

The time defined in the foregoing is given in terms of the Fourier number ( $Fo$ ), which is expressed as a function of the independent variables of the system by using the Nusselt number ( $Nu$ ) and the Biot number ( $Bi$ ). Thus, we have

$$Fo = f(Bi, Nu, x/d_o) \quad (11)$$

where  $d_o$  is the dimension of the specimen (sphere diameter or plate thickness), and  $x$  is distance from the center (sphere) or midplane (flat plate) of the specimen to the material whose heating time is referred to in  $Fo$ . This relationship, representing the solution of the differential equation describing the

heat-transfer process, is given in graphical form in the literature [8]. Therefore, for a given specimen of known thermal diffusivity, the heating time for material at a given position within a specimen is obtained by first calculating the Biot and Nusselt numbers.

#### CALCULATION OF NUSSOLT NUMBER

The Nusselt number, which is a measure of the rate of heat transfer from the ambient gas to the surface of the specimen, is given by  $Nu = hd_o/\lambda_g$  for spheres and  $Nu = hL/\lambda_g$  for flat plates, where  $d_o$  is the sphere diameter,  $L$  is the plate length,  $h$  is the heat-transfer coefficient for convection from the ambient gas to the surface of the specimen, and  $\lambda_g$  is the thermal conductivity of the ambient gas. The following semi-empirical relationships are known:

For sphere [10]:

$$Nu = 2 [1 + 0.3Re^{1/2}Pr^{1/3}] \quad (12)$$

For flat plate [11]:

$$Nu = 0.664Re^{1/2}Pr^{1/3} \quad (13)$$

$Pr$  is the Prandtl number of the ambient gas, and  $Re$  is Reynolds number based on the relative velocity between the specimen and the ambient gas. Equation (13) is limited to laminar flow over the surface of the slab, a condition which is expected to be satisfied in most all incinerators.

Prandtl number, which is essentially independent of both temperature and pressure, has a value of about 0.7 for air.  $Pr^{1/3}$  is approximated by unity in this calculation.

In calculating Reynolds number, the dimension of the specimen is taken to be the diameter of spheres and the length of plates. The length and width of the plate are assumed to be much larger than the thickness, and the plate is assumed to be oriented with its length parallel to the velocity of the ambient gas. Specific values of width are of no consequence in this calculation. The properties of the ambient gas are assumed to be identical to those of dry air.

## CALCULATION OF BIOT NUMBER

The Biot number is a measure of the relative rates of surface and internal heat transfer and is given by  $Bi = hr_o/\lambda_s$ , where  $\lambda_s$  is the thermal conductivity of the solid material, and  $r_o$  is the radius of spheres and the half-thickness of flat plates. Bi is expressed in the following in terms of Nu. In the case of flat plates, the length has been assumed to be 10 times the thickness.

For sphere:

$$Bi = (1/2)(\lambda_a/\lambda_s) Nu \quad (14)$$

For flat plate:

$$Bi = (1/20)(\lambda_a/\lambda_s) Nu \quad (15)$$

The thermal conductivity of a wide range of carbonaceous materials, including various woods, plastics, rubber, and coal, is within the range  $2.8 \times 10^{-4}$  to  $3.8 \times 10^{-4}$  cal/cm-deg C-sec [13,14]. It is assumed here that a value of

$$\lambda_s = 2.5 \times 10^{-4} \text{ cal/cm}^\circ\text{C sec (0.06 BTU/hr}^\circ\text{F ft)}$$

is representative of solid refuse. Pieces of refuse with conductivities much higher than this, such as tin cans and nails, may be neglected in this calculation, since they exert little influence in determining heating time.

Biot number is calculated using the values of Nu calculated in the foregoing and assuming the ambient gas to be air.

## CALCULATION OF FOURIER NUMBER

The Fourier number is given by  $Fo = \alpha t_h/r_o^2$ , where  $\alpha$  is the thermal diffusivity of the solid material, and  $t_h$  is the heating time. Fo is calculated using the values of Bi obtained in the foregoing and graphs of equation (11) found in reference [8].

## CALCULATION OF HEATING TIME

The heating time of a specimen of given dimension is obtained from the Fourier number and the thermal diffusivity of the material. This analysis uses the value  $\alpha = 1.0 \times 10^{-3}$  sq cm/sec ( $3.9 \times 10^{-3}$  sq ft/hr) which should be appropriate for refuse, since it is approximately valid for coal, wood, and many other carbonaceous materials [13,14].

The extreme case, where surface heat transfer is infinitely faster than heat transfer within the specimen (i.e.,  $\lambda_s/hr_o = 0$ ), represents an upper limit to the heating rate obtained by increasing without bounds the relative velocity between the specimen and the ambient gas. Heating times for this case are found in a similar manner to that described in the foregoing.

## APPENDIX B

### DERIVATION OF BURNING TIME EQUATIONS

#### INTRODUCTION

As was done in the analysis of heating time in Appendix A, two extreme specimen geometries are considered here: flat plates and spheres. In the case of each geometry, the equations for burning time are derived for cases of complete mass-transfer control and complete chemical control.

#### FLAT PLATE: MASS-TRANSFER CONTROLLED BURNING RATE

The plate is assumed to be oriented with its length parallel to the velocity of the ambient gas. Combustion of the edges of the specimen is assumed to be negligible with respect to both total burning rate and changes in the dimensions of the specimen.

The molar flux of oxygen reaching the burning surface is

$$\dot{N} = k_f (f_a - f_s)$$

where  $k_f$  is the mass transfer coefficient (g-moles/sq cm-sec), and  $f_a$  and  $f_s$  are the mole fractions of oxygen in the ambient gas and at the solid surface. Owing to the assumption that burning rate is mass-transfer controlled,  $f_s = 0$ . Therefore,

$$\dot{N} = k_f f_a \quad (16)$$

For the case of laminar flow at the surface of the specimen, which will almost always be the case,  $k_f$  is given by the following semi-empirical equation [12]:

$$k_f = 0.664 (PD/RTL) Re^{1/2} Sc^{1/3}$$

where P is absolute pressure, D and Sc are the coefficient of diffusion and Schmidt number for oxygen in the ambient gas, R is the ideal gas constant, and T is absolute temperature.

The Schmidt number is essentially independent of both temperature and pressure and has a value of about 0.9 for oxygen in air. Since the ambient gas of the refuse has properties similar to air,  $Sc^{1/3}$  is assumed to be unity. Therefore,

$$k_f = 0.644 (PD/RTL) Re^{1/2} \quad (17)$$

The specific burning rate (g/sq cm-sec) is given by

$$\dot{R}_s = FM_s \dot{N} \quad (18)$$

where F is the moles of solid material consumed per mole of oxygen used, and  $M_s$  is the molecular weight of the solid material.

Combining equations (16), (17), and (18) gives

$$\dot{R}_s = (0.664)FM_s (D/L) (P_f/RT) Re^{1/2} \quad (19)$$

The specific burning rate is also given as follows in terms of the density of the solid material ( $\rho_s$ ) and the rate of decrease of specimen thickness (dr/dt):

$$\dot{R}_s = \rho_s dr/dt$$

Assuming temperature pressure, oxygen concentration, and ambient velocity to be independent of time,  $\dot{R}_s$  is constant, and integration of the foregoing gives

$$t_b = (\rho_s/\dot{R}_s)r_0 \quad (20)$$

The desired burning-time equation is obtained by replacing  $\dot{R}_s$  in equation (20) with equation (19). In making this substitution, it is convenient to express D and Re in terms of temperature and pressure as follows:

$$D = D_o(T/T_o)^{3/2} (P_o/P) \quad (21)$$

$$Re = (VL/\nu_o) (T_o/T)^{3/2} (P/P_o) \quad (22)$$

where V is the relative velocity between the ambient gas and the specimen,  $\nu$  is the kinematic viscosity of the ambient gas, and the subscript o denotes STP conditions (0 C and 1 atm).

The temperature and pressure dependence of the relative velocity is not clearly known. If we express V as

$$V = V_o(T/T_o)^m (P/P_o)^n$$

then values of m ranging from -1/2 to 1 and values of n ranging from 0 to -1 are obtained depending upon the conditions chosen with regard to: 1) the size of the specimen, 2) whether the specimen is stationary with respect to the combustion chamber or suspended in the flow, 3) the extent to which the suspended specimen interacts with other specimens, and 4) the fractions of the time that the suspended plate is oriented parallel with and perpendicular to the main flow. Since the answers to these questions are now tenuous, the velocity of the ambient gas relative to the specimen will be treated as though it is the average linear flow rate through the chamber. Hence,

$$V = V_o(T/T_o)(P_o/P) \quad (23)$$

Since this equation is not necessarily correct, it should be remembered that the burning-time equation resulting from this analysis may not reveal the actual influence of pressure and temperature on burning time.

Substituting equations (21) to (23) into equation (20) gives

Flat plate; mass-transfer control:

$$t_b = [K_3 K_4 (T_o/T)^{1/4} (L/\nu_o)^{1/2} (1/f_a)] d_o \quad (24)$$

where

$$K_3 = \rho_s/FM_s, \quad K_4 = RT_o \nu_o^{1/2} / 1.328 D_o P_o$$

and  $d_o$  is the initial thickness of the plate.

For combustion in air,  $K_4 = 3.19 \times 10^4$  sq cm-sec<sup>1/2</sup>/g-mole. The value of  $K_3$  depends upon the material being burned. For example, if the products of combustion of aluminum, carbon, and iron are  $Al_2O_3$ ,  $CO_2$ , and  $Fe_3O_4$ , then the following values of  $K_3$  are found. Aluminum combustion:  $K_3 = 0.0752$  g-moles/cc; carbon combustion:  $K_3 = 0.129$  g-moles/cc; and iron combustion:  $K_3 = 0.105$  g-moles/cc.

#### SPHERE: MASS-TRANSFER CONTROLLED BURNING RATE

The sphere is assumed to burn uniformly over its surface, and the ambient gas is assumed to remain constant with respect to temperature, pressure, oxygen concentration, and velocity relative to the burning specimen. The following analysis is very similar to that performed in the foregoing for flat plates, except that Re changes during burnout for the case of spheres.

Assuming that Schmidt number is unity, the mass-transfer coefficient for a sphere may be written [12]

$$k_f = (DP/RT_r) [1 + 0.276 Re^{1/2}]$$

where  $r$  is the radius of the sphere at any time  $t$ . Using this equation and equating the rate of oxygen transport to the surface of the sphere to the equivalent rate of decrease of the sphere radius, we have

$$-\rho_s dr/dt = (DP/RT_r) [1 + .276 Re_0^{1/2} (r/r_0)^{1/2} (T_0/T)^{1/2}] f_a FM_s$$

where  $Re$  has been expressed in terms of its initial, STP value with velocity assumed to be  $V = V_0(T/T_0)(P_0/P)$ . This equation is arranged for integration in the following manner:

$$(DPf_a/RTK_3) \int_0^{(t_b)_{m.t.}} dt = \int_{r_0}^0 [r/(1+zr^{1/2})] dr$$

where  $z = 0.276 (Re_0 T_0/r_0 T)^{1/2}$ ,  $r_0$  is the initial sphere radius and  $(t_b)_{m.t.}$  is the burning time under mass-transfer controlled conditions. The substitution  $zr^{1/2} = y-1$  allows this equation to be integrated to give

Sphere; mass-transfer control:

$$(t_b)_{m.t.} = [K_1 K_2 K_3 (T_0/T)^{1/2} (1/f_a)] d_0^2 \quad (25)$$

where  $d_0$  is the initial sphere diameter and

$$K_1 = RT_0/8D_0P_0$$

$$K_2 = [(4/3)U^3 - 2U^2 + 4U - 4\ln(1+U)]/U^4$$

$$U = 0.276 Re_0^{1/2} (T_0/T)^{1/2}$$

$$K_3 = \rho_s/FM_s$$

The value of  $K_1$  is  $1.273 \times 10^4$  cm-sec/g-mole for combustion in air. The value of  $K_2$  is unity for the case of no convection (i.e., for  $V = 0$ ), and decreases as  $Re_0$  increases. For values of  $Re_0$  greater than about 1500,  $K_2$  becomes inversely proportional to  $Re_0^{1/2}$ , so that burning time becomes proportional to  $d_0^{3/2}$  and inversely proportional to  $V^{1/2}$ . The stoichiometric constant  $K_3$  is evaluated in the analysis of flat-plate combustion.

#### CHEMICALLY CONTROLLED BURNING OF CARBON: SPHERES AND FLAT PLATES

Combustion is assumed to occur only on the outer surface of specimens, thus neglecting reaction in pores. Assuming that oxygen concentration and temperature are constant, the specific burning rate,  $\dot{R}_s$ , is also constant, and the burning time of a

spherical or flat-plate specimen is obtained by integrating the equation  $\dot{R}_s = -\rho_c dr/dt$ , where  $\rho_c$  is the density of carbon, and  $r$  is either the sphere radius or the plate half-thickness. The burning time under conditions of chemical rate control is found to be

$$(t_b)_{c.c.} = (\rho_c/2\dot{R}_s) d_0$$

From the chemistry of the carbon-oxygen reaction,  $\dot{R}_s$  is given as follows:

Adsorption control:

$$\dot{R}_s = M_c \eta f_a P (1/2\pi M_o RT)^{1/2} \exp(-E_1/RT)$$

Desorption control:

$$\dot{R}_s = M_c A_2 \exp(-E_2/RT)$$

where  $E_1$  and  $E_2$  are the activation energies for oxygen adsorption on carbon and desorption of carbon oxides (assumed to be solely  $CO_2$ ),  $M_c$  and  $M_o$  are the molecular weights of carbon and oxygen,  $\eta$  is the steric factor of the adsorption process, and  $A_2$  is the frequency factor of the desorption process. Substitution of these expressions into equation (26) gives the following results:

Carbon sphere or flat plate; adsorption control:

$$(t_b)_a = K_5 (P_0/P) (1/f_a) [1/(T_0/T)^{1/2} \exp(-E_1/RT)] d_0 \quad (27)$$

Carbon sphere or flat plate; desorption control:

$$(t_b)_d = K_6 [1/\exp(-E_2/RT)] d_0 \quad (28)$$

where

$$K_5 = \rho_c (2\pi M_o RT_0)^{1/2} / 2M_c \eta P_0 \text{ and } K_6 = \rho_c / 2M_c A_2$$

The following quantities, obtained by fitting the foregoing chemical model to the data of Tu, David, and Hottel [15], permit calculation of burning times:

$$E_1 = 3.4 \text{ kcal/g-mole}$$

$$E_2 = 40 \text{ kcal/g-mole}$$

$$K_5 = 19.9 \text{ sec/cm}$$

$$K_6 = 7.38 \times 10^{-5} \text{ sec/cm}$$

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