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Aspects of the Mechanisms of Smoke Generation by Burning Materials

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This paper is concerned with the investigation of the detailed aspects of smoke generation during the burning of natural and synthetic solid materials under simulated fire conditions. With this objective in mind, the first portion of the paper is devoted to a review of relevant basic smoke formation studies. This review identifies the complex physical, chemical, and electrical processes that are believed to be important in smoke particulate production. The remainder of the paper presents measured experimental data and discusses observed trends in terms of many of the processes set forth in the previous section. The resulting increase in particle concentrations as heating rates are increased in nonflaming combustion is related to nucleation and condensation processes. Significant fundamental differences in smoke characteristics were observed between flaming and nonflaming conditions, and this is attributed to specific differences in controlling mechanisms and resulting pathways leading to particulate formation. Measured differences in smoke properties resulting from increased environmental temperature are similarly explained. The effects of polymer substrate properties and effects of various additives for a given substrate on observed smoke particulate properties are also discussed in terms of basic processes, although the determination of the actual mechanisms responsible for the observed smoke characteristics require further study. Finally, results of chemical analyses of smoke particulates from a variety of materials conducted as part of this study indicate that notable differences in particulate formation mechanisms are likely among the materials studied.

INTRODUCTION

Awareness of the life hazards associated with smoke formation in fires has resulted in increased emphasis on smoke research in recent years [1, 2]. Special emphasis has been given to the determination of the amounts and properties of smoke particulates generated by different materials under different fire conditions. In addition, research efforts have been directed at the elucidation of the mechanisms responsible for observed smoke formation tendencies. However, the latter are concerned with mechanisms of smoke generation in situations involving relatively simple fuels and flame configurations and very little has been done to date to extrapolate the results of these studies to fire situations involving more complex configurations and fuels. This paper represents an attempt at filling this gap by presenting measured smoke characteristics data and relating the observed trends with postulated smoke formation mechanisms. Accordingly, a review of the mechanisms of smoke particulate formation that are relevant to the fire safety problem is presented in the following section. This review is followed by a discussion of the relationships between the mechanisms of interest and measured experimental data, which have been obtained in the Combustion Products Test Chamber (CPTC) at the Georgia Institute of Technology for a variety of burning natural and synthetic materials under a variety of conditions designed to simulate actual fire situations.

REVIEW OF SMOKE FORMATION MECHANISMS

Flaming Combustion

Due to the complexity of the smoke generation problem, the majority of past investigations dealing

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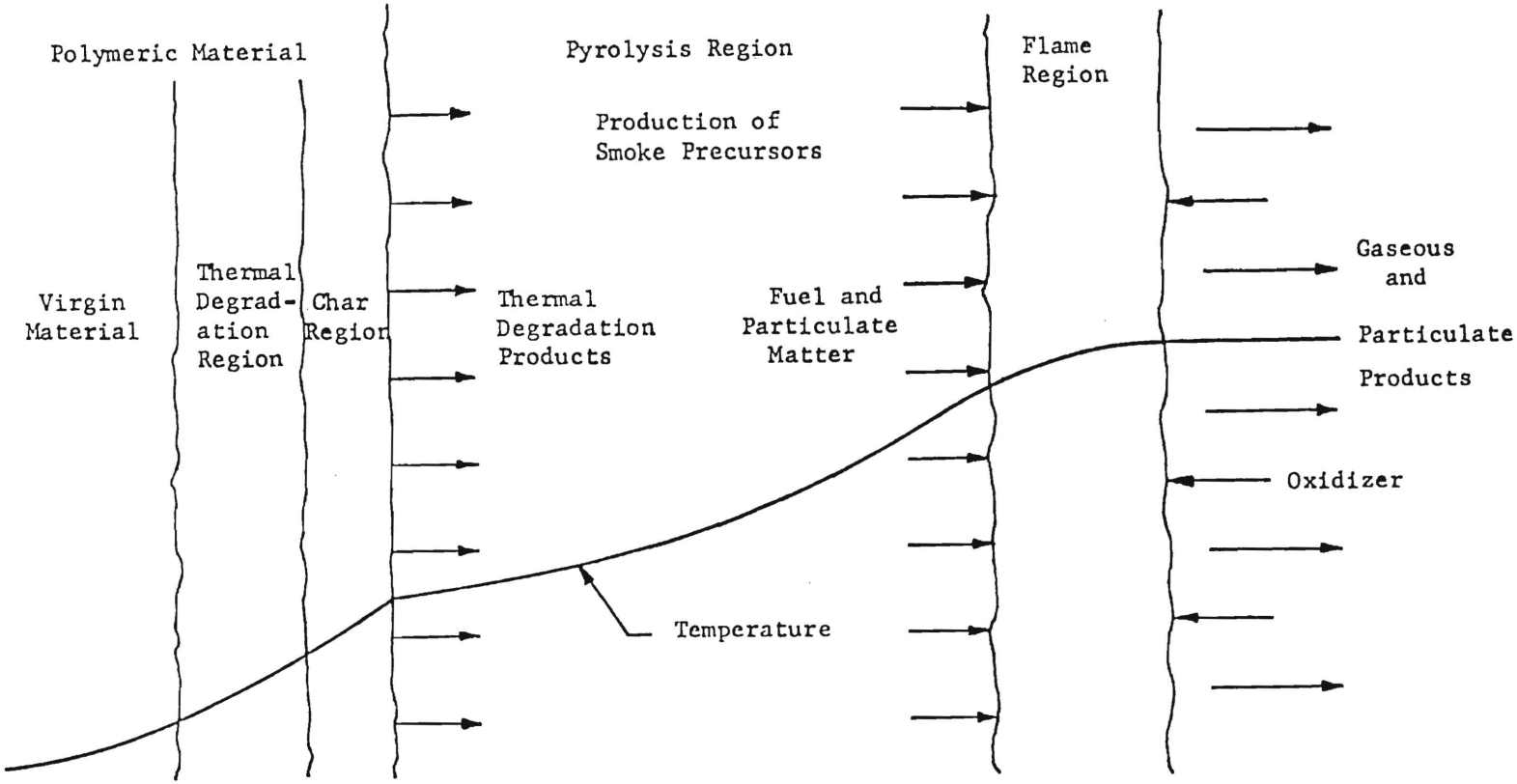

Fig. 1. Schematic of a polymer flame.

with this problem have restricted themselves to the investigation of soot formation in premixed or diffusion flames involving relatively simple fuels or fuels believed to be important intermediates in the soot generation process. In order to help relate the results of these studies to the combustion of polymers, we have provided an idealized schematic of the flame structure of a burning polymeric material in Fig. 1. For the indicated burning configuration, the fuel provided by the solid phase is moving by convection and diffusion toward the flame zone where it mixes with the incoming oxidizer and burns. This combustion process results in the generation of gaseous and (under certain conditons) particulate products, which are then transported away from the flame zone. The heat generated in the flame is fed back by conduction and radiation mechanisms to the solid phase; this heat feedback is essential, of course, for maintaining the flame. Under such conditions the solid phase can be characterized by three regions; namely, the virgin material, the thermal degradation region,[1] and the char region. The existence and thickness of all three regions depends on the nature of the material and many materials (e.g., polymethyl methacrylate) do not have a char region.

As shown in Fig. 1, the region between the solid phase and the flame is characterized by a variable temperature field. In most situations this region will contain little or no oxidizer and presumably the fuel moving through it undergoes further pyrolysis reactions as it moves from regions of lower to higher temperature. As discussed subsequently, it is also likely that particulate formation is initiated in this zone.

Based on existing understanding of particulate formation in relatively simple diffusion flames, it is generally believed [3, 4] that particles may be generated in both the preflame (i.e., pyrolysis) and flame regions of the configuration under consideration. Furthermore, it has been hypothesized that the particulate formation in the two regions is controlled by different mechanisms. In the pyrolysis region particulate formation is believed to be due to supersaturation and condensation of the pyrolyzing and to reacting hydrocarbons. Once nuclei have been formed, the supersaturation condition is relieved and further particulate growth occurs by surface deposition of gaseous hydrocarbons. The particulates thus formed undergo further dehydrogenation as they move through higher temperatures and enter the flame region. It is also believed that the condensing species are large hydrocarbon molecules with a high C/H ratio. These particles may also burn as they move through the flame regions.

In the flame region, positively charged hydrocarbon ions are believed to be the nucleation sites that attract other hydrocarbons to form soot particles [3,4,5]. The combustion region is the source of the needed positive ions and the nucleation and particle growth processes are expected to result in a large number of small diameter particles. In the preflame region it was postulated that supersaturation and condensation processes lead to particulate formation [3, 4], where a smaller number of larger diameter particles would be expected for a given amount of fuel. Abrahamson [6], however, argues against the condensation mechanism in the preflame region and instead proposes that other intermediates named "saturated platelets" are responsible for soot formation under pyrolytic conditions. These intermediates are large neutral and negatively charged hydrocarbons, which could act as nucleation sites for particulate formation in the pyrolysis (preflame) zone.

In these regards it should be pointed out that after the initial thermal degradation step, the sequence of particulate formation by burning polymers could be expected to follow one or more of the pathways indicated in Fig. 2, depending on the encountered thermal environment. This proposed overall scheme is a modified version of the one first proposed by Street and Thomas [7] and will be referred to continually in the discussions that follow. Also, note that those described pathways are usually followed by further collisional agglomeration, which results in the growth of soot particulates in flames from small primary units to the larger particles described later in this paper. However, particle agglomeration rates are dependent on

[1] This region is sometimes referred to as being a pyrolysis region. It is referred to here as a thermal degradation region to distinguish it from the region in the gas phase where pyrolysis reactions take place.

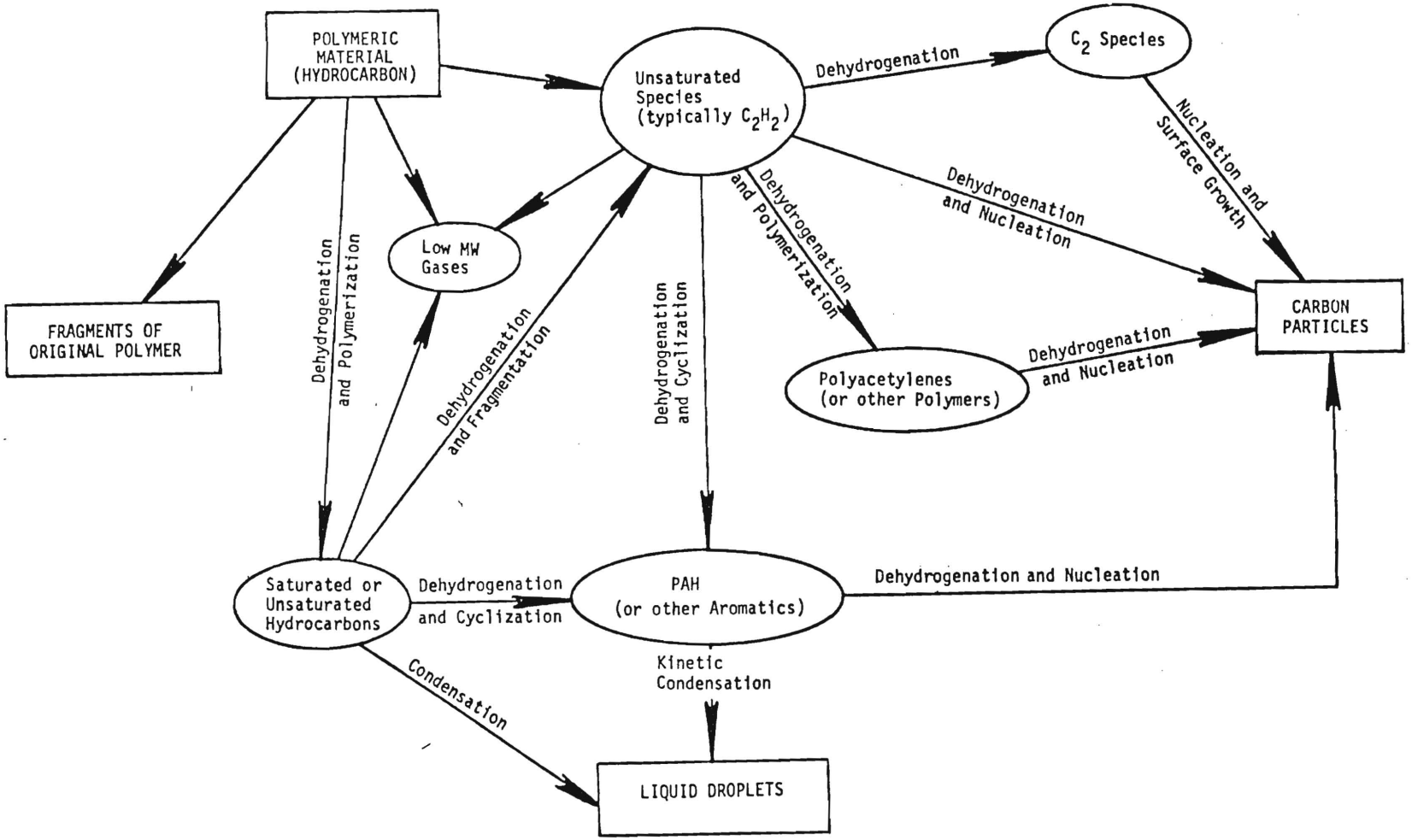

Fig. 2. Postulated mechanisms for smoke particulate formation.

the concentration and size of the primary sites, and thus the presence of the larger particles is directly related to rates of formation and growth of the primary sites.

Studies of soot formation in flames have included a variety of gaseous and liquid fuels such as methane, acetylene, isoprene, ethylene, propane, and benzene [7-16]. Although these compounds are chemically much simpler than the polymeric materials of interest in fire research, the pyrolysis products of polymers usually consist of a wide variety of organic species [1], which may be expected to include some of the fuels previously mentioned. Furthermore, because it is likely that simple molecules represented by classes of saturated (e.g., CH_4) and unsaturated (e.g., C_2H_2 and C_2H_4) compounds are involved in the smoke formation process (i.e., see Fig. 2), smoke formation pathways associated with these simple species must form at least a portion of the overall reaction process in the combustion of polymers.

The role of polyacetylenes [8, 10] and polycyclic aromatics (PAH) [13, 14] as precursors to soot formation is widely postulated (see Fig. 2). However, the relative importance attached to their roles as intermediates seems to be very dependent on the nature of the starting material. Where aromatic nuclei already exist (as with benzene), PAH may assume a major role as intermediates. By contrast, with acetylenic fuels, polyacetylenes are major components in the reaction scheme [17, 18]. It is possible, however, that soot formation from acetylenic fuels involves PAH as intermediates and intermediates in the formation of aromatics could be acetylene, ethylene, 1,3-butadiene [19], and/or their associated radicals.

Although, as previously mentioned, it has been suggested that PAH compounds can play a major role in soot formation, the precise mechanisms are not yet clear. Generally, the most likely route would follow dehydrogenation of substituted PAH, arising possibly from radicals or ions of benzenes or polyacetylenes following cyclization [9]. Benzene or unsubstituted PAH may be too unreactive to play a significant part in this process.

In the case of the polyacetylenes it is believed that they are formed by polymerization of unsaturated species (e.g., C_2H_2) via radical reactions or ionic mechanisms [5, 10]. These polyacetylenes then grow by successive addition of radicals, lower molecular weight unsaturated species, and other polyacetylenic species. This process is characterized by an increasing C/H ratio, which presumably results in the nucleus of a soot particle [5, 10]. Finally, it should be noted that it is possible that other unknown short-lived unstable chemical species also act as precursors or intermediates to smoke formation rather than the detectable PAH and polyacetylenes (e.g., Abrahamson's saturated platelets [6]).

For the polymer flame model discussed previously (Fig. 1) it was suggested that supersaturation and condensation processes in the pyrolysis (preflame) region and ionization in the flame region are the controlling particulate generation mechanisms in flames. In regard to ionic mechanisms, Salooja [20] has shown that the introduction of alkali or alkaline earth metals into the "primary reaction region" of a hydrocarbon flame results in considerable smoke reduction whereas the introduction of the same metallic compounds into regions downstream from the primary reaction zone of the flame increased smoke formation. The effects of the various tested metals have been correlated with their ionization potentials, and the generation of electrons by the ionizing metals in the primary reaction region has been argued by Salooja [20] to be responsible for the observed smoke reduction. Haynes et al. [21] have also studied the effects of metallic additives; however, they argue that soot reduction by addition of alkali metals in *premixed* flames is due to enhanced ionization of incipient soot particles rather than to the effects of generated electrons. Other investigators [22, 23] propose that the reaction of metal additives with water results in hydroxyl radical formation in the preflame region and these radicals react with smoke precursors and thus reduce their concentrations.

For diffusion flames (of primary interest in burning polymers) the work of Bowser and Weinberg [24] tends to support the conclusion that electrons play a significant role in soot growth processes. These authors found that the tendency of a gaseous diffusion flame to generate soot could be controlled through the application of electric field potentials or the addition of a metal additive (both separately and simultaneously). Soot forma-

tion tendencies are explained [24] by analyzing the probable effects on particulate agglomeration processes of the relative concentrations of neutral and positively charged particles; and how these processes may be affected by varying electron concentrations in the region of interest.

Smoke production could also be affected by chemical additives that affect some of the preceding processes in the gas phase. For example, inert additives may change the temperature and composition gradients in the flame due to their heat capacity and their effects on diffusion and local concentrations. Such changes can affect pyrolysis, condensation, and reaction rates, which depend on the temperature and local concentrations of the smoke forming species. Also, differences in smoke production among different materials may be due to these flame temperature and concentration effects. Heterogeneous condensation can occur when seeds are available in the flame region. Such seeds can presumably be provided by breakup of the polymeric material or by release of additive particulates to the gas phase. Additives may also affect the nucleation and smoke formation rates by interacting with condensable species, thus leading to condensation at partial pressures much lower than those required for the condensation of the surrounding pure vapors [25]. This phenomenon is known as heteromolecular nucleation and may also occur between species generated in the pyrolysis (preflame) region.

Finally, additives that modify the thermal decomposition characteristics in the polymer solid phase will affect the production of smoke according to how the degradation rate of the material is affected. For example, the presence of an additive that will decompose endothermically could deprive the polymer of energy for decomposition and thereby reduce the degradation rate. Local fuel/oxidizer ratios would then decrease and smoke formation presumably reduced. Also, Ramohalli [26] has shown that the application of coated fillers to modify thermal conductivity can result in reduced polymer degradation rates and less smoke production.

Nonflaming Combustion

The research on the mechanisms of smoke formation already discussed has been primarily concerned with the formation of black carbonaceous soot. Although these mechanisms are applicable to situations in which flames are present, they are probably not applicable to smoldering combustion situations in which the generated smoke appears as a complex mixture of liquid and/or solid organic materials [27-30]. In this case the generated smoke may consist of liquid drops generated by the condensation of high molecular weight compounds present in the pyrolysis products of the polymer. When this occurs, the dehydrogenation step that is most likely present in the soot formation process is probably absent or of negligible importance. Also, the absence of a flame in a smoldering situation results in a thermal environment that is cooler than the environment in a flaming situation, resulting in the absence of high temperature gas-phase pyrolysis reactions that lead to carbon formation and its subsequent growth into soot particles. In addition, the solid (but not carbonaceous) fraction that is found in some nonflaming smokes may be the result of large macromolecules or fragments of the substrate polymer being emitted directly from the surface of the decomposing material [31]. These routes of particulate formation in nonflaming combustion are also indicated in Fig. 2.

TRENDS IN MEASURED SMOKE CHARACTERISTICS

With reference to the proposed smoke formation mechanisms previously discussed, measured smoke characteristics are reviewed in this section. These data, which include both previously published [27-30, 32-36] and new results, have been taken over a wide range of burning conditions for several classes of natural and synthetic materials as part of a smoke research program carried out at the Georgia Institute of Technology. The dependence of the data on a selected number of environmental and material variables is considered and the results are analyzed in light of the proposed smoke formation mechanisms, which are reviewed in the previous section, thus leading to further insight into the detailed aspects of smoke generation. The smoke properties have been measured in the ventilated Combustion Products Test Chamber; where material samples are combusted under well-controlled

ambient conditions and the smoke properties measured in the final combustion products as they are exhausted through a sampling and optical analysis section. Measured properties include: fraction (Γ) of sample weight loss converted to particulates, particle size distribution, mean particle diameters (D_{32}), particle mass concentration, smoke optical density (*OD*) (which gives a relative measure of particulate product concentration [34, 37]), and chemical composition. Details of the test methods and procedures used to obtain the results discussed here can be found in Refs. 27, 29, 32, and 37.

Effects of Heating Rate on Nonflaming Combustion

In nonflaming tests of different materials at room temperature it has been observed that the weight loss rate of tested samples increases with increases in the radiant heating rate [27, 29, 30, 32]. This generally results in greater mass concentrations of smoke particulates in the form of larger smoke particle diameters. Examples of these trends are presented for wood and a rigid polyurethane foam in Figs. 3 and 4 and Tables 1 and 2, respectively. Moreover, because these data are for nonflaming conditions, the measured smoke particulates, as discussed previously, are characterized by liquid (and possibly some solid) organic compounds, which are not predominatly carbonaceous or "sooty." Thus it is likely that the larger particles that accompany high particle concentration levels are the result of either the following mechanisms: (1) increased nucleation rate of condensable species followed by enhanced agglomeration due to high particle concentrations or (2) accelerated surface growth by condensation. Identification of the precise controlling mechanism requires, however, further elucidation. In this regard it should be noted that for most materials tested, the *overall* smoking propensity (Γ) of a sample (or fraction of sample weight loss converted to particulates) also tends to increase with increasing heating rate (nonflaming) for the conditions and heating rates studied in this program.

Differences Between Flaming and Nonflaming Combustion

Results of flaming tests of different materials in 25°C ventilation air must be divided into charring and noncharring categories when compared with nonflaming results. First, tests of charring materials (e.g., wood, urethane foams, and charring PVCs), which were conducted under both flaming and nonflaming conditions with *comparable weight loss rates,* show that the particulate fractions are lower and particle sizes are smaller under flaming conditions than under nonflaming conditions [28–30]. This can be attributed to the fact that smoke formation processes in flaming combustion follow a different route of particle formation than in the nonflaming situation as discussed earlier in this paper (Fig. 2). More specifically, assuming that the properties of the initial pyrolysis products of the polymer are similar in both situations, most of the pyrolysis products that follow the condensation route in the nonflaming situation undergo further reactions in the flaming case, resulting in lower particulate (soot) concentrations. Such reactions would include further pyrolytic decomposition, greatly enhanced dehydrogenation, and possible "burnout" in the flame region. Typical results that illustrate these observations are presented in Fig. 5 and Table 3 for wood and in Fig. 6 and Table 4, for a rigid PVC.

In the second category of materials it was found that several common polymers that do not char generate larger particles in the flaming case than the previously mentioned charring materials. The data presented in Table 5 show that for these materials the characteristic particle diameters (D_{32}) are greater than one micron, and thus are more comparable with particle diameters measured under nonflaming conditions. On the other hand, the smoking parameter Γ is consistently lower under flaming conditions as before. These trends may be explained by noting that the burning rates of the polymers listed in Table 5 are much higher under flaming conditions than in the compared nonflaming conditions. Also, the burning rates were generally higher than for the charring materials studied. Accordingly, the rapid generation of pyrolysis products leads to a more fuel-rich flame region during the burning of these materials. The greater concentrations of species in the pyrolysis zone (Figure 1) thus generate more particulates that quickly grow (agglomerate) to the observed large diameters; although subsequent reaction or "burnout" results in the still low mass fractions

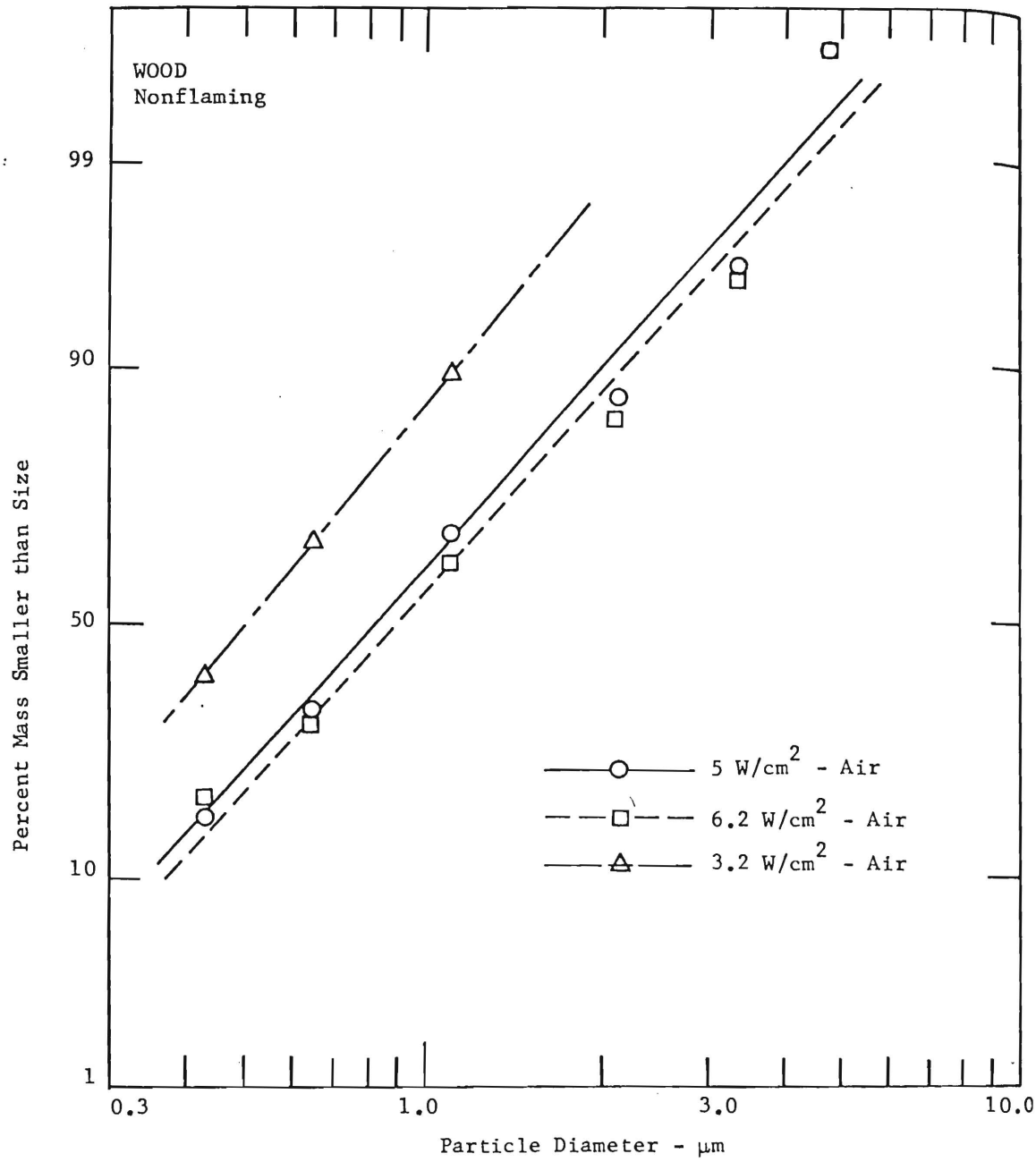

Fig. 3. Particle size distributions for wood smoke generated under nonflaming conditions.

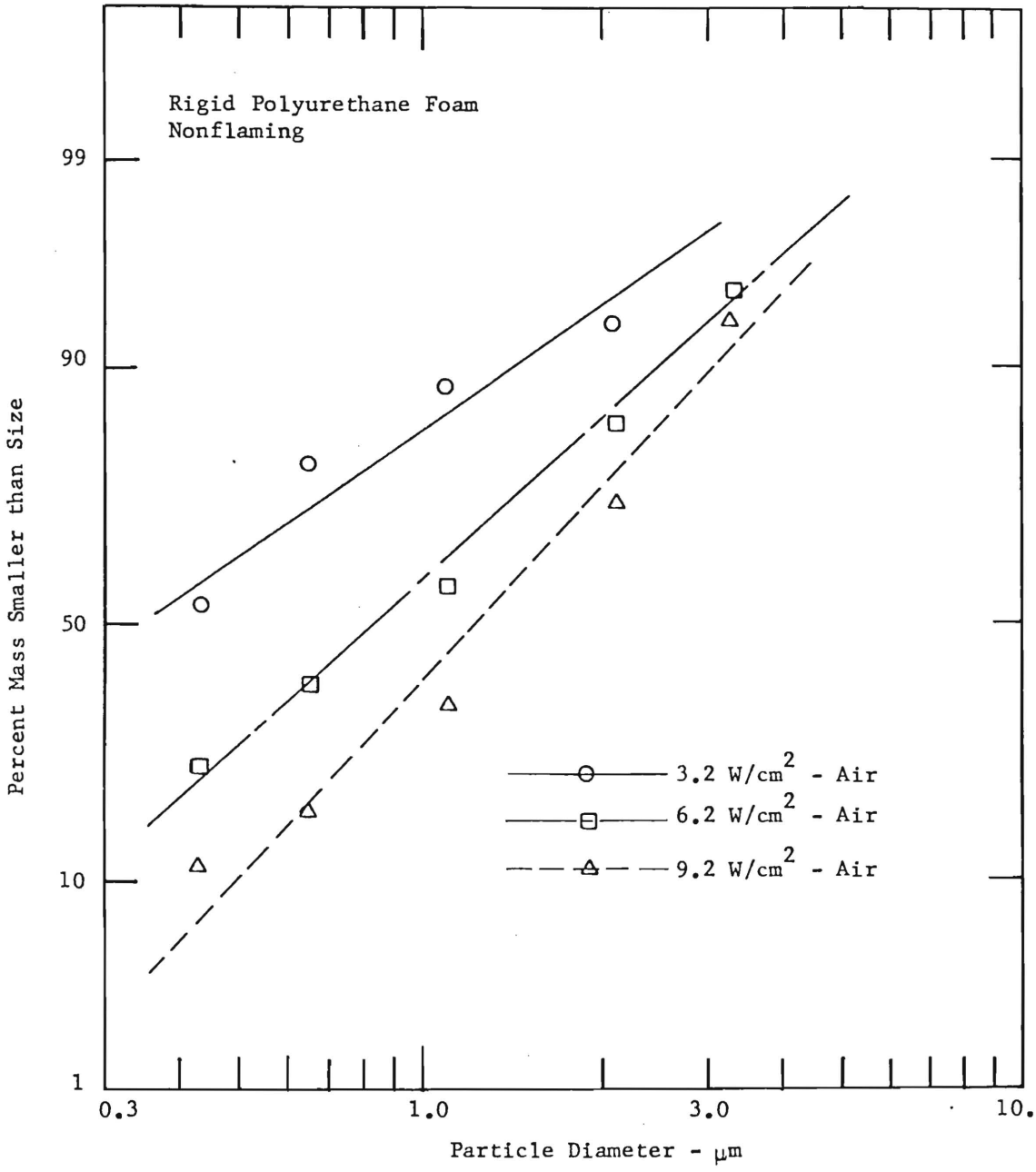

Fig. 4. Particle size distributions for rigid urethane foam smoke generated under non-flaming conditions.

TABLE 1

Wood Smoke Properties at Different Radiant Heating Rates–Nonflaming Conditions

	Γ	D_{MMD} μm	*OD* (Blue) m^{-1}	*OD* (Red) m^{-1}	D_{32} μm
Douglas fir nonflaming (3.2 W/cm²) air	0.031	0.5	NM[a]	NM	NM
Douglas fir nonflaming (5 W/cm²) air	0.154	0.82	1.57	1.07	0.75
Douglas fir nonflaming (6.2 W/cm²) air	0.165	0.90	2.48	2.04	0.80

[a] NM = Not measured.

(Γ). These conclusions are supported further by noting that scanning electron microscope photographs of particles from flaming polystyrene show very long chainlike agglomerates. The fact that these particles are generated rapidly over a relatively brief period of time (when compared to characteristic nonflaming times) also explains the very high maximum optical densities observed in Table 5.

Effects of Ventilation Gas (Air) Temperature

High temperature tests [30, 34] of several materials under flaming and nonflaming conditions have produced the following opposite trends. In flaming tests, higher ventilation gas temperatures often result in greater smoke optical densities and larger smoke particles. In nonflaming tests, higher temperatures generally result in lower smoke densities and smaller particles. Measured data also show that the increased environmental temperature in the high temperature tests results in increased weight loss rates for both modes of combustion.

First, for flaming conditions the accelerated burning (weight loss) rates result in more rapid supply of fuel to the flame zone. This implies greater concentrations of fuel species in the flame region

TABLE 2

Rigid Polyurethane Foam Smoke Properties at Different Radiant Heating Rates–Nonflaming Conditions

	Γ	D_{MMD} μm	*OD* (Blue) m^{-1}	*OD* (Red) m^{-1}	D_{32} μm
Rigid urethane foam nonflaming (3.2 W/cm²) air	0.057	0.34	NM[a]	NM	NM
Rigid urethane foam nonflaming (6.2 W/cm²) air	0.082	0.83	0.22	0.20	0.96
Rigid urethane foam nonflaming (9.2 W/cm²) air	0.191	1.20	NM	NM	NM

[a] NM = Not measured.

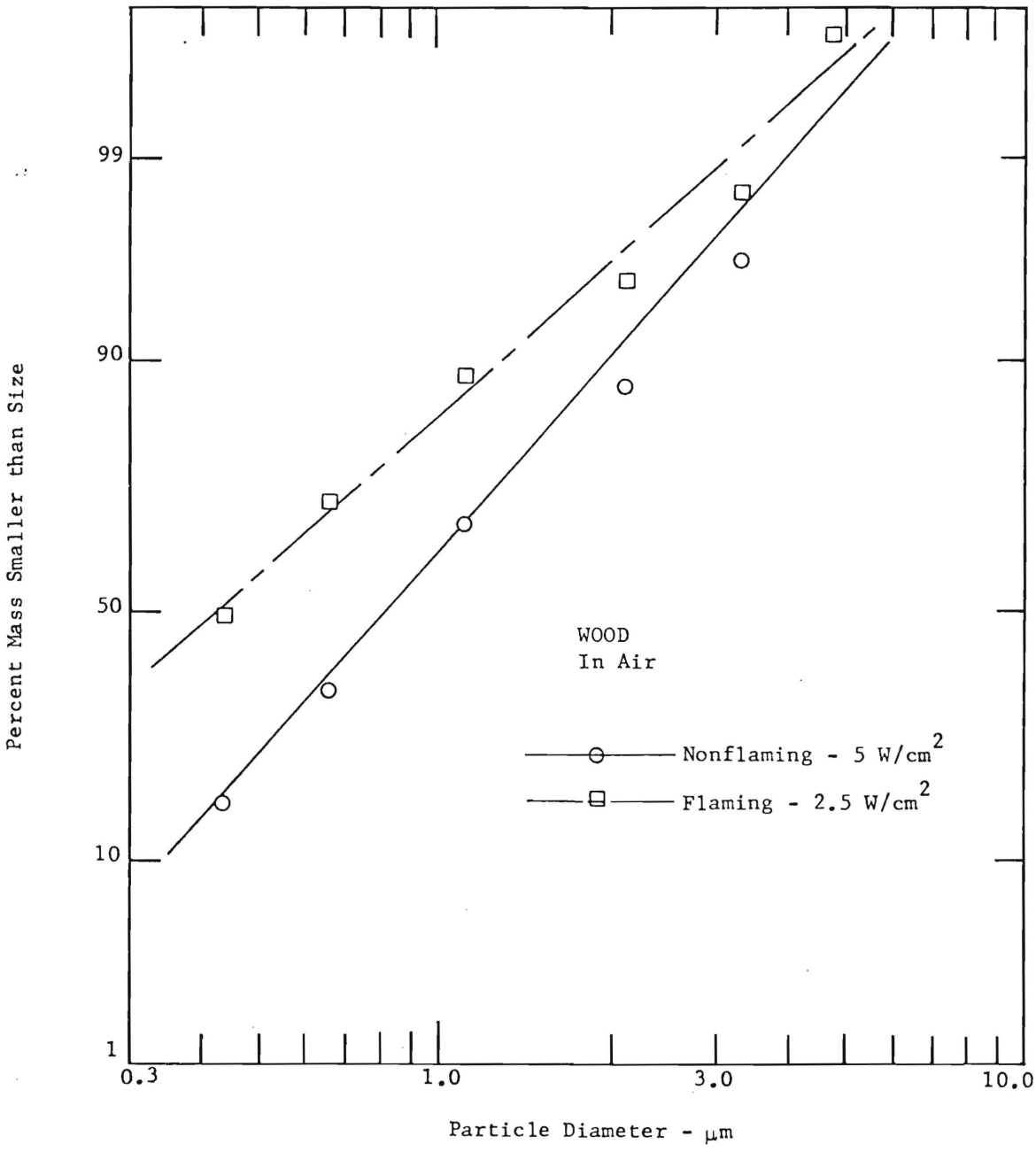

Fig. 5. Particle size distributions for wood smoke generated under flaming and non-flaming conditions.

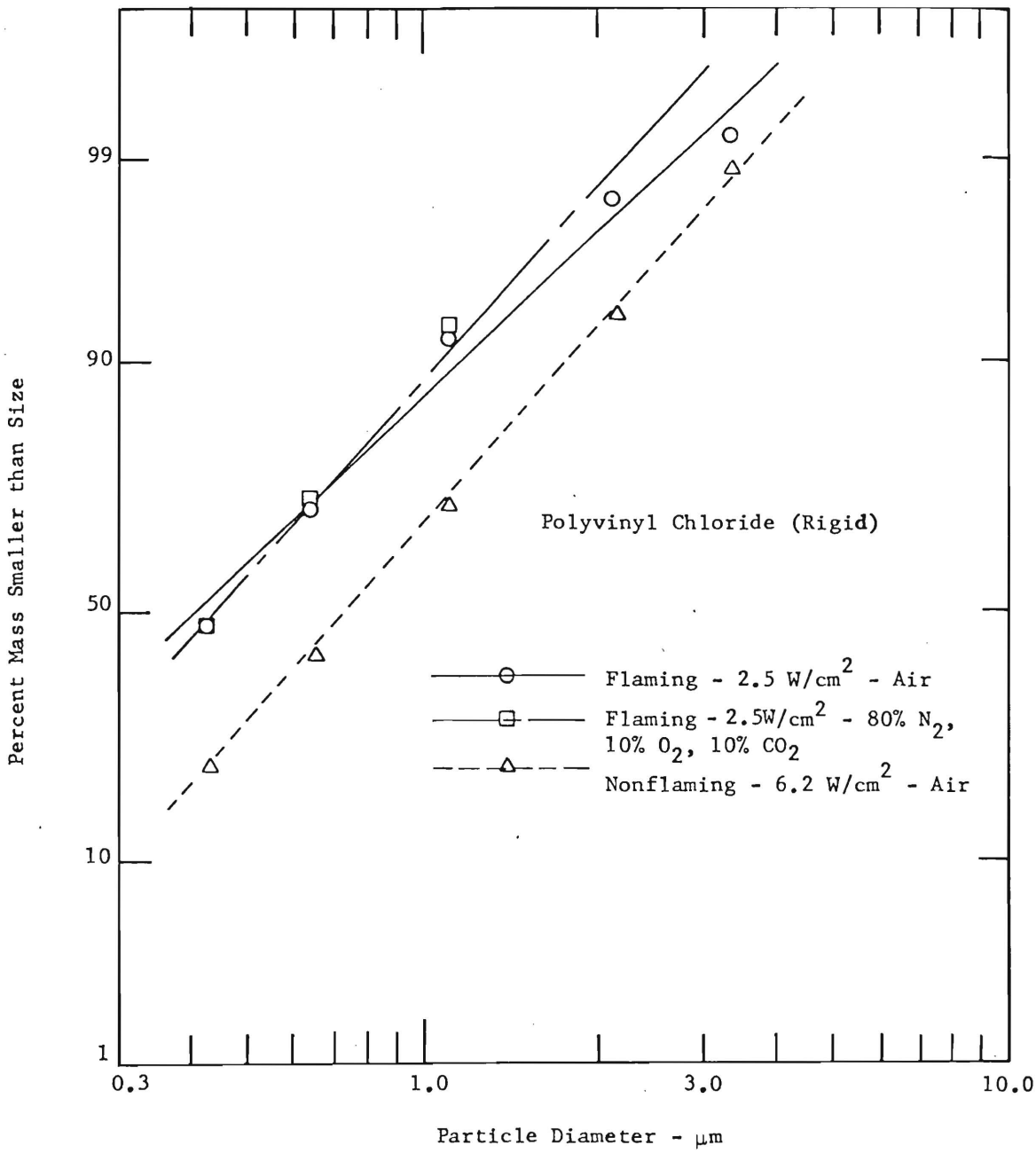

Fig. 6. Particle size distributions for PVC (rigid) smoke generated under flaming and nonflaming conditions.

TABLE 3

Wood Smoke Properties Compared for Flaming and Nonflaming Conditions

	Γ	D_{MMD} μm	*OD* (Blue) m^{-1}	*OD* (Red) m^{-1}	D_{32} μm
Douglas fir flaming (2.5 W/cm^2) air	0.025	0.43	0.61	0.32	0.52
Douglas fir flaming (5 W/cm^2) air	<0.01	NM[a]	NG[b]	NG	0.47
Douglas fir nonflaming (5 W/cm^2) air	0.154	0.82	1.57	1.07	0.75

[a] NM = Not measured.
[b] NG = Negligible values.

and thus similar conditions to those described in the previous paragraph for a group of noncharring materials (Table 5). However, as the environmental temperature increases, charring materials also begin to burn more rapidly, generating higher concentrations of fuel species that result in greater smoke densities (see Table 6 and Ref. 34). In the case of the materials in Table 5 that already burn very rapidly at room temperature, little effect is noted on smoke characteristics when environmental temperature increases as would be expected. Finally, because condensation processes are probably the dominating particulate formation mechanism in the nonflaming mode, the increased environmental temperatures will thus tend to hinder the condensation step and the associated particulate formation, as is confirmed by the experimental data in Table 7 (see also Ref. 34). Note, however, that in cases where mechanisms other than condensation are also responsible for the formation of particulates generated under nonflaming conditions, these trends may not hold. Hence when the generated nonflaming particulates are observed to be a complex mixture of liquid *and solid* compo-

TABLE 4

Rigid PVC Smoke Properties Compared for Flaming and Nonflaming Conditions

	Γ	D_{MMD} μm	*OD* (Blue) m^{-1}	*OD* (Red) m^{-1}	D_{32} μm
Rigid PVC flaming (2.5 W/cm^2) air	0.012	0.41	0.95	0.56	0.58
Rigid PVC flaming (2.5 W/cm^2) 80% N_2, 10% CO_2, 10% O_2	0.012	0.44	1.39	0.68	0.33
Rigid PVC nonflaming (6.2 W/cm^2) air	0.072	0.73	1.17	0.95	0.73

TABLE 5

Smoke Properties for Different Materials–Comparison of Flaming and Nonflaming Conditions

	Γ	*OD* (Blue) m^{-1}	*OD* (Red) m^{-1}	D_{32} μm
Polystyrene flaming (5 W/cm²) air	0.032	11.29	8.84	1.30
Polystyrene nonflaming (5 W/cm²) air	0.084	0.58	0.63	1.39
PVC flaming (5 W/cm²) air	0.026	2.55	2.02	1.05
PVC nonflaming (5 W/cm²) air	0.093	2.08	2.24	0.99
Polypropylene flaming (5 W/cm²) air	0.016	3.34	2.53	1.21
Polypropylene nonflaming (5 W/cm²) air	0.121	2.12	2.08	1.56
PMMA flaming (5 W/cm²) air	<0.01	1.43	1.05	1.18
PMMA nonflaming (5 W/cm²) air	<0.01	0.07	0.05	0.56

TABLE 6

Flexible Polyurethane Foam Smoke Properties at Different Environmental Temperatures–Flaming Conditions

	OD (Blue) m^{-1}	*OD* (Red) m^{-1}	D_{32} μm
Flexible polyurethane foam flaming (5 W/cm²) air (25°C)	0.26	0.21	0.66
Flexible polyurethane foam flaming (5 W/cm²) air (100°C)	0.34	0.23	0.91
Flexible polyurethane foam flaming (5 W/cm²) air (200°C)	0.56	0.41	0.96
Flexible polyurethane foam flaming (5 W/cm²) air (300°C)	0.94	0.71	1.10

TABLE 7

Flexible Polyurethane Foam Smoke Properties at Different Environmental Temperatures–Nonflaming Conditions

	OD (Blue) m^{-1}	*OD* (Red) m^{-1}	D_{32} μm
Flexible polyurethane foam nonflaming (5 W/cm²) air (25°C)	2.49	2.35	1.03
Flexible polyurethane foam nonflaming (5 W/cm²) air (100°C)	1.19	0.94	0.79
Flexible polyurethane foam nonflaming (5 W/cm²) air (200°C)	0.35	0.19	0.72
Flexible polyurethane foam nonflaming (5 W/cm²) air (300°C)	NG[a]	NG	0.69

[a] NG = Negligible Values.

nents [34], other processes that may be responsible for the solids must be considered (e.g., emission of polymer fragments from the polymer substrate).

Dependence upon Material Composition

Tests with a variety of polymeric materials have shown that the presence of additives affect the characteristics of the smoke generated under flaming and nonflaming conditions. For example, under nonflaming conditions, large quantities of fillers in PVCs reduce both the total (overall) quantities (per gram of initial sample mass) of smoke particulates generated and the resulting smoke particle sizes [30, 33]. The latter may be related to the high filler content, which substantially reduces the concentrations of condensable pyrolysis products, which are produced in the nonflaming case. It should be pointed out, however, that the *normalized* smoking tendency (Γ) is not necessarily reduced in these instances and, in fact, the effects of additives on Γ in nonflaming combustion exhibit no clearly definable trends for the materials tested in this program.

In flaming combustion the data in Table 8 show that the PVC sample (#4) containing Al_2O_3·

TABLE 8

Effect of Sample Composition on PVC Smoke Properties–Flaming Conditions

PVC
Flaming (5 W/cm^2)
Air

Composition of PVC Samples (PHR)							Smoke Properties		
	Resin	Stabilizer	Plasticizer	$CaCO_3$	$Al_2O_3 \cdot 3H_2O$	Lubricant	Γ	*OD* (Blue) m^{-1}	*OD* (Red) m^{-1}	D_{32} μm
1	100	5					0.025	2.55	2.02	1.06
2	100	5	45			1.5	0.028	7.75	6.33	1.08
3	100	5	45	50		1.5	0.023	3.66	2.84	1.11
4	100	5	45		50	1.5	0.010	2.16	1.70	1.04

$3H_2O$ generated significantly less smoke than three other PVC compositions. Moreover, less smoke was generated by sample #4 than was produced by the sample containing an equal amount (by weight) of $CaCO_3$ (#3), although both reduced the thermal decomposition rates of PVC samples by comparable amounts [33]. These results suggest that the aluminum compound, in addition to acting as a flame retardant, also tends to interrupt the path to soot formation by possibly intervening through mechanisms similar to those reviewed earlier in the paper for other metal compounds and flame configurations. Finally, the results shown in Table 9 for flexible polyurethane foams show that in room temperature flaming tests the effect of chlorinated and brominated flame retardants is to increase the smoking tendency of the material [30]. Although the possible mechanisms responsible for these results are not yet clear, it is interesting to note that when the same material compositions are tested at increased ventilation gas temperatures, the influence of the flame retardant on smoke formation becomes negligible at 100°C and above.

Further evidence exists in the results of the Georgia Tech program and others [38, 39] that

TABLE 9

Effect of Sample Composition on Flexible Polyurethane Foam Smoke Properties–Flaming Conditions

Flexible Polyurethane Foam
Flaming (5 W/cm^2)
Air

Flame Retardant Composition	Γ	Smoke Properties *OD* (Blue) m^{-1}	*OD* (Red) m^{-1}	D_{32} μm
1 Non flame retarded	<0.01	0.26	0.21	0.66
2 Chlorinated diphosphate ester–8%	0.015	2.37	1.32	0.47
3 Tris (2,3 dibromo propyl) phosphate–8%	0.035	2.26	1.14	0.45
4 Tetrakis (2-chloro ethyl) ethylene diphosphate–8%	0.010	1.30	0.62	0.53

TABLE 10

Smoke Properties Compared for Different Materials—Flaming Conditions

	Γ	*OD* (Blue) m^{-1}	*OD* (Red) m^{-1}	D_{32} μm
Polystyrene				
Flaming (5 W/cm²)	0.032	11.29	8.84	1.30
Air				
PVC				
Flaming (5 W/cm²)	0.026	2.55	2.02	1.05
air				
Polypropylene				
Flaming (5 W/cm²)	0.016	3.34	2.53	1.21
air				
Polyethylene				
Flaming (5 W/cm²)	0.012	2.70	2.05	1.27
Air				
PMMA				
Flaming (5 W/cm²)	<0.01	1.43	1.05	1.18
Air				
Douglas Fir (Wood)				
Flaming (5 W/cm²)	<0.01	0.06	0.03	0.47
Air				
Rigid Polyurethane Foam				
Flaming (2.5 W/cm²)	0.091	2.58	1.73	0.60
Air				
Flexible Polyurethane Foam				
Flaming (5 W/cm²)	<0.01	0.26	0.21	0.66
Air				
Rigid Trimer Foam				
Flaming (5 W/cm²)	0.060	2.15	1.63	1.10
Air				

the fundamental smoking characteristics also differ among different materials. When compared to three other olefin and vinyl polymers (PVC, polyethylene, and polypropylene), polystyrene is observed to generate the greatest quantities of smoke in flaming combustion (Table 10). The recent data of Pagni [39] for burning solid polymers verifies the very high polystyrene soot production from measurements made in the flame itself. A possible explanation involves the attached phenyl group present in polystyrene, which may act to increase the fraction of aromatics in the pyrolysis products. As indicated in Fig. 2, aromatics are believed to act as intermediates in the soot formation process. Also compared in Table 10 are the smoking characteristics for five other materials of different substrate structure: polymethyl methacrylate, Douglas fir (wood), flexible and rigid polyurethane foams, and a rigid trimer foam. These data indicate a wide range of smoking tendencies, where the rigid foam materials exhibit the highest smoking parameters (Γ). Clearly, these data indicate considerable differences in the composition of pyrolysis products that supply the flame, among materials with different substrate chemical structures.

Chemical Analysis of Smoke Particulates

The contents of the previous discussions emphasize the fact that there are no clear boundaries dividing the chemical and physical aspects of smoke formation. The transformation of one group of compounds (the polymer) through a variety of extremely complex reactions into another group of compounds (the smoke) involves a series of parallel competitive reactions (Fig. 2). The initial macromolecules of the polymer are thermally fragmented into smaller, highly reactive species, which often polymerize to yield carbonaceous soot, and also produce unreactive lower molecular weight compounds as by-products to this reaction chain. At all stages, physical and chemical processes interact.

Thus in order to understand mechanisms of smoke formation, it is essential to have accurate information concerning the chemical composition of the smoke. Ideally, one would obtain chemical analyses of the species present at various stages in the combustion process by sampling spatially resolved fractions of the smoke precursors. This could be accomplished by direct coupling of quartz microprobes in various zones of the combustion region (as in Fig. 1) with a mass spectrometer. Samples taken from regions below, within, and immediately above the "flame front" would be observed. However, such data are extremely difficult to obtain without disturbing the measurement regions and are often unreliable in nature due to the extreme reactivity of the species of interest (e.g., free radicals, reactive unsaturated species, etc.). As a consequence, in order to obtain reliable data on a rigorously comparative basis between various polymer samples only

stable species have been examined and all of the chemical analyses have been performed on the particulate smoke itself. A variety of polymers have been burned under different conditions of flaming and nonflaming combustion and the major classes of compounds have been separated using a scheme of the type shown in Fig. 7.

To date, the most complete data have been obtained for polynuclear aromatic hydrocarbons (PAH). These were selected as a group of interest because of their suggested intermediacy in smoke formation mechanisms for certain classes of polymers [9]. (Polyacetylenes are the other principal suggested intermediates [10].) A further reason for examining PAH is that data for PAH in the literature are fragmentary and comparison between different classes of polymers cannot be made from literature values. However, this type of comparison can lead to information regarding possible mechanisms.

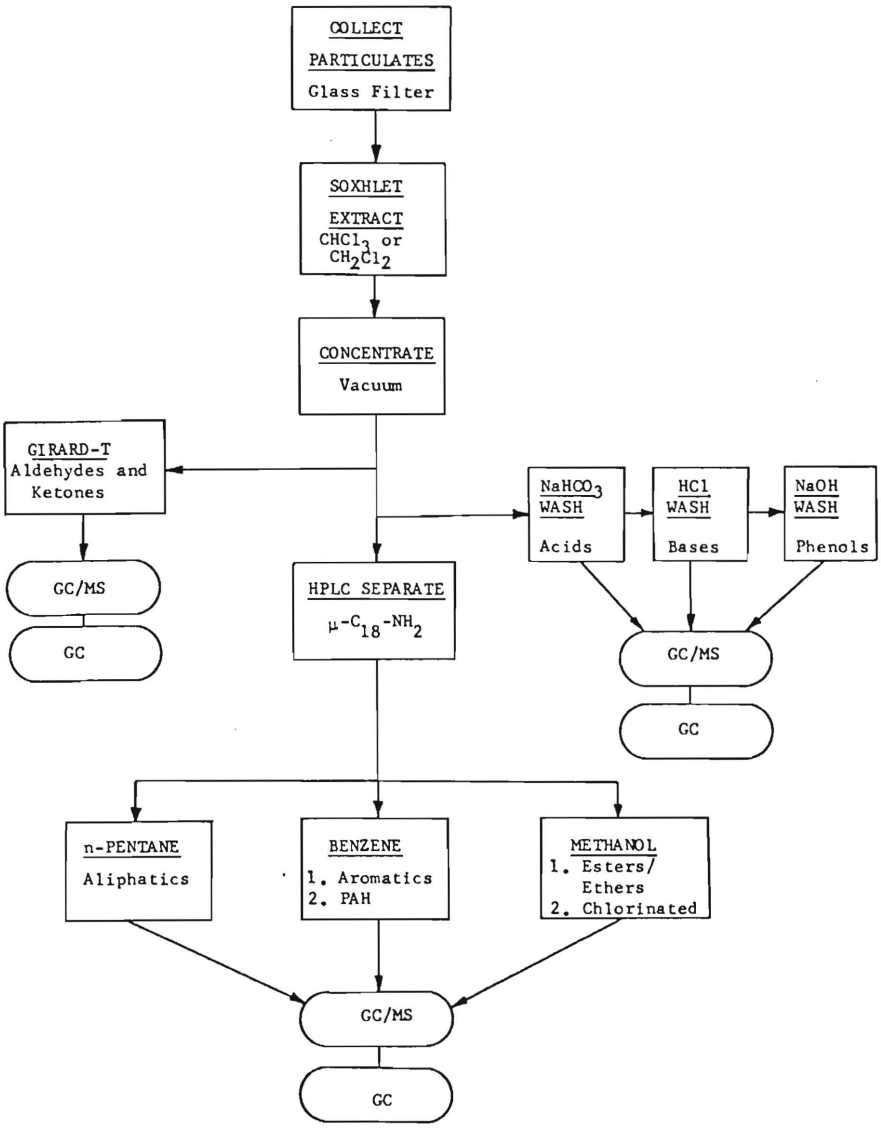

Fig. 7. Methodology for chemical analysis of smoke particulates.

The methodology for the analytical scheme has been described in the literature [35]. The samples examined were PVC, in a variety of formulations (see Table 8), polyurethene, polyethylene, polystyrene, polypropylene, and polymethyl methacrylate. The only samples yielding significant amounts of PAH were the PVC samples. In addition to the PVC samples shown in Table 8, two further samples, PVC-0 (pure PVC resin) and PVC-5 (PVC-2 + 5 PHR Sb_2O_3), were burned.

The data revealed some interesting trends. The yields of two-ring aromatics (mainly substituted naphthalene derivatives) were too low to be quantitatively measured for all samples burned. Presumably these were either two volatile to be retained on the particulate smoke or were too reactive to survive the high temperature pyrolysis and flame front zones. In the case of PAH with more than two rings, flaming and nonflaming modes of combustion were studied both at 5W/cm^2 radiant flux. For the pure resin (PVC-0), PAH were detected with molecular weights from 166 (fluorene) to 252 (perylene). Remarkably, PVC-0 gave comparable yields of PAH in both flaming and nonflaming modes (Table 11). The other formulations of PVC (PVC-1 to PVC-5) give similar yields of total PAH in the nonflaming mode, but greatly reduced yields (per gram of pure resin burned) in the flaming mode. This indicates that the additives either alter the predominant pathways in smoke formation or change the reaction kinetics along a given pathway to affect smoke formation dramatically. Complete analytical data on the remaining portions of the smoke from these samples will allow further examination of possible mechanisms responsible for the observed trends.

TABLE 11

PAH Yields in Smoke Particulates Generated from PVC Samples

Sample	Total PAH Yield (3-5 Membered Rings)[a]	
	Nonflaming[b]	Flaming[b]
PVC-0	183	149
PVC-1	205	40
PVC-2	155	39
PVC-3	203	18
PVC-4	177	2
PVC-5	225	12

[a] Units are μg PAH/g of pure resin.

[b] All heat fluxes are 5 W/cm^2, corresponding to an initial polymer surface temperature of approximately 470°C.

TABLE 12

Influence of Sample Composition on PAH Yield (Flaming Mode)–PVC Samples

Sample	Sample PAH Yield/PVC-0 PAH Yield[a]			
	Total	3-Ring	4-Ring	5-Ring
PVC-1	0.32	0.23	0.32	0.74
PVC-2	0.26	0.05	0.36	1.0
PVC-3	0.12	0.01	0.17	0.86
PVC-4	0.02	0.01	0.03	0.35
PVC-5	0.08	0.03	0.13	0.03

[a] Ratio of 1.0 indicates no difference between sample and PVC-0 PAH yield.

Significant differences in the yields of 3, 4, and 5-membered ring PAH were found for different PVC formulations (Table 12). When the PAH yields for the different ring numbers are normalized to the yields of pure PVC resin (PVC-0), it can be seen that all additives dramatically reduce 3-ring yields (except where stabilizer was added in PVC-1). Aluminum trihydrate ($Al_2O_3 \cdot 3H_2O$) has the most significant influence on the yield of 4-ring compounds but only Sb_2O_3 has any significant influence on yields of 5-ring compounds (approximately a 30-fold reduction). If the total PAH yields are considered, it can be seen that all additives reduce PAH yields in the flaming mode (compared to the resin) but that $Al_2O_3 \cdot 3H_2O$ and Sb_2O_3 have by far the strongest effect.

In conclusion, these chemical data indicate that smoke formation routes for PVC are different from the smoke formation routes followed when other materials studied were burned. This is suggested by the relatively high concentrations of PAH found in PVC smoke when compared to smoke particulates from all of the other materials. Also, PVC additives apparently alter smoke formation mechanisms such that the chemical composi-

tion of the particulates changes dramatically. In order to provide further insight into possible mechanisms, the detailed analysis of particulates generated by the other materials (than PVC) studied is also necessary.

SUMMARY

This paper represents new data and summarizes existing knowledge regarding the detailed properties of smoke particulates generated by burning materials under a variety of combustion conditions. Furthermore, it has been shown that many of the measured trends can be interpreted by considering postulated mechanisms of particulate formation in combustion systems. As such, this information may be useful in the planning of future smoke-related research and the development of polymeric materials with reduced smoke production capabilities.

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NOMENCLATURE

Γ	fraction of sample weight loss converted to airborne particulates
D_{MMD}	mass median particle diameter (μm)
D_{32}	volume-surface mean particle diameter (μm)
OD	smoke optical density (m^{-1})
PHR	parts per hundred (mass) units of resin

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