

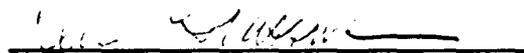
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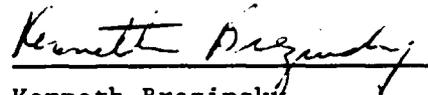
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13. ABSTRACT (Maximum 200 words) Upon completion of a major study of the oxidation of benzene and its mono- and di-alkylated derivatives, a major effort was directed at the oxidation of 1-methyl naphthalene. Completed work on the xylenes indicated the oxidation of one side chain at a time before the ring is attacked. The rate of xylene decay follows a linear profile and the major intermediates detected were toluene, benzene, p-tolualdehyde, p-ethyl toluene and CO. Naphthalene, indene, phenylacetylene and benzene were found to be the major aromatic intermediates in the oxidation of 1-methyl naphthalene. The general characteristics of 1-methyl naphthalene oxidation showed that it was very much an analog of toluene. Extensive work with normal and inverse diffusion flames revealed that vinyl acetylene, allene and benzene were the key intermediates in soot formation. Experiments performed by diluting normal diffusion flames until all soot disappeared led to the conclusion that irrespective of the fuel, soot forms when the pyrolysis zone reached a specific temperature - about 1700K. Fuels evaluated were acetylene, allene, ethene, benzene, 1-3 butadiene, 2-butene and toluene.				
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FUELS COMBUSTION RESEARCH



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SUMMARY

Present and anticipated variation in fuels require greater understanding of the chemical phenomena associated with the feed system and combustion aspects of the air breathing propulsion systems under consideration by the Air Force. With AFOSR support an integrated, fundamental program on fuel research had been established at Princeton. Research emphasis had been on understanding soot formation and destruction processes and the oxidative characteristic of aliphatic and aromatic hydrocarbon fuels.

During the three year period of this report, extensive progress has been made in both active aspects of the program. After completing a major study of the oxidation kinetics of benzene, mono- and di-alkylated aromatics, a major effort was directed at the oxidation of the polynuclear aromatic hydrocarbons (PAH's), specifically 1-methyl naphthalene. Work on the oxidation of the xylenes was completed. The results indicate the oxidation of one side chain at a time before the benzene ring is attacked. The rate of fuel decay follows a linear profile and the major species detected were toluene, benzene, p-tolualdehyde, p-ethyl toluene and CO. The mechanism for the formation of these intermediates has been elucidated and a general mechanistic format for the xylenes based on the earlier results for benzene and toluene is given. Results on 1-methyl naphthalene oxidation have been obtained and a preliminary mechanism proposed.

The early detailed work on sooting tendency of fuels in pre-mixed and diffusion flames was followed with a major study of near and slightly sooting inverse diffusion flames to gain insights as to possible key intermediates (precursors) to soot formation. Additional work using an opposed jet diffusion flame burner evaluated the effect of small quantities of oxygen on

the sooting tendencies of fuels under diffusion flame conditions. The results obtained in the inverse diffusion flame study indirectly confirm that the initial number density of soot particles which form, scales with the aromatic formation just prior to soot inception. Correlations exist between a fuel's sooting tendency as measured by the Princeton smoke height experiment and the extent of aromatic formation measured in both inverse and normal diffusion flames.

Sooting trends were measured in a counter flow system as a function of equivalence ratio of fuel/oxygen mixtures over the range of infinity (pure diffusion flame) to values as low as 2.6. Thus the flames ranged from pure diffusion to double flames, which had a rich premixed flame inside the diffusion flame. This effort has resolved the outstanding dilemma as to why oxygen affects the sooting tendency of ethene and not propane and most other aliphatic fuels and explains the very interesting variation with equivalence ratio for all fuels tested.

During past periods attention was focused, as well, on the important finding that soot inception in diffusion flames occurred at a definitive temperature on or about 1600 K. The variation in temperature is due to the physical characteristic of the flames used to make the inception temperature measurement. The diffusion flame temperature variation approach developed in this program was to dilute the fuel with inert. That such a technique caused alteration of the sooting tendency of a fuel due to a variation in temperature came under criticism by many other experimenters, who argued that the effect was simply due to a diluted fuel concentration. Definitive experiments in the program now show that indeed dilution causes a minor lowering of the temperature, but temperature is the major effect in sooting tendency.

I. INTRODUCTION

Interest in improving performance/emission characteristics of propulsion systems requires better understanding of the coupling between fluid mechanical and chemical kinetic processes which occur in these devices. Modelling of the necessary combustion chemistry is impeded by the lack of adequate knowledge of the general and detailed features of the kinetic mechanisms. More recently, uncertainties in the future sources and characteristics of fuels have emphasized the need to better understand fuel effects on combustion, e.g. energy release distribution, soot formation, emissions, feed system fouling, etc. Such information has been particularly lacking for aromatic species which now comprise a major fraction of present fuels and could be a dominant factor in future jet propulsion fuels. The flow reactor developed at Princeton has had the versatility to provide various aspects of combustion chemistry information related to all types of airbreathing engines and even to the understanding of rocket propellant processes. The research endeavors at Princeton covered in this final report include the pyrolysis and oxidation of aromatics and mechanistic studies of soot formation/destruction.

II. RESEARCH PROGRESS

A. The Oxidation and Pyrolysis of Aromatic Hydrocarbons

The initial efforts on this aspect of the fuels research program was to challenge what most thought to be an extremely complex area of chemical kinetics, that is, the oxidation process of the aromatic hydrocarbons. The approach used was to survey and analyze the literature in order to guide the experimentation. The motivation was that again the unique characteristics of the Princeton turbulent flow reactor would permit insights into the complex system. This flow reactor shown in Figure 1 has been described in detail in

various publications [1,2,3] and earlier reports. Most of the very early published work on aromatics by others was performed at low temperatures, nevertheless, proceeding to higher temperatures closer to combustion process levels was thought of as possibly clarifying the mechanism. High temperature mechanisms were needed. The analysis of the low temperature work created enough outside interest to warrant publication [4]. This review raised the question of the applicability at the higher temperatures of the earlier mechanism proposed and reviewed.

Specifically, the objectives of this aspect of the program have been to elucidate the mechanisms of the oxidation of all types of aromatic fuels with a particular emphasis on those aspects of the mechanisms which lead to soot and other pollutant formation, and to develop, where possible, specific chemical kinetic data on the individual reactions which make up the complex reaction history of the aromatic hydrocarbons. These results would then permit the development of overall rate expressions for combustor modellers, as had so successfully been done earlier for the aliphatic hydrocarbons [5].

As detailed below, great progress has been made during the contract period covered here and during the earlier period of support for the oxidation of such fuels as benzene, toluene and other alkylated aromatics. This success is due in large part to the successful continued development and operations of the Princeton flow reactor; a unique high temperature sampling system; an automated gas chromatographic apparatus, and the gas chromatographic/mass spectrographic apparatus purchased under the program.

Earlier investigations (6-8) of the high temperature (1000-1200K) oxidation of the fuels methyl, ethyl and n-propyl benzene in the flow reactor had indicated that three primary processes are instrumental in removing the

alkyl side chain from the aromatic ring: 1) abstraction of a hydrogen from the alkyl group, decomposition of the radical and, oxidation of the subsequently formed species; 2) displacement of the alkyl group by a radical species - usually an H atom; 3) thermal cleavage (homolysis) of part of the side chain followed by oxidation of the resultant radicals. Since the side chain is removed initially by these three processes without any major attack on the aromatic ring (9,10), it was also found that the oxidation of alkylated aromatics eventually reduces simply to the oxidation of the phenyl radical and/or benzene. Much of the basic understanding of the reactions important in the removal of the side chain was gained from observing that the chemistry of the oxidation of methyl, ethyl and n-propyl benzene was analogous in many ways to the oxidation chemistry of methane (11), ethane (12) and propane (13). Further experimental work in relation to earlier work on the oxidation of butane (14) showed that similar analogies could be made with n-butyl benzene (15). The consequence of this extensive work on the mono-alkylated aromatics was the formulation of a simple, generalized, mechanistic model for the oxidation of the monoalkylated aromatics that certainly should be valid in the temperature and pressure range of the turbulent flow reactor (15).

The main effort on this aspect of the overall program, particularly in the past three year period, then concentrated on the multi-substituted aromatics with particular attention given to ortho, meta and paraxylene. This effort led to a Ph.D. thesis and a series of publications (16-20).

Similar to previous low temperature studies, extensive research revealed that the o-xylene isomer was more reactive than either p- or m-xylene. Two distinct routes involving the oxidation of methyl side chains were found.

The primary decay path for all three xylenes was determined to be

abstraction of a benzylic hydrogen from the methyl side chain to form the resonantly stable methylbenzyl radical. Displacement of a methyl group by hydrogen atom was secondary, and oxygen atom addition to the aromatic ring was determined to be unimportant as a fuel decay path.

A single consumption path for *m*-xylene was identified in which this fuel was attacked mainly through sequential oxidation and removal of the methyl side chains. After removal of the first side chain, the resulting methylphenyl radical was oxidized further to methylphenoxy radical. Pyrolysis experiments with methylanisole, in which methylphenoxy is a decomposition product, showed that methylphenoxy decomposes to CO and methylcyclopentadienyl and that the latter product rearranges and decomposes very quickly to benzene and an H atom.

P-xylene reacted through both sequential oxidation and simultaneous oxidation of the methyl side chains. The simultaneous route involved the formation of *p*-xylylene and oxidation to *p*-phthaldehyde. Separate oxidation studies of *p*-tolualdehyde were performed to insure that the *p*-phthaldehyde detected in the *p*-xylene experiments was a product of *p*-xylene and not *p*-tolualdehyde. Although the xylene formation route was unavailable to *m*-xylene, the oxidation of *p*-xylene was only slightly faster than *m*-xylene.

The oxidation of *o*-xylene was found to proceed through both the sequential and simultaneous oxidation routes; for this isomer the simultaneous route led to a significant increase in the rate of fuel decay. The fast isomerization of *o*-xylylene to styrene was believed to be responsible for this increase in reactivity. Multi-ring species such as naphthalene, indene, and benzofuran were also formed during the *o*-xylene studies. Mechanisms for their formation involving the proximity of the alkyl groups on the ring were

proposed. The naphthalene formation route was tested using acetylene addition experiments which supported the role of acetylene in the build up of multi-ring aromatics.

The latest effort has concentrated on the oxidation of the polynuclear aromatic hydrocarbons which form an important component of jet fuels. In particular, the oxidation of 1-methylnaphthalene was studied. This aspect of the program was a particularly difficult challenge because of the high molecular weight of the fuel and many of its oxidation intermediates. Condensation in sampling lines has posed very difficult problems. After a thorough experimental analysis of the flow reactor, these difficulties were resolved, and very interesting data were and are being obtained.

The recent experimental oxidation tests (21) revealed that naphthalene, indene, phenylacetylene, and benzene were the major aromatic intermediates in the oxidation of 1-methylnaphthalene, with naphthalene reaching a maximum concentration first, then indene, phenylacetylene, and finally benzene (see Fig. 2). The major aliphatics detected were acetylene, methane, ethylene, vinylacetylene, and cyclopentadiene. Significant quantities of 1-naphthaldehyde were found, as well as small concentrations of 1-naphthol and 1,2-dimethylnaphthalene. Just as 1-methylnaphthalene is the doubly-ringed aromatic analog of the singly-ringed toluene, 1-naphthaldehyde, 1-naphthol, naphthalene, indene, and phenylacetylene are the analogs of the major intermediates in the oxidation of toluene, whose mechanism was previously studied in the flow reactor. By analogy then, major mechanistic steps in the oxidation of 1-methylnaphthalene have been proposed (21): once an initiation process has established a radical pool of H, OH, O, and HO₂, the fuel is attacked by radical abstraction of an H atom from the methyl group, forming

the 1-naphthylmethyl radical (see Fig. 3). Displacement of the methyl group by a H atom is probably an additional mechanism of attack of the fuel and leads directly to the formation of naphthalene. The 1-naphthylmethyl radical, resonantly stabilized to even a greater extent than the benzyl radical in toluene oxidation, undergoes radical-radical reactions with O and HO₂ to form 1-naphthaldehyde. Abstraction reactions with radicals and O₂ break the weak C-H bond of naphthaldehyde, and subsequent unimolecular decomposition yields the 1-naphthyl radical (which quenches to naphthalene in the sample probe) and CO. Reaction of the 1-naphthyl radical or naphthalene with radicals or O₂ gives 1-naphthoxy (observed as 1-naphthol), which rearranges and decomposes to the indenyl radical (observed as indene) and CO. Further radical attack finally ruptures the second aromatic ring and produces the styrene radical, which undergoes β-scission to form phenylacetylene or the phenyl radical (observed as benzene) and acetylene. Support for this mechanism is given by the presence of all of the suggested species (or quenched forms of the radicals) and the lack of any other significant peaks, in the GC analysis of the flow reactor runs. Further support is evident in the successive attainment of maximum concentration in the profiles of naphthalene, indene, phenylacetylene, and benzene, consistent with the predictions of the mechanism.

B. Soot Formation and Destruction Processes

The program's contribution to the understanding of soot processes has been well established. The Princeton studies were the first to clearly distinguish the difference between sooting tendencies of pre-mixed and diffusion controlled combustion processes and to emphasize the importance of considering temperature in analyzing the sooting tendency of fuels (22). The

work on pre-mixed flames was completed and a correlation developed between the critical sooting equivalence ratio of fuels and mixtures and a single property of the fuel, namely the "number of C-C bonds" (23). Work on diffusion flames also has largely been completed. The importance of temperature was particularly significant for this type of combustion process. The results of the program make it possible to determine from a fundamental knowledge of the pyrolysis kinetics of component fuels their tendency to soot under diffusion flame conditions (24,25).

The key to controlling soot formation irrespective of controlling the temperature is a knowledge of the mechanism of soot formation, but, perhaps, as important, also knowledge of the precursors that control the soot formation process. Thus during the period of this report, most attention had been directed towards this objective by the chemical sampling of "unique" inverse diffusion flames and making use of the chemical instrumentation available in the oxidation kinetics aspect of the program. The sampling for these flames was performed at a near sooting condition which was developed by nitrogen dilution of the flame (22).

All hydrocarbon fuels, except methane, tend to form so much soot in the standard co-flow laminar flame geometry employed that a near sooting flame is usually unattainable; with large dilution, most flames lift-off before soot formation can be eliminated. However, by simply interchanging the fuel and oxidizer streams and choosing the dilution of the streams appropriately, stable flames with no visible soot loading were readily attained. Measurements of temperature and intermediate hydrocarbon species for these so-called "inverse diffusion flames" (IDFs) of ethene, propene and 1-butene in near and slightly sooting conditions have been made. The effects of flame

temperature and fuel structure on these profiles have also been measured.

Of all the fuels tested in this aspect of the program, one ethene flame was sampled in detail and is considered as a base flame from which the effects of perturbations of the flame conditions can be observed. In all cases, the flame structure is kept similar by keeping the flame height and the parameter $S = X_{O_2} / [X_f(n+m/4)]$ constant. X_{O_2} and X_f are the oxygen and fuel inlet mole fractions, and n and m are the carbon and hydrogen number of the fuel (26). For a given fuel, by changing the O_2 and fuel concentrations together, flames of similar structure but uniformly higher temperatures are obtained so that the effects of increased temperature on intermediate hydrocarbon concentrations at fixed residence times (27) are observed.

Many of the original measurements were described in a previous annual report (28). Since this work has been completed and has appeared as a Ph.D. Thesis (29), it appears appropriate to discuss the inverse diffusion flame results with respect to the early work on normal diffusion flames because in this manner the application of this research approach is most readily seen.

Detailed results of tests performed with normal diffusion flames (NDF) have been reported extensively in the papers listed in the references. Earlier results on the inverse diffusion flames were reported in an annual report and the recent Ph.D. Thesis (29) mentioned. It should be noted, since the objectives of the two efforts were different that the same fuels were not studied in the two flames; the NDF study was of heavily sooting flames using high sooting tendency fuels, and the IDF study was of incipient sooting flames of lower sooting tendency fuels. Nevertheless, there are several comparisons of these drastically different flames which are very insightful.

The first comparison is that the inception of particles occurs only when

a critical temperature ($\sim 1300\text{K}$) is exceeded for both flame types. Some further insight was afforded by the IDF test, where it was observed that soot inception does not occur too far from the reaction zone. The unique geometry of the IDF allowed this important observation. These results suggest the importance of H atoms in soot formation.

The second group of comparisons, and perhaps the more important, is related to the concentrations of various intermediates that could be soot precursors. To more directly compare the concentrations, a histogram plot of several intermediate concentrations is shown in Figure 4 for all the flames (except methane) just prior to inception. Although the soot loading and fuel's temperature/time history are drastically different in the two flame geometries, a comparison of the chemical fields just prior to soot inception is revealing. The local temperature is approximately the same due to the critical inception temperature and allows a fair comparison of chemical fields. The subsequent soot loading, however, is quite different, and the differences in chemical fields are responsible.

A striking feature of Figure 4 is that di-acetylene has similar concentrations in all flames and vinyl-acetylene is only different in the butadiene NDF. In general, the concentrations of the three important stable C_4 species are similar regardless of the fuel, flame geometry or soot loading and indicate that the chemistry depicted for C_4 species by Frenklach, et al. (30) is a common feature. At first glance it might be thought that di-acetylene is the important precursor species for soot since its concentration is the same for all flames just prior to soot inception. However, it must be emphasized that the initial number density of soot particles formed is responsible for the soot formation rates observed in flames. If a specific

species controlled whether or not inception occurred and that species had similar concentrations in different flames (such as di-acetylene), the subsequent soot formation rates should be the same also. Based on this argument, di-acetylene is clearly not a controlling species since the soot formation rates in the flames are drastically different.

The explanation for di-acetylene being similar in all flames is that di-acetylene is closely tied to both acetylene concentrations and local temperature. In an ethene IDF test with argon to separate fuel concentration from temperature effects, it was observed that di-acetylene concentrations, unlike most other species, were closely tied to temperature and little affected by fuel concentration. Also, the ratio of di-acetylene to acetylene was observed to be very similar in all flames (implying that acetylene also has similar concentrations, which is to a large extent true). Modelling results (Singh and Kern (31) and Frenklach et al. (30)) demonstrate that, as observed in these flames, an equilibrium between acetylene and di-acetylene tends to be approached.

While the inception of soot in these flames is tied to the location of the 1300K isotherm, except for methane, the soot formation rates are related to the concentration field at inception. In particular, the aromatic content of the flames seems to scale with soot loading. In order to observe this result more closely, Figure 4 can be considered a plot of the fuel's sooting tendency as a function of the measured aromatic concentrations prior to soot inception. The sooting tendency is obtained from previous smoke height tests at a common inverse flame temperature of 4.32 (2315K). The results of both IDF and NDF tests indirectly confirm that the initial number density of soot particles which form scales with the aromatic content just prior to soot

inception. It is not surprising that the aromatic content is so important to the soot loading. What is unique is that the aromatic content does not determine whether or not inception will occur (provided a threshold of intermediate species concentrations exists). The results of the smoke height tests using mixtures of benzene and hexene are in agreement with these observations. Adding small amounts of benzene to hexene probably does not change the location of the soot inception point but increases the number density of particles formed there and therefore increases the sooting tendency proportionally. All details are in Ref. (29).

Why oxygen accelerates the sooting tendency of ethene and not propane under diffusion flame conditions has been an unresolved fundamental question for a long time. One could question the results of all co-flow experiments of either normal or inverse diffusion flames as due to leakage (diffusion) of oxygen across the central tube lip to the fuel side. Because of the importance of this point, an apparatus built under a previous sponsor support was integrated into this AFOSR effort. This apparatus was an opposed jet or counterflow diffusion flame system with laser diagnostics for the measurement of soot volume fractions and average particle size. This apparatus has a cylindrical fuel injector very similar to one initially developed by Tsuji (32). The detailed description of the particular device has appeared in the literature (29).

Initially small quantities of oxygen were added to ethene and propane and the soot volume fractions measured essentially at the same temperature by diluent control. The counterflow (CFDF) results (33) indicated, as this laboratory (34) and others (35) have shown on co-flow diffusion flames (CDF), that the sooting tendency of ethene increased substantially with oxygen

addition and that of propane decreased very slightly. To understand this result a chemical program for the pyrolysis of these fuels was run with trace amounts and without oxygen present. These results clearly illustrated the fact that small quantities of oxygen greatly increased the radical pool in the ethene case early in the pyrolysis stage and led to rapid fuel decay. In the case of propane there was no effect on the radical pool due to oxygen presence. The oxygen simply acted as a diluent. These results seem very reasonable in that the ethene molecule is tightly bound whereas propane has a weak C-C bond. Thus propane forms a radical pool readily and early in the pyrolysis process whether oxygen is present or not. The analytical results from the program indicated that any fuel which is tightly bound should be affected by the presence of O_2 . When the calculations were made for acetylene, indeed this statement was verified. Consequently, the proposal was made in the preceding section that these calculations be verified experimentally by studies in the flow reactor.

Thus, it is believed that the important question as to the effect of oxygen has been resolved. The intriguing question then arose as to what would occur as one continued to add oxygen to both of these fuels. Eventually the system would have to take on the characteristics of a pre-mixed flame. An effort to resolve this latter question was undertaken with both CDF and CFDF apparatus and the whole effort completed (36).

In the counterflow diffusion flames (CFDF's), the equivalence ratio (ϕ) of the fuel oxygen mixtures ranged from infinity to 2.60. As the results in Fig. 5 show, oxygen addition increased the soot formed in ethene flames as ϕ was decreased to about 6. Greater oxygen addition resulted in rapid reduction of soot loadings, and no soot was detected in flames with a $\phi < 3.0$. In

contrast to ethene, oxygen addition to propane CFDF's first decreased the soot loadings until a ϕ of about 6.0 was approached. The soot loadings then increased and subsequently decreased sharply with the peak occurring at a ϕ of 3.5, and no soot was present with $\phi < 2.60$.

In the regime of large oxygen addition the rapid increase followed by the sharp decrease in soot loadings in ethene and propane CFDF's can be explained on the basis of the formation of double flames in the reaction zone and changes in the aerodynamic and thermal structure of the flame. Double flames (an independent inner premixed flame and an outer diffusion flame) definitely exist in the frontal stagnation region for fuel/oxygen mixtures within the rich flammability limit (between 2.6-3.03 for propane and 4.84-5.61 for ethene on the CFDF burner). Moreover, Tsuji (32,37) has shown that a reaction zone inside the main diffusion flame is also present for mixtures outside the rich flammability limit. The outer flame is a source of heat and radicals to sustain the reactions in the inner zone.

As the fuel/oxygen mixture approaches the rich flammability ϕ , the inner reaction zone (which cannot yet exist as an independent premixed flame) becomes an increasing source of pyrolysis products which are ejected into a high temperature, relatively oxygen free region. This condition should lead to higher particle inception rates. Moreover, in the CFDF's the stagnation point is located further away from the burner, and this position change leads to a much longer soot residence time in the high temperature region and results in intense soot surface growth. In both ethene and propane CFDF's the maximum soot formation occurred at ϕ 's which were slightly greater than the ϕ 's at which premixed flames could be stabilized on the cylindrical burner. In the CDF's maximum soot emission occurred at the rich flammability limit for

propane, and for ethene flames peak soot emissions were observed slightly before the rich limit. Therefore, it is concluded that maximum soot formation in both CFDF's and CDF's occurs in an interacting double flame when the fuel/oxygen mixture is slightly outside the rich flammability limit.

Once the ϕ is less than the rich limit, the inner reaction zone becomes physically, chemically, and thermally separate from the outer diffusion flame. As in the pure pre-mixed flame studies, the dominance of oxidation reactions over pyrolysis processes reduces the concentrations of the soot precursors and results in lower soot formation. In the CFDF's, a dark zone between the soot and the outer violet zone appeared once the inner premixed flame was established. Moreover, the stagnation point moved outside the soot zone. This change not only reduces the residence time for the soot polymerization reactions, which results in lower particle inception rates, but also leads to oxidation (by hydroxyl radicals) of the soot particles, which are now convected towards the oxidizer. The change from peak soot formation/emission to no soot formed/emitted occurred in a very small range of ϕ 's on the CDF burner and a relatively larger range of ϕ 's in the CFDF burner and reflects the differences in the flame geometry and the greater heat losses in the water-cooled CFDF burner. These results resolve the supposed dilemma about oxygen effects on sooting tendencies of various fuels.

Since the smoke height test was considered a qualitative measurement, soot volume fraction was measured (38) by laser scattering/extinction; velocity and residence time information were obtained by laser-induced vaporization; temperature was measured in the soot-free region of the flame by thermocouples. The fuels tested in this manner were: butene, acetylene, butadiene and benzene. The results show that of all fuels tested, at a given

adiabatic flame temperature, benzene has the highest soot formation rate per unit volume and mass flow rate of fuel; butadiene, butene and acetylene follow in decreasing order. This finding holds even if the comparison were made with respect to the (radiatively corrected) measured average peak temperature in the control volume, instead of the calculated temperature. The measured soot formation rates are in agreement with qualitative indications obtained exclusively from smoke height tests and with purely pyrolytic studies reported in the literature. These results were the first quantitative confirmation of the controlling role of pyrolysis in the soot formation process. Furthermore, for a given fuel, nitrogen dilution decreases the maximum conversion of fuel into soot and the soot formation rates. This effect is attributed to a prevailing temperature decrease which causes a decrease in the pyrolysis rate and, in turn, in the soot formation rate.

The appearance of soot on the centerline of axisymmetric laminar diffusion flames of the same four fuels was studied by monitoring (i) the gas temperature by thermocouples; (ii) the soot particle field by laser scattering/extinction; (iii) the presence of polycyclic aromatic hydrocarbons (PAH) by laser-induced fluorescence (39). All but one flame were at the smoke height condition and were characterized by different levels of N_2 dilution aimed at controlling the temperature field.

It was observed that (i) soot nucleation occurs at the center; (ii) the soot onset on the centerline occurs when a characteristic temperature in the region is measured, regardless of fuel type or level of dilution; (iii) butene and benzene have similar fluorescence patterns, in contrast with premixed flame environments. These last two observations are consistent with the proposal that, though the extent of conversion of fuel into soot may

significantly change from fuel to fuel, there is a common mechanism of soot formation for all fuels. That a characteristic temperature could exist was a most important finding, and to explicitly determine this temperature (or temperature range) was the major effort in the current contract year.

The soot-onset point discussed above was measured by noting the first appearance of soot on the thermocouple as it moved along the centerline. It was realized that this point was not necessarily the true inception point since particles could reach the position by thermophoresis. As well, it was difficult for the experimenter to make the observation. Thus a unique approach was devised. In an overall view of soot formation (40), the principal investigator pointed out that sooting from a hydrocarbon diffusion flame could be eliminated by extensive dilution. Such flames appear blue in comparison to the bright orange of a non-diluted hydrocarbon flame. It was rationalized that if dilution was limited to the condition that the flame would just turn completely blue (specifically along the center streamline) then the temperature of the flame would be the inception temperature of the soot for that particular fuel. The procedure was to establish a 1 cm high luminous diffusion flame for each fuel, then to dilute with nitrogen until the tip of the flame turned blue. Then the centerline temperature profile was measured. The value at the observed flame height led to the latest results obtained for various fuels, as shown in the following table.

<u>Fuel</u>	<u>Inception Temperature°K</u>
Acetylene	1665
Allene	1586
Ethene	1700
Benzene	1580
1,3 Butadiene	1650
2-Butene	1684
Toluene	1570

There is about 150 K spread in the data. Most interesting is the observation that the temperature variation is oriented so that the least sooting fuel (ethene) has the highest temperature and the most heavily sooting fuel (toluene) has the lowest. Obviously dilution affects the flame somewhat. The inception point under non-diluted conditions thus is close to 1700.

There have been some published results (41,42) that nitrogen dilution was more of a concentration effect than temperature effect. The manner in which investigators conducted their experiments could have affected their conclusions. Since it could be the soot observation technique that causes the disparity between the results of those investigators' and the early results obtained in this program, it became apparent that an adoption of the completely diluted flame to eliminate soot which was described above could be a good technique to resolve the question. In the experiments which were performed, Ar and CO₂ were used as diluents, as well as N₂. To achieve the blue flame with Ar requires greater dilution than N₂. Likewise CO₂ requires less. If dilution were an important effect a different inception temperature would be found for each diluent and fuel. Fig. 6 reveals that within experimental error for four fuels evaluated the same incipient temperature is obtained.

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FIGURES

- Figure 1. The Princeton University high temperature, adiabatic, turbulent plug flow, chemical kinetic reactor.
- Figure 2. Time histories of major aromatic intermediates in the flow reactor oxidation of 1-methyl naphthalene $\phi = 0.47$.
- Figure 3. Proposed mechanism of 1-methyl naphthalene oxidation.
- Figure 4. Intermediates in near sooting and smoke point conditions of normal and inverse diffusion flames.
- Figure 5. Peak extinction coefficient (1/cm) vs. equivalence ratio of the fuel/oxygen mixture in propane and ethene CFD's.
- Figure 6. Soot inception temperatures of various fuels with various diluents. $Z/H = 1$ designates temperature at flame tip.
- Figure 7. General mechanisms for soot formation.

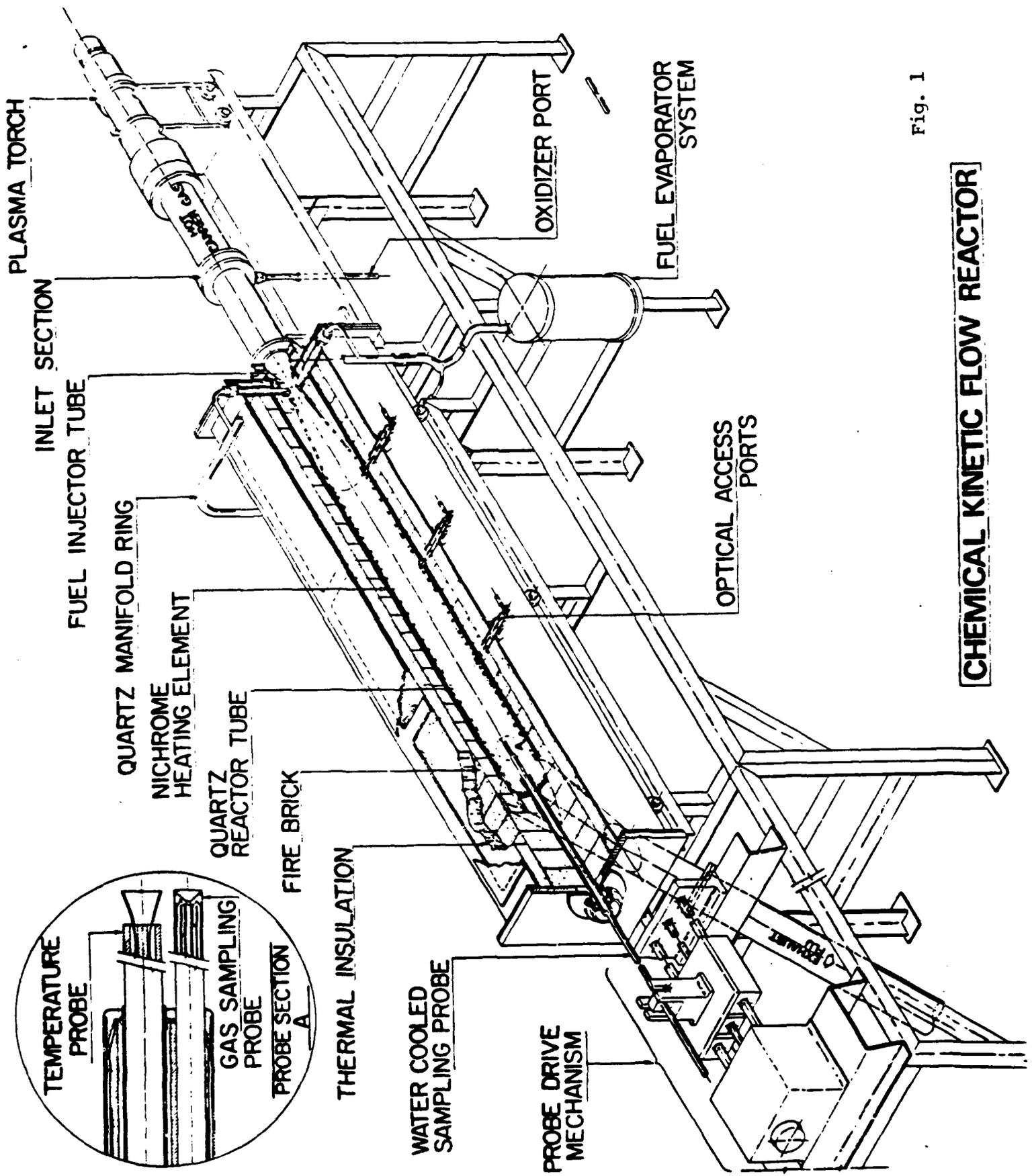


Fig. 1

CHEMICAL KINETIC FLOW REACTOR

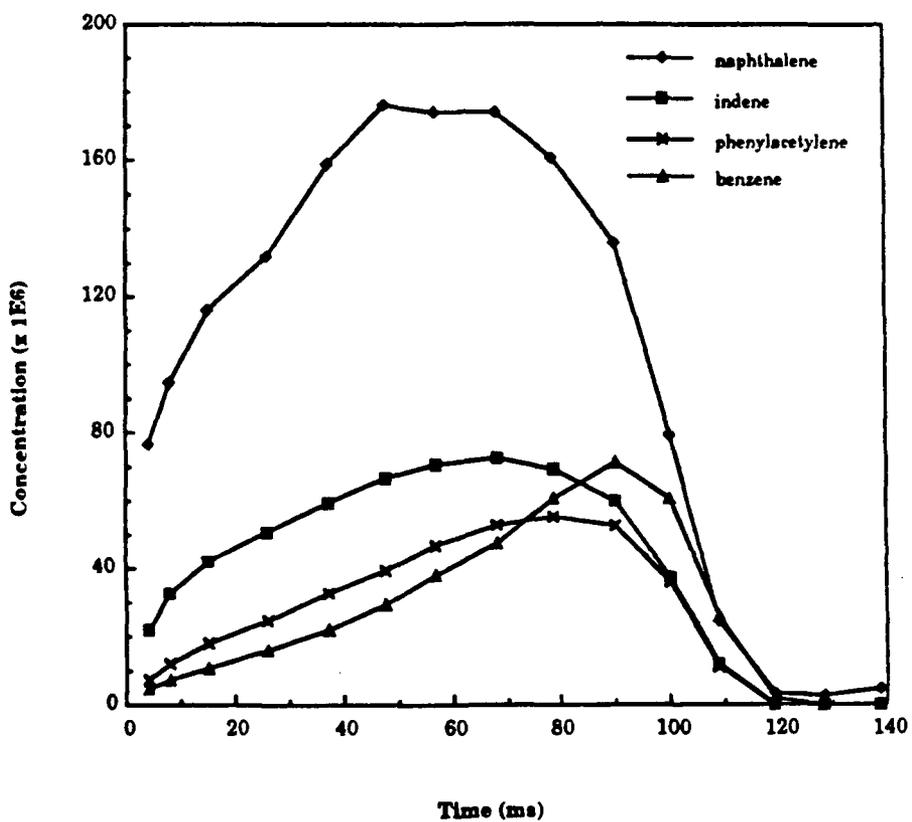
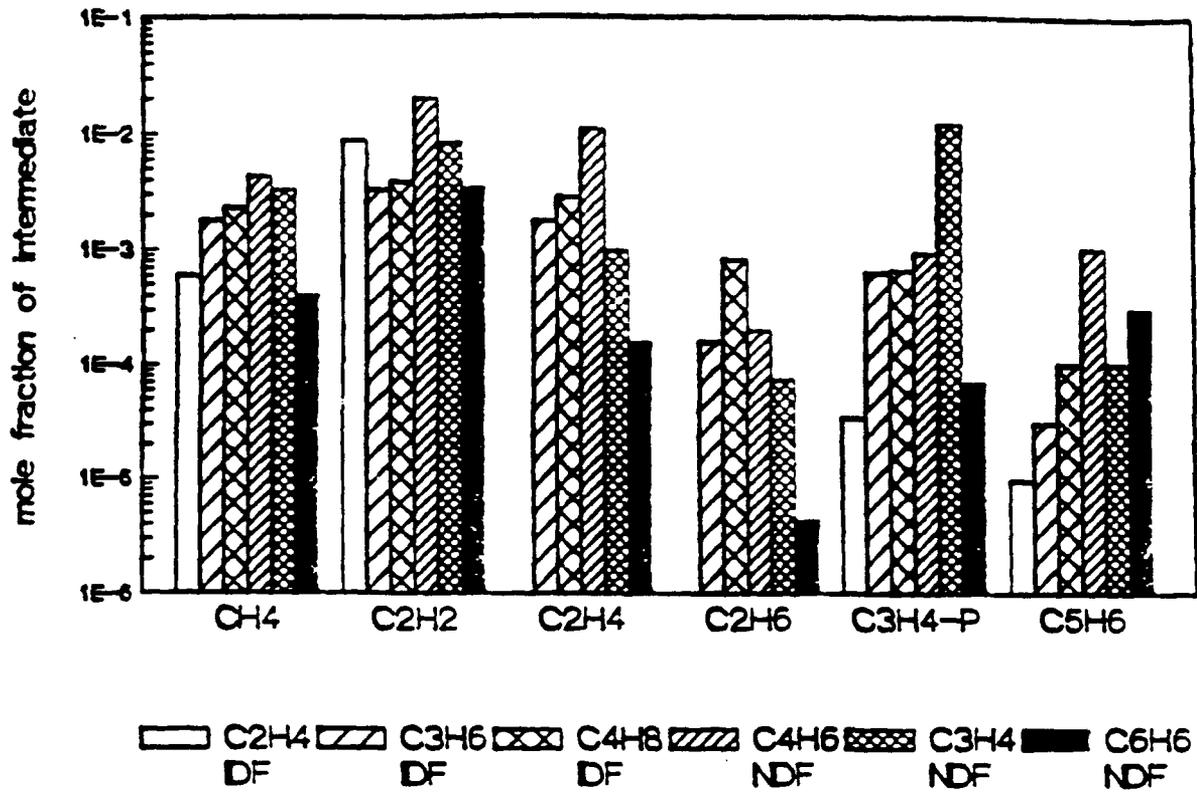


Fig. 2. Time histories of major aromatic intermediates in the flow reactor oxidation of 1-methylnaphthalene, $\phi = 0.47$.

IDFs and NDFs
near sooting and smoke point



IDFs and NDFs
near sooting and smoke point

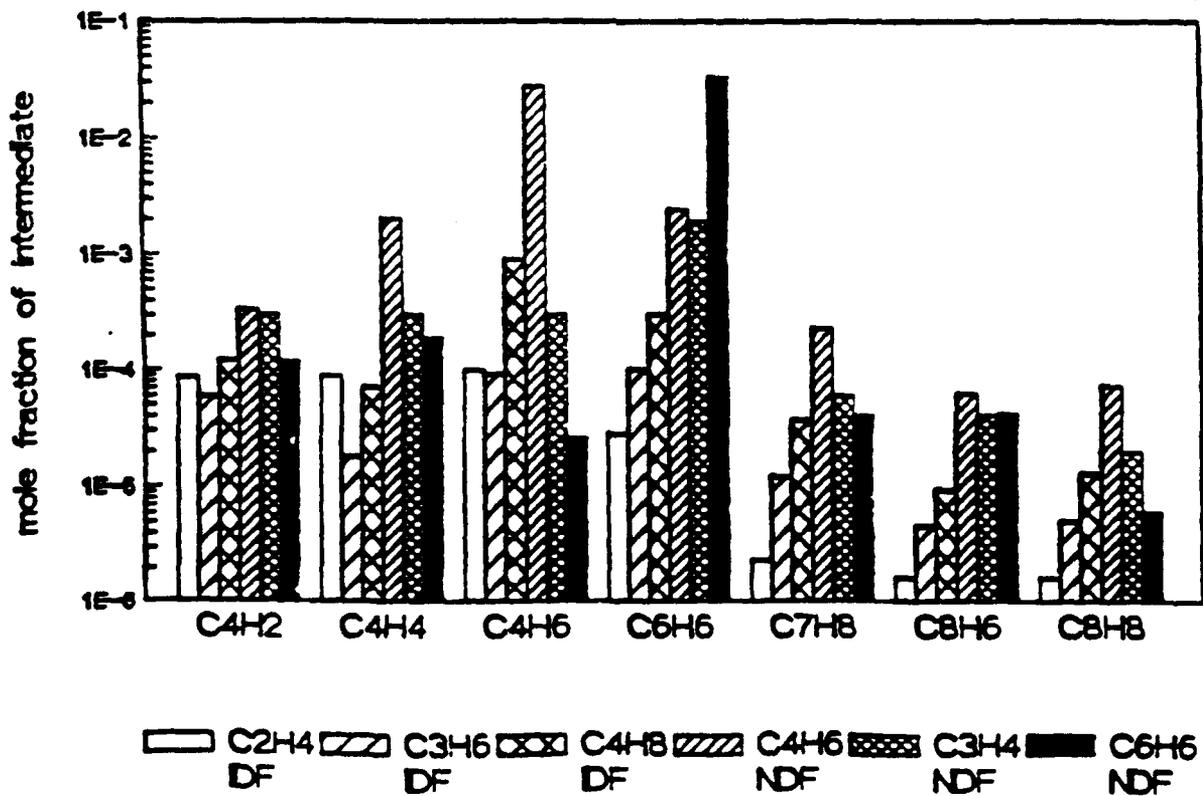


Fig. 4

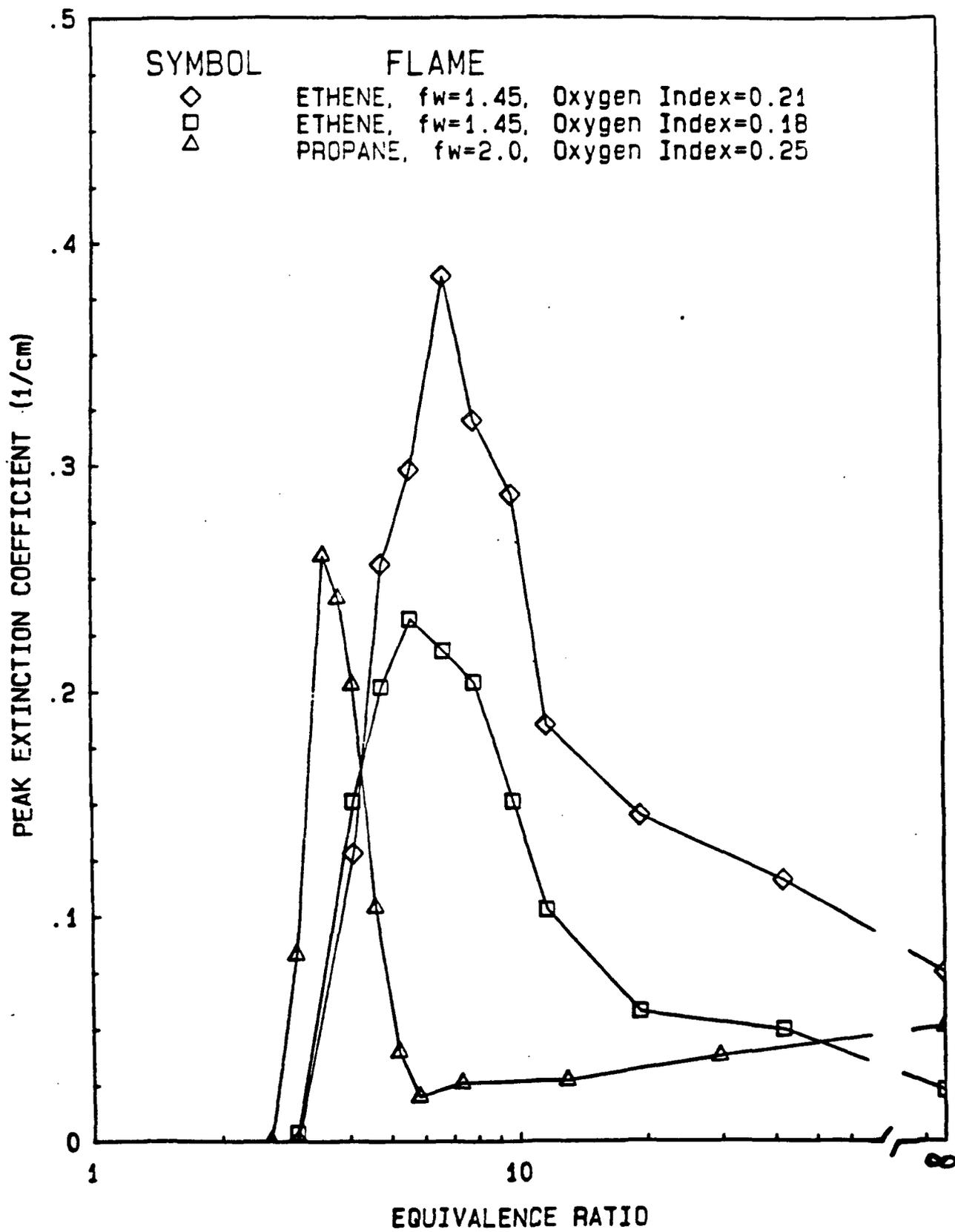


Fig. 5

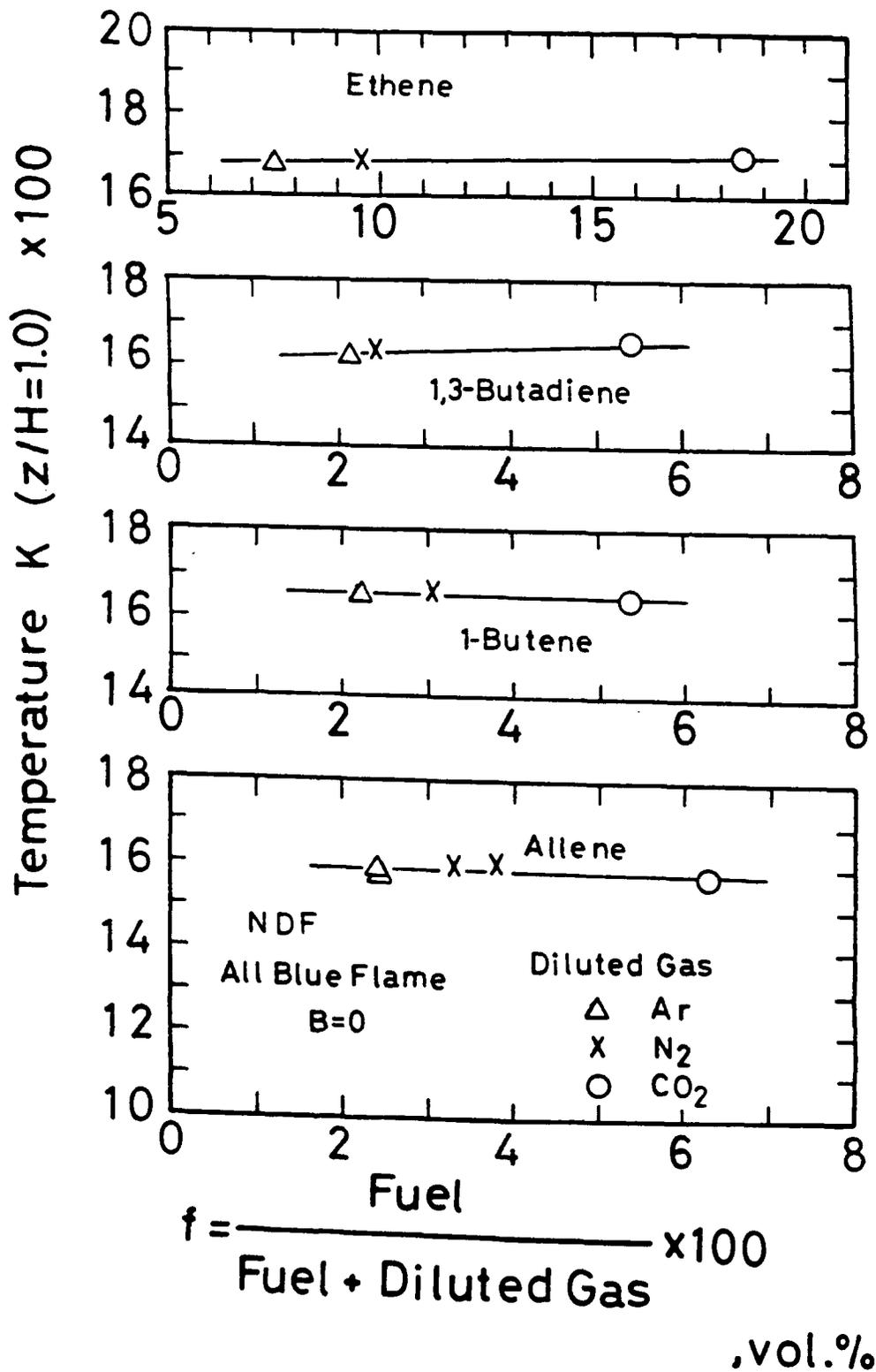


Fig. 6

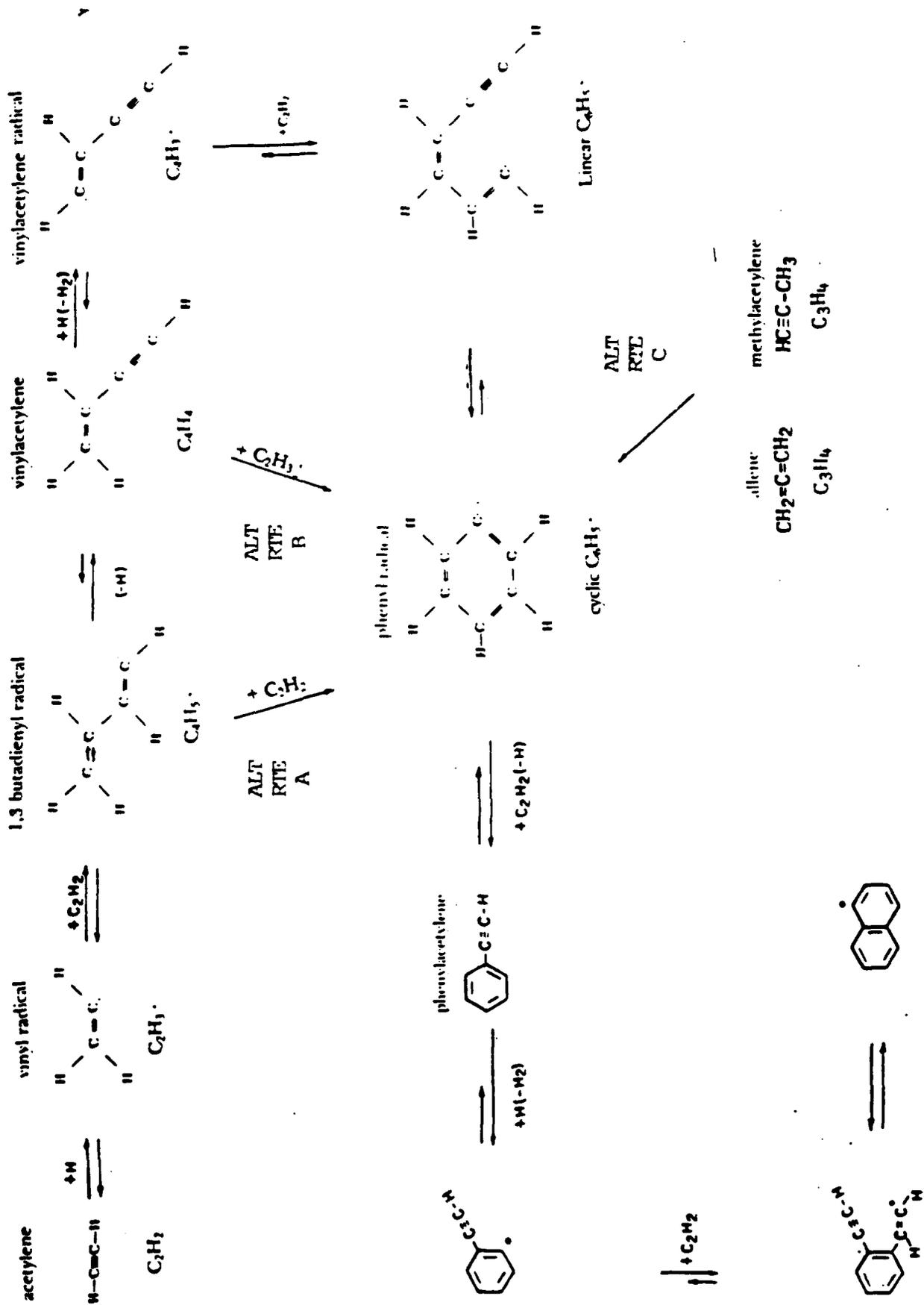
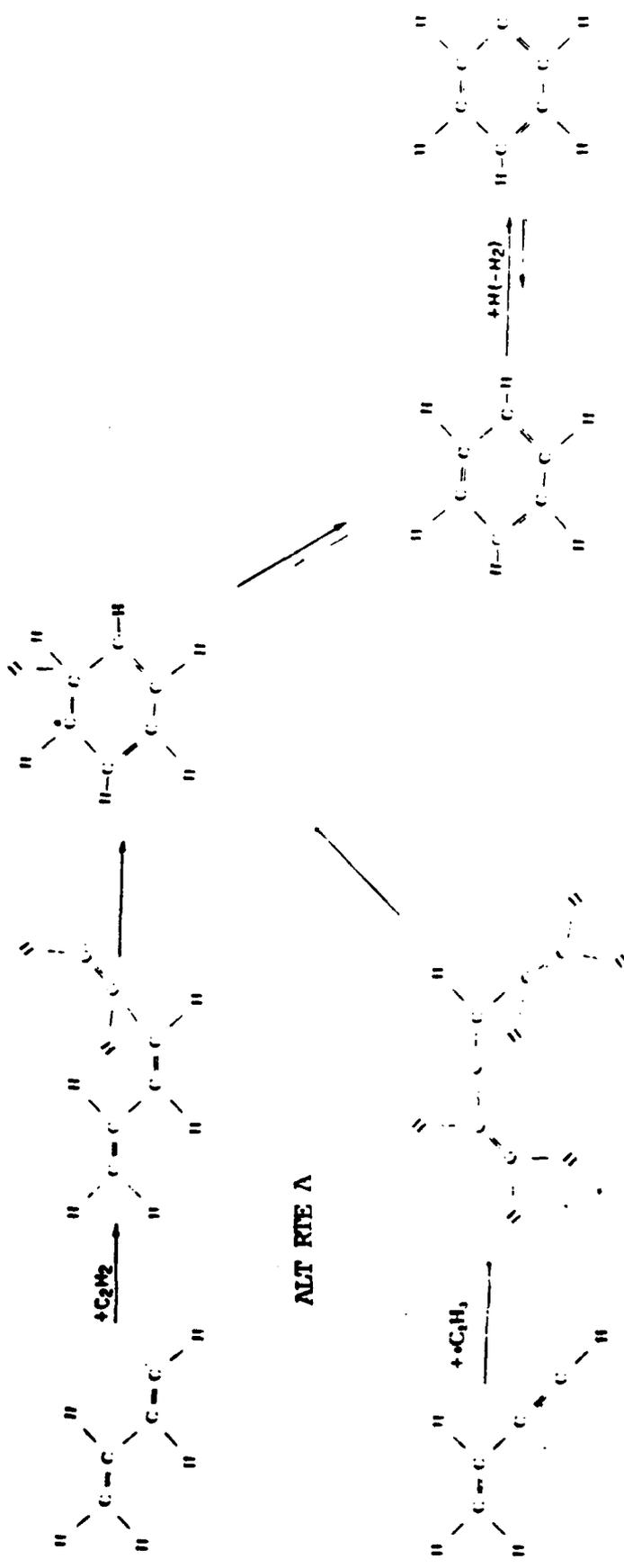


Fig. 7a



ALT RTE A

ALT RTE B

ALT RTE C

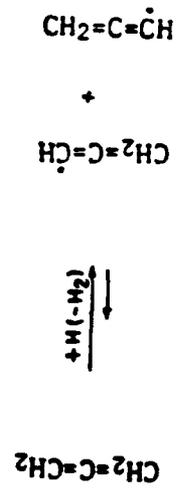


Fig. 7b

IV. PUBLICATIONS DURING CONTRACT PERIOD

K. Brezinsky, H.S. Hura, and I. Glassman, "Oxidation/Pyrolysis Chemistry as Related to Fuel Sooting Tendencies," *Energy and Fuels* 2, 487, 1988.

J.L. Emdee, K. Brezinsky, and I. Glassman, "Oxidation of Para-Xylene at 1160-1183 K," *Eastern States Section, Combustion Institute Meeting, Extended Abstract #19*, 1988.

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"Soot Formation in Combustion Processes," 22nd Symp. (Int'l.) on Combustion, The Combustion Institute, Pittsburgh, 1988, p. 295.

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J.L. Emdee, K. Brezinsky, and I. Glassman, "The High Temperature Oxidation of Toluene: Experiment and Model Compared", *Eastern States Section/Combustion Institute Meeting, Extended Abstract #4*, 1990.

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K. Saito, G. Sidebotham, and I. Glassman, "Pyrolysis Zone Structure of Allene, 1,3 Butadiene and Benzene Smoke Point Flames", accepted for publication in *Comb. Sci. and Tech.*, 1991.

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F.N. Egolfopoulos, K. Brezinsky, J.L. Emdee, C.K. Law, and I. Glassman, "Benzene/Toluene Oxidation Models: Studies Based on Flow Reactor and Laminar Flame Speed Data", *ACS Symp. on Combustion Chemistry*, Aug. 1991.

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J.L. Emdee, K. Brezinsky, and I. Glassman, "A Kinetic Model for the Oxidation of Toluene Near 1200 K", accepted for publication, Journal of Physical Chemistry, 1991.

C.R. Shaddix, K. Brezinsky, and I. Glassman, "Oxidation of 1-Methylnaphthalene", accepted for presentation/publication, Twenty-Fourth International Symposium on Combustion, 1991.

V. PROFESSIONAL PERSONNEL AND GRADUATE STUDENTS THESES

Staff

Prof. I. Glassman, Robt. H. Goddard Professor
Dr. K. Brezinsky, Research Scientist
Prof. O. Nishida, Visiting Scientist
Mr. J.A. Sivo, Technical Associate

Graduate Students

Dr. G. Sidebotham (currently Asst. Prof., Cooper Union)
Dr. J. Emdee (currently at Aerospace Corp.)
Dr. H. Hura (currently at AVCO Everett)
Mr. C.A. Smith (current at G.E. Cincinnati)
Mr. C. Shaddix (completing Ph.D., August 1992)

THESES

G.W. Sidebotham, "An Inverse Co-Flow Approach to Sooting Laminar Diffusion Flames", Dept. of Mech. and Aero. Eng., Princeton University Ph.D. Thesis, 1988.

H.S. Hura, "A Study of the Fuel Oxygen Effect on Soot Formation in Counterflow Diffusion Flames", Dept. of Mech. and Aero. Eng., Princeton University Ph.D. Thesis, 1988.

C.A. Smith, "On Incipient Particle Formation in Laminar Diffusion Flames", Dept. of Mech. and Aero. Eng., Princeton University Ph.D. Thesis, 1990.

J.L. Emdee, "An Experimental and Modeling Study of the High Temperature Oxidation of the Xylenes", Dept. of Mech. and Aero. Eng., Princeton University Ph.D. Thesis, 1991.

VI. PRESENTATIONS - SEMINARS

I. GLASSMAN

"Soot Formation in Combustion Processes", Invited Lecture, 22nd Symp. (Int'l.) on Combustion, Seattle, WA, August 18, 1988.

"Comparison of Fuel Pyrolysis Trends on Soot Formation in Premixed and Diffusion Flame", workshop on 'Current Problems in Soot Formation During Combustion, Goetingen, Germany, March 29, 1989.

"Soot Formation of High Density Fuels", invited presentation, ONR Meeting, Memphis, TN, Feb. 19, 1991.

"The Oxidation of Cyclopentadiene", Basic Energy Sciences, DOE, Contractors Meeting, Lake Geneva, MI, May 30, 1991.

"What are the Critical Out-of-Engine Soot Measurements Needed", Army Research Office Particulates Conference, Boulder, CO, June 13, 1991.

KENNETH BREZINSKY

"Oxidation Chemistry of Aromatics," Invited Talk, New Jersey Institute of Technology, Newark, N.J., October 18, 1988.

"Fuels Combustion Research", AFOSR Contractors Meeting in Propulsion, Atlanta, Georgia, June 15, 1990.

"Chemical and Physical Aspects of Gasoline Combustion", BP Research Centre, Sunbury, United Kingdom, July 3, 1990.

"The High Temperature Oxidation of Toluene: Experiment and Model Compared", Paper #4, Eastern States Section/The Combustion Institute Meeting, Orlando, Florida, December 3, 1990.

"Fuels Deposit Formation and Supercritical Fluids", A.F.O.S.R., Bolling Air Force Base, Washington, D.C., February 20, 1991.

"Reactor Designs for Studies of Fuels Deposit Formation", Wright Research and Development Center, Wright-Patterson AFB, Dayton, Ohio, March 4, 1991.

J.L. EMDEE

"Oxidation of Para-Xylene at 1160-1183K", Eastern States Section/The Combustion Institute Meeting, Dec. 1988.

"Evidence of Side Chain Interaction in the Oxidation of O-Xylene", Eastern States Section/The Combustion Institute Meeting, Nov. 1989, Albany, NY.

"Oxidation of O-Xylene", 23rd Symp. (Int'l.) on Combustion, Orleans, France, Aug. 1990.

C. SHADDIX

"The High Temperature Oxidation of 1-Methylnaphthalene", 2nd Int'l. Congress on Toxic Combustion By-Products, Salt Lake City, UT, March, 1991.

C.A. SMITH

"Preliminary Results on Incipient Particle Formation in Laminar Diffusion Flames", Eastern States Section/The Combustion Institute Meeting, Albany, NY, October, 1989.

VII. SIGNIFICANT INTERACTIONS

With respect to the work on soot formation processes there have been significant interactions with Wright-Patterson AFB, ONR, OAR, McDonnell-Douglas TRW, UTRC, and NIST. Prof. Glassman's review paper presented at the 22nd Symposium on Combustion attracted world-wide attention and well over 200 requests for reprints were received.

With respect to the work on hydrocarbon oxidation processes, there have been significant interactions with BP, Mobil, TRW, Exxon, and UTRC.

Contacts in both areas were with many other AFOSR contractors.