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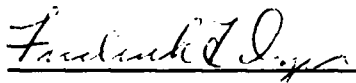
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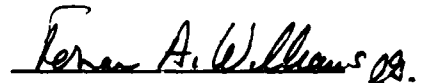
FUELS COMBUSTION RESEARCH



Frederick L. Dryer
Professor
Principal Investigator



Irvin Glassman
Professor
Principal Investigator



Forman A. Williams
Professor
Principal Investigator

School of Engineering and Applied Science
Department of Mechanical and Aerospace Engineering
PRINCETON UNIVERSITY
Princeton, New Jersey 08544

30 November 1988

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SUMMARY

Studies of near and slightly sooting inverse and normal co-flow diffusion flames determined aromatics as the key intermediates to soot formation. The extent of aromatic formation correlated with the earlier Princeton smoke height test results. The effect of oxygen addition to tightly bound fuels (ethene, ethyne and benzene) in diffusion flames was found to accelerate the pyrolysis and thus the sooting tendency, but not to affect other fuels in the temperature range of soot formation.

Flow reactor experiments determined oxidation kinetic results for the mono and dialkylated aromatic components of jet fuels. Succinctly, it was found that the alkyl chains are attached initially and in the case of dialkylated compounds not simultaneously. Mechanisms have been presented.

Results on boron slurry droplet combustion were obtained and provided a basis for calculating when droplet disruption would occur. Questions with respect to boron cloud combustion addressed mechanisms of ignition and combustion in the regime of chemical kinetic control.

Free droplet experiments have shown that the solid particles within commercial boron slurry droplets concentrated as the liquid phase was preferentially vaporized, that at some stage the droplet diameter variation with time departed from the classical d^2 law and that, after some further burning, the droplet underwent disruptive combustion. The stabilizing surfactants in the slurries were found to be responsible for the disruptive combustion.

I. RESEARCH OBJECTIVES

Present and anticipated variations in fuels and trends toward high performance propellants require greater understanding of the chemical phenomena associated with the combustion aspects of the various propulsion systems of current and future interest to the Air Force. Under AFOSR an integrated, fundamental program on fuel research was established at Princeton. Emphasis and research objectives during the contract period were directed towards understanding soot formation and destruction processes; on related pyrolysis and oxidation studies of hydrocarbons, particularly the various types of aromatics that aggravate soot conditions and are the components of heavy fuels, and mastering high energy density boron and slurry combustion problems.

Subsequent sections of this report detail the progress made during the contract period and the publications which have emanated from the work.

II. PROGRESS

A. Introduction

This progress section will not give an extensive review and history of the efforts previous to this contract period, nor dwell on the more than hundred publications which have been a result of continued AFOSR support. Many of these publications are identified in the reference section of this document. But, for clarity sake, some review material will be repeated.

In the following sections the principal tasks of the program discussed are:

1. aromatic pyrolysis and oxidation
2. soot formation and destruction mechanisms
3. high energy density (boron) slurry vaporization/combustion processes

B. The Oxidation and Pyrolysis of Aromatic Hydrocarbons

The objective on this aspect of the fuels research program was to challenge what most thought to be a most complex area of chemical kinetics, that is, the oxidation process of the aromatic hydrocarbons. The early 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]. Most of the very early published work on aromatics 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 opened 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 had been to elucidate the mechanisms of the oxidation of all types of aromatics 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 in the following paragraphs, great progress has been made during the contract period on understanding of the oxidation of mono and dialkylated aromatics after the earlier success of the study of benzene

oxidation. This success was 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.

During the initial period the contract investigations (6-8) of the high temperature (1000-1200K) oxidation of the mono-alkylated fuels methyl, ethyl and n-propyl benzene in the flow reactor were undertaken. The results 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).

Latter efforts then concentrated on the multi-substituted aromatics with particular attention given to para xylene(16). Most of the oxidation experiments on p-xylene were conducted in the range of 1163-1183K at a mixture ratio that was essentially stoichiometric. Data taken indicated that the stoichiometry did not affect the oxidation mechanism noticeably.

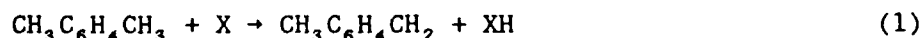
The major species detected during the experiments were toluene, benzene, p-tolualdehyde, p-ethyltoluene, CO, and fuel (Fig. 2). The major aliphatic found was methane. The concentration of CO increased throughout the oxidation process, hence, no CO₂ was formed and the experiments were essentially isothermal.

During the oxidation process, the xylene fuel decayed linearly and suggested a zero order decomposition. This result appeared to be caused by the p-methylbenzyl radical ($\text{CH}_3\text{C}_6\text{H}_4\text{CH}_2$). The intermediates formed during the oxidation indicated that this radical could have been present in large amounts due to resonant stability. Consider the formation of ethyltoluene. The most likely means to form ethyltoluene would be by the reaction between methylbenzyl and a methyl radical (the methyl would come from a side chain displacement by hydrogen). For the radical-radical reaction to be significant, relatively large amounts of methylbenzyl and methyl would have had to be present. The stability of methyl is well known. It was thus postulated that methylbenzyl is resonantly stabilized, similar to the benzyl radical ($\text{C}_6\text{H}_5\text{CH}_2$), and hence allowed it to form and remain in relatively large concentrations for a radical. Further support of this concept would be the presence of large aromatics such as 1,2-di-(4-tolyl) ethane which could be formed by the dimerization of two methyl-benzyl radicals. The positive

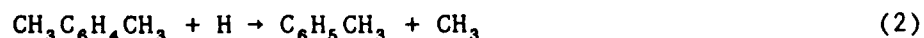
identification of this species is currently being investigated through the use of mass spectrometry.

In order to explain the linear fuel decay one should note that the sampling probe quenched the sample at 70C so that unstable species quickly recombined to form stable species. Thus if methylbenzyl were sampled, it would most likely recombine with any hydrogen or abstract hydrogen from other species and be detected as xylene. This effect could explain the apparent linear rate of fuel decay seen in the data. This hypothesis is being verified through estimation of the methylbenzyl radical concentration. Previous oxidation experiments of toluene ($C_6H_5CH_3$) in the reactor also produced a linear fuel decay and its benzyl radical was estimated to achieve relatively high concentrations.

The proposed oxidation mechanism of p-xylene involves the oxidation of one side chain at a time before the ring is broken in a manner not unlike the oxidation of the single side chain species, toluene. The major reaction route is the abstraction of the side chain hydrogen by a radical (X)



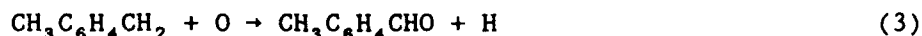
Reaction (1) has been observed by other investigators to dominate over addition of X at the temperature of this study. Trace amounts of dimethylphenol were detected though, probably due to the addition of O atom to the ring. Competing with Reaction 1, but less likely, is the displacement of the methyl group by hydrogen



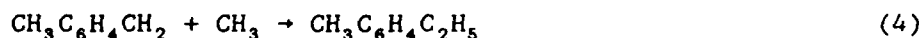
which has also been documented. This postulate is supported by the early appearance of large amounts of toluene and, as discussed earlier, the presence of ethyltoluene. Detailed experimentation has revealed that abstraction

accounts for about 75% of the xylene decay, displacement about 20% and homolysis about 5%.

The methylbenzyl subsequently reacts with O atom to form tolualdehyde, another major intermediate,

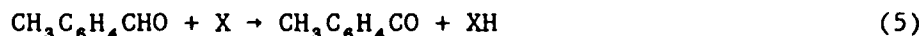


or ethyltoluene



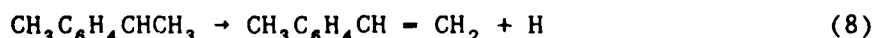
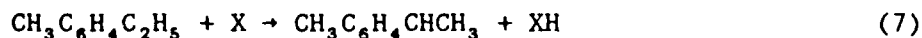
The methylbenzyl can also dimerize, as noted, but this step is not a significant reaction route.

The fate of the tolualdehyde is most likely abstraction of the formyl H and the decomposition to CO and the tolyl radical



This route is supported by the presence of early CO continuing throughout the oxidation from the beginning. The tolyl radical probably abstracts an H (e.g. from the fuel) and oxidizes as toluene since no aromatic ring fragments which contain the extra methyl group are detected.

Small amounts of p-methylstyrene were detected and are believed to come from the decomposition of the ethyltoluene via the abstraction of the benzylic hydrogen



Similar to Reaction (2), the ethyltoluene can also have the ethyl group displaced by a hydrogen. The fate of the methylstyrene is probably displacement of the ethenyl group again leading to the tolyl radical.

The side chain of the toluene formed then oxidizes in a similar manner as

the xylene until the phenyl radical (C_6H_5) is formed. As shown in earlier work (9) this radical oxidizes to cyclopentadiene which breaks down into the aliphatics.

So, as can be seen by the suggested mechanism, it is believed that p-xylene oxidizes one side chain at a time and leads to formation of CO before the aromatic ring breaks up and the subsequent formation of toluene. The trend the mechanism suggests is supported by the experimental data obtained.

C. Soot Formation and Destruction Process

Extensive progress and understanding of soot processes have developed. These 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 (18). 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" (19). 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 (20,21).

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 current contract period, most attention was directed towards this objective by chemical sampling "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 is developed by nitrogen dilution of the flame (18).

All hydrocarbon fuels, except methane, tended to form so much soot in the standard co-flow laminar flame geometry employed that a near sooting flame was usually unattainable; with large dilution, most flames lifted 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.

The ready achievement of an inverse diffusion flame measurement makes a description of the experimental apparatus worthwhile. The geometry of the burner was similar to that of previous investigations on "normal diffusion flames" (NDFs) and consisted of a 1 cm diameter stainless steel central tube and an 8 cm outer shroud. The oxidizer was a controllable mixture of O_2 and N_2 and flows through the central tube. The fuel flows in the outer stream and was heavily diluted with N_2 . The inlet velocities of the two streams were always comparable.

The system was enclosed by a plexiglass chimney with mounted sampling probes and thermocouples fixed with respect to the chimney. The system was sealed to prevent ambient air contamination of the fuel. The entire chimney assembly was movable vertically and the probes were mounted on vernier scales

so that profiles both axially (by moving the chimney) and radially were possible.

Gaseous samples were taken using an uncooled quartz micro-probe with an orifice of roughly 75 micrometers. The probe was vertical in the flame environment, roughly parallel to the streamlines. Samples were expanded from the flame to approximately 100 torr and subsequently compressed to 1 atmosphere for analysis using an HP-5840 Gas Chromatograph employing an FID. The GC/MS system was used to identify some unknown species. Some measurements of the permanent gases O_2 , N_2 , CO and CO_2 were made with a Varian 920 GC employing a TCD. H_2 concentrations were not measured.

Temperature measurements were made with a 6% Rh-Pt/30% Rh-Pt thermocouple with a 0.002 inch wire and coated with quartz to a diameter of 0.004 inches to prevent catalytic effects. No corrections for conduction or radiation were made.

Of all the fuels tested, 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 (22). For a given fuel, by changing the O_2 and fuel concentrations together, flames of similar structure but uniformly higher temperatures were obtained so that the effects of increased temperature on intermediate hydrocarbon concentrations at fixed residence times (23) were observed.

Many of the original measurements were described in a previous annual report (24). Since most of this work is nearly completed and has appeared as

a Ph.D. Thesis (25), 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 (25) 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 suggested the importance of H atoms in soot formation.

The second group of comparisons, and perhaps the more important, was 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 3 for all the flame (except methane) just prior to inception. Although the soot loading and fuel's temperature/time history were drastically different in the two flame geometries, a comparison of the chemical fields just prior to soot inception

was revealing. The local temperature was approximately the same due to the critical inception temperature and allowed a fair comparison of chemical fields. The subsequent soot loading, however, was quite different and the differences in chemical fields are responsible.

A striking feature of Figure 3 is that di-acetylene had 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 were similar regardless of the fuel, flame geometry or soot loading and indicated that the chemistry depicted for C_4 species by Frenklach, et al. (26) was a common feature. At first glance it might be thought that di-acetylene is the important precursor species for soot since its concentration was the same for all flames just prior to soot inception. However, it must be emphasized that the initial number density of soot particles formed was responsible for the soot formation rates observed in flames. If a specific specie controlled whether or not inception occurred, and that specie 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 was clearly not a controlling specie since the soot formation rates in the flames are drastically different.

The explanation for di-acetylene being similar in all flames was that di-acetylene was 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 was to a large extent true). Modelling results (Singh and Kern (27) and Frenklach et al. (26)) demonstrated that, as observed in these flames, an equilibrium between acetylene and di-acetylene was approached.

While the inception of soot was tied to the location of the 1300K isotherm, except for methane, the soot formation rates were related to the concentration field at inception. In particular, the aromatic content of the flames seemed to scale with soot loading. In order to observe this result more closely, Figure 3 is essentially then a plot of the fuel's sooting tendency as a function of the measured aromatic concentrations prior to soot inception. The sooting tendency was 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 confirmed that the initial number density of soot particles which formed scales with the aromatic content just prior to soot inception. It was not surprising that the aromatic content was so important to the soot loading. What was unique is that the aromatic content does not determine whether or not inception will occur (provided a threshold of intermediates specie concentrations exists). The results of the smoke height tests using mixtures of benzene and hexene were in agreement with these observations. Adding small amounts of benzene to hexene probably did not change the location of the soot inception point, but increased the number density of particles formed there and therefore increased the sooting tendency proportionally. All details are in Ref. (25).

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 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 the latter phase of 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 (28). 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 (29) indicated as this laboratory (30) and others (31) 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 undertaken 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 seemed very reasonable in that the ethene molecule was tightly bound whereas propane had a weak C-C bond. Thus propane formed a radical pool readily and early in the pyrolysis process whether oxygen was present or not. The analytical results from the program indicated that any fuel which was tightly bound should be affected by the presence of O_2 . When the calculations were made for

acetylene, indeed this statement was verified.

Thus, 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 the current contract (32).

In the counterflow diffusion flames (CFDF's) established, the equivalence ratio (ϕ) of the fuel oxygen mixtures ranged from infinity to 2.60. As the results in Fig. 4 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 an ϕ of about 6.0. The soot loadings then increased and subsequently decreased sharply with the peak occurring at an 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 could 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 existed 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 (28,33) had shown that a reaction zone inside the main diffusion flame is also present for mixtures outside the rich flammability limit. The outer flame was a source of heat and

radicals to sustain the reactions in the inner zone.

As the fuel/oxygen mixture approached the rich flammability ϕ , the inner reaction zone (which cannot yet exist as an independent premixed flame) became an increasing source of pyrolysis products which were ejected into a high temperature relatively oxygen free region. This condition should have led to higher particle inception rates. Moreover, in the CFDF's the stagnation point was located further away from the burner and this position change led to a much longer soot residence time in the high temperature region and resulted 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 was concluded that maximum soot formation in both CFDF's and CDF's occurred in an interacting double flame when the fuel/oxygen mixture was slightly outside the rich flammability limit.

Once the ϕ was less than the rich limit, the inner reaction zone became 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 reduced the concentrations of the soot precursors and resulted 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 reduced the residence time for the soot polymerization reactions which resulted in lower particle inception rates, but also led to

oxidation (by hydroxyl radicals) of the soot particles which were 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 reflected the differences in the flame geometry and the greater heat losses in the water-cooled CFDF burner.

These results have resolved the supposed dilemma about oxygen effects on sooting tendencies of various fuels.

D. High Energy Density (Boron) Slurry Vaporization/Combustion Processes

The potential advantages of boron as a high energy density fuel for use in volume-limited air breathing combustion systems had stimulated numerous research and development studies to address the three principal issues which must be solved: 1) developing a means to simplify storage and delivery of the fuel to the combustion environment; 2) improve the ability to ignite boron fuels; 3) obtain full condensation of the combustion products so that the largest amount of energy is extracted from the combustion.

1. Combustion of Boron Suspensions

This part of the overall contract effort was initiated by Prof. Williams and his colleagues because realization of improved performance was hampered by difficulties in achieving efficient combustion of boron. Problems in combustion of boron slurry droplets and of boron clouds were addressed by both theory and experiment. The research on slurry droplets focused on burning histories and on providing a basis for calculating when droplet disruption will occur, since disruption enhanced performance by reducing burning times. The research on cloud combustion addressed mechanisms of ignition and combustion in the regime of chemical-kinetic control, since fine particles

were known to burn more slowly than was predicted by analyses that assume diffusion control. The objective was to obtain improved understanding of the combustion that may suggest practical methods for increasing performance by reducing burning times.

The project had begun by taking a new look at the overall process of boron particle combustion (34). In this theoretical study the combustion of boron was considered from both physical and chemical points of view. The overall combustion process was separated into an ignition phase, during which the particle is covered by a layer of boron oxide, and a clean-particle burning phase. It was inferred that, contrary to earlier accepted ideas, during the ignition phase boron oxide production results from boron diffusion across the oxide layer, rather than by oxygen diffusion. During the clean-particle burning phase, boron oxidation was found to be similar to that of carbon. The chemistry of boron oxide production during this phase and the regions of kinetic and diffusion control of the burning rate were delineated and provided the starting point for the rest of the research.

Attention was next turned to problems in the combustion of slurry droplets. Matched asymptotic expansions in a parameter representing the ratio of the energy required for liquid heating to that required for liquid vaporization were applied to slurry-droplet combustion for solid loadings sufficiently large that the droplet diameter remains approximately constant (35,36). Subsequently the same kind of analysis was extended to smaller solid loadings for which the droplet diameter decreased with time during part of the combustion history, and implications concerning burning of pure liquid droplets were drawn (36,37). These theoretical investigations, which identified conditions under which a d -cube law replaces the familiar d -square

law, as well as conditions under which the average droplet temperature decreased rather than increasing during burning, are all contained in a Ph.D. thesis (36).

Single fiber-support slurry droplets composed of boron in JP-10 were ignited and burned in room-temperature air in an effort to test these theoretical predictions (36,38). Initial droplet diameters ranged from 1.2 to 3.0 mm and initial boron weight fractions f from 0 to 0.7 in these studies. It was observed that although the liquid fuel apparently burns completely, the boron did not ignite under these experimental conditions. For the pure liquid the combustion was observed to be smooth with a measured burning-rate constant of $0.43 \text{ mm}^2/\text{s}$. At low f there was periodic swelling of the droplet with mildly disruptive emission of gas from the interior; the severity of this irregularity was found to be greatest for $f \approx 0.1$ and negligible for $f \geq 0.2$. For $f \leq 0.4$ a reduction in droplet diameter, according to a d -square law, was observed for a period of time, followed by a burning period of essentially constant diameter. For $f \geq 0.5$, the droplet diameter remained practically constant during combustion, although the measured burning time conforms to a d -square law. These observations were compared quantitatively with the theoretical predictions and were found to agree within accuracies ranging from 10% to 25%.

As a further test of the concept of boron slurry droplet combustion, observations were made of the combustion properties of isolated and unsupported droplets of both pure JP-10 and boron/JP-10 slurries in high temperature, atmospheric-pressure, oxidizing gas streams (39). Droplets of initial diameter of 0.3-0.5 mm and solid mass fraction of 0-0.3 were projected downward into post-combustion gases of about 1900 K and oxygen mole fraction

of 0.07-0.39 under conditions of low Reynolds number (<2). The d -square law held for the combustion of JP-10 droplets, and the burning-rate constant was measured as a function of the oxygen mole fraction. Boron slurry droplets burned quiescently for short periods of time with an envelope flame of vaporized JP-10, but then experienced disruption. As the environmental oxygen content was increased, the disruption occurred more intensely and earlier, largely because of the increased diffusion-flame temperature; repeated disruptions were observed. For flame temperatures exceeding the boiling point of B_2O_3 , boron particles emitted during disruption ignited. At low solid loading there was an initial stage during which the d -square law applied, followed by a stage of nearly constant diameter that terminated in disruption; at high solid loading only this second stage occurred. These various studies of boron slurry droplet combustion provided a basis for describing the combustion histories of the slurry droplets under practical combustion conditions.

After development of this reasonable understanding of the slurry droplet combustion, attention was again focused on the combustion of the boron particles themselves. An experiment was designed and constructed in which a steady nitrogen jet transporting fine ($0.04\sim0.15\mu$ diameter) boron particles at low loading densities was injected coaxially into the hot combustion products of a flat-flame burner to study the kinetics of boron ignition and combustion (40,41). Three types of boron flame-plumes were found: a dark-yellow plume emitting dark-brown smoke from its tip, at measured maximum flat-flame temperatures below 1800 K; a yellow plume surrounded in its lower part by green emission, between approximately 1800 K and 1900 K; and a bright-yellow plume entirely surrounded by bright-green radiation, above 1900 K. In these

patterns, which were independent of the oxygen mole fraction in the product gas, over the range 0.08 to 0.80, the bright yellow was interpreted as boron ignition and the bright green as BO_2 emissions from boron combustion products. Based on a theory for a one-step, Arrhenius, ignition process, a theoretical analysis of the jet flow was employed to extract overall rate parameters from measurements of the height of the yellow plume as a function of the flat-flame temperature. The results were interpreted in terms of existing and new potential models for the ignition and combustion of boron particles.

This research on the combustion of boron particles and clouds continued until the end of the program (41). It resulted in improved understanding of chemical-kinetic mechanisms and rates of boron particle combustion. These results can be used for estimating burning times for boron under combustion conditions of practical interest.

2. Combustion of Isolated, Unsupported Boron Slurry Droplets

The work conducted under this aspect of the program by Prof. Dryer and his colleagues (Takahashi et al., (39); Takahashi et al., (42); Cho et al., (43,44)) addressed the combustion properties of JP-10/boron slurries and in particular isolated droplets as they related to the issues discussed at the beginning of Section D.

Takahashi et al., (39) reported the first fundamental isolated free droplet combustion observations made on commercial JP-10/boron slurries, and in particular on their disruptive burning character. In other research (supported by Mobil Research Corporation) co-incidental to this work (Green et al., (45)), an aerodynamic based shearing technique was derived specifically to generate small (300 - 600 micron diameter) monodisperse, isolated droplets of very viscous fuels and/or fuels containing high densities of solid particles

such as slurries from a liquid capillary jet. A stream of free, monodisperse isolated droplets of JP-10/boron slurries manufactured by Sun Tech, Inc., UOP, Inc., and Atlantic Research Corp. was injected into a co-flowing, high temperature, atmospheric pressure oxidizing environment.

While the manufactured slurries contained approximately 70% boron particles of about 0.1 micron diameter, all slurries were diluted with pure JP-10 ($C_{10}H_{16}$, exo-tetrahydrodicyclopentadiene) to boron mass fractions of 0.05, 0.1, 0.2, and 0.3. Various oxygen concentrations (0.07-0.39 oxygen mole fraction) were studied, without significant variations in the gas temperature and relative gas/droplet velocity, and visual as well as single-lens-reflex/back-lighted and high speed (5200 f.p.s.) color cine photography were used to study the combustion properties.

Most importantly, this work was the first to demonstrate that while the solid particles within the liquid slurry droplets of these commercial slurries were concentrated as the liquid phase was preferentially vaporized, at some stage the droplet diameter variation with time departs from the classical d^2 law behavior, and after some further burning, the droplet subsequently underwent disruptive combustion. As, the solid loading of the initial slurry droplet was increased, the time over which the classical d^2 behavior occurred and the time to disruption decreased.

The disruptive phenomena resulted in three types of fragments: individual and agglomerated boron particles which produced a greenish flash and popping sound when ignited (ignition only occurred when the corresponding diffusion flame temperature surrounding the original slurry droplet exceeded the boiling point of B_2O_3); small fragments (less than 1/10 of the original slurry droplet diameter) which continued to burn with an envelope diffusion flame; and a

major fragment of the original droplet which continued to burn with an envelope diffusion flame. Further disruptions of the the major and minor fragments were also noted, and disruption was also observed to increase in intensity and occur earlier in droplet burning time with increasing oxygen concentration. The characteristics of these phenomena were observed to vary with slurry manufacturer but were noted with all materials.

The process leading to disruption was speculated to be the formation of a dense shell of boron particles as the liquid slurry droplet surface regresses. Either from physical binding or dense agglomeration, the shell was suggested to become impervious to the transport of JP-10 liquid from the droplet interior, causing the surrounding flame structure to move closer to the droplet surface. An estimate of the shell thickness was derived from the amount of material which had undergone vaporization to be about 0.02 mm. As the outer surface of the slurry shell was depleted of liquid, the droplet temperature was suggested to rise and it was speculated that the JP-10 in the interior might superheat, nucleate and vaporize.

While some physical understanding leading to speculations concerning the observed slurry droplet burning and disruption behavior was obtained, the lack of physical property data on the commercial slurries caused difficulty in developing further understanding. While it was established that available theories could approximate the burning constants in regimes where the d^2 law was obeyed, estimations of the conditions under which departure and disruptive burning occurred were not able to be obtained.

Takahashi et al., (39) reported further experimental work in which JP-10/boron slurries prepared in the laboratory were studied using the same isolated droplet combustion techniques. Un-stabilized JP-10/boron slurries

which were continuously agitated using an ultrasonic transducer were also studied. It was found that the solids in un-stabilized slurry droplets agglomerated completely as the droplet burned, and no disruptions were evident. The addition of high molecular weight dispersants to stabilize the JP-10/boron slurry led to violent disruption of the burning slurry droplets.

While the role of dispersants in stabilizing slurries and in producing appropriate flow characteristics have been recognized and utilized in the manufacture of fuel slurries, this was the first occasion that dispersants had been shown to also play an influential role in slurry combustion properties. Dispersant selection had never been optimized previously with combustion behavior considered.

For a constant weight loading of boron solids, the time to disruption was observed to increase as the dispersant concentration was decreased, a dispersant with a higher initial pyrolysis temperature was employed, or the mean diameter of the dispersed solid particles was increased. The quiescent burning of the un-stabilized slurry generated spherical solid boron particle agglomerates, while the disruptive burning of the stabilized slurries produced quasi-spherical hollow shells along with their fragments.

On the basis of this and earlier experimental work (Takahashi et al., (39), a refined model for the processes leading to disruptive burning of slurry droplets was developed. The disruptive burning process was divided into three consecutive stages: a d^2 burning stage, a shell formation stage, and a disruption stage. At low solid particle loadings, all three stages were observed in droplet burning, while at high solid loadings, only the latter two stages were apparent. The critical solid loading separating these two regimes depended on the type and amount of dispersing agent(s) used in stabilizing the

slurry as well as the physical characteristics of the slurry solid particles themselves.

In the d^2 law combustion stage, the liquid fuel portion of the slurry vaporized and burned with an envelop diffusion flame, without any influence of the solids and dispersant; the burning rate constant of the slurry droplet was the same as that of the pure liquid. This stage corresponded to the contracting sphere model proposed by Antaki (36,37). As the slurry surface regresses, particles near the surface were retained in the liquid and regressed with it, concentrating particles at the liquid/gas interface. This concentration of particles was contrary to the uniform particle concentration assumption of Antaki. At the same time, dissolved, less volatile dispersant agents were concentrated at the surface as the more volatile JP-10 was vaporized. When the cross-linked layer of particles near the surface became thick enough to support itself structurally in the form of a shell (through the assistance of the concentrated dispersant in the layer), the d^2 law stage ended and the shell formation stage was initiated. The liquid surface began to regress through the dense layer of particles at the shell surface. When the shell was porous, as proposed in the rigid-porous shell model of Antaki (35,36), vapor of the liquid fuel was able to pass through the shell. However, in contrast to the constant shell temperature assumption of Antaki, the shell outer surface was no longer constrained to be at the saturation temperature of the JP-10 as the liquid surface regressed through the shell. Since the shell thermal diffusivity was low, the outer shell surface increased in temperature substantially. This result was of little consequence if the particles in the slurry had no low temperature reactivity (as in the cases of boron as well as aluminum and carbon particles) and no non-volatile additives

were present. However, when dispersants were present on and in the interstices between the particles in the shell, pyrolysis temperatures of the dispersant may have been exceeded, and the dispersant may have undergone coking reactions which leads to a severe reduction in the permeability of the shell. Internal vaporization may have resulted at heterogeneous nucleation sites just beneath the shell, promoting pressure build-up and fragmentation. A diameter increase was observed just prior to disruption, indicating that a swelling caused by the internal vaporization leads to disruption.

On the basis of the above mechanism, a simple numerical model had been formulated to predict the shell formation and disruption time, as well as the shell thickness at the time of disruption (Cho et al., (43,44)).

A simple quasi-steady, spherically symmetric, constant property model with no droplet heating and unity Lewis number in the gas phase (Law, (46)) was used to calculate the d^2 behavior in the first stage of combustion of the slurry droplet. A flame sheet approximation at the adiabatic flame temperature and droplet surface temperature at the boiling point of JP-10 were assumed, and the properties of the gas phase were determined using the approximation procedures of Law and Williams (47). The heat balance equations for the porous shell were identical to those equations used for the gas phase, with the exception that the boundary conditions for the outer surface of the shell were such that the temperature was not held at the saturation temperature of JP-10, and the boiling point of JP-10 was used to approximate the temperature at the inner shell surface. An effective thermal conductivity was used for the shell which reflected both fluid and solid heat transport as well as radiative heat transfer mechanisms.

Given the shell formation time and the disruption time from the

experimental data of Takahashi et al., (39), the temporal variation of droplet diameter, the critical packed region thickness of the shell when the d^2 law region ended, the temperature at which additive pyrolysis began, and the shell thickness at the disruption could be calculated. The temperature of pyrolysis of the additive was assumed to be the same as the temperature of the outer surface of the shell at disruption. Temperatures obtained were in general agreement with measurements reported in Takahashi et al., (39), and the remaining model predictions were found to be self-consistent with the shell formations and disruption times experimentally determined for two different JP-10/boron slurries studied by Takahashi et al. (39). The model calculations also showed that the disruption time increases as the initial solid loading decreased, as the environmental oxygen concentration decreased, or as the initial slurry droplet diameter increased. Finally, the thickness of the fragmented shell was predicted to increase as the initial solid loading or the initial slurry droplet diameter was increased.

In order to apply the mathematical model developed in the present work for predictive purposes to various slurry systems, particularly in terms of the particle size and the type and amount of additives, the quantification of the critical conditions for the shell formation and for the pyrolysis of additives had to be made. Therefore, further studies of the agglomeration processes leading to the shell formation and the additive pyrolysis need to be made and characterization of physical properties of additives need to be determined. Through both theoretical and experimental efforts to optimize the combustion properties of additives used in stabilizing slurries, further reductions in the burning time required for JP-10/boron slurry combustion are possible. Combined with special techniques to modify the particles

themselves, the use of high energy density liquid boron fuels might be substantially improved. Unfortunately further work on this subject is beyond the scope of the present effort.

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FIGURES

- Figure 1. The Princeton University high temperature, adiabatic, turbulent plug flow, chemical kinetic reactor.
- Figure 2. Major species profiles from the oxidation of p-xylene.
- Figure 3. Intermediates in near sooting and smoke point conditions of normal and inverse diffusion flames.
- Figure 4. Peak extinction coefficient (1/cm) vs. equivalence ratio of the fuel/oxygen mixture in propane and ethene CFDF's.

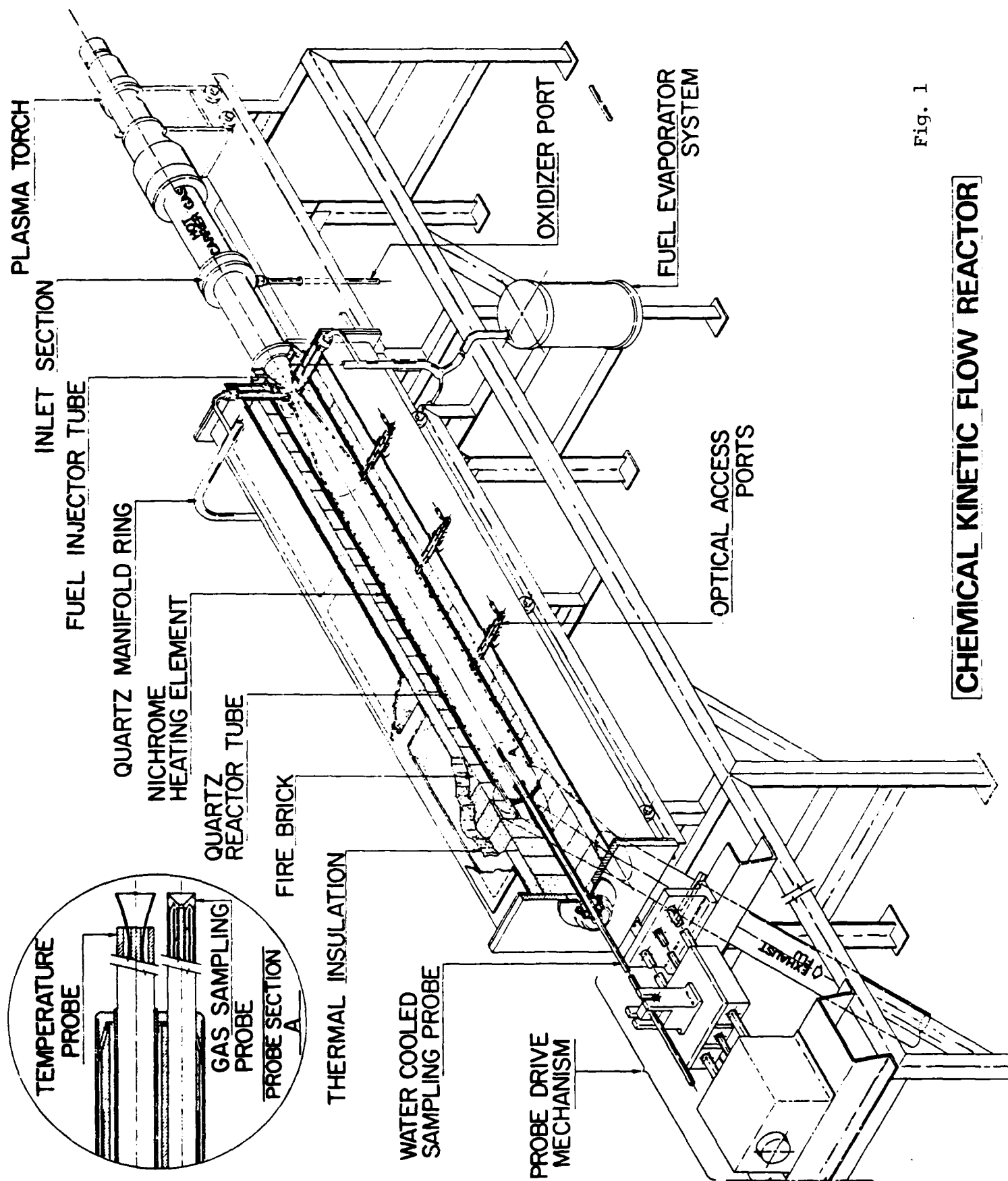


Fig. 1

CHEMICAL KINETIC FLOW REACTOR

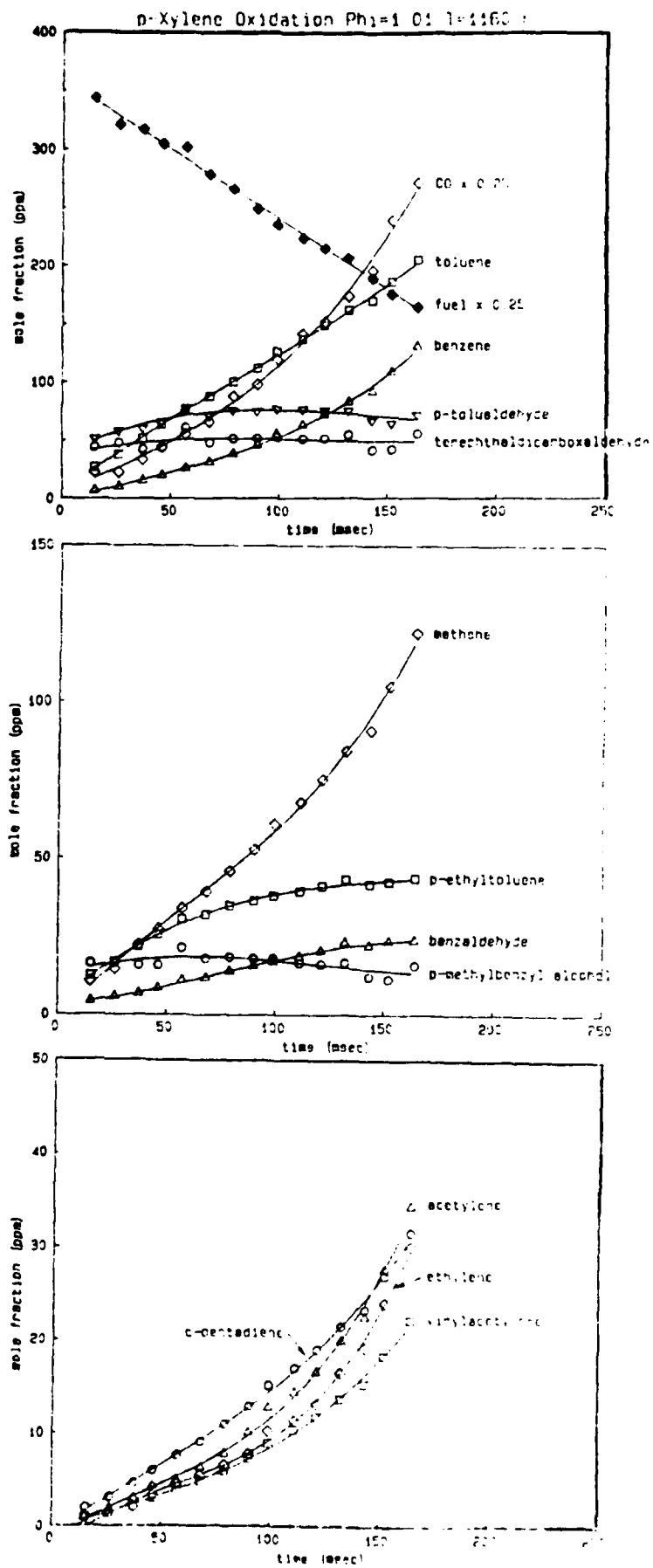
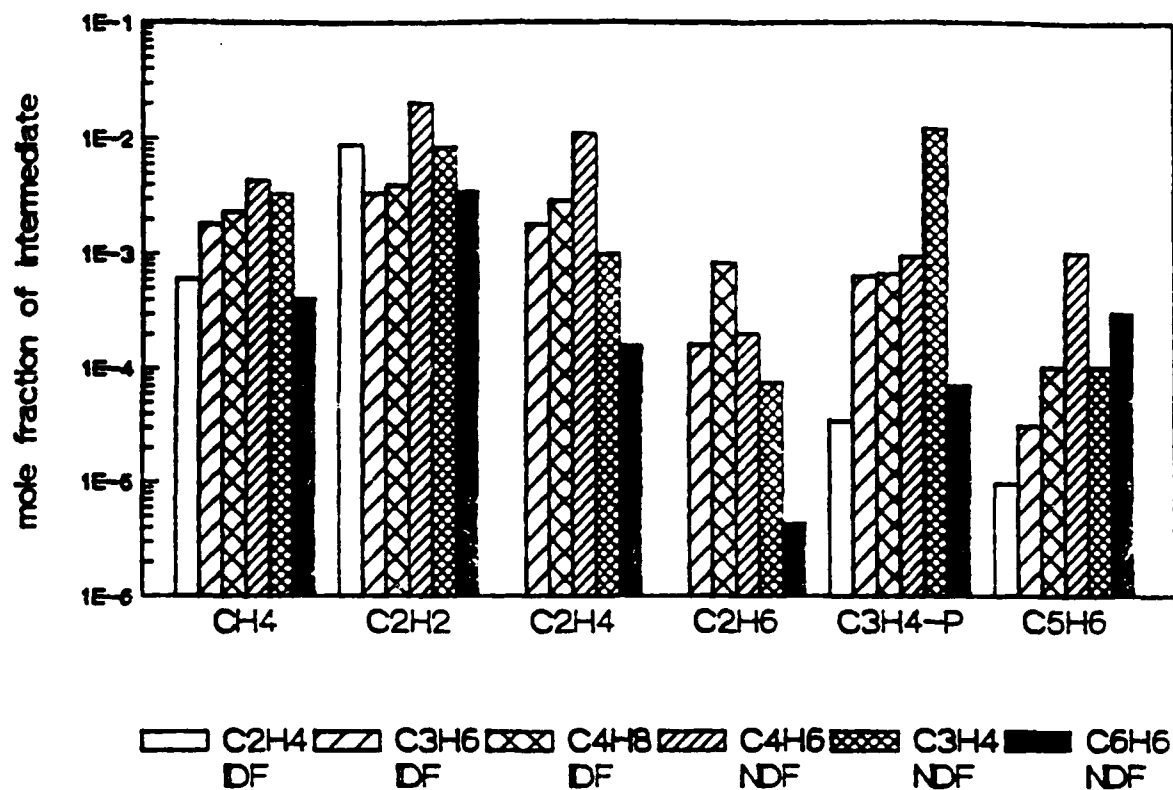


Fig. 2

IDFs and NDFs near sooting and smoke point

37



IDFs and NDFs near sooting and smoke point

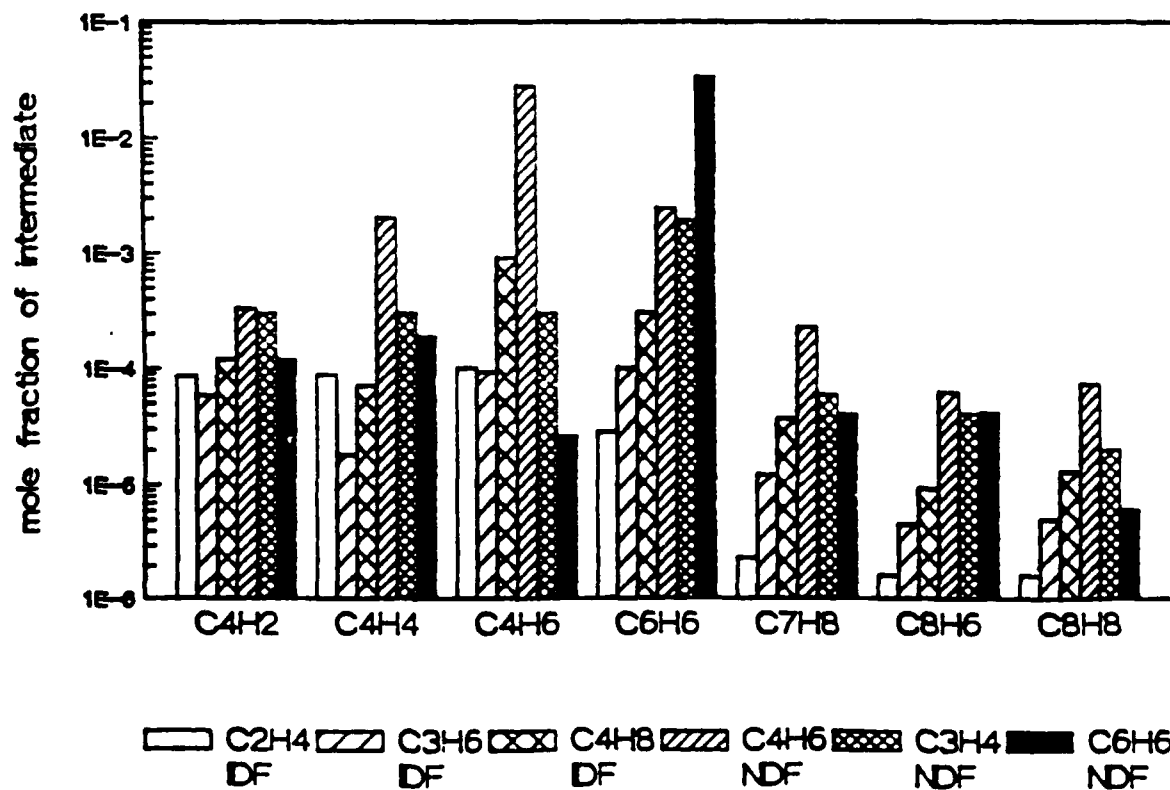


Fig. 3

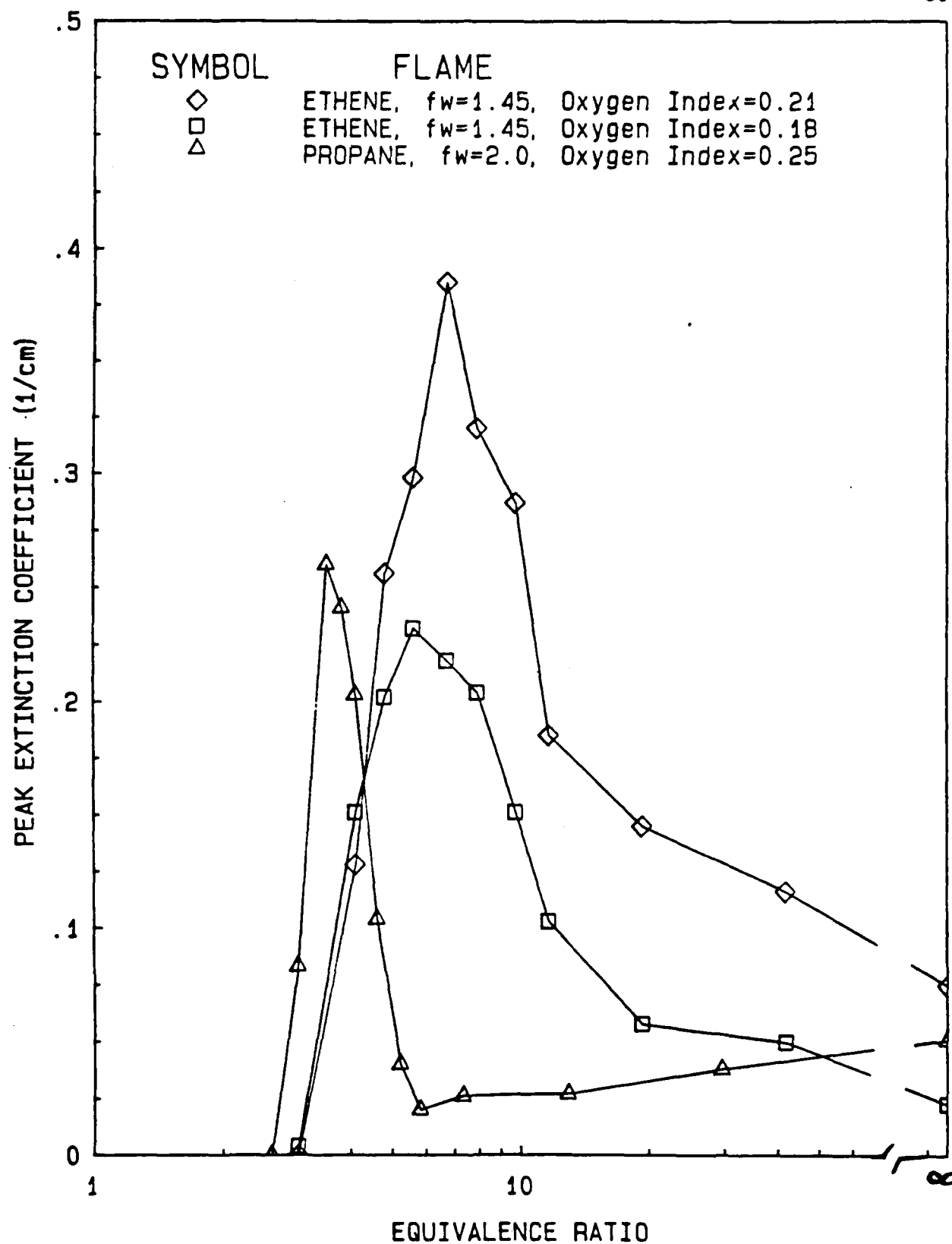


Fig. 4

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31. Takahashi, F., Heilweil, I.J., and Dryer, F.L., "Disruptive Burning Mechanism of Free Slurry Droplets," Combustion Science and Technology, in review (1988).

V. PROFESSIONAL PERSONNEL AND GRADUATE STUDENTS THESES

Prof. F.L. Dryer
Prof. I. Glassman, Coordinator
Prof. F.A. Williams
Dr. K. Brezinsky
Dr. F. Takahashi
Dr. C.Y. Cho

1. T. Litzinger, "The High Temperature Oxidation of Alkylated Aromatic Hydrocarbons," Princeton University, Department of Mechanical and Aerospace Engineering, Ph.D. Thesis (1985).
2. P. Antaki, "Studies of Slurry Droplet Combustion and Boron Particle Ignition," Princeton University, Department of Mechanical and Aerospace Engineering, Ph.D. Thesis (1985).
3. G.W. Sidebotham, "An Inverse Co-Flow Approach to Sooting Laminar Diffusion Flames," Princeton University, Department of Mechanical and Aerospace Engineering, Ph.D. Thesis (1987).
4. H.S. Hura, "Soot Formation in Diffusion Flames of Fuel/Oxygen Mixtures," Department of Mechanical and Aerospace Engineering, Ph.D. Thesis (1987).
5. S.C. Li, "Fundamental Studies of Boron Particle and Cloud Combustion," Princeton University, Department of Mechanical and Aerospace Engineering, Ph.D. thesis (in preparation).

VI. PRESENTATION - SEMINARS

K. Brezinsky

"High Temperature Oxidation of n-Alkyl Benzene", 21st Symp. (Int'l.) on Comb., August 5, 1986, Munich, W. Germany

"Chemical Species Measurements in a High Temperature Flow Reactor," Standard Oil Research and Development, Warrenville, OH, March 19, 1987.

"Oxidation and Pyrolysis Chemistry of Hydrocarbon Fuels," GM Research Laboratories, Warren, MI, June 18, 1987.

"Oxidation/Pyrolysis Chemistry as Related to Fuel Sooting Turbulence," American Chemical Society, National Meeting, Sept. 1, 1987, New Orleans, LA.

I. Glassman

"Physical and Chemical Aspects of Soot Formation"

- Dept. of Mech. Eng., Rutgers U., Oct. 3, 1985
- Invited Lecture, Eastern States/The Combustion Institute Meeting, Nov. 5, 1985.
- Dept. of Mech. Eng., University of Florida, Jan. 30, 1986
- Research Center, Phillips Petroleum Co., Bartlesville, OK, Feb. 21, 1986.

"Soot Formation in Combustion Processes"

- Invited lecture, 22nd Symp. (Int'l.) on Combustion, Aug. 18, 1988

F.L. Dryer

"Combustion Behavior of Free Boron Slurry Droplets"

- Air Force Air Breathing Propulsion Contractor's Review Meeting, Pennsylvania State University, State College, PA, June 16-20, 1987. Abstract.
- AFOSR and ONR Air Breathing Combustion Research Contractor's Meeting, June 18-20, 1986, Stanford University, Palo Alto, CA. Extended Abstract.

T.A. Litzinger

"Preliminary Experiments with n-Methylnaphthalene near 1180K", Eastern States Section/Combustion Institute Meeting, Nov. 5, 1985.

F. Takahashi

"Further Experiments on the Combustion Behavior of Free Boron Slurry Droplets," Eastern States Section: The Combustion Institute Meeting, Paper No. 19, Philadelphia, PA, November 1985.

"Combustion Behavior of Free Boron Slurry Droplets," 21st Symp. (Int'l.) on Comb., August 5, 1986, Munich, W. Germany.

F.A. Williams

"Observations on the Combustion of Boron Slurry Droplets in Air," presented at a Poster Session of the 21st International Symposium on Combustion, Munich, Germany, August 7, 1986.

VII. INTERACTION WITH OTHER LABORATORIES

Discussion about soot formation in dump combustors with NASA Langley, June 1987.

Discussion about soot formation in aircraft gas turbines with Wright Patterson AVB, Boeing AVCO-Lycoming, UTRC, McDonnell-Douglas, June 1986-1987. Interest in this work came as well from many of the major oil companies who are suppliers of residual fuels such as JP4. Liaison was maintained over the whole contract period with other AFOSR contractors, in particular TRW, Cal-Davis, Penn State, Michigan and UTRC.

Discussions about hydrocarbon oxidation processes with Standard Oil Research and G.M. Research, March-June 1987.

Numerous government laboratories requested Prof. Glassman's review paper on soot formation presented at the 22nd Symp. (Int'l.) on Combustion.