

Chapter 3

Soot

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3.1 Sources

The major source of carbonaceous soot released into the environment is from the incomplete combustion of fossil fuels and other organic matter. Principal sources of soot emissions are coal burning furnaces, refuse burning, coke production processes, wood burning in home fireplaces, the open burning of waste, and gasoline and diesel powered engines.

The solids formed in the combustion of organic fuels include char, coke, ash, and soot. The differences in these products are chemical, morphological, and related to the combustion processes which lead to their formation. The smallest soot particles are the result of gas phase chemical reactions which lead to the inception of a solid particle. Gas phase reactions on the particle surface lead to its growth and oxidation. Char is a solid residue formed through heterogeneous combustion of a solid fuel. Coke is the material which results through heat cracking and subsequent evaporation of the lighter components of an organic condensed fuel. Coke consists mainly of carbon, is hard, porous, and grey in appearance. Ash is the agglomerated salts which remain after the combustion of organo-metallic fuels such as coal or wood.

From a thermodynamic perspective, the generation of soot represents an energy loss associated with incomplete combustion. From an environmental point of view, the emission of soot (commonly called smoke) from combustors represents a significant health problem, primarily associated with the respiratory system.

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3.2 Health effects

It has been known for more than 200 years that the emission of carbonaceous soot represents a health risk. In 1775, medical observers concluded that the incidence of scrotal cancer in chimney sweeps was due to their exposure to soot [135]. Many studies, both epidemiological and experiments in laboratory animals, have linked exposure to soot with various cancers and respiratory problems. Soot particles are typically of a size (20–500 nm) which can be respired deep into the lung.

A large amount of research has been conducted on the poly-aromatic hydrocarbons that are associated with soot particles. It has been shown that some of these molecules promote the development of cancerous tumors in laboratory animals.

3.3 Influence on the radiation character of flames

The presence of soot particles alters the radiation characteristics of a flame and influences the overall energetics of a combustion system. Differences in the radiative emission characteristics of fires burning different fuels can be attributed to differences in the concentration of soot particulates in the fire. At flame temperatures, soot behaves not unlike a black body, emitting visible and infrared radiation following Planck's Law.

A large portion ($\approx 50\%$) of the carbon atoms present in a hydrocarbon fire exist in the form of soot. A fraction of the soot from within the flame zone in a turbulent hydrocarbon fire is ejected laterally by eddy motion through the sides of the fire or escapes from the top in the form of smoke. The escaping soot particles indicate that incomplete combustion is occurring. Other chemical species may also be escaping from the flame or combustor. There is a strong correlation between the mass of soot and CO escaping laminar and turbulent diffusion flames [136, 137]. The escaping smoke represents inefficient combustion, as a portion of the enthalpy associated with the fuel does not go to complete combustion.

In a non-sooting methyl alcohol fire, radiative emission is principally in the infrared and is due exclusively to gaseous species, primarily water vapor and carbon dioxide. The blue emission is due to high temperature gas molecules. Whereas gas species are also emitting radiation in a hydrocarbon fire, the total radiation intensity emitted by soot far exceeds that of gaseous emission. The total energy emitted by radiation from the methyl alcohol fire to the surroundings is about a factor of four less than that from a typical hydrocarbon fire. A methyl alcohol fire also is not a perfect combustor, and can emit small amounts of unburnt carbon monoxide (CO).

3.4 The structure of soot

The formation of soot has been extensively studied for a large number of fuels and in a variety of combustion configurations. Research has been conducted in laminar and turbulent, (rich and lean) premixed and nonpremixed flames, momentum and buoyancy driven flames, stirred reactors, spray flames, shock tubes, and common combustor devices such as engines and furnaces. The soot formed in these configurations possess many similar morphological characteristics [138] including fractal dimension, size, and shape. For example, the soot number density, particle size, and soot volume fraction in rich ($\phi \approx 2.7$) low pressure (150 mbar) propane–oxygen and acetylene–oxygen premixed flames [139] are all within an order of magnitude of the value of these parameters in a laminar atmospheric coflowing nonpremixed ethene–air flame [140]. These similarities, as well as similarities in soot morphology suggest that a common developmental history governs the formation process, even in very different combustion configurations.

3.4.1 Appearance and size

Soot particles are usually described in terms of average number density, N (m^{-3}), average volume fraction, f_v (m^3 of soot per m^3 of gas), and average diameter, D (m). For particles that are assumed to be spherical, these parameters are related such that: $f_v = (\pi/6)ND$. It may be reasonable to approximate early particles as roughly spherical as well as the individual primary particles that compose soot agglomerates, yet aggregates themselves are far from spherical. Instead, these structures are three dimensional and very irregular.

The nature of this irregularity has been characterized by a fractal description of soot particles, with an emphasis on the parameter known as the fractal dimension (FD). The limiting length scales associated with the fractal nature of a soot cloud are greater than the size of its individual components (≈ 2 nm) but less than the total soot cluster (≈ 1 to 1000 μm) [141]. A fractal can be defined as a structure that is characterized by an invariant symmetry with scale; the object appears similar on a variety of length scales [141].

The fractal nature of an aggregating cloud of soot particles has been quantified using Transmission Electron Microscopy (TEM) as well as laser scattering techniques [142, 143]. The soot fractal dimension has been measured to be similar for a number of different fuels and combustion configurations [143, 142]. A useful quantitative description of the fractal nature of an object is given by:

$$N_p \approx R^{FD}$$

where N_p is the number of primary particles inside an agglomerate sphere of radius R . For soot, FD has been found to take on values ranging from 1.6 to 2.6 with the larger values thought to be an artifact of the sample preparation method [142]. However, independent studies characterizing soot clusters inside of a premixed methane oxygen flame ($FD = 1.6$), and those escaping from an acetylene diffusion flame ($FD = 1.7$) exhibit a highly similar fractal nature. A fractal description of soot facilitates improved estimates of soot surface area, number density, and rates of particle growth and oxidation. A fractal view of the size distribution of soot aggregates has been exploited to develop improved models of the character of radiation emitted from flames [144]. A fractal perspective on soot promises to lead to further insight into particulate related phenomena.

3.4.2 Morphology and chemical structure

The soot generation process leads from the pyrolysis of a fuel molecule typically containing a few carbon atoms and many hydrogen atoms to the formation of particles within tens of milliseconds that contain millions of carbon atoms. The structure and the evolving nature of the morphology of soot in diffusion flames has been studied by extracting samples from flames and analyzing the deposits by various techniques including scanning electron micrography (SEM) and Xray photoelectric spectroscopy (ESCA) [145]. The results show that the youngest particles are highly fuel specific, but mature particles are quite similar for all fuels.

Soot samples emitted and extracted from flames are black and similar to a fine powder in appearance. When examined by Electron Microscopy (magnifications up to 200,000) the smallest soot samples are extracted from flame locations which correspond to early times in the soot formation process and are nearly spherical (3 to 12 nm diameter). At later times in the soot development process, particles take on a chain like appearance, the chain typically composed of hundreds or thousands of primary particles each 2 to 35 nm in diameter [146]. Some agglomerates are as large as several millimeters. For example, Fig. 3.1 is an electron micrograph of soot which has been emitted from an atmospheric pressure ethylene-air nonpremixed flame. At flame locations characterized by low and intermediate temperatures, a tar-like soot precursor (≈ 1 nm diameter and less) has been observed [146, 145]. Differences in fuel type seem to affect the early but not ultimate chemical character of a soot particle [145].

Besides carbon, soot particles also contain hydrogen (10 to 25%), oxygen ($\mathcal{O}(1\%)$) and nitrogen atoms ($\mathcal{O}(0.1\%)$). The proportion of these elements varies for different fuel molecules and changes as a soot molecule

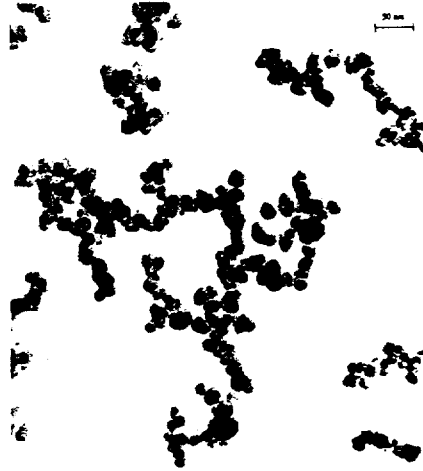


Figure 3.1: Electron photomicrograph of carbonaceous soot aggregates collected from an atmospheric pressure ethylene–air nonpremixed flame. Courtesy of Professor C. M. Megaridis of the University of Illinois at Chicago.

grows and matures [145]. The composition of soot is attributed to the reactive surface of the particle which readily adsorbs gas phase species, enabling the formation of surface complexes with carbon [80]. The highly stable polyaromatic hydrocarbons (PAH) are adsorbed on the soot and maintain their structure as the particle is emitted from a flame [147]. Younger particles have a much higher hydrogen content and possess a larger number of reactive radical sites [148]. The density of soot probably changes during its development with a value between 1 to 2 g/cc. This rather low value is attributed to large spaces between the lattice like structure in a typical soot particle [138].

3.4.3 Optical diagnostics

Laser extinction and scattering are the most common diagnostic used to measure local soot volume fractions in flames. Extinction data are typically interpreted in terms of the Rayleigh scattering assumption. The soot aggregate is assumed to be composed of a uniform lattice of primary particles, spherical in shape with constant refractive indices. The theory relates extinction to the soot volume fraction:

$$f_v = -\lambda/L \ln(I/I_o)/(6\pi Im(m^2 - 1)/(m^2 + 2))$$

where λ is the wavelength of the incident light, L is the optical path length, I and I_o are the incident and transmitted beam intensities, and m is the complex refractive index which can vary with particle shape and size [149]. For this expression to hold, light scattering must be small and the Rayleigh condition must be, valid which requires that the ratio of the diameter of primary particles (d_p) to the wavelength of light (λ) be small; i.e. $(d_p/\lambda) \ll 1$. Other models use an assumed particle size distribution and consider particle scattering. Light extinction experiments are generally line of sight measurements. Some investigators use a pair of hollow tubes as light guides to define small measurement volumes in order to obtain local f_v information [150]. Still, f_v is the characteristic best quantified by experimental measurements.

Improved theories are needed to account for the effects of nonuniform, nonspherical particles and scattering which may have a large impact on the soot volume fractions determined by laser extinction measurements [137].

3.5 Soot evolution

The evolution of soot can be mechanistically divided into several stages, involving fuel pyrolysis, the formation of particle nuclei, particle growth, agglomeration or coagulation, and oxidation. The formation and growth of soot particles, however, is not as organized a process as implied by a mechanistic description and it is not absolutely clear where one stage starts and another ends. This description of soot formation processes, however, serves as a basis for comparison with experimental measurements.

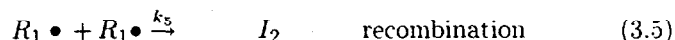
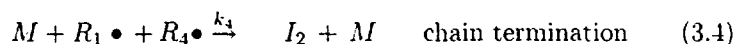
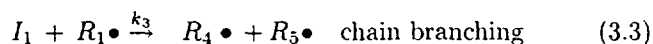
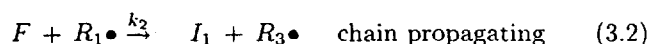
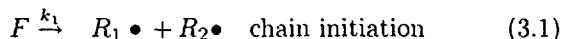
Soot particles form, grow and are oxidized as the result of a series of complex chemical reactions. These chemical processes may occur simultaneously on the same particle, some promoting particle growth while others may cause decreased particle mass. These reactions occur through essentially unverified chemical routes. As these reactions take place on the particle surface, the character of the particle changes. For example, the hydrogen/carbon content changes by almost an order of magnitude with time in a flame.

While an enormous amount of experimental measurements have investigated soot formation processes and a large number of measurement techniques are used to characterize soot, model verification is hampered by a "missing link" in information between the largest observable gas phase molecules which are about 300 atomic mass units, typically composed of 25 carbon atoms and the smallest observable particles which are approximately 5 nm in diameter or 2.5×10^5 carbon atoms. While this missing link has not prevented the development of molecular growth and

soot generation models, it does call attention to the need for improved diagnostics for validation of these models.

3.5.1 Free radical mechanism

Pyrolysis occurs when a fuel molecule breaks into smaller stable molecules or radical species by nonoxidative thermal degradation. As pyrolysis occurs, typically, a chain initiation reaction occurs whereby the fuel molecule dissociates to form free radicals. Radicals are neutrally-charged chemical species with a nonbonded or free electron which makes them highly reactive. Flame radicals participate in a series of chemical reactions which lead to the formation of larger molecules. This process is known as molecular growth. Several classes of reactions important in molecular growth can be schematically represented as:



where F is a fuel molecule, $R_i \bullet$ is a radical species. I_i is a stable chemical intermediate, M is a third body and k_i is the reaction rate constant for the i th reaction in the forward direction. The " \bullet " placed next to the name of the chemical species is the common convention for designating a radical species.

Very little fuel reaches the high temperature combustion zone in diffusion flames. Typically a fuel is pyrolyzed, leading to the formation of intermediate species. It is these intermediates, primarily CO and H_2 , that are oxidized before they escape the flame. Radical species are destroyed by chain termination reactions. Chemical reactions between two stable species are not generally important in the molecular growth process because the overall reaction rate is too slow to compete with reactions between radicals and stable species. Recombination of radicals, however, can have an impact on the formation rate of larger stable species although usually the rate of radical-radical interactions are not competitive with radical-stable species interactions.

Figure 3.2 shows an idealized pyrolysis path for methane (CH_4), which leads to the formation of chemical species with two, four, six and more carbon atoms. The arrows represent chemical reactions. Arrows connecting reactant and product species on the same row in Fig. 3.2 represent interactions with non-carbon containing species such as the free radical $H \bullet$. Arrows connecting reactant and product species in

different rows represent interaction with a carbon containing species such as C_2H_2 . The bottom of Fig. 3.2 also shows how the interaction of large aromatic species may lead to the formation of molecules with a three-dimensional structure.

As intermediates are formed, a competition occurs between molecular growth and oxidative reactions. Whereas the majority of pyrolysis intermediates are eventually oxidized, a large portion of the carbon in a flame at any one time is tied up in the molecular growth process. Oxidative reactions lead to a variety of oxygen containing intermediates and products including CO , CO_2 , and H_2O .

The schematic shown in Fig. 3.2 is not complete, principally because fuel pyrolysis research is an active field of study. Recently, for example, a chemical model for methane pyrolysis has suggested that a new route (via C_3H_3) is significant in the formation of benzene [151, 152]. Particle inception is the result of fuel pyrolysis which forms the first soot precursors. The identification of a soot precursor would provide a basis for the prediction of soot generations rates. A large number of candidates have been proposed as precursors in hydrocarbons flames. These include large positive hydrocarbon ions [153], reactive free radicals C_2H^\bullet , C_2^\bullet , and C_3^\bullet [154], polyaromatic hydrocarbons (PAH) [155], acetylene (C_2H_2) and its heavier analogues (C_2H_{2+N}), macromolecules with an aromatic character undergoing condensation [156] and the phenyl radical [157]. Many others have investigated the details of fuel pyrolysis chemistry as it leads to precursor formation [80], [158]–[161]. While positive identification of soot precursors may never occur, such a construct invites refinement as measurements of key chemical species in flames become more possible with improvement of diagnostic capabilities.

Figure 3.3 is the mass spectrometer signal for masses from 35 to 200 amu in a methane–air diffusion flame and is a representation of the relative concentration of chemical species in the flame. The line cutting across the spectrum depicts values where the signal to noise ratio is equal to a value of 2.0. The measurement was made at a spatial location where molecular growth processes are very active. Some of the key species that stand out have been labeled. They are the aromatic species benzene, toluene, naphthalene, etc. As the mass increases the concentration falls.

A popular scheme models molecular growth chemistry as dependent on acetylene addition with subsequent aromatization [157]. In this mechanism, aromatic species like benzene, toluene, naphthalene, etc. are viewed as islands of stability in an infinite sea of possible molecular structures which might be formed through molecular growth. The inception process is calculated to be the rate limiting step in the formation of soot [83, 157, 162]. Particle growth occurs as heterogeneous chemical reactions take place and gas phase species react on the soot surface. Acetylene has been identified as a likely candidate for the sur-

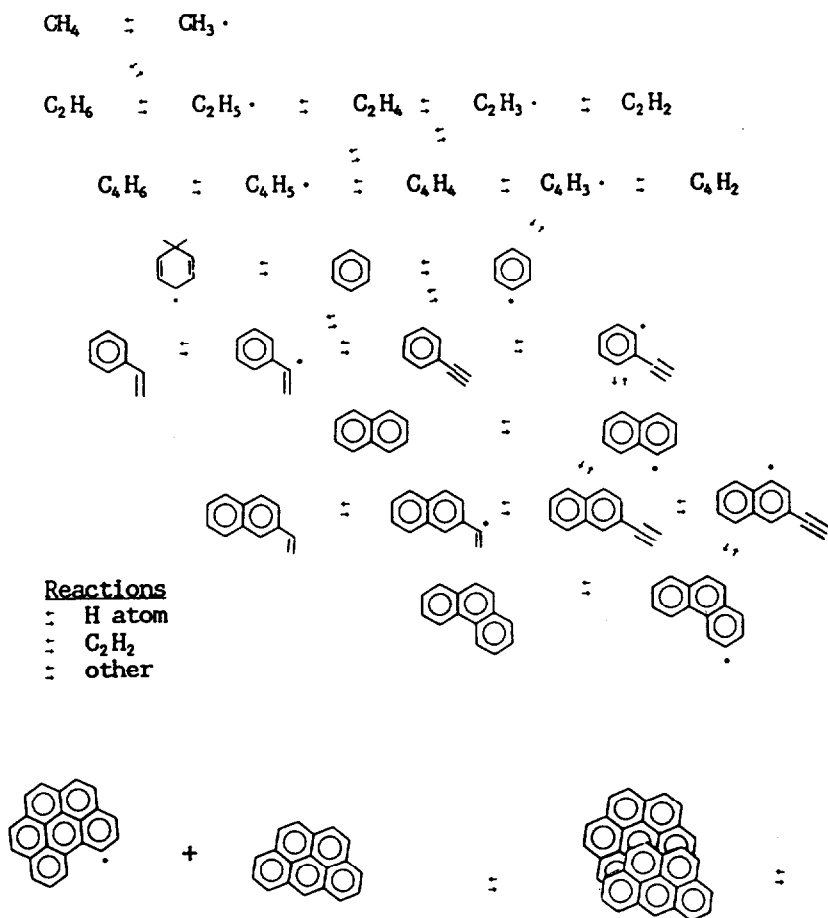


Figure 3.2: A schematic representation of the nonoxidative molecular growth processes leading from methane (CH_4) to benzene (C_6H_6).

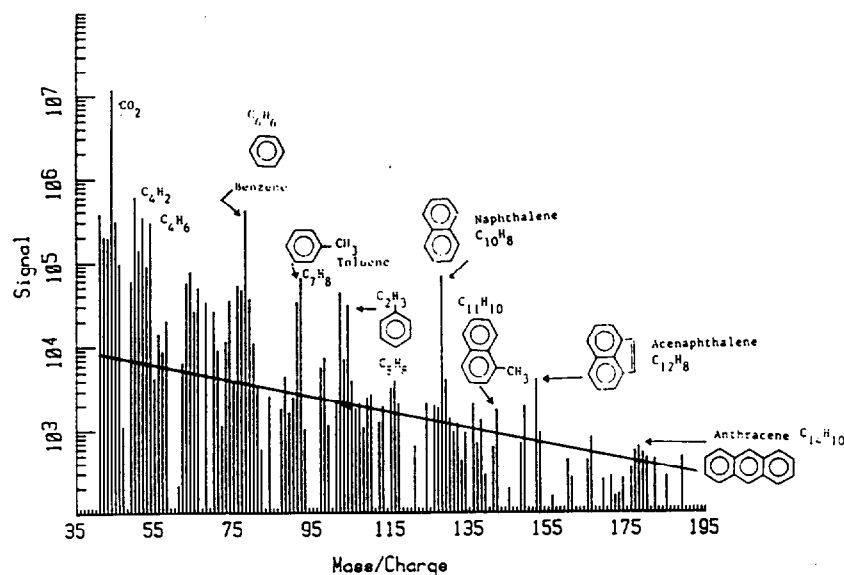


Figure 3.3: Mass spectrometer signal for masses from 35 to 200 amu sampled from the fuel side of a methane-air diffusion flame.

face reactions [83, 157], [162]–[164] although other molecules could also react on the particle surface. Recently, particle surface growth by poly aromatic hydrocarbons (PAH) has been identified as competitive with an acetylenic growth mechanism [165]. The physical processes of agglomeration and coagulation yield increased particle mass and diameter and decreased number density while not affecting soot volume fraction.

While most soot mass is due to particle growth reactions on the soot surface, it is conjectured that particle inception chemistry controls or limits the amount of soot ultimately produced. Harris and Weiner [163, 164, 166] measured surface growth rates in premixed flames and found that the initial surface area (the product of particle number density and average surface area) controlled the soot fraction distribution in a flame. Thus, soot concentrations, soot radiation, the temperature field, and the final smoke emission from a hydrocarbon flame are all likely to be closely linked to the early particle inception steps [140, 167].

Based upon modelling considerations, Kennedy *et al.* disagree that particle inception controls soot production [168]. Instead, they propose that surface growth is the most important factor. The relative importance of surface growth and particle inception is a key issue in quantitative models of soot formation.

3.5.2 Ionic growth model

The existence of ionized particles in flames has been clearly demonstrated, whereas their role in the soot evolution process has been controversial [169]. Although many studies have failed to categorically show that chemi-ions do not play a significant role in the soot formation process, recent work has shown that ions may not play a significant role. Bertrand and Delfau [170] imposed a voltage potential from their burner, which acted as cathode, to the anode situated in the gas products. The density of soot was measured with no field, with a small field which did not disturb the chemion charge distribution, and for a strong disturbing electric field. The soot volume fractions were the same within 5% suggesting that enhanced chemion concentrations associated with the electric field had little effect on soot formation.

3.5.3 Oxidation

As soot particles are transported towards the high temperature combustion zone, soot oxidation reactions become competitive with soot growth processes. Soot mass is reduced by oxidation of particles principally by $OH\cdot$ and O_2 although other oxygenated species such as O atoms can also have a role depending on the combustion environment [171, 172].

During its oxidation, the physical structure of soot changes as particle size and mass decreases. In lean premixed flames and smoking nonpremixed flames, an increase in particle concentration occurs when a large portion of the soot mass has been oxidized [173, 174]. This is hypothesized to be a consequence of oxidation by O_2 inside of the soot pores. In rich premixed flames, no change in particle concentration is observed [173].

The rate of oxidation is highly dependent on the relationship between the temperature field and the concentration distribution of $OH\cdot$ and other oxidizing species. In diffusion flames, for example, smoke is emitted when the temperature in the oxidation region *drops below 1300 K* [167]. A full understanding of the oxidative processes is complicated because the flame temperature, the concentration of oxidizing species and the soot volume fraction are coupled. Formally this can be understood by considering the conservation equations for mass, momentum and energy. Empirically, increased soot concentrations promote radiative losses, decreasing flame temperatures and lowering reaction rates associated with oxidation. This promotes soot breakout which represents an enthalpy loss from the combustion system, further decreasing flame temperature.

Because the formation and growth of soot particles is closely coupled to the hydrocarbon chemistry occurring in the reaction zone of the flame, a better understanding of the soot formation and destruction processes

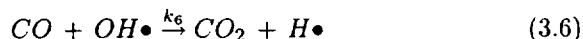
necessitates a complete description of the flame or combustion structure. Thus, the soot volume fraction depends on the time-temperature-species concentration history of a particle.

Particle formation and destruction rates depend on flame structure and are dependent on the temperature field and the concentration distribution of oxidizing molecular species, principally OH , O_2 and O atoms. Along these lines, measurements of the temperature, the soot concentration, and the $OH\bullet$ concentrations in the high temperature oxidative region of laminar hydrocarbon diffusion flames have been recently reported [175]. These results show that as soot levels increase, the $OH\bullet$ concentration and temperature decreases. An equilibrium approach for predicting $OH\bullet$ concentrations is shown to be grossly inadequate. This implies that detailed considerations of finite rate kinetics may be necessary to accurately predict $OH\bullet$ concentrations.

There have been a great number of experimental measurements conducted in the last twenty years on the soot formation processes in premixed flames, nonpremixed flames, shock tubes, engines, and flow reactors. These studies have focussed on the chemical kinetics associated with fuel pyrolysis, molecular growth chemistry and particle growth. Yet, only a handful of studies have been performed on soot oxidation processes. Further studies are needed to unravel this very fundamental flame process.

3.6 Soot and CO emission

The amount of soot emitted in both laminar and buoyancy dominated turbulent flames is closely correlated with CO emission [136, 137]. Details of the flame structure have been important in understanding the link between the smoke and carbon monoxide emission from a flame. Measurements of the $OH\bullet$ and CO concentration in sooty regions of laminar hydrocarbon flames have provided an improved understanding of pollutant emissions. The primary mechanism thought to be responsible for the oxidation of CO in hydrocarbon flames can be represented by:

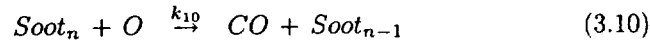
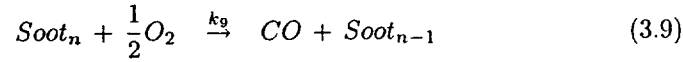
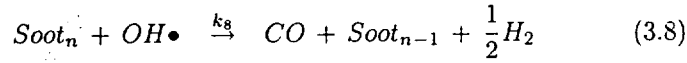


The kinetic scheme for the oxidation of soot has not been described in detail. Leung *et al.* [176], however, schematically represent soot oxidation by:



where C represents carbonaceous soot. Experimental results from Neoh and Howard [173] observed CO , CO_2 and H_2 as the only stable species in the combustion products of the secondary burning of a gaseous stream

laden with soot particles. Their results suggest that the overall kinetics may be effectively represented as follows:



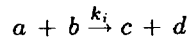
where k_i represents the reaction rate constant for the i th reaction and Soot_n represents a soot particle with n carbon atoms. Such a representation may be a fair approximation for soot escaping a flame when the C/H ratio of the particle is large (≈ 8).

Nagle and Strickland-Constable [171] formulated a semi-empirical expression for the rate of oxidation of pyrolytic graphite by O_2 (R8) for a temperature range 1000–2000°C. In their analysis, they assumed that oxidation by $\text{OH}\bullet$ was negligible. For temperatures less than 1800 K and oxygen concentrations greater than a few percent, the Nagle and Strickland-Constable expression for the oxidation rate R_{ox} ($\text{g}/\text{cm}^2\text{-s}$) reduces to:

$$R_{ox} = 11.3 \exp(-17,000K/T)$$

where T is the flame temperature.

Recall that for a bimolecular reaction:



the chemical rate of reaction in the forward direction is defined as:

$$R_i = k_i N_a N_b$$

where R_i is the rate of reaction, k_i is the rate constant for the forward reaction, and N_i is the number density of the i th species.

Neoh *et al.* [173] have shown that the rate constant (k_8) and the reaction rate (R_8) for the oxidation of soot by $\text{OH}\bullet$ in rich premixed flames is much higher than by O_2 (R_9, k_9) and that the Nagle and Strickland-Constable expression drastically underestimates the rate of soot oxidation. In lean premixed flames, they found $R_8 \approx R_9$ and that oxidation by O atom (k_{10}) cannot be discounted.

From Reactions (6) and (8), a kinetic competition occurs between CO and soot particles for oxidation by $\text{OH}\bullet$. Furthermore, as soot is oxidized in Reactions (8)–(10), more CO is formed. For soot to escape from a nonpremixed flame, it must pass through a relatively hot reaction zone where the concentration of $\text{OH}\bullet$ is relatively large. If the temperature is low (<1300 K) then the reaction rate is typically not fast enough to fully oxidize mature soot particles [167].

3.6.1 Smoke yield

Köylü and Faeth [137] have observed that a strong correlation exists between the mass of CO and soot emitted from buoyant turbulent hydrocarbon and alcohol diffusion flames. Puri and Santoro [136] have studied the formation of CO due to oxidation of soot by $OH\bullet$ and O_2 in laminar hydrocarbon flames. Using the result of Neoh *et al.* [173] that approximately 28% of the collisions between $OH\bullet$ and soot lead to reaction for temperatures in the range 1575–1865 K, they derive an expression for the soot oxidation rate (or the CO production rate) by applying a fundamental kinetic theory approach:

$$d[\text{soot}]/dt = d[CO]/dt \approx [OH\bullet]f_v T^{0.5}/D$$

where f_v is the soot volume fraction, D is related to the particle diameter and the CO concentration is in moles/cm³. In their formulation, the oxidation rate is assumed to be proportional to the soot concentration [136].

Smoke is emitted when the temperature near the soot oxidation region drops below 1300 K [167]. A large database of the smoke yield escaping flames exists for many fuels, but is based on small scale fires only (0.1m diameter in a horizontal orientation) [177]. The smoke yield, defined as the percentage of fuel carbon which is converted to particulates emitted from the flame varies from $\approx 0.1\%$ for wood to $\approx 10\%$ for polymethylmethacrylate [177]. While fuel type is a key parameter, the fire scale is also important [178]. For heptane pool fires, the soot yield increases almost linearly with scale [179]. The smoke yield can be correlated to the smoke point height [177].

Santoro and Miller [174] have determined conversion efficiencies for various hydrocarbons going to soot when added to ethylene and methane diffusion flames. Harris and Weiner [166] and Hamins *et al.* [180] have reported high conversion efficiencies of aromatic fuels into soot particles in premixed and diffusion flames, respectively.

3.7 Flames

The evolution of soot in chemically reacting flow systems is an area of active interest, and an extensive literature exists on many aspects of the topic. While many questions remain unanswered, recent studies in premixed and nonpremixed flames have led to advances in our fundamental understanding of the soot formation and growth processes.

Because the soot formation process is influenced both by chemistry and fluid mechanics, these effects must be independently considered before a predictive model of soot evolution can be detailed.

3.7.1 Premixed flames

Premixed flames facilitate the study of flame chemistry and soot evolution, independent from mixing processes. One dimensional laminar premixed flames also allow control of the temperature environment through preheating of the reactants or cooling through the addition of an inert gas. The concentration of oxidative species can be varied in order to study its effect on soot evolution. Premixed flames are representative of combustion in some practical devices.

Sooting tendency

In premixed flames, comparison of the tendency for different fuels to form soot is based on the onset of flame luminosity and can be often correlated with a critical fuel equivalence ratio (ϕ_c). The equivalence ratio is defined as:

$$\phi = (F/A)/(F/A)_s$$

where F is the number of moles of fuel, A is the moles of air and the subscript s denotes the stoichiometric value. A premixed flame is characterized by the value of ϕ . For $\phi < 1$, the flame is fuel lean; if $\phi = 1$ then the flame is stoichiometric, for $\phi > 1$ the flame is fuel rich.

The critical fuel equivalence ratio (ϕ_c) is usually determined by increasing the fuel flow rate until the onset of yellow luminosity (or some other observable) just occurs. For all fuels, $\phi_c > 1$, but its value varies for different fuel types. Those fuels that appear luminous at lower equivalence ratios are considered to have a higher sooting tendency. For premixed flames burning at 1 atm in air this tendency is characterized as [181]:

aromatics > alcohols > paraffins > olefins > acetylene.

Although the luminosity is attributed to the onset of soot, the luminosity is actually due to a combination of parameters including particle temperature and soot volume fraction. Furthermore, particle temperatures are not necessarily equilibrated to gas temperature [182].

3.8 Nonpremixed flames

Nonpremixed or diffusion flames contain a wide range of temperatures (300 to 2500 K) and stoichiometries (ϕ) varying in value from $\mathcal{O}(0)$ to $\mathcal{O}(10)$. Diffusion flames are complicated because of the sharp gradients in temperature and species concentrations. Stoichiometry in a nonpremixed flame must be defined locally, rather than globally as for a premixed flame. The local equivalence ratio is determined from the

measured concentration of major chemical species. For a CH_4 -air flame, ϕ can be defined as the ratio of the stoichiometric number of O atoms to the actual number of O atoms available [183]:

$$\phi = \frac{[H_2] + 2[CO_2] + 4[CH_4] + 2[CO] + 6[C_2H_4] + [H_2O]}{2[CO_2] + 2[O_2] + [CO] + [H_2O]}$$

As the fuel flow rate is increased in a hydrocarbon diffusion flames, the flame height increases and the flame character changes. Initially the flame is laminar and almost completely blue in appearance. As the fuel flow rate increases, the flame height grows and the flame tip becomes yellow [182]. Further increasing the fuel flow rate increases the length of the yellow zone until a small orange zone appears [182]. The orange zone appears at approximately 1700 K for hydrocarbon fuels. Whereas the soot in the orange zone is thought to be in equilibrium with gas temperatures, the soot in the yellow zone may be at higher temperatures than the gas due to chemical reactions on the particle surface [182]. Increased soot concentration is associated with increased maximum temperature and residence time, where residence time is defined as the time a molecule spends travelling along a streamline leading from the burner duct to the end of the flame. Further increases in the fuel flow rate leads to a critical value when soot escapes the luminous zone. The sooting tendency is typically quantified by measuring this critical smoke point height. The standard ASTM Smoke Point Height device incorporates a wick and is designed solely for liquid fuels [184]. Gaseous and solid fuels have also been tested using modified devices [177].

The smoke point height test has been used as an indicator of the sooting tendency for fuels burning in air at 1 atm. The sooting tendency is related to the initial fuel structure. The ranking determined by many researchers is related to fuel structure [185]–[187]

polyaromatics > aromatics > alkynes > alkenes > alkanes > alcohols.

Fuels that have a high tendency to soot, such as benzene, emit smoke at a low mass flow rate, as compared to fuels characterized by a low tendency to soot, like ethane, which requires a relatively high flow rate. The causes for the differences in smoke point height have been examined by careful measurements of the temperature and soot field in smoke point flames. Schug et al. [158] determined that the smoke height does not directly correlate to the fuel C/H ratio as found for premixed flames [181].

It should be emphasized that the smoke point height is a relative rather than an absolute ranking method. With preheated fuel and controlled fuel flow rates such that the smoke point is maintained, the maximum soot volume fraction in these flames decreases with increased preheating [188]. This underscores the importance of flame structure in determining the soot field.

The fuel pyrolysis mechanism has a strong impact on the sooting tendency of diffusion flames [159, 160]. The ranking given above for different fuel types indicates the importance of fuel structure (which is linked to chemical mechanisms of fuel pyrolysis) in the sooting propensity of a fuel. Other evidence supports this claim. Benzene, for example, is a prominent chemical intermediate in the pyrolysis of cyclohexadiene. These two fuels have very similar smoke point heights.

A fuel will not necessarily have the same relative sooting tendency in a premixed as in a nonpremixed flame. This is because the flame structure is completely different in premixed and nonpremixed flames. Thus, the kinetics controlling the soot formation and oxidation processes cannot be expected to yield parallel results even for the same test fuels.

Increases in flame temperature have very different consequences for the soot concentration field in nonpremixed and premixed flames burning the same fuel. As the temperature field in a flame is increased, f_v increases in nonpremixed flames, whereas it decreases in premixed flames. Glassman [80] suggests that in premixed flames as the temperature rises, oxidative attack on soot precursors increases at a faster rate than precursor formation. This is consistent with studies [181] which have determined that soot oxidation is characterized by a large activation energy, and thus is highly temperature sensitive. In nonpremixed flames increased flame temperatures increase fuel pyrolysis rates which gives rise to increased soot precursor formation and ultimately to elevated soot concentrations.

Glassman and Yaccarino [159] determined that the flame temperature must be considered when ranking fuels according to sooting propensity. For example, acetylene, which is considered a highly sooting fuel has a sooting tendency similar to butane (a paraffin) when the sooting tendency is compared at a fixed adiabatic flame temperature which was controlled through nitrogen dilution [160].

Dilution and thermal effects

The effects of dilution and temperature on the soot field have been carried out in both counterflowing [189, 190] and coflowing diffusion flames [140, 160, 167, 188, 191, 192]. Although many questions remain unanswered, several unifying trends emerge from these experiments. The maximum soot volume fraction increases with increasing flame temperature obtained through reactant preheating, but the relative increase depends on the fuel type. Nitrogen dilution affects the soot formation rate due to both thermal and kinetic effects. The addition of an inert decreases the flame temperature and the probability of a given chemical reaction is reduced because the collision probability is reduced.

The relative magnitude of these effects was quantified by Gülder and

Snelling [188] who measured the impact of two experiments on the soot volume fraction in nonpremixed flames. This was accomplished by either cooling the reactants from the base temperature of 600 K or by diluting the reactants with an inert gas. A reduction in soot formation was observed in both series of experiments. The difference between the two sets of results at a particular adiabatic flame temperature condition is an indication of the importance of dilution. The effect of dilution on the maximum soot volume fraction is greater than that of temperature until rather large amounts of dilution when the two effects have approximately the same impact.

Glassman [80] suggests that in premixed flames as the temperature rises, oxidative attack on soot precursors increases at a faster rate than precursor formation. This is consistent with other studies [181] which have determined that soot oxidation is characterized by the largest activation energy of all soot processes and thus is the most temperature sensitive.

3.8.1 Fuel structure and thermal effects

The initial fuel/air equivalence ratio (ϕ) and the maximum flame temperature have been emphasized as key parameters [159] in controlling the tendency of a premixed flame to soot. Yet, the initial chemical structure is thought to play little or no role in premixed flames. The parameter ϕ_c was determined for nondiluted and nitrogen diluted premixed flames [181] and the adiabatic flame temperatures were calculated. Values of ϕ_c were found to be well correlated with the total number of carbon bonds in the initial fuel molecule when all fuels are compared at the same calculated adiabatic temperature. This result is consistent with a study by Harris and Weiner [166] who have shown that increments of carbon added to premixed flames in the form of ethylene (C_2H_4) or toluene (C_7H_8) yield the same amount of additional excess soot produced.

Yet, some disagreement exists as to the importance of the initial chemical structure of the fuel molecule in the soot formation process in premixed flames. With the same data, Calcote and Olson [193] concluded that the initial fuel structure plays a major role in determining soot formation and that fuel dilution experiments are not the correct way to think about sooting tendency.

3.8.2 Pressure effects

Although many combustion processes occur at elevated pressures (diesel engines for example), only a few flame studies have been carried out under these conditions (e.g. Refs. [194, 195]). These studies indicate that combustion at enhanced pressures result in increased soot volume

fractions, number densities and particle diameters.

Many flame structure studies of premixed flames have been undertaken at reduced pressures in order to cause a broadened reaction zone in an effort to increase the resolution of the measurements. For a constant temperature, as pressure increases so does the reactant number density, as well as the rate of chemical reactions.

3.8.3 Oxygen effects

Hura and Glassman [196, 197] studied the addition of oxygen to the fuel side of diffusion flames and found that small amounts of oxygen addition significantly enhanced soot formation for some fuels but not for others. These results were explained in terms of the details of fuel pyrolysis chemistry. In similar experiments, Wey *et al.* [198] concluded that the enhanced soot formation was due to increased catalysis of the pyrolysis reactions by trace oxygen.

3.8.4 Flow effects

Although kinetic processes including fuel pyrolysis, surface growth and particle oxidation govern soot formation, transport processes such as diffusion and convection influence the structure of a combustion system and thereby influence the soot formation process. The velocity field is important because particle growth is dependent on residence time in the flame. The path traversed by soot is a function of inertial, drag and thermophoretic forces on the particle. The relative magnitude of these forces depends on the particle size, local temperature gradient and convective velocity of the flow field [199]. Whereas large molecules typically follow flow streaklines in hydrocarbon diffusion flames, drag forces on large particles preclude this from occurring.

Practical combustion normally involves turbulent flames. Differences in the mechanisms controlling soot formation and oxidation in laminar and turbulent flames has been outlined by Kent and Wagner [167]. One approach to modelling turbulent combustion treats such situations as an ensemble of well characterized laminar flamelets. This method assumes that the structure of these flamelets in the limit of fast chemistry can be characterized by the mixture fraction, which is a nondimensional parameter directly related to the local equivalence ratio [200]. Empirically, it has been shown that many flame scalars, such as the temperature field and the concentration distribution of many chemical species can be adequately predicted using this treatment [201]. Use of the mixture fraction concept has gained popularity mainly due to its computational simplicity. Chemical species associated with slow chemistry, however, do not obey mixture fraction relationships. The fast chemistry condition is typ-

ically met when a flame species is either fully or partially equilibrated. It is rare, however, for species concentrations to be equal to their full equilibrium values.

The mixture fraction correlation is appropriate when the controlling chemical rates for the formation and destruction of a particular chemical species are fast relative to transport rates. All chemical species present at a particular flame location are the sum of a chemical source or sink and/or transport into that volume. Net chemical production is due to the sum of chemical reactions leading to formation or destruction of a particular species, whereas transport is due to the sum of convection and molecular diffusion. Slow chemistry implies that the sum of the chemical formation rates are slower than species transport. For example in hydrocarbon diffusion flames, the chemistry associated with the formation and destruction of carbon monoxide, benzene as well as other large molecules is slow and these species do not obey mixture fraction correlations [202].

It has been shown that the application of a direct mixture fraction correlation to the soot volume fraction in the fuel rich soot production region in nonpremixed flames does not hold [203]–[205]. Instead, other approaches are being tested. These seek to relate the rate of change of the soot volume fraction and number density to the mixture fraction [206].

In order to better understand flow field effects on the soot field, experiments have been conducted in diffusion flames burning in a counterflow configuration [189, 207]. The counterflow geometry is particularly useful because scalar properties such as temperature and species concentration are one dimensional. In addition, the flow field is amenable to mathematical analysis. Streams of fuel and oxidizer flow towards each other resulting in a stagnation type flow. A thin steady laminar flame is established which lies on the oxidizer side of the stagnation plane in hydrocarbon flames. With a flame established between the reactant streams, increases in the velocity of the fuel or oxidizer increase the strain rate which has been shown to significantly effect the concentration distribution of chemical species in the flame.

Increases in the strain rate lead from a flame that is yellow in appearance to one that is blue. Measurements by Du *et al.* [189] show that as the velocity of the reactant streams is increased (i.e. the strain rate is increased), a critical strain rate exists such that disappearance of the yellow luminosity associated with soot particles, the laser induced fluorescence associated with PAH, and the light scattering from soot particles occurs. The critical strain rates for luminosity and light scattering are similar and less than that from the fluorescence signal (thought to be from large PAH molecules). The soot volume fraction and the maximum particle size decrease with increasing oxidizer velocity, which has been interpreted as being due to reduced particle residence time that is

necessary for coagulation and surface growth [207].

Recent developments in detailed models of soot generation have focussed on simple combustion systems such as laminar hydrocarbon premixed and nonpremixed flames. At the same time, studies in turbulent flames are yielding correlations relating soot generation rates to residence times [208] with the goal of predicting soot levels and radiant fractions in turbulent flames.

3.9 Integrated models of soot formation

While a great deal of work has focussed on various aspects of the generation of soot, few attempts have been made to integrate the submodels into a predictive tool. An integrated soot formation model must possess certain capabilities, depending on the application.

3.9.1 One step models

A very basic model, for example, might predict the rate of soot formation for a particular fuel type considering a one-step chemical reaction. A simple quantitative expression describing soot formation is based on a global one step chemical reaction leading from reactants (fuel and oxidizer) to soot, expressed by Arrhenius type kinetics as:

$$R_{soot} = Y_{ox} Y_f B \exp(E_a/RT_f)$$

where Y_{ox} and Y_f are the mass fraction of oxidizer and fuel respectively, E_a is the global activation energy for the sooting limits of a particular fuel, R is the universal gas constant, T_f is the calculated adiabatic flame temperature and B is a preexponential factor in the Arrhenius rate expression. In this formulation, the sum of all of the processes leading to the formation and oxidation of soot are described by a single irreversible chemical reaction. This global model describes effective kinetic rate parameters which may control soot formation and oxidation kinetics near the sooting limit. Flames near the sooting limit are defined as those flames in which the yellow flame luminosity (or some other observable limiting soot condition) is just evident. For laminar hydrocarbon diffusion flames, Du *et al.* [189] found $E_a \approx 30$ Kcal/mole, depending on fuel type.

The soot formation process has also been modeled by global kinetics in shock tubes where the activation temperature (E/R in units of temperature) associated with the early formation process has been found to be 15,000 to 25,000 K depending on the pressure range and fuel type [148]. On the other hand, soot oxidation exhibits the highest global activation energy of the several stages in soot formation [181]. Thus, the oxidation process is the most sensitive to the local flame temperature.

For many applications, a model must be able to predict radiative emission as a function of fire size and fuel type. Because the temperature field and the soot concentration are coupled, a model must account for transport, mass, momentum and energy conservation. Thus, a comprehensive soot model must be coupled with a model that predicts flame structure. A model should consider fuel pyrolysis, molecular growth kinetics, surface growth rates as well as particle oxidation. Global kinetic soot models are limited in their utility. They are valid only within the range of parameters (temperature, pressure, fuel type) for which they were developed and cannot be used to predict particle size or radiative emission from a flame.

Because the rate of particle inception is thought to control the amount of soot ultimately produced, the rate of particle nucleation must be predicted with some accuracy. Since about 90% of soot mass is due to growth reactions, a model must also predict the concentration of the species responsible for soot growth. More detailed models may also consider a particle's time-temperature history, total residence time, and dependence on other parameters such as pressure.

3.9.2 Quantitative soot formation models

The ultimate challenge of soot formation research is to develop predictive models of the soot distribution within a flame and the radiative, smoke and toxic gas emission from a flame or fire to the surroundings. Several quantitative integrated soot formation models have been proposed [168], [176] [209]–[211]. All of these models address the essential physics in the evolution of a soot field including nucleation, surface growth and oxidation. These models have been developed and validated for specific experimental conditions and thus are limited in their application. For example, the global soot growth model [210] was developed for isothermal systems. To date, the models by Syed *et al.* [211], Kennedy *et al.* [168] and Moss *et al.* [206] require some empirical input to describe the soot formation process and different constants for each new fuel. Some also emphasize the local mixture fraction [168, 211] whereas others emphasize the C_2H_2 concentration [176]. A key parameter in all of the models is the local temperature which has a dramatic impact on the rates of these temperature dependent processes.

It may be illustrative to consider a quantitative model in detail. The model by Leung *et al.* [176] takes C_2H_2 as the soot particle growth species, following the results of Frenklach [157] and Harris [212]. The model uses detailed chemistry to determine the local C_2H_2 concentration and then determines local soot volume fraction, particle growth and soot number density for counterflowing propane and ethylene diffusion flames burning in enriched and depleted oxygen environments. The model does

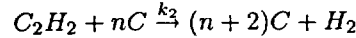
not couple the radiative heat losses associated with the soot volume fraction to the calculated temperature field.

The rate of nucleation of soot particles assumed to contain roughly 100 carbon atoms approximately 1 nm in diameter, is taken from the measurements by Vandesburger *et al.* [207] and is correlated to the local C_2H_2 concentration:

$$R_1 = k_1(T)[C_2H_2]$$

where $k_1(T)$ is a rate constant ($\approx \exp[-21,100K/T]$) that is highly temperature sensitive. Because of the large activation temperature, a change of a few hundred degrees in temperature can easily yield an order of magnitude change in the inception rate. Others have chosen to treat the rate of inception as an empirical constant [211].

The model relates surface growth to C_2H_2 in an exclusive manner:



and the rate of reaction is taken as:

$$R_2 = k_2 f(S)[C_2H_2]$$

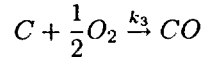
where $k_2 \approx \exp(12,000K/T)$. The rate of growth is taken to be a function (f) of the surface area (S) or active sites available for growth reactions. Here, the number of active sites are taken to be equal to the square root of the locally available surface area (S):

$$S = \pi D^2 \rho N$$

where ρ is the gas density, N is the particle number density, and D is the diameter of the particles that are assumed to be spherical:

$$D = (6Y_c/\pi N \rho_c)^{1/3}$$

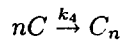
Y_c is the soot mass fraction, and ρ_c is the soot density. Leung *et al.* [176] represent soot oxidation by:



where soot is taken to be oxidized exclusively by O_2 with the rate constant taken to be proportional to the soot surface area and the oxygen concentration, i.e.,

$$R_3 = k_3 S[O_2]$$

and k_3 is taken from the work of Garo *et al.* [213]. An improved model would also include oxidation by $OH\bullet$. A fourth rate term is given for particle agglomeration, which can be represented as:



and R_4 is taken to be proportional to ρ . The reactions form a closed system of four equations (for mass formation, mass destruction, agglomeration, and particle number density) and four unknowns, i.e., $[C]$, ρ_n , $[C_n]$ and Y_c . The pre-exponential factors for the nucleation (R_1) and growth (R_2) steps were calibrated from a preliminary set of experiments on ethene. A comparison of computed and experimental values using the model for both propane and ethene counterflow flames yielded good agreement when compared to the profiles of experimentally measured temperature, soot volume fraction and soot number density. These results are extremely encouraging.

3.10 Future challenges

Over the last two decades, a large number of fundamental studies have investigated the formation and structure of soot in a variety of combustion configurations. Progress has been made in unravelling a variety of key processes including fuel pyrolysis chemistry, particle inception, surface growth, particle oxidation and the effects of flame temperature, dilution and strain rate. These studies have provided key information, facilitating the development of a new generation of integrated flame/soot models which endeavor to quantitatively predict the formation and evolution of soot in hydrocarbon diffusion flames. A number of these models approximately predict key characteristics of flames including the temperature field, soot volume fraction, number density and rate of particle growth in simple counterflowing laminar flames [176]. Integrated flame models are also being developed for turbulent flames [214].

It is still not possible to accurately predict the soot emission from a fire or other practical combustion configurations. Yet, these models are young. Comparison with experimental measurements will certainly improve as quantitative understanding of the parameters affecting the soot formation process increases.

The challenge of the next generation of integrated soot models will be to predict the soot and temperature fields and consequent burning rate, radiative emission and soot yield from a growing turbulent fire. The current models are an initial step in addressing this interesting and practical problem.

3.10.1 New technologies

The development of generalizable new models should lead to improved combustor design and fire growth models. In the interim, however, transfer and application of knowledge to the development of new technologies continues. The wood burning stove is an interesting example of recent improvements in combustion technology. Wood burning stoves, which

were not regulated until 1988, contributed to air pollution in the form of unburnt particulates. The pollution was so grave that partial bans of wood burning occurred in certain areas of the United States.

The pyrolysis of wood yields a vast array of gas phase molecules which contain carbon, hydrogen as well as oxygen and nitrogen. Because of this, the chemical details of the pyrolysis mechanism are not well understood. Yet, combustion engineering solutions to the problem of incineration have been known for many years. Thus, it is surprising that stoves were not redesigned to burn cleaner before 1988. The new stove possesses secondary and tertiary combustion zones which oxidize particulates and hydrocarbons not fully oxidized in the primary combustion section. Through the use of obstacles, turbulence is generated in the secondary and tertiary combustion zones, allowing better mixing between the unburnt particulates and the fresh air supplied to the auxiliary sections. New stoves will not allow an operator to cut off the air supply, which allowed slow burning embers to smolder and heat a room for hours and at the same time release unburnt hydrocarbons and particulates. Finally, catalytic combustors in the chimney of many stoves catalyze further reduction of particulate emissions. The example of the wood stove demonstrates that solvable combustion problems exist which still have not been addressed. Recent emphasis on clean air, global warming, and energy conservation may provide the impetus which leads to the development of improved combustion technologies.

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