

[This manuscript is dedicated to the memory of C. Y. Wen]

Fluidized Combustion of Char and Volatiles from Coal

This paper reviews the literature about fluidized combustion of char and volatiles from coal. While the rate of combustion of particles bigger than about 2 mm is mainly limited by the rate of diffusion of oxygen, there is usually an effect of chemical rate. As particle diameter decreases, the influence of chemical rate increases. Char particles are porous and combustion occurs in pores near their exterior. Char reactivity can be modelled by using an effective pore area for combustion.

At high bed temperatures ($>1,150$ K), the rate of combustion of volatiles is limited by the rate of mixing of fuel and oxygen. At low bed temperatures ($<1,000$ K), combustion reactions are inhibited by the inert particles in the bed.

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SCOPE

The primary objective and focus of this review is to provide perspective and understanding of the combustion of char and of volatile products from coal in dense bed fluidized combustors. The analysis is based on data from small-scale batch experiments using fundamental models of fluidized bed behavior. The method is that of classical reaction engineering.

The review also includes a broad brush picture of the appli-

cation of these results to predict the behavior of large fluidized combustors by means of comprehensive models. Such predictions are uncertain, notwithstanding the numerous intricate and elaborate models that have been promulgated. The uncertainties arise from incomplete knowledge of bed behavior, volatiles combustion and scale-up problems.

CONCLUSIONS AND SIGNIFICANCE

Char particles produced in a fluidized bed from coal are porous. If the diameter of these particles is larger than about 2 mm, their rate of combustion is mainly limited by the rate of diffusion of oxygen to the burning particles. For smaller particles the effect of chemical rate can be significant.

Combustion occurs within pores near the external surface of the particle. The effect of char reactivity can be allowed for, approximately, by using an effective pore area for combustion. For highly reactive chars the pore area is large and combustion tends to be controlled by diffusion. The pore area is small for unreactive chars and chemical rates can have a significant influence on the rate of combustion.

The reactivity of a char largely determines the inventory of carbon; the more reactive the char, the smaller the inventory. Combustion efficiency is sensitive to the inventory of carbon because carbon loss is mainly from small particles formed by attrition; these small particles burn slowly and may be elutriated

from the bed.

Three regimes can be identified for combustion of volatiles from coal. At low bed temperatures (<970 – $1,020$ K) the volatiles do not burn within the bed; combustion is inhibited by the inerts that comprise the majority (e.g., 99.5%) of the particles in the bed. At moderate bed temperatures ($\sim 1,100$ – $1,170$ K) the volatiles burn only in bubbles whose diameter exceeds a critical value. At high bed temperatures ($>1,170$ K) combustion occurs within bubbles and in the particulate phase.

If the bed temperature is above about 1,150 K, the rate of combustion of volatiles is limited mainly by the rate of mixing of fuel and oxygen. There is evidence to suggest that volatiles are released in bubbles and hence that the rate of interphase mass transfer may limit the rate of combustion. If this is true, the designer should aim to reduce the size of the bubbles of fuel.

INTRODUCTION

Work on the fluidized combustion of coal began in the 1950s (Skinner, 1970) but interest in the process remained subdued until the oil crisis of the 1970s. Since then the following systems, incorporating fluidized beds and based on coal, have received considerable attention.

(1) Plants for producing liquid or gaseous fuels, which are not dealt with in this paper.

(2) Combustors at atmospheric pressure for raising steam or process heat. The main advantages of these systems are: (i) the ease with which they can be adapted to reduce emissions of sulfur dioxide, e.g., by adding limestone; and (ii) their insensitivity to the type and quality of fuel.

(3) Combustors at elevated pressure for generation of electricity. As well as the advantages of fluidized combustion at atmospheric pressure, there are advantages of operation at elevated pressure: (i) thermal output per unit volume of bed is approximately proportional to absolute pressure, so the system is compact which should reduce capital costs; and (ii) by incorporating a gas turbine, such power cycles have the promise of appreciably higher thermal efficiency than those with atmospheric coal burners now in use (National Coal Board, 1980).

Professor Wen's house had many mansions. Important among these were his comprehensive models of fluidized bed combustion (Rajan and Wen, 1980; Chen and Wen, 1982). Here we consider the bricks from which these models were constructed: the literature on fluidized combustion of char and volatiles from coal. Particular attention will be given to applications (2) and (3) above, the areas in which it is generally agreed that fluidized combustion could have a major impact. Additional information can be found in the reviews of char combustion by Mulcahy (1978), Laurendeau (1979), Essenhigh (1981), and Smith (1982). The review of coal pyrolysis by Howard (1981) is also recommended, as are the reviews of fluidized combustion by Howard (1983), Yates (1983), and La Nauze (1984).

COMBUSTION OF SOLID CARBON

Reactions at Surface of Carbon

Avedesian and Davidson (1973) used the "two film" model of Hougen and Watson (1947) to describe the concentration gradients for O_2 , CO_2 and CO around burning particles. In this model oxygen diffusing towards a burning particle is consumed before it reaches the particle by,



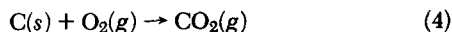
One of the CO_2 molecules produced diffuses away from the burning particle while the other diffuses back to the particle where it reacts with solid carbon,



Basu (1977), Chakraborty and Howard (1978, 1979), Roscoe et al. (1980), and Ross et al. (1981) have shown that the temperature of particles burning in a fluidized bed at ambient pressure is at most 250 K above that of the bed. This is too low for reaction 2 to be of importance. The current view is that oxygen diffuses to the burning particle where it reacts to form carbon monoxide,



which is subsequently oxidized in the gas phase around the particle by reaction 1. Therefore, not all of the heat produced by reaction 1 may get back to the particle. This is important because reaction 1 contributes approximately two thirds of the heat produced by the overall reaction,



The order of the heterogeneous oxidation reaction (Eq. 3) is uncertain. Reaction orders from experiment vary from 0.5 to 1.0, so Essenhigh (1981) suggests that the rate expression for this reaction should be of the Langmuir-Hinshelwood type. However, both he and Smith (1978) use Arrhenius-type rate expressions to relate rate constant with temperature and assume that reaction order is 0.5 for temperatures less than 1,000 K and 1.0 for temperatures greater than 1,000 K. Consequently, the order of the reaction is normally taken to be 1.0.

Rate of Combustion of Solid Carbon

The rate of combustion of single particles of carbon, in a bed of inert particles such as sand fluidized by air, may be affected by the rate of diffusion of oxygen to the particle and/or the rate of consumption of oxygen at the surface of the particle. Let the rate of

consumption per unit of external surface be

$$R_p = Kc_p \quad (5)$$

where c_p is the gas-phase oxygen concentration in the particulate phase, and K is an overall rate constant. When combustion of $CO(g)$ occurs close to the particle, the reaction at the surface of the particle is effectively Eq. 4 and,

$$1/K = 1/k_o + d_p/ShD_G \quad (6)$$

Here k_o is an overall chemical rate constant; d_p is the diameter of the carbon particle; and Sh is a local Sherwood number defining mass transfer to the burning particle. The Sherwood number is likely to be of order 2-4. Avedesian and Davidson (1973) assumed that the rate of combustion is limited by the rate of diffusion of oxygen to the particle; they assumed k_o was very large. Ross and Davidson (1982) assumed that reaction only occurs at the exterior surface of the particle. They put $k_o = k_F$ where k_F is the rate expression proposed by Field et al. (1967),

$$k_F = 595 T_p \exp(-149,200/RT_p) \quad (7)$$

Turnbull et al. (1984) assumed that oxygen diffuses a small distance into the burning particle and, using an analysis similar to that of Wicke (1955), showed that

$$k_o = (S_E D_E k_i)^{0.5} \quad (8)$$

Here k_i is on intrinsic rate constant which is based on the work of Smith (1978),

$$k_i = 470 T_p \exp(-179,400/RT_p) \quad (9)$$

slightly different from Eq. 7 because of experimental difficulties in measuring rate constants.

Avedesian and Davidson (1973) used the two-phase theory of Davidson and Harrison (1963); they assumed that solid carbon burns in the particulate phase and hence derived an expression for the burnout time for a batch of monosized char particles injected into a bed of inert particles fluidized by air. This analysis was extended by Ross and Davidson (1982) to include the effect of chemical rate. The resulting equation is

$$t_b = \frac{m}{12c_o A(U - (U - U_{mf})e^{-X})} + \frac{\rho_c d_i^2}{48ShD_G c_o} + \frac{\rho_c d_i}{24k_o c_o} \quad (10)$$

The terms in this equation represent the processes that may limit the rate of combustion of solid carbon. They are, in the order in which they appear in this equation: (i) the rate of transfer of oxygen from bubbles to the particular phase; (ii) the rate of diffusion of oxygen locally around the burning particle; and (iii) the rate of consumption of oxygen at the surface of the particle.

Equation 10 applies only if Sh and T_p , and hence k_o , are constant during burnoff. The particle temperature used in this equation is that predicted by Eq. 11 with $d_p = d_i$ and $c_p = c_o$. The validity of these assumptions is examined by discussing these parameters in general.

Particle Temperatures. An energy balance on a burning particle is complicated because CO produced at the surface of the particle burns in the gas phase around the particle. Consequently, it is difficult to predict how much of the energy from this reaction heats the particle.

If ΔH_T is the heat of combustion for carbon burnt to CO_2 and $\eta\Delta H_T$ is the heat that reaches the particle from this reaction, a particle energy balance can be written,

$$\eta\Delta H_T c_p / (1/d_p k_o + 1/ShD_G) = Nuk(T_p - T_b) + \sigma \epsilon_p d_p (T_p^4 - T_b^4) \quad (11)$$

The lefthand side of this equation represents the rate of heat production by the particle. This is equal to the molar rate of consumption of carbon, given by Eq. 5, times the effective molar heat of combustion of carbon and the surface area of the particle.

The validity of Eq. 5 was confirmed by combustion experiments by Ross and Davidson (1982) from which they deduced $Sh = 3.5$.

The righthand side of Eq. 11 represents the rate of loss of heat from the burning particle; the first term is the convective component and the second the radiative. The thermal conductivity k is an effective value. Heat is conducted first through a stagnant layer of gas of thickness δ around the particle and then the particulate phase (Xavier and Davidson, 1978). Ross et al. (1981) showed that,

$$1/k = 1/k_g - d_p/k_g(d_p + 2\delta) + d_p/k_{mf}(d_p + 2\delta) \quad (12)$$

The thermal conductivity k_{mf} of the particulate phase is uncertain but can be estimated from the relationships of Yagi and Kunii (1957) or Yagi et al. (1961) for an incipiently fluidized bed with Kunii and Smith's (1960) effective thermal conductivity for a packed bed. The simplified form of the radiation term is justified because the emissivity of a burning particle, 0.85 (Ross et al., 1981), is close to the value, 0.80, given by Lindsay (1983) for the particulate phase.

Turnbull (1983) showed that the equation for heat loss with $Nu = 7$ (Ross et al., 1981) is valid for particles whose diameter is bigger than that of the bed material if $\delta = d_a/5$. Then, using particle temperatures and combustion rates measured by Ross (1979), he deduced $\eta = 0.71$.

Equation 11 can be used to predict the effect of particle diameter on particle temperature. The results, with k_p from Eq. 8, show the following: 1) for unreactive carbons ($S_e \sim 0.3 \times 10^6 \text{ m}^{-1}$), the particle temperature approaches that of the bed as diameter decreases below about 0.8 mm; 2) for reactive carbons ($S_e \sim 10 - 15 \times 10^6 \text{ m}^{-1}$), the particle temperature does not decrease until the diameter is less than about 0.4 mm. The rate of combustion of small particles is mainly controlled by the rate of chemical reaction, so small particles of a reactive carbon burn much faster than those of an unreactive carbon. These predictions are important because combustion efficiency is largely determined by the rate of combustion of small particles.

Ross (1979) observed that small particles of coke (an unreactive carbon) burn at a temperature close to that of the bed. He suggested that this is because the Sherwood number is nearly constant so small particles have a large mass transfer coefficient, consequently CO produced at the particle combusts some distance from the particle. The particle temperature drops because little of the heat produced by the combustion of CO heats the particle. The predictions from Eq. 11 suggest an alternative explanation. The particle temperature drops because the Nusselt number is nearly constant so the heat transfer coefficient for small particles is large. Both factors probably contribute to the decrease in particle temperature but the calculations of Caram and Amundson (1977) show that the escape of CO does not occur until the diameter of the articles is about 50–100 μm . This is much smaller than the diameter ($\sim 500 \mu\text{m}$) at which the temperature of most carbons begins to fall. The temperature of 50–100 μm particles will usually be close to that of the bed so the effect of CO escaping from the vicinity of the particle will be small.

Because the particle temperature, and hence the rate of combustion per unit surface area, drops as the diameter of the particle decreases below some critical value, the CO_2 trace produced when a batch of carbon is introduced into a fluidized bed can have a long tail. The length of the tail gives an indication of the amount by which the rate of combustion is limited by the rate of chemical reaction; the more reactive the char or the higher the bed temperature, the smaller the tail. Turnbull (1983) showed that, unless the rate of combustion is limited mainly by the rate of chemical reaction, the assumption of constant particle temperature during burnoff gives reasonable estimates for the burnout time. In general, carbons burnt in fluidized beds are reactive because they are from low-grade fuels, so Eq. 10 can be used.

Sherwood Number for Mass Transfer. Equation 10 is for Sherwood number constant. If the equation for Sherwood number has the form suggested by Frossling,

$$Sh = a + b Re^{0.5} Sc^{0.3} \quad (13)$$

the equation for burnout time is more complicated (Chakraborty and Howard, 1981).

Chakraborty and Howard (1981) and Turnbull (1983) examined data for burnout times for particles in the size range 0.25–5 mm and concluded that burnout times are insensitive to Sherwood number. For many cases, Eq. 10 will therefore give satisfactory estimates for burnout time, though for large particles ($+10 \text{ mm}$) the equation for variable Sherwood number deserves attention. The following is a brief discussion of the equations for Sherwood number in the literature.

The theoretical minimum for Sherwood number occurs in a stagnant medium and is the constant a in Eq. 13. For an isolated sphere, $a = 2$. For a sphere in a fluidized bed, the theoretical minimum for Sherwood number is uncertain. Avedesian (1972) argued that the inerts around a burning particle hinder mass transfer, so $a = 2\epsilon_{mf}$; this has been used by many workers. On the other hand, it could be argued that $a = 2$ because particles in fluidized beds seem to be surrounded by a stagnant layer of gas (Xavier and Davidson, 1978).

Ross's (1979) Sherwood number of 3.5 implies mass transfer by forced convection and various relationships between Sherwood number and Reynolds number have been published. The two-phase theory of Davidson and Harrison (1963) assumes that the velocity of the gas in the particulate phase is U_{mf}/ϵ_{mf} . If this velocity is used in an equation of the form of Eq. 13 to calculate the Reynolds number in the particulate phase, too small a value for Sherwood number is obtained. Consequently, many workers have used the velocity U/ϵ_b to calculate the Reynolds number. This may often give satisfactory results but is not based on sound reasoning.

The work of Clift et al. (1984) may provide a solution of this discrepancy. There is a flow of gas through bubbles in a fluidized bed. Because of this, the superficial velocity in the particulate phase close to bubbles is greater than that at incipient fluidization. For combustors, the fluidizing velocity is usually far in excess of that required for incipient fluidization. For these conditions, Clift et al. (1983) show that the average superficial velocity in the particulate phase, taking into account the flow through bubbles, is about $2.5 U_{mf}$. The value given to b in Eq. 13 is usually 0.6. The Reynolds number suggested by the two-phase theory, $Re_{mf} = \rho_g d_p U_{mf} / \mu \epsilon_{mf}$, can be used in Eq. 13 with $b = 0.6 \times 2.5^{0.5} = 0.95$. The resulting equation is

$$Sh = 2\epsilon_{mf} + 0.95 Re_{mf}^{0.5} Sc^{0.3} \quad (14)$$

Support for this equation comes from the work of La Nauze and Jung (1982) who obtained Sherwood numbers from carefully controlled combustion experiments, as discussed below. They could only obtain satisfactory agreement with their data if they used the fluidizing velocity U to calculate Reynolds number. By coincidence, their beds were fluidized at velocity $U = 2.5 U_{mf}$, at which velocity the Sherwood numbers calculated by their method equal those calculated using Eq. 14.

Experimental

The rate of combustion of solid carbon in fluidized beds has been studied by two main methods.

First, the time t_b to combust batches of monosized carbon particles injected into an air-fluidized bed of sand has been measured either by: i) direct observation of burning particles or ii) measurement of CO_2 concentration in the flue gas. The interpretation of these data is best considered by reference to Eq. 10.

(a) Plots of t_b vs. m for constant U should, on the basis of Eq. 10, be straight. The intercept of such plots is approximately the time t_{bs} for combustion of a single particle and is the sum of the last two terms in Eq. 10. The effect of bed temperature and bed pressure on t_{bs} shows the degree of control by chemical rate. If the effect of bed temperature on t_{bs} is small, the effect of chemical rate is also small; if t_{bs} increases rapidly as bed temperature drops, the effect of chemical rate is significant. Similarly for bed pressure, if the rate of combustion is controlled by the rate of chemical reaction, increasing pressure has a significant effect. This is because the increased concentration of oxygen gives faster rates of chemical reaction.

On the other hand, if the rate of combustion is controlled by the rate of diffusion of oxygen to the particle, increasing pressure has little effect because while $c_o \propto P$, $D_G \propto P^{-1}$ so the product $c_o D_G$ is unchanged; thus the second term in Eq. 10, the diffusion term, is independent of pressure.

(b) Plots of t_b vs. d_i for constant m and U should give an indication of the rate controlling step. If the plot is linear, Eq. 10 shows that control by chemical rate is suggested. If the plot is linear in d_i^2 , control by diffusion is suggested.

Second, the rate of combustion of single particles has been followed by: i) fixing particles to a fine wire; ii) using a gauze basket to retrieve the partly burnt particles; or iii) quenching and sampling the whole bed. These data are used to obtain plots of: i) combustion rate; ii) Sherwood number; iii) density of the burning particle; and iv) fraction control by diffusion vs. diameter of the burning particle.

There are advantages and disadvantages of both methods. The major objection to the use of burnout times is that conditions vary during burnoff, in particular the bed temperature and oxygen concentration. The time-resolved approach allows conditions to be steady, but the particles have to be repeatedly heated and cooled which could affect their reactivity. Also, burnout times can be determined over a much wider range of conditions than can be used for the second method. For example, it would be difficult to use the second method to study the effect of bed pressure on combustion rate and the combustion of particles smaller than about 2 mm; the smaller sizes are frequently of interest because the rate of combustion of particles bigger than 2 mm is mainly limited by the rate of diffusion. Conclusions reached from both methods usually agree, and both methods have helped develop the present ideas concerning fluidized combustion of solid carbon.

The main aim of studying the fluidized combustion of solid carbon has been to determine the extent to which the rate of combustion is limited by either the rate of chemical reaction or the rate of diffusion of oxygen locally around the burning particle. One method of determining this is to deduce from experimental data the exponent n in either of the relationships,

$$\begin{aligned} R &\propto d_p^n \\ t_b &\propto d_i^n \end{aligned} \quad (15)$$

For pure diffusion control the relationships are,

$$\begin{aligned} R_{\text{dif}} &\propto d_p \quad (\text{see Eqs. 5 and 6}) \\ t_{b\text{dif}} &\propto d_i^2 \quad (\text{see Eq. 10}) \end{aligned} \quad (16)$$

and for control by chemical rate,

$$\begin{aligned} R_{\text{kin}} &\propto d_p^2 \quad (\text{see Eqs. 5 and 6}) \\ t_{b\text{kin}} &\propto d_i \quad (\text{see Eq. 10}) \end{aligned} \quad (17)$$

Avedesian and Davidson (1973) showed that for char in the size range 1.5–3.0 mm, burnout times are linearly related to diameter squared. They, therefore, concluded that the rate of combustion is mainly limited by the rate of diffusion of oxygen locally around the burning particle. It was generally agreed that this conclusion was valid for particles bigger than about 3 mm, but for smaller particles the rate of chemical reaction was thought to have an effect.

The data of Basu et al. (1975) suggested, but did not confirm, that chemical kinetics affect the rate of combustion. They used POCl_2 , which inhibits the combustion of CO to show that the reaction at the surface of burning particles is most likely Eq. 3. They also measured the temperature of burning particles and these were low enough to suggest that the rate of chemical reaction is of the order the rate of diffusion.

Basu (1977), Borghi et al. (1977), and Pillai (1982a) used their combustion data to determine values for n in Eq. 15. The values for n were within the range 1–2 predicted by theory and were generally closer to the value for control by diffusion. The conclusion was that, while the rate of combustion is mainly limited by the rate of diffusion, chemical kinetics have an effect. These analyses appear convincing, but Tomeczek (1979) and Chakraborty and Howard (1981) showed that usually such data could with equal confidence be correlated against either diameter or diameter squared.

Ross and Davidson (1982) used a different approach to determine the relative rates of diffusion and chemical reaction. They plotted the overall resistance to combustion, given by Eq. 6, against particle diameter. The intercept at $d = 0$ of such a plot shows the effect of chemical rate. They found that for coke burnt at 1,173 K the rate constant from experiment was close to that from Field et al.'s (1967) rate expression. The data of Ross and Davidson (1982) show that for coke burnt at 1,173 K in gas containing about 8% oxygen (vol./vol.) the fractional kinetic resistance to combustion decreases almost linearly from 0.9 for a 0.15 mm particle to about 0.3 for a 3 mm particle.

The influence of chemical kinetics complicates matters because the rate constant and particle temperature for the carbon need to be known. Most of the above workers used the rate constant of Field et al. (1967) with particle temperature about 140–150 K above that of the bed. Jung and La Nauze (1983, 1984) have performed useful experiments with a carbon

whose reactivity is well characterized. They obtained plots of particle temperature vs. diameter for various oxygen concentrations and used these in the rate constant for the carbon to calculate the rate of chemical reaction. The results of these carefully controlled experiments support the conclusions of Ross and Davidson (1982) and suggest internal pore combustion. The results show that while particles appear to shrink at approximately constant density, there is a slight reduction in density.

Turnbull et al. (1984) also concluded that combustion occurs in a thin shell near the exterior of the particle and showed that this has several important consequences. They measured burnout times for several carbons, whose reactivities differed, in fluidized beds of sand at pressures up to 17 bar absolute and temperatures of 1,023–1,173 K. As explained above, the effects of bed pressure and temperature should show the importance of chemical kinetics. The conclusions from this work are:

(1) As pressure is increased, the rate of combustion approaches a limit set by the rate of diffusion of oxygen locally around the burning particle. This is because increased pressure gives higher oxygen concentration and therefore faster reaction rates. On the other hand, the rate of diffusion is, as shown above, unaffected by pressure because the higher oxygen concentration is offset by the decrease of diffusion coefficient due to higher pressure.

(2) The reactivity of a carbon may be approximated by using an effective pore area S_E for combustion. BET areas comprising all pores give an area greater than S_E : the data suggest that only pores bigger than 150 Å are effective.

(3) Burnout times over the range of conditions given above were predicted by Eq. 10 with k_o from Eq. 8 and k_i from Eq. 9. Particle temperatures were obtained from Eq. 11. These equations only apply if $S_E > 0.3 \times 10^6 \text{ m}^{-1}$, as it is for most chars formed in a fluidized bed from medium- or low-rank coals. For $S_E \gg 0.3 \times 10^6 \text{ m}^{-1}$ combustion tends to be diffusion-controlled. For $S_E < 0.3 \times 10^6 \text{ m}^{-1}$ combustion is restricted to the external carbon surface and is likely to be controlled by chemical rate.

(4) The activation energy in the rate expression (Eq. 7) proposed by Field et al. (1967) is too large for fluidized combustion. The observed activation energy is about half this value (Eqs. 8 and 9).

(5) The reactivity of a char is affected by its treatment at high temperature if annealing of active sites is allowed to occur. The BET method detects this effect.

The rate of combustion of solid carbon in fluidized beds is controlled to varying extents by the rate of chemical reaction. Control by diffusion is favored by high bed temperatures and pressure, large particles (>3 mm) and reactive carbons.

Applications of Theory

As confidence in the models for combustion has increased, workers have attempted to predict the performance of combustors to which coal is added continuously. In particular the aim has been to predict the combustion efficiency and control characteristics of a fluidized bed. Both of these are related to the inventory of carbon in the bed.

Combustion Efficiency and Carbon Inventory. As carbon particles burn in a fluidized bed, they either shrink or break up until they are small enough to be blown out of the bed. The combustion efficiency, defined as the percentage of feed carbon converted to CO_2 , is therefore less than 100%.

Many complex models for predicting combustion efficiency have been published (Gibbs, 1975; Horio and Wen, 1978; Donsi et al., 1978; Ross, 1979; Garbett and Hedley, 1980; Turnbull, 1983). In all of the models, the range of char sizes is divided into a number of intervals over which mass or population balances are performed. The calculations require complicated numerical methods and are iterative.

There are three mechanisms by which the size of carbon particles in fluidized beds decreases. First, the particle may shrink due to combustion. Second, the particle may fragment to produce a few new particles. Third, the size of the particle may decrease because small pieces are broken from it by the process of attrition. Shrinkage due to combustion can be described by the models outlined previously. Fragmentation is difficult to model, and fortunately it is generally agreed that this process has little effect on the performance of a combustor. The effect of attrition can be modelled if it is assumed that particles formed by this process are so small that they are instantaneously elutriated. Then, using the approach of Massimilla and coworkers (Chirone et al., 1982; Arena et al., 1983),

the shrinkage term in the population or mass balances described above can be written as

$$\left(\frac{-dd_p}{dt}\right) = \left(\frac{-dd_p}{dt}\right)_{\text{combustion}} + \left(\frac{-dd_p}{dt}\right)_{\text{attrition}} \quad (18)$$

Beer et al. (1980), Chirone et al. (1982), Arena et al. (1983), and Turnbull (1983) show that reduced combustion efficiency is mainly caused by loss of carbon particles formed by attrition. Combustion efficiency is, therefore, a balance between the rates of combustion and attrition; the model for elutriation has little effect because attrited particles are rapidly elutriated. This is important because it suggests that combustion efficiency increases as the inventory of carbon decreases. The data of Beer et al. (1980) support this view; they show that the combustion efficiency increases as the inventory of carbon decreases. Since the inventory of carbon decreases as reactivity of the char increases, this is one reason why high combustion efficiencies have been observed for low-grade fuels (Beer et al., 1980).

Control Characteristics of a Combustor. The unsteady behavior of fluidized combustors has received little attention in the literature but is of theoretical interest and of practical importance. An understanding of transient behavior gives insight into the mechanisms of combustion and provides time constants for the system which are necessary for the proper design of control systems.

Van der Post et al. (1980) present a model to predict the response of a fluidized combustor to changes in operating conditions. The model does not include elutriation or breakage of particles but is otherwise general and the results are calculated by a computer program. Predictions from the model are compared with data from a pilot plant. Theory and experiment show that the response of a bed to changes in operating conditions is a function of the inventory (and hence burnout time) of carbon in the bed and the weight of the bed material.

Davidson (1982) considered a fluidized combustor for which the rate of injection of coal varies sinusoidally about some steady value. He used a population balance on the carbon particles in the bed to show that the burnout time of these particles affects both the attenuation and phase lag of the size distribution for carbon in the bed. The analysis also showed that the attenuation and phase lag differs according to whether the rate of combustion is controlled by diffusion of oxygen to the particle or by chemical rate.

Two time constants for a fluidized combustor were identified by Davidson (1982). First, there is the "mixing tank" time constant which depends on the heat capacity of the bed and the rate of heat removal from it. This time constant affects the response of the bed temperature to changes in operating conditions. Second, the behavior of the bed depends on the burnout time of carbon in the bed. This burnout time also influences the bed temperature response and determines the response of concentrations in the offgas to changes in operating conditions.

The usefulness of Davidson's (1982) analysis in its original form is limited because it is difficult to measure the amount of carbon in the bed and its size distribution. However, Gray (1981) has used the theory to predict how the bed temperature varies with operating conditions. The theory has been compared with data from frequency response tests performed on pressurized combustors at C.U.R.L. and the initial results are promising.

Overall System Models. The aim of overall system models is to predict the performance of fluidized combustors and boilers. These models use results from, but generally do not contribute to, the study of basic mechanisms of combustion and fluidization. Hence, they are not central to the theme of this review but a brief description and commentary is included.

Park et al. (1980) and La Nauze (1984) give useful summaries of the assumptions used in published models; there are a wide variety of assumptions. This is because the models need to described the following processes which are incompletely understood: i) fluid dynamics of the bed; ii) combustion of solid and gaseous fuels; iii) elutriation of material from the bed; iv) reactions between pollutants and materials added to remove them; and v) heat transfer to tubes immersed in the bed.

A model describing all of these processes in detail would be extremely complex, requiring special techniques to ensure convergence and considerable computer time for execution. The present understanding of the processes i-v above does not justify such an elaborate treatment.

A typical model for combustion of coal with low volatiles content makes a number of assumptions with respect to fluid mechanics and combustion, e.g.: a) no volatile matter in the coal; b) char evenly distributed throughout the particulate phase; c) combustion only in the particulate phase; and d) gases in the particulate phase perfectly mixed. Such assumptions simplify the analysis, but, nevertheless, such a model has several convergence loops. Analysis of this type, which was pioneered by Wen, is given by Louis (1978) and by Congalis and Georgakis (1981).

Other models in the literature aim to examine specific effects. The level II model of Horio et al. (1977) examines the effect of the rate of dispersion of coal on the temperature profile within the bed and the distribution of char throughout the bed. The main assumption in this model is that the size distribution of char particles within the bed is known. Van der Post et al. (1980) aim to model the unsteady behavior of fluidized combustors so that control characteristics can be determined; the assumptions in this model are similar to a-d noted above.

In most system models, the combustion of volatile matter is either (i) ignored, (ii) assumed to occur close to the distributor, or (iii) assumed to occur throughout the particulate phase. Park et al. (1980) consider the combustion of volatile matter, as mentioned previously; to simplify the analysis, they assume that the gases pass through the bed in plug flow. The model of Bywater (1980) extends the analysis of Park et al. (1980) by discarding the assumption of instantaneous release of volatiles at the coal injector and considering the rate of dispersion of the coal.

The agreement between predictions and observations for models such as those discussed above is usually disappointing. Reasonable agreement can be obtained only by adjusting parameters, for example, bubble diameter, cross-flow factor, and volume of solids in the bubble wakes. Even after the adjustment of parameters, there is a scale-up problem because there are few data from large units. Hence, the predictive power of even the most elaborate models is rather uncertain.

In spite of these doubts about the value of elaborate models of fluidized combustion, it is believed that the designer has much to learn from fundamental studies. Examples of how basic studies can explain large-scale behavior and influence design are as follows.

(1) Volatiles combustion and char burnout time probably determine the space between fuel injection points; fundamental studies suggest that wider spacing can be used for anthracite than for coal of high volatile content.

(2) The mechanism of char burnout explains why low-rank coals have a better carbon combustion efficiency than high-rank coals.

(3) The time constants, needed for the design of control systems, are influenced by char burnout.

COMBUSTION OF VOLATILES FROM COAL

Introduction

When coal is introduced into a fluidized combustor it decomposes to produce: (i) hydrogen-rich gas (Kossakowski, 1981) derived from the volatile matter in the coal; and ii) carbon-rich residue, the char. As discussed earlier, the char remains in the bed until it burns away, is elutriated, or is lost via overflow. The residence time in the combustor of the volatile matter is of the order (bed height)/(fluidizing velocity) which is less than 5 s. It is usually considered desirable to burn all of the volatile matter within the bed; failure to do so may give overbed burning and reduced thermal efficiencies.

While the volatile content of the coal can account for up to 40% of the heat input to the bed, the release and combustion of volatiles are not well understood. The time for devolatilization cannot be

predicted accurately, and on release it is not clear into which phase the volatiles enter nor in which phase they combust.

The rate of combustion of volatiles is normally considered to be limited by the rate of mixing of fuel and oxygen. If the volatiles do not burn within the bed, they are generally assumed to burn in the freeboard, so causing a rise in the temperature of this region. But these suppositions are not always valid: (i) at low bed temperatures, the rate of mixing may not limit the rate of combustion of volatiles; and (ii) freeboard temperature rises may be suppressed by solids thrown up from the bed into the splash zone and returning to the bed conveying sensible heat.

Behavior in the Freeboard

Bubbles project particles into the freeboard when they erupt at the surface of the bed. On a weight basis, the proportion of particles returning to the bed from the splash zone is greater than the proportion carried out of the freeboard. The splash zone should not be confused with the region between the minimum and maximum bed heights, H_{\min} and H_{\max} , called the fluctuating height zone.

Various relationships for the flux of solids across H_{\max} have been published: Martens et al. (1982) used the relationship of George and Grace (1978); Turnbull (1983) used that of Pemberton (1982). By considering heat transfer to these particles, both of these workers showed that about 70% of heat produced in the splash zone returns to the bed via these solids. Consequently, Martens (1983) observed only a 40 K freeboard temperature rise when sufficient natural gas was burnt in the freeboard to maintain the bed at 1,070 K. This suggests that the large freeboard temperature rises calculated by Park et al. (1980) are unrealistic. However, it is known that large industrial units may suffer from freeboard temperature rises of several hundreds of degrees Kelvin.

This anomaly is explained by ghost bubbles. Pemberton (1982) observed that gas from bubbles behaves as a discrete entity for some distance into the freeboard; following Kehoe (1969) he called these entities ghost bubbles. If bubbles of fuel are formed and reach the top of the bed, fuel-rich ghost bubbles will enter the freeboard. The rate of combustion in the freeboard will then be limited by the rate at which these ghost bubbles entrain oxygen. This is described by Pemberton's (1982) work. Consequently, fuel that enters the freeboard need not be burnt close to the top of the bed. If most of the fuel is not consumed within the splash zone, high freeboard temperatures can be expected. Turnbull (1983) showed that, if the concentration of fuel in a bubble at the surface of the bed is greater than about 50% vol./vol., complete combustion in the splash zone is unlikely. The data of Martens et al. (1982) support this view. They observed that combustion of CO in the freeboard is "retarded," causing higher freeboard temperatures than expected.

Combustion at Low Bed Temperatures

The rate of combustion of volatiles from coal in a fluidized bed is normally assumed limited by the rate of mixing of fuel and oxygen (Park et al., 1980; Stubington, 1981). The amount of over-erbed burning increases rapidly as the bed temperature falls below a critical value. The above assumption is, therefore, not always valid.

Turnbull's (1983) observation is consistent with the work of Baskakov and Makhorin (1975) and Dennis et al. (1982) on gas-fired fluidized combustors. They reported that it is difficult to burn gaseous fuels in fluidized beds whose temperature is less than some critical value.

To explain why combustion is unstable two questions need to be answered: (i) What is the mechanism by which combustion is inhibited and (ii) do the gases burn in the bubble phase or the particulate phase?

Consider the heatup of a bed of sand fluidized by a mixture of propane and air. Initially, at low bed temperatures, the mixture does not burn within the bed. Rather, it travels through the bed, (i) as bubbles which explode loudly just below the surface of the bed and (ii) in the particulate phase; this fuel can be seen burning with a blue flame just above the surface of the bed. Combustion

is said to be unstable. Ignition is maintained because the exploding bubbles ignite those that follow. The noise begins to subside at a bed temperature called the critical temperature T_{c1} , of about 1,090 K, at which the bubbles begin to burn within the bed (Dinnage and Kershaw, 1982). When the bed temperature reaches 1,120 K the bed is quiet; the propane can be seen burning with a blue flame in the jets which form above the distributor and in bubbles within 40 mm of the distributor.

The observation that at a particular temperature bubbles begin to burn within the bed is the basis of the model by Dennis et al. (1982). They suggested that, for temperatures close to T_{c1} , homogeneous combustion only occurs in bubbles whose diameter exceeds a critical value D_{emin} . For combustion inhibited by either (i) radical terminating reactions on the surface of particles in the bed or (ii) rapid removal of heat which prevents the large temperature jump normally associated with ignition, Dennis et al. (1982) showed that the equation for D_{emin} was of the form,

$$D_{emin} = K_c U_{mf} \exp(E_c/RT_{c1}) \quad (19)$$

Dennis et al. (1982) suggested that radical removal probably limits the rate of combustion, but van der Vaart (1983) has shown that both mechanisms, i.e., radical terminating reactions or heat removal, are possible.

Equation 19 predicts that T_{c1} decreases, so that it becomes easier to burn gaseous fuel, as (i) bed height increases, (ii) U_{mf} (and hence d_a) decreases, and (iii) $(U - U_{mf})$ increases. The first prediction agrees with experiment (Dinnage and Kershaw, 1982; Turnbull, 1983). However, the model fails to predict the effect of particle size (Dinnage and Kershaw, 1982; Turnbull, 1983) and fluidizing velocity (Baskakov and Makhorin, 1975; van der Vaart, 1983).

Aoyagi and Kunii (1974) and Yoshida (1975) suggest that the influence of particles raining through bubbles can be significant for exothermic reactions. If this is so, Turnbull (1983) has shown that the model of Dennis et al. (1982) could be modified to predict the effect of particle size.

The discrepancy between theory and experiment for the effect of fluidizing velocity is more serious. Van der Vaart (1983) suggests that ignition delay τ , which is the time for the concentration of radicals to reach that required for ignition may be important. For temperatures near that required for ignition, delays of the order 90 s have been observed, much longer than the residence time of gases in fluidized beds. Simple thermal theory gives the following expression for ignition delay,

$$\ln \tau = A/T + B \quad (20)$$

Using the two-phase theory of Davidson and Harrison (1963) and Eq. 20, van der Vaart (1983) showed that ignition delay could explain the observed effect of increasing fluidizing velocity.

The two models (i.e., ignition delay or transfer from bubbles of radicals or heat) have different, and plausible, criteria for stable combustion. Perhaps both criteria need to be satisfied before combustion can proceed. Combustion may not occur if either (i) the bubbles in the bed are smaller than D_{emin} or (ii) the residence time of gases in the bed is less than τ . The mechanism by which combustion is inhibited could depend upon the operating conditions.

If combustion is inhibited by removal of either radicals or heat, it is likely that combustion begins to occur in the particulate phase at some temperature T_{c2} which is higher than T_{c1} . Dennis et al. (1982) estimated T_{c2} by letting gas in the voids of the particulate phase have an equivalent bubble diameter. They predicted that for 0.4 mm sand T_{c2} is about 120 K higher than T_{c1} . The authors admit that this calculation is approximate, but it does give an idea of the magnitudes that could be involved.

Three regimes for combustion of gases in fluidized beds can, therefore, be identified: regime A, $T_b < T_{c1}$, gases do not burn within the bed; regime B, $T_{c1} < T_b < T_{c2}$, gases only burn within bubbles; regime C, $T_b > T_{c2}$, combustion occurs in both the bubble and particulate phases.

For combustion of volatiles the temperature T_{c2} cannot yet be estimated, but T_{c1} seems to be around 1,050 K (Turnbull, 1983).

This figure must be treated with caution because experiments with pure gases have shown that the temperature for stable combustion can be affected by the type of bed material (Turnbull, 1983; Stephenson and Ellwood, 1983) and the gas being burnt (Stephenson and Ellwood, 1983).

Combustion at High Bed Temperatures

The following discussion is for regimes B and C above. Turnbull (1983) has shown that, in most cases, particularly if the coal is well dispersed throughout the bed, the amount of overbed burning will be approximately the same for both regimes.

The mixing process that limits the rate of combustion of volatiles depends on the phase into which the volatiles are released and the rate of their release compared to the rate of dispersion of solids.

For fluidized beds at about 1,150 K, devolatilization times for 1–2 mm coal particles are of the order 10–20 s (Morris and Keairns, 1979; Atimtay, 1980; Jung and Stanmore, 1981; Pillai, 1981). These times have been compared to solids mixing time to justify assumptions regarding dispersion of volatiles (Borghi et al., 1977; Pillai, 1981), but this is not justified for the following reason. Devolatilization has been observed (Peters and Bertling, 1965; Morris and Keairns, 1979; Jungten and Van Heek, 1979; Jung and Stanmore, 1980) to occur in two stages: (i) a period of rapid decomposition during which most of the volatiles are released is followed by (ii) a period of slow degasification during which the major product is hydrogen. About 70% of the volatiles are released during the first 25–30% of the time for complete devolatilization, that is 3–6 s. This is the time that should be compared to the time for mixing of solids.

The rate and pattern of solids circulation cannot be predicted accurately (Masson et al., 1981; Jin et al., 1982). Assume that, after injection, coal particles move to the surface of the bed from where they are mixed throughout the bed. The time t_s to reach the surface of the bed determines the amount of volatile matter released into the region above the injector. The average rise velocity \bar{U}_R of a 3 mm coal particle is given by Nienow et al. (1978),

$$\bar{U}_R = 0.15(U - U_{mf})^{0.5}$$

Let $t_s \sim (H_{\max} - H_f)/\bar{U}_R$. For $(H_{\max} - H_f) = 0.5$ m, $(U - U_{mf}) = 1$ m·s⁻¹, $t_s = 0.5/0.15 \sim 3$ s. The time for completing the first stage of devolatilization is about 3–6 s, so most of the volatiles should have been released by the time the particle reaches the surface of the bed.

This is the situation modelled by Park et al. (1980) and Stubington and Davidson (1981). Both groups (i) assume the volatiles are released instantaneously to form a fuel-rich region above the injector, (ii) ignore the bubble and particulate phases; all gas is assumed to travel through the bed in plug flow with velocity U_T , and (iii) assume that combustion occurs at the interface between the oxygen- and fuel-rich regions of the bed.

The model of Park et al. (1980) is based on the tracer experiments of Jovanovic et al. (1980). The tracer experiments suggested that gases in fluidized beds pass through the bed as a meandering plume. Using this model, Jovanovic et al. (1980) deduced radial diffusion coefficients for gases in fluidized beds. These diffusion coefficients are about two orders of magnitude larger than molecular diffusion coefficients and are used by Park et al. (1980). Stubington and Davidson (1981) used experimental data for the amount of overbed burning with their model for combustion to deduce radial diffusion coefficients. These diffusion coefficients are of the order of molecular diffusion coefficients, much smaller than those of Jovanovic et al. (1980).

Turnbull (1983) suggested that this difference was the result of bypassing of fuel in bubbles. Yates et al. (1980) observed that volatiles are released as bubbles. Pillai (1982) discounts this observation because the position of the particle in Yates et al.'s (1980) experiment was fixed. However, it is difficult to believe that volatiles released into a fuel-rich region during the initial period of rapid devolatilization do not become detached from the particle.

If bubbles of fuel are formed during devolatilization, the region

above the coal injector contains fuel-rich bubbles and oxygen-rich bubbles from the fluidizing air. The diameter of the bubbles of fuel is determined by the volatile matter content of the coal and the method of injecting the coal. If the coal is injected in batches cyclically, for example by a rotary valve, the particles in each batch are not well dispersed so bubbles of fuel from the individual particles coalesce. Consequently, one or more large bubbles of fuel are likely to be formed. This is important because the rate of interphase mass transfer is slow for large bubbles (Davidson and Harrison, 1963). The particulate phase above the injector becomes oxygen-rich and combustion occurs as oxygen is transferred to the fuel-rich bubbles and as fuel is transferred to the particulate phase. If the coal is injected particle by particle, the bubbles of fuel are smaller because the probability of coalescence is reduced. As a result, interphase mass transfer is more rapid and the particulate phase above the injector is fuel-rich. Combustion occurs: (i) as oxygen is transferred to the particulate phase from bubbles of fluidizing air within the plume; (ii) as fuel is transferred to oxygen-rich bubbles; and (iii) at the interface between the fuel- and oxygen-rich regions of the bed. Theory predicts that the smoother the method of injection the more rapid the rate of combustion of volatiles.

Data from a 0.3 m combustor into which the coal was injected by a rotary valve agree with predictions from a model based on the above ideas (Turnbull, 1983). The data also show that the amount of overbed burning decreases with: (i) decreasing volatile matter content of the coal, (ii) increasing bed height, and (iii) increasing excess air. Finally, the data suggest that oxygen supplied to the region above the injector with the gas for conveying the coal is consumed by volatiles. This implies that the amount of overbed burning of volatile matter could be reduced by matching the flow of conveying air to the volatile matter content of the coal.

Turnbull (1983) also presents models for the combustion of volatiles in which the coal is assumed well dispersed. Comparing predictions from these models to those from the models above shows that in general overbed burning of volatiles would be reduced if the coal was dispersed throughout the bed.

Thus, it is of vital importance to get good distribution of coal over the whole cross-section of a large fluidized combustor. This is a long standing engineering problem for which no satisfactory practical solution has yet been found.

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NOTATION

a	= constant in equation for Sherwood number, Eq. 13
A	= cross-sectional area of combustor, m ²
A	= constant in equation for ignition delay, Eq. 20, s·K
b	= constant in equation for Sherwood number, Eq. 13
B	= constant in equation for ignition delay, Eq. 20, s
c_o	= oxygen concentration of the inlet gas, mol·m ⁻³
c_p	= oxygen concentration in the particulate phase, mol·m ⁻³
d_a	= diameter of inerts that comprise the bed, m
d_i	= initial diameter of particle, m
D_{emin}	= minimum bubble diameter for ignition, m
D_E	= diffusion coefficient of oxygen in solid carbon, m ² ·s ⁻¹
D_G	= gas-phase diffusion coefficient of oxygen, m ² ·s ⁻¹
E_c	= activation energy for a combustible mixture, J·mol ⁻¹
H_f	= height of coal injection point above distributor, m
H_{\max}	= maximum bed height, m
H_{\min}	= minimum bed height of a bubbling bed, m
ΔH_T	= heat of combustion for carbon burnt to carbon dioxide, J·mol ⁻¹

k	= effective thermal conductivity of particulate phase, $W \cdot m^{-1} \cdot K^{-1}$
k_F	= rate constant proposed by Field et al. (1967) for combustion of impure solid carbon, $m \cdot s^{-1}$
k_g	= thermal conductivity of gas, $W \cdot m^{-1} \cdot K^{-1}$
k_i	= intrinsic rate constant for combustion of impure solid carbon, $m \cdot s^{-1}$
k_{mf}	= thermal conductivity of particulate phase, $W \cdot m^{-1} \cdot K^{-1}$
k_o	= overall chemical rate constant, $m \cdot s^{-1}$
K	= overall rate constant for combustion, $m \cdot s^{-1}$
K_c	= constant in Eq. 19, s
m	= mass of carbon injected into bed, g
n	= exponent for diameter in Eq. 15
Nu	= Nusselt number for heat transfer
P	= absolute pressure, bar
R	= universal gas constant = $8.314, J \cdot mol^{-1} \cdot K^{-1}$
R	= rate of reaction for one particle, $mol \cdot s^{-1}$
R_{dif}	= rate of reaction for one particle for rate limited by diffusion of oxygen to the particle, $mol \cdot s^{-1}$
Re	= Reynolds number
Re_{mf}	= Reynolds number for particles in particulate phase
R_{kin}	= rate of reaction for one particle for rate limited by chemical kinetics, $mol \cdot s^{-1}$
R_p	= rate of reaction for one particle per unit of its external surface area, $mol \cdot m^{-2} \cdot s^{-1}$
Sc	= Schmidt number
SE	= effective pore area for combustion, determined by adsorption of N_2 at 77 K, $m^2 \cdot m^{-3}$
Sh	= Sherwood number for mass transfer to burning carbon particle
t	= time, s
t_b	= burnout time for batch of carbon, s
t_{bdf}	= burnout time for batch of carbon whose rate of combustion is limited by rate of diffusion of oxygen to the particle, s
t_{bkin}	= burnout time for batch of carbon whose rate of combustion is limited by chemical kinetics, s
t_{bs}	= burnout time for single particle of carbon, s
t_s	= time for coal particle to travel from injector to surface of bed, s
T	= temperature, K
T_b	= bed temperature, K
T_{c1}	= minimum temperature at which gaseous fuel burns in the bed. Combustion in bubbles, not in the particulate phase, K
T_{c2}	= temperature at which gaseous fuel begins to burn in the particulate phase, K
T_p	= particle temperature, K
U	= fluidizing velocity, $m \cdot s^{-1}$
U_{mf}	= minimum fluidizing velocity $m \cdot s^{-1}$
\bar{U}_R	= average rise velocity of particles in a fluidized bed, $m \cdot s^{-1}$
U_T	= total superficial fluidizing velocity, $m \cdot s^{-1}$
X	= bubble/particulate-phase cross-flow factor

Greek Letters

δ	= thickness of gas film around a burning particle, m
ϵ_b	= bubble voidage
ϵ_{mf}	= voidage of particulate phase
ϵ_r	= emissivity of particle
η	= ratio of heat that reaches particle from combustion of carbon to carbon dioxide to heat of combustion of carbon (= ΔH_T)
μ	= gas viscosity, $N \cdot s \cdot m^{-2}$
ρ_c	= carbon density, $g \cdot m^{-3}$
ρ_g	= gas density, $g \cdot m^{-3}$
σ	= Stefan-Boltzmann constant, $W \cdot m^{-2} \cdot K^{-4}$
τ	= ignition delay, time for concentration of radicals to reach that required for ignition, s

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