Some Unresolved Fire Chemistry Problems

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ABSTRACT

Six areas of fire science are selected for discussion which involve chemistry in an important way. The areas are: rate of pyrolysis of a solid combustible; generation of toxicants in a fire; fire luminosity (radiative output) and smoke generation; fire retardation of wood and synthetics; flammability of a hot gas layer in a compartment before flashover; and chemically active extinguishing agents. In each case, highlights of knowledge and remaining unsolved questions are touched upon, and 35 references to the recent literature are provided.

INTRODUCTION

This paper will describe six important areas of fire science in which chemistry is heavily involved. In each case, highlights of the present state of knowledge will be indicated, references will be provided to current work, and unresolved problems will be mentioned.

Because of coverage elsewhere in this symposium, fire toxicology and fire detection will not be discussed here, although generation of toxicants and of smoke in flames will be discussed. In addition to the foregoing, the review will include rate of pyrolysis, flammability of the hot gas layer in a burning compartment, and mechanisms of retardation and extinguishment.

RATE OF PYROLYSIS

For flaming fires involving solids the rate of burning is essentially the rate of pyrolytic gasification, referred to as the rate of pyrolysis. This rate is the net result of complex heterogeneous chemical kinetics, usually involving many reaction steps, some of which have high activation energies and are very temperature-dependent. These reaction steps have not yet been quantified completely for most combustible solids, and are not likely to be in the near future.

Fortunately, however, an approximate method may be used in many cases to describe the pyrolysis rate, which does not require knowledge of the chemical kinetics. It is based on four assumptions: (I) the overall pyrolytic gasification process is endothermic; (II) the overall heat of gasification is independent of the rate of gasification; (III) the overall activation energy of gasification is high enough so that the temperature at which gasification occurs is only weakly dependent on the rate of gasification; (IV) the burning is a "steady-state" process.

The approximate method is simply based on a heat balance. The rate of gasification is assumed to be the ratio of the net heat flux absorbed by the pyrolyzing region to the heat of gasification. This heat of gasification is considered to be a material property, and may be measured by applying a known heat flux to a weighed sample in an inert atmosphere. For a polymer, it would be equal to the sum of the heat needed to raise the polymer to the decomposition temperature, including the latent heat of any phase transitions, plus the heat of depolymerization to the monomer or oligomer vapors which form. For combustible substances, it is always substantially less than half the heat of combustion.

The validity of this concept for thermopolastic polymers is strongly supported by experiments of Tewarson and Pion (1) who find linear relations between burning rate and applied radiant heat flux for polystyrene, polyoxymethylene, polymethyl methacrylate, polyethylene, polypropylene, and flexible polyurethane foam, the slopes being consistent with independently measured heats of gasification. Vovelle et al. (2) have confirmed this result for polymethyl methacrylate. An extensive list of apparent heats of gasification for many substances has been published recently by Tewarson (3). The values are seen to range from one to four kilojoules per gram.

However, many combustible solids, including cellulosics and cross-linked synthetic polymers, pyrolyze with char formation. The char layer, which has low thermal conductivity, becomes progressively thicker as heating continues, so a "steady-state" approximation is an extremely crude way to describe the time-varying pyrolysis. A proper understanding of the burning of a charring substance will require substantial further research. Some complicating features will be discussed, in addition to the effect of the time-dependent thermal barrier just mentioned.

In general, many organic substances will release gases rapidly at 300–450°C, which would correspond to the temperature on the inner side of the char layer. The outer side of the char layer will be expected to be several hundred degrees hotter. This will have at least three likely consequences. Firstly, the pyrolysis gases passing through the pores of the char may undergo further chemical change, either depositing carbon on the char or removing carbon from the char. Secondly, the high surface temperature of the char and the corresponding high rate of radiant heat loss from the char to any cold ambient within the field of view will have a strong effect on the overall energy balance and may lead to extinguishment. Thirdly, when and if oxygen contacts the char surface, char oxidation (glowing combustion) will result, again with strong effect on the energy balance.

Another complication is structural, relating, in the case of wood, to the direction of the grain and consequent effect on the char. Even for homogeneous substrates, crack development in chars is common.

Yet other complications, chemical in nature, are the tendency of wood to pyrolyze by at least a two-stage mechanism (4) and the strong influence of even low concentrations of inorganic compounds to promote or inhibit char formation.

Various mathematical models of charring pyrolysis have been developed (5-7), but none attempts to treat all these factors.

GENERATION OF TOXICANTS

A computer model of a fire often requires an answer to the following

question. Given that a specified material is burning at a known rate, what is the rate of generation of toxicants of interest (carbon monoxide, hydrogen cyanide, hydrogen chloride, acrolein, dioxin, etc.)? This is not only of interest from a toxicological viewpoint but also because the energy released per unit mass consumed in a fire is affected by incomplete combustion.

Of the various toxicants, carbon monoxide is the only one which has been proven to cause large numbers of fire fatalities (on the basis of carboxyhemoglobin data from autopsies) and deserves the major attention.

For a fire burning under conditions where excess air is present, thermodynamic considerations would predict essentially no carbon monoxide. Experimentally, it is found that the CO/CO_2 molar ratio in products of well-ventilated pool fires may be as low as 0.001 to 0.002 for oxygenated combustibles such as methanol, polyoxymethylene, and wood, or as high as 0.1 or 0.2 for aromatic or highly chlorinated combustibles, which tend to burn incompletely, producing black smoke as well as CO, even when ample air is available. Table I shows CO/CO_2 ratios for a variety of materials burning with adequate ventilation and shows a 200-fold variation of this CO/CO_2 ratio.

TABLE 1. Molar CO/CO_2 ratio found in various combustion products
(Pool configuration, well ventilated)*

Substance	Molar CO/CO_2 Ratio
Methanol	0.001
Wood	0.001-0.003
Polyoxymethylene	0.002-0.004
N-heptane	0.004-0.02
Polymethyl methacrylate	0.007-0.02
Rigid polyurethane foam	0.03 -0.04
Coal	0.05
Styrene-butadiene rubber	0.07
Polystyrene	0.08
Polyvinyl chloride	0.17
Benzene	0.18
Polyethylene, 48% chlorinated	0.27

*Unpublished data from Factory Mutual Research Corporation. Results such as these are sensitive to experimental conditions.

Three mechanisms have been proposed for incompleteness of combustion in a well-ventilated diffusion flame: (I) rapid heat loss by radiation from highly luminous flames; (II) partial quenching by the action of steep velocity gradients as in turbulent flames; and (III) partial quenching by heat conduction to adjacent cold surfaces. The ranking of combustibles in Table 1 strongly suggests a correlation between CO/CO_2 ratio and flame luminosity or soot-forming tendency (characteristic of aromatic or halogenated combustibles). Indeed, correlations between CO and smoke particle formation have often been reported. However, more detailed understanding is needed.

While the foregoing relates to well-ventilated fires, a fire burning in a compartment will generally fall outside this category. The upper portion of

the compartment will become filled with an oxygen-deficient hot gas layer, and if the flames project into this layer the combustion chemistry is dramatically affected. Furthermore, some mixing occurs between the upper and the lower layer, which may affect combustion occurring entirely in the lower layer.

Experimental data on wood cribs and heptane pools burning with restricted ventilation give CO/CO_2 molar ratios of the order of unity in some cases, or two orders of magnitude higher than for full ventilation of the same combustibles. When CO/CO_2 ratios are high, high concentrations of a variety of organic molecules are also found (2), generally including toxicants.

The foregoing statements refer to <u>flaming</u> combustion. In a fire, it is likely that radiant heat from a burning region will cause pyrolysis in a not-yet-burning region, with copious CO production. Lee et al. (8) have pyrolyzed wood by laser heating and found that the pyrolysis gases consisted of 75% CO, 15% H_2, and 10% CH_4. Yoshizawa and Kubota (9) reported that the pyrolysis gases from cardboard subjected to 30 W/cm contained 70% CO, 20% CO_2 and 10% light hydrocarbons; they found no H_2. Cullis et al. (10) report CO yields from cellulose pyrolysis under helium varying with flow rate and temperature. Furthermore, <u>smoldering combustion</u> of porous cellulosic material or polyurethane foam will produce substantial CO; few quantitative data are available, presumably because smoldering is strongly affected by experimental conditions, especially air movement and impurities. However, it has been reported that cigarette smoke contains about 3 to 4 percent by weight of CO (11). Cullis et al. (12) have heated cellulose at heating rates of about $10°$/second, drawing air through, and found that the percentage of CO in the product gas increased and then decreased as the temperature increased with a maximum of about 20% CO at 450° C (the primary constituent being nitrogen). When 5% oxygen in nitrogen was used instead of air, the CO maximum was only 9% CO, under their conditions.

To summarize the experimental information on CO production in fires: radiative quenching appears responsible for CO yield from fully ventilated laminar flames; poorly ventilated flames produce as much CO as CO_2; pyrolysis and smoldering combustion of cellulosics produce CO as the dominant product.

Bilger and Starner (13) have tried a theoretical approach to the generation of CO in diffusion flames with a partial equilibrium model, which assumes equilibration of $CO + H_2O = CO_2 + H_2$ in the flame while burnout of CO is determined by three-body recombination of H, OH and O radicals in a partially equilibrated radical pool. Unfortunately, however, this model is in disagreement with predictions of complex numerical models by Miller and others (14, 15) which take into account the kinetics of more than 100 individual reaction steps as well as transport properties. These various models are tested by comparing with measured concentration profiles within a diffusion flame; they all predict that ultimately the CO is consumed. The next step would be to develop an even more complex model, perhaps including radiative quenching, which could predict the rate of release of unconsumed CO from the flame.

As for other toxicants, the chemical facts for HCl are somewhat simpler, as essentially all the chlorine in combustion products of chlorine-containing polymers is in the form of HCl. In the pyrolysis of polyvinyl chloride, the primary vapor products are HCl and benzene (16) with a carbon-rich char left behind.

Hydrogen cyanide, more than an order of magnitude more toxic than CO, would only be expected in combustion products of polymers containing CN groups, such as polyurethane and acrylonitrile polymers. Tewarson (17) has

found HCN/CO$_2$ ratios of the order of 0.01 and HCN/CO ratios of roughly 1/3 in combustion products of rigid polyurethane foam. Levin et al. (18) heated flexible polyurethane foam containing fire retardant to 800° C, with resulting flaming combustion; the HCN produced was 16% of the maximum possible yield, based on the 4.25% N content of the foam. On subsequent reheating of the resultant char, more HCN was produced. HCN yields would be expected to vary over the same wide range as CO yields, depending on ventilation conditions, flaming combustion vs. pyrolysis or smoldering, and flame luminosity (soot-forming tendency).

FIRE LUMINOSITY AND SMOKE GENERATION

The luminous character of a diffusion flame of a given combustible may be quantified in terms of radiative emission, or absorptivity per unit depth, or soot volume fraction, or smoke point (ASTM D 1322) if the combustible is liquid or gaseous. Soot (carbonaceous particles) formed from pyrolysis of fuel vapors in the flame is the primary source of this luminosity. The radiative heat transfer rate from the flame to the pyrolyzing solid fuel and to the environment is strongly influenced by this luminosity. Of course, the radiative heat transfer rate from a flame to a target is also strongly affected by any intervening cold smoke.

The soot which forms may or may not subsequently be consumed by oxidation; the unconsumed soot becomes smoke in the fire products. However, the fire products may also contain aerosol particulates resulting from condensation of pyrolysis vapors, as well as ash particles in some cases. The smoke is important in that it will be a source or sink for infrared radiation in the fire compartment. Furthermore, it will obscure vision, hindering escape. Again, it provides an important means for detecting a fire. The smoke may be measured by optical transmission or scattering, by collection followed by mass measurement, or by ionization with measurement of a current.

Since a flame which is highly luminous will have a low smoke point and have a strong tendency to emit unburned carbonaceous material, there is a close connection between flame luminosity and smoke generation. The chemistry of the combustible material is of crucial importance. For example, on comparing two materials, polyoxymethylene and polystyrene, the former burns without soot formation while the latter burns with a yellow flame rich in soot, producing smoke-laden products. The latter flame produces more than 8 times as much thermal radiation as the former flame, at the same total heat release rate. Many materials, such as cellulosics, will burn with flames intermediate between these extremes.

Much more quantitative data are available for radiative and smoke-forming properties of gaseous fuels than for solid fuels. Markstein (19) has shown that the radiative fraction of the heat-release rate of a turbulent jet flame correlates very closely with the laminar smoke-point, for six hydrocarbon fuels. The radiative fraction of these six fuels ranges from 21% for ethane to 42% for 1, 3-butadiene. The corresponding smoke-point lengths are 245 mm and 20 mm. Methane would have an even greater smoke-point length (not measurable in Markstein's apparatus) and an even lower radiative fraction.

If these various fuels are burned in "air" of adjusted O$_2$/N$_2$ ratio so that the calculated adiabatic flame temperature of all fuels was the same, then Markstein finds that the radiative fraction of heat release for the laminar flame at the smoke point appears to be independent of the nature of the fuel (∿24% for 2200 K and ∿37% for 2600 K). The significance of this is not yet

completely clear, but there is hope that current research will yield some basic understanding of this soot-forming process in diffusion flames (20).

The foregoing refers to gases and vaporized liquids. De Ris (21) has suggested that an apparatus could be built to pyrolyze a small solid sample in an inert or reducing atmosphere and then to continuously burn the evolved vapors in a laminar diffusion flame so as to obtain a smoke point. This would lead to characterization of solid materials in regard to radiative output of their flames. A presently mising link would then be filled so that a fundamental relation between material properties and flammability could be developed.

A group of 20 recent papers on soot formation and flame luminosity were presented in a symposium in 1984 (22) and provide a picture of the current state of knowledge. A survey paper on fire radiation was presented by de Ris (23) in 1978.

As for the smoke produced in either flaming or smoldering combustion, an enormous amount of literature exists. Seader and Einhorn (24) have prepared a review article with 81 references. One generalization, for _flaming_ combustion of nine different cellulosic and plastic materials, is that the optical density of the smoke (= $\log_{10} 1/T$, where T is the fraction transmitted) per meter of beam length is directly proportional to the particulate concentration (g/m^3), the proportionality constant being 3.3 m^2/g. For _nonflaming_ combustion/pyrolysis of 13 materials, the same relation is valid except that the proportionality constant is now 1.9 m^2/g and the scatter is somewhat greater. On considering this proportionality constant from the viewpoint of the theory of absorption and scattering of light by particles, it is seen that the underlying factors are particle diameter and complex refractive index. Apparently, the variation of these properties from one smoke to another is not sufficiently great to cause large changes in the proportionality mentioned above. This needs confirmation.

For combustion of any given material, the percentage yield of particulates varies widely with conditions of heat flux, ventilation, ambient oxygen concentration, and extent of cooling of the smoke. For wood, the particulate yield may be as low as 0.2%, while it may be as high as 20% for polyisoprene or polystyrene. The factors influencing CO yield previously discussed will also influence smoke yield. However, the ratio of optical density to CO concentration is not absolutely constant from material to material, but varies by about a factor of three in the most extreme cases.

FIRE RETARDATION

Wood is the most extensively studied organic solid of interest to fire researchers. The literature is enormous. To summarize the highlights: on being heated in an inert atmosphere, wood pyrolyzes mainly in the range 250–400.°C, leaving behind a char comprising 20 or 30% of the original weight. The volatile products include simple gases (H_2O, CO, CO_2) and a wide variety of organic molecules, including tars. The tar to char ratio is strongly affected by heating rate and by chemical additives. An additive which decreases the tar to char ratio is a fire retardant. It has been known for hundreds of years that inorganic salts are effective as fire retardants when impregnated into wood. The effective salts have ammonium, sodium, potassium, or zinc as cations and phosphate, borate, silicate, sulphate, or sulphamate as anions. The chemical mechanisms of retardation are not fully understood. Wood itself has two major chemical constituents, cellulose and lignin, which are quite different from one another in pyrolysis characteristics. The retardants are

intended to: (1) reduce ignitability and flame spread; (2) reduce heat generation; (3) reduce smoke generation; (4) prevent afterglow. The practical problems in the use of the various retardants are: (1) leachability by water; (2) reduction of strength of structural wood; and (3) interference with gluing or painting.

Organic retardants have been developed more recently in the attempt to overcome the foregoing problems with inorganic salts. Organic compounds with retardancy power may contain phosphorous, boron, halogens, or nitrogen (generally as amines). Hundreds of such compounds have been reported in the literature (25-27).

Instead of impregnating wood, it may be protected with fire-retardant paints, including intumescent paints. Again, a large literature exists. The coating may be effective by virtue of providing a barrier, by releasing a suppressing gas, by affecting the char process, by providing a heat sink (such as aluminum hydroxide), or by any combination of these. These fire-retardant coatings often have special difficulty in surviving in wet or very humid environments.

Synthetic polymers as well as wood may be fire-retarded (27). One approach is to incorporate halogens, phosphorus, boron, silicon, or sulphur into the polymer structure. Alternately, additives may be introduced, of a great variety of types. One important class of retardants is a synergistic combination of an antimony compound and a chlorine compound. Apparently a volatile compound, either $SbCl_3$ or $SbOCl$, forms and inhibits the gaseous flame. An unfortunate by-product of halogenated retardant systems is the corrosive effect of the acid produced on any nearby sensitive equipment.

A major problem in evaluating fire retardants is the choice of the fire test method(s) employed. Small-scale tests are characterized by low levels of radiative heat flux impinging on the sample (unless a radiant heater is included in the test procedure). Retardants often appear effective in small-scale tests while they may be less effective in tests involving high radiative heat flux, such as would be present in a compartment approaching flashover.

FLAMMABILITY OF HOT GAS LAYER

In a compartment fire before flashover, there is a horizontal interface with air below and partly consumed combustion products above. A local fire plume is pumping combustion products, unburned combustibles and air into this oxygen-deficient upper region, but flames are not propagating along the horizontal interface.

In actual fires it is occasionally observed that, at a particular moment, a reddish flame initiated at the fire plume spreads across the compartment along the interface between the hot ceiling layer and the air below. The immediate consequences are a large increase in radiative heat flux to not-yet-ignited objects in the compartment, and a change in temperature and composition of gases leaving the compartment.

Presumably, the explanation of the phenomenon is that the hot layer underwent a transition from nonflammable to flammable, because of a change of temperature or composition or both. There was very little knowledge on how a relevant criterion for flammability could be specified, prior to a recent study by Beyler (28).

Beyler reviewed correlations for flammability limits of mixtures of both premixed and diffusion flames (Le Chatelier's rule, Burgess and Wheeler's constancy of adiabatic flame temperature at the limit, and Simmons and Wolfhard's study of diluents producing extinguishment of diffusion flames). Based on these, he proposed an "ignition index" requiring knowledge of the total hydrocarbons, the CO, and the hydrogen in the hot layer, and the hot-layer temperature. The value of the index increases with increasing concentrations of the combustible species. When the index reaches unity, combustion should be able to propagate along the interface, if an ignition source is available.

Beyler compared his predictions with experimental data obtained with a variety of liquid-fuel pool fires under a one-meter-diameter hood. He obtained very encouraging agreement. An extension of the model predicted that the critical condition would be reached when the fire size and location were such that the actual air entrained by the plume below the layer was less than a calculable fraction of the stoichiometric air required for the fuel supply.

Beyler did not treat the soot and aerosols present in the hot layer; furthermore the effect of reactant temperature was not explored. Follow-on studies of these effects as well as possible effects of volatile fire retardants should be investigated in future researches. The applicability of the correlation to solid combustibles should be investigated.

CHEMICALLY ACTIVE EXTINGUISHING AGENTS

Many of the most common extinguishing agents, including water, aqueous foams, steam, carbon dioxide, nitrogen, powdered limestone, and sand, are well established to act by physical mechanisms, either serving as heat sinks or providing a barrier between combustible and air. However, two classes of extinguishing agents, namely completely halogenated carbon compounds, such as $CF_3 Br$, $C_2F_4Br_2$, or $CF_2 C\ell Br$, and chemical powders, such as ammonium or alkali metal salts or acid salts of carbonates, phosphates, or halides, are believed to act at least partially by chemical mechanisms. Research to delineate these mechanisms has been conducted sporadically over the past 40 years.

The action of compounds such as $CF_3 Br$ is now fairly well understood (29-31). The agent decomposes in the flame, with some absorption of energy, but, more important, the species HBr is formed. HBr is believed to remove chain-propagating radicals H and OH by the reactions $H + HBr \rightarrow H_2 + Br$ and $OH + HBr \rightarrow H_2O + Br$. Thus, the rate of the key chain-branching reactions in the flame, $H + O_2 \rightarrow OH + O$ (followed by $OH + H_2 \rightarrow H_2O + H$), would be reduced, making extinguishment easier. The radical removal process may also be enhanced by the regeneration of the chain-breaking species HBr via Br recombination to Br_2 followed by $H + Br_2 \rightarrow HBr + Br$. In addition to the HBr effect, an agent such as $CF_3 Br$ may also remove H atoms by formation of HF. Values for the rates of these various radical reactions are now known, to a reasonable accuracy, and the overall set of reactions may be modelled with a computer.

The increase in soot formation caused by the presence of halogens would increase the radiative heat loss from the flame and also encourage extinguishment. The actual extinguishment process depends in a complicated way on fluid-mechanical strain rates, often buoyancy-driven, and heat losses. However, the reduction in burning velocity of a fuel-air mixture, such as CH_4-air, when HBr or a compound decomposing to form HBr is added, may be measured as well as calculated from flame theory with good agreement. (It is known that addition of HF or $HC\ell$ is far less effective than addition of an equal volumetric percentage of HBr to a flame, thus providing further confirmation of a chemical

mechanism. Furthermore, CF_4 is much less effective than CF_3Br, suggesting that removal of H atoms by HF formation is not too important.)

The next step in more sophisticated understanding of extinguishment by bromine compounds might be to extend a computer-modeling approach, which Dixon-Lewis et al. (15) have applied to the strain-rate-induced extinction of a counterflow diffusion flame in the forward stagnation region of a porous cylinder, by including HBr in the kinetics. Further progress could also be made by quantifying the radiative heat loss stimulated by halogen addition to a hydrocarbon flame.

The chemical mechanisms by which powders extinguish flames are much more obscure. It is well established that effectiveness of a powder agent is correlated with specific surface area of the powder, but this leaves open the question of whether fine particles are more effective because they volatilize faster, or because there is more surface area for heterogeneous catalysis, or because of increased radiative heat loss, or simply because heat is absorbed more rapidly from the flame by a larger number of smaller particles passing through the flame. Very possibly, all of these effects are important.

Tests with a variety of chemically different powders of the same particle size show differences of effectiveness; the most effective powders ($NH_4H_2PO_4$, $KHCO_3$, and $KHCO_3$ plus $CO(NH_2)_2$) all decompose readily to form gases at elevated temperature. Clearly the endothermic decomposition will reduce the flame temperature and promote extinguishment, but the possibility that the volatile decomposition products enter into the flame chemistry cannot be excluded. It has been suggested that potassium salts are particularly effective agents, possibly because KOH vapor destroys H or OH atoms by $KOH + H \rightarrow H_2O + K$, or $KOH + OH \rightarrow H_2O + KO$, but Friedman and Levy (32) added potassium vapor to methane (1:16 molar ratio) and found no effect on flame strength of a diffusion flame.

Some recent researches on extinguishment by powders are those of Mitani and Niioka (33), Kim and Reuther (34) and Hertzberg et al. (35). The challenge for the future is to characterize the relative importance of thermal energy absorption, gas-phase or surface chemical kinetics, and radiative energy loss on the extinguishment process when powders are added to flames.

REFERENCES

1. Tewarson, A. and Pion, R. F.: Combustion and Flame, 26, 85-103, 1976.

2. Vovelle, C., Akrich, R., and Delfau, J. L.: Combustion Sci. and Tech, 36, 1-18, 1984.

3. Tewarson, A.: in Flame Retardant Polymeric Materials, Vol. 3, 92-153, Plenum Press, New York, 1982.

4. Vovelle, C., Mellottee, H., and Delbourgo, R.: Nineteenth Symposium (Int'l.) on Combustion, Pittsburgh, 1982, 797-805.

5. Kung, H. C.: Fifteenth Symposium (Int'l.) on Combustion, The Combustion Institute, Pittsburgh, 1975, 243-253.

6. Kansa, E. J., Perlee, H. E., and Chaiken, R. F.: Combustion and Flame, 29, 311-324, 1977.

7. Becker, H., Phillips, A. M., and Keller, J.: Combustion and Flame, 58, 163-189, 1984.

8. Lee, C. K., Chaiken, R. F., and Singer, J. M.: Sixteenth Symposium (Int'l.) on Combustion, The Combustion Institute, Pittsburgh, 1977, 1459-1470.

9. Yoshizawa, Y. and Kubota, H.: Nineteenth Symposium (Int'l.) on Combustion, The Combustion Institute, Pittsburgh, 1982, 787-793.

10. Cullis, C. F., Hirschler, M. M., Townsend, R. P., and Visanuvimol, V.: Combustion and Flame, 49, 235-248, 1983.

11. Summerfield, M., Ohlemiller, T. J., and Sandusky, H. W.: Combustion and Flame, 33, 268, 1978.

12. Cullis, C. F., Hirschler, M. M., Townsend, R. P., and Visanuvimol, V.: Combustion and Flame, 49, 249-254, 1983.

13. Bilger, R. W. and Starner, S. H.: Combustion and Flame, 51, 155-176, 1983.

14. Miller, J. A., Kee, R. J., Smooke, M. D., and Grcar, J. F., Sandia National Laboratories, Livermore, CA: Paper presented at Western States Section, The Combustion Institute, April 1984 (WSS/CI 84-20).

15. Dixon-Lewis, G., Fukutani, S., Miller, J. A., Peters, N., and Warnatz, J.: Twentieth Symposium (Int'l.) on Combustion, The Combustion Institute, Pittsburgh, 1984, 1893-1903.

16. Lum, R. M.: J. Appl. Polymer Sci, 20, 1635, 1976.

17. Tewarson, A. and Newman, J. S. This symposium.

18. Levin, B. C., Paabo, M., Fultz, M. L., Bailey, C., Yin, W., and Harris, S. E.: NBS IR 83-2791, November 1983.

19. Markstein, G. H.: Twentieth Symposium (Int'l.) on Combustion, The Combustion Institute, Pittsburgh, 1985, 1967-1973.

20. Kent, J. H. and Wagner, H. G.: Combustion Science and Technology, 41, 245-270, 1984.

21. De Ris, J.: Fire and Materials, in press, 1985.

22. Twentieth Symposium (Int'l.) on Combustion, The Combustion Institute, Pittsburgh, 1985.

23. De Ris, J.: Seventeenth Symposium (Int'l.) on Combustion, The Combustion Institute, Pittsburgh, 1979, 1003-1016.

24. Seader, J. D. and Einhorn, I. N: Sixteenth Symposium (Int'l.) on Combustion, The Combustion Institute, Pittsburgh, 1977, 1423-1445.

25. Lyons, J. W.: The Chemistry and Uses of Fire Retardants, Wiley-Interscience, New York, 1970.

26. Canadian Wood Council, Ottawa, Canada. Wood Fire Behaviour and Fire Retardant Treatment. Forest Products Laboratory, Ottawa, Canada, 1966.

27. Cf. Flame Retardant Polymeric Materials, Vol. 1, 1975, Vol. 2, 1978, Vol. 3, 1982, Plenum Press, New York.

28. Beyler, C. L.: Combustion Science and Technology, 39, 287-303, 1984.

29. Westbrook, C. K.: Nineteenth Symposium (Int'l.) on Combustion, The Combustion Institute, Pittsburgh, 1982, 127-141.

30. Safieh, H. Y., Vandooren, J., and Van Tiggelen, P. J.: Nineteenth Symposium (Int'l.) on Combustion, The Combustion Institute, Pittsburgh, 1982, 117-126.

31. Westbrook, C. K.: Combustion Science and Technology, 34, 201-225, 1983.

32. Friedman, R. and Levy, J. B: Combustion and Flame, 7, 195-201, 1963.

33. Mitani, T. and Niioka, T.: Combustion and Flame, 55, 13-21, 1984.

34. Kim, H. T. and Reuther, J. J.: Combustion and Flame, 57, 313-317, 1984.

35. Hertzberg, M., Cashdollar, K. L., Zlochower, L., and Ng, D. L.: Twentieth Symposium (Int'l.) on Combustion, The Combustion Institute, Pittsburgh, 1985, 1967-1973.