

PART B: ANALYTICAL PROGRAM PROGRESS

R. B. Edelman, E. Y. Wong
Science Applications, Inc,
Combustion Science and
Advanced Technology Department
21133 Victory Boulevard, Suite 216
Canoga Park, California 91303

1. INTRODUCTION

The objective of the model development effort is to provide user-oriented tools to aid in accelerating the implementation of alternative fuels in stationary gas turbines. Fundamental information is being translated into a form that relates the important performance criteria to the flame structure with emphasis on fuel property effects. The practical results are models that will relate efficiency and emissions to controllable design parameters. At the same time the models will provide important information on fuel/air distribution, aerodynamic flow patterns and heat transfer.

The approach of relating fundamental combustion phenomena to fuel properties involves the application of analytical models developed with and ultimately verified by data obtained from specially designed experiments. The models are being developed through the integration of chemical and fuel related elements, thermodynamic and heat transfer elements, and aerodynamic elements. The physical processes include droplet and spray combustion, heat transfer by convection and radiation, aerodynamic flow patterns, and turbulent mixing.

The work reported upon here emphasizes the approach to the model development for fuel related elements. The engineering model for this element is based on extending the quasiglobal kinetics model. The concept of this sub-model involves the coupling of a set of subglobal reaction steps to a set of detailed steps for those reaction chains for which substantial information already exists for their kinetics and mechanism. While the original quasiglobal kinetics model consisted of a single global partial oxidation step coupled to the detailed "wet CO mechanism", the extended model includes fuel pyrolysis, soot formation and oxidation and fuel-bound nitrogen conversion steps.

The effort during this phase of the program has concentrated on the development of the extended quasiglobal kinetics model with particular emphasis on soot emissions.

2. EXTENDED QUASIGLOBAL KINETICS MODEL*

The details of the kinetics and mechanism of the combustion of most hydrocarbon fuels, particularly heavy hydrocarbons, is not fully understood at this time. The quasiglobal kinetics model represents an intermediate level of detail and involves the essential features of the coupling of a set of subglobal steps to a set of detailed steps for which sufficient information to accurately describe their kinetics and mechanism exists. The original quasiglobal kinetics model, however, consists of a single subglobal partial oxidation step coupled to the detailed wet CO mechanism.

That model has been used with reasonable success in accounting for the variation in fuel type, i.e. aliphatic versus cyclic in fuel lean systems. Consistent with the general quasiglobal concept, the current model has been extended to include important combustion characteristics in fuel rich systems. The extended model, illustrated in Table 1, includes subglobal steps for fuel pyrolysis, fuel bound nitrogen conversion, partial oxidation, soot formation and oxidation. Furthermore, the products of partial oxidation, CO and H₂, are allowed to react toward completion through a set of elementary steps. In addition, detailed NO_x formation steps are included. Many of these detailed steps, together with their rate constants have been recently compiled and updated in an SAI report published by Gelinas, et al, (Ref. 1).

For the fuel nitrogen conversion step, it is assumed that a nitrogen-containing intermediate (NX) is released through hydrocarbon pyrolysis. The intermediate might be NH₂, N, or even HCN, as Fenimore, et al, (Ref. 2), and Corrett, et al, (Ref. 3) have suggested. As the intermediate is formed, it may further react to produce other nitrogen containing compound(s) (e.g. NCH and NH₃), or nitric oxide, or a stable nitrogen compound (e.g. N₂). The kinetic steps under "NO_x Formation" in Table 1 illustrate our approach to the fuel nitrogen conversion process. Foster (Ref. 4) has proposed a rather detailed mechanism for the fate of fuel bound nitrogen and these results will be included in our model. In addition, nitric oxide can also form through a direct thermal process and is accounted for by the extended Zeldovich mechanism given by the last three reactions in Table 1.

Finally, the rate constants for the subglobal steps are expressed in modified Arrhenius form and the rate of production (consumption) is given by expressions of this type:

$$R = AT^b C_1^a C_2^c \exp (-E/RT)$$

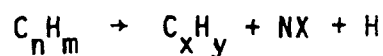
where the constants A, b, a, c and E are the rate parameters for the particular subglobal reaction. For the partial oxidation steps, C₁ and C₂ are the concentrations of the particular hydrocarbons and oxygen, respectively. For pure pyrolysis, c is zero and a is unity for first order decomposition. The rate parameters are being determined from literature values, but mainly in conjunction with ER&E data.

During this period emphasis was on the analysis of the net soot emissions data measured in the jet stirred combustor described in Part A of this report. In terms of the quasiglobal scheme, the work concentrated on the two steps comprising soot formation and soot oxidation given in Table 1.

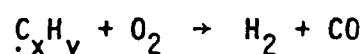
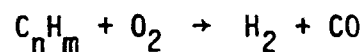
* This section is drawn from the AGARD paper written jointly by R. B. Edelman, A. Turan, P. T. Harsha, and E. Wong of SAI and W. S. Blazowski (Exxon) which is included in the Appendix to this report.

TABLE 1 - SKELETAL SYSTEM FOR THE EXTENDED QUASI-GLOBAL MODEL

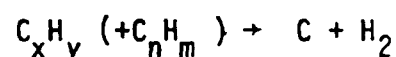
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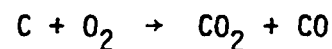
Hydrocarbon Partial Oxidation



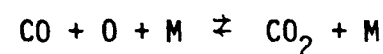
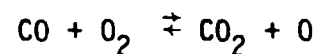
Soot Formation



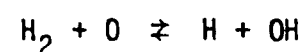
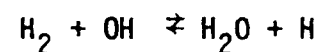
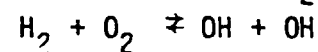
Soot Oxidation



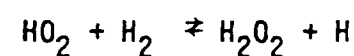
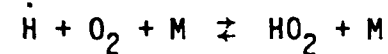
Elementary Steps for CO/O₂ Reaction Mechanism



Elementary Steps for H₂/O₂ Reaction Mechanism

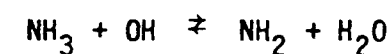
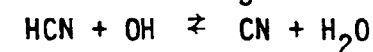


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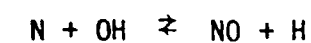
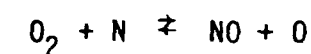
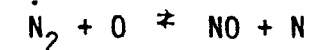


⋮

NO_x Formation



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3. EXISTING SOOT FORMATION MODELS

Many studies on soot formation have been carried out but few lead to quantitative predictions of soot production. Furthermore, there is little agreement as to the details of the intermediate steps involved in the production of soot. Nevertheless, there seems to be general agreement that the overall soot formation reaction is triggered by hydrocarbon pyrolysis and involves subsequent soot nuclei formation, soot particle formation, and particle growth and coagulation. A model that treats these in some detail has been considered by Jensen (Ref. 5). Application of the model to a methane flame has led to qualitative agreement with experimental observations. Although this approach represents an attempt to deal with the problem at a mechanistic level the uncertainty of intermediate species, reactions and rates requires long term development to provide quantitative predictions. Tesner, et al (Ref. 6) have proposed a model in which soot formation is characterized by three rate-limited steps. The feature of the model is that all the complex elementary steps associated with pyrolysis, nuclei formation and soot formation are grouped into three subglobal steps. The model includes a first order (with respect to hydrocarbon concentration) pyrolysis rate, a chain branching and chain termination rate, and a soot formation rate:

$$\text{Pyrolysis} \quad n_0 = 10^{13} C_{\text{HC}} \exp(-170,000/RT) \quad 2$$

$$\text{Nuclei Formation} \quad \frac{dn}{dt} = n_0 + (f-g)n - g_0 Nn \quad 3$$

$$\text{Soot Formation} \quad \frac{dN}{dt} = (a-bN)n \quad [\text{particle/cm}^3\text{sec}] \quad 4$$

The values of the kinetic parameters (f, g, g₀, a, b) for Toluene (Ref. 7) are:

$$\begin{aligned} (f-g) &= 500.0 \\ g_0 &= 10^{-8} \\ a &= 10^5 \\ b &= 3 \times 10^{-6} \end{aligned}$$

In contrast to this three-step scheme, Greeves, et al, (Ref. 8) proposed a single step soot formation rate,

$$\frac{dC_s}{dt} = 0.468 p_{\text{HC}} \phi_u^3 \exp(-40,000/RT) \quad [\text{gm/cm}^3\text{sec}] \quad 5$$

where p_{HC} and φ_u represent the partial pressure of unburnt hydrocarbon and the unburnt equivalence ratio. The rate parameters given in this equation were selected by Greeves to fit data obtained under conditions designed to simulate typical diesel operation. The fuel was an unspecified diesel fuel.

Comparisons between computations using the Tesner and Greeves models and a set of ER&E soot measurements are shown in Fig. 1. Soot emissions become detectable at φ = 1.3 and the soot concentration level increases as the equivalence ratio increases. The relatively horizontal curve obtained using the Tesner model shows no discernible trend. In contrast to the experimental observation, the Tesner model appears to be insensitive to the equivalence ratio. Fig. 1 also shows the predictions based upon the Greeves model. In this case the predicted soot concentration appears to be overly sensitive to the equivalence ratio and the predictions are generally one order of magnitude higher than the experimental data.

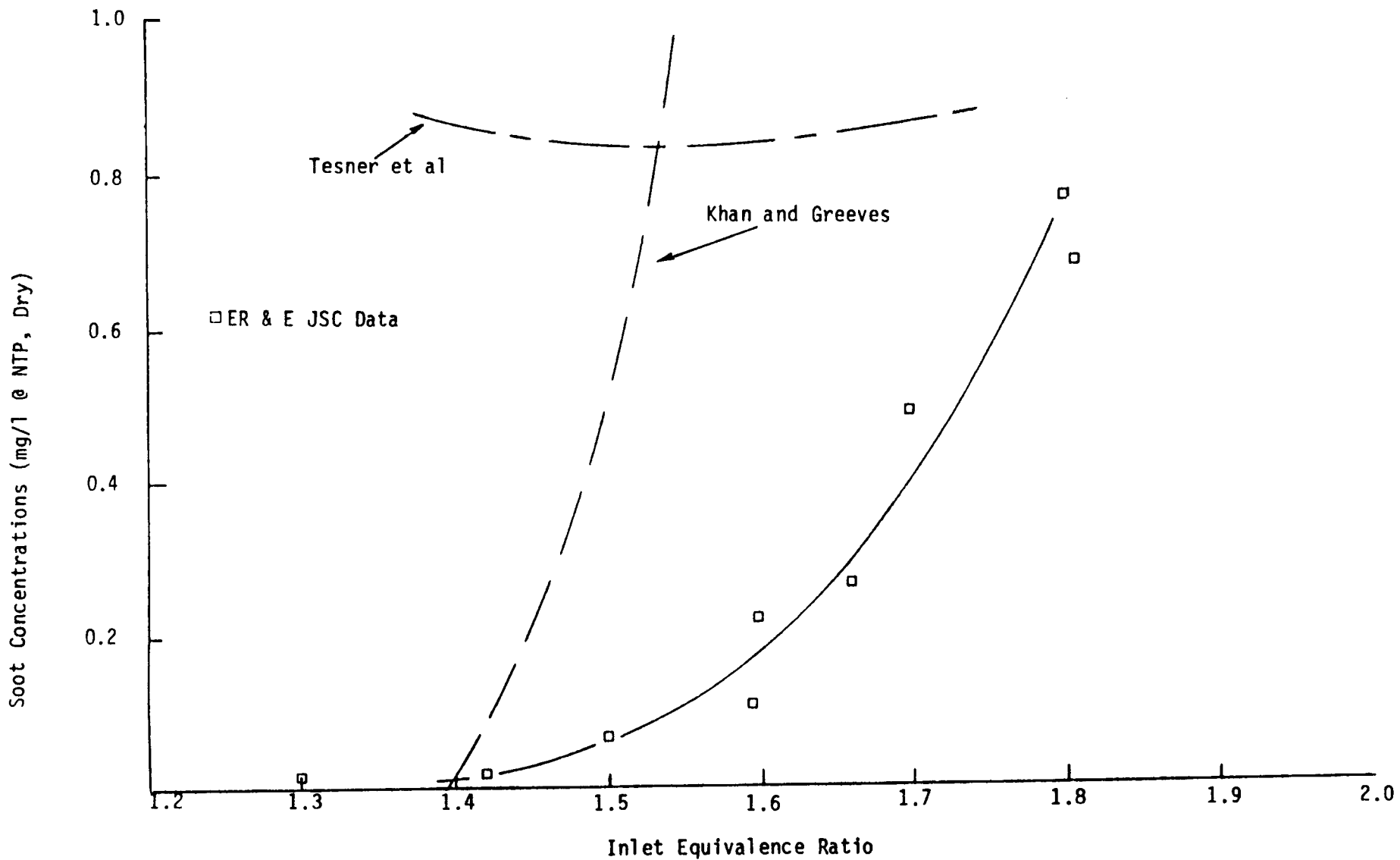


Figure 1. Comparison of Predicted with Measured Soot Concentrations, Toluene

The disparity between the ER&E data and Tesner model has not been fully reconciled. However, an examination of the method used in obtaining the rate constants suggests that they may have been influenced by aerodynamic effects including turbulent mixing. Furthermore, the Tesner model has treated the kinetic parameters (a , b , f , g , g_0) as constants throughout the range of conditions covered in their experiments. However, in studies on explosion limits, Semenov and coworkers (Ref. 9) have shown that these parameters are, in fact, functions of local conditions, such as temperature and radical concentrations, suggesting that for this model to have practical use considerably more information is required concerning these dependencies.

Furthermore, a significant deficiency of these models is that they do not account for the effect of soot oxidation. In high temperature combustion systems where soot burnout is expected to be significant and might possibly be controlled, it is important that the formation and the oxidation reactions be considered simultaneously in the prediction of net soot emission.

4. NET SOOT EMISSIONS

As a result of the above investigation, a somewhat more general two step model comprised of a formation and an oxidation step has been developed. For the prediction of net soot emissions under well-stirred environments, however, these reaction steps are coupled into the species conservation equations in order to provide the desired net soot emissions relationship. The species conservation equation for soot can be expressed as follows:

$$\frac{\dot{m}}{\rho V} (C_S - C_{S_0}) = R_f - A_t R_{Ox} \quad [\text{gm/cm}^3\text{sec}] \quad 6$$

where \dot{m} , ρ , V , C_S , C_{S_0} , are total mass flow rate, exhaust gas density, reactor volume, outlet and inlet soot concentrations. As a whole, $\dot{m}/\rho V$ represents the reciprocal of residence time. A_t which can be expressed in terms of C_S , soot density (ρ_S) and soot particle diameter (D) is the total surface area available for oxidation. Finally, R_f and R_{Ox} are the reaction rates for the soot formation and oxidation steps.

The formation step assumes the following form:

$$R_f = AT^\alpha C_{HC}^a C_{O_2}^b \exp(-E/RT) \quad [\text{gm/cm}^3\text{sec}] \quad 7$$

where C_{HC} and C_{O_2} are concentrations of unburnt hydrocarbon and oxygen, and A , α , a , b , E are rate constants. Tentative values for these constants have been determined by using ER&E jet-stirred reactor data (Ref. 10). These data comprise three residence times, i.e. three mass flow rates corresponding to 112.5, 80.0 and 50.0 gm/min. The set of data having air flow rates of 112.5 gm/min was used to determine these rate constants. These data comprising the unburnt hydrocarbon and oxygen concentrations are illustrated on Figs. 2 and 3. Because the nature of the data does not allow a direct determination of these rate constants, a series of Arrhenius type plots were constructed by systematically varying the value of these rate parameters. This procedure produced the following set of rate constants:

$$\begin{aligned} A &= 1.33 \times 10^{14} \\ \alpha &= -1.94 \\ a &= 1.81 \\ b &= -0.5 \\ E &= 32,000 \end{aligned}$$

Regarding the oxidation step, various oxidation models have been reviewed. In particular, models developed by Lee, Thring, and Beer (Ref. 11) and Nagle, Strickland-Constable (Ref. 12) have been examined in some detail. These models were of particular interest because the rate constants were determined using data obtained from soot or soot-like combustion experiments. Since the model of Lee, et al, can be deduced from that of Nagle and Strickland-Constable when the oxygen concentration is small, the more general model of Nagle and Strickland-Constable has been tentatively adopted. This model gives the rate of soot consumption as follows:

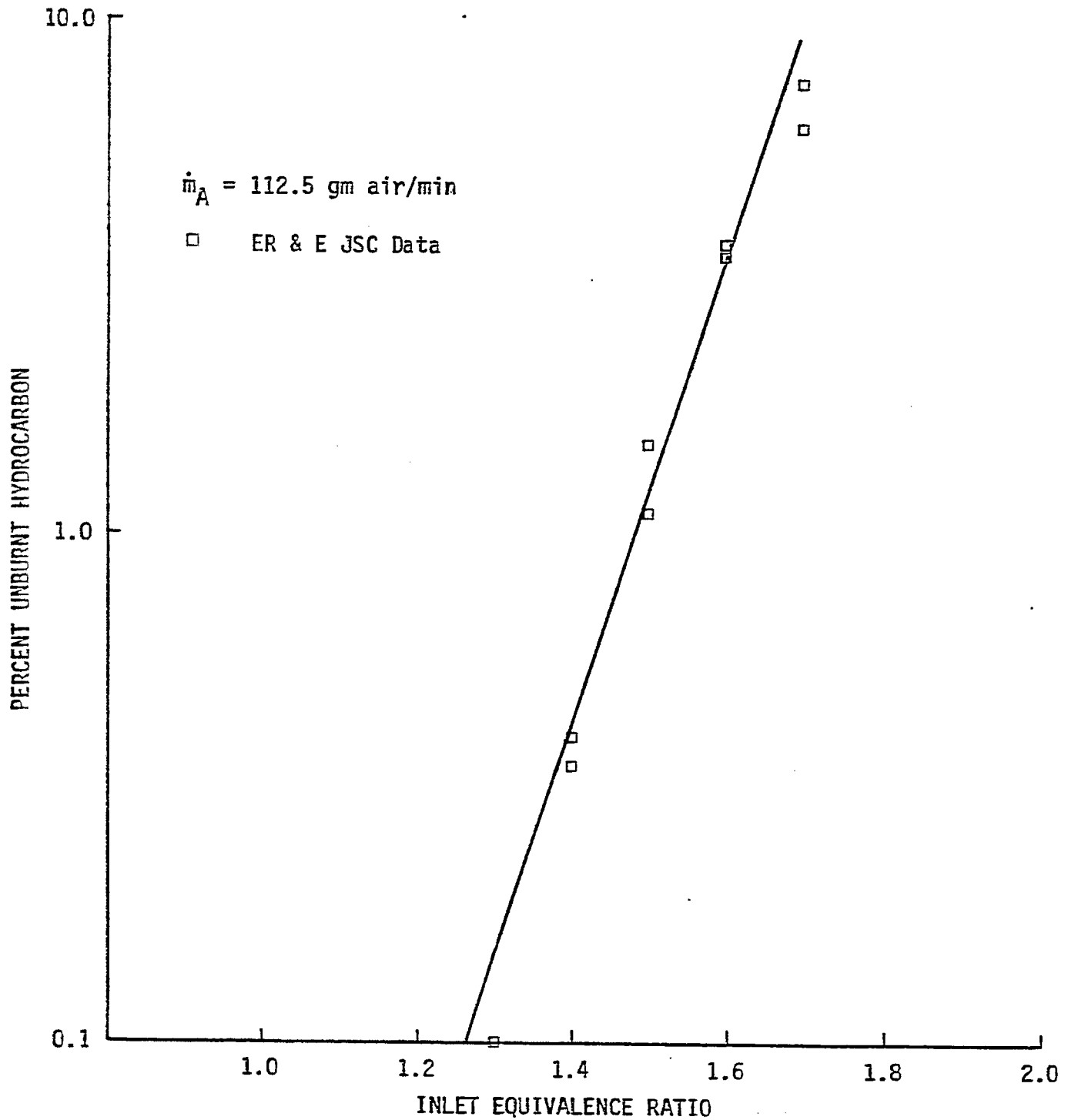


Figure 2: Measured Unburnt Hydrocarbon Concentration in Jet Stirred Reactor, Air Flow = 112.5 gm/min, Toluene

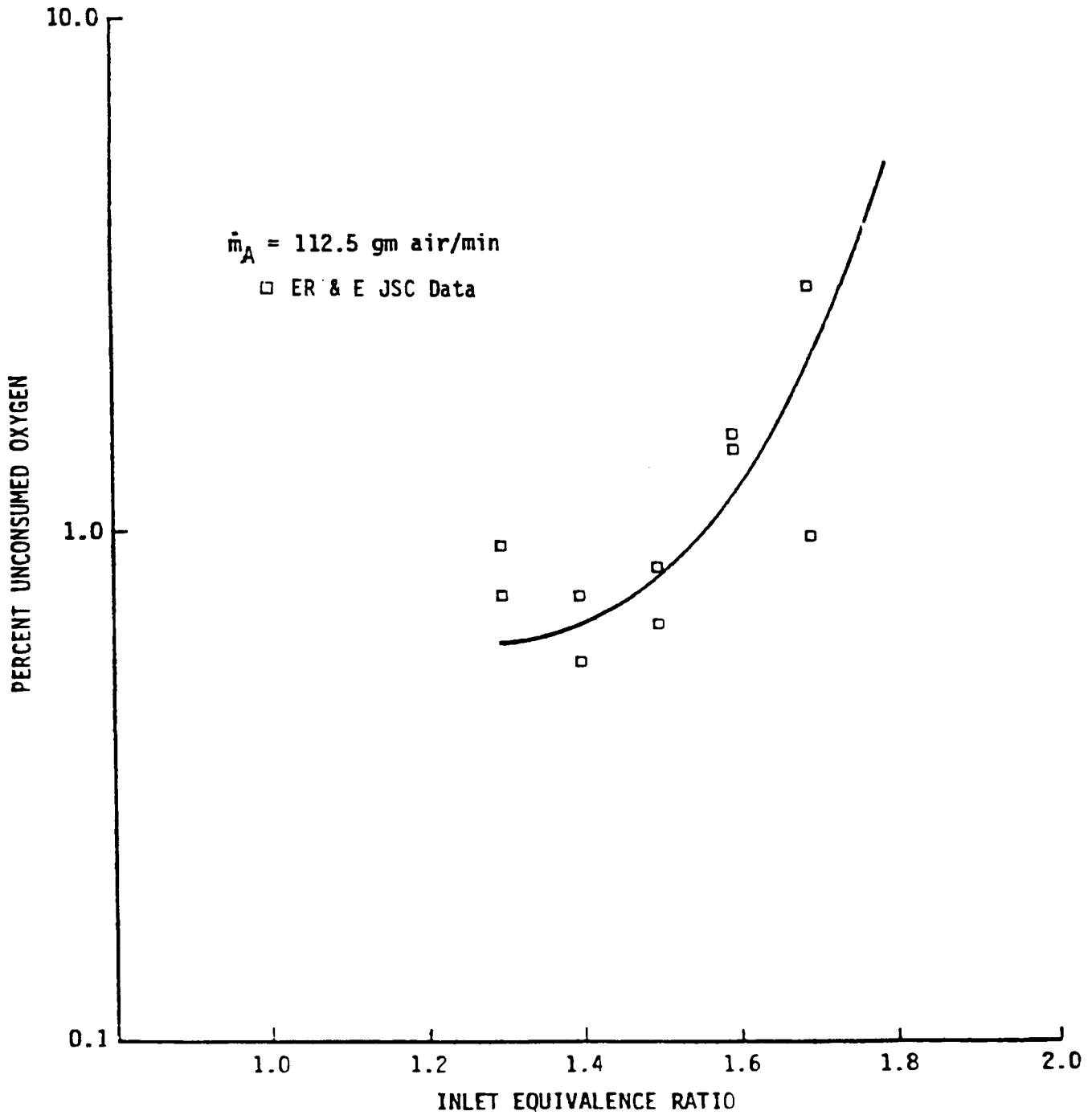


Figure 3: Measured Unconsumed Oxygen Concentration in Jet Stirred Reactor, Air Flow = 112.5 gm/min, Toluene

$$R_{ox} = 12 \left[\left(\frac{k_Z P_{O_2}}{1 + k_Z P_{O_2}} \right) \chi + k_B P_{O_2} (1 - \chi) \right] \text{ [gm/cm}^2 \cdot \text{sec]} \quad 8$$

$$\text{where } \chi = \left[1 + k_T / (k_B P_{O_2}) \right]^{-1} \quad 9$$

$$k_A = 20 \exp (-30,000/RT)$$

$$k_B = 4.46 \times 10^{-3} \exp (-15,200/RT)$$

$$k_Z = 1.51 \times 10^5 \exp (-97,000/RT)$$

$$k_T = 21.3 \times \exp (4100/RT)$$

Substitution of the formation and oxidation rates into equation 6 gives the desired result for the concentration of the soot emission

$$C_s = \frac{\left(\frac{V}{\rho \dot{m}} \right) \times 1.33 \times 10^{14} T^{-1.94} C_{HC}^{1.81} C_{O_2}^{-0.5} \exp (32,000/RT)}{1 + \left(\frac{\rho V}{\dot{m}} \right) \left(\frac{6}{\rho_s D} \right) R_{ox}} \text{ [gm/cm}^3 \text{]} \quad 10$$

The relationship was used in the prediction of the soot emission data obtained from ER&E JSC experiments. For this purpose, a single soot particle size of 250 Å was assumed. The results of our calculations are shown in Fig. 4. It can be seen that the predictions based upon the above equation generally agree with the data over the range of operating conditions covered. In addition, Figs. 5 thru 7 show the comparison between predictions and data recently obtained from ER&E isothermal experiments. These data were obtained for constant reactor temperatures at various inlet equivalence ratios. Even for these cases the agreement is good for soot concentrations above 0.1 mg/l. Below this level the trend in the data is generally predicted but the scatter suggests the desirability of obtaining additional data at these low emissions level conditions. Finally, Fig. 8 shows a comparison of computed and measured soot concentration as a function of residence time. Again, the predictions follow the trend of the data very well.

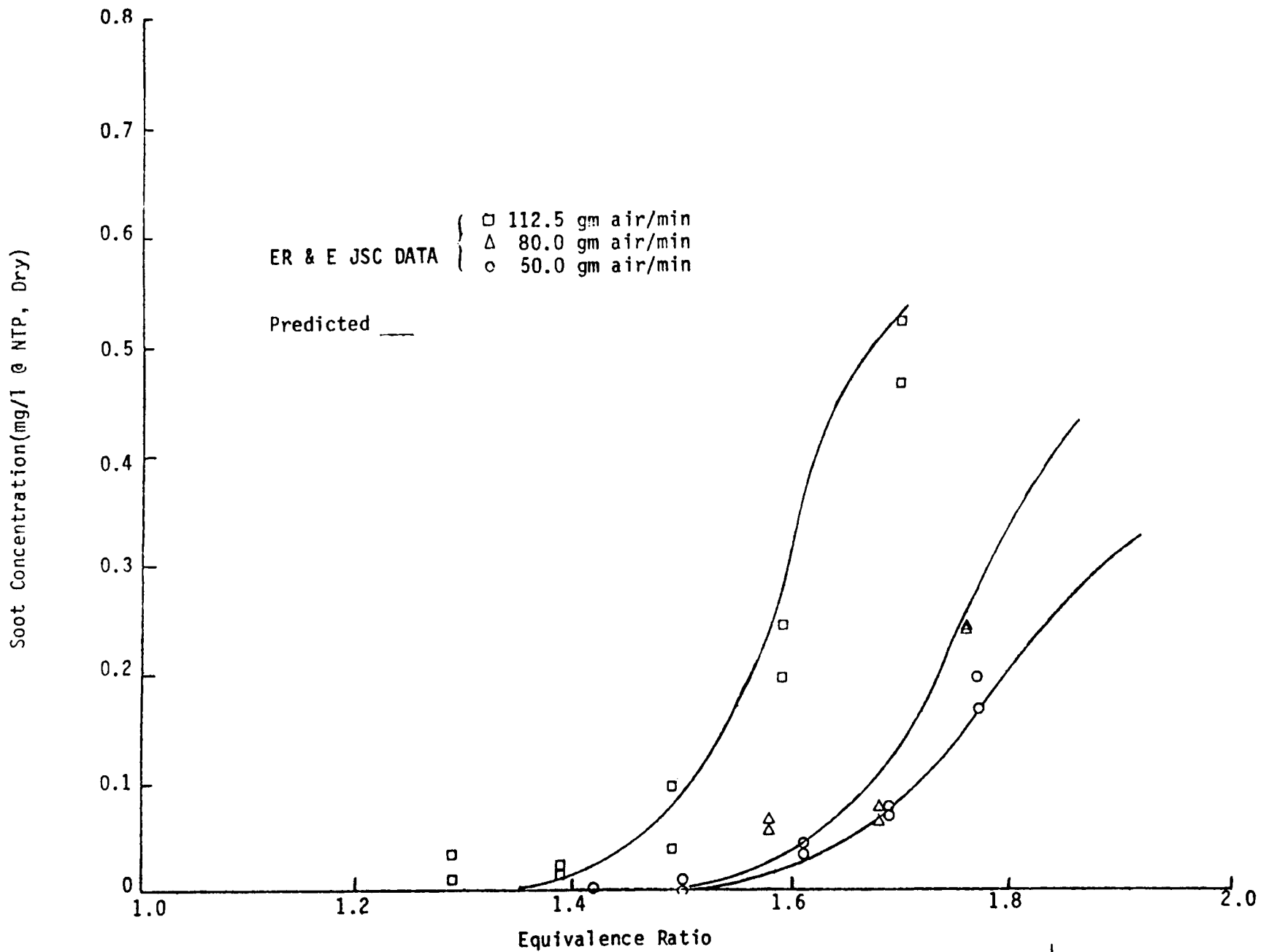


Figure 4. Comparison of Predicted with Measured Soot Concentrations, Toluene

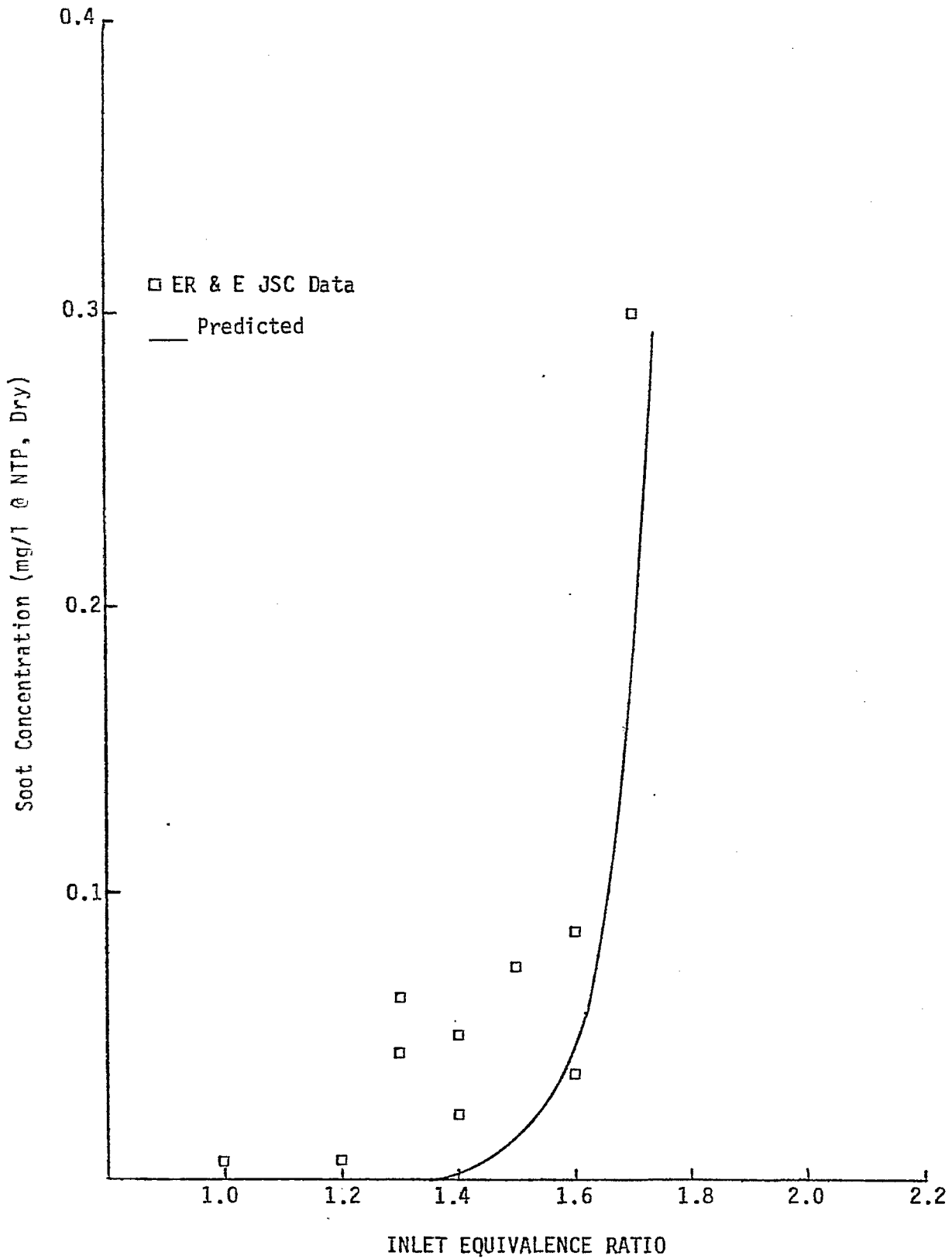


Figure 5: Comparison of Predicted with Measured Soot Concentrations, Controlled Reactor Temperature = 1700°K, toluene

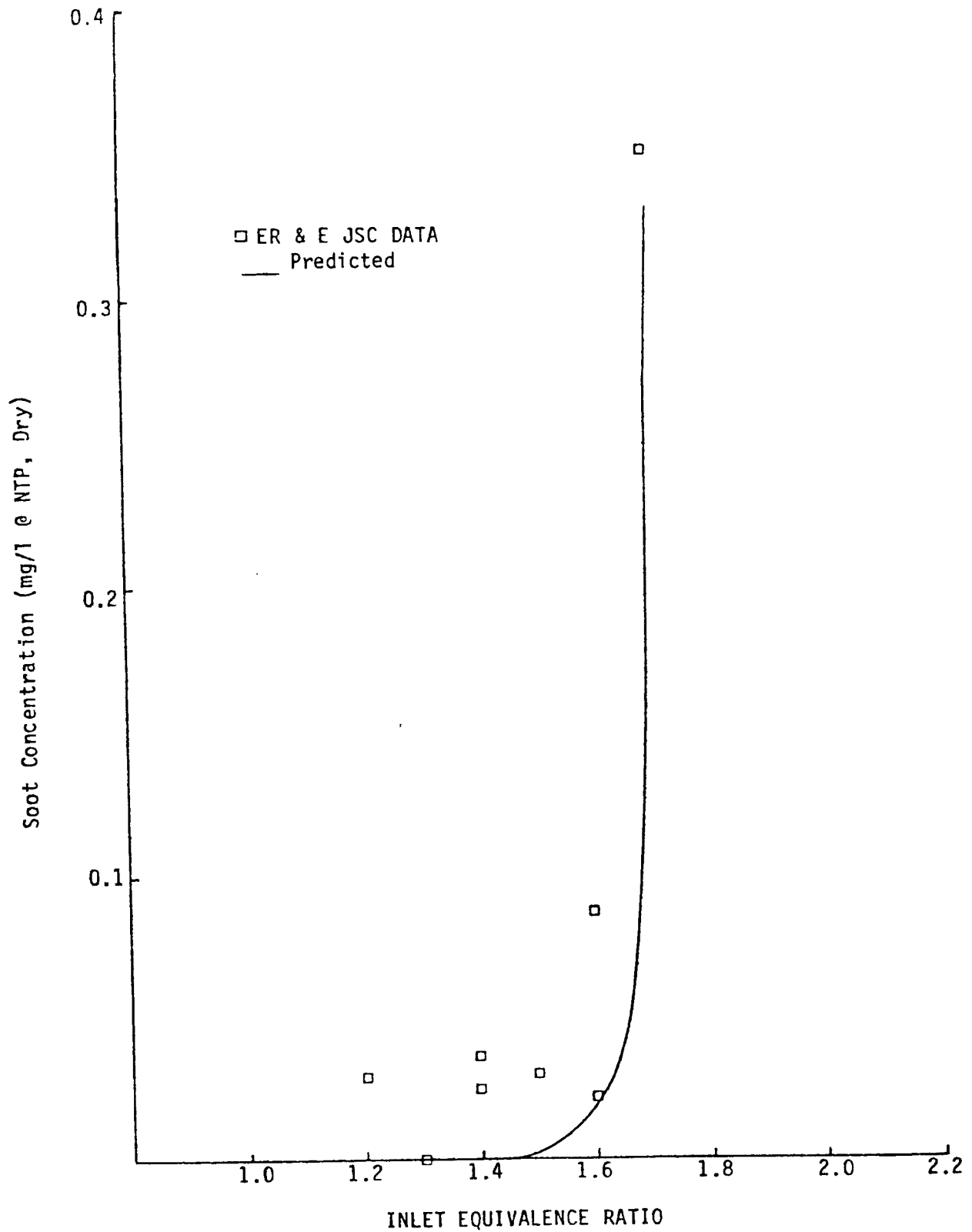


Figure 6: Comparison of Predicted with Measured Soot Concentrations, Controlled Reactor Temperature = 1800°K, Toluene

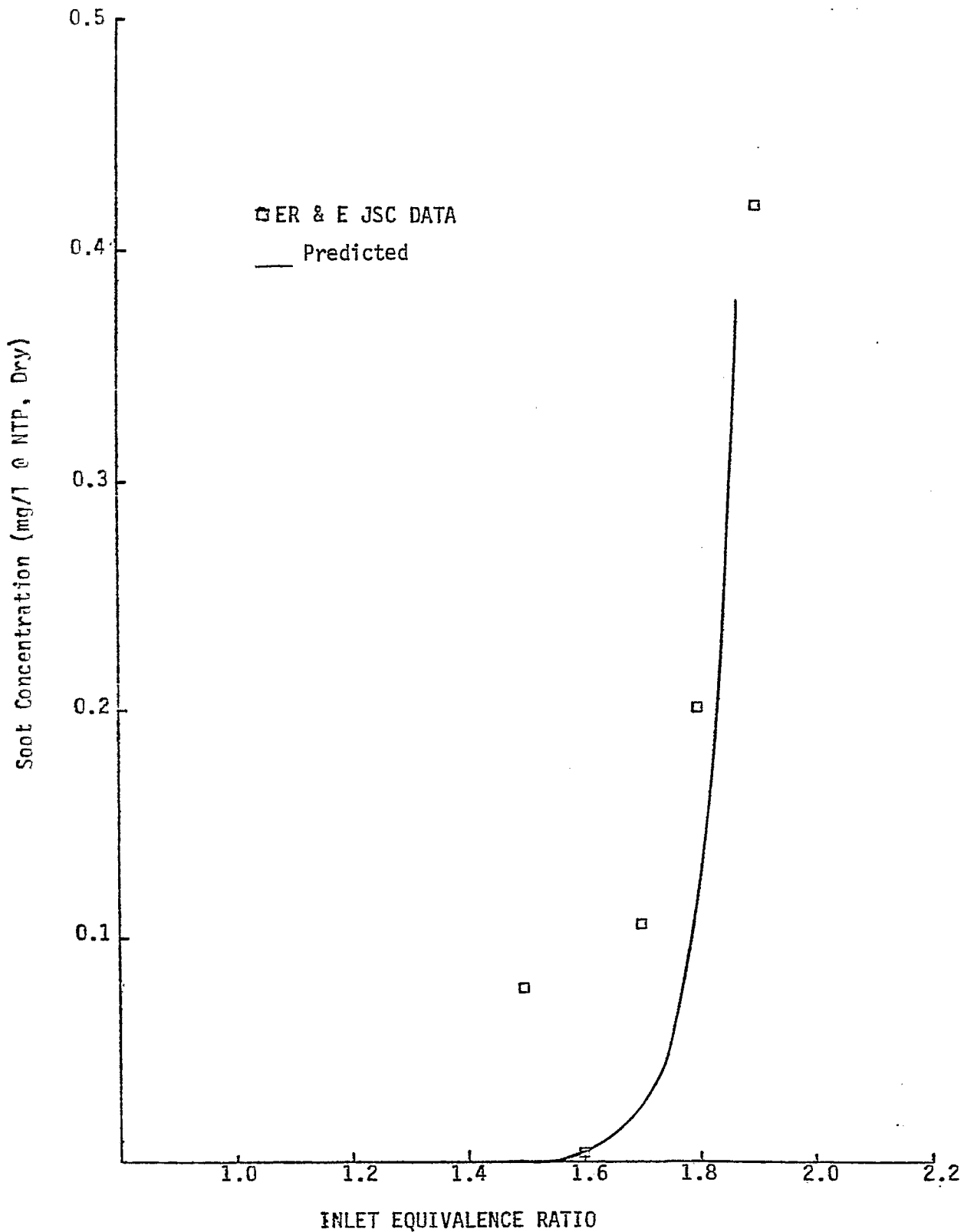


Figure 7: Comparison of Predicted with Measured Soot Concentrations, Controlled Reactor Temperature = 1900^oK, Toluene

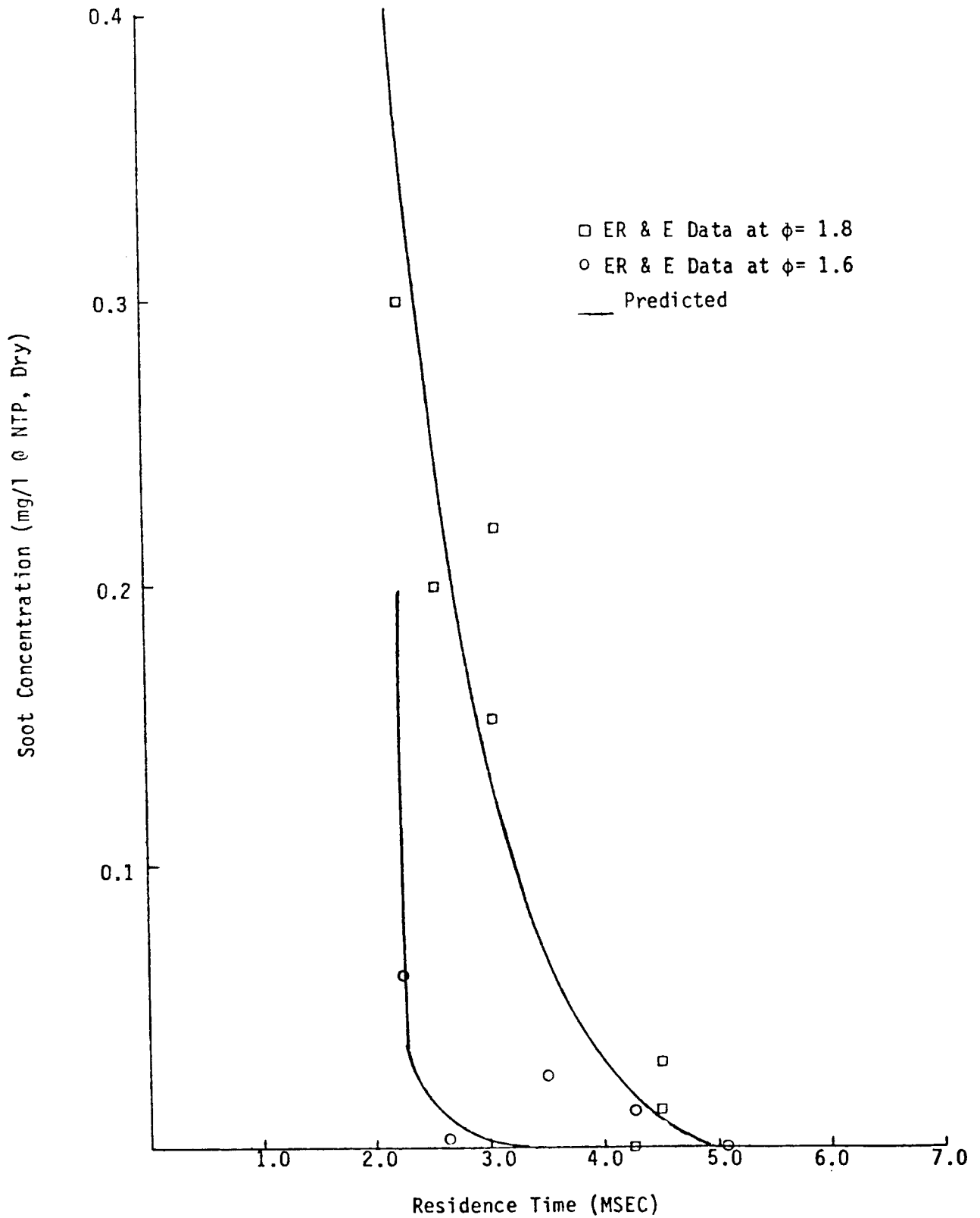


Figure 8: Comparison of Predicted with Measured Soot Concentrations, Controlled Reactor Temperature = 1900°K, Toluene

5. DISCUSSION OF RESULTS

The results of the investigations conducted to date on toluene show that a relatively simple engineering model for net soot emissions is feasible. Furthermore, the iterative procedure used in developing the model in conjunction with the ER&E jet-stirred combustor experiments is providing the basis for the establishment of guidelines for the control of sooting characteristics from combustor primary zones characterized by intense backmixing under kinetically controlled conditions. Although the rate parameters have been determined for a limited range of conditions the results are applicable to certain of the important operating characteristics encountered in gas turbine combustors. Residence times span the range from 2-7 milliseconds for fuel/air equivalence ratios in the range of from 1 to 2. The temperature levels covered were predominantly in the 1800-2000°K range and much of this data was obtained by independently varying the equivalence ratio and residence times under isothermal conditions.

While a broad base of information has been established it represents only part of the modeling required in the development of the overall engineering model for gas turbine combustors. The work required includes expanding the chemical kinetics modeling to cover fuel property variations, through the investigation of other fuels and fuel blends and NO_x emissions. Of particular importance is the effect of pressure on net soot emissions as well as the physical processes of spray combustion and the aerodynamics of the combustion process including flow patterns and turbulence.

6. FUTURE WORK

This section summarizes work to be conducted in the next phase of the program. Technical data required to accomplish the work will be provided by ER&E jet-stirred reactor and continuous flow reactor facilities. In cases where the type of experiment required for model development is still uncertain, particularly for soot emission in fuel blend systems and fuel nitrogen conversion to NO_x , some preliminary analytical work will be performed in advance, and guidance in experimental design will be provided. In general, work related to the following technical areas will be performed.

A. Quasiglobal Model Development

- (1) Soot emissions for the methylnaphthalene system
- (2) Soot emissions from fuel blend systems
- (3) Fuel nitrogen conversion to NO_x
- (4) Pressure effect on soot emissions
- (5) Fuel pyrolysis
- (6) Soot oxidation

B. Other Submodel Development

- (1) Gas dynamics
- (2) Spray interaction
- (3) Flame radiation

C. Modular Model Development

It should be noted that the order of tasks identified above does not necessarily constitute the actual priority of work.

Soot production for toluene systems has been studied extensively in the last phase of the program; as a result we have successfully developed a tentative model capable of predicting the soot emissions under typical ER&E JSC conditions. However, for the methylnaphthalene systems, experimental data have shown that soot emissions in such systems is much heavier than those of toluene under similar conditions. This suggests that methylnaphthalene, being structurally different from toluene in terms of the number of aromatic rings, is likely to follow a different route to produce soot. Therefore, independent modeling for this fuel is required and this probably will involve the determination of an independent set of rate constants.

Soot emissions for fuel blends will be studied in order to provide a broad base of modeling capability for a range of possible practical fuels to be encountered in the future. It is expected that experience gained from the modeling of each parent fuel will provide guidance on modeling the blends. In addition, the effect of mixture ratio on unburnt hydrocarbon emissions, as well as soot formation will be determined.

Fuel nitrogen conversion to NO_x will be studied, as the practical fuels of interest in the future will have high nitrogen content. The

currently available JSC data on fuel bound nitrogen conversion will be analyzed and data requirements for further model development will be established.

As observed by various researchers, soot emission is enhanced as the total pressure increases. Therefore, the effect of pressure on unburnt hydrocarbon, oxygen emission and soot production will be determined. Work related to fuel pyrolysis and soot oxidation has already been initiated and this work will continue with some parametric studies on pyrolysis. However, when experimental data becomes available, models for these reactions will be developed. Finally, the structure of the products of pyrolysis will also be determined.

Under the Other Submodel Development, work related to gas dynamics, spray interaction and flame radiation will be studied in parallel with other model developments.

The modular model for the overall gas turbine combustion system constitutes the framework for the coupling of the chemical and physical submodels. Work on the development of this modular model will be initiated during the next phase of the program.

7. REFERENCES

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