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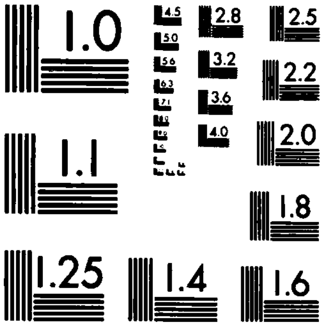

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Annual Report Under AFOSR Contract

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Air Force Systems Command

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FUELS COMBUSTION RESEARCH

For the Period 1 March 1982 to 28 February 1983

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ABSTRACT

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 has been impeded by the lack of adequate knowledge as to the general and detailed features of the kinetic mechanisms. More recently, uncertainties in the future sources and characteristics of fuels has emphasized the need to better understand fuel effects on combustion, e.g. energy release distribution, soot formation, emissions, etc. Such information is particularly lacking for aromatic species which could comprise a major fraction of future alternative fuels. Recent interest in high performance, high density fuels such as boron and carbon slurries has made it evident that the combustion characteristics of these fuels must be understood before their alternate potential can be reached in use. This document discusses Princeton's AFOSR research endeavors which include pyrolysis and fuel-rich oxidation of aliphatic hydrocarbons, pyrolysis and fuel-rich oxidation of aromatics, mechanistic studies of soot formation/destruction, and boron and carbon slurry combustion in turbulent reacting flows.

The specific objectives discussed and results obtained for the year of this report are:

1. To initiate quantitative studies on the pyrolysis and oxidation of aromatics. Results are reported for benzene, toluene, and ethyl benzene and general mechanisms have been proposed.
2. To continue studies of the pyrolysis reactions of the higher aliphatic hydrocarbons with and without the presence of small concentrations of oxygen. Results are reported on eight different fuels and their relation to the sooting problem has been evaluated.
3. To study soot formation and destruction processes in premixed and diffusion limited systems. A complete phenomenological model has been developed and refined. Extensive experiments have identified the importance of flame temperature and fuel structure as the major controlling parameters in soot formation.
4. To initiate work on boron and carbon slurries, both on a particle and cloud basis, and in consideration with turbulent reacting flow. A new theory of boron ignition and combustion has been developed and is reported.

I. INTRODUCTION

This annual report discusses the research objectives and progress made at Princeton under its fuel research program for AFOSR. An extensive review and history of Princeton's efforts previous to this most recent initiative will not be given, nor will the report dwell on the more than hundred publications which have been a result of continued A.F.O.S.R. support. These publications are listed in the reference section of this document. In order to keep the size of this report reasonable, only brief reviews of progress and discussion of original objectives will be given.

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

1. aromatic pyrolysis and oxidation
2. aliphatic hydrocarbon pyrolysis kinetics in the presence of various oxygen concentrations
3. soot formation and destruction mechanisms
4. boron and carbon slurry combustion in turbulent reacting flows

II. THE OXIDATION AND PYROLYSIS OF AROMATIC HYDROCARBONS

A. Objective

The initial objective on this aspect of the fuels research program was to challenge what most thought to be a more complex area of chemical kinetics, that is the oxidation processes of the aromatic hydrocarbons. The approach used was to survey and analyze the literature 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 earlier 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 are needed. This analysis of the low temperature work created enough outside interest to warrant publication [4]. The results lead one to question the earlier mechanism proposed and reviewed, certainly at the higher temperatures.

Specifically, the objectives of this aspect of the program have been to elucidate the mechanisms of the oxidation of some 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 one to develop overall rate expressions for combustor modellers, as had been so successfully done at Princeton for the alkyl hydrocarbons [5].

As detailed below, great progress was made during this current contract year. This success is due in large part to the successful development and operations of the flow reactor; a new unique high temperature sampling system; an automated gas chromatographic apparatus, and the gas chromatographic/mass spectrographic apparatus purchased under the program.

B. Research Progress

More extensive experimental results have been obtained for the oxidation of benzene, toluene and ethyl benzene. The equivalence ratio (ϕ) range for benzene and toluene was extended from very lean mixture up to $\phi = 1.5$. For ethyl benzene to date, the range covered varied from $\phi = 0.39$ t 0.79. Typical flow reactor results are shown in Figures 2,3 and 4. These results led to a new, more detailed mechanism for these three aromatics. As was reported [6], it has become quite apparent that a dominant factor in the oxidation rate of these compounds is specifically the oxidation of the phenyl radical. Indeed, the Princeton work led to one of the first proposed high temperature oxidation mechanisms for these compounds. Shown in Tables I, II and III are the mechanisms proposed earlier [6]. These mechanisms were derived by analyzing the peaks of the experimental data such as seen in Figures 2-4. Without dwelling into an extensive discussion in analyzing the phenyl oxidation mechanism as shown in Table I, the following brief synopsis of the proposed system is offered. The initiating step proposes a mechanism apparently overlooked by others; that is, the phenyl radical reacts with O_2 in an exothermic chain branching step to form a phenoxy radical and an oxygen atom. The phenoxy isomerizes into the ketocyclohexadiene radical, which expels CO and forms a cyclopentadienyl radical, which reacts with O_2 in a manner analogous to phenyl and forms a compound which due to resulting delocalization of an electron forms a ketone radical. The stable form of this radical is 2-cyclopentene-1-one and was found in trace amounts in our mass spectroscopic examination of the reaction products. The radical was then postulated to once again follow the ring rupture step of CO expulsion and this time to form a butadienyl radical. The butadiene radical undergoes pyrolysis to form vinyl acetylene, acetylene and ethylene and an addition reaction to form butadiene. With respect to soot formation considerations this result is significant in that these four products of aromatic oxidation are all known to have a great tendency to soot. So it becomes apparent that the aromatics soot extensively not only because of their initial structure, but also because of the intermediates which form during their oxidation.

If there is great commonality among many of the aromatics, then the possibility of developing overall reaction mechanisms for a wide variety of compounds looked attractive. Such overall reactions would be of great importance to modellers. Consequently much of the current work was directed to developing in more detail the complete oxidation mechanism of the alkyl part of the alkylated benzenes (essentially toluene and ethyl benzene). Figure 3 shows that an early intermediate in toluene oxidation is benzaldehyde. This result led to the mechanism recommended in Table II. The question of how benzaldehyde was formed was not definitive and this concern was the motivation of more extensive work on toluene. Refinement of gas chromatographic analysis techniques to identify higher molecular weight compounds subsequently permitted the discovery of substantial amounts of dibenzyl, as shown in Figure 5. This observation was a good indication that the benzyl radical undergoes a slow oxidative reaction steps similar to methyl radical oxidation. Due to its high endothermicity it is now believed that the benzyl plus O_2 reaction is highly unlikely [7]. New experimental results would now indicate that the radical plus radical reactions of benzyl plus O, OH and HO_2 are the important paths to benzaldehyde formation and the relative significance of each individual oxidizing radical depends on its concentration which is a function of the equivalence ratio and temperature. As oxidation proceeds, benzyl plus O is definitely the more important reaction at lean equivalent ratios; rich equivalence ratios await further evaluation. Thus the important conclusion is reached that just as methane is unrepresentative of the general mechanism of alkane oxidation, so toluene is probably unrepresentative of alkylated aromatic oxidation [6].

More insight has also been obtained with respect to the oxidation of ethyl benzene and the more extensive operation has led to the proposed mechanism in Table III. Conversion of this aromatic fuel to styrene is extensive and extremely fast and suggests that under the driving force of attaining the highly delocalized styrene configuration, the second H atom is readily lost from the side chain.

Significant amounts of ethylene were also obtained too early in the reaction sequence to be from the usual oxidative decay of the ring into smaller fragments. Furthermore, the concentration profiles for the intermediates benzene and ethylene follow each other almost exactly and suggest, under the conditions of experimentation, cleavage of the unsaturated C_2 side chain may predominate over oxidative attack of the double bond. The benzaldehyde found could form as a result of the oxidation of benzyl radicals formed in the initiation process and thus its presence offers no direct evidence for the oxidation of styrene. However, if benzaldehyde is produced from styrene then the interesting implication is that the process is quite like that of the oxidation of ethylene in that phenyl ethylene oxide forms. Steric factors would dictate that the oxide pyrolyze into benzaldehyde and a methylene radical rather than isomerize to phenylacetaldehyde.

More detailed work on the alkylated benzenes and 1-methyl naphthalene is proceeding during the continuation year.

III. PYROLYSIS OF ALIPHATIC HYDROCARBONS

A. Objective

The initial motivation behind this element of the total effort was to provide basic rate data and mechanisms to an element of the fuel combustion process not studied as extensively as so many others. Fuel pyrolysis studies and the effect of small concentrations of oxygen on fuel pyrolysis were considered essential to understanding the burning processes in fuel-rich pockets. That this concept was an important and necessary element of the combustion system, was vindicated by the results obtained in the aromatic oxidation and soot formation efforts of this program. It seems now, as shown earlier, that ethene and acetylene, as well as vinyl acetylene and butadiene, are important intermediates in the oxidation of all aromatics. As will be shown in the next section, the results give strong indication that fuel pyrolysis is the controlling element in soot formation in diffusion flame systems. Also, the presence of oxygen on the fuel side of a diffusion flame apparently accelerates the sooting process. It was and is crucial to verify whether the trends in soot formation reported correspond to the rates of pyrolysis (with and without small concentrations of oxygen) measured in flow reactor kinetic studies. Thus these kinetic studies will contribute as well to the understanding of the very complex mechanism of soot nucleation.

B. Research Progress

As stated above the need to strengthen the present understanding of how pure and oxidative pyrolysis affect soot formation in a laminar diffusion flame provided the motivation for this study. The major objectives were to understand the oxidative pyrolysis phenomenon and to identify the conditions when it becomes important, to compare overall pyrolysis rates of several fuels and to explain the observed trends, and to use the knowledge obtained to help improve the understanding of soot formation in the diffusion flame. Again extensive experimentation has taken place during the current contract year. All flow reactor experiments in this aspect of the program used a high dilution (>99.5% N_2) and short residence time (<.2 sec) in the temperature range 970-1150K. Details of all experiments, results and analyses are given in a recent thesis [8].

Oxidative pyrolysis refers to an accelerated fuel decomposition rate in the presence of oxygen. The literature (see Table IV) reveals the importance of small amounts of oxygen in non-dilute, relatively low temperature systems. Researchers have usually proposed new accelerative propagation paths to explain the oxygen effect. (the accelerative effect (Rate [OX]/Rate [PYR]), or oxygen effect, will equal the overall rate in the presence of oxygen divided by the pure pyrolysis rate).

Three key factors in determining the importance of oxygen emerged from the literature review: fuel type, temperature, and concentration. The particular experimental study undertook to investigate the concentration effect, given a fuel type, temperature, and total pressure (1 atm). Interestingly, using propane, propylene and butene an oxygen accelerative effect was only found at the higher concentrations. A consensus of results from the literature and the flow reactor showed that the oxygen effect decreases with increasing temperature and decreasing concentrations. The temperature trend can be explained by considering the changing relative importance of a few important elementary reactions. It was apparent from all the experimental results obtained that the lower limiting temperature of the flow reactor was too high to find a pronounced effect of oxygen.

Nevertheless, the importance of fuel pyrolysis rates in understanding high temperature fuel rich oxidation processes, as well the exact pyrolysis role in sooting tendencies, led to a study of the pure thermal decomposition of six fuels (C_3H_8, 1-C_4H_8, n-C_4H_{10}, i-C_4H_{10}, 1-C_6H_{12}, n-C_6H_{14}). The extensive results obtained have been summarized by the first order Arrhenius parameters, based on fuel decomposition, derived from Arrhenius plots of the data (Figure 6), listed in Table V. Overall rates of the above six fuels and a few other fuels (C_2H_4, C_3H_6, i-C_4H_8, 1,3-C_4H_6) were compared at 1073 K. Due to similar activation energies observed within the experimental temperature range, the ranking of rates at 1073 K should also apply to other temperatures within this range (970-1150 K). The following ranking of first orders rate constants was found:

$$C_2H_4 < C_3H_6 < i\text{-}C_4H_8 < 1,3\ C_4H_6 < C_3H_8 < (i\text{-}C_4H_{10} \sim n\text{-}C_4H_{10} \sim 1\text{-}C_4H_8) < n\text{-}C_6H_{14} < 1\text{-}C_6H_{12}$$

The trend within the alkane and alkene series can be explained through a comparison of relative stabilities. The larger molecules are less stable due to their less compact bonding structure. Furthermore, the ranking between alkanes and alkenes can be explained through a comparison of relative initiation rates and weakest C-C bond strengths. Assuming the chain reactions for an alkane and alkene of the same C number are similar, an imbalance in initiation rates, leading to higher radical concentrations, would result in a similar imbalance in product formation rates and hence fuel decomposition rates.

Consequently it was concluded that the trends in fuel structure for both overall rates of pyrolysis and soot emissions do not appear to be the same.

One explanation is that the original fuel pyrolysis rate is not as important as the quality, i.e. structure, of the products formed. Under typical diffusion flame conditions, most aliphatics decompose quickly to smaller stable hydrocarbon products. The character of these products, if similar to strong sooters or key soot precursors, could lead to more rapid soot formation than indicated directly by the overall pyrolysis rate.

IV. SOOT FORMATION AND DESTRUCTION PROCESSES

A. Objectives

The major objectives of the soot effort have been:

a. a complete and critical review of the soot literature in order to evolve phenomenological models and understanding of the overall processes so that control strategies could be developed.

b. experimental investigations with gaseous fuel jets (laminar diffusion flames) in order to evaluate the effects of water and other additives on the soot formation process and to scrutinize the models developed.

c. experimental investigations with premixed laminar flames for the same purposes as (b).

d. the development of a rapid experimental test to permit evaluation of the sooting tendency of practical liquid fuels, particularly those containing fractions of aromatics.

Items (a) and (d) have been completed and reported as part of five major publications [9-13] in this area during the contract period this report covers. The phenomenological models and the results obtained under Items (b) and (c) have given substantial understanding of soot processes, much of which has practical application. Indeed, it is believed that this A.F.O.S.R. work has had substantial influence on the direction and thinking of many investigators in the soot field.

B. Research Progress

1. General Background

The review and phenomenological models developed have been published as an A.F.O.S.R. report [9]. Again the extensive information reported will not be repeated but the major conceptual ideas promulgated will be reviewed.

The complete soot mechanism in a combustion system is truly very complex. The process may be described in a cursory fashion as follows. Whether starting in a premixed or diffusion flame system, a fuel undergoes pyrolysis and eventually forms a specie which is the precursor to the actual soot nucleation process. The precursor then reacts or polymerizes in some manner so that soot nuclei form. During this process it is feasible that some of the precursors (or even the species forming the precursors) can be oxidized. Nuclei which form can absorb other high molecular weight hydrocarbons which exist in the combustion system. Since the particles exist in high temperature regions, they can undergo condensed phase reactions which can reduce their hydrogen content and eventually give the highly complex aromatic structure known as soot. The soot particles can conglomerate and agglomerate while these processes are proceeding. Simultaneously, there can also be oxidation of the particles.

Although the overall soot formation process as defined above seems very complex, the Princeton research has been governed by the essential idea that the controlling factors in most sooting combustion systems are the rate of formation of the precursors and the rate of oxidation of the formed particulates.

Most investigators have been concentrating their efforts on the nucleation process. Although nucleation is obviously an important step, recent results under this program seem to confirm that it is not the controlling one. Nevertheless, the initial review focused on this question and it was considerations which grew out of this study that guided much of the original Princeton experimentation on sooting diffusion flames.

The two primary mechanisms that have been suggested in the past have been the polyacetylene route and ion-neutral route. Doubts have been raised about the polyacetylene route because it is known that in flame processes soot forms very early. The time required for the numerous free radical-neutral acetylene reactions, the energy required for cyclization, etc. have led many to question this type of mechanism. There is substantial evidence that polyacetylenes form in flames, but their fate may simply be to be destroyed or absorbed on particles already formed. The concept of fast ion-neutral reactions being the nucleation route is also open to serious question. Firstly, there are much smaller ion concentrations in diffusion flames than in premixed flames, yet the propensity to soot in diffusion flames is far greater than in premixed flames. More importantly, the ion concentrations in flames are orders of magnitudes lower than the formed particle density. Thus it would appear that there simply is not sufficient ions present to nucleate all particles.

In the search for an appropriate mechanism a suggestion of Thomas [14] that Diels-Alder (condensation) type reactions were fast and this possible nucleation route for soot formation was considered. The thinking followed the lines that any soot precursor must be highly conjugated to be stable at the high temperatures in flames, and, indeed the high molecular weight species forming from these precursors must be conjugated as well. Conceptually then one could understand why the aromatics had a strong tendency to soot. In a very classical sense, Diels-Alder reactions are very much like electrostatic reactions and if one examines the resonance structures of most compounds which undergo Diels-Alder reaction, one can understand from the polar nature of some of these structures the possibilities of these reactions. If this conceptual idea were correct, then certain compounds such as butadiene and vinyl acetylene should have a great propensity to soot.

Indeed, Schalla, et.al. [15] reported that butadiene had a greater tendency to soot than the aromatics. (Although experimental work at Princeton had shown butadiene to be prolific sooter but opposite in trend to Schalla's results, work at the time of this writing has shown agreement with her results). The evidence appears to support the contention that vinyl acetylene and butadiene may be the main precursors to soot nucleation. The fact that vinyl acetylene can undergo a Diels-Alder like addition to form the aromatic molecule styrene can lead to the belief it was the more important of the two. Indeed the importance of the kinetic studies on the oxidation of aromatics, reported in the previous section, is now most evident. The fact that vinyl acetylene and butadiene form in the oxidation of aromatics may be the key to understanding soot formation processes in an aromatic-fuel, premixed combustion system. However, recent estimates of the A factor in the rate expression indicate that simple Diels-Alder reactions may be too slow for the soot forming process. There is a possiblity that the butadiene radical could readily become ionized whereby its dissociation products would also be so and very fast Diels-Alder reactions could proceed.

Most of the early work on soot formation in premixed flames (Street and Thomas [16]) compared the relative tendency of fuels to soot and reported the tendency as:

aromatics > alcohols > paraffins > olefins > acetylenes

It was observed that, except for the aromatics, the trend was not just a matter of a homologous series trend or the C/H ratio, but the greater the flame temperature the less the tendency to soot. This conclusion was consistent with what Milliken [17] had reported from his considerations of premixed ethylene-air flames that the tendency to soot was a function of the flame temperature. Milliken calculated that the rate of "pyrolysis" of acetylene to form the soot precursors rose more slowly with temperature than the rate of oxidative attack on the precursor forming system. Thus under premixed conditions, the only reason that acetylene seems to have little tendency to soot compared to other fuels is its high flame temperature compared to the other alkyls. Since the work on the oxidation kinetics of alkyls inidicated that under rich conditions all compounds break down to acetylene, it was postulated that to a first order the sooting tendency of the alkyl compounds under premixed conditions are independent of fuel structure and primarily a function of the temperature of the combustion system. It was this conceptual idea that guided the experimental work on premixed flames to be discussed subsequently.

The question of how the aromatics behave with respect to sooting is apparently a different one. Benzene, for example, has a temperature close to ethene, yet, its tendency to soot is greater. From the initial review of aromatic oxidation [4], the conclusion was reached that the mechanism was such that carboxyl structures formed and these led to radicals which eventually formed CO_2 directly. Thus, the demands for two carbon atoms in the ring was for two oxygen atoms each compared to the fact that all alkyl compounds eventually take a route through a formyl group and only form CO. Thus it was stated that benzene at a given equivalence ratio was richer than an alkyl compound of the same C/H ratio. This condition was thought to give the great tendency of benzene to soot and not to have correspondence with respect to the temperature trend of the alkyl compounds. Again, the experimental results on the oxidation of the aromatics has helped clarify this point. The results show that it is not likely carboxyl structures will form during the oxidation of the aromatics, certainly not at the high temperatures of combustion systems. However, the analyses also show that vinyl acetylene and butadiene form as well as acetylene. The postulate has been that acetylene must form such compounds to undergo soot nucleation steps. Milliken's concept was that acetylene pyrolysis to soot versus rate of oxidative attack determined the trend to soot with respect to temperature. His concept apparently holds for the alkyl compounds because they follow the same degradation route to acetylene. The aromatics do not follow this route. Instead they go directly to important soot precursors. Thus the competitive trend with respect to precursor formation and oxidative attack can be altered substantially. (New evidence found at the time of this writing indicates that this concept holds only for diffusion flame systems and that it is the size and C/H ratio of the aromatics that govern its tendency to soot under premixed conditions).

The reasoning on the temperature effect under premixed conditions can be extended, quite simply, to diffusion flame systems in order to determine the temperature effect. Since there is no oxidative attack on the soot precursor process in diffusion flames, then the pyrolysis rate increase with temperature is not counteracted by any other effect. Thus the higher the fuel stoichiometric flame temperature the greater the tendency to soot. The general tendency as reported by Schalla et.al. [15] long ago shows the trend according to homologous series:

aromatic > acetylenes > olefins > paraffins > alcohols

Again, except for the aromatics, the trend is the greater the stoichiometric flame temperature the greater the tendency to soot. However Schalla, et.al. results show that the C_4 olefins had the greater tendency to soot among the olefins. Further branched chain isomers had a greater tendency to soot than the corresponding straight chain compounds. Again the characteristic of benzene pyrolysis would have to be different from the alkanes. These facts led to the conclusion that the tendency to soot in diffusion controlled systems was dominated by the stoichiometric flame temperature and the fuel structure. Indeed this concept guided much of the experimentation with fuel jet diffusion flames to be discussed next.

2. Sooting Tendency in Diffusion Flames

During the course of the earlier A.F.O.S.R. program and during the present program a significant amount of experimental results had been produced on a diffusion flame burner which permits determination of the so-called smoke point.

In the earlier work it had shown that addition of an inert did not alter the flame characteristics of a diffusion controlled system [18]. Thus by the addition of an inert to the gasified fuel the temperature of the diffusion flame could be controlled independently. The actual measurements proceed by measuring the smoke heights (and the mass flow rate at this height) with various vamounts of a nitrogen diluent. Since the model of soot formation was that fuel pyrolysis kinetics control, the data were plotted as the $\ln$ (1/fuel mass flow rate (FFM)) vs 1/T and it was found that straight lines were obtained for all fuels tested. In a major publication [19] results on acetylene, ethene, butane, propene, n-butene, pentene and hexane were published. In the current year's program data were taken on the xylenes, ethyl benzene and 1,3 and 1,4 cyclohexadiene in addition to the earlier work on benzene and toluene. All the diffusion flame data taken to date are plotted in Figure 7.

Some direct conclusions can be drawn from Fig. 7. First, one must note that the highest temperature point for all fuels, except ethylene, is the case of no inert addition. For ethylene there was fuel preheating to increase the flame temperature. Acetylene is thus observed to be a prolific sooting fuel in diffusion flames only because its flame temperature is so high. At a fixed temperature acetylene is seen to soot less than the C_4, C_5 and C_6 olefins. Further, at a fixed temperature the C_4 and C_5's have the greatest tendency to soot of all the olefins. This result is consistent with that of Schalla, et.al. [15]. The aromatics and the cyclohexadienes soot more than the aliphatics, even butadiene. The butadiene result is contrary to what Schalla and co-workers [15] report, but at the time of writing the butadiene was repeated and found consistent with Schalla's results. The butadiene used in the earlier experiments is now believed to have been contaminated.

Considering the experimental scatter it is difficult to separate the tendency among the aromatics. The trend does appear to follow ethyl benzene > xylenes > toluene > benzene, which would be the order expected for ease of initiation of pyrolysis. 1,3 and 1,4 cyclohexadiene were tested because one (1,3) is conjugated and the other is not and it was initially thought that the conjugated species would have the more noticeable tendency to soot. The experimental results do not indicate any difference. Review of the literature subsequently showed that the cylohexadienes immediately pyrolyze to benzene [20] and it is rewarding to note that the experimental results show that all three compounds have the same tendency to soot.

It is debatable whether the slopes of the lines in Figure 7 represent any realistic activation energies. Nevertheless, the activation energy obtained [19] from the curves for acetylene was 118 kcal/msec, for ethene 114 and all other aliphatics between 80-90. It is interesting to observe that the weakest bond in acetylene is the C-H with a value of ~110, the weakest bond in ethene is also a C-H with a value ~108, the weakest bond in all others is a C-C bond which will always have a value around 85 [see Refs. 19,21].

The slopes for the aromatic fuels are all about 25-30 kcal/mole. There is no bond strength in any of the fuels that has a value so low. Another interesting observation from the literature is that the activation energy for the oxidative pyrolysis of benzene has been reported as ~35 kcal/mole [22]. Assuming that the type of agreement shown in these last two paragraphs is not fortuitous, it is feasible to speculate that considering the temperatures which exist and the normal activation energies of the pure pyrolysis processes of the fuels examined that O_2 induction in the fuel stream does not play a role for the aliphatics, but may for the aromatics.

The above results would appear to be good confirmation that pyrolysis kinetics govern the tendency of fuels to soot and that the smoke point apparatus developed is an excellent tool for evaluating the tendency of a fuel to soot and the effect of fuel structure on this tendency.

3. Sooting Tendency in Premixed Flames

The qualitative procedure for evaluating the sooting tendency of fuels under premixed conditions has been to observe the C/O ratio (or equivalence ratio ϕ) at which luminosity just begins in a laminar flame. Bunsen and flat flame burners have been used. The larger the C/O or equivalence ratio at which luminosity begins the less the tendency to soot. The most extensive published data of this type have been that of Street and Thomas [16]. Milliken's interpretation of the competing phenomena in premixed flames made it evident that the C/O ratio was not necessarily the primary variable for categorizing fuels with respect to there tendency to soot under premixed conditions. Indeed from oxidation kinetics one would expect acetylene certainly not to have the least tendency to soot amongst the alkyls. Thus experiments of the Street and Thomas type were repeated with temperature control of the flame at each C/O ratio. This control was achieved by varying the nitrogen concentration in the air. Thus for a given fuel, a temperature higher or lower than the value for air could be obtained.

During the year that this report covers the simple Bunsen burner test apparatus was modified to improve the stability of the flame at the very rich equivalence ratios of operation and to prevent cellular flame formation for some of the fuels tests. This great stability of operation was accomplished by making the burner a long stainless steel tube of 7.6 mm i.d. equipped with a double-concentric annular channel through which flows a very small amount of air just sufficient to stabilize the flame. The opening between the main burner and surrounding concentric channel is approximately 0.5 mm. A pyrex tube of 43 mm i.d. and 220 mm long surrounds the whole assembly to exclude secondary air from the ambient atmosphere. This new design has permitted highly reproducible results with a Bunsen type experiment in a range in which others have not been successful. Results for 10 different fuels obtained with this new experimental technique are shown in Figure 8 in which ϕ is plotted versus the calculated adiabatic flame temperature T_f. (Substantially more fuels have been used in the months past the dates this report covers). It is important to note that the ϕ plotted is the actual fuel-oxygen ratio divided by the stoichiometric fuel-oxygen ratio for all the carbon and hydrogen in the fuel being converted to carbon dioxide and water, respectively.

There are many interesting observations to be made by examining Figure 4. First note that the cross point on every fuel line represents the results for air. One thus observes for air, that acetylene has the least tendency to soot, ethylene next and then ethane, exactly the same as the early trend reported [16]. Indeed all the cross data are in good agreement with the results of Street and Thomas [16]. However, notice that for a fixed temperature, acetylene has the smallest ϕ, for C_2 hydrocarbons. Thus as one would expect from the understanding of the kinetic mechanism, given a temperature, acetylene has the greatest tendency to soot of the C_2 hydrocarbons. Indeed Figure 8 shows as well that for the C_2, C_3, C_4 hydrocarbons the olefins have a greater tendency to soot than the paraffins. What is unusual about these results is that the C_2's appear to have a lesser tendency to soot than the C_3's and the C_4's. It would appear that the size of the fuel molecule plays a role and certainly this trend is inconsistent with oxidation kinetic results. Here again one must realize the fundamental kinetic realities of the process. All data obtained are in the very fuel rich region, thus normalizing the data on the basis of an equivalence ratio where stoichiometric is defined as the carbon going to CO_2 is unrealistic. Kinetically, in most cases the H must be abstracted by an oxygen species and it is somewhat realistic to assume each 2 hydrogens will consume one oxygen atom. A more realistic normalization procedure would be to use a stoichiometric relation in which the carbon is converted to carbon monoxide and the hydrogen to water []. Figure 9 is a replot of the data in Figure 8 in a manner in which the equivalence ratio is based on C to CO and H to H_2O; that is, the term is the ordinate of Figure 9 written as $[C + (H/2)]$ is the stoichiometric oxygen requirement on this new basis and the O is the actual experimental value at the sooting point. Simple analysis will show that the normal equivalence ratio (Figure 8) written in the same manner would be $[2C + (H/2)]/O$. It is kinetically unrealistic [23] to plot the data such that the ordinate would be simply $[C/O]$. In pre-mixed flames the hydrogen in the fuel consumes some of the oxygen and it is for this reason that experimental data for air mixtures do not correlate [13] with (C/O) = 1.

The data trends in Figure 9 are much more appealing. The trends among the C_2, C_3 and C_4's themselves are as one would expect. In general, the paraffins soot less than the olefins and acetylene. More importantly, the data indicate that the C_4 olefins, butadiene and acetylene have the greatest tendency to soot. This trend gives some credence to the postulated importance of these molecules in the nucleation process discussed earlier. Comparison of Figures 8 and 9 reveals the importance of the basic oxidative pyrolysis and combustion mechanisms of the fuel. The importance of the ordinates used is that they to a first order normalize the results with respect to the number of carbon atoms in the fuel. However, it is also apparent that the kinetic mechanism also prevails. For paraffins the hydrogens are abstracted by an oxidative specie. For the multi-bonded compounds, the oxidative species can add directly to the multiple-bond and thus not all the hydrogens must be abstracted initially by an oxidizing specie. Thus, in reality due to kinetics, there is no totally correct standard normalization procedure based on an equivalence ratio for the data presented in Figures 8 and 9.

The major point above is that the combustion temperature may be one of the most significant parameters in sooting pre-mixed systems and that the higher the temperature the less the tendency to soot. The conclusion, however, holds only for aliphatic fuels. The aromatics have adiabatic flame temperatures close to the olefins, yet they have a far greater propensity to soot than do all aliphatics. It is very apparent then that their basic mechanisms leading to the soot nucleation process must be very much different than that of the aliphatics just as our recent flow reactor results show. The trend of the sooting equivalence ratios of the aromatics as a function of the controlled flame temperature is under investigation.

V. BORON AND CARBON SLURRY COMBUSTION IN TURBULENT REACTING FLOWS

A. Objectives

The possible performance improvements associated with the addition of boron and carbon hydrocarbon fuels were indicated in the original proposal for support of this research which is directed towards addressing problems of burning of carbon and boron-containing fuels and problems of turbulent combustion in general. The work is intended to provide fundamental information needed in solving associated problems of combustion design.

Four specific items were identified viz., a) Slurry Droplet Combustion, b) Boron Suspension Combustion, c) Carbon Slurry Combustion and d) Turbulent Flame Theory. Prof. Williams and Dryer co-direct these experimental efforts. Progress will be reviewed here for each of the three items separately.

B. Progress

Appreciable success has been achieved in the work on boron suspension combustion and in turbulent flame theory. A recent paper [24] on boron particle combustion has commanded great attention and is apparently a stimulus for other research programs in the area. The efforts in the area of slurry combustion have been proceeding and are mainly concerned with establishing the proper experiment approach to the complex combustion situation this type of fuel imposes. The status of each of the main three areas of this aspect of the program are summarized below.

1. Slurry Droplet Combustion

Boron slurries represent a complex combustion problem because they present a three phase medium (a solid fuel, a liquid fuel, and a gaseous oxidizer) which burns both homogeneously and heterogeneously. Consequently it appeared appropriate to consider carefully how to gain the most understanding from single particle studies. It is still believed that it is very important to achieve this understanding in order to properly analyze experimental results with spray clouds. The essential approach is to understand single slurry particle combustion, cloud combustion of boron particles carried on a gaseous medium and then actual slurry sprays.

As originally proposed, the slurry droplets were to be supported on fine fibers to gain the associated experimental convenience. Increasing concerns about the effect of fiber supports arose from results obtained in other Princeton programs. Considering the complexity of the problem at hand, possibility that fiber supports could interfere with the boron related processes during droplet burning was an important concern and thus alternative means of supporting droplets during their combustion were sought. Under study in particular have been the possibility of using hot gas flow or acoustic levitation to accomplish this purpose. Development of such a technique would be a major contribution to the slurry combustion field. These studies of the optimum techniques are still in progress.

2. Boron Suspension Combustion

The first step in the studies of ignition and combustion of clouds of boron particles was identified to be the design and construction of a reliable generator of well-characterized suspensions. It was estimated that one full year of effort would be necessary in developing the generator. This work has gone more quickly than anticipated, and a suitable generator is now available in the laboratory.

This generator, the design and construction of which has now been completed, is based on a fluidizing principle in which the boron is maintained in a uniform suspension by gas circulation, and a gas-boron mixture flows out of the suspension chamber at a controllable rate. This rate is controlled by the rate at which nitrogen is fed into the suspension chamber at the bottom. For safety reasons, the fluidization is performed entirely by use of nitrogen, and the oxygen needed for combustion is to be added to the boron-nitrogen stream after it leaves the chamber. The system was tested by use of inert Al_2O_3 particles, sized such that 90% were in the 2 to 5μ diameter range, and flow rates up to 3×10^{-2} g/s were achieved with variations below 5% over a 5 minute period. Thus, the generator system appears to be suitable for future testing and use with boron particles.

In addition to this progress towards future performance of ignition and combustion experiments with boron clouds, theoretical studies on the ignition and combustion of individual boron particles were advanced. Much of this work has been summarized in a recent publication [24]. Although because of this publication not all results will be detailed, the major findings will be identified.

Two new findings concern the ignition and the combustion of boron particles. In the past, it has generally been assumed that during the ignition phase oxygen dissolves in a liquid layer of B_2O_3 on the surface of the boron particle and diffuses to the boron surface where it reacts. It has been found that it is much more likely that instead the boron dissolves in the liquid B_2O_3 and migrates toward the surface of the liquid where it reacts with oxygen. Suboxides may well be formed during this migration process. Concerning diffusion-controlled burning in the absence of an oxide layer, it has been shown that for a simplified model originally identified independently by Mohan and Williams and by Glassman and adopted more recently by King, the calculated burning rate varies very little if details of the model are varied. In this model, oxygen reacts with gaseous BO at a flame sheet in the gas and forms gaseous B_2O_3 which diffuses to the liquid boron surface where reaction occurs to produce gaseous BO. The key high-temperature problem was identified as the chemical rate-controlled burning of small particles, and possible chemical mechanisms were postulated. The reader is referred to Reference 24 for details.

3. Turbulent Flame Theory

The work on turbulent flame theory has resulted in by far the largest number of publications [References 25 to 31]. This theoretical work has treated both premixed turbulent flames and turbulent diffusion flames by asymptotic methods. Although it is unreasonable to attempt to summarize all of the results here, it is of interest to highlight the most important findings, with reference to the publications requested for further details and additional results.

A new finding of the work on premixed turbulent flames concerns the influences of the density change associated with the heat release on the flame structure and on the flame dynamics. In the absence of this fluid-dynamical density change effect, the reaction zone is readily subjected to significant influences from nonadiabaticity or from differing diffusive conductances for heat and reactant species (Lewis numbers different from unity). In the presence of the effect, the expansion associated with the density change lessens gradients locally and thereby greatly reduces the sensitivity of the reaction zone to external perturbations. Conditions for instability of wrinkled flames thereby are modified significantly. Many of the resulting modifications have now calculated.

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[All are program contributions except 14,15,16,17,20 and 22]

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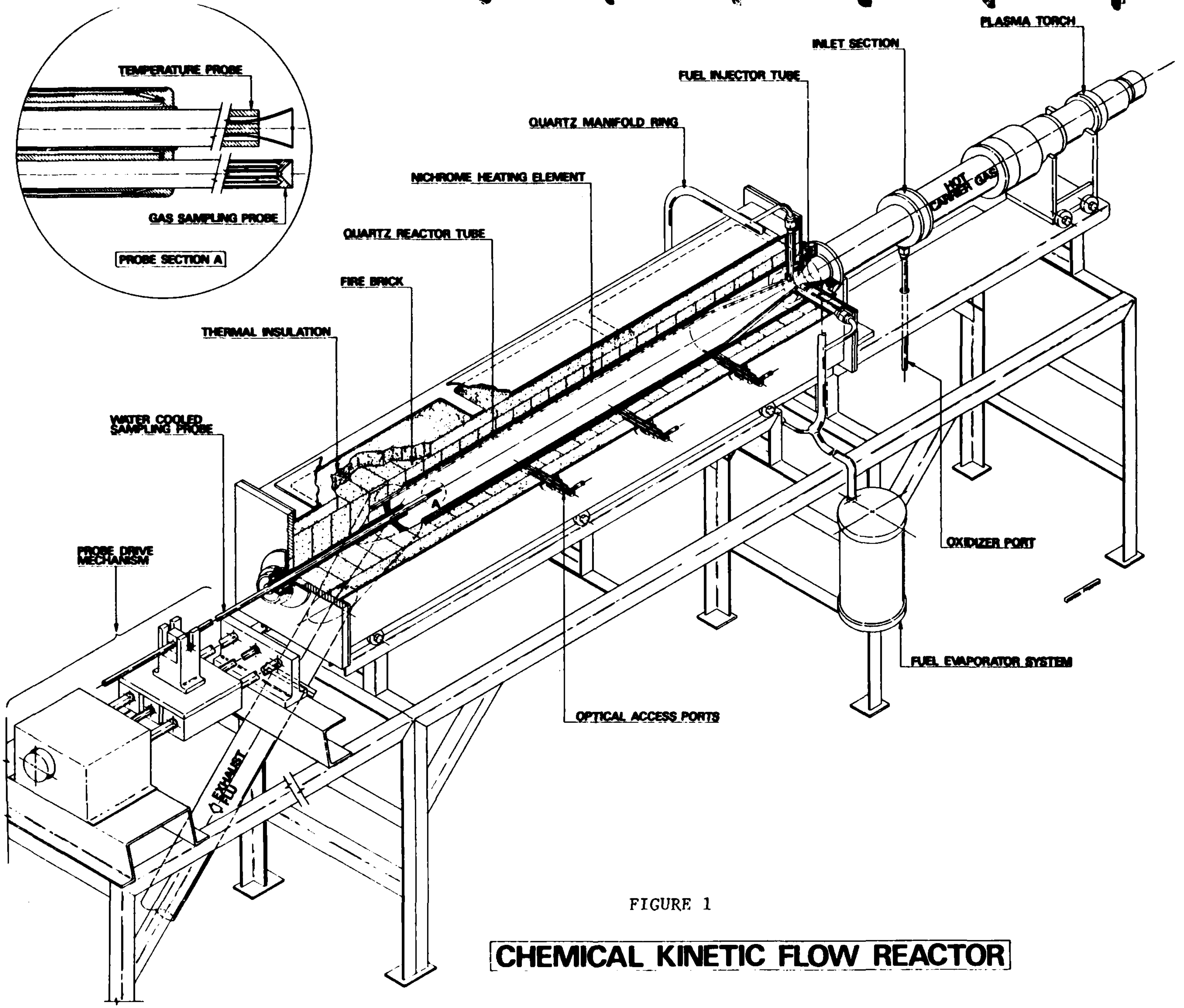


FIGURE 1

CHEMICAL KINETIC FLOW REACTOR

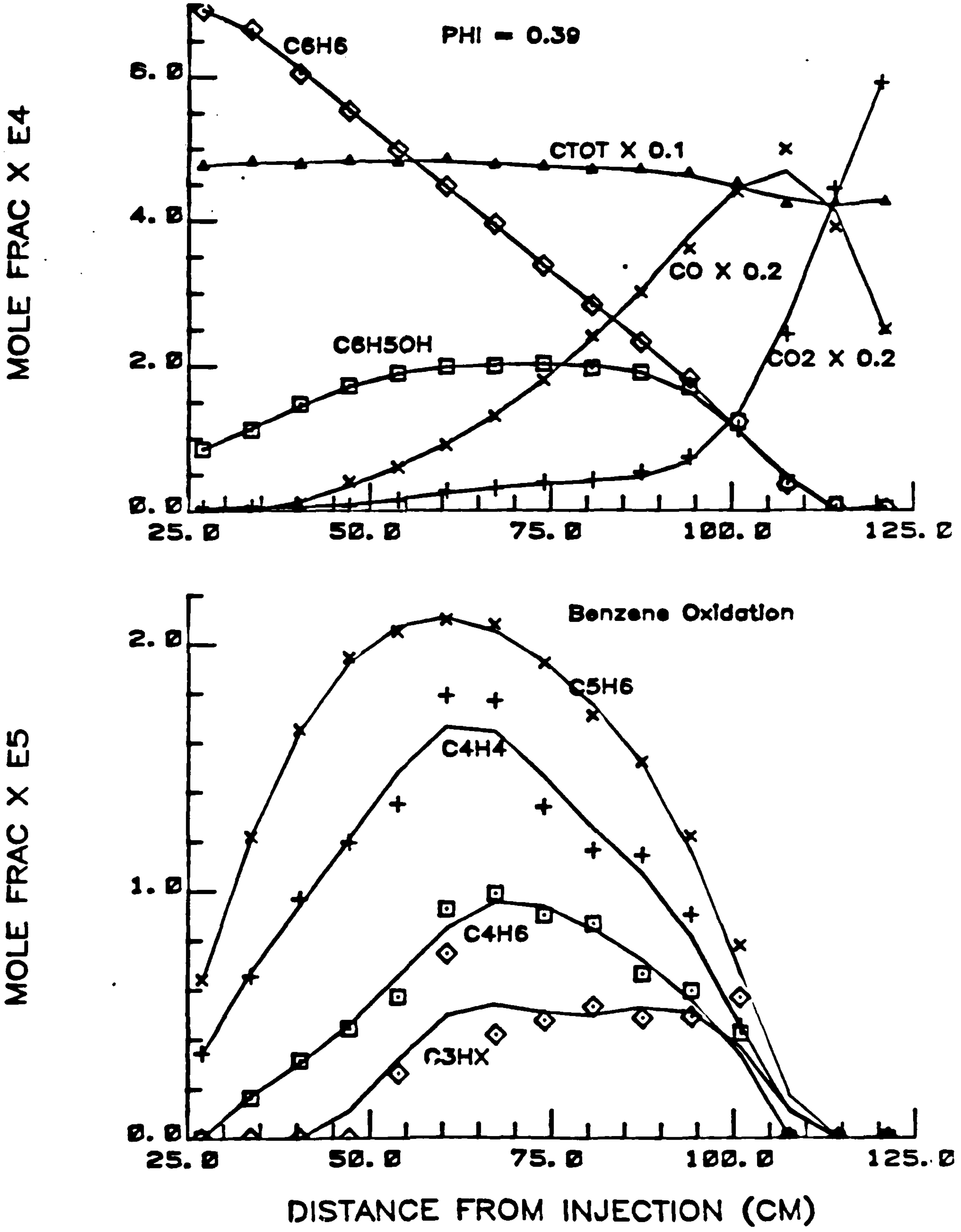


FIGURE 2 Benzene Oxidation: Phi = 0.39,
1 cm ≅ 0.74 msec.

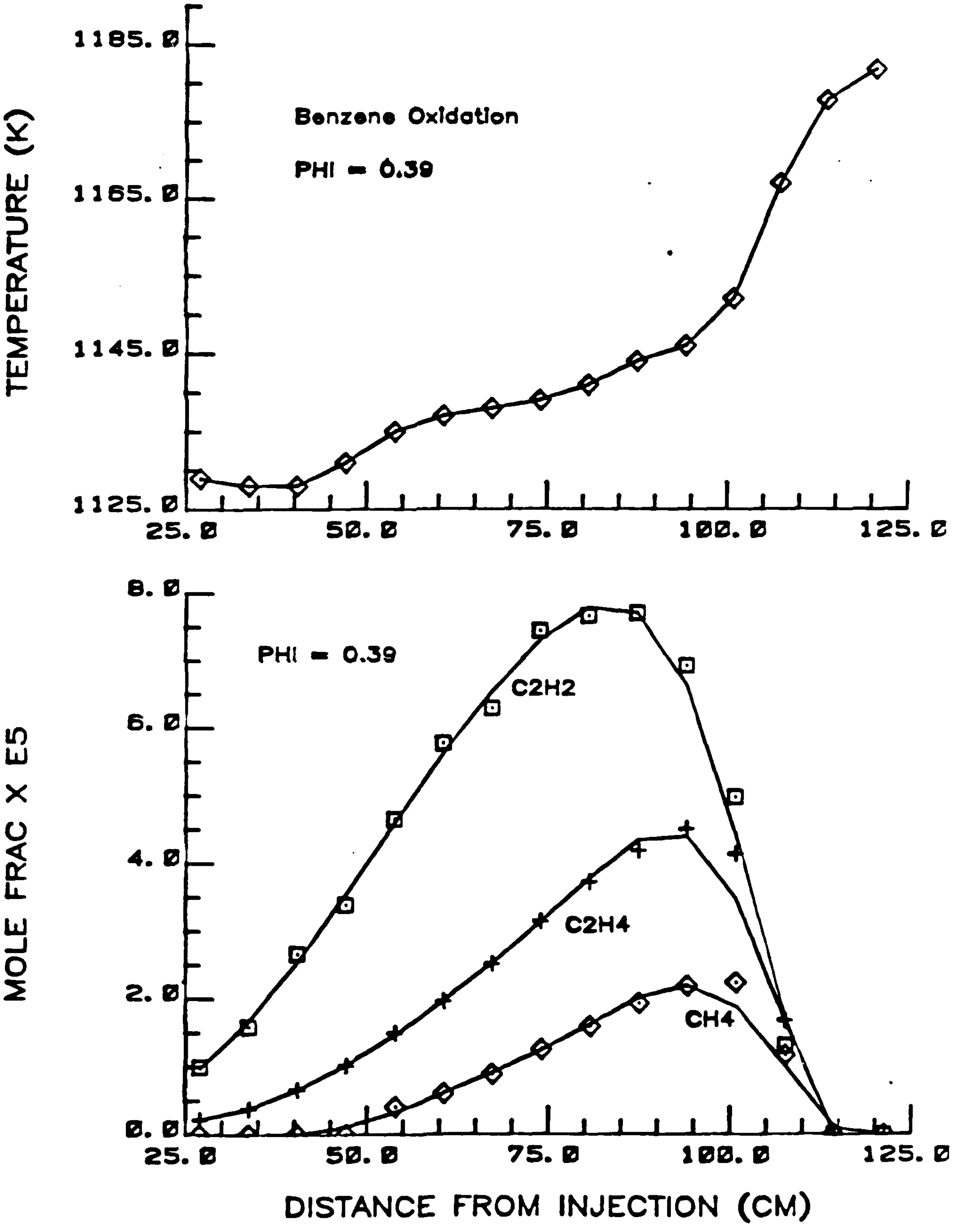


FIGURE 2 continued

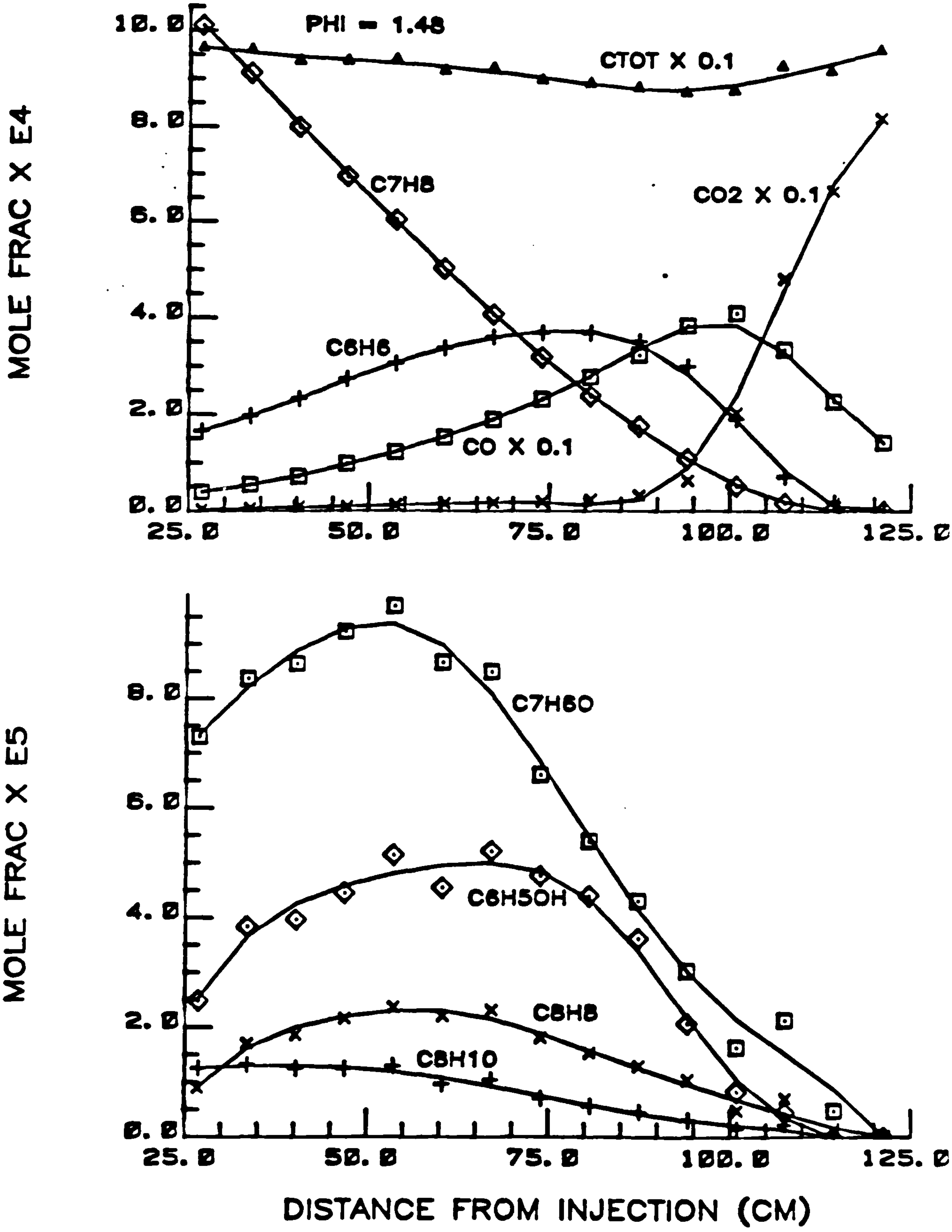


FIGURE 3 Toluene Oxidation: Phi = 1.48, 1 cm $\hat{=}$ 1.2 msec.

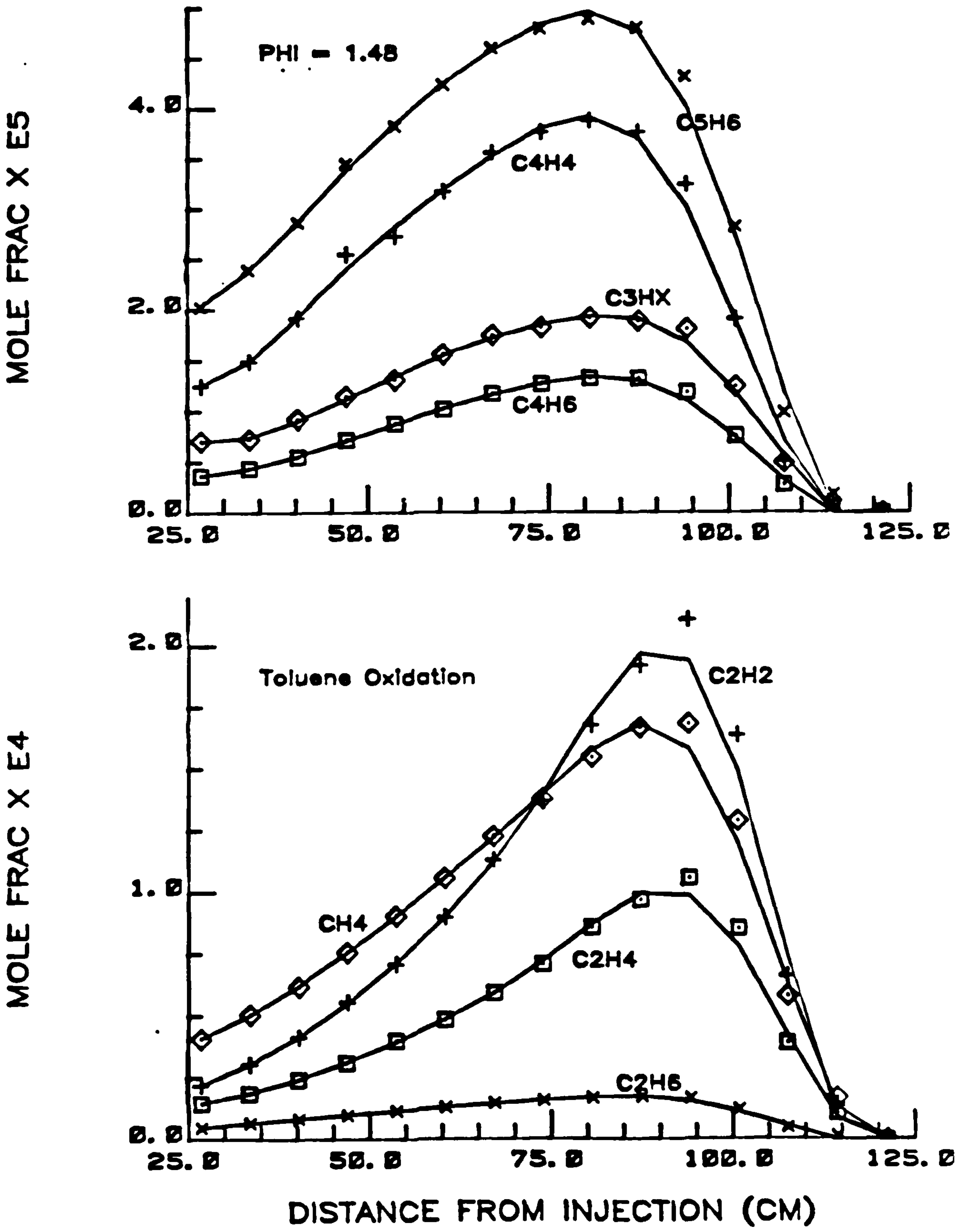


FIGURE 3 continued

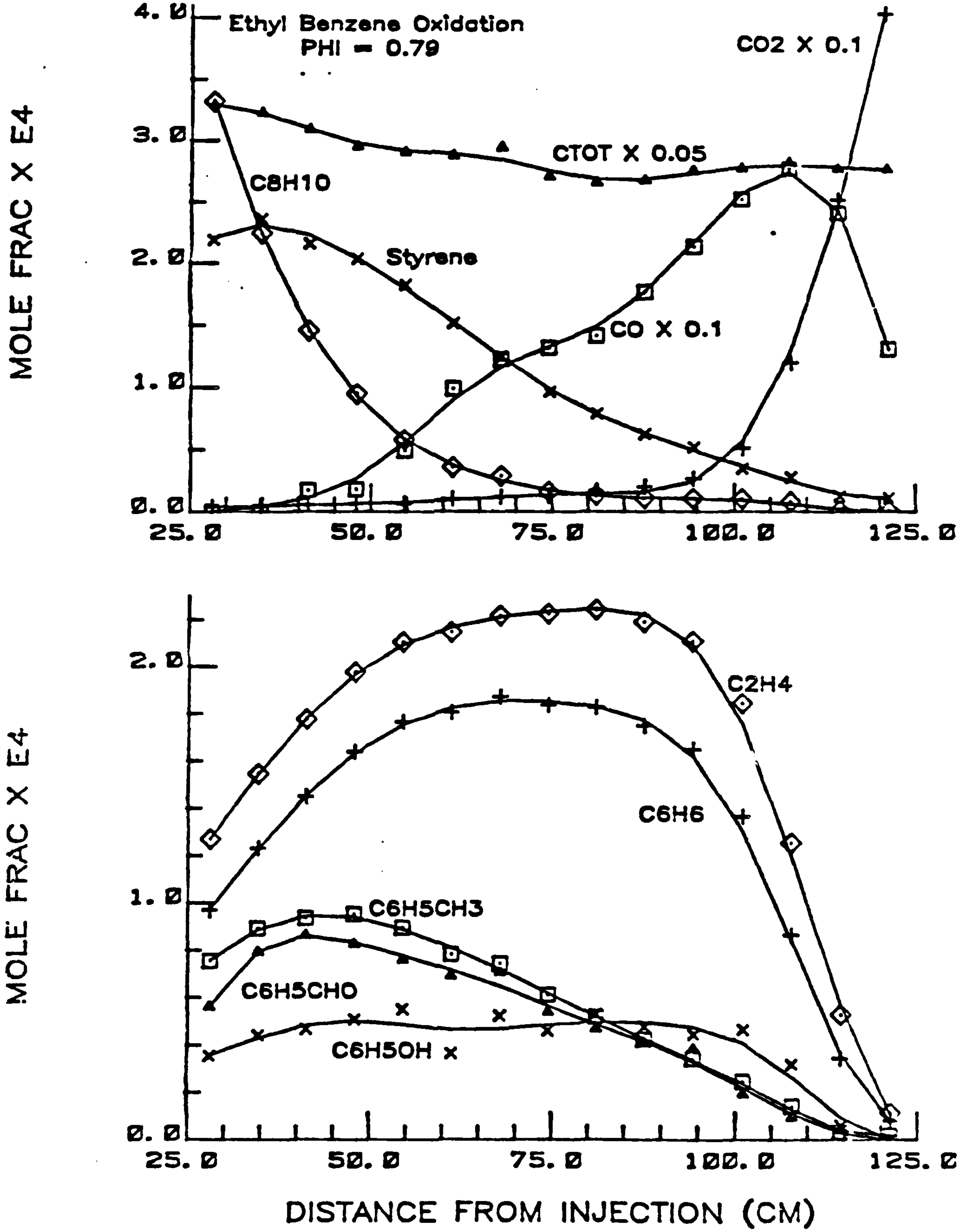


FIGURE 4 Ethyl Benzene Oxidation: Phi = 0.79, 1 cm $\hat{=}$ 0.85 msec.

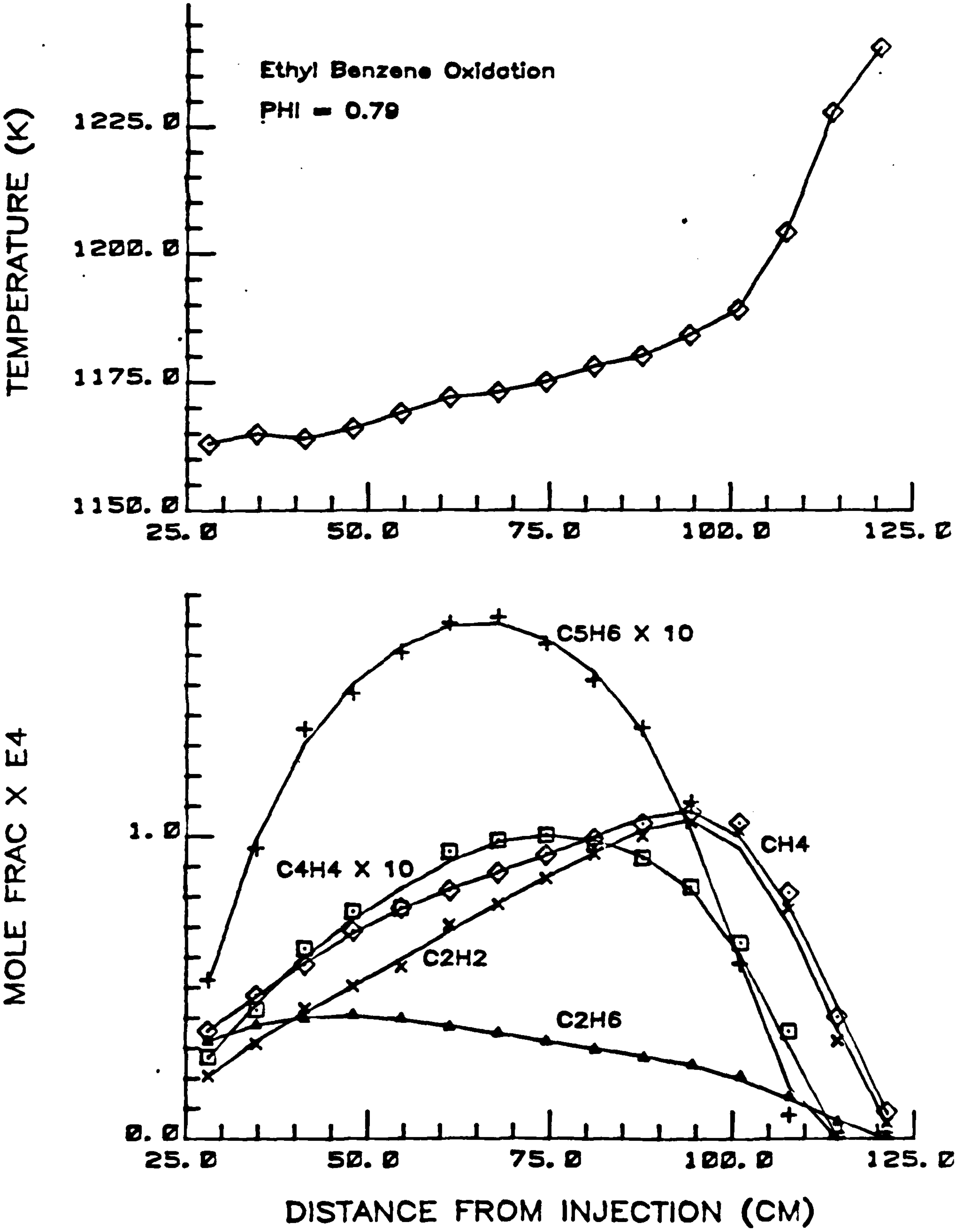


FIGURE 4 continued

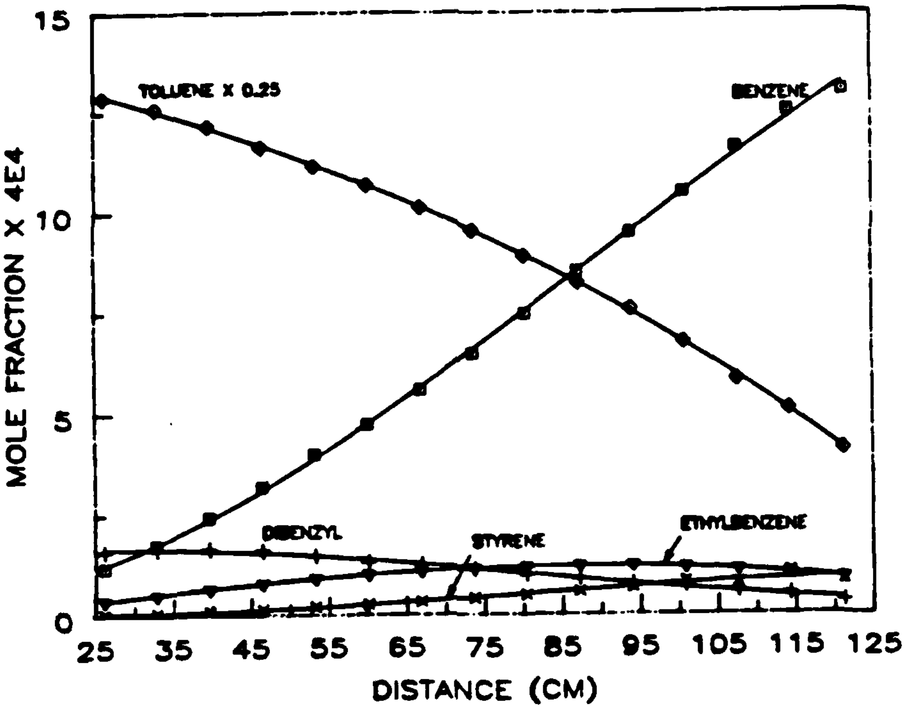


FIGURE 5

Fuel consumption and formation of products in Toluene oxidation at $\phi = 0.63$ and T ≅ 1180 K versus distance from fuel injection point.

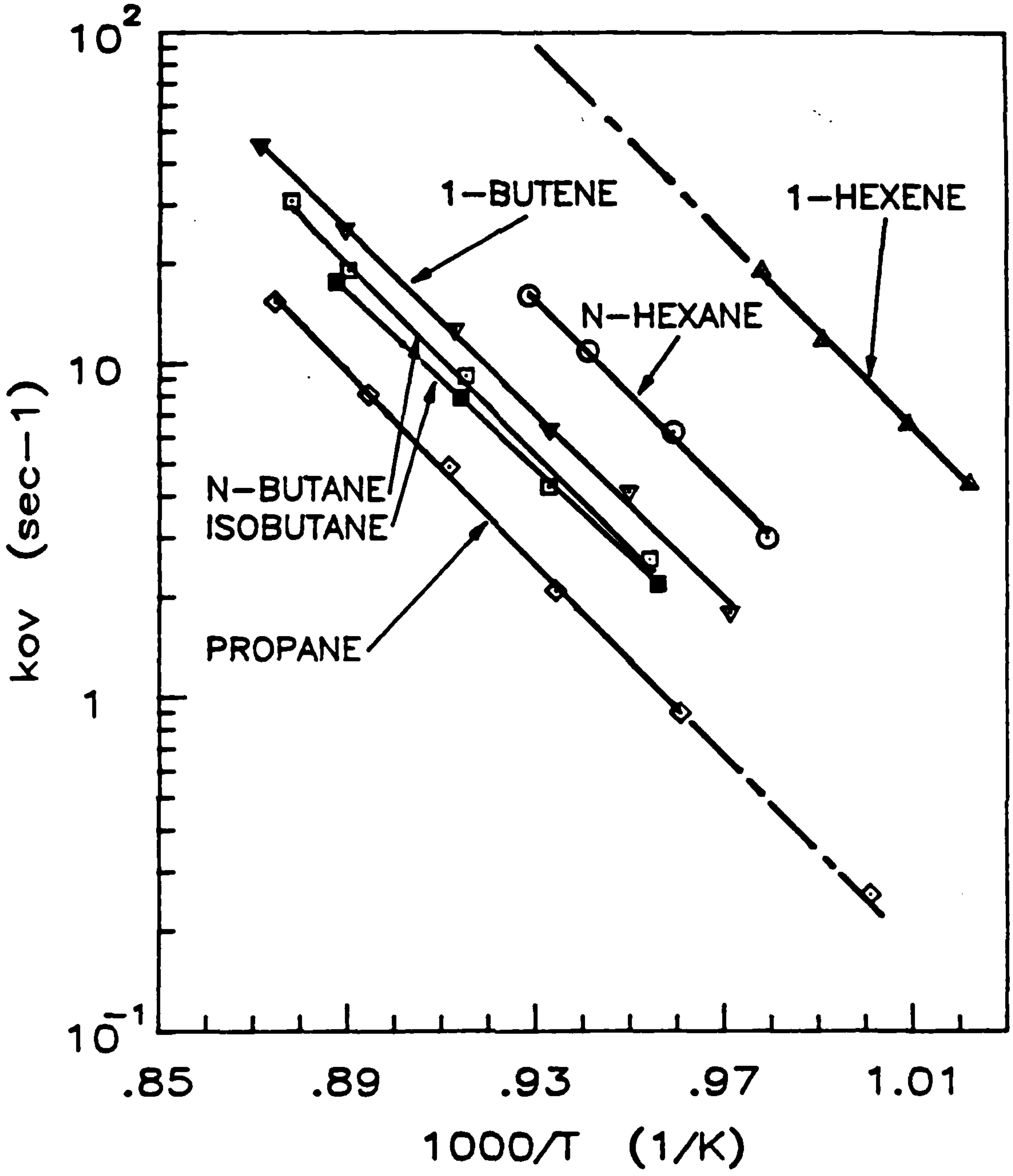


FIGURE 6 **Arrhenius Plot of Flow Reactor Pure Pyrolysis Results for Six Fuels: C3H8, 1-C4H8, n-C4H10, i-C4H10, 1-C6H12, and n-C6H14**

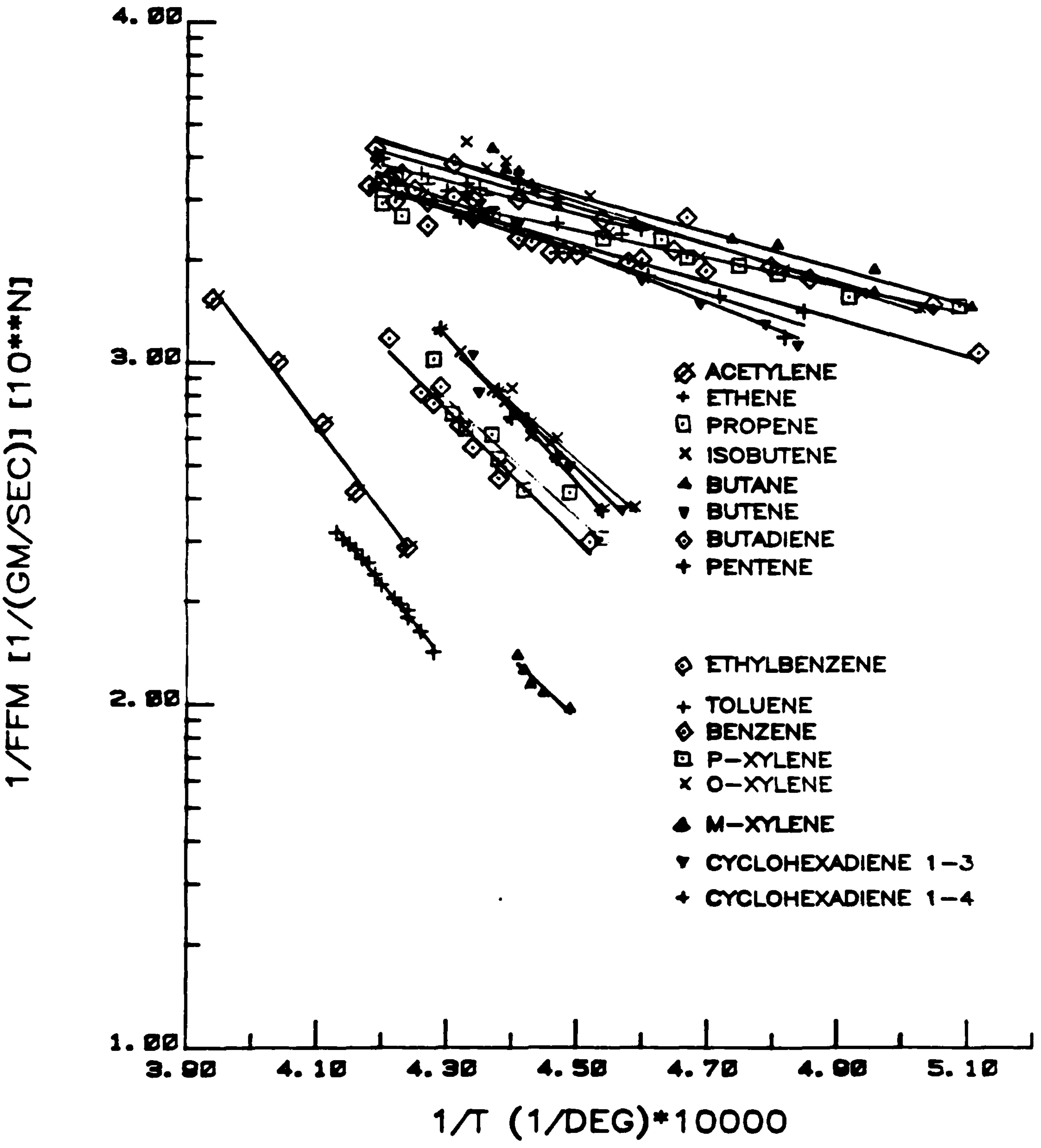


FIGURE 7 The Sooting Mass Flow Rate-Temperature Dependency Plotted as Arrhenius Parameters for Various Fuels.

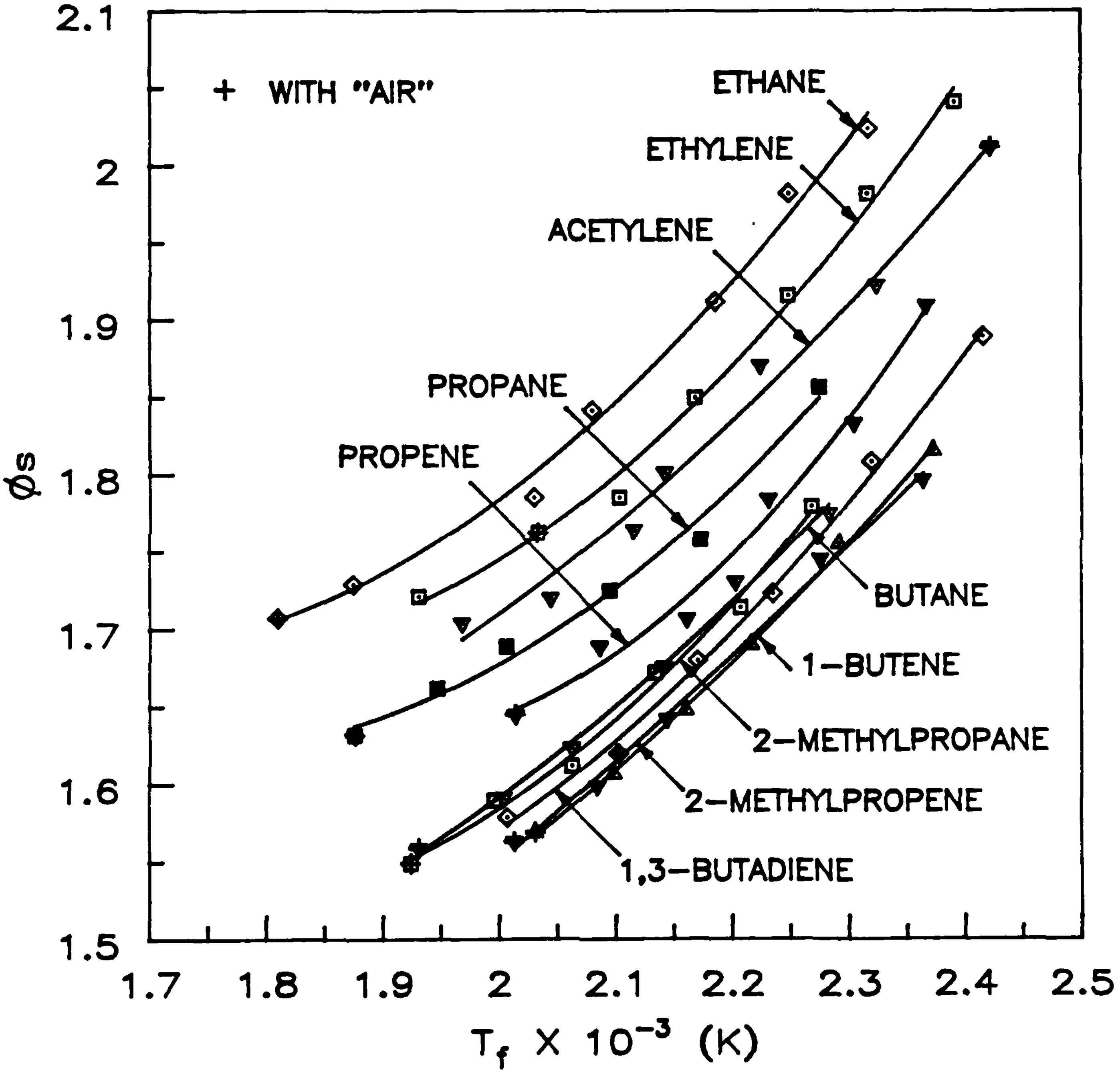


FIGURE 8 Sooting Equivalence Ratios for Various Fuels in Premixed Flames as a Function of Temperature. Equivalence Ratio Based on Carbon Conversion to CO_2.

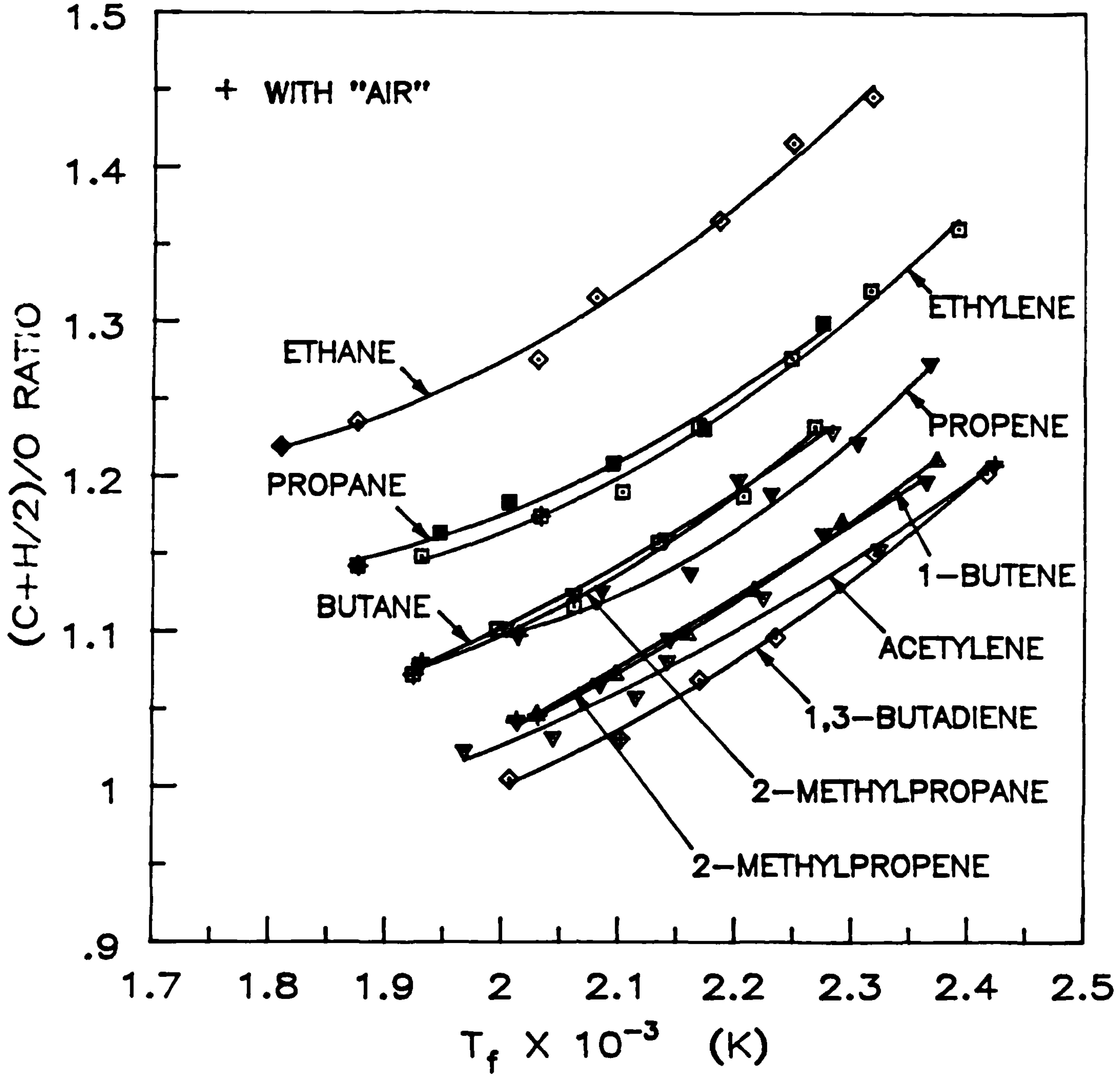
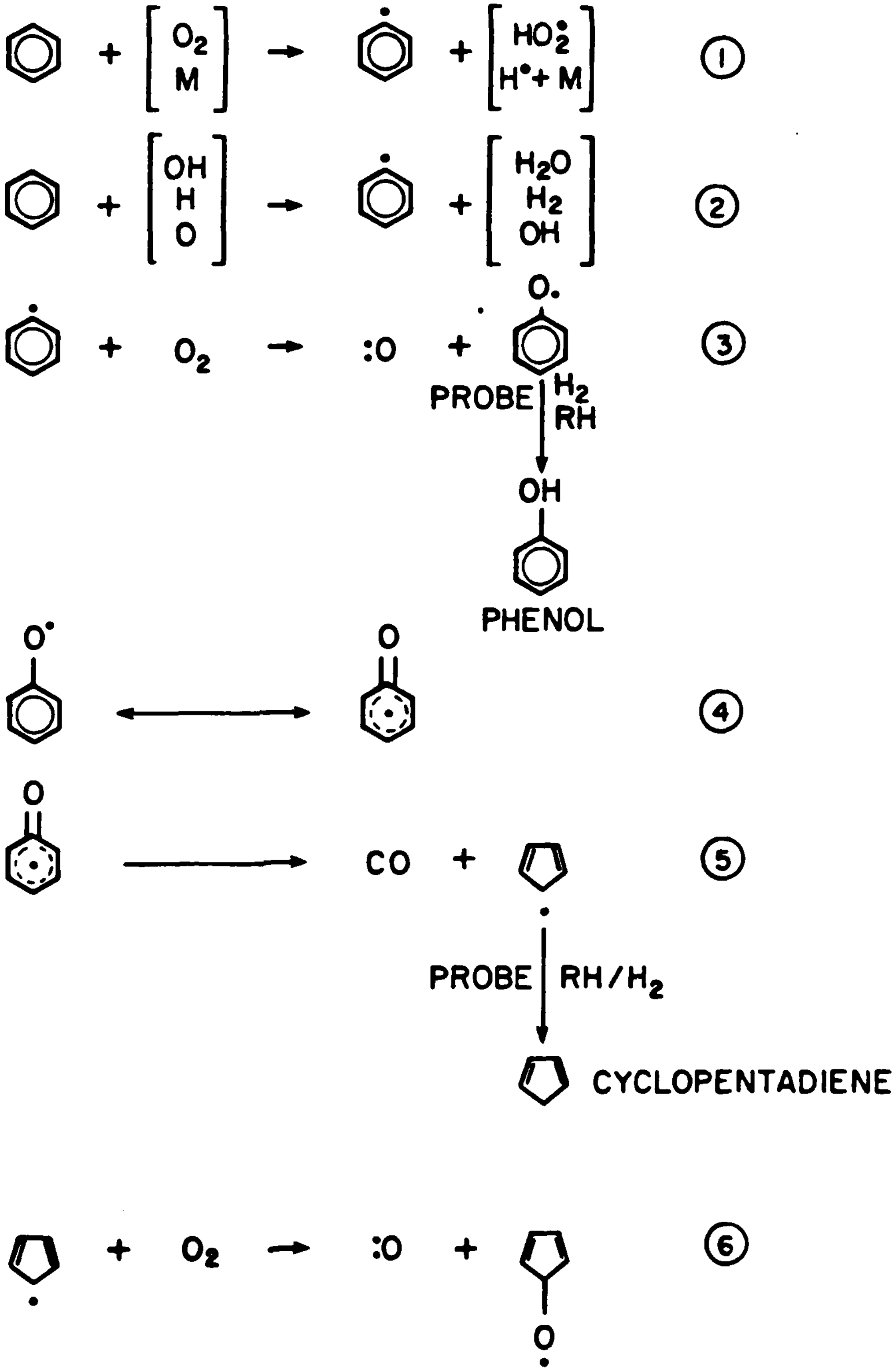
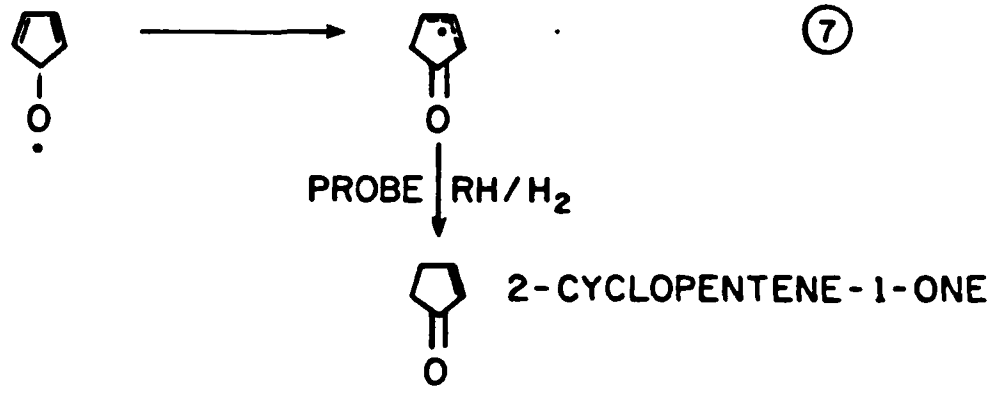


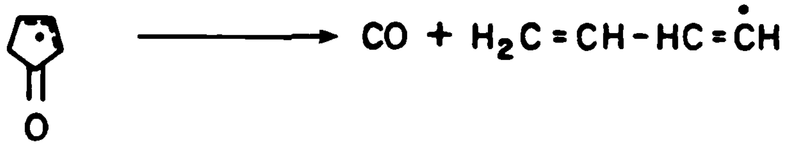
FIGURE 9 Sooting Equivalence Ratios for Various Fuels in Premixed Flames as a Function of Temperature. Equivalence Ratio Based on Carbon Conversion to CO.

TABLE I
BENZENE OXIDATION: PROPOSED MECHANISM

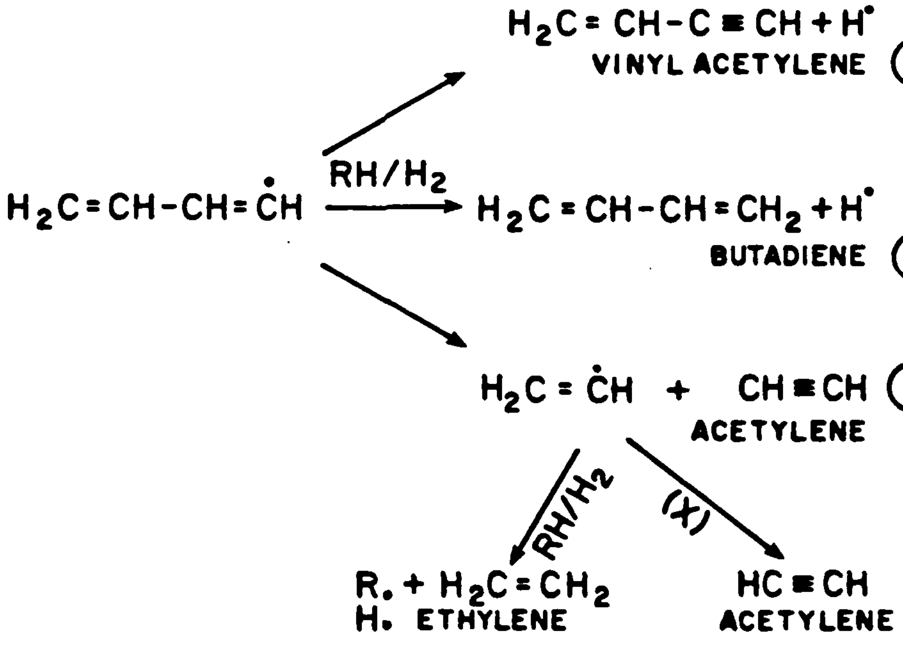



PROBE
RH/H2
2-CYCLOPENTENE-1-ONE

⑦


CO + H2C=CH-HC=ĊH

⑧


H2C=CH-C≡CH+H•
VINYL ACETYLENE
H2C=CH-CH=ĊH
RH/H2
H2C=CH-CH=CH2+H•
BUTADIENE
H2C=ĊH + CH≡CH
ACETYLENE
RH/H2
(X)
R. + H2C=CH2
H. ETHYLENE
HC≡CH
ACETYLENE

⑨
⑩
⑪
⑫
⑬

TABLE II

TOLUENE OXIDATION : PROPOSED MECHANISM

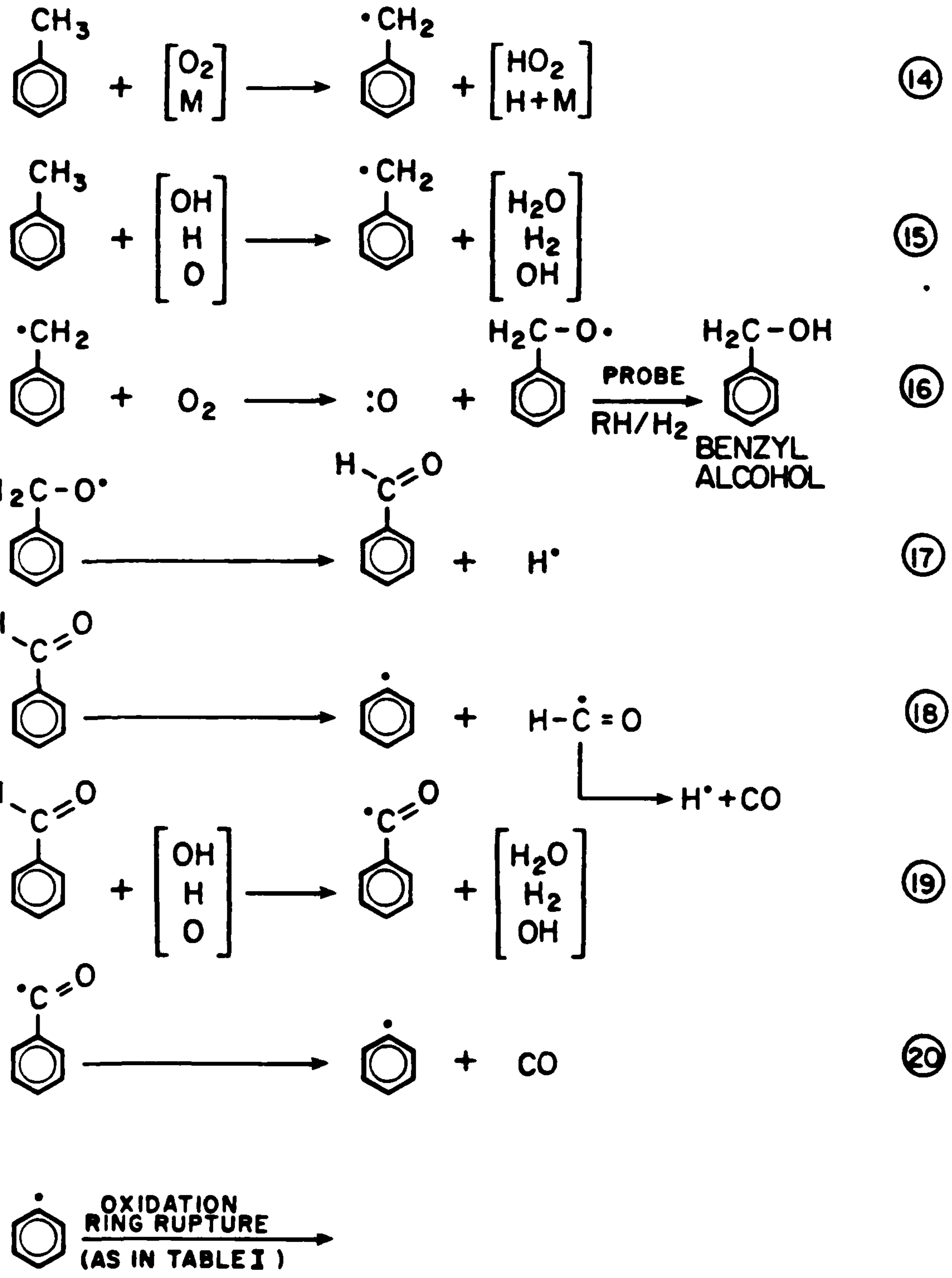


TABLE III
ETHYL BENZENE OXIDATION: PROPOSED MECHANISM

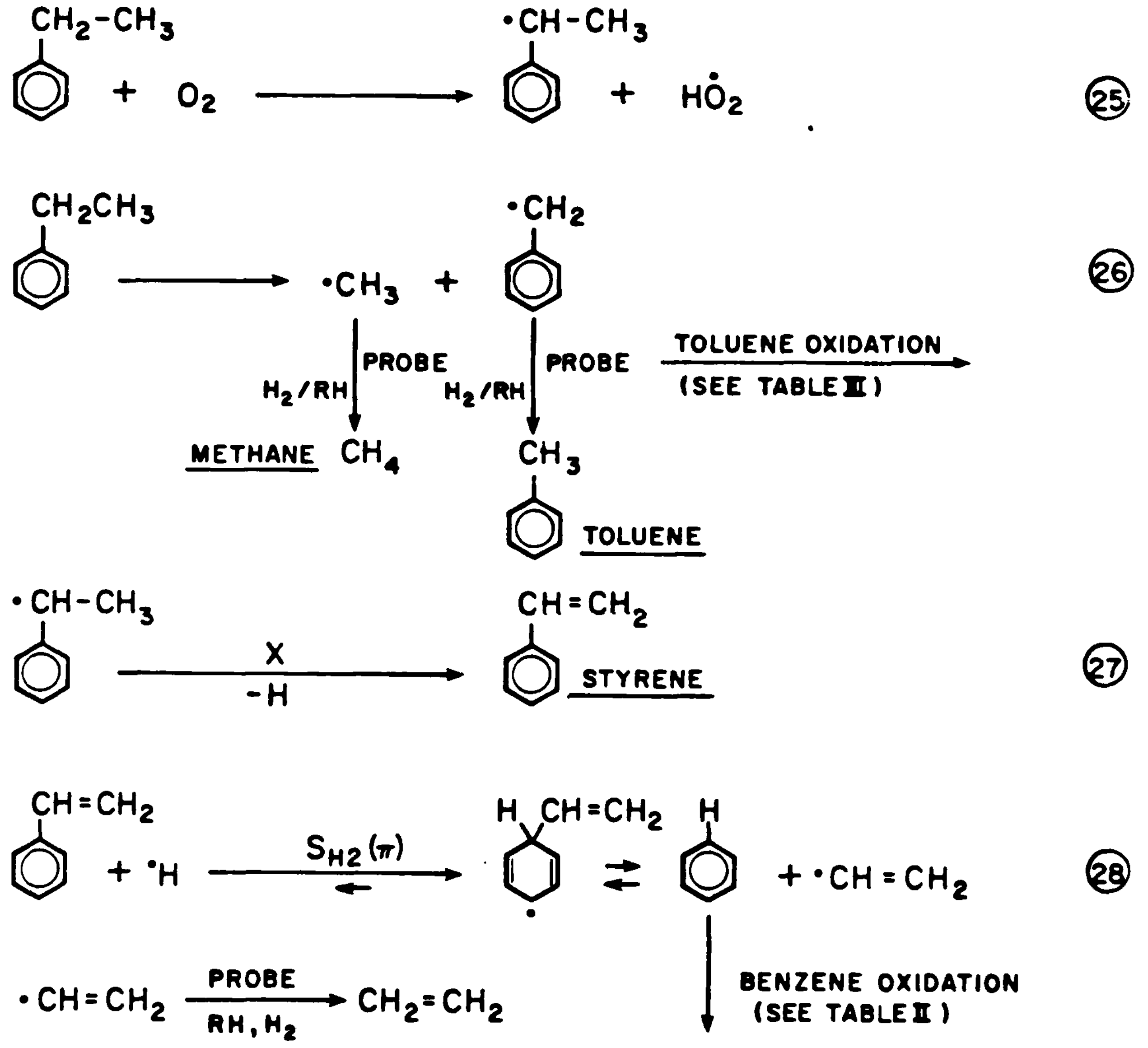


TABLE IV Oxidative Pyrolysis Literature

SOURCE	FUEL	% FUEL BEFORE OXYGEN ADDIT.	TOTAL P (atm)	TEMPERATURE RANGE (K) 700→	800→	1000→	[ox]/[fuel] RANGE <.001 <.1	Rate(OX)/Rate(PYR) strong (>2X)	
GROUP I:									
[4]	C2H4	100	.33	XXXX			XXXXX	SSS	
[5]	C2H4O	100	.3	XXXX			XXXXX	SSS	
[6]	C3H8	50	.33	XXXX			XXXX	SSS	
[7]	C3H8	100	.07		XXXX		XXXX	SSS	
[8]	C3H8	90	1		XXXX		XXXX	SSS	
[9]	i-C4H8	100	1		XXXX		XXXX	SSS	
[10]	n-C4H10	100	.75	XXXX			XXXX	SSS	
[11]	C2H6 i-C4H10 i-C5H12	100	.07	XXXX			XXXX	SSS	
[83]	ETHYL-BENZENE	10	1		XXXX		XXXX		WWW
GROUP II:									
[84]	BENZENE	10	1			XXXX	XXXX	SSS	
[85]	BENZENE	100	1		XXXX		XXXX		WWW
[86]	C2H6 C3H8	1	1		XXXX		XXXX	SSS	
[87]	C2H4	.25	3			XXXX	XXXX		WWW
[48]	C2H4O	.7	1			XXXX	XXXX		WWW

TABLE V First Order Overall Arrhenius Parameters

FUEL	NUMBER OF RUNS (Appendix C)	TEMPERATURE RANGE (K)	ARRHENIUS PARAMETERS log(A)*	E* (kcal/mole)
C_3H_8	5	1041 - 1143	13.8	66.0
1-C_4H_8	6	1053 - 1148	13.7	63.2
n-C_4H_{10}	5	1048 - 1139	14.0	65.3
i-C_4H_{10}	3	1046 - 1126	13.0	60.6
1-C_6H_{12}	4	978 - 1022	15.4	66.0
n-C_6H_{14}	4	1021 - 1077	14.5	65.4

Average Activation Energy for normal alkanes and alkenes = 65.2

* Calculated from slope and intercept of plots in Figure 2

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soot formation
boron and carbon combustion
turbulent reacting flow

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

A qualitative mechanism of aromatic oxidation has been developed and is of significant importance for the understanding of soot processes and combustor modelling. Kinetic results on toluene and ethyl benzene have elucidated how aromatic side chains are oxidized and contribute further towards developing overall mechanisms for combustor modellers. Extensive results on fuel pyrolysis rates have been obtained. These results reveal that pyrolysis rates alone do not control sooting intensity, but also the pyrolysis intermediates formed. A complete phenomenological model of soot formation has been developed and refined by comparison with the experimental results. This model has permitted the identification of the phenomena controlling soot formation in both premixed and diffusion flame combustion systems and has great immediate practical applications. In particular, lengthy experimentation has shown that the combustion temperature is one of the most significant parameters in determining sooting tendencies in both diffusion and premixed flame situations and with temperature as a controlled parameter the real

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effect of fuel type can be determined.

A reliable generator of well characterized suspensions of boron slurries has been designed and constructed well ahead of schedule. Two significant new findings with respect to the ignition combustion of boron particles have been reported. The first shows that the solubility of boron, not oxygen, in the molten B_2O_3, determines the oxide growth during the ignition phase. The second is that at the surface of the clean boron particle, at steady state, the B_2O_3 reacts with the boron to form BO only. The theoretical work on turbulent combustion has treated both premixed and diffusion flames by asymptotic methods. The major new findings for premixed flame concerns the influences of the density change associated with the heat release on the flame structure and on the flame dynamics.