# COMBUSTION SCIENCE AND TECHNOLOGY

## 1. Introduction

Fuel combustion is a complex process, the understanding of which involves knowledge of chemistry (structural features of the fuel), thermodynamics (feasibility and energetics of the reactions), mass transfer (diffusion of fuel and oxidant molecules), reaction kinetics (rate of reaction), and fluid dynamics of the process. Therefore, the design of combustion systems involves utilizing information and data generated in a range of disciplines. Often, the design of practical combustion systems is based on experience rather than on fundamental mechanistic understanding. However, for certain fuels such as methane, the combustion mechanism is better understood than for other more complex fuels such as coal. To accommodate the variety of approaches used to solve practical problems, this article is divided into two subsections: combustion science and combustion technology.

## 2. Combustion Science

### 2.1. Definitions and Terminology.

*Higher Heating Value.* The heating value of a fuel is the amount of heat released during its combustion and is expressed in two forms: higher heating value (HHV) or gross calorific value and lower heating value (LHV) or net calorific value. The higher heating value of a fuel is the heat of combustion at constant pressure and temperature (usually ambient) determined by a calorimetric measurement in which the water formed by combustion is completely condensed (1–3). The lower heating value is the similarly measured or defined heat of combustion in the absence of water condensation. The higher heating value is most often used in combustion and flame calculations. The difference between HHV and LHV is numerically equal to the corresponding enthalpy difference, due to latent heat of vaporization. For example, in the complete combustion of methane with $O_2$ at 298 K, $CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O$ (g), for one mole of fuel the enthalpy change is $\Delta H = -802.1$ kJ/mol. This value is equal to the lower heating value of methane, and the higher heating value for the above reaction is obtained by adding the heat of vaporization of water at 298 K (44.01 kJ/mol). Thus the higher heating value of methane is $802.1 + 2(44.01) = 890.1$ kJ/mol of $CH_4$ (212.7 kcal/mol). The evaluation of $\Delta H$ for use in thermochemical calculations is more generally performed with the use of tables such as the Joint Army Navy Air Force (JANAF) Tables.

*FAR or AFR.* The composition of a mixture of fuel and air or oxidant is often specified according to the Fuel to Air Ratio (FAR), and can be expressed on a mass, molar, or volume basis. The FAR is normalized to the stoichiometric composition by defining the equivalence ratio $\phi$ as in equation 1, where

$m_f$ = mass of fuel, kg; and $m_o$ = mass of oxidizer, kg.

$$\phi = \frac{\left(\frac{m_f}{m_o}\right)}{\left(\frac{m_f}{m_o}\right)_{\text{stoich}}} \tag{1}$$

If $\phi < 1$, the mixture is said to be lean (in fuel) and the products of combustion contain unreacted or excess $O_2$. If $\phi > 1$ the mixture is said to be rich (in fuel) and the products of combustion contain CO and possibly $H_2$ because of incomplete combustion caused by the oxygen deficiency (1–3).

*Flammability Limits.* Any given mixture of fuel and oxidant is flammable (explosive) within two limits referred to as the upper (rich) and lower (lean) limits of flammability (Fig. 1). Most mixtures are flammable when the fuel to air volume ratio lies between 50 and 300% of the stoichiometric ratio (2). The stoichiometric ratio is the exact theoretical ratio of fuel to air required for complete combustion. The flammability region widens with increasing temperature, and usually with increasing pressure, although the effect of pressure is less predictable. The region within the flammability limits of a fuel–air mixture can be divided into two subregions, the slow oxidation region and the explosion region, separated by the spontaneous ignition temperature. To determine this temperature for liquid fuels, standard tests are used in which the liquid fuel is dropped into an open-air container heated to a known temperature. The lowest temperature at which visible or audible evidence of combustion is observed is defined as the spontaneous ignition temperature (1).

*Flash Point.* As fuel oil is heated, vapors are produced which at a certain temperature "flash" when ignited by an external ignition source. The flash point is the lowest temperature at which vapor, given off from a liquid, is in sufficient quantity to enable ignition to take place. The flash point is in effect a measure of the volatility of the fuel. The measurement of flash point for pure liquids is relatively straightforward. However, the measured value may depend slightly on the

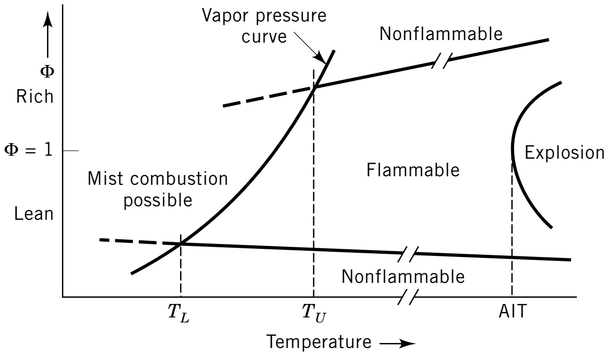


**Fig. 1.** Effect of temperature on limits of flammability of a pure liquid fuel in air, where $T_L$ = lean (or lower) flash point; $T_U$ = rich (or upper) flash point; and AIT = auto ignition temperature (4,5).

method used, especially for liquid mixtures, since the composition of the vapor evolved can vary with the heating rate. Special problems arise when the liquid contains a mixture of fuels and/or fuels and inhibitors. In these cases the vapor composition will be different from the liquid composition. Consequently, successive tests with the same sample can lead to erroneous results because the composition of the liquid in the sample holder changes with time as a result of fractional distillation (4–7).

*Ignition.* To understand the phenomenon of ignition it is necessary to consider the following concepts: ignition source, gas temperature, flame volume, and presence of quench wall surfaces. In general, there are two main methods of igniting a flammable mixture. In the self-ignition method, the mixture is heated slowly so that the vapor released as the temperature is raised ignites spontaneously at a particular temperature. In the forced ignition method, a small quantity of combustible mixture is heated by an external source and the heat released during the combustion of this portion results in propagation of a flame. The external ignition source can be an electric spark, pilot flame, shock wave, etc. For ignition to take place the following conditions should be satisfied: (*1*) the amount of energy supplied by the ignition source should be large enough to overcome the activation energy barrier; (*2*) the energy released in the gas volume should exceed the minimum critical energy for ignition; and (*3*) the duration of the spark or other ignition source should be long enough to initiate flame propagation, but not too long to affect the rate of propagation. Ignition models fall into two categories: the thermal model explains the ignition as resulting from supplying the mixture with the amount of heat sufficient to initiate reaction. In the chemical diffusion model the main role of the ignition source is attributed to the formation of a large number of free radicals in the preheat zone, where their diffusion to the surrounding region initiates the combustion process. The thermal model is applied more widely in the literature and shows better agreement with experimental data.

At ambient temperatures, reaction rates for gaseous mixtures of fuel and oxidant are extremely slow. As temperature is increased gradually, slow oxidation begins and as a result of the exothermic reactions that occur, the temperature keeps increasing. With further temperature increase, the reaction rate suddenly increases causing rapid combustion reactions to occur. This is providing, of course, that the rate of heat release is greater than the rate of heat loss through the container walls. The temperature at which the heat released by the reaction exceeds the heat loss is commonly referred to as the ignition temperature. The spontaneous ignition temperature (SIT), on the other hand, is the lowest temperature at which ignition occurs. Increasing the pressure results in a decrease in the spontaneous ignition temperature (1) (Fig. 2 and Table 1). This temperature is highly dependent on the material of construction, apparatus configuration, and test procedure, therefore reported test values vary widely (2,6,7).

From the chemical diffusion model standpoint, the usual values of ignition temperatures of mixtures often do not correlate well with other flame properties. Nevertheless, the following highly simplified, even speculative, qualitative description may be useful in thinking about flames. Early in the ignition or induction period, the attack of fuel by $O_2$ is initially slow, but generates free radicals (OH, H, O, $HO_2$, hydrocarbons) and other intermediate species (CO, $H_2$, and

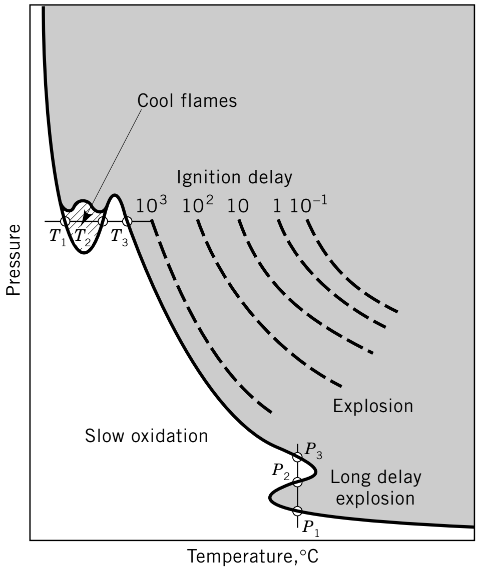


**Fig. 2.** Slow oxidation, spontaneous ignition, and explosion as a function of pressure and temperature variations in hydrocarbon mixtures (1).

partial oxidation and decomposition products of hydrocarbons, if present). For some time, there may be little or no temperature rise, the energy essentially being stored in the free radicals. In this stage the reactions may be similar to those that occur in very slow and nearly isothermal oxidation and cool flames observed in very rich hydrocarbon–$O_2$ mixtures, usually at lower temperatures and pressures. These reactions often stop at the production of stable oxidation and decomposition products, such as aldehydes, peroxides, lower hydrocarbons, etc, but under some conditions may lead to explosions. In a variety of chain

Table 1. **Spontaneous Ignition Temperatures**[a]

| Fuel | SIT, K |
|---|---|
| propane | 767 |
| butane | 678 |
| pentane | 558 |
| hexane | 534 |
| heptane | 496 |
| octane | 491 |
| nonane | 479 |
| decane | 481 |
| hexadecane | 478 |
| isooctane | 691 |
| kerosine (JP-8 or Jet A)[b] | 501 |
| JP-3 | 511 |
| JP-4 | 515 |
| JP-5 | 506 |

[a] Ref. 1.

[b] See AVIATION AND OTHER GAS TURBINE FUELS.

reactions, the fuel and any intermediates are rapidly attacked by radicals, some of which are also undergoing very fast chain-branching reactions. Evidence for the behavior of such free radicals is provided by studies of the mechanism of $H_2/O_2$ and similar explosions. These free radicals can multiply rapidly and attain high transient concentrations, initiating chain reactions that can eventually lead to the explosion of the flammable mixture. They are eventually consumed to form stable species by three-body recombination reactions in which most of the heat release occurs. An example of such a reaction, where M is any atom or molecule in the gas, is represented by

$$\mathrm{H} + \mathrm{OH} + \mathrm{M} \longrightarrow \mathrm{H_2O} + \mathrm{M} \qquad \Delta H = -498\ \mathrm{kJ/mol}\ (119\ \mathrm{kcal/mol})$$

Numerous other reactions of this type, including a sequence involving $HO_2$, exist and the relative importance of each reaction depends on the mixture composition. The rates of these termolecular processes increase with increasing pressure but have little or no temperature dependence.

When the partial pressures of the radicals become high, their homogeneous recombination reactions become fast, the heat evolution exceeds heat losses, and the temperature rise accelerates the consumption of any remaining fuel to produce more radicals. Around the maximum temperature, recombination reactions exhaust the radical supply and the heat evolution rate may not compensate for radiation losses. Thus the final approach to thermodynamic equilibrium by recombination of OH, H, and O, at concentrations still many times the equilibrium value, is often observed to occur over many milliseconds after the maximum temperature is attained, especially in the products of combustion at relatively low ($<2000$ K) temperatures.

The radicals and other reaction components are related by various equilibria, and hence their decay by recombination reactions occurs in essence as one process on which the complete conversion of CO to $CO_2$ depends. Therefore, the hot products of combustion of any lean hydrocarbon flame typically have a higher CO content than the equilibrium value, slowly decreasing toward the equilibrium concentration (CO afterburning) along with the radicals, so that the oxidation of CO is actually a radical recombination process.

In most hydrocarbon flames there are many radical consumption reactions that interfere with the chain-branching reactions, and the peak radical concentrations are therefore always lower than in analogous flames of $H_2$, $H_2/CO$, or moist CO. Consequently, the overall reaction rates for hydrocarbon flames at a given temperature are lower than the overall reaction rates for $H_2$, $H_2/CO$, or moist CO flames. In general, variations in the concentrations of such radicals are believed to interfere with the flame chemistry and can account for inhibition of flames by various additives, notably halogen-containing substances. Such additives can narrow flammability limits and reduce burning velocities, even when they cause little or no reduction in the ignition temperature. Those additives containing bromine are particularly effective, and brominated organic compounds are extensively used in extinguishing devices to suppress unwanted diffusion flames (fires). Although most of the chemistry summarized here has evolved from the study of flames and explosions in premixtures, it also applies semiquantitatively to many nonpremixed systems.

The fundamental parameters in the two main methods of achieving ignition are basically the same. Recent advances in the field of combustion have been in the development of mathematical definitions for some of these parameters. For instance, consider the case of ignition achieved by means of an electric spark, where electrical energy released between electrodes results in the formation of a plasma in which the ionized gas acts as a conductor of electricity. The electrical energy liberated by the spark is given by equation 2 (1), where $V$ = the potential, V; $I$ = the current, A; $\Theta$ = the spark duration, s; and $t$ = time, s.

$$E = \int_0^Q VI\,dt \tag{2}$$

The electrical energy is rapidly transformed into thermal energy, and because the temperature of the ionized gas is generally above 300 K, the ignition delay time is short compared with the spark duration, $\Theta$. Ignition only takes place if the electrical energy exceeds the critical value, $E_c$, and if this energy is liberated within a critical volume, $v_c$ (1,8,10,11).

Ignition can also be produced by a heated surface. During the process of heat transfer from a hot surface to a flammable mixture, reactions are initiated as the temperature rises and the combination of additional heat transfer from the surface and heat release by chemical reactions can lead to ignition of the mixture.

In experiments in which a heated cylinder was introduced into a propane–air mixture, it was found that approximately 11 μs were required for ignition. During this time, heat released by chemical reactions is negligible. This time interval before ignition is referred to as the ignition delay or induction time and is a function of the physical properties of the fuel, the rate of heat conduction, and the pressure of the combustion chamber (1,3,8,10,11). Ignition is characterized by a rapid change in temperature (eq. 3), where $t_{\text{ignition}}$ = ignition delay time, s; $E_a$ = activation energy, J/mol; $R$ = universal gas constant, J/(K·mol); and $T_i$ = ignition temperature, K.

$$t_{\text{ignition}}\, \alpha \exp\left(\frac{E_a}{RT_i}\right) \tag{3}$$

For liquid fuels, ignition delay times are of the order 50 μs at 700 K and 10 μs at 800 K. At low temperatures most of the ignition delay is the result of slow, free-radical reactions, and a distinction between the initiation and explosion periods within the ignition delay time can be made. With increasing ignition temperature for a given mixture, these times become comparable and at temperatures as high as 1500 K, both times may be of the order of $10^{-4}$ s. Consequently, the reaction zone in the flame of a mixture is observed to be one continuous event (12–14).

Another important concept is that of the critical ignition volume. During the propagation of the combustion wave, the flame volume cannot continually grow beyond a critical value without an additional supply of energy. The condition that controls the critical volume for ignition is reached when the rate of increase of flame volume is less than the rate of increase of volume of the combustion products. In this condition a positive exchange of heat between the flame and the fresh mixture is achieved.

For a point spark source, the flame volume is initially spherical and the critical ignition volume is determined by calculating the rate of change of flame volume with respect to radius compared to the rate of change of volume of the combustion products (eq. 4)

$$\frac{d}{dr}\left(\frac{4}{3}\pi\left((r+e)^3 - r^3\right)\right) \leq \frac{d}{dr}\left(\frac{4}{3}\pi r^3\right) \tag{4}$$

where $r$ = radius of flame, m; $e$ = thickness of flame front, m; and $r_c$ = radius of the critical spherical volume for ignition, m. This gives equations 5 or 6.

$$2\,er + e^2 \leq r^2 \tag{5}$$

$$r_c = e + \sqrt{2} \tag{6}$$

For a line spark source, the flame volume is initially cylindrical with the cylinder length equal to the separation distance between the electrodes. Thus, for a cylindrical flame, $r_c = e$, and the critical ignition volumes are equation 7 for a spherical flame and equation 8 for a cylindrical flame where $v_c$ = critical ignition volume, $m^3$/kg; $e$ = thickness of flame front, m; and $d$ = flame height, m.

$$v_c = \frac{4\pi e^3 \left(1+\sqrt{2}\right)^3}{3} \tag{7}$$

$$v_c = \pi e^2 d \tag{8}$$

In order to control and monitor the amount of energy required to achieve ignition, the concept of the minimum ignition energy as the smallest quantity of energy that will ignite a mixture is defined (15–17). The minimum ignition energy is calculated using the assumption that sufficient energy must be supplied from the exterior to the critical volume, $v_c$, to raise the mixture from its initial temperature, $T_i$, to the flame temperature, $T_f$(1). The critical energy is given by equation 9: where $E$ = critical energy, J; $v_c$ = critical ignition volume, $m^3$/kg; $\rho$ = density, kg/$m^3$; $c_p$ = specific heat capacity at constant pressure, J/(kg · K); $T_f$ = flame temperature, K; and $T_i$ = initial temperature, K.

$$E = v_c\,\rho\,c_p\left(T_f - T_i\right) \tag{9}$$

Because of heat being transferred to the exterior of the critical volume, only a fraction of the total spark energy, $E$, is utilized as ignition energy.

Minimum ignition energies are determined experimentally by means of a combustion bomb with two electrodes. Both the ignition energy and the quenching distance can be varied in this device. By using high performance (usually airgap) condensers, the majority of the stored energy will appear in the spark gap.

The stored energy can be calculated using equation 10 (1,2,9), where $E$ = total spark energy released/stored, J; $C$ = capacity of the condenser; and $V$ = voltage just before the spark is passed through the gas, V.

$$E = \frac{CV^2}{2} \tag{10}$$

The spark must always be produced by a spontaneous breakdown of the gas because an electronic firing circuit or a trigger electrode would either obviate the measurement of spark energy or grossly change the geometry of the ignition source (1,2,9).

Once ignition has been achieved, flame propagation can be controlled. This is achieved by the use of the concept of the quenching distance, defined as the minimum orifice diameter, wall separation, or mesh spacing just sufficient to prevent flame propagation (Fig. 3). Experiments carried out on spark ignition of mixtures between parallel plates show that, with sufficiently powerful sparks, a flame develops in the immediate neighborhood of the spark but does not propagate through the mixture unless the plates are separated by more than the quenching distance (1,2).

*Cool Flames.* Under particular conditions of pressure and temperature, incomplete combustion can result in the formation of intermediate products such as CO. As a result of this incomplete combustion, flames can be less exothermic than normal and are referred to as cool flames. An increase in the pressure or

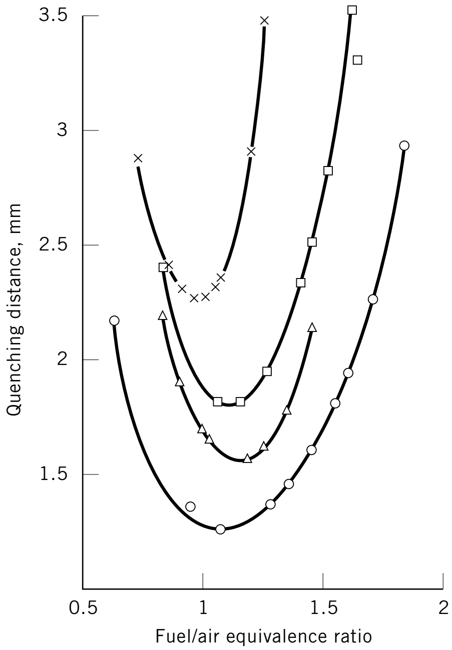


**Fig. 3.** Quenching distance as function of equivalence ratio for hydrocarbon mixtures with air (1), where x = methane, □ = propane, △ = propylene, and ○ = ethylene.

temperature of the mixture outside the cool flame can produce normal spontaneous ignition (1).

*Flame Temperature.* The adiabatic flame temperature, or theoretical flame temperature, is the maximum temperature attained by the products when the reaction goes to completion and the heat liberated during the reaction is used to raise the temperature of the products. Flame temperatures, as a function of the equivalence ratio, are usually calculated from thermodynamic data when a fuel is burned adiabatically with air. To calculate the adiabatic flame temperature (AFT) without dissociation, for lean to stoichiometric mixtures, complete combustion is assumed. This implies that the products of combustion contain only carbon dioxide, water, nitrogen, oxygen, and sulfur dioxide.

Actual temperatures in practical flames are lower than calculated values as a result of the heat losses by radiation, thermal conduction, and diffusion. At high temperatures, dissociation of products of combustion into species such as OH, O, and H reduces the theoretical flame temperature (7). Increasing the pressure tends to suppress dissociation of the products and thus generally raises the adiabatic flame temperature (4).

Adiabatic flame temperatures agree with values measured by optical techniques, when the combustion is essentially complete and when losses are known to be relatively small. Calculated temperatures and gas compositions are thus extremely useful and essential for assessing the combustion process and predicting the effects of variations in process parameters (4). Advances in computational techniques have made flame temperature and equilibrium gas composition calculations, and the prediction of thermodynamic properties, routine for any fuel-oxidizer system for which the enthalpies and heats of formation are available or can be estimated.

*Flame Types and Their Characteristics.* There are two main types of flames: diffusion and premixed. In diffusion flames, the fuel and oxidant are separately introduced and the rate of the overall process is determined by the mixing rate. Examples of diffusion flames include the flames associated with candles, matches, gaseous fuel jets, oil sprays, and large fires, whether accidental or otherwise. In premixed flames, fuel and oxidant are mixed thoroughly prior to combustion. A fundamental understanding of both flame types and their structure involves the determination of the dimensions of the various zones in the flame and the temperature, velocity, and species concentrations throughout the system.

The development of combustion theory has led to the appearance of several specialized asymptotic concepts and mathematical methods. An extremely strong temperature dependence for the reaction rate is typical of the theory. This makes direct numerical solution of the equations difficult but at the same time accurate. The basic concept of combustion theory, the idea of a flame moving at a constant velocity independent of the ignition conditions and determined solely by the properties and state of the fuel mixture, is the product of the asymptotic approach (18,19). Theoretical understanding of turbulent combustion involves combining the theory of turbulence and the kinetics of chemical reactions (19–23).

*Laminar Premixed Flames.* The structure of a one-dimensional premixed flame is well understood (1). By coupling the rate of heat release from chemical reaction and the rate of heat transfer by conduction with the flow of the unburned mixture, an observer moving with the wave would see a steady laminar flow of unburned gas at a uniform velocity, $S_u$, into the stationary wave or flame. Hence $S_u$ is defined as the burning velocity of the mixture based on the conditions of the unburned gas. The thickness of the preheating zone and the equivalent reaction zone is found to be inversely proportional to the burning velocity. By considering the heat release from the chemical reaction, it is possible to calculate the thickness of the effective reaction zone. For example, at atmospheric pressure, for hydrocarbon flames, the thicknesses of the preheat and reaction zones are found to be 0.7 and 0.2 mm, respectively (1–3). A propagating, premixed flame is in essence a thin wave in which the temperature rise is continuous and rapid. The thicknesses of the wave depend on $\phi$ and on pressure; for a typical hydrocarbon–air mixture at $\phi = 1$ at 101.3 kPa (1 atm), the entire rise, from the initial temperature to the adiabatic temperature, occurs in 0.01 mm, and the concentration and temperature gradients are accordingly very steep.

$S_u$ has been approximated for flames stabilized by a steady uniform flow of unburned gas from porous metal diaphragms or other flow straighteners. However, in practice, $S_u$ is usually determined less directly from the speed and area of transient flames in tubes, closed vessels, soap bubbles blown with the mixture, and, most commonly, from the shape of steady Bunsen burner flames. The observed speed of a transient flame usually differs markedly from $S_u$. For example, it can be calculated that a flame spreads from a central ignition point in an unconfined explosive mixture such as a soap bubble at a speed of $(\rho_o/\rho_b)S_u$, in which the density ratio across the flame is typically 5–10. Usually, the expansion of the burning gas imparts a considerable velocity to the unburned mixture, and the observed speed will be the sum of this velocity and $S_u$.

By applying the conservation equations of mass and energy and by neglecting the small pressure changes across the flame, the thickness of the preheating and reaction zones can be calculated for a one-dimensional flame (1).

There are a number of sources of instability in premixed combustion systems (23,24).

1. System instabilities involve interactions between flows in different parts of a reacting system. Although these instabilities can cause turbulence, they cannot be analyzed on their own and the whole system should be considered as a unit (11,25).
2. Acoustic instabilities involve the interactions of acoustic waves with the combustion processes. These instabilities are of high frequency and can be significant in certain situations but can successfully be avoided by suitable design (11,24).
3. Taylor instabilities involve effects of buoyancy or acceleration in fluids with variable density; a light fluid beneath a heavy fluid is unstable by the Taylor mechanism. The upward propagation of premixed flames in tubes is subject to Taylor instability (11).
4. Landau instabilities are the hydrodynamic instabilities of flame sheets that are associated neither with acoustics nor with buoyancy but instead involve only the density decrease produced by combustion in incompressible flow. The mechanism of Landau instability is purely hydrodynamic. In principle,

Landau instabilities should always be present in premixed flames, but in practice they are seldom observed (26,27).

5. Diffuse-thermal instabilities involve the relative diffusion reactants and heat within a laminar flame. These are the smallest-scale instabilities (11).

Laminar flame instabilities are dominated by diffusional effects that can only be of importance in flows with a low turbulence intensity, where molecular transport is of the same order of magnitude as turbulent transport (28). Flame instabilities do not appear to be capable of generating turbulence. They result in the growth of certain disturbances, leading to orderly three-dimensional structures which, though complex, are steady (1,2,8,9).

*Turbulent Premixed Flames.* Combustion processes and flow phenomena are closely connected and the fluid mechanics of a burning mixture play an important role in forming the structure of the flame. Laminar combusting flows can occur only at low Reynolds numbers, defined as

$$RE = \frac{\rho u d}{\mu} \tag{11}$$

where, $\rho$ = density, kg/m$^3$; $u$ = velocity, m/s; $d$ = diameter, m; and $\mu$ = kinematic viscosity, kg/ms. When $Re > Re_{cr}$ the laminar structure of a flow becomes unstable and when the Reynolds number exceeds the critical value by an order of magnitude, the structure of the flow changes. Along with this change of structure from an orderly state to a more chaotic state, the following parameters begin to fluctuate randomly: velocity, pressure, temperature, density, and species concentrations. Overall, with increasing Reynolds number, laminar flow becomes unstable as a result of these fluctuations and breaks down into turbulent flow. Laminar and turbulent flames differ greatly in appearance. For example, while the combustion zone of a laminar Bunsen flame is a smooth, delineated and thin surface, the analogous turbulent combustion region is blurred and thick (1).

Turbulent flame speed, unlike laminar flame speed, is dependent on the flow field and on both the mean and turbulence characteristics of the flow, which can in turn depend on the experimental configuration. Nonstationary spherical turbulent flames, generated through a grid, have flame speeds of the order of or less than the laminar flame speed. This turbulent flame speed tends to increase proportionally to the intensity of the turbulence.

In high speed dusted, premixed flows, where flames are stabilized in the recirculation zones, the turbulent flame speed grows without apparent limit, in approximate proportion to the speed of the unburned gas flow. In the recirculation zones the intensity of the turbulence does not affect the turbulent flame speed (1).

In the reaction zone, an increase in the intensity of the turbulence is related to the turbulent flame speed. It has been proposed that flame-generated turbulence results from shear forces within the burning gas (1,28). The existence of flame-generated turbulence is not, however, universally accepted, and in unconfined flames direct measurements of velocity indicate that there is no flame-generated turbulence (1,2).

The balanced equation for turbulent kinetic energy in a reacting turbulent flow contains the terms that represent production as a result of mean flow shear, which can be influenced by combustion, and the terms that represent mean flow dilations, which can remove turbulent energy as a result of combustion. Some of the discrepancies between turbulent flame propagation speeds might be explained in terms of the balance between these competing effects.

To analyze premixed turbulent flames theoretically, two processes should be considered: (*1*) the effects of combustion on the turbulence, and (*2*) the effects of turbulence on the average chemical reaction rates. In a turbulent flame, the peak time-averaged reaction rate can be orders of magnitude smaller than the corresponding rates in a laminar flame. The reason for this is the existence of turbulence-induced fluctuations in composition, temperature, density, and heat release rate within the flame, which are caused by large eddy structures and wrinkled laminar flame fronts.

A unified statistical model for premixed turbulent combustion and its subsequent application to predict the speed of propagation and the structure of plane turbulent combustion waves is available (29–32).

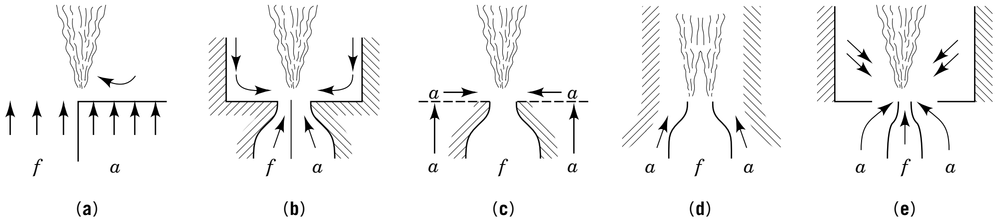
*Laminar Diffusion Flames.* Generally, a diffusion flame is defined as one in which no mixing of the fuel and oxidant takes place prior to emission from the burner. However, it can also be defined as a flame in which the mixing rate is sufficiently slow compared to the reaction rate, that the mixing time controls the burning rate. Since a continuous spectrum of flames exists between the perfectly premixed flame and the diffusion flame, the term diffusion flame is reserved for those flames in which there is a total separation between fuel and oxidant (1,5). Some of the practical advantages of diffusion flames include high flame stability, safety (as there is no need for the storage of the combustible mixture), intense radiation and hence high heat exchange with the surroundings. It is difficult to give a general treatment of diffusion flames largely because no simple measurable parameter, analogous to the burning velocity for premixed flames, can be used to characterize the burning process (3).

Many different configurations of diffusion flames exist in practice (Fig. 4). Laminar jets of fuel and oxidant are the simplest and most well understood diffusion flames. They have been studied exclusively in the laboratory, although a complete description of both the transport and chemical processes does not yet exist (2).

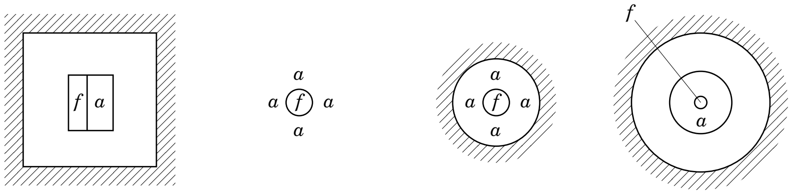
The discussion of laminar diffusion flame theory addresses both the gaseous diffusion flames and the single-drop evaporation and combustion, as there are some similarities between gaseous and liquid diffusion flame theories (2). A frequently used model of diffusion flames has been developed (34), and despite some of the restrictive assumptions of the model, it gives a good description of diffusion flame behavior.

The Displacement Distance theory suggests that since the structure of the flame is only quantitatively correct, the flame height can be obtained through the use of the displacement length or “displacement distance” (35,36) (eq. 12), where $h$ = flame height, m; $V$ = volumetric flow rate, m$^3$/s; and $D$ = diffusion coefficient.

$$h = \frac{V}{2\pi D} \tag{12}$$



Side views



Top views

**Fig. 4.** Various configurations (**a–e**) used to obtain gaseous diffusion flames where $a$ = air and $f$ = fuel (33).

In addition to the Burke and Schumann model (34) and the Displacement Distance theory, a comprehensive laminar diffusion flame theory can be written using the equations of conservation of species, energy, and momentum, including diffusion, heat transfer, and chemical reaction.

Evaporation and burning of liquid droplets are of particular interest in furnace and propulsion applications and by applying a part of the Burke and Schumann approach it is possible to obtain a simple model for diffusion flames.

Combustion chemistry in diffusion flames is not as simple as is assumed in most theoretical models. Evidence obtained by adsorption and emission spectroscopy (37) and by sampling (38) shows that hydrocarbon fuels undergo appreciable pyrolysis in the fuel jet before oxidation occurs. Further evidence for the existence of pyrolysis is provided by sampling of diffusion flames (39). In general, the preflame pyrolysis reactions may not be very important in terms of the gross features of the flame, particularly flame height, but they may account for the formation of carbon while the presence of OH radicals may provide a path for $NO_x$ formation, particularly on the oxidant side of the flame (39).

Combustion chemistry in diffusion flames also accounts for the smoke formation process. Characteristic behavior of smoking diffusion flames includes: (*1*) the first appearance of smoke is generally at the flame tip, the width of the smoke trail increasing as the amount of smoke increases; (*2*) the appearance and quantity of smoke increases with increasing flame height; (*3*) the smoking tendency changes with oxidant flow rate and the oxygen content of the oxidant stream; (*4*) the smoking tendency is a function of fuel type; and (*5*) the smoking tendency generally increases with increasing pressure (39).

*Diffusion Flames in the Transition Region.* As the velocity of the fuel jet increases in the laminar to turbulent transition region, an instability develops at the top of the flame and spreads down to its base. This is caused by the shear forces at the boundaries of the fuel jet. The flame length in the transition region is usually calculated by means of empirical formulas of the form (eq. 13): where $l$ = length of the flame, m; $r$ = radius of the fuel jet, m; $v$ = fuel flow velocity, m/s; and $C_1$ and $C_2$ are empirical constants.

$$l = \frac{r}{C - \dfrac{C_2}{v}} \tag{13}$$

*Turbulent Diffusion Flames.* Laminar diffusion flames become turbulent with increasing Reynolds number (1,2). Some of the parameters that are affected by turbulence include flame speed, minimum ignition energy, flame stabilization, and rates of pollutant formation. Changes in flame structure are believed to be controlled entirely by fluid mechanics and physical transport processes (1,2,9).

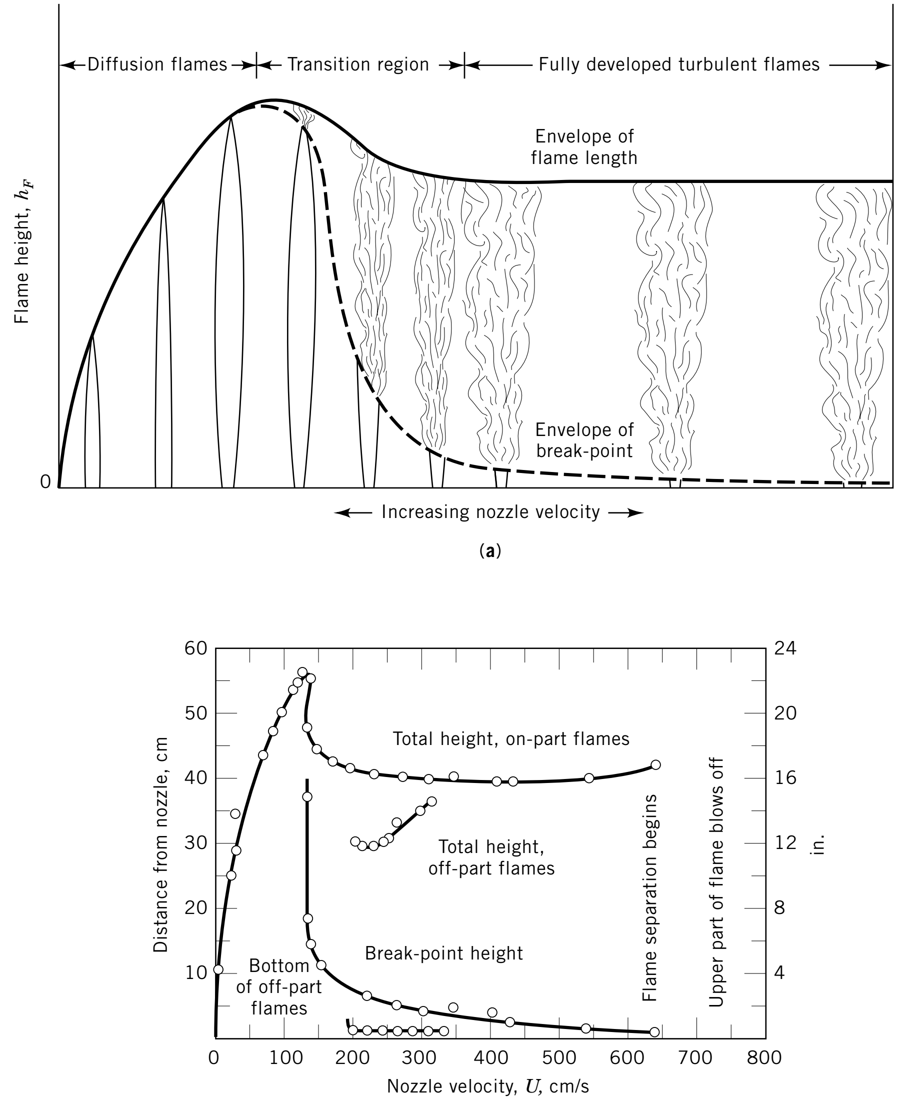
Consider the case of the simple Bunsen burner. As the tube diameter decreases, at a critical flow velocity and at a Reynolds number of about 2000, flame height no longer depends on the jet diameter and the relationship between flame height and volumetric flow ceases to exist (2). Some of the characteristics of diffusion flames are illustrated in Figure 5.

The preferred models for predicting the behavior of turbulent-free shear layers involve the solution of the turbulent kinetic energy equation in order to obtain the local turbulent shear stress distribution (1,2,9). These models are ranked according to the number of simultaneous differential equations that need to be solved. The one-equation model considers the turbulent kinetic energy equation alone, whereas the two-equation model considers the turbulent kinetic energy equation plus a differential equation for the turbulence length scale, or equivalently, the dissipation rate for turbulent kinetic energy. These equations are solved along with the conservation equations (momentum, energy, and species) to model turbulent flows.

The physics and modeling of turbulent flows are affected by combustion through the production of density variations, buoyancy effects, dilation due to heat release, molecular transport, and instability (1–3,5,8). Consequently, the conservation equations need to be modified to take these effects into account. This modification is achieved by the use of statistical quantities in the conservation equations. For example, because of the variations and fluctuations in the density that occur in turbulent combustion flows, density weighted mean values, or Favre mean values, are used for velocity components, mass fractions, enthalpy, and temperature. The turbulent diffusion flame can also be treated in terms of a probability distribution function (pdf), the shape of which is assumed to be known a priori (1).

In general, comprehensive, multidimensional modeling of turbulent combustion is recognized as being difficult because of the problems associated with solving the differential equations and the complexities involved in describing the interactions between chemical reactions and turbulence. A number of computational models are available commercially that can do such work. These include FLUENT, FLOW-3D, and PCGC-2.

The various studies attempting to increase our understanding of turbulent flows comprise five classes: moment methods disregarding probability density functions, approximation of probability density functions using moments,



(a)

(b)

**Fig. 5.** Effects of nozzle velocity on flame appearance in laminar and turbulent flow: (**a**), flame appearance; (**b**), flame height and break-point height (40).

calculation of evolution of probability density functions, perturbation methods beginning with known structures, and methods identifying coherent structures. For a thorough review of turbulent diffusion flames see References (41–48).

**2.2. Fundamentals of Heterogeneous Combustion.** The discussion of combustion fundamentals so far has focused on homogeneous systems. Heterogeneous combustion is the terminology often used to refer to the combustion of liquids and solids. From a technological viewpoint, combustion of liquid hydrocarbons, mainly in sprays, and coal combustion are of greatest interest.

Most theories of droplet combustion assume a spherical, symmetrical droplet surrounded by a spherical flame, for which the radii of the droplet and the flame are denoted by $r_d$ and $r_p$, respectively. The flame is supported by the fuel diffusing from the droplet surface and the oxidant from the outside. The heat produced in the combustion zone ensures evaporation of the droplet and consequently the fuel supply. Other assumptions that further restrict the model include: (*1*) the rate of chemical reaction is much higher than the rate of diffusion and hence the reaction is completed in a flame front of infinitesimal thickness; (*2*) the droplet is made up of pure liquid fuel; (*3*) the composition of the ambient atmosphere far away from the droplet is constant and does not depend on the combustion process; (*4*) combustion occurs under steady-state conditions; (*5*) the surface temperature of the droplet is close or equal to the boiling point of the liquid; and (*6*) the effects of radiation, thermodiffusion, and radial pressure changes are negligible.

In order to obtain an expression for the burning rate of the droplet, the following parameters are needed: physical constants such as the specific heat, and the thermal conductivity of the droplet, the radius of the flame, and the temperature of the flame. To determine these quantities, heat conduction, diffusion, and the kinetics of the chemical processes associated with droplet combustion need to be analyzed. This is achieved mathematically by solving the equations of mass continuity, mass continuity for components, and the energy equation. The solving of these equations can be facilitated if the following simplifying assumptions are made: the flame surrounding the droplet is a diffusion flame and, by definition, is formed where the fuel and oxidant meet in stoichiometric proportions; the temperature of this flame is very close to the adiabatic flame temperature; and the heat required for evaporation of the droplet and the heat loss to the surroundings through the burned gas are small and can therefore be neglected. These equations are usually solved in spherical coordinates for a one-dimensional case. However, since the flame is relatively thick, and the droplet is relatively small, the one-dimensional model of the process may not be a particularly accurate representation. Nevertheless, the values obtained for burning rates provide useful information (9).

The burning rate of the droplet (kg/s), and its rate of change of radius are related by:

$$m_e = -4\pi r_d^2 \rho_f \frac{dr_d}{dt} \tag{14}$$

where $m_e$ = burning rate of the droplet, kg/s; $\rho_f$ = density of fuel, kg/m$^3$; and $r_d$ = radius of droplet, m. This equation can be simplified, assuming $r_t/r_d \simeq$ constant and $m_e \simeq r_d$.

$$\frac{d(d_d^2)}{dt} = K = \text{constant} \tag{15}$$

Hence, the constant $K$ is termed the "burning-constant of the droplet." Integration of the equation 15 produces the droplet burning law:

$$d_d^2 = d_0^2 - Kt \tag{16}$$

where $d_0$ = the initial diameter of the droplet, m, and $t$ = burnout time, s.

The amount of data available on droplet combustion is extensive. However, the results can be easily summarized, because the burning rate constants for the majority of fuels of practical interest fall within the narrow range of 7 to $11 \times 10^{-3}$ $\mathrm{cm}^2/\mathrm{s}$. An increase in oxygen concentration results in an increase in the burning rate constant. If the burning takes place in pure oxygen, the values for burning rate are increased by a factor of about 2.0, compared to when the burning takes place in air (9).

The convective gas flow around a burning particle affects its burning rate. It has been postulated that in the absence of convection, the burning rate is independent of pressure. Forced convection, on the other hand, is believed to increase the burning rate.

During the final stages of the combustion of a droplet, coke remains, and although it represents a relatively small percentage of the mass of the original oil droplet, the time taken for the heterogeneous reaction between the oxygen-depleted combustion air and the coke particle is generally the slowest of all the combustion steps (9).

The reaction between a porous solid, such as a coke sphere, and a gas, such as oxygen, occurs in the following stages: (*1*) the main reactant species diffuse thoroughly through the boundary layer toward the solid surface and the products of reaction diffuse away from the surface; (*2*) diffusion and simultaneous chemical reaction take place within the pores of the solid proceeding from the external surface toward the interior, and gaseous products diffuse in the opposite direction; and (*3*) at the participating surfaces, the reacting gas chemisorbs, some intermediate species are formed, then the final products of the reaction desorb from the surface. Thus the observed reaction rate is a function of the individual resistances–boundary layer diffusion, pore diffusion, and chemical kinetics, and the rate controlling process is the slowest of them or a combination of these processes. Even though a number of gas reactions may take place at the surface of a burning carbonaceous solid, the reaction forming CO is most often assumed, $\mathrm{C} + 1/2\ \mathrm{O}_2 \longrightarrow \mathrm{CO}$. Coke combustion is treated mathematically like char combustion.

In a practical combustion chamber, the droplets tend to burn in the form of sprays, hence it is important to understand the fundamentals of sprays. In the most simple case, a fuel spray suspended in air will support a stable propagating laminar flame in a manner similar to a homogeneous gaseous mixture. In this case, however, two different flame fronts are observed. If the spray is made up of very small droplets they vaporize before the flame reaches them and a continuous flame front is formed. If the droplets are larger, the flame reaches them before the evaporation is complete, and if the amount of fuel vapor is insufficient for the formation of a continuous flame front, the droplets burn in the form of isolated spherical regions. Flames of this type are referred to as heterogeneous laminar flames. Experimental determination of burning rates and flammability limits for heterogeneous laminar flames is difficult because of the motion of droplets caused by gravity and their evaporation before the arrival of the flame front.

In modern liquid-fuel combustion equipment the fuel is usually injected into a high velocity turbulent gas flow. Consequently, the complex turbulent flow and spray structure make the analysis of heterogeneous flows difficult and a detailed analysis requires the use of numerical methods (9).

The combustion of a coal particle occurs in two stages: (*1*) devolatilization during the initial stages of heating with accompanying physical and chemical changes, and (*2*) the subsequent combustion of the residual char (49). The burning rate or reactivity of the residual char in the second stage is strongly dependent on the process conditions of the first stage. During pulverized coal combustion the devolatilization step usually takes about 0.1 s and the residual char combustion takes on the order of 1 s. Since char combustion occurs over ~90% of the total burning time, its rate can affect the volume of the combustion chamber required to attain a given heat release and combustion efficiency. The rate of devolatilization, and the amount and nature of volatiles can significantly affect the ignition process and hence the onset of char combustion. During devolatilization or thermal decomposition, rupture of various functional groups bonded to the macromolecular structure leads to the evolution of gases and the formation and opening of pores. Also, depending on its thermoplastic properties, a coal particle may undergo softening and swelling resulting in a change in size and physical characteristics. Diffusion of oxygen to, and within, a char particle depends on its physical structure and accessible surface area (char morphology). Attempts have been made to explain the combustion rates of chars in terms of their morphologies (50–52).

The ignition mechanism is rather complex and is not well understood in terms of actually defining the ignition temperature and reaction mechanisms. The ignition temperature is known, however, not to be a unique property of the coal and depends on a balance between heat generated and heat dissipated to the surroundings around the coal particle. Measuring the ignition characteristics is complicated by the fact that they are strongly dependent on the physical arrangement of the particles, eg, single particle, clouds of coal dust, or coal piles. Reported ignition temperatures range from 303 to 373 K in the case of spontaneous ignition of coal piles at ambient temperature to 1073–1173 K in the case of single coal particle ignition (53,54). Characteristics such as coal type, particle size and distribution of mineral matter, and experimental conditions such as gas temperature, heating rate, oxygen, and coal dust concentration are some of the important factors that influence values obtained for ignition temperatures. Ignition of coal particles can occur either homogeneously, with ignition of the volatiles released and the subsequent ignition of the char surface, or heterogeneously, with both volatiles and the char surface igniting simultaneously. Heating rate and particle size affect the mode of ignition. The early theories of ignition were based on an energy balance per unit volume of reactive mixture (55,56). Later, a generalized theory of flame propagation in laminar coal dust flames was proposed (57). Good reviews in this area include References (58–60).

A variety of techniques has been used to determine ignition temperatures: fixed beds, the crossing point method, the critical air blast method (61), photographic techniques (62,63), entrained flow reactors (64), electric spark ignition (65), luminous glow observations (66), plug flow reactors (67), shock tubes (68), and thermogravimetric analysis (69). The techniques mostly used are constant temperature methods (66,70,71) in which coal particles are introduced into a preheated furnace maintained at a fixed temperature. If ignition of the coal particles is not observed by the appearance of a glow, flame, or sharp temperature rise, the test is then conducted at a higher temperature and the procedure is repeated until the ignition of the sample is observed. It has been a matter of controversy as to whether the value of the critical temperature determined using this method for these low temperature tests represents the ignition tendency or the combustibility of the coal during the high heating rates encountered in a pulverized coal flame.

The structure of residual char particles after devolatilization depends on the nature of the coal and the pyrolysis conditions such as heating rate, peak temperature, soak time at the peak temperature, gaseous environment, and the pressure of the system (72). The oxidation rate of the char is primarily influenced by the physical and chemical nature of the char, the rate of diffusion and the nature of the reactant and product gases, and the temperature and pressure of the operating system. The physical and chemical characteristics that influence the rate of oxidation are chemical structural variations, such as the concentration of oxygen and hydrogen atoms (73–75), the nature and amount of mineral matter (76–79), and physical characteristics such as porosity, particle size, and accessible surface area. The rate of diffusion of the reactant gas is governed by the temperature and pressure of the operating system.

The rate limiting step in the combustion of char is either the chemical kinetics (adsorption of oxygen, reaction, and desorption of products) or diffusion of oxygen (bulk and pore diffusion). Variations in the reaction rate with temperature for gas–carbon reactions have been grouped into three main regions or zones depending on the rate limiting resistance (80) (Figs. 6 and 7).

The overall reaction rate is determined by equation 17,

$$q = \frac{1}{\dfrac{1}{k_{\text{diff}}} + \dfrac{1}{k_s}} p_g \tag{17}$$

where $q$ = rate of removal of carbon atoms per unit external surface area, kg/m$^2$s; $p_g$ = partial pressure of oxygen in the free stream, Pa; $k_{\text{diff}}$ = diffusional

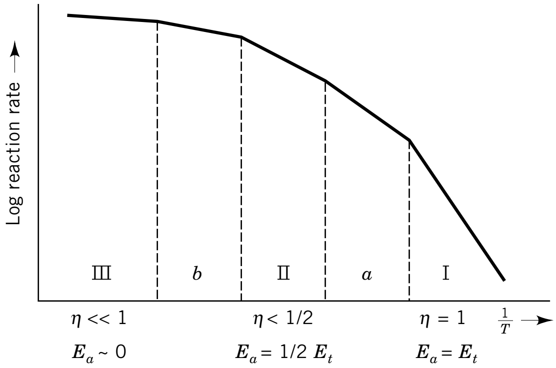


**Fig. 6.** The three ideal zones (I–III) representing the rate of change of reaction for a porous carbon with increasing temperature where $a$ and $b$ are intermediate zones, $E_a$ is activation energy, and $E_t$ is true activation energy. The effectiveness factor, η, is a ratio of experimental reaction rate to reaction rate which would be found if the gas concentration were equal to the atmospheric gas concentration (80).

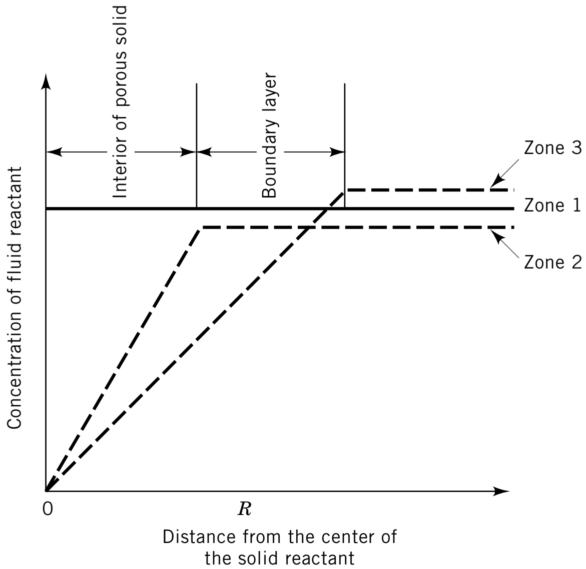


**Fig. 7.** The concentration of the reacting fluid as a function of the distance from the center of the solid reactant in various reaction zones.

reaction rate coefficient, kg/(m$^2$ · Pa); and $k_s$ = surface reaction rate coefficient, kg/(m$^2$ · Pa).

In Zone 1, the low temperature zone, the reaction rate is slow and the concentration of the reactant gas is uniform throughout the interior of the solid. The overall rate is controlled by the chemical reactivity of the solid, the kinetics are not influenced by mass transfer, and the kinetics are the intrinsic kinetics. The measured activation energy is equal to the true activation energy. In a higher temperature zone, Zone 2, the concentration of the gaseous reactant becomes zero at a point somewhere between the surface and the center of the particle, and the reaction rate is controlled by both the chemical kinetics and the diffusion rate of the gaseous reactant. The measured activation energy in this zone is one-half of the true activation energy. At still higher temperatures, in Zone 3, the chemical reactivity is so high that oxygen is consumed as soon as it reaches the surface of the solid and the concentration of the gaseous reactant approaches zero at the surface, indicating that the reaction rate is controlled by bulk diffusion of the reacting gas. The measured activation energy approaches a value of zero in this zone.

Burning times for coal particles are obtained from integrated reaction rates. For larger particles (>100 μm) and at practical combustion temperatures, there is a good correlation between theory and experiment for char burnout. Experimental data are found to obey the Nusselt "square law" which states that the burning time varies with the square of the initial particle diameter ($t_c \sim D_o^{2.0}$). However, for particle sizes smaller than 100 μm, the Nusselt relationship seems to predict higher burning times than those observed and it has been noted that burning times are proportional to the initial diameter of the particles raised to the power of 1.4 ($t_c \sim D_o^{1.4}$) (54).

## 3. Combustion Technology

Technology addresses the more applied, practical aspects of combustion, with an emphasis on the combustion of gaseous, liquid, and solid fuels for the purpose of power production. In an ideal fuel burning system (*1*) there should be no excess oxygen or products of incomplete combustion, (*2*) the combustion reaction should be initiated by the input of auxiliary ignition energy at a low rate, (*3*) the reaction rate between oxygen and fuel should be fast enough to allow rapid rates of heat release and it should also be compatible with acceptable nitrogen and sulfur oxide formation rates, (*4*) the solid impurities introduced with the fuel should be handled and disposed of effectively, (*5*) the temperature and the weight of the products of combustion should be distributed uniformly in relation to the parallel circuits of the heat absorbing surfaces, (*6*) a wide and stable firing range should be available, (*7*) fast response to changes in firing rate should be easily accommodated, and (*8*) equipment availability should be high and maintenance costs low (49–51).

**3.1. Combustion of Gaseous Fuels.** In any gas burner some mechanism or device (flame holder or pilot) must be provided to stabilize the flame against the flow of the unburned mixture. This device should fix the position of the flame at the burner port. Although gas burners vary greatly in form and complexity, the distribution mechanisms in most cases are fundamentally the same. By keeping the linear velocity of a small fraction of the mixture flow equal to or less than the burning velocity, a steady flame is formed. From this pilot flame, the main flame spreads to consume the main gas flow at a much higher velocity. The area of the steady flame is related to the volumetric flow rate of the mixture by equation 18 (81,82)

$$\dot{V}_{\mathrm{mix}} = A_f S_u \tag{18}$$

where $\dot{V}_{\mathrm{mix}}$ = volumetric flow rate, m$^3$/s; $A_f$ = area of the steady flame, m$^2$; and $S_u$ = burning velocity, m/s.

The volumetric flow rate of the mixture is, in turn, proportional to the rate of heat input (eq. 19):

$$\dot{V}_{\mathrm{mix}} \cdot (HHV) = \dot{Q} \tag{19}$$

where $\dot{V}_{\mathrm{mix}}$ = volumetric flow rate, m$^3$/s; $HHV$ = higher heating value of the fuel, J/kg; and $\dot{Q}$ = rate of heat input, J/s.

In the simple Bunsen flame on a tube of circular cross-section, the stabilization depends on the velocity variation in the flow emerging from the tube. For laminar flow (parabolic velocity profile) in a tube, the velocity at a radius $r$ is given by equation 20:

$$v = \mathrm{const}\left(R^2 - r^2\right) \tag{20}$$

where $v$ = laminar flow velocity, m/s; $R$ = tube radius, m; $r$ = flame radius, m; and const = experimental constant.

The maximum velocity at the axis is twice the average, whereas the velocity at the wall is zero. The effect of the burner wall is to cool the flame locally and decrease the burning velocity of the mixture. This results in flame stabilization. However, if the heat-transfer processes (conduction, convection, and radiation) involved in cooling the flame are somehow impeded, the rate of heat loss is decreased and the local reduction in burning velocity may no longer take place. This could result in upstream propagation of the flame.

To make the flame stable against the flow in a thin annular region near the rim, the flow velocity $v_r$ should be made equal to the burning velocity at some radius $r$. This annulus serves as a pilot and ignites the main flow of the mixture, ie, the flame gradually spreads toward the center. In most of the mixture flow, $v_r > S_u$ which results in a stable flame. With increasing mixture flow, the height and area of the flame increase. Measurement of the area of a stable Bunsen flame is the basis for the method most commonly used to determine $S_u$ (81–83).

By feeding the mixture through a converging nozzle, the velocity profile may be made nearly flat or uniform. A Bunsen flame in such a flow has a smaller range of stability but the mechanism is essentially the same and the flame very closely approximates a cone. If the apex angle of the flame is Θ, then $S_u$ can be obtained from equation 21

$$S_u = v_r \sin\left(\frac{\Theta}{2}\right) \tag{21}$$

where $S_u$ = burning velocity, m/s; $v_r$ = mixture velocity at the nozzle exit, m/s; and $\Theta$ = the apex angle of the flame in degrees.

If the tube diameter is appreciably larger than the quenching distance, $S_u$ will exceed $v_r$ in some parts of the flowing mixture due to a lack of quenching, and the flame will then propagate down the tube as far as there is mixture to consume. This undesirable condition is referred to as flashback. If, on the other hand, $v_r$ exceeds $S_u$ in the mixture flow, the flame lifts from the port and blows off. This condition is referred to as blowoff and like flashback should be avoided (Fig. 8). The velocity gradient at the wall, $g_w$, is defined as

$$g_w = \left(\frac{dv}{dr}\right)_{r=R}$$

For example, in a laminar or Poiseuille flow in a round tube of radius $R$, $g_w = 4g_{av}/R$, and for a given initial mixture composition, flashback (or blowoff) will occur at the same value of $g_w$ in tubes of various sizes, whereas the corresponding average velocity at flashback (or blowoff) is proportional to $R$. Typical velocity gradient values for stoichiometric methane–air flames are at flashback about 400 $\mathrm{s}^{-1}$ and at blowoff 2000 $\mathrm{s}^{-1}$. Thus, if the mixture is burned on a 1-cm diameter tube, the average velocity of flashback is $400 \times 0.5/4 = 50$ cm/s and at blowoff the average velocity is 250 cm/s, or the range of stability would be roughly one and a half to seven times the burning velocity. At flashback, $g_w$ is at a maximum around $\phi = 1$. If the burner is operated such that the surrounding inert atmosphere is inert, $g_w$ is at a maximum at blowoff.

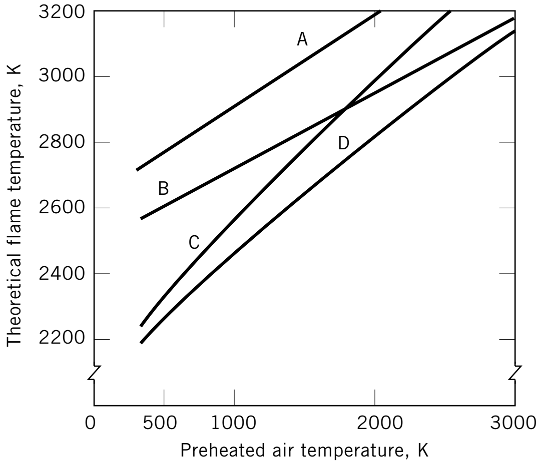


**Fig. 8.** Flashback and blowoff critical velocity gradients for a natural gas flame (10), where A is $N_2/O_2 = 2$, $p = 1.01$ MPa (10 atm); B, $N_2/O_2 = 2$, $p = 101.3$ kPa (1 atm); C, air, $p = 1.01$ MPa; and D, air, $p = 101.3$ kPa.

The behavior of rich mixtures is complicated by the entrainment of air at the burner port that sustains combustion of hot combustion products of the primary flame near the port. The blowoff velocity is found to increase continuously with $\phi$, or richer mixtures are more stable with respect to blowoff. They also have a lesser tendency toward flashback. Hence, a Bunsen flame has more latitude for stable operation if the primary mixture is rich. For this reason many appliance burners that involve assemblies of such flames are routinely adjusted by first making the primary mixture so rich that soot just forms in the burned gas (yellow-tipping), and then increasing the air until the yellow luminosity disappears. The primary equivalence ratio is then perhaps 1.5 or more; the rich products of that primary flame are burned in the secondary diffusion flame in the surrounding air, or the faintly luminous outer mantle of a Bunsen flame.

Most of the commercial gas–air premixed burners are basically laminar-flow Bunsen burners and operate at atmospheric pressure. This means that the primary air is induced from the atmosphere by the fuel flow with which it mixes in the burner passage leading to the burner ports, where the mixture is ignited and the flame stabilized. The induced air flow is determined by the fuel flow through momentum exchange and by the position of a shutter or throttle at the air inlet. Hence, the air flow is a function of the fuel velocity as it issues from the orifice or nozzle, or of the fuel supply pressure at the orifice. With a fixed fuel flow rate, the equivalence ratio is adjusted by the shutter, and the resulting induced air flow also determines the total mixture flow rate. The desired air–fuel volume ratio is usually seven or more, depending on the stoichiometry. Burners of this general type with many multiple ports are common for domestic furnaces, heaters, stoves, and for industrial use. The flame stabilizing ports in such burners are often round but may be slots of various shapes to conform to the heating task.

Atmospheric pressure industrial burners are made for a heat release capacity of up to 50 kJ/s (12 kcal/s), and despite the varied designs, their principle of stabilization is basically the same as that of the Bunsen burner. In some cases the mixture is fed through a fairly thick-walled pipe or casting of appropriate shape for the application and the desired distribution of the flame. The mixture issues from many small and closely spaced drilled holes, typically 1–2 mm diameter, and burns as rows of small Bunsen flames. It may be ignited with a small pilot flame, spark, or heated wire, usually located near the first holes to avoid accumulation of unburned mixture before ignition. The rated heat release for a given fuel–air mixture can be scaled with the size and number of holes. For example, for 2-mm diameter holes it would be 10–100 J/(hole) or, in general, 0.3–3 $kJ/cm^2s$ (72–720 $cal/cm^2s$) of port area, depending on the fuel. The ports may also be narrow slots, sometimes packed with corrugated metal strips to improve the flow distribution and reduce the tendency to flashback.

Gas burners that operate at high pressures are usually designed for high mixture velocities and heating intensities and therefore stabilization against blowoff must be enhanced. This can be achieved by a number of methods such as surrounding the main port with a number of pilot ports or using a porous diaphragm screen.

In order to achieve high local heat flux the port velocity of the mixture should be increased considerably. In burners that achieve stabilization using pilot ports, most of the mixture can be burned at a port velocity as high as 100 $S_u$ to produce a long pencil-like flame, suitable for operations requiring a high heat flux.

High local heat flux can also be obtained with Bunsen flames using mixtures with high burning velocities as in $H_2/O_2$ and $C_2H_2/O_2$ torches. Their stabilization mechanism is essentially the same as it is for slower burning mixtures but the port or nozzle of the torch is usually much smaller, in part to avoid turbulence in the mixture flow. The consequences of flashback are also much more severe since most such mixtures are detonatable, and the premixing chamber or tube must accordingly be more rugged. For this reason, many large hydrogen–oxygen and hydrocarbon–oxygen flames are not premixed. They actually consist of assemblies of closely spaced diffusion flames, produced from separately fed but contiguous fuel and oxidizer flows. In such surface-mixing burners, the surface is an array of very small and closely packed alternating fuel and oxidizer ports. The arrangement and number of the ports and the complexity of the required manifolding of the reactant passages vary with the application and the desired geometry of the burned gas flow. With a very fast burning fuel-oxidizer combination, the individual diffusion flames may be so short that the assembly approximates a large, flat, premixed flame, as is the case with some rocket engine injectors (84,85). The most frequently used modern burners are the circular type, capable of burning oil and gas.

It is often desired to substitute directly a more readily available fuel for the gas for which a premixed burner or torch and its associated feed system were designed. Satisfactory behavior with respect to flashback, blowoff, and heating capability, or the local enthalpy flux to the work, generally requires reproduction as nearly as possible of the maximum temperature and velocity of the burned gas, and of the shape or height of the flame cone. Often this must be done precisely, and with no changes in orifices or adjustments in the feed system.

If the substitute fuel is of the same general type, eg, propane for methane, the problem reduces to control of the primary equivalence ratio. For nonaspiring burners, ie, those in which the air and fuel supplies are essentially independent, it is further reduced to control of the fuel flow, since the air flow usually constitutes most of the mass flow and this is fixed. For a given fuel supply pressure and fixed flow resistance of the feed system, the volume flow rate of the fuel is inversely proportional to $\sqrt{\rho_f}$. The same total heat input rate or enthalpy flow to the flame simply requires satisfactory reproduction of the product of the lower heating value of the fuel and its flow rate, so that $WI \equiv Q_p/\sqrt{\rho_f}$ remains the same. *WI* is the Wobbe Index of the fuel gas, and is a commonly used criterion for interchangeability in adjusting the composition of a substitute fuel. The units of *WI* are variously given, but, if used consistently, are unimportant since only ratios of the Wobbe Indices are ordinarily of interest. Sometimes $\rho_f$ is taken as the specific gravity relative to some reference gas, eg, air, or average molecular weights may be used.

The Wobbe Index criterion also applies to substitution with aspirating or atmospheric pressure burners in which the volume flow of primary air induced by momentum exchange with the fuel increases with $\sqrt{\rho_f}$. Because the volumetric air requirement for a given $\phi$ is nearly proportional to the heating value of the fuel, an adjustment of $Q_p$ and $\phi_f$ to the same *WI* results in about the same stoichiometry of the primary flame. For example, if propane is an available substitute for methane or natural gas, it is common practice to prepare a mixture of approximately 60% propane–40% air (which of course is well above the upper flammability limit) to use as the fuel supply; though the heating value of the mixture is $1.53/\sqrt{2.36} = 1.0$ so that its Wobbe Index is the same. Though there would be slight differences in the stoichiometry of the flame, arising from the air mixed with the propane, and in $S_u$ of the final mixture, substitution with the same supply conditions would be quite satisfactory. On the other hand, if a mixture of the same heating value as that of methane were used (39.2% propane in air) at the same supply pressure, the flame would be much leaner and generally unsatisfactory (84,85).

There are direct substitutions of possible interest that would not be feasible without drastic changes in the feed system or pressure. Thus if the available substitute for natural gas is, eg, a manufactured gas containing much CO, there would almost always be a mismatch of the *WI*s unless the fuel could be further modified by mixing with some other gaseous fuel of high volumetric heating value (propane, butane, vaporized fuel oil, etc). Moreover, if there are substantial differences in $S_u$, eg, as a result of the presence of considerable $H_2$ as well as CO in the substitute gas, the variation in flame height and flashback tendency can also make the substitution unsatisfactory for some purposes, even if the *WI* is reproduced. Refinements and additional criteria are occasionally applied to measure these and other effects in more complex substitution problems (10,85).

Turbulence in the flow of a premixture flattens the velocity profile and increases the effective burning velocity of the mixture; eg, at a pipe-Reynolds number of 40,000 the turbulent burning velocity is several times the laminar burning velocity and it can be perhaps fifty times larger at very high Reynolds numbers. A turbulent flame is always somewhat noisy, the apparent flame surface becomes diffuse owing to the fluctuations in the actual or flame surface about its average position, and its stability tends to be less predictable. The instantaneous flame surface may be thought of as wrinkled by velocity variations in turbulent flow, or by the average distribution over a greater thickness (or time). Although the resulting enhancement of the mixture consumption rate may be considerable, turbulence is often considered undesirable in Bunsen-type flames. For this and other reasons, a large number of burner ports of small characteristic dimension, rather than a single large port, are frequently used to assure laminar flow to the individual flames. However, turbulence has an essential role in facilitating the mixing of fuel, oxidizer, and flame products, and serves an important function in the various types of flame-stabilizers of practical importance.

**3.2. Combustion of Liquid Fuels.** There are several important liquid fuels, ranging from volatile fuels for internal combustion engines to heavy hydrocarbon fractions, sold commercially as fuel oils. The technology for the combustion of liquid fuels for spark-ignition and compression-ignition internal combustion engines is not described here. The emphasis here is primarily on the combustion of fuel oils for domestic and industrial applications.

In general, the combustion of a liquid fuel takes place in a series of stages: atomization, vaporization, mixing of the vapor with air, and ignition and maintenance of combustion (flame stabilization). Recent advances have shown the atomization step to be one of the most important stages of liquid fuels combustion. The main purpose of atomization is to increase the surface area to volume ratio of the liquid. This is achieved by producing a fine spray. The finer the atomization spray the greater the subsequent benefits are in terms of mixing, evaporation, and ignition. The function of an atomizer is twofold: atomizing the liquid and matching the momentum of the issuing jet with the aerodynamic flows in the furnace (86–88). Some of the more common designs of atomizers are shown in Figure 9.

Atomizers for large boiler burners are usually of the swirl pressure jet or internally mixed twin-fluid types, producing hollow conical sprays. Less common are the externally mixed twin-fluid types (89,90).

The principal considerations in selecting an atomizer for a given application are turn-down performance and auxiliary costs. An ideal atomizer would possess all of the following characteristics: ability to provide good atomization over a wide range of liquid flow rates; rapid response to change in liquid flow rate; freedom from flow instabilities; low power requirements; capability for scaling (up or down) to provide desired flexibility; low cost, light weight, easily maintained, and easily removed for servicing; and low susceptibility to damage during manufacture and installation (89,90). There are differences in the structures of the sprays between atomizer types which may affect the rate of mixing of the fuel droplets with the combustion air and, hence, the initial development of a flame.

For distillate fuels of moderate viscosity 30 $mm^2/s$ (= cSt), at ordinary temperatures, simple pressure atomization with some type of spray nozzle is most commonly used. Operating typically with fuel pressure of 700–1000 kPa (7–10 atm) such a nozzle produces a distribution of droplet diameters from 10–150 μm. They range in design capacity of 0.5–10 $cm^3/s$ or more and the

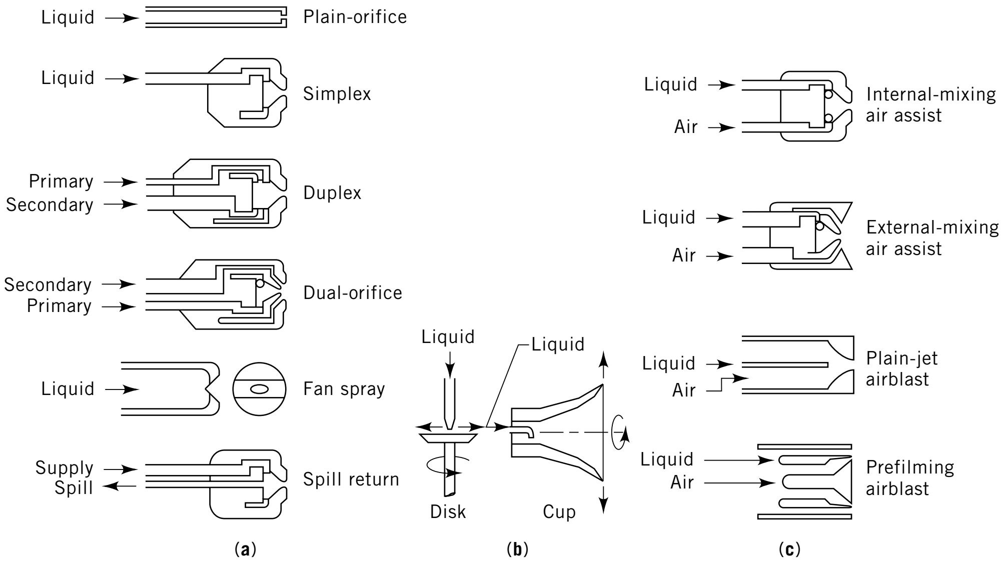


**Fig. 9.** (**a**) Pressure atomizers; (**b**) rotary atomizer; and (**c**) twin-fluid atomizers (89,90).

pumping power dissipated is generally less than 1% of the corresponding heat release rate. A typical domestic oil burner nozzle uses about 0.8 $cm^3/s$ of No. 2 fuel oil at the design pressure. Although pressure-atomizing nozzles are usually equipped with filters, the very small internal passages and orifices of the smallest units tend to be easily plugged, even with clean fuels. With decreasing fuel pressure the atomization becomes progressively less satisfactory. Much higher pressures are often used, especially in engine applications, to produce a higher velocity of the liquid relative to the surrounding air and accordingly smaller droplets and evaporation times. Other mechanical atomization techniques for the production of more nearly monodisperse sprays or smaller average droplet size (spinning disk, ultrasonic atomizers, etc) are sometimes useful in burners for special purposes and may eventually have more general application, especially for small flows.

Conventional spray nozzles are relatively ineffective for atomizing fuels of high viscosity, such as No. 6 or residual fuel oil (Bunker C) and other viscous, dirty fuels. In order to transfer and pump No. 6 fuel oil, it is usually heated to about 373 K, at which temperature its viscosity is about 40 $mm^2/s$. Relatively large nozzle passages and orifices are necessary to accommodate the possibility of suspended solids. Atomization of such fuel is often accomplished, or at least assisted, by the use of atomizing air, pumped at high velocity through adjacent passages in or around the liquid injection ports. Much of the relative velocity required to shear the liquid and form droplets is thus provided by the atomizing air; its mass flow is usually comparable with the fuel flow and thus a small fraction of the stoichiometric combustion air, although it is sometimes called primary air. In a typical high pressure, air-atomizing nozzle designed for injecting residual oil in a gas turbine combustor, the atomizing air is supplied by an auxiliary compressor with a power usage of about 1% of the combustion heat release rate.

Dry steam, if available, may also be used in a similar way, as is common practice in the furnaces of power plant boilers using residual oil (89,90).

Air atomization with low pressure and relatively low velocity air is also used in some burners for low viscosity distillate oils. In most aircraft gas turbines some, or even a large part, of the atomization is done in this way by a small fraction of the warm, compressed combustion air supplied in swirling flow around the fuel nozzles. Imparting swirl to at least some of the air flow around fuel injectors of all types is a common feature of many burners and combustors; in some, swirl is introduced on a larger scale in all of the primary combustion air. The velocity gradients or shear in the resulting vortexlike flow promote mass transfer or mixing, including the recirculation of hot products of combustion to the rich mixture or suspension in the low pressure core that contributes to stabilization of the primary combustion zone (25). The angular or swirl velocity imparted to the air and the strength of such flows are of course limited by the available pressure drop; eg, in gas turbine combustors the allowable pressure loss is usually $<4\%$ of the absolute pressure.

Combustion of fuel oil takes place through a series of steps, namely vaporization, devolatilization, ignition, and dissociation, which finally lead to attaining the flame temperature. Vaporization and devolatilization of the fine spray of fuel droplets take place as physiochemical processes in the combustion chamber. The vaporization temperature for fuel oil is in the range of 311–533 K, depending on the grade of the fuel. Devolatilization takes place at about 700 K. The final flame temperature attained is between 1366–1918 K. Complete combustion of an oil droplet can occur in 2–20 ms depending on the size of the droplet. A typical characteristic of an oil flame is its bright luminous nature which is the result of incandescent carbon particles in the fuel rich zone.

The study of the combustion of sprays of liquid fuels can be divided into two primary areas for research purposes: single-droplet combustion mechanisms and the interaction between different droplets in the spray during combustion with regard to droplet size and distribution in space (91–94). The wide variety of atomization methods used and the interaction of various physical parameters have made it difficult to give general expressions for the prediction of droplet size and distribution in sprays. The main fuel parameters affecting the quality of a spray are surface tension, viscosity, and density, with fuel viscosity being by far the most influential parameter (95).

The following general expression (eq. 22) is commonly used to describe the droplet size distribution in a spray:

$$dn = ar\,\alpha\,\exp(-br\,\beta)\,dr \qquad (22)$$

where $dn$ = number of droplets with radii between $r$ and $r + dr$. The constants $a$, $b$, $\alpha$, and $\beta$ are independent of $r$ and are usually determined empirically. The best-known special case of this general equation is the Rosin-Rammler distribution (95–97).

Theoretical modeling of single-droplet combustion has provided expressions for evaporation and burning times of the droplets and the subsequent coke particles. A more thorough treatment of this topic is available (88,91–93,98).

Experimental techniques used for studying the combustion of single droplets can be divided into three groups: suspended droplets, free droplets, and porous droplets, with ongoing research in all three areas (98).

### 3.3. Combustion of Solid Fuels.

Solid fuels are burned in a variety of systems, some of which are similar to those fired by liquid fuels. In this article the most commonly burned solid fuel, coal, is discussed. The main coal combustion technologies are fixed-bed, eg, stokers, for the largest particles; pulverized-coal for the smallest particles; and fluidized-bed for medium size particles (99,100) (see COAL).

*Fixed-Bed Technology.* Fixed-bed firing of coal by means of stokers consists of a solid bed of large (2–3 cm) coal particles on moving grates with combustion air passing through the grates and ash removal from the end of the grate. The use of a grate limits the application of this technique to small units, as grates are restricted to a maximum size of about 100 $m^2$ for structural reasons. Mechanical stokers can be classified into the following groups, based on the method of introducing fuel to the furnace: spreader stokers, underfeed stokers, water-cooled vibrating-grate stokers, and chain-grate and traveling-grate stokers. For a thorough review of stokers see Reference 81.

*Pulverized-Coal Firing.* This is the most common technology used for coal combustion in utility applications because of the flexibility to use a range of coal types in a range of furnace sizes. Nevertheless, the selection of crushing, combustion, and gas-cleanup equipment remains coal dependent (54,100,101).

Prior to being fed to a pulverized fuel burner, coal is ground to a size generally specified such that at least 70% passes a 200 mesh screen (75 μm) and less than 2% is retained on a 52 mesh screen (300 μm). The top size is determined by the classifying component of the crushing mill, oversize material being retained for further grinding (54, 100, 101).

Suspensions of pulverized coal or coal dust in air can be explosive, hence, it is essential to have adequate guidelines and procedures to ensure safe and stable operation during pulverized-coal (PC) firing. Some of these guidelines include: (*1*) coal dust should never be allowed to accumulate except in specified storage facilities; (*2*) coal and dust suspensions in air should not exist except in drying, pulverizing, or burner equipment and the necessary transportation ducts; (*3*) the furnace and its setting should be purged before introducing any light or spark; (*4*) before introducing the fuel into the furnace, a lighted torch or spark-producing device should be in operation; (*5*) a positive flow of secondary air should be maintained through the burners into the furnace and up the stack; and (*6*) a positive flow of primary air-coal to the burner should be maintained (81,82).

As for oil and gas, the burner is the principal device required to successfully fire pulverized coal. The two primary types of pulverized-coal burners are circular concentric and vertical jet-nozzle array burners. Circular concentric burners are the most modern and employ swirl flow to promote mixing and to improve flame stability. Circular burners can be single or dual register. The latter type was designed and developed for $NO_x$ reduction. Either one of these burner types can be equipped to fire any combination of the three principal fuels, ie, coal, oil and gas. However, firing pulverized coal with oil in the same burner should be restricted to short emergency periods because of possible coke formation on the pulverized-coal element (71,72).

The self-igniting characteristics of pulverized coal vary from one coal to another, but for most coals it is possible to maintain ignition without auxiliary fuel when firing above the capacity of the boiler. The igniters may have to be activated in the following cases: (*1*) when firing pulverized coal with volatile matter less than about 25%, (*2*) when firing excessively wet coal, and (*3*) when feeding coal sporadically into the pulverizer (81,102–104).

Compared to natural gas and oil, complete combustion of coal requires higher levels of excess air, about 15% as measured at the furnace outlet at high loads, and this also serves to avoid slagging and fouling of the heat absorption equipment.

The process of coal ignition in the flame involves a number of steps. Initially, the pulverized coal is heated by convection as the flame jet entrains and mixes with the furnace gases and also by radiation from the hotter furnace gases. On heating to temperatures above about 773 K, the coal starts to decompose, and evolves a mixture of combustible gases such as CO, $H_2$, and hydrocarbons ($C_nH_m$) as well as noncombustible gases such as $CO_2$ and $H_2O$. At temperatures of about 1173 K most of the volatile matter has been evolved and, given adequate mixing of air in the jet, its combustion will sustain the ignition of the flame. The char residue remaining after the devolatilization is then burned relatively slowly in the flame and furnace. Char combustion has been the subject of intensive investigation since the early 1930s and is one of the least understood areas in coal combustion. Good reviews on char combustion are available (49,105,106). For more information on the industrial applications of coal, References (107–110) are recommended and for a thorough review of coal devolatilization see References (111–114) (see COAL CONVERSION PROCESSES).

As pulverized-coal combustion potentially has a significant impact on the environment, the 1980s saw the employment of techniques such as coal washing and beneficiation to reduce the emissions of fly-ash, $SO_x$, and water-soluble metallic oxides. Fly-ash emissions can be reduced by means of electrostatic precipitators and fabric fillers, with efficiencies higher than 99.8%. $SO_x$ emissions are reduced considerably by means of gas scrubbing which employs water slurries of lime and limestone. Staged combustion is an effective method of reducing $NO_x$ emissions from coal combustion. In this method, combustion takes place in two zones: a low temperature fuel-rich zone and a high temperature fuel-lean zone, where hydrocarbons and CO are afterburned. In the fuel-rich zone the fuel bound nitrogen is converted to $N_2$ rather than to $NO_x$ as in the case at high values of $\phi$.

The environmental impact associated with pulverized-coal firing has given rise to efforts to develop other combustion technologies such as fluidized beds or the use of coal-water slurry fuels (CWSF), which can be burned as substitutes for certain liquid fuels (115–117). CWSFs were developed as alternatives to more expensive and increasingly scarce conventional hydrocarbon fuels. In their most common form, they are composed of 70–75% by weight of coal (usually high volatile A bituminous), 24–29% water, and 1% chemical additives. The principal potential market for CWSF is as a replacement for residual fuel oil, ie, heavy fuel oil and No. 6 fuel oil, in utility and large industrial boilers. CWSFs offer all the advantages of liquid fuels in addition to the cost advantages associated with the use of coal. The main challenge in the utilization of CWSFs is obtaining stable mixtures that can be successfully atomized and burned. Much research has been carried out in the area of CWSF atomization but this phenomenon is far from being well understood. On the combustion front, novel techniques such as the coupling of a high intensity acoustic field have been employed to enhance the convective processes occurring during the combustion of CWSF (116,117).

*Fluidized-Bed Technology.* In fluidized-bed combustion of coal, air is fed into the bed at a sufficiently high velocity to levitate the particles. This velocity is referred to as the minimum fluidizing velocity, $u_{mf}$. At this velocity, the volume occupied by the bed increases abruptly and the bed exhibits some of the characteristics of a fluid. The two predominant designs of fluidized beds are bubbling and recirculating, with most theories of fluidization being based on the simpler bubbling bed concept.

Fluidized combustion of coal entails the burning of coal particles in a hot fluidized bed of noncombustible particles, usually a mixture of ash and limestone. Once the coal is fed into the bed it is rapidly dispersed throughout the bed as it burns. The bed temperature is controlled by means of heat exchanger tubes. Elutriation is responsible for the removal of the smallest solid particles and the larger solid particles are removed through bed drain pipes. To increase combustion efficiency the particles elutriated from the bed are collected in a cyclone and are either re-injected into the main bed or burned in a separate bed operated at lower fluidizing velocity and higher temperature.

Fluidized beds are ideal for the combustion of high sulfur coals since the sulfur dioxide produced by combustion reacts with the introduced calcined limestone to produce calcium sulfate. The chemistry involved can be simplified and reduced to two steps, calcination and sulfation.

*Calcination*

$$\mathrm{CaCO_3} \longrightarrow \mathrm{CO_2} + \mathrm{CaO}$$

*Sulfation*

$$\mathrm{SO_2} + \mathrm{CaO} + \tfrac{1}{2}\,\mathrm{O_2} \longrightarrow \mathrm{CaSO_4}$$

The main steps associated with coal combustion (heating, devolatilization, volatiles combustion, and char burnout), occur sequentially to some extent; however, there is always some overlap between the stages. Char burnout is the slowest step so there is practical interest in determining the factors that influence its rate. In order to determine the char combustion rate and time, it is necessary to understand the interaction between the rate of oxygen diffusion to the reacting surface and the inherent chemical kinetics of char oxidation. In the case of fluidized beds the use of a simplified rate coefficient overestimates the burnout time substantially. The enhancement of mass transfer through the boundary layer as the result of an applied velocity must be considered in order to predict char combustion times under conditions relevant to fluidized-bed combustion. Char combustion in fluidized beds is believed to be controlled by both diffusional and chemical kinetic parameters, ie, mixed control. This indicates that models attempting to predict char burnout times in fluidized beds must consider both oxygen diffusion rates and inherent chemical kinetics (117–120).

The main stages of coal combustion have different characteristic times in fluidized beds than in pulverized coal combustion. Approximate times are a few seconds for coal devolatilization, a few minutes for char burnout, several minutes for the calcination of limestone, and a few hours for the reaction of the calcined limestone with $SO_2$. Hence, the carbon content of the bed is very low (up to 1% by weight) and the bed is 90% CaO in various stages of reaction to $CaSO_4$. About 10% of the bed's weight is made up of coal ash (91). This distribution of 90/10 limestone/coal ash is not a fixed ratio and is dependent on the ash content of the coal and its sulfur content.

Devolatilization and combustion occur close to the coal inlet tubes. However, because of rapid mixing in the bed the composition of the solids in the bed may be assumed to be uniform.

*Atmospheric Pressure Fluidized-Bed Boilers.* A typical bubbling fluidized-bed is usually 1.2 m deep in its expanded or fluidized condition. Normally, the heat-transfer surface is placed in the bed in the form of a tube handle to achieve the desired heat balance and bed operating temperature. For fuels with low heating values the amount of surface can be minimal or absent. Coal-fired bubbling-bed boilers normally incorporate a recycle system that separates the solids leaving the economizer from the gas and recycles them to the bed. This maximizes combustion efficiency and sulfur capture. Normally, the amount of solids reacted is limited to about 25% of the combustion gas weight. For highly reactive fuels this recycle system can be omitted. Bubbling-beds that burn coal usually operate in the range of 2.4 to 3 m/s superficial flue gas velocity at maximum load. The bed material size is 590 μm and coarser, with a mean size of about 1000–1200 μm.

Circulating fluidized-beds do not contain any in-bed tube bundle heating surface. The furnace enclosure and internal division wall-type surfaces provide the required heat removal. This is possible because of the large quantity of solids that are recycled internally and externally around the furnace. The bed temperature remains uniform, because the mass flow rate of the recycled solids is many times the mass flow rate of the combustion gas. Operating temperatures for circulating beds are in the range of 816 to 871°C. Superficial gas velocities in some commercially available beds are about 6 m/s at full loads. The size of the solids in the bed is usually smaller than 590 μm, with the mean particle size in the 150–200 μm range (81).

Some of the advantages of fluidized beds include flexibility in fuel use, easy removal of $SO_2$, reduced $NO_x$ production due to relatively low combustion temperatures, simplified operation due to reduced slagging, and finally lower costs in meeting environmental regulations compared to the conventional coal burning technologies. Consequently, fluidized-bed combustors are currently under intensive development and industrial size units (up to 150 MW) are commercially available (Fig. 10).

The modeling of fluidized beds remains a difficult problem since the usual assumptions made for the heat and mass transfer processes in coal combustion in stagnant air are no longer valid. Furthermore, the prediction of bubble behavior, generation, growth, coalescence, stability, and interaction with heat exchange tubes, as well as attrition and elutriation of particles, are not well understood

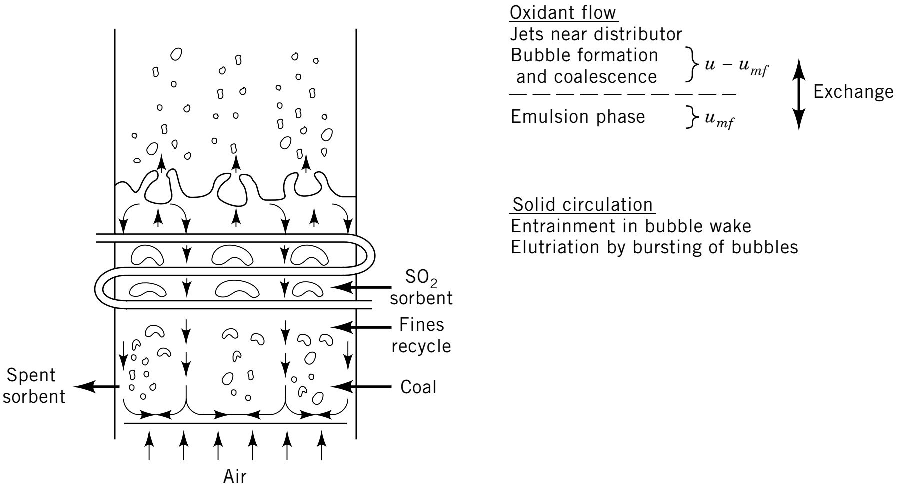


**Fig. 10.** The main processes taking place in a fluidized bed (92). Heat transfer to immersed tubes is 30% by radiation.

and much more research needs to be done. Good reviews on various aspects of fluidized-bed combustion appear in References 121 and 122 (Table 2).

### 3.4. Design Considerations in Fossil Fuel Combustion Systems.

One of the most important considerations in the design of a combustion chamber for a boiler is the fuel that is to be burned in the chamber (see FURNACES, FUEL-FIRED). Although all fuels burn and release heat during combustion, the rate at which a fuel burns and releases heat, and the impurities associated with the fuel have to be considered.

*Furnaces for Oil and Natural Gas Firing.* Natural gas furnaces are relatively small in size because of the ease of mixing the fuel and the air, hence the relatively rapid combustion of gas. Oil also burns rapidly with a luminous flame. To prevent excessive metal wall temperatures resulting from high radiation rates, oil-fired furnaces are designed slightly larger in size than gas-fired units in order to reduce the heat absorption rates.

*Furnaces for Pulverized Coal Firing.* The main differences between boilers fired with coal and those fired with oil or natural gas result from the presence of mineral matter in coals. The volume of the coal-fired furnace is higher because of the longer residence time required for the complete combustion of coal particles, the requirement of a controlled combustion rate to reduce $NO_x$ formation, the provision for a larger heat-transfer surface area resulting from decreased heat-transfer rates because of ash deposits on the surfaces, and increased spacing of heat-transfer tubes to reduce flue gas velocities and thereby erosion of heat-transfer surfaces. Even when firing coal, depending on the reactivity of the coal (rank), the size of the combustion chamber required can vary (Fig. 11).

The combustion chamber of a modern steam generator is a large water-cooled chamber in which fuel is burned. Firing densities are important to ensure

Table 2. **Operating Conditions for an Atmospheric Pressure Fluidized-Bed Combustor**[a]

| Process | Representative value | Comments |
|---|---|---|
| excess air, % | ≈30 | values selected to maintain CO emissions at acceptable levels |
| bed height, m | ≈1.5 | trade-off between pressure drop and gas residence time |
| bed temperatures, K | ≈1100 | higher values favor higher combustion efficiencies, higher rates of NO reduction by char; high values reduce $SO_2$ capture |
| calcium/sulfur (stoichiometric ratio) | ≈2.5 | value may be reduced by use of more active stone, lower gas velocities, deeper beds |
| gas velocity, m/s | ≈2 | high values are favored by high energy release rates per unit plan area; lower values are favored by higher efficiencies of combustion and $SO_2$ capture |
| sorbent particle top size, mm | ≈3 | low values are favored by shorter reaction times; size determined by consideration of elutriation at operating velocities |
| coal particle top size, mm | ≈3 | trade-off between elutriation rate and reaction time |
| sorbent residence time, s | $\approx 5 \times 10^4$ | determined by stone reactivity and Ca/S ratio |
| gas residence time in bed, s | $\approx\frac{1}{4}$ | an additional residence time of 1–2 s is available in the free board |
| coal particle burning time, s | ≈400 | dependent on temperature, size, and excess air |
| solid circulation time, s | ≈2 | short relative to solid reaction time |

[a] Ref. 122.

that the chamber wall metal temperatures do not exceed the limits of failure of the tubes. Firing densities are expressed in two ways: volumetric combustion intensities and area firing intensities. The volumetric combustion intensity is defined by equation 23,

$$I_v = \frac{J_f h_f}{V_c P} \tag{23}$$

where $I_v$ = volumetric combustion intensity, kJ/(m$^3$ · h); $J_h$ = fuel feed rate, kg/h; $h_f$ = heating value of the fuel, kJ/kg; and $V_c$ = volume of the combustion chamber, m$^3$.

The area firing density is defined by equation 24,

$$I_a = \frac{J_f h_f}{A_c} \tag{24}$$

where, $I_a$ = area firing density, kJ/(m$^2$ · h); $J_h$ = fuel feed rate, kg/h; $h_f$ = heating value of the fuel, kJ/kg; and $A_c$ = cross−section of a fluid-bed distributor plate or grate area of a mechanical stoker or plan area in pulverized-coal combustors. Table 3 provides some design parameters for fossil fuel burners.

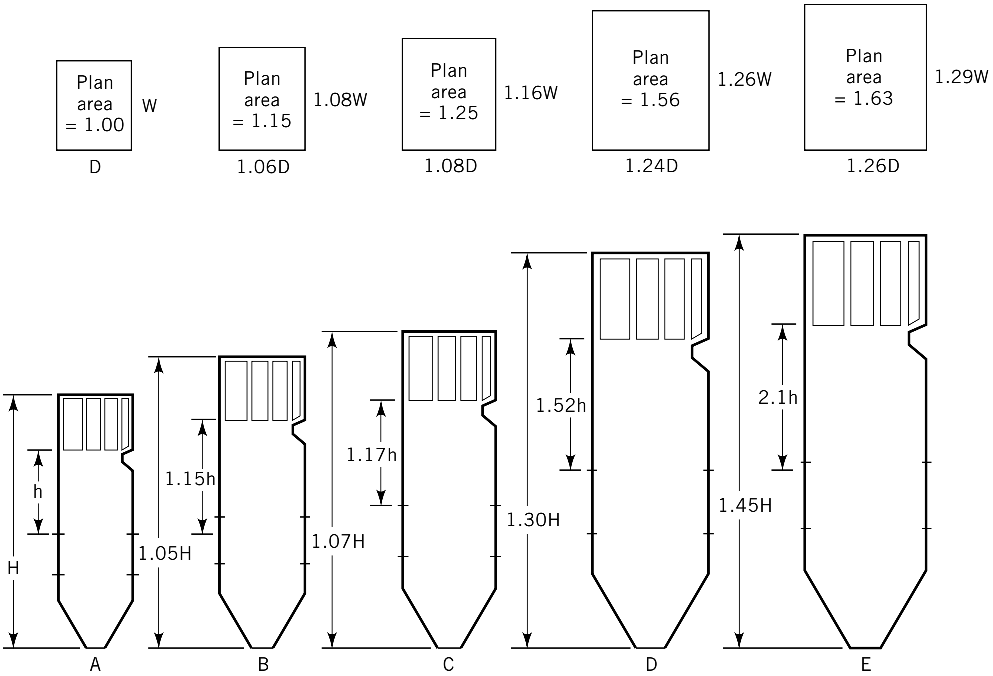


**Fig. 11.** Effect of coal rank on furnace sizing (constant heat output) (82), where W = width, D = depth, and h and H are the heights indicated. A represents medium volatile bituminous; B, high volatile bituminous or subbituminous; C, low sodium lignite; D, medium sodium lignite; and E, high sodium lignite.

Table 3. **Comparison of Design Parameters for Fossil Fuel Boilers**

| | | | Coal | | |
|---|---|---|---|---|---|
| Parameter | Gas | Oil | Grate | Fluid bed | Pulverized coal |
| heat rate, mW (t) | 0.03–3000 | 0.03–3000 | 0.3–30 | up to 30 | 30–3000 |
| volumetric combustion intensity, kW/m$^3$ | 250–450 | 250–450 | 250–750$^a$ | up to 2000$^a$ (based on bed volume) | 150–250 |
| area combustion intensity, kW/m$^2$ | 280–500 | 280–500 | 2000 | 3000 | 7500 |
| fuel firing density, kg/m$^3$h | | | 30–100 | ≈250 | 15–30 |
| kg/m$^2$h | 6–11 | 6–11 | 40–250 | up to 500 | up to 1000 |
| practical combustion temperature, °C | 1000–1600 | 1100–1700 | 1200–1300 | 850–950 | 1600–1700 |
| combustion time, s | $10 \times 10^{-1}$ | $20 - 25 \times 10^{-1}$ | up to 5000 | 100–500 | $\approx 1 - 2$ |
| particle heating rate, °C/s | | | <1 | $10^3$–$10^4$ | $10^4$–$10^5$ |

$^a$Based on the total combustion volume which includes space between the bed and the convective tubes.

### 3.5. Environmental Considerations.

Atmospheric pollutants released by combustion of fossil fuels fall into two main categories: those emitted directly into the atmosphere as a result of combustion and the secondary pollutants that arise from the chemical and photochemical reactions of the primary pollutants (see AIR POLLUTION).

The main combustion pollutants are nitrogen oxides, sulfur oxides, carbon monoxide, unburned hydrocarbons, and soot. Combustion pollutants can be reduced by three main methods depending on the location of their application: before, after, or during the combustion. Techniques employed before and after combustion deal with the fuel or the burned gases. A third alternative is to modify the combustion process in order to minimize the emissions.

*Nitrogen Oxides.* From the combustion of fuels containing only C, H, and O, the usual air pollutants or emissions of interest are carbon monoxide, unburned hydrocarbons, and oxides of nitrogen ($NO_x$). The interaction of the last two in the atmosphere produces photochemical smog. $NO_x$, the sum of NO and $NO_2$, is formed almost entirely as NO in the products of flames; typically 5 or 10% of it is subsequently converted to $NO_2$ at low temperatures. Occasionally, conditions in a combustion system may lead to a much larger fraction of $NO_2$ and the undesirable visibility thereof, ie, a very large exhaust plume.

NO is formed to some extent from $N_2$ and $O_2$ in flame products when N atoms are produced at a significant rate. Above 1700 K, the important step in the much studied Zeldovitch (thermal) mechanism is the production of N atoms by:

$$\mathrm{O} + \mathrm{N}_2 \longrightarrow \mathrm{NO} + \mathrm{N}$$

This is followed by a very fast reaction:

$$\mathrm{N} + \mathrm{O}_2 \longrightarrow \mathrm{NO} + \mathrm{O}$$

When $[NO] \ll [NO]_{eq}$, as is usually true in practice, its formation is essentially irreversible, and its rate is proportional to $[NO][N_2]$ with a large temperature dependence, an activation energy of 316 kJ/mol (75.5 kcal/mol). Unfortunately, the rate becomes appreciable just in the range of typical hydrocarbon–air flame conditions. If it is also assumed that $[O] = [O]_{eq}$, the observed rate in most lean-flame products in which $N_2$ is roughly 75 mol % of the gas can be approximated by

$$\frac{d[NO]}{dt} = \left(\frac{3.3 \times 10^{18}}{T}\right) \exp\left(\frac{-68700}{T}\right) (x_{O_2})^{1/2}$$

Here, $x_{O_2}$ is the mole fraction of $O_2$ in the products at temperature $T$, and the rate is given in ppm/ms. The exponential implies a large effective activation energy of 570 kJ/mol, the sum of that for the $O{-}N_2$ reaction and half the dissociation energy of $O_2$. In typical hydrocarbon–air flames, the rate of NO formation by the thermal mechanism can be shown to be about 8 ppm/ms, or in a 10 ms residence time the thermal NO would be about 80 ppm. If preheating the mixture were to raise the gas temperature by 100 K, the rate of NO production would be nearly tripled, making the NO concentration unacceptable. Conversely, the rate can be reduced by the same amount by a 100 K reduction in temperature by precooling or heat abstraction from the flame itself, or by dilution of the mixture with excess air, steam, or other inert gas such as recirculated, relatively cool exhaust gas. Control of thermal $NO_x$ thus involves reduction of the maximum attainable temperature, or the residence time at high temperature, or both. Such measures, however, always entail some compromise in stability and control, and possibly also in the efficiency of the combustion process. The afterburning of CO tends to be quenched by rapid temperature reduction, and the resulting increase in the emission of CO must be balanced against the desired $NO_x$ reduction. Heat abstraction or cooling of the flame always occurs to some extent by radiation from the highly luminous flames produced by pulverized-coal or oil combustion, as is typical in boilers and similar furnaces. When heat is rejected, eg, by a boiler fluid, and not returned or recuperated to the unburned mixture, the maximum temperature and thermal $NO_x$ formation will be reduced. An extension of this effect has been applied to achieve low $NO_x$ emissions in some furnaces and boilers in which combustion occurs in a very rich, relatively low temperature primary stage, followed by heat abstraction by convection as well as radiation to reduce the gas enthalpy (two-stage combustion). Secondary products and any excess air are then introduced to complete the combustion and, owing to the previous heat transfer, the maximum temperature attainable in that stage will never approach the adiabatic flame temperature. Much soot, which is responsible for the radiative heat loss, may be present in the rich primary flame products. To avoid smoke from such two-stage processes, care must be taken to assure its oxidation in the second stage. In practice $[O]/[O]_{eq}$ is seldom unity as assumed. Though $[O]$ is decreased in the burned gas, its average value may be several times $[O]_{eq}$ and NO formation may be correspondingly higher than predicted from the $[O]_{eq}$. Similarly, the very high radical concentration, eg, $[O]$, in the reaction zone of a flame often leads to almost instantaneous NO production, even though the temperature is still relatively low and the residence time is relatively short. Other fast reactions involving transient flame species producing N atoms, for example, $CH + N_2 \longrightarrow HCN + N$, can also contribute to the production of some NO. In any case, the NO inevitably formed by these species is called prompt NO. The total concentration of prompt NO is usually not large, 10–50 ppm depending on the composition of the flame, but is significant if very low $NO_x$ emission levels are sought.

A different and often more serious source of $NO_x$ is chemically bound nitrogen in the fuel, eg, $NH_3$, amines, nitrites, pyridine, a fraction of which is always converted to NO. Most coals contain at least 1% N, of which 50% or more is retained in gaseous or liquid fuels derived from coal. The N content of distillate and gaseous petroleum fuels from most sources is usually very low, but it can reach 0.5% and if such a fuel were burned with air under stoichiometric or lean conditions, the conversion of its fuel N to NO in the flame would yield up to 400 ppm of NO in the burned gas. $NO_x$ production levels from fuel N and $NO_x$ control measures are now well established from correlations of data from flames and combustors. Formation occurs in the flame reaction zone by OH radical oxidation of intermediate species formed by the decomposition of the fuel N, eg, $NH_2$, NH, N, which if unoxidized would in a short time simply form stable $N_2$.

Whether NO or $N_2$ formation prevails depends on the flame conditions as well as on the concentrations of the intermediates. At high levels of fuel N, NO can also be converted directly to $N_2$. In general, the yield (mol of NO/mol of fuel N) is much higher in lean and stoichiometric flames than in rich flames, and asymptotically approaches unity at low fuel N concentrations. It decreases with increasing fuel N, and at some level that depends on $\phi$, the NO concentration becomes constant, albeit rather high, and any additional fuel N is converted rapidly to $N_2$, from which NO can then be formed only by the relatively slow thermal process with oxygen.

Thus if combustion can be effected in two stages, with or without the intermediate heat rejection for thermal $NO_x$ control discussed above, the conversion of fuel N to NO can be largely circumvented by first, a primary stage at $\phi = 1.5 - 2$ with a modest residence time to allow formation of $N_2$ in the hot primary products, followed by rapid addition of secondary air to complete the combustion at an effective $\phi \approx 0.8$. There will of course be a maximum in the temperature near $\phi = 1$ in the course of the secondary air addition, but if the residence time at that condition is minimized, the production of thermal NO will also be minimized.

Combustion system developments for reducing $NO_x$ formation include: low $NO_x$ burners, staged burning techniques, and flue gas recirculation (FGR). Some postcombustion techniques for reducing $NO_x$ include: selective noncatalytic reduction (SNCR) and selective catalytic reduction (SCR). In either technology, $NO_x$ is reduced to nitrogen ($N_2$) and water ($H_2O$) through a series of reactions with a chemical agent injected into the flue gas. The most common chemical agents used commercially are ammonia and urea for SNCR and ammonia for SCR systems. Most ammonia-based systems have used anhydrous ammonia ($NH_3$) as the reducing agent. However, because of the hazards of storing and handling $NH_3$, many systems use aqueous ammonia at 25–28% concentration. Urea can be stored as a solid or mixed with water and stored in solution (81).

These ideas form the basis of most approaches to $NO_x$ control with N-containing fuels. In principal, they are readily applicable to the modification of certain combustors in which the desired divisions in the combustion process exist for other reasons. Although such improvements have been demonstrated, it is difficult in practice to make the required revisions in the air and fuel distribution without adverse effects on other emissions or on performance. It has also been shown that when steam is used to reduce thermal $NO_x$ production, the formation of $NO_x$ from fuel N is enhanced, or the reduction is less than otherwise expected.

*Sulfur Oxides.* Oxides of sulfur are also pollutants of concern. When present in the fuel as inorganic sulfides or organic compounds, sulfur is converted almost completely to $SO_2$ in the products of complete combustion. There are no known techniques for the elimination of this conversion process in flames, and emission control measures necessarily involve either desulfurization of the fuel or removal of the $SO_2$. Up to 10% of the $SO_2$ is oxidized to $SO_3$ at low temperatures in most combustion processes, and the total sulfur oxides emission is often given as the sum of the concentrations of $SO_2$ and $SO_3$, or $SO_x$. The presence of $H_2O$ in the combustion products is inevitable and at low temperatures $SO_3$ combines with $H_2O$ to form $H_2SO_4$, which is both a highly corrosive agent to heat exchange surfaces and a highly undesirable stack emission.

*Soot.* Emitted smoke from clean (ash-free) fuels consists of unoxidized and aggregated particles of soot, sometimes referred to as carbon though it is actually a hydrocarbon. Typically, the particles are of submicrometer size and are initially formed by pyrolysis or partial oxidation of hydrocarbons in very rich but hot regions of hydrocarbon flames; conditions that cause smoke will usually also tend to produce unburned hydrocarbons with their potential contribution to smog formation. Both may be objectionable, though for different reasons, at concentrations equivalent to only 0.01–0.1% of the initial fuel. Although their effect on combustion efficiency would be negligible at these levels, it is nevertheless important to reduce such emissions.

Neither soot nor unburned hydrocarbons are found in the products of a lean or stoichiometric premixed flame with air or $O_2$, although hydrocarbons may be formed or survive unburned in lean flames partially quenched, eg, by the cold wall of a combustion chamber. A moderately rich flame also should yield only the water-gas equilibrium products (and $N_2$); but with increasing equivalence ratio, at some $\phi$ still well below the upper flammability limit, the burned gas becomes faintly luminous with precipitated soot particles that increase in number density and luminous intensity with further increase in $\phi$. The appearance of the condensed phase (soot) is connected with appreciable nonequilibrium concentrations of fairly stable low molecular-weight hydrocarbons, notably acetylene, from the decomposition of unoxidized fuel. These polymerize (condense with elimination of $H_2$) to form high molecular-weight products, mostly with ring structures. If these intermediates are not consumed, eg, by OH, in simultaneous and competing oxidation reactions, they grow until nucleation, and eventually precipitation occurs as visibly radiating soot, typically over a period of several milliseconds after the main flame reaction zone. The particle growth and competing oxidation then continue in the burned gas.

The composition, properties, and size of soot particles collected from flame products vary considerably with flame conditions and growth time. Typically the C–H atomic ratio ranges from two to five and the particles consist of irregular chains or clusters of tiny spheres 10–40 nm in diameter with overall dimensions of perhaps 200 nm, although some may agglomerate further to much larger sizes.

Whether soot particles form at all and grow depends on $\phi$, the fuel type, and other variables, eg, the growth is easier and faster at a given $\phi$ with fuels of higher C–H ratio and at elevated pressure. Given sufficient residence time to attain equilibrium at the burned gas condition, the soot and hydrocarbons would eventually be consumed. In practice, their rapid oxidation occurs in a secondary flame in which the hot primary products are burned with the required excess air, which is added by diffusion or by more intensive mixing. However, if a large excess of air is added too rapidly, the cooling can, in effect, quench the oxidation of both unburned hydrocarbons and the accompanying soot, which would then persist as visible smoke. The blackness of the smoke depends on the size and number density of the particles when quenched, their further aggregation, etc. Some may also survive as much smaller invisible particles, or condensation nuclei. For thorough reviews on the mechanisms of pollutant formation see References (123–125).

*Diffusion Flame Chemistry.* Since most combustion systems employ mixing-controlled diffusion flames, which are characterized by very high pollutant emissions, it is imperative to look into the chemistry occurring in diffusion flames. In a typical diffusion flame the mixture composition in the reaction zone is close to the stoichiometric proportion and the temperature is at a maximum resulting from the large volume of this zone, thus $NO_x$ production is favored. If, however, the surrounding gas cools the combustion products rapidly, further reactions of CO and NO are eliminated. This fixes the concentrations of these pollutants at unfavorable levels. Furthermore, the fuel diffuses into the combustion zone through the burned gases and thus is heated in the absence of oxygen. This creates ideal conditions for the formation of soot and the reduction of the $CO_2$ produced in the combustion zone to CO. Additionally, diffusion flames have low combustion intensity and efficiency and hence release large amounts of unburned hydrocarbon emissions. In general, despite the fact that the structure of the diffusion flame is more complex and difficult to analyze, the same basic description of soot formation and oxidation should apply to diffusion flames as for premixed flames.

*Emissions Control.* From the combustion chemistry standpoint, lean mixtures produce the least amount of emissions. Hence, one pollution prevention alternative would be to use lean premixed flames. However, lean mixtures are difficult to ignite and form unstable flames. Furthermore, their combustion rates are very low and can seldom be applied directly without additional measures being taken. Consequently the use of lean mixtures is not practical.

Another potential solution is the use of catalytic combustors, which produce extremely low levels of emissions by the use of combustion catalysts such as platinum. The main disadvantage of catalytic combustors, however, is their high cost.

More advanced techniques for emissions control include electrical or plasma jet augmentation of flames based on radical production. Since in two-phase, heterogeneous combustion the flames are always diffusion flames on the microscale, ie, the individual droplets or particles burn as diffusion flames, and since at the characteristic times for evaporation, decomposition and burning of individual particles can be comparable with the characteristic times for mixing and pollutant formation, prevaporization or gasification of the fuel can reduce pollutant emissions. For this reason catalytic systems for liquid-fuel decomposition and coal gasification are being considered seriously as alternatives to conventional combustion technology (126–128).

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