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PHENOMENOLOGICAL MODELS

OF

SOOT PROCESSES IN COMBUSTION SYSTEMS

by

Irvin Glassman

Department of Mechanical and Aerospace
Engineering Report 1450
AFOSR TR No. (applied for)

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The fuel sooting trends in pre-mixed and diffusion flames follow opposite
directions due to the different influences of temperature. In pre-mixed flames
as the temperature rises the rate of oxidative attack on the soot precursors
increases faster than the rate of precursor formation through pyrolysis. Thus
the higher the temperature the less is the tendency to soot. In the pre-mixed
flame all aliphatics form some acetylene which is the monoelement for precursor
formation and all fuels essentially follow the same nucleation route.
Aromatics oxidize partially through carboxyl radicals formed during attack on the

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ring and thus aromatic mixtures burn "richer" than corresponding aliphatic
mixtures of the same stoichiometry.   The dominant factors in diffusion flames
are the temperature and fuel structure.   Here the higher the temperature, the
greater is the rate of fuel pyrolysis and the propensity to soot.   Thus fuel
structures which during pyrolysis form strongly conjugated (polar) species most
readily soot.   A pure acetylenic polymerization route is too slow to predict
the early nucleation of soot particles and the presence of ions cannot predict
the difference of isomers to soot in diffusion flames.   Thus it has been
postulated that only conjugated species which have polar resonance structures
can under go the fast reactions necessary.

aliphatic

PHENOMENOLOGICAL MODELS OF SOOT PROCESSES IN COMBUSTION SYSTEMS

By

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I. Objective and Introduction

A major element of this effort is to review from a fundamental point of view the complex literature and recent surge of experimental results in the field of soot formation and destruction in flames. Many excellent comprehensive reviews of this field exist [Palmer and Cullis (1965), Homann and Wagner (1967), Homann (1970), Wagner (1978), Lawton and Weinberg (1969), Gaydon and Wolfhard (1979), Schalla and Hibbard (1959)]. Two other recent reviews [Bittner and Howard (1978) and Calcote (1978)] concentrate on the roles of aromatic fuels and ions in flames. No attempt will be made to repeat all that appears in these reviews. The initial purpose here was to address the major experimental observations with respect to the physical and chemical variables and then to formulate a model or models of the soot processes with the objective that these models would serve as guideleines for control of the soot phenomena in practical devices. Although determining the effect of water on soot formation was one of the initial motivations of the author's interest, what has developed has far greater consequences than just explaining the role of this additive.

II. Review

To date the general consensus with regard to the complexities in this field has been expressed by Bittner and Howard (1978) who in a brief statement in their article comment, "A fact that has troubled researchers looking for a single unifying mechanism to explain soot formation (although it is not likely that such a mechanism exists) has been ...". The fact that many investigators

simply do not believe that soot formation is a unique process for
all fuels burning in flames is succintly stated by Cullis et al.
(1973),..." that there is no single mechanism for the formation of
carbon, and it is probable that many different radicals are in-
volved in these reactions." From a global point of view, given
the essential C/H ratio differences of virgin soot particles and
the fact that there is a wide discrepancy in the tendency of soot
among various fuels in diffusion flames, in the strictest sense
one would have to agree with Cullis, et al. (1973). But these au-
thors and others were seeking an understanding of the detailed
and precise steps which constitute the entire soot formation pro-
cess without endeavoring to analyze whether there were controlling
mechanisms in the various types of flames. It is rather re-
markable that, as Palmer and Callis (1965) point out, that: "With
diffusion flames and premixed flames investigations have been
made both of the properties of the carbon formed and of the extent
of carbon formation under various conditions. In general, however,
the properties of the carbons formed in flames are remarkedly
little affected by the type of flame, the nature of the fuel being
burnt and the other conditions under which they are produced.
Any complete and comprehensive theory of carbon formation must, of
course, be able to account for this striking experimental funding."
That the properties of the carbons formed are the same may be due
to the fact that, as it is now known (Homann, (1970)), the C/H
ratio of virgin soot particles decreases as the particles pass
through the hot burned gases of a combustor. It is possible, of
course, that the similarities referred to by Palmer and Cullis (1965)
come about from the later pyrolytic dehydrogenation in the combus-
tion gases. Nevertheless, the spirit of their insight is probably
correct and the conceptual approach developed here follows this
spirit that nature was not meant to be infinitely complex, that
sufficiently new experimental evidence was at hand or could be
obtained, and that a general, comprehensive, phenomenological
model could be developed which could explain the soot formation pro-
cesses of various type flames using significantly different fuels.

The basis of this feeling was augmented by recent results in the Fuels Research Laboratory at Princeton on the pyrolysis and oxidation of aliphatic hydrocarbons (Dryer and Glassman, 1972; Glassman, et al., 1975), aromatic oxidation (Santoro and Glassman, 1979), and sooting characteristics of diffusion flames (Glassman, et.al, 1978). These new results and the objective of this effort have fostered new thinking with respect to soot precursor reactions and nucleation which permits more order to be put in this complex field.

One of the key elements which has intrigued investigators in the soot field is the rapidity with which soot particles form in flames (essentially of the order of 1 msec or less). A prevailing sentiment (Homann and Wagner, 1967) is that the precursors to soot are acetylenic in character, that these acetylenics polymerize and go through a cyclization process to form the virgin soot particle elements. This mechanism relies heavily on free radical reactions. However, as Calcote (1978) points out, there appears to be some difficulty in accounting for the rapid production of soot by reasonable free radical reaction rates (Tanzawa and Gardner, 1978), some problems in explaining the rearrangement of CH chains to produce cyclic aromatic hydrocarbons (Cullis, 1976) and some thermodynamic constraints on the growth of aromatics from radicals (Stein, 1978). In order to circumvent these possible limitations to free radical mechanisms for soot formation a school of thought led by Weinberg of Imperial College and joined by Calcote and Miller of Aerochem has been proposing that ions in flames lead to a series of much faster ion-neutral reactions that account for the rapid soot production under appropriate stoichiometric conditions. Homann (1968) questioned whether ions can be the complete story since he argues that the concentration of ions in the absence of a field is several orders of magnitude lower than the concentration of hydrocarbon radicals, and that, if ions were important, the number of particles in the flames of rich mixtures should decrease as well as the ion concentration, but that this is contrary to observed facts. There is some question whether Homann's second point is valid since recent results show

only a slight decay in ion concentration as one proceeds from
stoichiometric to rich mixtures. Nor, in this writer's point of
view does one have to accept the concept that all persisting
hydrocarbon radicals be involved in the nucleation step. They
could add to surface growth, be oxidized in later stages of the
flame, or suffer other fates not contributing to soot process.
Still, however, theories based on ion concentration cannot ex-
plain the tendency in diffusion flames of isomers to soot dif-
ferently.

III. Some New Insights

An essential element appears to have been overlooked by many
previous investigators and this element forms the basis of one of
the new considerations offered here. This new element character-
izes a role both for free radicals and ions. Sufficient importance
just has not been given to the fact that aromatics and multiple
bonded aliphatics are conjugated and have resonance structures.
What is the new significant item is that some of these resonance
structures are polar and thus can undergo rapid reaction with each
other, ions and other neutral molecules and radicals. Since soot
forms in high temperature zones, it is necessary that the precur-
sors be stable at high temperatures. Thus it is necessary that
they be strongly conjugated and stabilized by resonance. For
example, benzene has the following three polar resonance struc-
tures (Pauling, 1959)
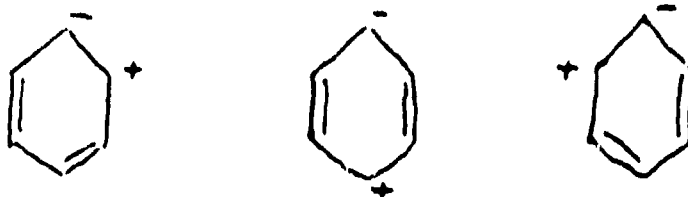
and others can be shown for toluene as well (Pauling, 1959).
Methyl acetylene has an alkene polar resonance structure (Pauling,
1940)
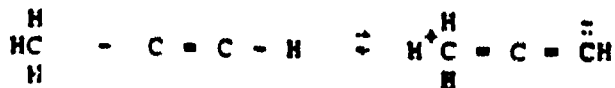
but acetylene has no such structure and is not conjugated. It is stable due to the strong C≡C bond. Because of the fact that acetylene is not conjugated, I do not believe it can be considered the primary precursor to soot formation. However, acetylene does quickly lead to butadiene which would now appear to be the essential precursor to soot. For one readily writes a polar resonance structure for the conjugated butadiene molecule

$$\begin{array}{c} H \\ H \end{array} C = C - C \begin{array}{c} H \\ H \end{array} \rightleftharpoons \begin{array}{c} H \\ H \end{array} \overset{+}{C} - C = C - \overset{-}{C} \begin{array}{c} H \\ H \end{array}$$

as well as neutral structures. Butadiene has less resonance energy than benzene and would not be considered as strongly resonance stabilized. However when a H^+ is added to butadiene, the situation changes. The resulting carbonium ion has almost the equivalent structure, and its structure is the hybrid of the two.

$$H_2C = CH - CH = CH_2 + H^+ \longrightarrow CH_3 - \overset{+}{CH} - CH = CH_2$$
$$\updownarrow \qquad +$$
$$H_3 - CH = CH = CH_2$$
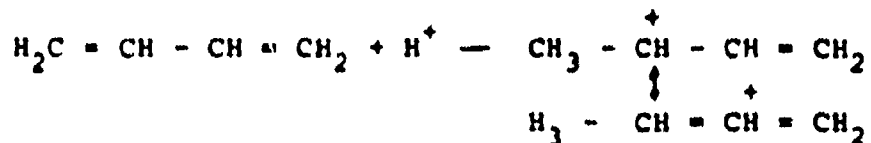
Many reactions of butadiene also proceed through intermediates that are strongly resonance stabilized. Thus, even though butadiene itself does not show major conjugation such effects may be important in its reactions. In the above case, for instance, the formation of a strongly stabilized (by conjugation) carbonium ion from a weakly stabilized diene makes the reaction favorable (Breslow, 1965).

The situation is similar for diacetylene

$$HC \equiv C - C \equiv CH \rightleftharpoons H\overset{..}{\overset{-}{C}} = C = C = \overset{+}{CH}$$

Thus, this new consideration appears to explain the greater propensity for butadiene and diacetylene to soot in diffusion flames relative to acetylene, and even the aromatics (Schalla, et al.,

1954, see Figure 1. Indeed mechanistically, one could evolve an aromatic soot structure from a butadiene derivative then from a benzene derivative as follows:
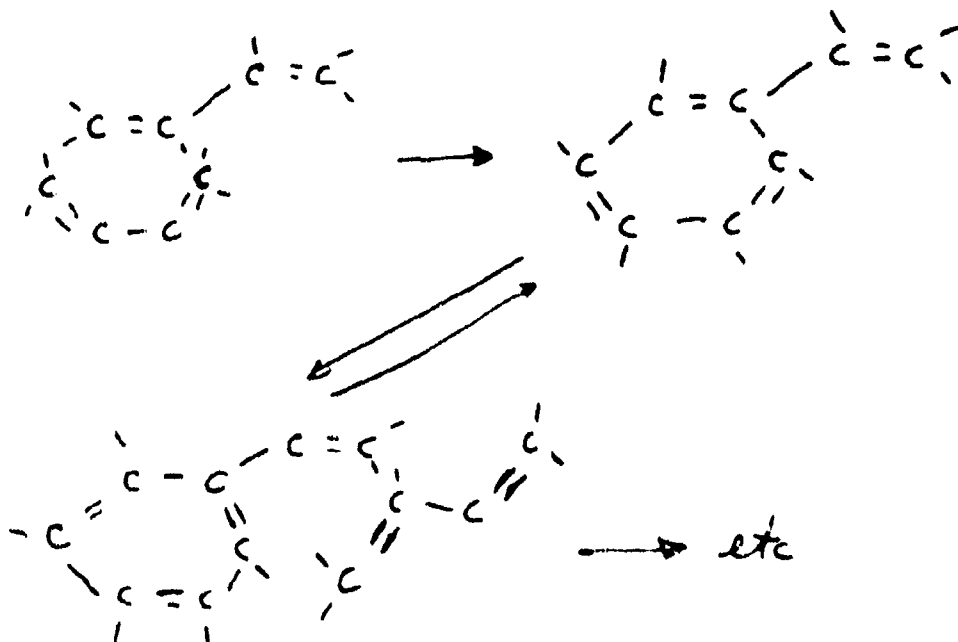
Thus not only would styrene and ethyl benzene soot more readily than benzene because they form phenyl and other radicals more readily as do all alkylated aromatics, but also from the strongly configurated (polar) structures which develop from these fuels in their pyrolysis. They should soot more readily than benzene in diffusion flames, and they do (Schalla, et al, 1954, see Figure 1).

It is, of course, worth pointing out that any compound
which is a chain of alternate single and double (or triple) bonds,
there could be conjugation (Rudd, 1973) which leads to the ef-
fects described and the thermal stability and reactivity required
for soot formation. Thus compounds such as diacetylene and vinyl
acetylene take on the same significance as butadiene. Indeed
these features exist in the qualitiative model already put forth
by Chanraborty and Long (1968), who drew upon the work of Thomas
(1962). This author now realizes that much of the phenomenological
considerations stated here are similar to those proposed by Thomas
in 1962. An important difference is that the conjugated struc-
tures are noted to be polar in nature so that not only can they
undergo fast Diels-Alder type reactions, but perhaps rapid simple
addition   reactions as well. The ability of butadiene to form
carbonium ions is another new feature.

Thus it is proposed that those fuels which because of their
structure have during oxidative and thermal pyrolysis the greatest
ability to form multi-bonded compounds or radicals which have po-
lar resonance structures (that is, take the character described for
butadiene and benzene) will have the greatest tendency to soot.
This concept applies to the nucleation phase of the soot formation
process and thus is similar for both pre-mixed and diffusion flames.
As will be explained later based on Princeton pyrolysis and oxi-
dative kinetics work (Dryer and Glassman, 1978), the effect and
particularly the role of butadiene, is most evident in distin-
guishing the features of sooting tendencies in diffusion flames,
particularly with the aliphatics. It is evident that the aroma-
tics have the pre-requisite (polar) features. The pyrolysis and
oxidative work mentioned argues that in pre-mixed flames all
fuels proceed with acetylene formation initially (and then a con-
jugated larger molecule, usually butadiene).

Explicitly the features of the previous Princeton work that
contribute to the overall model are first, that all paraffins dur-
ing their oxidation undergo an initial (oxidative) pyrolysis step
and are converted to a few simple olefins, which then undergo oxi-
dation to CO, or for very rich mixtures other possible steps such

as those leading to soot formation (Glassman, et al., 1975; Dryer
and Glassman, 1978; Glassman, 1979). Indeed in only slightly rich
ethane oxidation experiments, identifiable quantities of acetylene
are found. Further the explicit olefins which form can be pre-
dicted from the parent paraffin (Dryer and Glassman, 1978); this
element is of particular importance in predicting the different ten-
dencies of isomers to soot in diffusion flames. The second fea-
ture is the emphasis that has been given (Santoro and Glassman, 1979)
to the fact that benzene in undergoing oxidation in pre-mixed flames
proceeds through a low temperature ring fracture caused by oxidation
attack, as put forth by (Norris and Taylor, 1956) and results in
the formation of CO_2 directly and two acetylene elements.

Elements of the above new features in relation to the soot
formation processes will be evident as the major literature is
reviewed, and the more unified phenomenological models developed.
The required experimental research to verify what may be con-
sidered speculative elements of the model will be mentioned and
form the basis for the current experimental research in this area
at Princeton.

IV. The Use Of Flames in Soot Analyses

The basic soot literature has developed in a somewhat his-
torical manner. The earliest work developed procedures for mea-
suring the tendency of fuels to soot and the effect of additives
on this tendency. As chemical analytical equipment developed
work began an actual soot mechanisms to explain the general flame
observations. Laser developments then permitted analysis of the
particle growth problem (D'Alessio, et al., 1975, 1977, Haynes,
et.al., 1978). The pioneering work of Weinberg on ion effects
has finally taken hold and many recent research efforts appear to
be concentrating on the role of ions. As mentioned earlier, these
efforts have been initiated in an attempt to elucidate further the
soot nucleation process, but they are also endeavoring to explain
the interesting effect of certain metals (particularly the alkaline
earths) in the general sooting tendency of a fuel.

The tendency of fuels to soot has been measured by various means: laminar pre-mixed flames (Street and Thomas, 1951), laminar diffusion flames (Minchin, 1931; Clark, et al., 1946), turbulent diffusion flames (Magnussen and Hyertager, 1975), and stirred reactors (Wright, 1969). In a general sense the amount of soot which will emerge from a particular combustion process is a result of a series of sequential steps: (thermal and /or oxidative) pyrolysis of the fuel, the development and polymerization of precursor elements, precursor attack, nucleation, particle growth and partial particle burn-up. Although these processes will be discussed in more detail later, it is important to note that in laminar flame processes, the spacial distribution of the steps are such that they are essentially non-interfering (non-overlapping). Thus from a given laminar experiment one is more likely to determine which step is affected by a change in a given physical or chemical variable. In turbulent diffusion flames and stirred reactors the processes are mixed and although these type of experiments probably approach more realistic practical conditions, it is more difficult to compare results of various investigators because of the lack of detailed turbulence and degree of mixing measurements. The fact that stirred reactors give the same tendency to soot trends as do pre-mixed laminar flames, but somewhat different quantitative trends, points to the dominance of a step or steps which are not affected by back mixing. Similarly the tendency of turbulence to reduce soot formation in diffusion flames can be seen from a most simplified phenomenological model. Thus most attention is given here to the results from laminar, premixed and diffusion flames and was the reason for the choice of laminar diffusion flame experimental work at Princeton (Glassman, et al., 1978).

In pre-mixed flames the tendency to soot is correlated with the equivalence ratio at which noticeable sooting just begins (luminous, continuum radiation). When the equivalence ratio is defined as the actual fuel-air ratio to the stoichiometric value, the smaller the equivalence ratio at the sooting point, the greater the tendency to soot (Street and Thomas, 1951). In diffusion flames the tendency to soot is measured by the height of the fuel jet (Mincher, 1931; Clark, et al., 1946) or the mass flow of fuel (Schalla,

et al, 1954) at which the luminous flame breaks open at its
apex and emits a stream. The smaller the flame height at the break-
through (called sooting height) or the smaller the mass flow rate
the greater the tendency to soot. Glassman, et al., (1979) have
shown that the flame height or the volumetric flow rate of the fuel
is the more fundamental parameter. However, they point out that
if all experiments are carried out at the same initial fuel temp-
erature, the mass flow rate allows more convenient, overall corre-
lations.

Comparison of the sooting tendency of the aliphatic fuels
shows a change of order for pre-mixed and diffusion flames.
This result indicates a difference in the controlling mechanism
for soot formation between the two flame processes. Yet later,
consideration will be given to a pre-mixed flame which becomes
richer and richer and how the transition to diffusion flame soot-
ing characterization comes about (obviously for experiments con-
ducted in an ambient atmosphere).

V. Models for Soot Formation in Pre-Mixed Flames

The review of the literature completed has motivated me to
paraphrase the detailed sequential and partially overlapping
steps which affect the overall soot formation process in pre-mixed
flames in the manner presented in Figure 2. In this initial dis-
cussion of the processes attention is directly exclusively to the
aliphatic hydrocarbons in pre-mixed flames.

As has been reported earlier, the paraffin fuels undergo
oxidative and thermal pyrolysis as their initial step in their
oxidative process (Step a). This pyrolysis leads to the formation
of olefins (primarily, ethylene, propylene, and butylene). At
this stage of the combustion process the pool of oxidative radi-
cals (OH and O) is building up and begins to attack the olefins
to form CO, H_2O, aldehyde, etc. (Step b). It has been established,
as well, that as the olefins are being oxidized some undergo fur-
ther pyrolysis and form acetylene which is considered here the
initial precursor to soot formation. Certainly a molecule of this
type must be the precursor because only multiple bonded or strongly

conjugated compounds would be stable in the thermal environment which would exist in any flame. Thus I propose that Milliken's (1962) original speculation that the fate of the acetylene formed determines the tendency to soot is correct. Addition to the acetylene must form the important butadiene molecule or radical mentioned earlier. Others, of course, much earlier had proposed acetylene as the precursor to soot, but it is in the context that Milliken considered acetylene as the precursor that is important. Fenimore, et al. (1967) has argued that other species could play a similar role to acetylene at this stage, although he does not specifically state which species - only unburned hydrocarbons. A specific experiment will be proposed later that could give qualitative verification as to whether acetylene (or a compound derived from it) plays a unique role. I choose to call acetylene the precursor monoelement.

Two things could happen to the precursor monoelements or their immediate next products (such as butadiene). They can be oxidized (Step d) and leave the soot formation chain or they can be pyrolyzed or react further and form radicals which can react with the precursor monoelement to form a still larger precursor element which also can be a radical (Step c). Milliken essentially states that it is the competition of these two steps that determines the generally tendency to soot in premixed flames. He argues that the main oxidative attack is by OH radicals and that although the acetylene pyrolysis reaction is one of high activation energy, raising the temperature raises the OH concentration substantially so that the lower activation energy oxidation reaction is favored. It is really not important conceptually whether the oxidative attack is on acetylene or any compound which may form immediately after acetylene. By using the formula proposed by Milliken for estimating of the OH radical concentration and a activation energy for the acetylene process of 39 kcal/mole, I calculated that for a given mixture ratio in which the temperature is changed from 1722°K to 1890°K, the oxidation rate increases twice as fast as the pyrolysis rate. Going to still higher temperatures increases the difference further. The OH concentration used is the equilibrium one, and of course, it is known that

the radicals reach super equilibrium values in the reaction zone. It must be recognized as well that Peeters and Mahnen (1973) have shown that O radical attack on olefins and acetylenes is much faster than OH attack; however we are dealing with quite rich conditions and partial equilibrium could hold as well so that the actual trends should follow the OH equilibrium trends calculated. Thus Milliken's postulate leads us to the important conclusion that the dominant factor in determining the tendency to soot is the reaction zone (flame) temperature. In reality the OH or O concentration is the other important parameter and this concentration would depend as well on the initial C/H ratio of the system.

Street and Thomas (1951) found that the tendency to soot based on the increasing fraction of stoichiometric air to eliminate soot formation was:

naphthalenes > benzenes > alcohols > paraffins > olefines > acetylenes

For the aliphatics the stoichiometric temperature increases from the alcohols to the paraffins to the olefins to the acetylenes (see Table 1) supporting the hypothesis above. In order to verify this concept experiments will be performed with the following fuel mixtures:

(1) C_2H_6

(2) $C_2H_4 + H_2 + a \, N_2$

(3) $C_2H_2 + 2H_2 + b \, N_2$

where a and b are so chosen that the mixtures give the same flame temperature as C_2H_6. Thus a condition is obtained where the initial fuel has the same C/H ratio and flame temperature. The three mixtures should have qualitatively the same tendency to soot, with perhaps the acetylene mixture being a little greater tendency since it starts with the precursor monoelement. It is quite evident as well that many equilibrium flame temperature and product gas composition calculations should be made over a complete range of fuel to oxygen ratio. Of particular interest, of course, is the flame temperature at the experimental C/O soot limit.

The flame temperatures of the aromatics are of the same order as the olefins, yet they have a far greater sooting propensity. There are essentially two possible reasons for this apparent anamalous result. The first is postulated to be related to the fact that the oxidation in flames proceeds through a low temperature step leading to dihydroxy benzenes which are unstable to further oxidation and react to form acetylene and maleic acid from hydroquinone (Norris and Taylor, 1956)
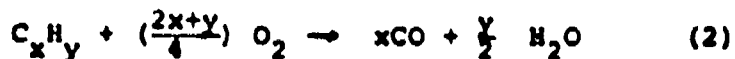

and to form acetylene and oxalic acid from pyrotatechol:
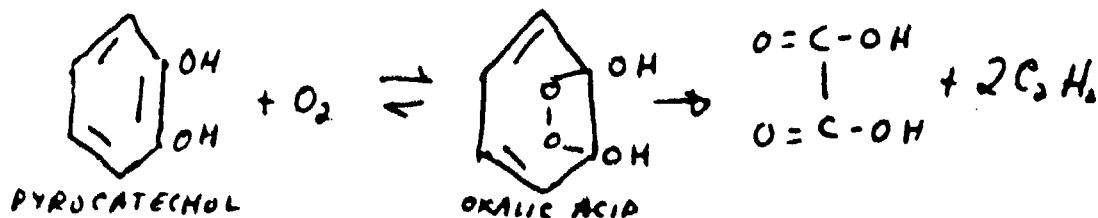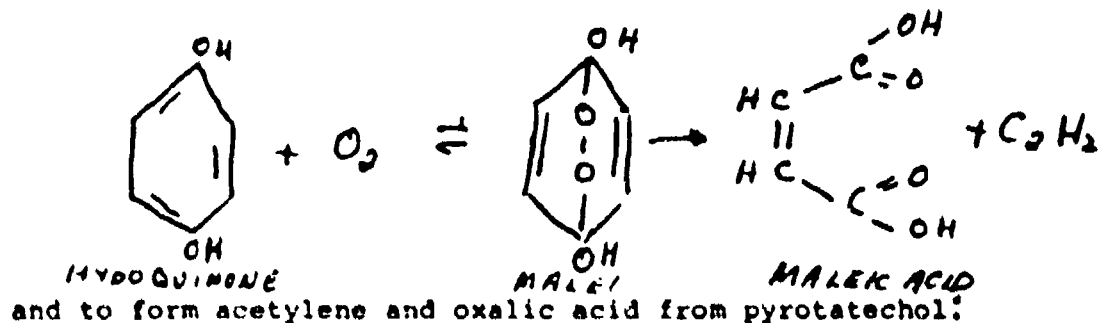
Santoro and Glassman (1979) have argued that carboxyl groups in the maleic and oxalic acids convert to CO_2 directly and that this is the reason Wright (1962) found the CO_2/CO ratio in the combustion of xylenes to decrease as one proceeds from a fuel rich condition towards stoichiometric. Thus it would appear that the aromatics under fuel rich conditions require more oxygen to have the same "richness" as aliphatics which only form CO directly.

On an equilibrium basis one would expect that a pre-mixed flame would begin to soot at a C/O ratio just greater than 1. But the processes leading to soot formation are kinetic and not purely equilibrium. Much of the hydrogen in the fuels must be stripped away by oxidizing radicals before the carbon can participate in the reaction schemes. Thus instead of the limiting C/O ratio being given by (C/O = 1)

$$C_xH_y + x/2\ O_2 \longrightarrow xCO + \frac{y}{2}\ H_2 \qquad (1)$$
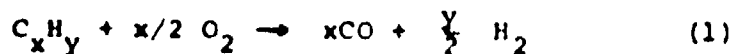
it should closely correspond to

$$C_xH_y + (\frac{2x+y}{4})\ O_2 \longrightarrow xCO + \frac{y}{2}\ H_2O \qquad (2)$$

For the aromatics, due to the low temperature oxidation process, it is postulated that the limiting C/O ratio should be close to

$$C_xH_y + (\frac{2x+4+y}{4})\ O_2 \longrightarrow (x-2)\ CO + 2CO_2 + \frac{y}{2}\ H_2O \qquad (3)$$
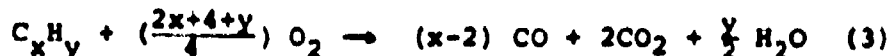
Table 2 shows the experimental results of Street and Thomas in terms of equivalence ratio in the first column. The limiting mixture based on Equ. 1 is Column 1. The limiting mixtures for aliphatics based on Equ. 2 and for the aromatics based on Equ. 3 are listed in Column 3. Recent experimental results by Miller and Calcote (1977) are reported in Column 4. The qualitative agreement between the experimental results and Column 3 is very good and would appear to support the simple mechanistic characteristics postulated. The one major variation between the results of the calculations proposed here and the experimental results of Street and Thomas are those for acetylene and ethylene. It is interesting to note that Gaydon and Wolfhard (1979) report that oxygen deficient explosion experiments with the paraffins formed water as well; whereas the experiments with acetylene and ethylene produced practially none. It is now well known that oxidative attack on these compounds is on the multiple bond and not on the hydrogens, that is the reactions are additive rather than abstractive.

The results for methyl napthalene in Table 3 would appear to be somewhat contradictory to the general agreement. However, here one must question Street and Thomas's results which indicate that the alkylated naphthalenes soot very near to stoichiometric. This result is at odds with the limiting ratio determined in stirred reactors (Blazowski, 1979) which although not giving the same C/O ratio as laminar flames for reasons explained earlier, do give qualitative agreement (Wright, 1969).

With this type of knowledge it is, of course, possible to work
out an empirical scheme to predict the sooting limits as Daniels (1968)
has done, but the point here is to understand the essential mechanism.
Fundamentally it is the temperature and the O or OH concentra-
tion which determines the limit and not any equilibrium stoichio-
metry (except for the aromatics as discussed). The equilibrium
stoichiometry gives a relative order. The sooting limit for a
given fuel will change if its flame temperature is artificially
altered. The most interesting point is that the postulated mech-
anism for aromatic oxidation would indicate that the actual oxi-
dative radical concentration is actually lower than one would
expect or would exist in aliphatic oxidation processes. The
proposed stoichiometry (Equ. 3) for aromatics is an indirect
measure of the lower oxidative radical concentration.

In particular, the above results with the aromatics have
great significance because they indicate that at the limiting
equivalence ratio the aromatics proceed through an acetylene
precursor route and that their apparent greater sooting tendency
is due to the fact that two carbon atoms in the ring oxidize
directly to CO_2 and that a given mixture ratio is not as lean as
it appears. Indeed, if the postulates were true, then in con-
sideration of the following fuel mixtures

$$C_2H_4 + a\ N_2$$

$$C_6H_6 + 3H_2 + b\ N_2$$

$$C_7H_8 + 3H_2 + c\ N_2$$
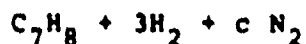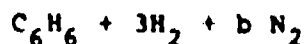
where a, b and c are adjusted so that the mixtures give the same
flame temperature, the benzene should soot at a mixture ratio
more lean by a factor 6/7 than ethylene. Without balancing the
initial C/H ratio, one sees that the experimental data in Table
2 for the aromatics and olefins are near this rate.

Unfortunately the only recent work on the oxidation of benzene has been carried out in shock tubes where the low temperature oxidation route is not followed (Fujii and Asabu, 1973). It is important to remember the difference between shock tube and flame oxidation processes. Of course, in diffusion flames the aromatic structure of the benzene can be retained as it undergoes pyrolysis probably with some ring fracturing leading to soot precursor elements. Again one must keep in mind the polar nature of the benzene ring and the suggestion proposed here that this characteristic leads to fast addition reactions with other radicals, ions and other polar molecules.

Even in pre-mixed flames, although it has been argued that benzene proceeds primarily through an acetylene route, it is also well to remember that some quantities of fuel are never destroyed. The amount of soot formed itself is indeed small at the initial sooting C/O ratio. Thus when burning aromatics in pre-mixed flames, a second possibility could be that at the limiting equivalence ratio quantities of the conjugated (polar) fuel could persist and provide excellent initial sights for addition to form the larger elements which lead to nucleation. Observations of sooting pre-mixed flames would confirm that this second possibility is so. With most of the paraffins tested a dark zone exists between the blue-green reaction zone in the flame and the onset of luminosity attributed to formation of soot particles (Street and Thomas, 1951). However the reaction and soot initiation zones merge for the aromatics; that is the dark zone disappears. It is the interpretation here that the dark zone is where the conjugated, polar compounds are forming. The aromatics having this character, and not all being consumed, thus form soot immediately in the reaction zone. Unfortunately there has been no observation of butadiene flames. Butadiene flames should appear similar to benzene flames, as would other fuels so conjugated. Experiments at Princeton will attempt to verify the postulate.

Thus it appears that in premixed flames all fuels follow an essentially acetylene precursor route to form soot. When the equilvalence ratio is such that Step c is favored over Step d,

the larger precursor radicals undergo further addition and dehy-
dration via a combination of radical, ion and polar compound reac-
tions giving either higher molecular weight, lower H content ali-
phatics (probably ionic in character)(Step e) or undergoing Diels-
Alder cyclization leading to polynuclear aromatics (Step f). Step
f is probably the dominant route according to the concepts already
put forth. Both the results of Step e and Step f undergo further
association reactions of the type described leading to condensed
phase nuclei either aliphatic (Step g) or aromatic (Step h) in
character.

As pointed out by Homann (1968), the Goetingen work shows
that the particulate formation is observed to be rapid only in
the region of the radical rich oxidation zone in the laminar flame
and the particulate formation slows down with decreasing concen-
tration of hydrocarbon radicals. Thus Steps c, e or f, and g or h
must take place very rapidly. As stated in the first section
Calcote (1978) inferred that there are some problems accounting for
this soot formation with neutral free radical mechanisms with rea-
sonable reaction rates (Tanzawa and Gardner, 1978), in explaining
the rearrangement of aliphatic chasis to produce cyclic aroma-
tics (Cullis, 1976), and avoiding thermodynamic bottlenecks asso-
ciated with the growth of aromatics (Stein, 1978). These problems
can be avoided with the chemi-ion or the chemi-ion-polar interac-
tion mechanisms.

The existence of ions in flames is well-established (Calcote,
1972) and that they played a role in pre-mixed and diffusion
flames had very early been shown by Weinberg and coworkers (see
Payne and Weinberg, 1959). The question which requires analysis
is whether the ion concentration is an essential element in the
particulate nucleation step. As mentioned earlier, in 1968 Homann
has essentially argued that since ions in the absence of a field
are several orders of magnitude lower than the concentration of
hydrocarbon radicals, the role of ions cannot be the essential
feature in the nucleation process. Yet is seems likely that neu-
tral free radical mechanisms may not be rapid enough. The following
reasoning would seem to support the chemi-ion model. Many (Salooja,
1973; Peugier, 1975, Bukwics, et.al., 1975) have shown that the

addition of the low ionization potential alkaline earth metals to
the flame could affect soot processes in different ways. When the
additives can be effectively placed in the reaction zone region,
the tendency to soot increases visibly. It would appear then that
many of the neutral free radicals do not undergo sufficiently fast
reactions to nucleate in the reaction zone and have other fates
which will soon be discussed. The addition of material which af-
fect ion reactions in this zone then involves these otherwise non-
nucleating molecules in rapid nucleating steps. However, it would
appear to this observer that if all the nucleation sights must be
strictly ionic in character, then practically all the virgin par-
ticles formed in the flame would be charged. The evidence seems
to be to the contrary. For if all the particles were charged then
the pearl-like structure of the soot (Palmer and Cullis, 1965)
leaving the combustion process could not form, certainly not by the
logical mechanism that Howard (1969) has described. The parti-
cles would constantly repel each other. Similarly, the recent work
of Haynes, et.al., (1978) in which the alkaline earths were added
in the post reaction zone of the flame shows that the amount of
soot formed does not decrease as many had earlier expected from
this type additive, but there were larger amounts of much smaller
particles. The conclusion of Haynes, et.al., was that the low
ionization potential additives charged the particles and prevented
their agglomeration - thus more visible particles did not form.
This type of evidence seems to indicate that many of the virgin
soot particles formed have no charge. Thus many of the nucleated
particles rapidly formed must be formed by some fast reaction in
which the ion states of the precursor cannot persist - such as the
speculation that relates to the rapid reaction due to the polar
character of the many multi-bonded intermediates which must exist.

This present discussion must be related to the earlier im-
portant remark that the flame temperature (and the oxidative
radical concentration) are the dominant factors in predicting the
tendency to soot in pre-mixed flames. Since higher flame tempera-
tures decrease the tendency to soot through increased oxidative
radical attack on the precursors and also increase the concentra-
tion of ions in a flame (which should increase the tendency to soot),

it would appear that in natural systems the precursor competition
steps (c and d) are more important than the nucleation steps (e,
f,g,h). This conclusion does not mean that the extent of sooting
cannot be affected by altering the nucleating step.

The results of Steps g and h are condensed phase nuclei some
of which are charged. The cyclization route (Step h) appears
apparent and the important features of the other physical elements
of the overall soot process will be evident from following the
aliphatic Step g.

Before proceeding it is necessary to consider what is meant
by nucleation in the soot process. As Homann (1968) has discussed
the process of carbon formation takes place under non-equilibrium
conditions and is thus "intrinsically different from the condensa-
tion of a normal vapor where liquid lights represent an equili-
brium state. There is no critical size of carbon particles above
which the rate of growth (as in condensation) is greater than the
rate of evaporation and which could be correlated with a certain
degree of supersation of carbon vapor." However, Homann did not
proceed to define the concept of nucleation. Calcote (1978) has
put forth the most succinct definition,"Nucleation involves the
formation of an embryonic ion which grows faster than it decom-
poses or otherwise reacts". The definition would be more general
of the word "species" were substituted for "ion". Thomas (1962)
essentially had proposed the same earlier by also defining the
nucleus through its chemical nature. Again quoting from Thomas,
"It (the nucleus) should be added to the molecules or frag-
ments of fuel molecules at high temperatures to form a new larger
species that is just as reactive as the first. It must also grow
rather than split. So we are again back to the concept of a con-
jugated free radical which fulfills the role of a nucleus quite
well. The critical steps of nucleus formation may well be simply
the first few reaction steps necessary to produce a conjugated
polyolefin". This writer supports Thomas' interpretation strongly
with the essential idea that the conjugated species can be ionic, or
readily form ions by addition, as well,and that di-acetylene and
vinyl acetylene could fit his idea of a "conjugate" polyolefin".
One must be careful as to the meaning of soot. The chemical com-

position of the soot particulate changes as it proceeds through
the flame process. The newly born particle in the flame can have
a very high hydrogen content. Sampled very young compounds have
been found to have a hydrogen content as high as 3% by weight which
converts to 36% in an atomic basis (Thomas, 1962). Considering
the now accepted evidence that ions increase nucleation, it would
appear that the young particles do not necessarily have to be
strictly large polybenzoid hydrocarbons as Thomas suggests, al-
though this probably is the fate of aromatics in diffusion flames.
The large hydrogen content of the young carbon particles argues
strongly against a strictly polyacetylene route. Given that a
new particle will probably have a free radical character, cycli-
zation of aliphatics must take place in the condensed phase as the
particle thermally dehydrogenates and ages. Thus it appears the
fate of many of the low molecular weight hydrocarbon radicals being
identified in flames is not that of participating in the nucleation
process. The fact that one can identify these compounds argues
against their participating in the very rapid reactions leading to
condensed phase nuclei. Butadiene, and higher molecular weight
compounds derived from it, have not been identified in flames.
The reason may be that they react and form particles so quickly,
identification is not possible. The fate of the acetylenic type
compounds identified in flames may be one of three: adding on
to the nucleus, surface addition to a young particle, or non-
participation in the soot process at all.

Returning to the flow chart represented by Figure 2, we will
now consider those steps which concern the growth of the particle.
Since many of the particles are positively charged, they repel
each other and their growth is by addition of radicals to surface
and by surface absorption of those species which have not found
sufficient fast routes to nucleate in the active flame zone (Step
i). Many charged and neutral particles will agglomerate (Step j)
and will also have radical and absorption surface reactions as
Step i. Step j leads to much larger particle growth than Step i.
I shall call the result of Step i very small, young, virgin par-
ticles. As these young particles age in the burned gas zone very
near the flame front, they undergo further dehydrogenation, and,

as a postulate, if aliphatic in nature condensed phase cycliza-
tion (Step m). The result is small, old soot particles. These
particles have two fates. They are small enough so that they are
completely oxidized to gaseous products (Step n) or they escape
to the combustion environment and leave the process as soot (Step
o). That the latter sequence is feasible is evident from the pre-
mixed flame experiments to deter the limiting C/O ratio for sooting.
This limit is determined by appearance of luminosity in the flame,
however, the particles so formed do not persist, but are burned
completely, because the burned gas condition on an equilibrium
basis is still oxidative with respect to carbon. Recall the ac-
tual limiting C/O ratio is much less than 1.

The agglomerated particles, the result of Step j, consist
comparatively of a variety of much larger size particles. They
undergo Step 1 exactly similar to Step m and either escape intact
(Step p) or are partially oxidized to gaseous products (Step q)
and only very slightly reduced in size. It does not appear nec-
essary to detail the agglomeration process as this phase has been
more than adequately detailed by Howard and coworkers (Howard,
et.al., 1972).

The work of Hyanes, et.al., (1978) is particularly signi-
ficant in showing that the addition of low ionization potential
additives in the right position in flames can substantially in-
crease the flow process in the direction of Step i over Step j
and thus favor the formation of a larger mass of small particles.
This result has great practical consequences when it is desired
to reduce soot effux in a given combustion scheme. Very small
soot particles, even in a flow field, would follow in practical
combustion situation a "d^2" burning rate law. Thus the indica-
tions are, if the particles are kept small, for sufficient, but
not necessarily large, stay times in an atmosphere oxidizing to
them and at sufficiently high temperatures, they can be com-
pleted converted to harmless gaseous products. Many modern in-
dustrial plants that operate sufficiently fuel rich so that the
combustion process is luminous for increased radiant heat trans-
fer burn off the soot formed in another process stage before
emitting the stack gases.

The complex flow scheme in Figure 2 can be reduced to three significant elements which control the amount of soot formed in a given, pre-mixed combustion process: the temperature and oxidizing radical concentration (O or OH), the amount of nucleation sights, and the extent of agglomeration of the particulates formed. The first effect is the dominant one particularly near the limiting mixture ratio for sooting and for systems which contain no additive.

It would appear that the only effect of fuel structure under pre-mixed conditions arises from the means by which aromatics are oxidized in pre-mixed situations. The sooting tendency of the aliphatics follows the trend, the higher the temperature, the less the tendency to soot. Further Street and Thomas (1955) have shown that the branched-chain paraffins have the same C/O limit as the straight-chains.

The experimental results on the effect of pressure are not clear. Schalla and Hibbard (1959) have reported that the most quoted work (Smith, 1940) gave results that were open to question. Gaydon and Wolfhard (1979) concluded that the effect of pressure was only slight. More recent work by Fenimore, et.al., (1957) over a small pressure range indicates the higher the pressure, the greater the tendency to soot. In order to estimate whether these results are consistent with the major controlling step discussed just previously, one would have to make an equilibrium calculation to determine how the hydroxyl radical concentartion changes with pressure. The temperature will rise due to a pressure increase, but if in an eqilibrium context the O and OH radicals are considered products of dissociation then Le Chatelier's principle indicates that the radical concentration will tend to decrease with pressure. These appear to be compensating effects and thus the effect of pressure should be slight.

The addition of inert additives should reduce the temperature and thus increase the tendency to soot; enrichment with oxygen should thus decrease the tendency. Street and Thomas (1955) found these explicit trends. Most chemical additives in small percentages have little or no effect on the sooting tendency

(Palmer and Cullis, 1965). The one exception is sulfur trioxide, which is small percentages appreciably accelerates the soot forming process. Palmer and Cullis state that SO_3 induces chain reactions leading to polymerization and decomposition of the fuel. I have derived another explanation from the possible reactions of SO_3 with those radicals which affect the O, H and OH pool. The thermal dissociation of SO_3 is slow so it can be present in the active reaction zone and do as Palmer and Cullis suggest or undergo the following two reactions (Glassman, 1977)

$$O + SO_3 \longrightarrow O_2 + SO_2 \qquad -37 \text{ kcal/mole}$$
$$H + SO_3 \longrightarrow OH + SO_2 \qquad -19 \text{ kcal/mole}$$
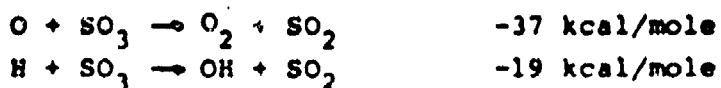
Although more H radicals are present in rich mixtures, the rate of the first is more than two orders of magnitude faster than the second and could remove the pool of O radicals, which could also reduce the others through the H_2-O_2 chain steps

$$O + H_2 \longrightarrow OH + H$$
$$H + O_2 \longrightarrow OH + O$$
$$OH + H_2 \longrightarrow H_2O + H$$
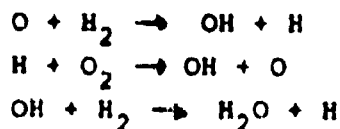
With removal of O and OH radicals near and above the limiting equivalence ratio, the tendency to soot would increase appreciably.

VI   Diffusion Flames

The soot formation process in diffusion flames nearly follows the same flow scheme as in pre-mixed flames except for one very, very important difference. The oxidative Steps b and d do not exist; that is, the fuel and precursor monoelements only undergo thermal pyrolysis. This aspect is most significant in that the rate of thermal pyrolysis increases with temperature, and since no competitive oxidative step increases faster, the tendency to soot increases with increasing flame temperature. Thus the sooting order of the aliphatics in diffusion flames is exactly the reverse of that in pre-mixed flames

$$\text{acetylenes} > \text{olefins} > \text{paraffins}$$

The general order of all fuels in

$$\text{naphthalene} > \text{benzenes} > \text{acetylenes} > \text{olefins} > \text{paraffins}$$

Although diolefins of 10 carbon atoms or more would place these species between the acetylenes and mono-olefins (Clark, et. al., 1946), it appears to have gone unnoticed that the diolefins of 4 or 5 carbon atoms soot more readily than the aromatics and acetylenes (Schalla, et.al., 1954). It is important to note here that in diffusion flames the structure of the fuel is most important in determining the sooting tendency.

Glassman, et.al., (1979) have completed a careful study of the effect of inert additives on the tendency of diffusion flames to soot. By adding monoatomic, diatomic, linear and non-linear triatomic inert species to the fuel side of ethylene and acetylene flames, they were able to show that the tendency to soot decreased with increasing heat capacity of inert; i.e. with decreasing temperature. There were only minor deviations from the quantitative trend due to the effects of the inerts on the mass diffusivity of the fuel jet. It is further interesting to note that one of the additives, water, did not play any chemical role. It had been proposed earlier (Glassman, 1976) that water could produce OH radicals via

$$H + H_2O \rightarrow H_2 + OH$$

and reduce the tendency of soot by introduction of an oxidative radical on the fuel side of the diffusion flame. The heat capacity experiments showed that there was no validity to this suggestion. It is now apparent that any H radical present reacts with the more abundant fuel, rather than the H_2O additive. Indeed the reaction

$$H + RH \rightarrow R + H_2$$

is faster than the previous one as well.

As given above the trend of the aliphatics is that the greater the flame temperature the greater the tendency to soot. But the order of these compounds is such that one could conclude the greater the C/H ratio the greater the tendency to soot. Since the flame temperatures of the aromatics are lower than the acetylenes, it would appear the C/H ratio correlation would be better than the temperature condition. In pre-mixed flames it was found that the C/H ratio had an effect because of its role in determining the OH and O radical concentrations. Since there is no role for oxidative attack in diffusion flames, what is the significance of the trend in C/H ratio? The overall hydrogen content could possibly play a role in the sooting tendency in diffusion flames because of the unusual diffusivity of H_2 and H (Homann, 1970) or it could alter (lower) the overall fuel pyrolysis and polymerization rates. Clark, et.al. (1946) reported that for diffusion flames their experiments showed the higher the C/H ratio the greater the tendency to soot. But, the question is, does the C/H ratio reflect the structure of the fuel or simply the overall carbon to hydrogen content present. To paraphrase this concept simply, does an equal molar mixture of ethylene and hydrogen have the same sooting hei ;ht as ethane? The question is important in that it it has been known that addition of H_2 to a fuel does decrease its tendency to soot in diffusion flames (Thorp, et.al., 1951). The recent experiments of Glassman, et.al., (1979) have also shown that the addition of H_2 to both ethylene and acetylene decreases their tendency to soot; however, when ethane is compared to with ethylene-hydrogen and acetylene-hydrogen mixtures so that all three systems have equal C/H ratios, the acetylene mixture has a far greater propensity to soot than the ethylene mixture, which soots more extensively than the ethane. These results would indicate the great importance of fuel structure, but the new mixtures follow the proper temperature trend for sooting as well. Thus not only must C/H be kept constant, but also the flame temperature as well, if one is to determine a fuel structure effect. Such experiments are essentially underway at Princeton.

In dealing with this question of fuel structure one must take into consideration the aromatics. It has been reported by Schalla, et.al. (1954), that since benzene soots more readily than acetylene (equal C/H ratio) and benzene has a lower flame temperature than acetylene, flame structure is important. However, as reported earlier, not only does benzene follow an oxidative route different from the aliphatics, but also its pyrolysis route varies with temperature (Bittner and Howard, 1978). In order to perform their experiments with benzene, Schalla, et.al., had to vaporize this fuel. Glassman, et.al., (1979) have criticized the method of reporting of Schalla, et.al., as possibly giving misleading trends. There is enough practical evidence (van Teuren, et.al., 1978) to indicate that aromatics do have an unusual propensity to soot which is related to their structure. The only question in doubt would be to what extent. This question is currently under investigation at Princeton.

Probably the most conclusive evidence that structure is an important factor is the results of Schalla, et.al. (1954) with the paraffinic isomers. These isomers have the same C/H ratio and the same adiabatic flame temperatures, yet it appears the more branched, or compact, the molecule the greater the tendency to soot.

The concentration of ions in a diffusion flame should not vary among the different paraffinic isomers. Then although ions could play a role in diffusion flames (Place and Weinberg, 1967; Calcote, 1978) the results on the paraffinic isomers clearly indicate that they are not a key element. Dryer and Glassman (1978) have recently detailed the manner in which paraffinics are thermally and oxidatively pryolyzed. The interesting point is that the method that Dryer and Glassman suggest to predict the olefins formed from the paraffins show that the branched chain compounds give more intermediates that can become di-olefins, particularly butadiene. It is the smaller di-olefins that show the most polar resonance (conjugated) structure, the reaction (a - e) in Figure 2. It is somewhat surprising on first thought to recognize that butadiene soots more readily than benzene and acetylene. Since the temperature and C/H ratio would favor acetylene

to be the predominantly sooting compound, some other reason for
the general trend of butadiene, benzene and acetylene had to be
put forth. The most logical explanation at this time is that
put forth in this paper eariler that the polarity of butadiene,
its ability to undergo very rapid Diels Alder type reaction, and
its ability to accept a positive ion and form the even more reactive
carbonium can make it the logical soot precursor to nucleation.

Schalla, et.al. (1954) discusses the possibility of the
carbon-carbon bonding as a factor in explaining the sooting trends
of the aliphatics and of the isomers. The postulate breaks down
as expected since the comparative strengths of the C-C bonds to
the C-H bonds would only be a factor in the thermal pyrolysis step.
The general pyrolysis must be a chain and dominated by radical
reactions which could strip a hydrogen from the parent fuel. Thus
the trends predicted by Dryer and Glassman (1978) for oxidation
systems probably prevail to a great degree as well for the overall
thermal pyrolysis of the fuel. Applying the method of Dryer and
Glassman to dimethyl propane, isopentene and pentane, one finds
that in the initial stages of pyrolysis that the dimethyl pentane
should form predominantly butene and methane, isopentane should
form predominantly propene with some butene and ethene, and pentane
should form about equal amounts of propene and ethene. From this
result one would predict the following sooting tendency:

dimethyl propane > isopentane > pentane

which is exactly what Schalla, et.al. (1954) found and of course
what would be expected from compactness of the initial fuel mole-
cule. It is necessary to stress the importance of the formation
of butene as an intermediate since it would appear to pyrolyse
further in a reacting system to form butadiene. Further credance
for this line of reasoning is that the butenes have the greatest
tendency to soot of all the mono-olefins, followed by propene
(which will give allene or methyl acetylene in its next pyrolysis
step), and then pentene (Scalla, et.al., 1954). The often repro-
duced chart of Clark, et.al. (1946) is very misleading in that it
only depicts results for compounds with six atoms or more.

In the context of the reasoning put forth then the sooting order for the hexanes should be

2,2 demethyl butane }
3 methyl pentane } > 2 methyl pentane > 2,3 dimethyl butane
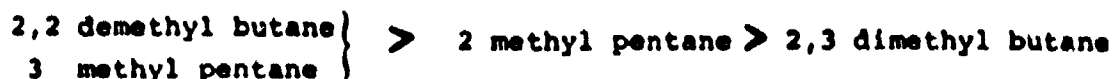
This prediction will be tested in the Princeton program.

The argument with respect to the aromatics are somewhat more diffuse because on the fuel rich side of a benzene diffusion flame, the temperature ranges from 2370°K to below 1000K. Studies on the pyrolysis of benzene reveal that there is ring fracture above 1800K (Bittner and Howard, 1978). Thus in a diffusion flames there is pyrolysis to phenyl radicals below 1800K and to acetylene and other aliphatics above 1800C. Undoubtedly the aromatic structure is retained in much of the fuel side of the flame and arguments as to its polarity, ability to form ions (Calcote, 1978) and the integral large size (6 carbon atoms) it retains for building blocks to form soot nuclei, all indicate a great propensity to soot. The fact that the aromatic structure is retained in diffusion flames is supported by the fact that toluene has a greater tendency to soot than benzene. The C-H bond in the methyl group in toluene is 85 kcal/mole compared to the CH bonding in the ring of .110 kcal/mole and C aromat-C alkyl bonding of 100kcal/mole. So toluene forms initial radicals much earlier than benzene.

The role of ions in diffusion flames must be very much like that in pre-mixed flames. In support for a more important role for a purely ion theory, Calcote (1978) points out that carbon monoxide, methyl alcohol, formaldehyde, formic acid and carbon disulfide do not produce soot in diffusion flames and that neither do these gases produce ions in diffusion flames. This agreement is fortuitous. No single carbon atom fuel, especially when bound to oxygen or other atoms besides hydrogen, will produce soot. Indeed C_2N_2 does not soot either (Gaydon and Wolfhard, 1979) and thus it is apparent that the soot formation process must proceed through a C-H precursor with multiple bonded C-C atoms. These fuels cannot produce these multiple bonded precursors. The only reason methane produces soot is that methyl radicals recombine to

form ethane, then ethene, etc. In fact methane would not form
soot in pre-mixed flames if it were not for the fact that methane
radicals are difficult to oxidize and thus recombine to form ethane
(Westbrook, et.al. (1977); Dryer and Glassman, 1978; Glassman, 1979).

Increasing the pressure of diffusion flames strongly increases
the tendency of a given fuel to soot. The effect is best ex-
plained through the flame temperature which increases strongly
with increasing pressure. Pressure could accelerate nucleation
reactions, but the effect of the temperature in pyrolysis is ex-
ponential in character and must dominate.

The most interesting additives to inject on the fuel rich
side of a diffusion flames are those which are oxidizing in nature.
The addition of a small amount of oxidizer strongly increases the
sooting tendency. This is the well known homogeneous catalytic
effect of small amounts of oxidizer on pyrolysis reactions. Both
Wright (1974) and Glassman, et.al. (1979) have shown that as the
oxygen addition to the fuel increases the tendency to soot increases
until a given concentration, above which the tendency to soot be-
gins to decrease. Obviously enough oxidizer can be added so that
the flame becomes pre-mixed in character. This trend explains
the so-called anamalous results in pre-mixed flames. When per-
forming soot experiments in pre-mixed flames at mixture ratios
richer than the critical limit, it has been observed that at
times the amount of soot formed increased with increasing temp-
erature of the flames and at other times it decreased. It is
apparent that very rich pre-mixed flames act as diffusion flames
which soot more profusely as the temperature increases. Those
flames just richer than the critical limit follow the pre-mixed
trend with temperature and decrease with temperature, as explained
earlier.

SO_3 tends to decrease the tendency to soot in diffusion
flames. This role could be related to one of the SO_3 reactions
given previously, namely,

$$H + SO_3 \rightarrow OH + SO_2$$

which is quite exothermic. This reaction not only removes H

radicals from the pyrolysis chain, but forms hydroxyl radicals.
The literature is unclear with respect to how much SO_3 reduces
the sooting tendency. If only small amounts were added then the
above argument falls apart since there is a critical concentration
above which hydroxyl attacks the precursors rather than accel-
erates the fuel pyrolysis.

VII Conclusions

The fuel sooting trends in pre-mixed and diffusion flames
follow opposite directions due to the different influences of
temperature. In pre-mixed flames as the temperature rises the
rate of oxidative attack on the soot precursors increases faster
than the rate of precursor formation through pyrolysis. Thus the
higher the temperature the less is the tendency to soot. In the
oxidative atmosphere of a pre-mixed flame all aliphatics form some
acetylene which is the monoelement for precursor formation and
all fuels essentially follow the same nucleation route. Thus
initial fuel structure plays little role in soot formation in
pre-mixed flames.

Aromatics oxidize partially through carboxyl radicals formed
during attack on the ring and thus aromatic mixtures burn "richer"
than corresponding aliphatic mixtures of the same stoichiometry.
Consequently aromatics appear, and do, have a greater sooting

tendency as measured by the critical C/O ratio.

The dominant factors in diffusion flames are the temperature
and fuel structure. However, here the rate of pyrolysis of the
fuel has no competitive oxidative attack. Thus the higher the
temperature, the greater is the rate of fuel pyrolysis and the
greater the propensity to soot. Thus fuel structures which
during pyrolysis form strongly conjugated (polar) species most
readily soot.

Since a pure acetylenic polymerization route is deemed too
slow to predict the early nucleation of soot particles in flames
and the presence of ions cannot predict the difference of isomers
to soot in diffusion flames, it has been postulated that only
conjugated species which have polar resonance structures can under-
go the fast reactions necessary. Thus butadiene, either by itself,

as a radical, or as a carbonium ion, is probably the crucial intermediate to soot nucleation. In pre-mixed flames it forms from acetylene monoelement and is probably not identified because it undergoes very fast reaction. Indeed, experimentally, butadiene has the greatest tendency to soot in diffusion flames of any fuel tested. The great tendency of aromatics to soot, besides the stoichiometry question mentioned, is also due to their initial high conjugation and polar character.

VIII Acknowledgements

IX. References

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TABLE I

Stoichiometric Flame Temperatures in °K

Paraffins		Olefins		Acetylene		Aromatics	
methane	2200						
ethane	2195	ethene	2340	acetylene	2560	benzene	2340
propane	2260	propene	2320	methyl-acetylene	2450		
cyclo	2350	butene-1	2320	ethyl acetylene	2413		
butane	2280	butadiene 1,3	2365				
pentane	2275	n pentene-2	2320				
iso	2250						
2,2 dimethyl pro.	2220	hexene	2286				
cyclo	2235						
hexane							
2,2 dimethyl but.	2220						
cyclo	2225						

TABLE 2
Sooting Limit Equivalence Ratios (ϕ)[a]

Compound	Theor (C/O=1)	S&T[b] Exp. ϕ	ϕ new Theory[c]	C&M[d] Exp ϕ
ethane	3.51	1.67	1.41	
propane	3.33	1.56	1.43	1.73
n-pentane	3.19	1.47	1.45	
iso-pentane	3.19	1.49	1.45	
n-hexane	3.17	1.45	1.47	
iso-hexane	3.17	1.45	1.47	1.73
n-octane	3.13	1.39	1.47	1.73
iso-octane	3.13	1.45	1.47	
iso-dodecane	3.09	1.41	1.47	
n-cetane	3.07	1.35	1.49	
acetylene	2.50	2.08	1.67	2.00
ethylene	3.03	1.82	1.50	
propylene	3.03	1.67	1.52	
butylene	3.03	1.56	1.52	
amylene	3.03	1.54	1.52	
cyclohexane	3.03	1.52	1.52	1.74
n-heptene	3.03	1.45	1.52	
ethyl alcohol	5.99	1.52	1.52	
propyl alcohol	4.50	1.37	1.52	
isopropyl alcohol	4.50	1.39	1.52	
isoamyl alcohol	4.50	1.54	1.52	
acetaldehyde	5.00	1.82	1.67	
proprion-aldehyde	4.00	1.75	1.61	
acetone	4.00	1.69	1.61	
methyl ethyl ketone	3.56	1.69	1.56	
diethyl ether	4.00	1.72	1.52	
di-isopropyl ether	4.00	1.56	1.52	
benzene	2.50	1.43	1.37	1.54
toluene	2.56	1.33	1.39	1.46
xylene	2.63	1.27	1.41	1.45
cumene	2.63	1.28	1.41	1.56
methyl naph-thalene	2.45	1.03	1.35	1.21 (Blazowski,1979)

a. $\phi = (F/O)$act./(F/O)Stoich. b. Smith and Thomas (1955)

c. ϕ for $[O/(C+(H/2))] = 1$ for aliphatics
   ϕ for $[O/((C+2) + (H/2))] = 1$ for alkylated benzenes
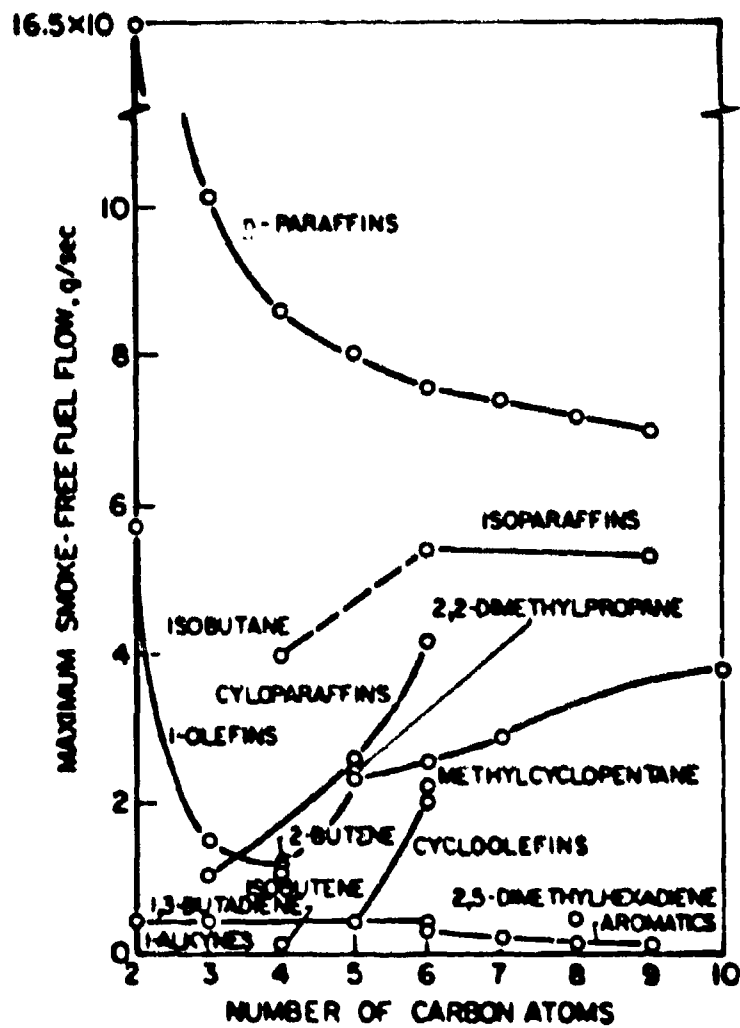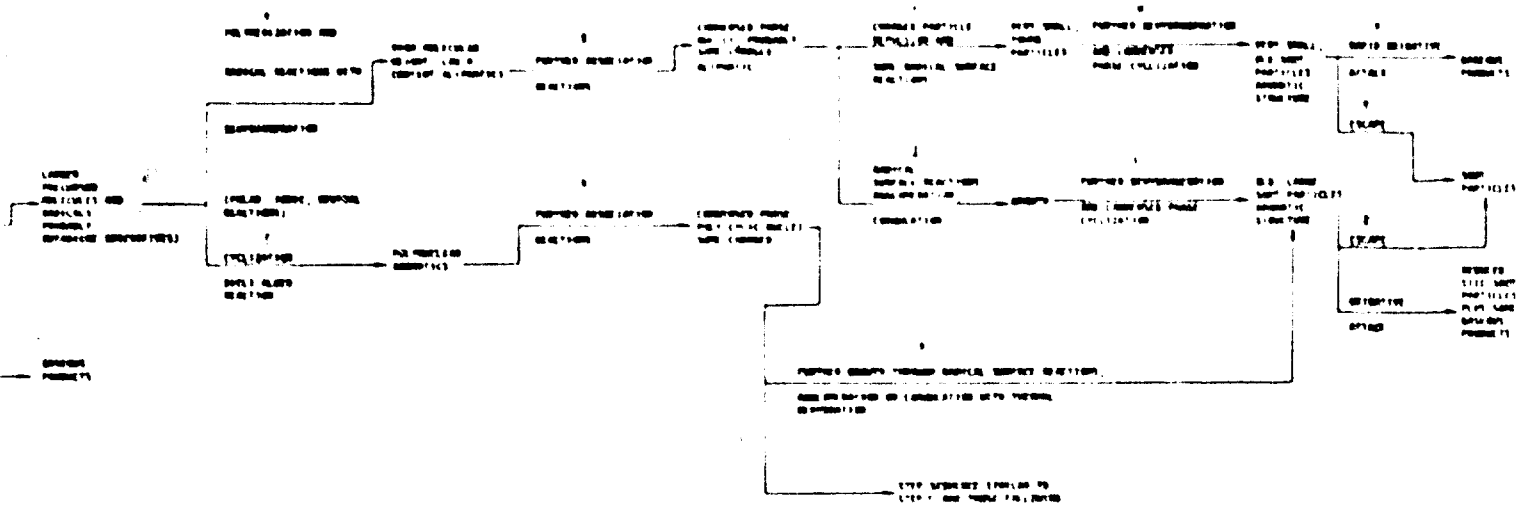 ϕ for $[O/((C+4) + (H/2))] = 1$ for alkylated naphthalenes

Figure 1.   Variation of Maximum Smoke-Free Fuel
Flow with Number of Carbon Atoms
(from Schalla, et.al., 1954).

Figure 7. Photomorphological Models of Root Processes in Cadmium-tin Systems Using Attached to Roots