2)

Modeling of Hazardous Waste Incinerator: Failure Diagnostic and Staged Combustion

by

Tai-Gyu Lee

B.S. in Chemical Engineering
Yonsei University, Seoul, Korea (1991)

Submitted to the Department of Chemical Engineering
in Partial Fulfillment of the Requirement for the Degree of

Master of Science in Chemical Engineering

at the

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

February 1995

Signature of Author____
Department of Chemical Engineering
February, 1995

Certified by____
Professor Adel F. Sarofim
Thesis Supervisor

Accepted by____
Professor Robert E. Cohen
Chairman, Committee for Graduate Studies

Modeling of Hazardous Waste Incinerator: Failure Diagnostic and Staged Combustion

by

Tai-Gyu Lee

Submitted to the Department of Chemical Engineering
on January 13, 1995 in partial fulfillment of the
requirements for the degree of
Master of Science in Chemical Engineering

Abstract

Numerical modeling of a perfectly stirred reactor (PSR) and a plug flow reactor (PFR) were performed by using PSR and SENKIN FORTRAN codes respectively. Outlet gas calculated by PSR were used as a baseline flow into the SENKIN to simulate the reactor consists of PSR followed by PFR.

Calculation of equilibrium state shows the Cl and Cl_2 are formed far less in the fuel-rich condition than in the fuel-lean condition. By introducing much more H radical in fuel-rich condition, most of Cl atoms formed HCl rather than forming Cl_2.

By staging the combustion process in Hazardous Waste Incinerator, the formation of PIC and subsequent formation of dioxin can be reduced less than the case of single stage combustion process. The efficiency of the staged combustion process was evaluated by comparing the concentration of Cl, Cl_2, HCl and the CO_2/CO ratio of both single and staged combustion process.

In the staged combustion, injection of steam or water reduced the concentration of Cl and Cl_2 which can potentially lead to the formation of dioxin in the homogeneous gas phase. Also the temperature drop by injection of steam or water reduced the reformation of Cl_2 from Cl in quenching process.

In SENKIN, various amount of CH_3Cl was injected into the baseline flow from the outlet of PSR. The richer the fuel gets by injecting more CH_3Cl, the more difference in the results of SENKIN (free of mixing constraints) and those of a actual PFR were founded only to explain the existence of mixing constraint in the actual PFR.

Based on the results from the SENKIN, failure diagnosis was developed for the incinerator. Existence of specific species and the comparison of selected ratio of species can be used as the failure diagnosis for mixing.

The effect of cooling rate in the PFR was simulated by dropping the temperature of flue gas in various rate in SENKIN. The faster the cooling occurs the more free radicals form molecules, especially the formation of Cl to Cl_2. The slower the cooling occurs the less PIC forms.

Thesis Advisor: Adel F. Sarofim
Title: Professor of department of Chemical Engineering

To Tae-Sup, Haing-Ja, Boong-Kyu, Ka-Young,

and

myself

Acknowledgments

First of all, I sincerely thank to my Lord and Savior Jesus Christ, the true source of all that I am and have. And I am grateful to many and acknowledge the following contributions to this thesis work:

- my parents, Mr. Tae-Sup Lee and Mrs. Haing-Ja Lee, who have been a constant source of love, support, cheerful inquiry, wisdom. And the endless prayer for me!
- my one and only brother Boong-Kyu Lee and sister-in-law Ka-Young Yoo, without whom, I know for sure, my life at MIT would have been miserable.
- my grandmother and uncles and aunts, who have always prayed for me.
- Professor Adel F. Sarofim, my mentors at MIT, who gave me a constant guidance not only on my academic life but also my personal life with support and kindness.
- Dr. Guido Sacchi, who definitely influenced me on my academic work and who is so much fun to be with and whom I would like to see anytime, anyplace.
- Professors John P. Longwell and Joseph W. Bozzelli, who always helped me and inspired me with their incredible knowledge on my work.
- Brian DiVasta and Fredderica Turner who lended invaluable support as UROPs.
- my friends with whom I shared may great times: Hiroshi Saito, Alex Diaz, Wei Liu, Yanping Zhang, Jonathan Allen, Angelo Kandas, Scott Macadam, Sergei Serbin.
- my Korean friends in dept. of chem. eng.: Chonghun Han, Sung Min Park, Taeshin Park, Heeyeop Chae, and Youngpil Han.
- Yuchul Rhim, Ikho Suh, Myungwoo Chun, Chunhyuk Lee, Sunghyuk Lee, who enlightend my life at Cambridge.

Table of Contents

Title Page........ 1
Abstract........ 2
Dedication........ 4
Acknowledgments........ 5
Table of Contents........ 6
List of Figures........ 8
List of Tables........ 11

Chapter 1. Introduction........ 12

Chapter 2. Numerical Modeling........ 15
  2.1. The PSR Model........ 15
  2.2. The SENKIN Model........ 20

Chapter 3. Application of the Numerical Models........ 25
  3.1. Chemical Kinetic Mechanism........ 27
  3.2. Cooling Rate........ 39
  3.3. Residence Time........ 42
  3.4. Temperature........ 46

Chapter 4. Failure Diagnosis (Mixing)........ 52
  4.1. Reaction Mechanism........ 52
  4.2. A Brief Discussion of Experimental Results........ 54
    4.2.1. Rayleigh Scattering Measurements........ 54
    4.2.2. Stable Species Concentrations........ 59
  4.3. The Failure Diagnosis (Mixing) Theory........ 60
  4.4. The Development of the Failure Diagnosis (Mixing)........ 60
    4.4.1. Detection of Particular Species........ 61
    4.4.2. Comparison of the Selected Molar Ratios of Species........ 62
  4.5. The Prediction Method Theory........ 62

Chapter 5. Theory of the Staged Combustion Process........ 67
  5.1. Chemistry in the Staged Combustion Process........ 67
  5.2. Background Calculations........ 68
  5.3. Cooling Rate........ 71
  5.4. Effect of Steam (or Water) Injection........ 76

Chapter 6. Staged Combustion Process........ 79
  6.1. First Stage........ 79

- 6.2. Second Stage 82
- 6.3. Third and Fourth Stages 82
- 6.4. Final Stage 83
- 6.5. Comparison with Conventional Process 86

Chapter 7. Summary and Conclusions 89

References 94

Appendix A. Post-SENKIN Program for Sensitivity Analysis 99

Appendix B. Chemical Kinetic Mechanism Set for Benzene 135

List of Figures

Figure 1.1. Block diagram of research interactions 13

Figure 2.1. Perfectly-Stirred Reactor (PSR) Schematic 15

Figure 3.1. Plug Flow Reactor (PFR) linked to the TJSC 26

Figure 3.2. Molar fraction versus residence time (CH_3Cl) 39

Figure 3.3. Molar fraction versus residence time (Cl_2) 40

Figure 3.4. Molar fraction versus residence time in SENKIN (CH_3Cl, ϕ=1.65, Cl/C=0.1, T=1500K) 44

Figure 3.5. Molar fraction versus residence time in SENKIN (C_2H_2, ϕ=1.65, Cl/C=0.1, T=1500K) 44

Figure 3.6. Molar fraction versus residence time in SENKIN (O_2, ϕ=1.65, Cl/C=0.1, T=1500K) 45

Figure 3.7. Molar fraction versus residence time in SENKIN (CH_4, ϕ=1.65, Cl/C=0.1, T=1500K) 45

Figure 3.8. Molar fraction versus residence time in SENKIN (C_2H_4, ϕ=1.65, Cl/C=0.1, T=1500K) 46

Figure 3.9. C_2H_2 conversion (%) versus CH_3Cl conversion (%) (ϕ=1.25, 1300K<T<1800K) 50

Figure 3.10. C_2H_2 conversion (%) versus CH_3Cl conversion (%) (ϕ=1.5, 1300K<T<1800K) 51

Figure 4.1. Rayleigh scattering PDF's evolution for cold flow experiment 55

Figure 4.2. Rayleigh scattering PDF's evolution for fuel-lean conditions (ϕ=0.75) 57

Figure 4.3. Rayleigh scattering PDF's evolution for fuel-rich conditions (ϕ=1.25) 58

Figure 4.4. Molar ratio versus equivalence ratio (CH_3Cl/CH_4) 64

Figure 4.5. Molar ratio versus equivalence ratio (CH_3Cl_{in}/CH_3Cl_{out}) 64

Figure 4.6. Molar ratio versus equivalence ratio (C_6H_6/C_2H_4)........ 65

Figure 4.7. Molar ratio versus equivalence ratio (O_2/CH_4)........ 65

Figure 4.8. Molar ratio versus equivalence ratio (O_2/H_2)........ 66

Figure 4.9. Molar ratio versus equivalence ratio (O_2/C_2H_2)........ 66

Figure 5.1. Molar ratio versus equivalence ratio (Cl & Cl_2/(Cl+Cl_2+HCl)) (T=1800K, equilibrium state)........ 69

Figure 5.2. Molar ratio versus equivalence ratio (HCl/(Cl+Cl_2+HCl)) (T=1800K, equilibrium state)........ 69

Figure 5.3. Molar ratio versus equivalence ratio (Cl & Cl_2/(Cl+Cl_2+HCl)) (T is cooled from 1800K to 400K, residence time=3.e-02 second)........ 70

Figure 5.4. Molar ratio versus equivalence ratio (HCl/(Cl+Cl_2+HCl)) (T is cooled from 1800K to 400K, residence time=3.e-02 second)........ 70

Figure 5.5. Molar ratio versus starting T of cooling (Cl & Cl_2/(Cl+Cl_2+HCl)) (ϕ=0.75, residence time=3.e-02 second)........ 72

Figure 5.6. Molar ratio versus starting T of cooling (HCl/(Cl+Cl_2+HCl)) (ϕ=0.75, residence time=3.e-02 second)........ 72

Figure 5.7. Molar ratio versus temperature (Cl & Cl_2/(Cl+Cl_2+HCl)) (ϕ=0.75, equilibrium state)........ 73

Figure 5.8. Molar ratio versus temperature (HCl/(Cl+Cl_2+HCl)) (ϕ=0.75, equilibrium state)........ 73

Figure 5.9. Molar ratio versus time of cooling (Cl & Cl_2/(Cl+Cl_2+HCl)) (T is cooled down from 1800K to 373K, ϕ=0.75)........ 74

Figure 5.10. Molar ratio versus time of cooling (HCl/(Cl+Cl_2+HCl)) (T is cooled down from 1800K to 373K, ϕ=0.75)........ 74

Figure 5.11. Molar ratio versus time of cooling (Cl & Cl_2/(Cl+Cl_2+HCl)) (T is cooled down from 1800K to 373K, ϕ=3.0)........ 75

Figure 5.12. Molar ratio versus time of cooling (HCl/(Cl+Cl_2+HCl)) (T is cooled down from 1800K to 373K, ϕ=3.0)........ 75

Figure 5.13. Cl/(Cl+Cl_2+HCl) molar ratio versus (O2 injected:H2O(g) injected)........ 77

Figure 5.14. $Cl_2/(Cl+Cl_2+HCl)$ molar ratio versus (O2 injected:H2O(g) injected)........... 77

Figure 5.15. CO/CO_2 molar ratio versus (O2 injected:H2O(g) injected)........................... 78

Figure 6.1. Molar fraction versus amount of steam injected (CO_2)................................. 81

Figure 6.2. Molar fraction versus amount of steam injected (HCl)................................. 81

Figure 6.3. $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratio versus O_2 injection temperature (H_2O 30%).. 84

Figure 6.4. $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratio versus O_2 injection temperature (H_2O 10%).. 84

Figure 6.5. $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratio versus O_2 injection temperature (H_2O 20%).. 85

List of Tables

Table 2.1. An example of PSR input file 18

Table 3.1. Modeling approach schematic........ 26

Table 3.2. C_1/C_2 Hydrocarbon and Chlorocarbon Reaction Mechanism........ 28

Table 3.3. Molar fraction versus cooling time (ϕ=0.8, final T=400K)........ 41

Table 3.4. Molar fraction versus cooling time (ϕ=1.5, final T=400K)........ 42

Table 3.5. Molar fraction versus temperature in PSR (ϕ=0.75)........ 47

Table 3.6. Conversion factor versus temperature in SENKIN (ϕ=1.25)........ 48

Table 3.7. Conversion factor versus temperature in SENKIN (ϕ=1.5)........ 49

Table 4.1. Benzene formation and oxidation reactions........ 53

Table 4.2. CH_3Cl molar fraction versus equivalence ratio........ 62

Table 6.1. Cl and Cl_2 over $Cl+Cl_2+HCl$ ratio versus equivalence ratio........ 80

Table 6.2. $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratio versus O_2 injection temperature (H_2O=10%)........ 86

Table 6.3. $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratio versus O_2 injection temperature (H_2O=20%)........ 87

Table 6.4. $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratio versus O_2 injection temperature (H_2O=30%)........ 87

Chapter One

1. Introduction

The advantages of a numerical modeling in the research of combustion are numerous. First of all, by modeling, one can be able to perform the same experiment over and over in considerably less time than the actual perform of experiments. Second, it is possible to vary the conditions of incinerator to see the relationship between parameters and the phenomena. Even off-optimal condition can be simulated, which cannot be done for the sake of public health in real waste incinerator. Third, errors by human in experiments can be prevented even the experiments are repeated for over and over again. For the same condition, it always gives the same result that one can count on.

The primary concern of this work is to develop a better understanding of the factors that govern the emissions of products of incomplete combustion from the secondary combustion chamber of incinerators by: 1) development of a model for reacting flows in a well stirred/plug flow reactor at MIT equipped with an extractive gas sampling probe to measure stable species, 2) application of the validated model to the development of failure diagnosis for waste incinerator, and 3) evaluation of the advantages of staged combustion process on formation of PIC and potential dioxin formation.

In order to address the above three aspects, this work is divided into three phases. The first phase addresses the theory and the background of numerical modeling used in the work and the application of this models to the evaluation of the effect of the cooling rate on the PIC and chlorine formation, and the effect of residence time and temperature.

Since this work is especially concentrated on the mixing constraints in PFR, any other parameters, such as temperature, residence time, cooling rate are addressed in one phase, while the failure diagnosis based on mixing constraint is addressed in a whole separate phase. The second phase addresses the effect of incomplete turbulent mixing by comparing the result of real PFR and that of the perfect mixing conditioned SENKIN model. Also, this phase involves the methodology of using the mixing failure diagnosis for waste incinerator. Finally, in third phase, the theory of staged combustion process and the advantage of applying the staged combustion process over single stage process are addressed. This phase involves the chemical kinetic effect on the formation of C_l and Cl_2 in the both fuel-lean and fuel-rich conditions. Also, the effects of steam or water injection, subsequent cooling, and temperature drop in quenching process on the fate of C_l and Cl_2 are addressed in this phase.

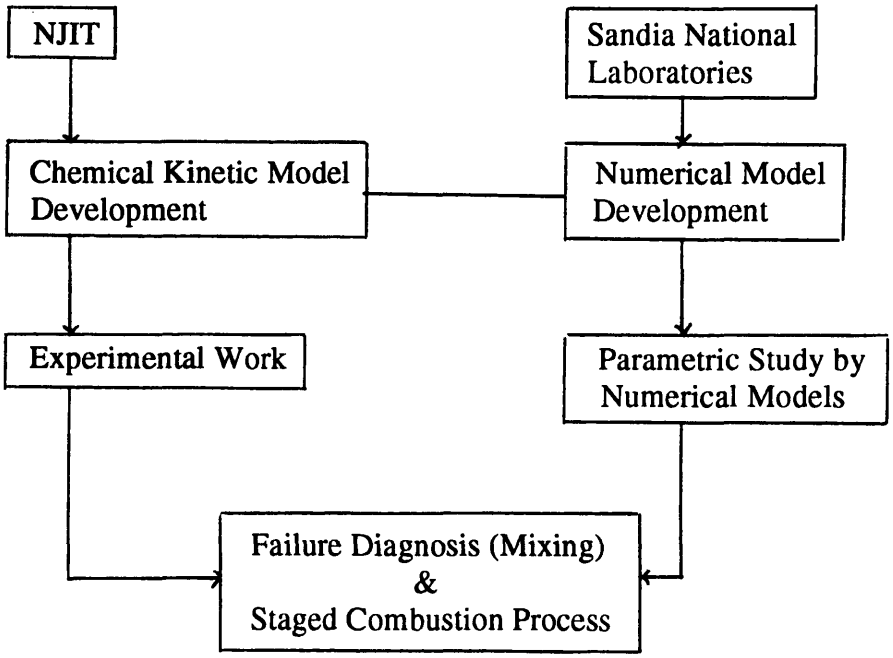


Figure 1.1. Block diagram of research interactions.

The thesis presentation reflects the division of research into three phases and is organized as follows. Chapter 2 presents the background and the theory of numerical modeling used in this work. Chapter 3 presents the application of this models to the evaluation of the effects of cooling rate, residence time and temperature on the formation of PIC and Chlorine. Chapter 4 presents the evaluation of the effect of the incomplete turbulent mixing and the development of mixing failure diagnosis for hazardous waste incinerator. Chapter 5 presents the background, theory of the staged combustion process. Also, the effect of steam or water injection and the effect of quenching on the formation of Chlorine is presented in this chapter. Chapter 6 presents the adopted staged combustion process in this work by following the each stage. Chapter 7 provides a short summary and list of recommendations for further investigation.

Chapter Two

2. Numerical Modeling

The model used to approximate conditions in a well stirred/plug flow reactor were PSR code followed by SENKIN code developed at the Sandia National Laboratory. Both the PSR and the SENKIN simulate the conditions free of mixing constraints in homogeneous gas phases. The result of the PSR calculation provides the base line flow into the SENKIN with or without the injection of specific species.

2.1. The PSR Model

A description of the process occurring within the ideal perfectly stirred reactor (PSR) is obtained by relating the conservation of mass and energy to the net generation of chemical species within the reactor volume. The general concept of a PSR is shown schematically in Figure 2.1.

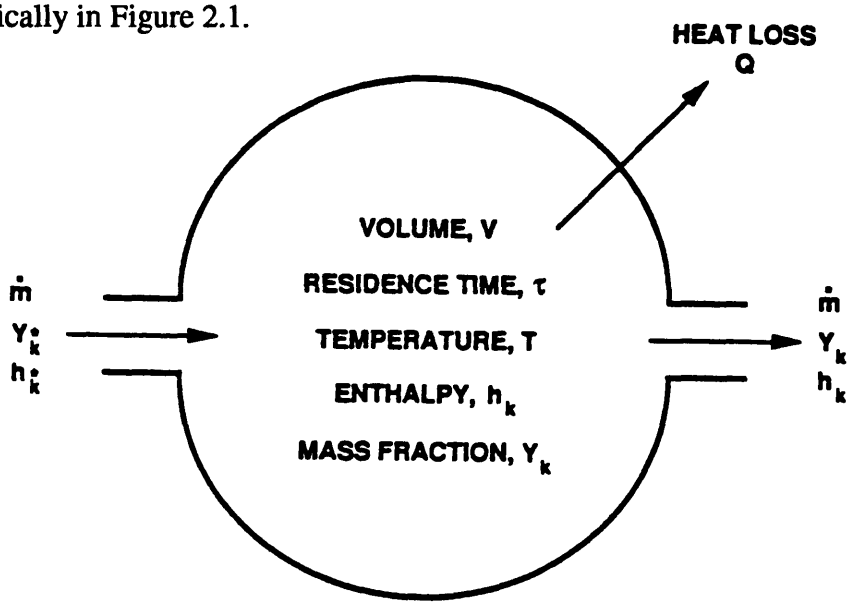


Figure 2.1. Perfectly-Stirred Reactor (PSR) Schematic

The mixing in the reactor chamber is intense, and thus it is assumed that the temperature and composition in the reactor is the same as that which exits the reactor volume. The mass flow rate through the reactor $\dot{m}$ is constant.

The species conservation equation is given by

$$\dot{m}\,(Y_k - Y_k^*) - \dot{\omega}_k W_k V = 0, \tag{2.1}$$

and the conservation of energy is stated as

$$\dot{m}\,\Sigma\,(Y_k h_k - Y_k^* h_k^*) + Q = 0. \tag{2.2}$$

In these equation Y_k is the mass fraction of the kth species (there are K species); W_k, the molecular weight of the kth species; V, the reactor volume; $\dot{\omega}_k$, the molar rate of production by chemical reaction of the kth species per unit volume; h_k, the specific enthalpy of the kth species; and Q, the reactor heat loss. The superscript (*) indicates the inlet conditions.

The nominal residence time is related to the reactor volume V and the mass flow rate by

$$\tau = \rho V/\dot{m}\,, \tag{2.3}$$

where the mass density ρ is calculated from the ideal gas equation of state,

$$\rho = P\overline{W}/RT. \tag{2.4}$$

Here P is the pressure, T is the temperature, R the universal gas constant, and $\overline{W}$ the mixture's mean molecular weight. The residence time is often used as a characteristic parameter of the reactor rather than the mass flow rate. When this is the case, $\dot{m}$ is computed from equation (2.3).

The net chemical production rate $\dot{\omega}_k$ of each species results from a competition between all the chemical reactions involving that species. Each reaction proceeds according to the law of mass action and the forward rate coefficients are in the modified Arrhenius form

$$k_f = AT^{\beta} \exp(-E_A/RT). \tag{2.5}$$

The details of the chemical reaction equations and the thermo-chemical properties are found in the user's manual for CHEMKIN (Kee, Rupley, and Miller, 1991).

Equations (2.1) and (2.2) form a set of K+1 nonlinear algebraic equations, the solution of which is the temperature and mass fractions. Even though we seek the solution to the steady-state equations stated above, the computational algorithm often requires a partial solution of the related transient problem. The analogous time-dependent equation for mass conservation of each species is

$$\rho V\,(dY_k/dt) = -\dot{m}\,(Y_k - Y_k^*) + \omega_k W_k V \tag{2.6}$$

or

$$(dY_k/dt) = -\,(Y_k - Y_k^*)/\tau + \dot{\omega}_k W_k/\rho \tag{2.7}$$

The energy balance for the reactor (assuming constant pressure) leads to

$$\rho V\, dh/dt = -\, \dot{m} \sum (Y_k h_k - Y_k{}^* h_k{}^*) - Q \tag{2.8}$$

or

$$dh/dt = -\, (1/\tau) \sum (Y_k h_k - Y_k{}^* h_k{}^*) - Q/\rho V \tag{2.9}$$

where h is the mass-weighted mean enthalpy. It is convenient to write the energy equation in terms of temperature rather than enthalpy. Since $h = \sum Y_k h_k$ and $c_p = \sum Y_k c_{pk}$,

$$dh/dt = c_p\, dT/dt + \sum h_k (dY_k/dt) \tag{2.10}$$

Combining equations (2.7), (2.9), and (2.10) leads to the form of the transient energy equation that is actually solved,

$$c_p\, dT/dt = (1/\tau) \sum Y_k{}^*(h_k{}^* - h_k) - \sum h_k \dot{\omega}_k W_k/\rho - Q/\rho V \tag{2.11}$$

where c_p is the mass-weighted mean specific heat.

Table 2.1. An example of PSR input file

Keyword	Value	Units & Description
TGIV	1500	K
EQUI	0.75	fuel/air ratio

Keyword	Value	Units & Description
FUEL	C_2H_4 1.0	reactant mole or molar fraction
OXID	O_2 0.21	reactant mole or molar fraction
OXID	N_2 0.79	reactant mole or molar fraction
PROD	CO_2	product of complete combustion
PROD	H_2O	product of complete combustion
PROD	N_2	product of complete combustion
VOL	250	cm^3
FLRT	10	g / second
END		

An example of PSR input is shown at Table 2.1. Keywords are in the first column, while sample values are in second column. Third column contains the units or description of keywords. An actual input file consists of only first and second column. Keyword TGIV is one of two choices for reactor temperature. Using keyword TGIV, the reactor temperature is held constant at given temperature, while ENRG allows the heat be transferred through the reactor wall. There are two choices of keyword (EQUI, REAC) for reacting flow information. EQUI specify the equivalence ratio of reacting gas. To use EQUI option, mole or molar fraction of fuel (FUEL) and oxidant (OXID) should be specified. Keyword REAC set the initial mole or molar fraction of reactant. For the product information, keyword PROD is used. With keyword PROD, only products of complete combustion should be specified. PRES and VOL are to set the pressure and the volume of the reactor. Residence time is set by either TAU or FLRT. Direct specifying of residence time is required for TAU. The residence time is calculated from reactor volume, mass flow rate and density of reacting gas in case of FLRT.

2.2. The SENKIN Model

SENKIN FORTRAN code is for the simulation of time evolution of a homogeneous reacting gas mixture in a closed system. The cases for the SENKIN can be stated as; 1) adiabatic system with constant pressure, 2) adiabatic system with constant volume, 3) adiabatic system with the volume a specified function of time, 4) a system with constant pressure and temperature, 5) a system with constant pressure and with the temperature a specified function of time.

The reacting mixture is treated as a closed system with no mass crossing the boundary, so that the total mass of the mixture $m = \sum m_k$ is constant, and $dm/dt = 0$. Here m_k is the mass of the kth species and K is the total number of species in the mixture. The individual species are produced or destroyed according to

$$dm_k/dt = V\dot{\omega}_k W_k \qquad k = 1,\dots,K \tag{2.12}$$

where t is time, $\dot{\omega}_k$ is the molar production rate of the kth species by elementary reaction, W_k is the molecular weight of the kth species, and V is the volume of the system, which may vary in time. Since the total mass is constant, this can be written in terms of the mass fraction as

$$dY_k/dt = v\dot{\omega}_k W_k \qquad k = 1,\dots,K \tag{2.13}$$

where $Y_k = m_k/m$ is the mass fraction of the kth species and $v = V/m$ is the specific volume. The species equations (2.13) are the same in all case, 1 through 5. For cases 4 and 5, the temperature is known, so the energy equation is unnecessary and the problem is completely defined by equations (2.13). For cases 1 through 3, the energy equation must be derived in light of the specific constraints used in each case.

The first law of thermodynamics for a pure substance in an adiabatic, closed system states that

$$de + pdv = 0, \tag{2.14}$$

where e is the internal energy per mass and p is the pressure. This relation holds for an ideal mixture of gases, with the internal energy of the mixture given by

$$e = \sum e_k Y_k, \tag{2.15}$$

where e_k is the internal energy of the kth species. Differentiating the internal energy of the mixture leads to the expression

$$de = \sum Y_k de_k + \sum e_k dY_k. \tag{2.16}$$

Assuming calorically perfect gases, $de_k = c_{v,k} dT$, where T is the temperature of the mixture, and $c_{v,k}$ is the specific heat of the kth species evaluated at constant volume. Defining the mean specific heat of the mixture, $c_v = \sum Y_k c_{v,k}$ and differentiating with respect to time, the energy equation becomes

$$c_v \, dT/dt + \sum e_k \, dY_k/dt + p \, dv/dt = 0. \tag{2.17}$$

Substitution of equation (2.12) for the species production rate gives

$$c_v \, dT/dt + p \, dv/dt + v \sum e_k \dot{\omega}_k W_k = 0, \tag{2.18}$$

where $c_v = \sum Y_k c_{v,k}$. The ideal gas equation of state is used to compute the pressure,

$$p = \rho RT/W \tag{2.19}$$

where R is the universal gas constant, W is the mean molecular weight of the mixture, and ρ is the mass density. In case 3, it is presumed that the volume is proved as a function of time, so the specific volume and its rate of change are

$$v(t) = V(t)/m \tag{2.20}$$

and

$$d\upsilon/dt = (1/m)\,(dV/dt). \tag{2.21}$$

The system of equation for the case 3 consists of equation (2.18) for the energy, and the K equations (2.13) for the species mass fractions. In case 2, the volume is held constant, so equation (2.18) reduces to

$$c_v \, dT/dt + v \sum e_k \dot{\omega}_k W_k = 0. \tag{2.22}$$

In case 1, the first law of thermodynamics reduces to the condition that enthalpy of the mixture is constant. The definition of enthalpy is $h = e + pv$, which differentiated becomes

$$dh = de + vdp + pdv \tag{2.23}$$

The pressure is constant, so the term involving dp drops out and the first law (equation (2.14)) simplifies to the condition

$$dh = 0. \tag{2.24}$$

The mixture enthalpy is

$$h = \sum Y_k h_k \tag{2.25}$$

where h_k is the specific enthalpy of the kth species. Proceeding as before, the energy equation for the constant pressure case becomes

$$c_p\, dT/dt + v \sum hk\dot{\omega}kWk = 0, \tag{2.26}$$

where the mean specific heat of the mixture is $c_p = \sum Y_k c_{p,k}$. The system of equations for case 1 consists of equation (2.26) for the energy, and the K equations (2.13) for the species mass fractions.

The net chemical production rate $\dot{\omega}_k$ of each species results from a competition between all the chemical reactions involving that species. Each reaction proceeds according to the law of mass action and the forward rate coefficients are in the modified Arrhenius form

$$k_f = AT^{\beta} \exp(-E/RT), \qquad (2.27)$$

where the activation energy E, the temperature exponent β, and the pre-exponential constants A are parameters in the model formulation.

The initial value problem for each of the different cases formulated above requires initial conditions for the temperature, pressure, and composition of the mixture. The initial density is computed from the equation of state. These are intensive variables, so the problem is independent of the absolute quantity of mixture in question. However, case 3 requires input of the system volume $V(t)$, which is an extensive variable. This forces the computation of another extensive variable, namely the mass of mixture, which is a constant during the solution. So in case 3, the mass is computed from the initial density and volume, $m = \rho(0)V(0)$.

Chapter Three

3. Application of the Numerical Models

The PSR and SENKIN models discussed in chapter 2 are applied to evaluate and understand the characteristics of several parameters. The reactor conditions used here are not relevant to those of the actual experiment. After a discussion about the chemical kinetic mechanism, parameters such as cooling rate, residence time, and temperature are examined by using the models. Though temperature, residence time, and turbulence level are often called "three Ts of combustion", only temperature and residence time are examined in this chapter. The effect of the turbulence level on the reacting gas will be evaluated later in chapter 4, when the failure diagnosis is developed.

The experimental facility at MIT is pilot scale model of real incinerator. It consists of a Toroidal Jet Stirred Combustor (TJSC) followed by a plug flow reactor which simulate the primary combustion chamber and the secondary combustion chamber at real waste incinerator, respectively (Figure 3.1). Hot gases exit the TJSC and are directed into the PFR through a flow straightener which counteracts the swirl imposed by the jet-stirred reactor. Mean flow velocities in the PFR range from 20 to 30 m/s for reacting flow. Oxidant and/or chlorinated hydrocarbons are introduced into the PFR via an injector positioned at the entrance of the PFR. The baseline PFR input is determined by strictly controlling the combustion conditions in the TJSC. Again, the TJSC and the plug flow reactor at MIT are simulate by PSR and SENKIN FORTRAN code respectively (Table 3.1).

The equivalence ratio is the measure of stoichiometry used in this work, which is defined as

$$\phi = \frac{(\text{fuel mass / oxidant mass})_{\text{actual}}}{(\text{fuel mass / oxidant mass})_{\text{stoich}}} \tag{3.1}$$

or the ratio of actual to stoichiometric fuel/oxidant mass ratios. The stoichiometric fuel/oxidant mass ratio is determined by writing the stoichiometric equation for conversion of the fuel/oxidant mixture completely to CO_2, H_2O, and HCl. For example, a mixture of 50% C_2H_4 and 50% CH_3Cl would have the stoichiometric equation

$$0.5C_2H_4 + 0.5CH_3Cl + 2.25O_2 \leftrightarrow 1.5CO_2 + 1.5H_2O + 0.5HCl \tag{3.2}$$

This leads to a stoichiometric fuel/oxidant mass ratio of

$$(\text{fuel mass/oxidant mass})_{\text{stoich}} = \frac{0.5\, MW(C_2H_4) + 0.5\, MW(CH_3Cl)}{2.25\, MW(O_2)} \tag{3.3}$$

where $MW(i)$ is the molecular weight of species i. Dividing the actual fuel/oxidant mass ratio bt this quantity gives ϕ. Fuel-lean conditions have equivalence ratios less than 1 ($\phi < 1.0$) and fuel-rich conditions have $\phi > 1.0$.

3.1. Chemical Kinetic Mechanism

The development of a chemical kinetic mechanism along with kinetic rate parameters was accomplished through a joint program with New Jersey Institute of Technology (NJIT). A reaction mechanism for the description of C_1 and C_2

hydrocarbon and chlorocarbon combustion was developed jointly with Professors Joseph Bozzelli and Robert Barat of NJIT. Results from these models were already validated through the experiment performed at MIT. The complete reaction mechanism that has been developed and used in this research is given in this section. This chemical kinetic mechanism, which is presented in Table 3.2, comprises 50 species and consists of 224 reversible reactions.

Table 3.2. C_1/C_2 Hydrocarbon and Chlorocarbon Reaction Mechanism

(k = A T**b exp(-E/RT))

REACTIONS CONSIDERED	**A**	**b**	**E**
1. $CH_3+CH_3=C_2H_6$	2.68E+29	-4.95	6130
2. $CH_3+H=CH_4$	7.09E+31	-5.77	5890
3. $CH_4+O_2=CH_3+HO_2$	7.9E+13	0	56000
4. $CH_4+H=CH_3+H_2$	2.2E+04	3	8750
5. $CH_4+OH=CH_3+H_2O$	1.6E+06	2.1	2460
6. $CH_4+HO_2=CH_3+H_2O2$	1.8E+11	0	18700
7. $CH_3+HO_2=CH_3O+OH$	2E+13	0	0
8. $CH_3+O_2=CH_3O+O$	2.05E+19	-1.57	29229
9. $CH_3+O=CH_2O+H$	8E+13	0	0
10. $CH_2OH+H=CH_3+OH$	1E+14	0	0
11. $CH_3O+H=CH_3+OH$	1E+14	0	0
12. $CH_3+OH=CH_2+H_2O$	7.5E+06	2	5000

REACTIONS CONSIDERED	**A**	**b**	**E**
13. $CH_3+H=CH_2+H_2$	9E+13	0	15100
14. $CH_3O+M=CH_2O+H+M$	1E+14	0	25000
15. $CH_2OH+M=CH_2O+H+M$	1E+14	0	25000
16. $CH_3O+H=CH_2O+H_2$	2E+13	0	0
17. $CH_2OH+H=CH_2O+H_2$	2E+13	0	0
18. $CH_3O+OH=CH_2O+H_2O$	1E+13	0	0
19. $CH_2OH+OH=CH_2O+H_2O$	1E+13	0	0
20. $CH_3O+O=CH_2O+OH$	1E+13	0	0
21. $CH_2OH+O=CH_2O+OH$	1E+13	0	0
22. $CH_3O+O_2=CH_2O+HO_2$	6.3E+10	0	2600
23. $CH_2OH+O_2=CH_2O+HO_2$	1.48E+13	0	1500
24. $CH_2+H=CH+H_2$	1E+18	-1.56	0
25. $CH_2+OH=CH+H_2O$	1.13E+07	2	3000
26. $CH_2+OH=CH_2O+H$	2.5E+13	0	0
27. $CH+O_2=HCO+O$	3.3E+13	0	0
28. $CH+O=CO+H$	5.7E+13	0	0
29. $CH+OH=HCO+H$	3E+13	0	0
30. $CH+CO_2=HCO+CO$	3.4E+12	0	690
31. $CH+H=C+H_2$	1.5E+14	0	0
32. $CH+H_2O=CH_2O+H$	1.17E+15	-0.75	0
33. $CH+CH_2O=CH_2CO+H$	9.46E+13	0	-515
34. $CH+C_2H_2=C_3H_2+H$	1E+14	0	0
35. $CH+CH_2=C_2H_2+H$	4E+13	0	0

REACTIONS CONSIDERED	**A**	**b**	**E**
36. $CH+CH_3=C_2H_3+H$	3E+13	0	0
37. $CH+CH_4=C_2H_4+H$	6E+13	0	0
38. $C+O_2=CO+O$	2E+13	0	0
39. $C+OH=CO+H$	5E+13	0	0
40. $C+CH_3=C_2H_2+H$	5E+13	0	0
41. $C+CH_2=C_2H+H$	5E+13	0	0
42. $CH_2+CO_2=CH_2O+CO$	1.1E+11	0	1000
43. $CH_2+O=CO+2H$	5E+13	0	0
44. $CH_2+O=CO+H_2$	3E+13	0	0
45. $CH_2+O_2=CO_2+2H$	1.6E+12	0	1000
46. $CH_2+O_2=CH_2O+O$	5E+13	0	9000
47. $CH_2+O_2=CO_2+H_2$	6.9E+11	0	500
48. $CH_2+O_2=CO+H_2O$	1.9E+10	0	-1000
49. $CH_2+O_2=CO+OH+H$	8.6E+10	0	-500
50. $CH_2+O_2=HCO+OH$	4.3E+10	0	-500
51. $CH_2O+OH=HCO+H_2O$	3.43E+09	1.18	-447
52. $CH_2O+H=HCO+H_2$	2.19E+08	1.77	3000
53. $CH_2O+M=HCO+H+M$	3.31E+16	0	81000
54. $CH_2O+O=HCO+OH$	1.8E+13	0	3080
55. $HCO+OH=H_2O+CO$	1E+14	0	0
56. $HCO+M=H+CO+M$	2.5E+14	0	16802
CO	Enhanced	by	1.9
H_2	Enhanced	by	1.9

REACTIONS CONSIDERED	**A**	**b**	**E**
CH	Enhanced	by	2.8
CO_2	Enhanced	by	3
H_2O	Enhanced	by	5
57. $HCO+H=CO+H_2$	1.19E+13	0.25	0
58. $HCO+O=CO+OH$	3E+13	0	0
59. $HCO+O=CO_2+H$	3E+13	0	0
60. $HCO+O_2=HO_2+CO$	3.3E+13	-0.4	0
61. $CO+O+M=CO_2+M$	6.17E+14	0	3000
62. $CO+OH=CO_2+H$	1.51E+07	1.3	-758
63. $CO+O_2=CO_2+O$	1.6E+13	0	41000
64. $HO_2+CO=CO_2+OH$	5.8E+13	0	22934
65. $C_2H_6+CH_3=C_2H_5+CH_4$	5.50E-01	4.0	8300
66. $C_2H_6+H=C_2H_5+H_2$	5.4E+02	3.5	5210
67. $C_2H_6+O=C_2H_5+OH$	3E+07	2	5115
68. $C_2H_6+OH=C_2H_5+H_2O$	8.7E+09	1.05	1810
69. $C_2H_4+H=C_2H_3+H_2$	1.1E+14	0	8500
70. $C_2H_4+O=CH_3+HCO$	1.6E+09	1.2	746
71. $C_2H_4+OH=C_2H_3+H_2O$	2.02E+13	0	5955
72. $CH_2+CH_3=C_2H_4+H$	3E+13	0	0
73. $H+C_2H_4=C_2H_5$	5.41E+35	-6.78	11700
74. $C_2H_5+H=2CH_3$	8.73E+14	-0.08	3080
75. $C_2H_5+H=C_2H_6$	5.18E+35	-6.83	6810
76. $C_2H_5+O_2=C_2H_4+HO_2$	8.43E+11	0	3875

REACTIONS CONSIDERED	A	b	E
77. $C_2H_2+O=CH_2+CO$	1.02E+07	2	1900
78. $C_2H_2+O=HCCO+H$	1.02E+07	2	1900
79. $H_2+C_2H=C_2H_2+H$	4.09E+05	2.39	864
80. $C_2H_3=C_2H_2+H$	5.62E+31	-6.06	51720
81. $C_2H_3+H=C_2H_2+H_2$	4E+13	0	0
82. $C_2H_3+O=CH_2CO+H$	3E+13	0	0
83. $C_2H_3+O_2=CH_2O+HCO$	4E+12	0	-250
84. $C_2H_3+OH=C_2H_2+H_2O$	5E+12	0	0
85. $C_2H_3+CH_2=C_2H_2+CH_3$	3E+13	0	0
86. $C_2H_3+C_2H=2C_2H_2$	3E+13	0	0
87. $C_2H_3+CH=CH_2+C_2H_2$	5E+13	0	0
88. $OH+C_2H_2=C_2H+H_2O$	3.37E+07	2	14000
89. $OH+C_2H_2=HCCOH+H$	5.04E+05	2.3	13500
90. $OH+C_2H_2=CH_2CO+H$	2.18E-04	4.5	
91. $OH+C_2H_2=CH_3+CO$	4.83E-04	4	
92. $HCCOH+H=CH_2CO+H$	1E+13	0	0
93. $C_2H_2+O=C_2H+OH$	3.16E+15	-0.6	15000
94. $CH_2CO+O=CO_2+CH_2$	1.75E+12	0	1350
95. $CH_2CO+H=CH_3+CO$	1.13E+13	0	3428
96. $CH_2CO+H=HCCO+H_2$	5E+13	0	8000
97. $CH_2CO+O=HCCO+OH$	1E+13	0	8000
98. $CH_2CO+OH=HCCO+H_2O$	7.5E+12	0	2000
99. $CH_2CO=CH_2+CO$	2.01E+35	-6.68	82990

REACTIONS CONSIDERED	A	b	E
100. $C_2H+O_2=2CO+H$	5E+13	0	1500
101. $C_2H+C_2H_2=C_4H_2+H$	3E+13	0	0
102. $H+HCCO=CH_2(1)+CO$	1E+14	0	0
103. $O+HCCO=H+2CO$	1E+14	0	0
104. $HCCO+O_2=2CO+OH$	1.6E+12	0	854
105. $CH+HCCO=C_2H_2+CO$	5E+13	0	0
106. $2HCCO=C_2H_2+2CO$	1E+13	0	0
107. $CH_2(1)+M=CH_2+M$	1E+13	0	0
H	Enhanced	by	0
108. $CH_2(1)+CH_4=2CH_3$	4E+13	0	0
109. $CH_2(1)+C_2H_6=CH_3+C_2H_5$	1.2E+14	0	0
110. $CH_2(1)+O_2=CO+OH+H$	3E+13	0	0
111. $CH_2(1)+H_2=CH_3+H$	7E+13	0	0
112. $CH_2(1)+H=CH_2+H$	2E+14	0	0
113. $C_2H+O=CH+CO$	5E+13	0	0
114. $C_2H+OH=HCCO+H$	2E+13	0	0
115. $2CH_2=C_2H_2+H_2$	4E+13	0	0
116. $CH_2+HCCO=C_2H_3+CO$	3E+13	0	0
117. $CH_2+C_2H_2=C_3H_3+H$	1.2E+13	0	6600
118. $C_4H_2+OH=C_3H_2+HCO$	6.66E+12	0	-410
119. $C_3H_2+O_2=HCO+HCCO$	1E+13	0	0
120. $C_3H_3+O_2=CH_2CO+HCO$	3E+10	0	2868
121. $C_3H_3+O=CH_2O+$C2H	2E+13	0	0

REACTIONS CONSIDERED	**A**	**b**	**E**
122. $C_3H_3+OH=C_3H_2+H_2O$	2E+12	0	0
123. $2C_2H_2=C_4H_3+H$	2E+12	0	45900
124. $C_4H_3+M=C_4H_2+H+M$	1E+16	0	59700
125. $CH_2(1)+C_2H_2=C_3H_3+H$	3E+13	0	0
126. $C_4H_2+O=C_3H_2+CO$	1.2E+12	0	0
127. $C_2H_2+O2=HCCO+OH$	2E+08	1.5	30100
128. $C_2H_2+M=C_2H+H+M$	4.2E+16	0	107000
129. $C_2H_4+M=C_2H_2+H_2+M$	1.5E+15	0	55800
130. $C_2H_4+M=C_2H_3+H+M$	1.4E+15	0	82360
131. $H_2+O_2=2OH$	1.7E+13	0	47780
132. $OH+H_2=H_2O+H$	1.17E+09	1.3	3626
133. $O+OH=O_2+H$	4E+14	-0.5	0
134. $O+H_2=OH+H$	5.06E+04	2.67	6290
135. $H+O_2+M=HO_2+M$	3.61E+17	-0.72	0
H_2O	Enhanced	by	18.6
CO_2	Enhanced	by	4.2
H_2	Enhanced	by	2.9
CO	Enhanced	by	2.1
N_2	Enhanced	by	1.3
136. $OH+HO_2=H_2O+O_2$	7.5E+12	0	0
137. $H+HO_2=2OH$	1.4E+14	0	1073
138. $O+HO_2=O_2+OH$	1.4E+13	0	1073
139. $2OH=O+H_2O$	6E+08	1.3	0

REACTIONS CONSIDERED	**A**	**b**	**E**
140. $2H+M=H_2+M$	1E+18	-1	0
H_2	Enhanced	by	0
H_2O	Enhanced	by	0
CO_2	Enhanced	by	0
141. $2H+H_2=2H_2$	9.2E+16	-0.6	0
142. $2H+H_2O=H_2+H_2O$	6E+19	-1.25	0
143. $2H+CO_2=H_2+CO_2$	5.49E+20	-2	0
144. $H+OH+M=H_2O+M$	1.6E+22	-2	0
145. $H+O+M=OH+M$	6.2E+16	-0.6	0
H_2O	Enhanced	by	5
146. $2O+M=O2+M$	1.89E+13	0	-1788
147. $H+HO_2=H_2+O_2$	1.25E+13	0	0
148. $2HO_2=H_2O_2+O_2$	2E+12	0	0
149. $H_2O_2+M=2OH+M$	1.3E+17	0	45500
150. $H_2O_2+H=HO_2+H_2$	1.6E+12	0	3800
151. $H_2O_2+OH=H_2O+HO_2$	1E+13	0	1800
152. $H+Cl+M=HCl+M$	1E+17	0	0
153. $H+Cl_2=HCl+Cl$	7.94E+13	0	1200
154. $Cl+H_2=HCl+H$	4.8E+13	0	5000
155. $Cl+CO=COCl$	1.95E+19	-3.01	8070
156. $Cl+Cl+M=Cl_2+M$	5.75E+14	0	-1600
157. $Cl+HCO=HCl+CO$	1.41E+14	-0.35	510
158. $ClO+H_2=HOCl+H$	1E+13	0	13500

REACTIONS CONSIDERED	**A**	**b**	**E**
159. $ClO+CO=CO_2+Cl$	6.02E+11	0	7400
160. $COCl+Cl=COCl_2$	3.4E+28	-5.61	3390
161. $COCl+Cl=CO+Cl_2$	1.49E+19	-2.17	1470
162. $COCl+H=CO+HCl$	3.54E+16	-0.79	1060
163. $COCl+H=HCO+Cl$	3.42E+09	1.15	-180
164. $COCl+O_2=CO_2+ClO$	7.94E+10	0	3300
165. $COCl+O=CO_2+Cl$	1E+13	0	0
166. $O+HCl=OH+Cl$	5.25E+12	0	6400
167. $O+Cl_2=ClO+Cl$	1.26E+13	0	2800
168. $O+ClO=Cl+O_2$	5.75E+13	0	400
169. $OH+HCl=H_2O+Cl$	2.2E+12	0	1000
170. $CH_3Cl+OH=CH_2Cl+H_2O$	1.32E+12	0	2300
171. $CH_3Cl+O=OH+CH_2Cl$	1.7E+13	0	7300
172. $CH_3Cl+H=H_2+CH_2Cl$	6.66E+13	0	10600
173. $CH_3Cl+O_2=HO_2+CH_2Cl$	4E+13	0	52200
174. $CH_3Cl+HO_2=H_2O_2+CH_2Cl$	1E+13	0	16700
175. $CH_3Cl+ClO=HOCl+CH_2Cl$	5E+12	0	8700
176. $CH_3Cl+Cl=HCl+CH_2Cl$	3.16E+13	0	3300
177. $CH_3Cl+CH_3=CH_4+CH_2Cl$	3.31E+11	0	9400
178. $CH3Cl+H=HCl+CH_3$	5.4E+13	0	6500
179. $CH_3Cl=CH_3+Cl$	5.53E+31	-5.63	88810
180. $CH_3Cl=CH_2+HCl$	1.82E+25	-4.69	132460
181. $CH_3Cl=CH_2Cl+H$	1.31E+30	-5.23	106100

REACTIONS CONSIDERED	**A**	**b**	**E**
182. $CH_2Cl+O_2=ClO+CH_2O$	8.46E+13	-1.03	8180
183. $CH_2Cl+H=CH_3+Cl$	1.68E+16	-0.68	1020
184. $CH_2Cl+HO_2=CH_2ClO.+OH$	5.19E+14	-0.51	840
185. $CH_2Cl+OH=CH_2O+HCl$	4.1E+21	-2.57	3740
186. $CH_2Cl+OH=CH_2OH+Cl$	9.24E+11	0.38	2970
187. $CH_2Cl+CH_3=C_2H_5Cl$	8.47E+34	-6.75	8080
188. $CH_2Cl+CH_3=C_2H_4+HCl$	4.8E+24	-3.44	7690
189. $CH_2Cl+O=CH_2ClO.$	2.55E+15	-2.02	1230
190. $CH_2Cl+O=CH_2O+Cl$	8.31E+13	-0.18	800
191. $CH_2ClO.=CH_2O+Cl$	2.51E+24	-4.78	10070
192. $CH_2O+Cl=HCO+HCl$	5E+13	0	500
193. $CH_2O+ClO=HOCl+HCO$	1.2E+13	0	2000
194. $CH_3+ClO=CH_3O+Cl$	2.28E+07	1.54	-820
195. $CH_3+ClO=HCl+CH_2O$	5.5E+14	-0.51	710
196. $CH_4+ClO=CH_3+HOCl$	1.4E+13	0	15000
197. $CH_4+Cl=HCl+CH_3$	2.57E+13	0	3850
198. $C_2H_2+Cl=HCl+C_2H$	1E+13	0	28800
199. $C_2H_3+Cl=C_2H_3Cl$	6.5E+34	-6.63	8610
200. $C_2H_3+Cl=C_2H_2+HCl$	2.4E+24	-3.22	9070
201. $C_2H_4+ClO=CH_2Cl+CH_2O$	9.26E+18	-1.98	8430
202. $C_2H_4+ClO=C_2H_4OCl$	1.75E+32	-6.32	7900
203. $C_2H_4+Cl=HCl+C_2H_3$	3E+13	0	5100
204. $C_2H_5+Cl=C_2H_5Cl$	8.39E+36	-7.38	9550

REACTIONS CONSIDERED	A	b	E
205. $C_2H_5+Cl=C_2H_4+HCl$	6.12E+24	-3.38	9040
206. $C_2H_5+Cl=CH_3+CH_2Cl$	1.5E+21	-1.94	17720
207. $C_2H_6+Cl=HCl+C_2H_5$	7E+13	0	1000
208. $Cl+C_2H_3Cl=HCl+CHClC.H$	5E+12	0	5870
209. $Cl+C_2H_5Cl=HCl+CH_2ClC.H_2$	1.12E+13	0	1500
210. $CHClC.H=Cl+C_2H_2$	8.23E+29	-5.99	25760
211. $CH_2ClC.H_2=Cl+C_2H_4$	6.24E+36	-8.05	26340
212. $H+C_2H_3Cl=HCl+C_2H_3$	1E+13	0	9800
213. $H+C_2H_3Cl=H_2+CHClC.H$	1.55E+13	0	4730
214. $H+C_2H_3Cl=C_2H_4+Cl$	3.01E+13	0	4223
215. $H+C_2H_3Cl=CH_3C.HCl$	5.5E+34	-6.56	11950
216. $H+CH_3C.HCl=C_2H_5Cl$	8.01E+11	0	-5090
217. $H+CH_3C.HCl=C_2H_5+Cl$	3.39E+21	-2.42	8880
218. $H+CH_3C.HCl=CH_3+CH_2Cl$	6.67E+19	-1.55	9430
219. $H+CH_3C.HCl=C_2H_4+HCl$	3.72E+30	-5.1	9330
220. $H+C_2H_5Cl=HCl+C_2H_5$	1E+13	0	8100
221. $HO_2+Cl=HCl+O_2$	1.58E+13	0	0
222. $HO_2+Cl=ClO+OH$	3.35E+14	-0.32	1470
223. $H_2O_2+Cl=HCl+HO_2$	1.02E+12	0	800
224. $H_2O_2+ClO=HOCl+HO_2$	5E+12	0	2000

3.2. Cooling Rate

All the incinerator has the quenching process at the end of secondary combustion chamber right before exiting the gas through the atmosphere. What can be interesting here is whether the cooling rate of quenching process has any effect on the formation of PICs or any other species.

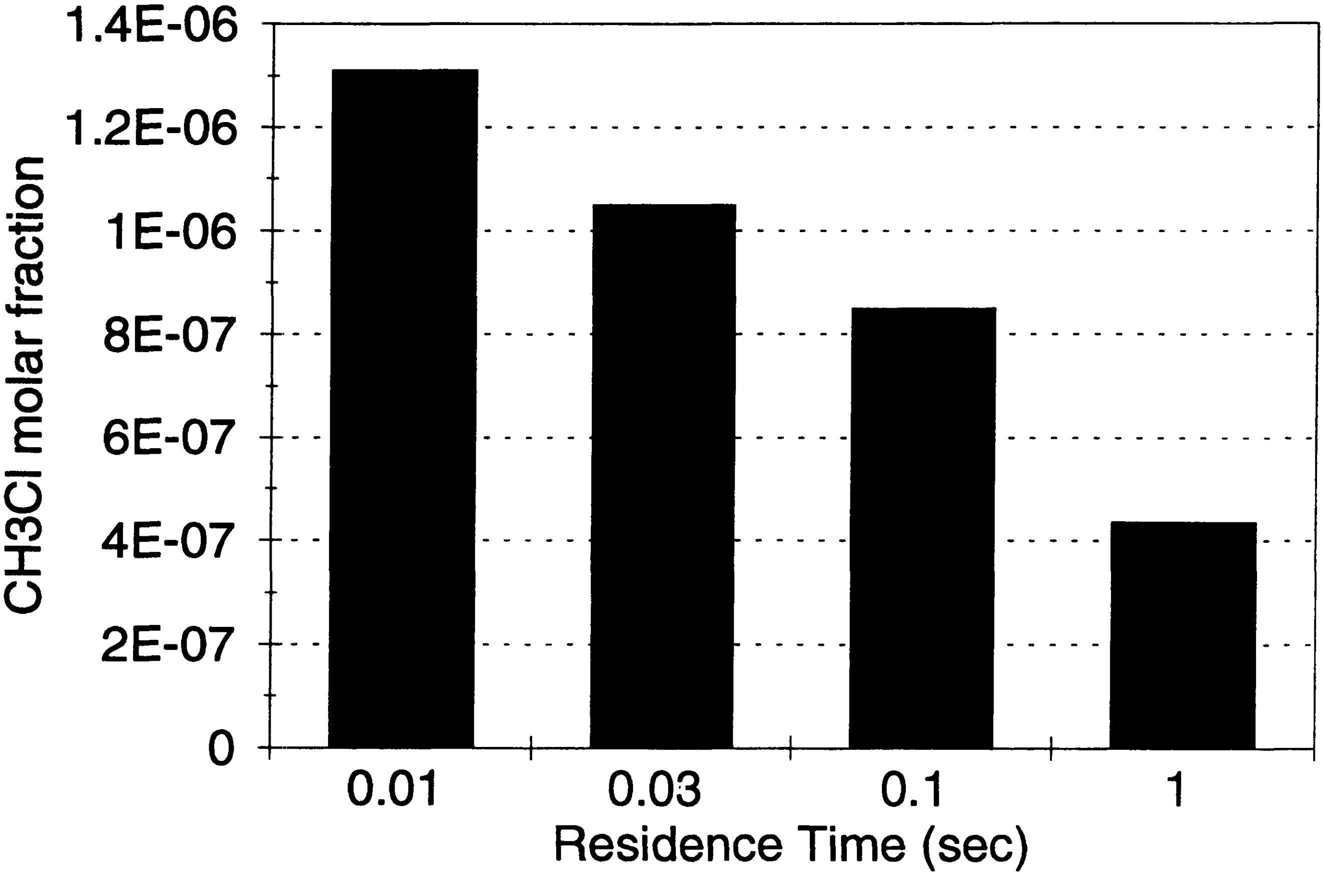


Figure 3.2. Molar fraction versus residence time (CH_3Cl)

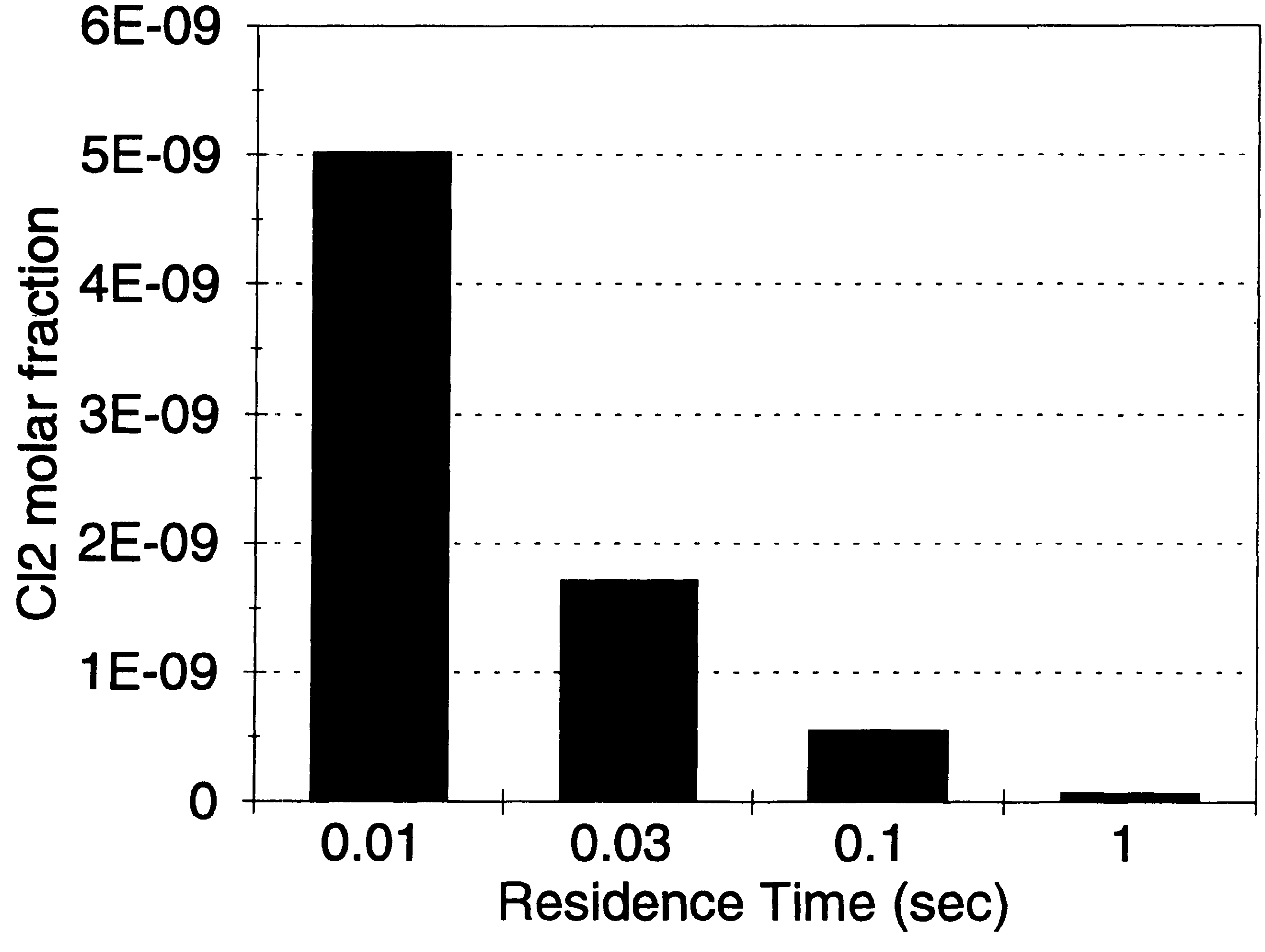


Figure 3.3. Molar fraction versus residence time (Cl_2)

Figure 3.2 and 3.3 show the advantage of slower cooling rate on the DRE of CH_3Cl and the formation of Cl_2 at fuel-rich conditions, which is cooled down from 1800K to 400K, respectively.

Table 3.3, 3.4 are the tables of molar fraction of CH_3Cl versus the cooling rate (same temperature decrease with different residence time). The unit of cooling rate is K / second. The temperature of reacting gas is dropped from 1500K, 1800K to the approximate atmospheric temperature of 400K at various residence times. Table 3.3, 3.4 show that the slower the cooling rate the more DRE of CH_3Cl which is suspected to be the result of longer time to burn the reacting gas. Also, it shows that the slower cooling rate the more reactor efficiency. The other interesting result is that the effect of cooling rate on the reformation of Cl_2 molecules in both fuel-lean and fuel-rich conditions. The same change in the cooling rate causes quite different results between fuel-lean and fuel-rich conditions. Table 3.3 shows that the decrease in cooling rate causes the decrease in the formation of Cl_2. However, the relationship between the CO/CO_2 ratio versus the cooling rate in fuel-lean condition shows that the faster the cooling rate the less efficient. Meanwhile, Table 3.4 shows that the increase in cooling rate results in the increase in the formation of Cl_2 and increase in DRE of CH_3Cl. Interestingly, when the temperature drops from 1500K at $\phi = 1.5$, the efficiency decreases as the cooling rate is slowed. It is believed that at the temperature at 1500K, the longer residence time the more O2 tend to react with chlorinated hydrocarbon rather than CO. The above results will be accounted into the decision of cooling rate for the staged combustion process in conjunction with the reactor volume, which depends on the residence time.

Table 3.3. Molar fraction versus cooling time (ϕ=0.8, final T=400K)

species residence time (s)	CH_3Cl	CO	CO_2	Cl_2	CO/CO_2
start at 1500K					
0.01	5.82E-26	7.86E-06	0.105	0.000111	7.486E-05
0.03	2.63E-26	6.99E-06	0.105	0.000114	6.657E-05
0.1	6.85E-27	4.95E-06	0.105	0.000102	4.714E-05
1.0	5.23E-28	5.95E-07	0.105	5.78E-05	5.667E-06

species residence time (s)	CH_3Cl	CO	CO_2	Cl_2	CO/CO_2
start at 1800K					
0.01	5.79E-26	8.55E-05	0.105	0.000308	0.0008143
0.03	1.14E-27	5.78E-05	0.105	0.000235	0.0005505
0.1	4.4E-30	2.22E-05	0.105	0.000153	0.0002114
1.0	1.01E-34	6.85E-07	0.105	6.02E-05	6.524E-06

Table 3.4. Molar fraction versus cooling time
(ϕ=1.5, final T=400K)

species residence time(s)	CH_3Cl	CO	CO_2	Cl_2	CO/CO_2
start at 1500K					
0.01	0.00219	0.0508	0.0861	5E-08	0.5900116
0.03	0.00201	0.051	0.0861	3.56E-08	0.5923345
0.1	0.00151	0.0517	0.0862	1.34E-08	0.599768
1.0	4.43E-05	0.0552	0.0868	2.51E-10	0.6359447
start at 1800K					
0.01	1.31E-06	0.0883	0.0619	5.02E-09	1.4264943
0.03	1.05E-06	0.0883	0.062	1.72E-09	1.4241935
0.1	8.49E-07	0.0883	0.0622	5.5E-10	1.4196141
1.0	4.36E-07	0.0886	0.063	7.29E-11	1.4063492

3.3. Residence Time

Residence time plays an important role in enhancing the burning efficiency. Generally, the longer the residence time the less the concentrations of the PICs. However, in most cases, the reaction is in the steady state after a certain amount of time. It is importune to find the time when the reaction fall into the steady state to get the minimize the PICs while keeping the reactor volume at its smallest value possible. Figure 3.4 shows that as the residence time increases the molar fraction of CH_3Cl

decreases until the residence time passes the 1.5e-02 seconds. After that point, the DRE of CH_3Cl remains same. All the residence times used for the purpose of; 1) development of mixing failure diagnosis, and 2) evaluation of the staged combustion process are matched to those of actual experimental works previously done at MIT and those of the real hazardous waste incinerator. Some of the results are plotted for the conditions of equivalence ratio of 1.65, Cl/C ratio of 0.1 and the temperature of 1500K for SENKIN. Figure 3.5, 3.6, 3.7 and 3.8 are the plots of residence time versus the molar fractions of C_2H_2, O_2, CH_4 and C_2H_4, respectively. C_2H_2 molar fraction shows the increase as the residence time increases except for the instant drop at the start of right after the CH_3Cl injection. It is believed that with the new fuel CH_3Cl, C_2H_4 destruction process, which results in the formation of C_2H_2, temporarily. For this same reason, Figure 3.8 shows the increase in C_2H_4 molar fraction for a short period of time right after CH_3Cl injection into SENKIN. After a while, C_2H_4 molar fraction starts to decrease again. Figure 3.6 and 3.7 show the gradual decrease of O_2 and increase of CH_4 until it starts to slow down and decrease very slowly, as expected.

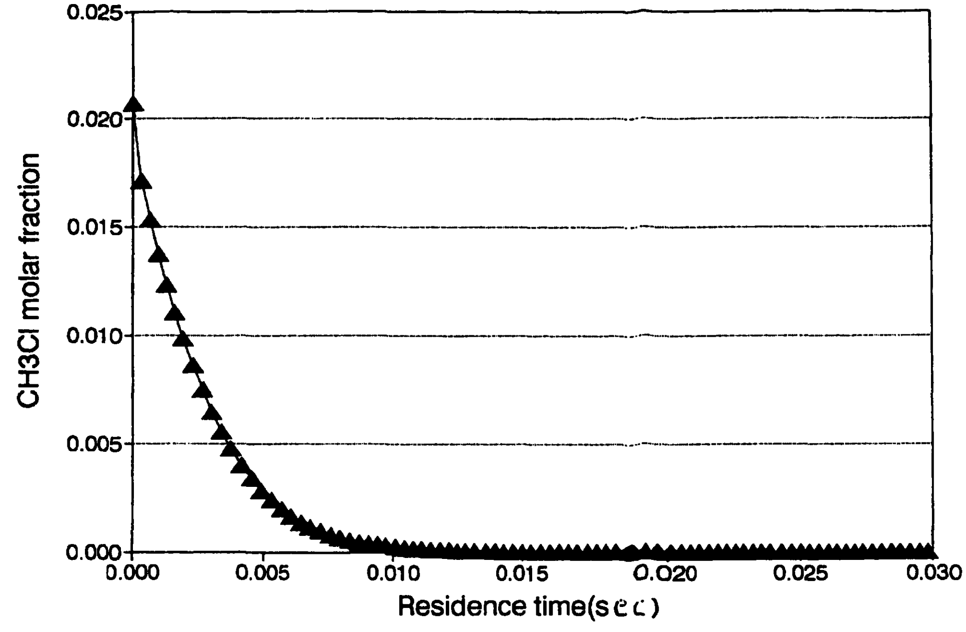


Figure 3.4. Molar fraction versus residence time in SENKIN (CH_3Cl, $\phi=1.65$, Cl/C=0.1, T=1500K)

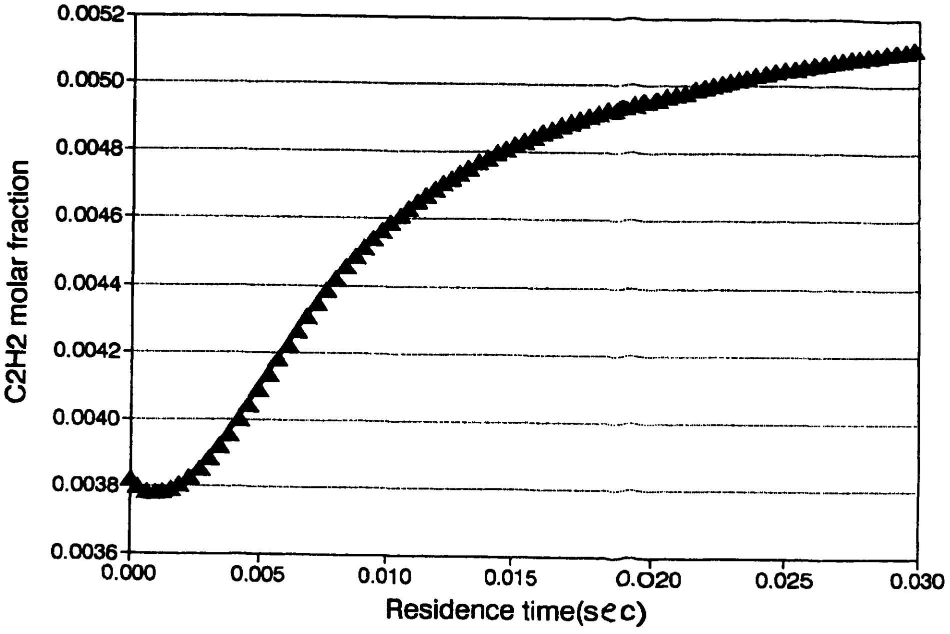


Figure 3.5. Molar fraction versus residence time in SENKIN (C_2H_2, $\phi=1.65$, Cl/C=0.1, T=1500K)

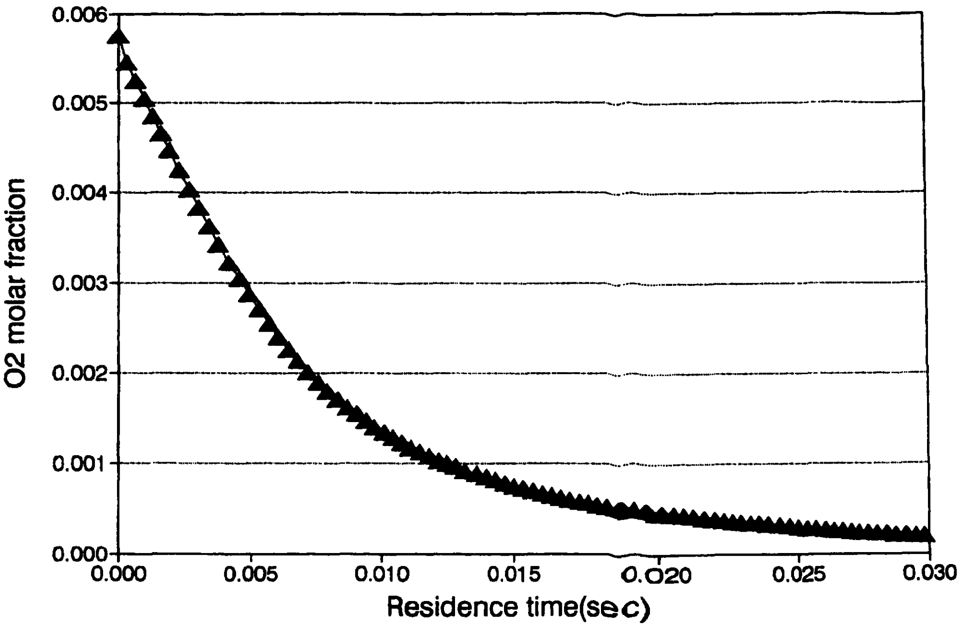


Figure 3.6. Molar fraction versus residence time in SENKIN (O_2, ϕ=1.65, Cl/C=0.1, T=1500K)

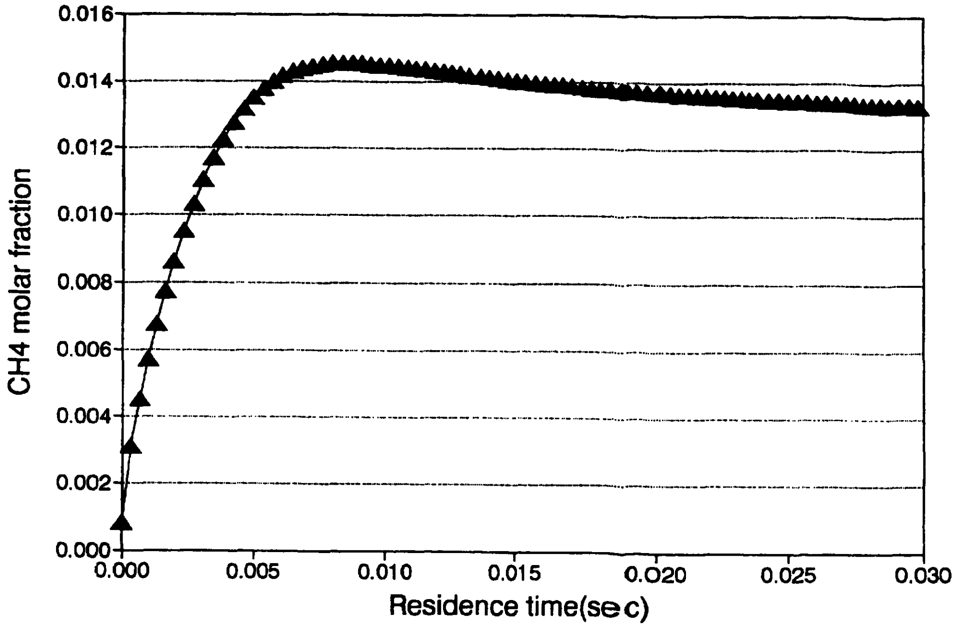


Figure 3.7. Molar fraction versus residence time in SENKIN (CH_4, ϕ=1.65, Cl/C=0.1, T=1500K)

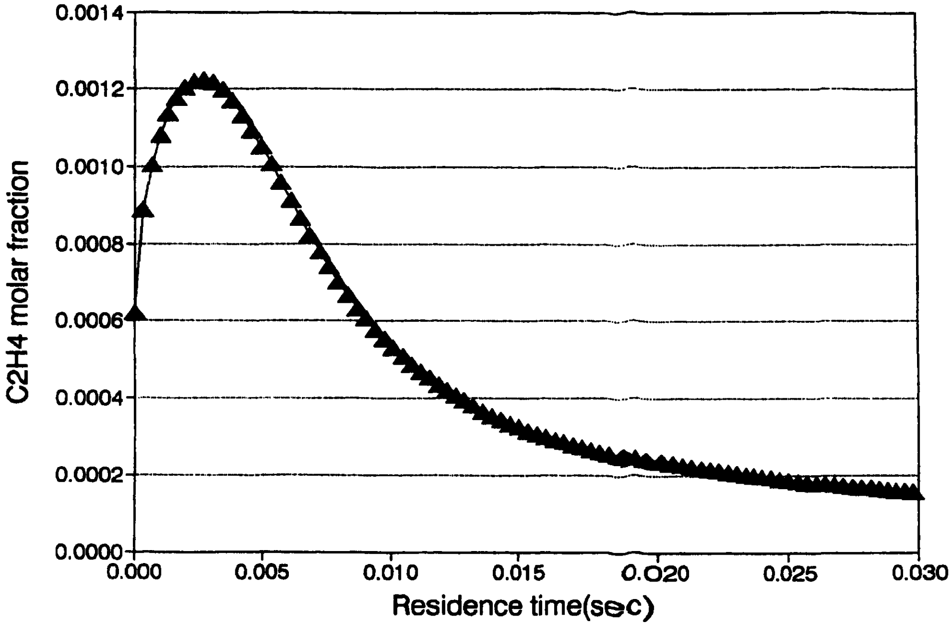


Figure 3.8. Molar fraction versus residence time in SENKIN (C_2H_4, ϕ=1.65, Cl/C=0.1, T=1500K)

3.4. Temperature

The effect of temperature on the PIC formation is expected to be the higher the temperature the less formation of PICs.

The conversion factor of several species are calculated from those gases leaving out of PSR. The temperature are in the range of 1000 to 1500K with the interval of 100K. The reactor conditions are mass flow rate of 11 g/sec, pressure of 1 atm, volume of 250 cm^3. Residence times are in the range of 1.14e-02 to 4.4e-03 seconds.

Equivalence ratio is 0.75. Fuel is 100% C_2H_4 and the oxidants are 21% O_2 and 79% N_2 in the form of air. Table 3.5 show the results of this calculations in terms of molar fractions.

Table 3.5. Molar fraction versus temperature in PSR (ϕ=0.75)

temperature(K)	$C_2H_{4\,out}$	$C_2H_{2\,out}$	$CH_{4\,out}$	CO/CO_2
1000	0	0	0	0
1100	4.98e-02	4.37e-05	9.14e-08	278.67
1200	3.11e-04	4.55e-06	5.31e-05	0.1877
1300	1.51e-04	3.66e-06	1.33e-05	0.1057
1400	9.80e-05	3.55e-06	5.00e-06	0.08
1500	6.99e-05	3.58e-06	2.26e-06	0.0714

The results shows that a meaningful combustion reaction starts at the temperature of 1200K. For the temperatures between 1200K and 1500K, results shows continuous increase or decrease in molar fractions except for C_2H_2 at 1400K. The CO/CO_2 ratios clearly indicate that the higher the temperature the higher reactor efficiency.

Second, the similar work is performed for the case of SENKIN model. The baseline is the gas flow coming out of PSR. CH_3Cl is injected at the start of SENKIN with the Cl/C ratio of 0.1. The overall equivalence ratio at fixed Cl/C ratio can be calculated as following;

1. For the case of Cl/C = 0.1, the (fuel/air)stoich of 0.368 is calculated from the overall stoichiometric reaction (PSR + SENKIN);

$$9C_2H_4 + 2CH_3Cl + 30O_2 \leftrightarrow 20CO_2 + 20H_2O + 2HCl. \tag{3.4}$$

2. For the case of PSR equivalence ratio = 1.0, the stoichiometric reaction in PSR is

$$9C_2H_4 + 27O_2 \leftrightarrow 18CO_2 + 18H_2O. \tag{3.5}$$

3. The actual overall reaction becomes

$$9C_2H_4 + 2CH_3Cl + 27O_2 \rightarrow \tag{3.6}$$

the $(\text{fuel/air})_{\text{actual}}$ ratio of 0.408 is calculated from above reaction and the overall equivalence ratio of 1.1 is calculated by $\{(\text{fuel/air})_{\text{actual}}/(\text{fuel/air})_{\text{stoich}}\}$.

With the equivalence ratios of 1.25, 1.5 (C_2H_2 converted)/(CH_3Cl converted) ratios (%) are calculated at various temperatures and at the CH_3Cl conversion of 50%, 60%, 70%, 80% and 90% (Table 3.6, 3.7). The conversion of both CH3Cl and C2H2 are calculated by {(Inlet molar fraction- Outlet molar fraction)/Inlet molar fraction} * 100.

Table 3.6. Conversion factor versus temperature in SENKIN (ϕ=1.25)

CH_3Cl (%) T (K)	50	60	70	80	90
1300	-0.58	-0.42	-0.23	*	*

1400	0.45	0.93	1.44	2.09	2.73
1500	2.91	3.73	4.95	6.08	7.58
1600	3.69	6.24	7.99	9.85	11.99

* indicates CH$_3$Cl does not convert over 80%

Table 3.7. Conversion factor versus temperature in SENKIN (ϕ=1.5)

CH$_3$Cl (%) T (K)	50	60	70	80	90
1300	-0.91	-0.85	-0.79	-0.69	-0.55
1400	-1.04	-0.87	-0.61	-0.24	0.32
1500	0.09	0.55	1.08	1.78	2.95
1600	1.71	2.37	3.32	4.44	6.16
1700	2.65	3.79	5.08	6.64	8.85
1800	2.84	4.11	5.21	7.52	10.37

Both Table 3.6 and 3.7 show that as the temperature increases (C_2H_2 converted/CH$_3$Cl converted) ratio increases, as expected. The relation between CH$_3$Cl converted and (C_2H_2 converted/CH$_3$Cl converted) ratio shows that the more CH$_3$Cl react the more C_2H_2 are produced. Figure 3.9 and 3.10 shows the C_2H_2 conversion versus CH$_3$Cl conversion at equivalence ratio of 1.25, 1.5, respectively. They indicate as the temperature increases and as CH$_3$Cl reacts away, the more C_2H_2 produced. The minus sign indicates C_2H_2 is produced. All the results from the above are going to be used as bases later in chapter 4, 5 and 6.

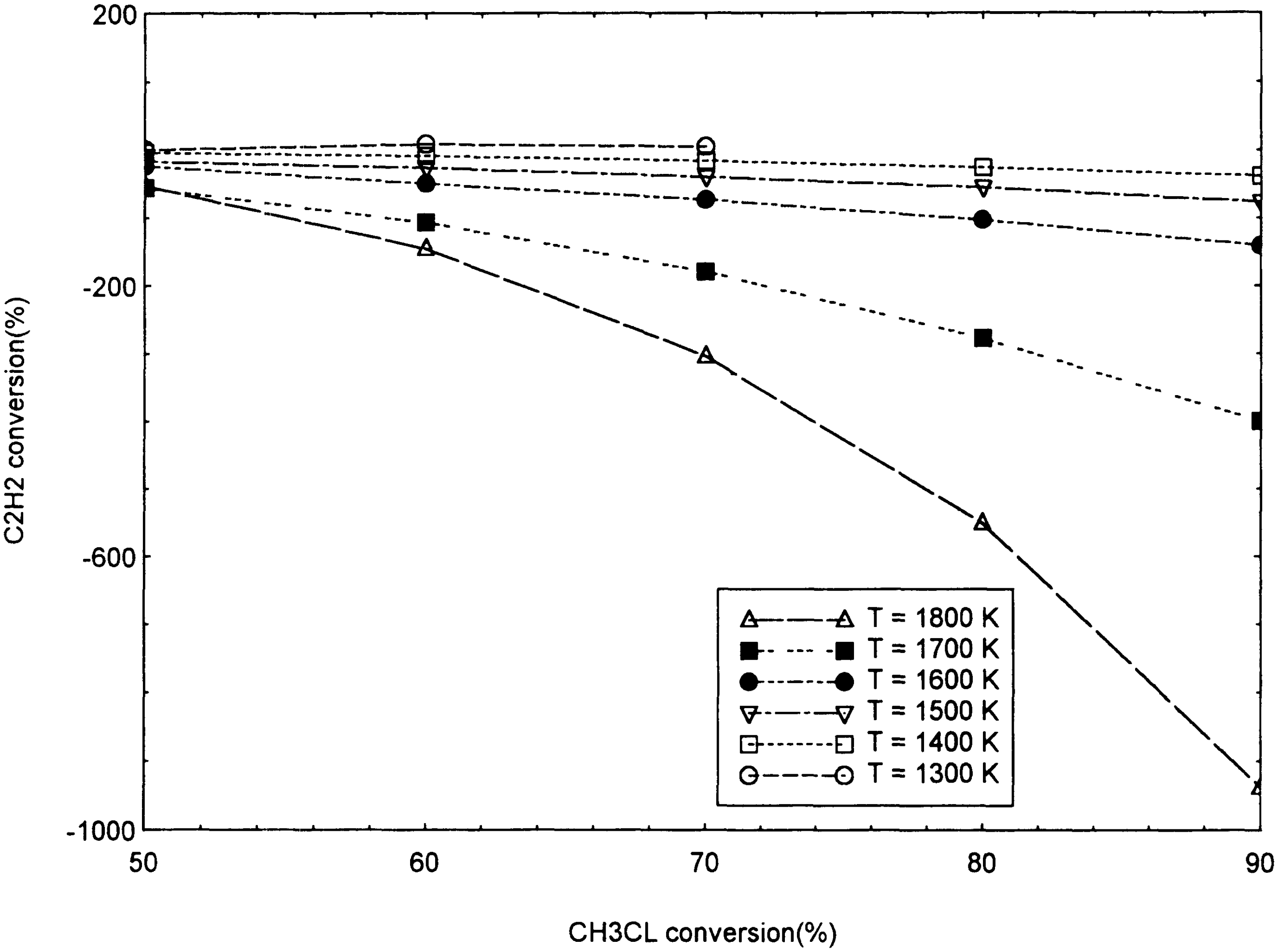


Figure 3.9. C_2H_2 conversion (%) versus CH_3Cl conversion (%) (ϕ=1.25, 1300K<T<1800K)

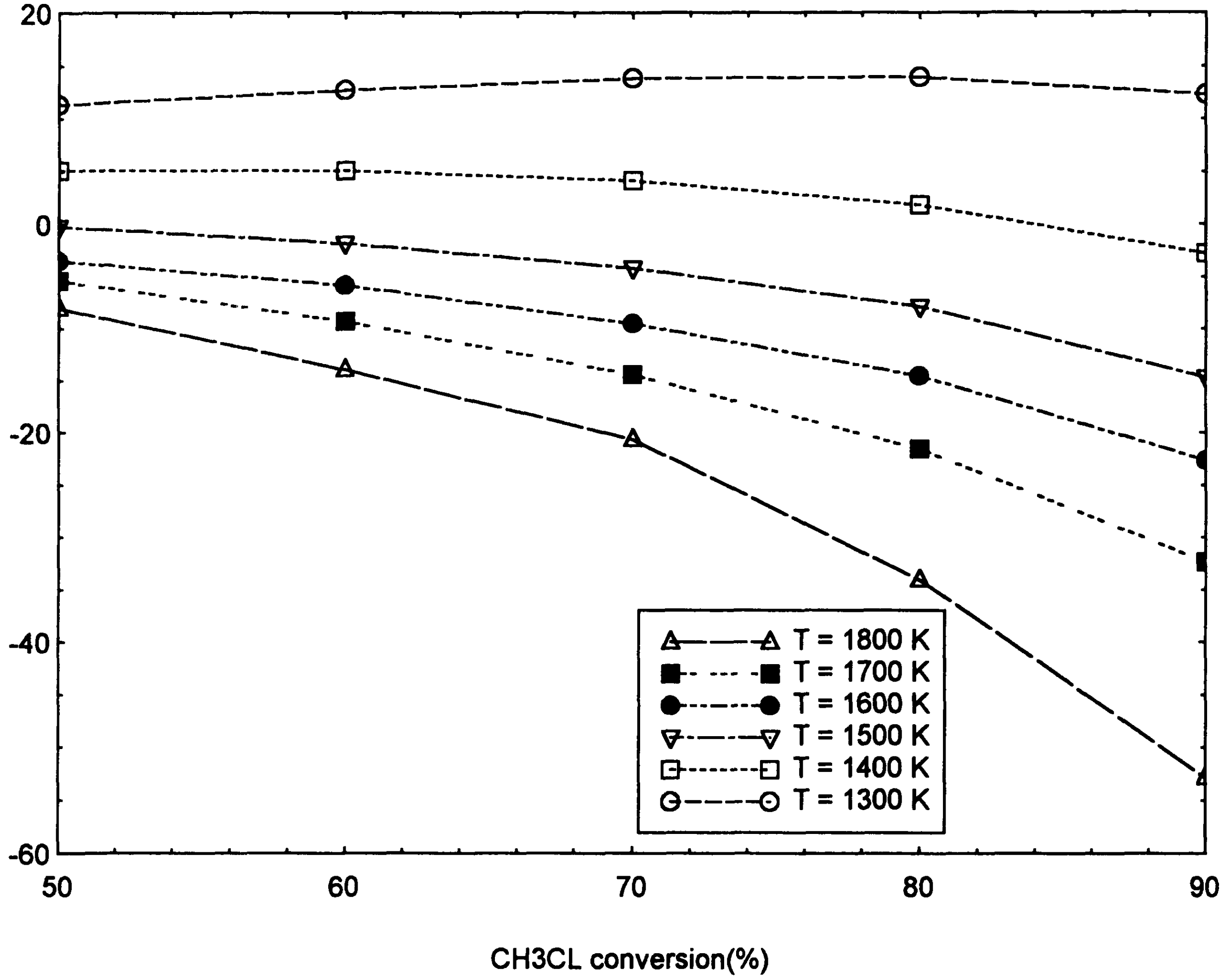


Figure 3.10. C_2H_2 conversion (%) versus CH_3Cl conversion (%) (ϕ=1.5, 1300K<T<1800K)

Chapter Four

4. Failure Diagnosis (Mixing)

One of the major concerns in hazardous waste incineration system is the emission of products of incomplete combustion (PICs). In order to reach the goal of minimizing PIC emission, it is important to operate the incineration systems under their optimum conditions. Significant effort has been made to develop the general method to detect any failure modes in incinerator systems by recognizing the links between specific observed PICs and particular incinerator afterburner failure modes. Monitoring CO as a surrogate for other stack emissions has been practiced until it has been proven inadequate for many PICs. To look at the relations between PICs and selected failure modes, it is necessary to operate the incinerator at off the optimal conditions (failure modes), and measure the amount and composition of the PICs of concern until one can get the general relations between them. However, operating the incinerator in failure modes on purpose can be a major threat to the public health, and also it is too expensive to monitor every species in combustion product gas. Pilot-scale experiments and its numerical modeling are applied here to resolve such problems. The current work focuses on the effects of incomplete turbulent mixing, development of diagnostic failure modes (mixing), and the prediction of the amount and composition of combustion products in a selected incineration system.

4.1. Reaction Mechanism

The reaction mechanism sets used here are; 1) the mechanism discussed in chapter 4, and 2) the mechanism of pure hydrocarbons including aromatics. The second reaction mechanism set includes the formation and the oxidation of benzene and several other aromatic compounds. Recalling the result from the experiment, the fact that aromatics are only formed under the fuel-rich condition, this reaction mechanism is perfect for validating the existence of mixing constraint. There are 18 reactions of formation and oxidation of benzene presented below in Table 4.1.

Table 4.1. Benzene formation and oxidation reactions

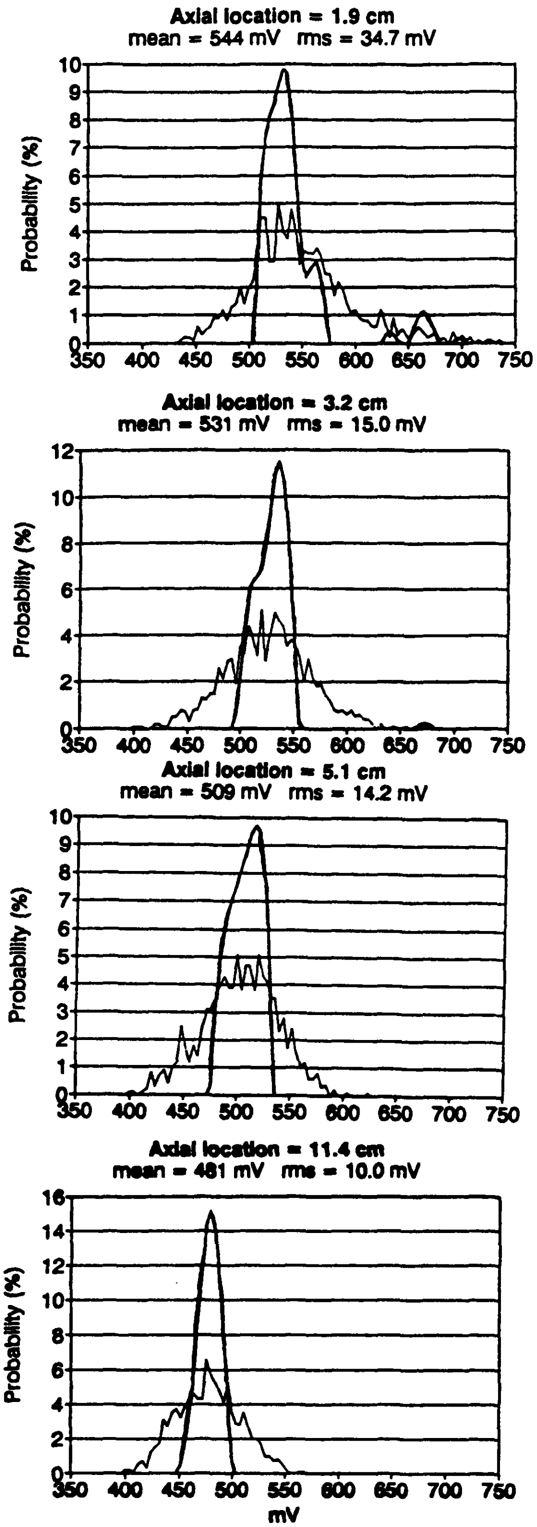
REACTIONS	A	b	E
1. CPDCRC = C_6H_6 + CH_3	1E+08	0.0	0.0
2. C_6H_6 + C*CC. = H + CPEBICHD	2E+10	0.0	0.0
3. C_6H_6 + NO_2 = C_6H_5 + HNO_2	3E+13	0.0	33000.0
4. $PHOCH_3$ + H = C_6H_6 + CH_3O.	4.77E+13	0.0	10800.0
5. $C_6H_5CH_3$ + H = C_6H_6 + CH_3	4.17E+13	0.0	11000.0
6. C_6H_5OH + C_6H_5 = C_6H_6 + C_6H_5O.	1E+13	0.0	6064.0
7. C_6H_5OH + H = C_6H_6 + OH	3.44E+13	0.0	9420.0
8. C_6H_6 + H = C_6H_5 + H_2	2E+13	0.0	18600.0
9. C_6H_6 + H = CYC_6H_7	1.6E+12	0.0	-2120.0
10. C_6H_6 + H = $BICYC_6H_7$	2.75E+10	0.0	7370.0
11. C_6H_6 + H = $CH_2CY_{24}PD$	2.26E+14	0.0	14100.0
12. C_6H_6 = C_6H_5 + H	1.67E+16	0.0	111500.0
13. C_6H_6 + H = $LINC_6H_7$	1.22E+22	-1.87	31200.0
14. C_6H_6 + H = $CYC_5H_4CH_3$	2.39E+27	-3.92	29200.0
15. C_6H_6 + O = C_6H_5O. + H	6.32E+14	-0.40	5640.0
16. C_6H_6 + O = C_6H_5OH	3.91E+04	1.59	17190.0
17. C_6H_6 + OH = C_6H_5 + H_2O	1.4E+13	0.0	4490.0
18. C_6H_6 + O_2 = C_6H_5 + HO_2	6.31E+13	0.0	67832.0

4.2. A Brief Discussion of Experimental Results

The experimental facility has been designed to simulate the conditions in actual incinerator systems; it consists of a Toroidal Jet Stirred Reactor (TJSC) followed by a Plug Flow Reactor (PFR). Gaseous CH_3Cl is injected into a baseline flow of hot products flowing in the PFR. Instantaneous temperature measurement, obtained by application of a laser Rayleigh scattering diagnostics, and stable species concentrations are then measured at various distances from the point of injection. The temperature probability density functions (PDFs) and stable species concentration measurements for fuel-lean and fuel-rich conditions show the evidence of mixing constraints in the PFR environment. Detection of aromatic species having a strong non-linear dependence on the equivalence ratio is interpreted as an effect of the variation of the local value of the equivalence ratio due to imperfect mixing. Temperature PDFs and stable species concentrations were measured at various distances from the point of injection of CH_3Cl into the PFR to observe the behavior of the fluid streams as they mixed and reacted while flowing downstream. Conditions were carefully controlled to achieve primary variations of the flow-field in the axial direction of the PFR, which approximated the one dimensional concentration field.

4.2.1 Rayleigh Scattering Measurements

The Rayleigh scattering diagnostics were evaluated for both cold flow and reacting flow conditions. To investigate the pure mixing constraints, cold flow experiments were performed by injecting CH_3Cl into the PFR with the baseline flow of N_2 keeping the dynamics similar to that of reacting flow conditions. The Rayleigh scattering PDFs for cold flow conditions are presented in Figure 4.1.


Axial location = 1.9 cm
mean = 544 mV rms = 34.7 mV

Axial location = 3.2 cm
mean = 531 mV rms = 15.0 mV

Axial location = 5.1 cm
mean = 509 mV rms = 14.2 mV

Axial location = 11.4 cm
mean = 481 mV rms = 10.0 mV

Figure 4.1. Rayleigh scattering PDF's evolution for cold flow experiment

Both the raw data and reconstructed PDFs are presented in each panel. The subsequent panels correspond to axial locations progressively distant from the injection point. Without CH_3Cl injection (baseline condition), the PDF is quite narrow with a mean value of 423 mV. Near the point of injection (1.9 cm, 3.2 cm locations) the PDF exhibits a higher signal peak and a multimodal distribution, which is attributed to CH_3Cl that is not completely mixed into the baseline flow of N_2, and to the presence of unmixed packets of material. The fluctuating component of the signal decreases further from the point of injection, indicating the progressive mixing of the injected material into the baseline flow. The results of non-reacting flow experiments show the evidence of mixing constraints and characterize the evolution of the turbulent system in the PFR by the decay of the fluctuating component of the concentration (represented by signal) distribution with the distance from the injection point.

The experimental data obtained for the variance of the concentration of CH_3Cl versus distance from the injection point are in good agreement with an exponential trend, describing the evolution of the variance of the concentration of a non-reactive tracer due to turbulent mixing, such as;

$$\sigma^2(x) = \sigma^2(0)\exp[-(1/\chi_d)x] + C \qquad (4.1)$$

where σ^2 is the variance in the distribution, x is the distance from the point injection, χ_d is the characteristic distance describing the approach of the concentration distribution to uniformity, and C is a constant to be determined experimentally.

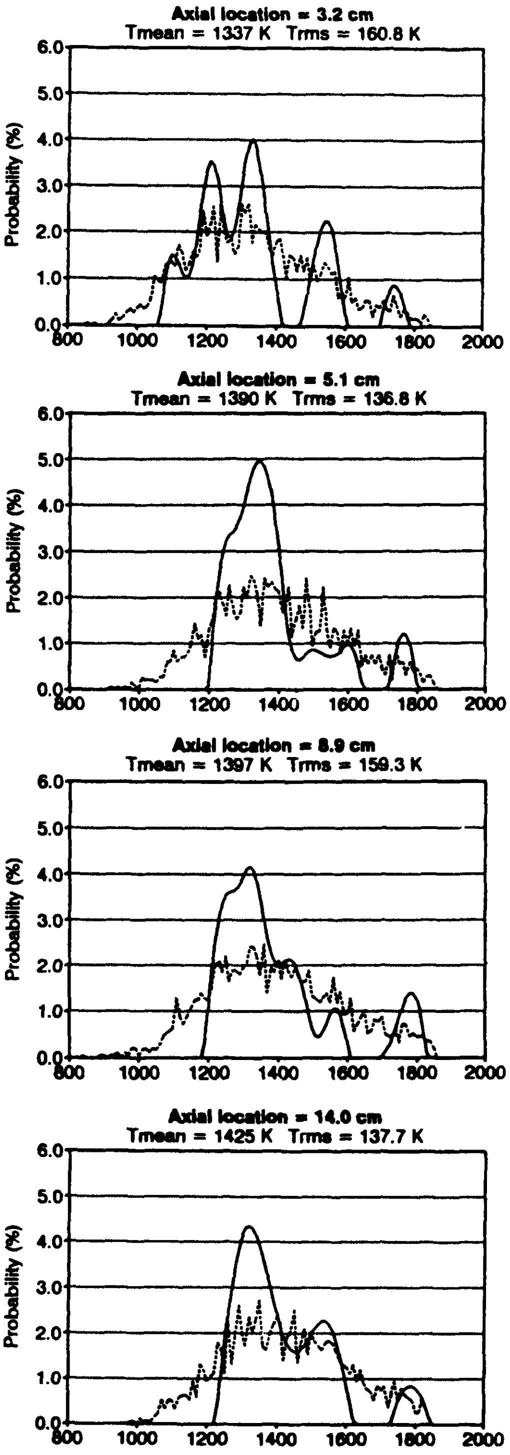


Figure 4.2. Rayleigh scattering PDF's evolution for fuel-lean conditions (ϕ=0.75)

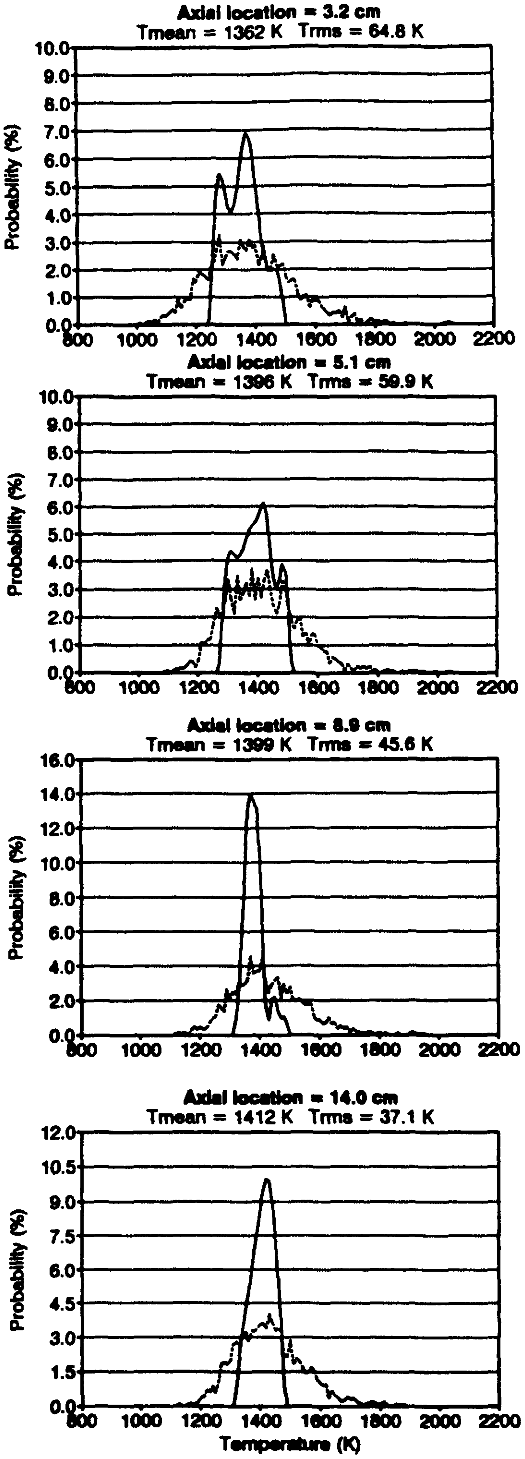


Figure 4.3. Rayleigh scattering PDF's evolution for fuel-rich conditions (ϕ=1.25)

The evolution of the temperature PDFs in reacting flow conditions show the evidence of mixing constraints in the PFR environment (Figure 4.2 and 4.3). The figures are interpreted similar to those of cold flow experiments. The reacting flow conditions were constructed by injecting CH_3Cl into both fuel-lean (ϕ=0.671) and fuel-rich (ϕ =1.17) baseline flows of combustion products from the TJSC. The corresponding overall equivalence ratios for both fuel-lean and fuel-rich cases are 0.75 and 1.25, respectively.

4.2.2. Stable Species Concentrations

The evolution of the temperature field in the PFR detected via Rayleigh scattering diagnostics has proven evidence of mixing constraints that are expected to interact with the chemistry of the system in two concurrent ways. First, since complete mixing conditions are reached at a certain distance from the injection point, mixing constraints have the effect of decreasing the extent of reaction, compared to the case of a premixed environment. Second, the detection of the distribution of temperatures in a PDF at a given location is interpreted as a distribution of the local equivalence ratio, compared to the theoretical ϕ value. Some of the high values of ϕ will result in pyrolytic pockets that can lead to the detection of species which have a strong non-linear dependence on the value of the equivalence ratio, compared to the conditions simulated by numerical modeling for a completely mixed flow field. Stable species concentration measurements were performed to give insight on these expectations on the effects of the presence of turbulent mixing constraints in the PFR environment.

4.3. The Failure Diagnosis (Mixing) Theory

The detection of chemical species which should not be formed under complete mixing conditions can be used as a tool for the development of a diagnostic failure modes in actual incineration systems.

Usually, these systems are operated under the excess air conditions; a feed back control system based on the presence of selected species, which are sensitive to variations in the distribution of the equivalence ratio at given residence time in the flue gases which is coming out of the secondary combustion chamber can be used to adjust the practical devices (for example, air injectors, fuel and air flow controllers, etc.) and quickly restore the optimal operating conditions.

The sensitivity of selected species to other parameters, such as temperature, cooling rate in quenching process, and residence time are already discussed in chapter 4.

The basic method for developing the mixing failure diagnosis are 1) detection of certain species, and 2) comparison of the selected molar ratios of species.

4.4. The development of the Failure Diagnosis (Mixing)

For a long time, people in this field have been tried to develop a methodology for locating any failure in hazardous waste incinerator. The feed-back control systems are adopted to maintain the appropriate incinerator conditions such as temperature, residence time and the composition and the feed rate of fuel into the incinerator. In recent years, the enormous amount of research have been performed on the importance of turbulent mixing in reacting gas to the formation of PICs. It is believed that PIC formation is highly dependent upon the local ratio of fuel and oxidant and is sensitive to both turbulent mixing and chemistry. Recalling those work already done on the effect of chemistry on the formation of PICs, following work is concentrated on that of turbulent mixing on the formation of PICs. The following work is based on those results of the experiment previously done at MIT. The basic approach is by comparing the results of numerical models, which is free of mixing constraints in homogeneous gas phase, and those of the actual experiment, the differences are explained in terms of the existence of mixing constraint in the actual incinerator.

4.4.1. Detection of Particular Species

As discussed in experimental results, there are some products such as aromatics (benzene), chlorinated aromatics, and higher molecular weight species that are only formed under pyrolytic conditions. These species were measured near the injection point where the injected material is not well mixed into the baseline flow and is thus allowed to establish localized pyrolytic conditions under overall fuel-lean and slightly fuel-rich conditions whose overall equivalence ratio would not lend themselves to pyrolysis. Detection of these species can be understood as the evidence of mixing failure in the PFR. Results of numerical modeling show that CH_3Cl was consumed for both fuel-lean and fuel-rich conditions with perfect mixing. In other word, detection of CH_3Cl at any conditions indicates the mixing failure mode in the PFR, which must be resulted from the slipping through the PFR wall. Table 4.2 shows that for both fuel-lean and fuel-rich conditions at 1600K, residence time of 3.e-02 seconds, Cl/C ratio of 0.1, CH_3Cl are almost zero in its molar fraction (concentration (ppm) can be calculated multiplying by factor, 10e-06).

Table 4.2. CH_3Cl molar fraction versus equivalence ratio

equivalence ratio	0.75	1.0	1.5	1.75	2.0
CH_3Cl molar fraction	0	1.29e-07	6.46e-06	6.94e-06	7.59e-06

4.4.2. Comparison of the Selected Molar Ratios of Species

Using numerical models, certain molar ratios of species that show characteristic behaviors with respect to equivalence ratio were found. Figure 4.4 shows that the molar ratios of CH_3Cl/CH_4 are quite different between the overall fuel-lean side and fuel-rich side. The conditions are T=1600K, residence time=3.e-02 seconds, Cl/C=0.1. By comparing the selected species' molar ratios of both the PFR and models, detection of any mixing problem in the PFR was possible. If the sleeted molar ratios of species at fuel-lean condition, which is the case for most incinerators, is matched to that of the fuel-rich region at the condition of fuel-lean, the reacting gas is expected to have fuel-rich pockets due to the imperfect mixing. Figure 4.5 shows the same insight as Figure 4.4 for the case of $CH_3Cl_{inlet}/CH_3Cl_{outlet}$ at the temperature of 1800K and Cl/C=0.1, residence time of 3.e-02 seconds. Several other ratios are calculated for the same purpose. Figure 4.6, 4.7, 4.8, 4.9 are the plots of C_6H_6/C_2H_4, O_2/CH_4, O_2/H_2 and O_2/C_2H_2 ratio versus equivalence ratio at 1500K, residence time of 1.e-02 seconds and Cl/C of zero.

4.5. The Prediction Method Theory

the method of predicting the amount and composition of PICs in a selected combustion system is discussed for the case of the experimental facility described above.

First, based on the insights on the mixing history provided by the temperature PDFs at various distances from the injection point, the corresponding PDFs of equivalence ratio were generated. Then the concentration of several species were obtained for the perfect mixing conditions using numerical modeling with various residence time indicating the distances along the PFR. Finally, by applying the PDFs of equivalence ratio to the results of numerical modeling , the concentration of the selected species at actual incineration system were predicted.

With this new prediction method, investigation of incinerator at various off-optimal conditions, such as temperature drop and slippage of unburned material along the reactor wall, existence of fuel-rich pocket, can be possible without causing any potential treat to the public health.

The prediction method can be described as; first, based on the temperature PDFs generated by Rayleigh scattering diagnostics, Gaussian distribution function was applied for the simplest PDF of the equivalence ratio of a flue gas in the PFR used in experiments. The equivalence ratios for baseline flows in both experimental and modeling case were matched. Second, the concentration of a species interested at various equivalence ratios were calculated by numerical models (in perfect mixing conditions) and the weighting factors for each equivalence ratio were calculated from the normalized PDF. Third, the concentrations were multiplied by the weighting factors and summed to the total. Finally, the total from previous step were compared to the concentration of a same species exited from the PFR. The above procedures were repeated for the PDFs of different variances until the concentrations of both PFR and models were matched. The validity of the PDF was examined by applying the same procedure to other species. Although the whole procedure are not yet examined and validated, the trial indicate the high possibility of practical use of this method.

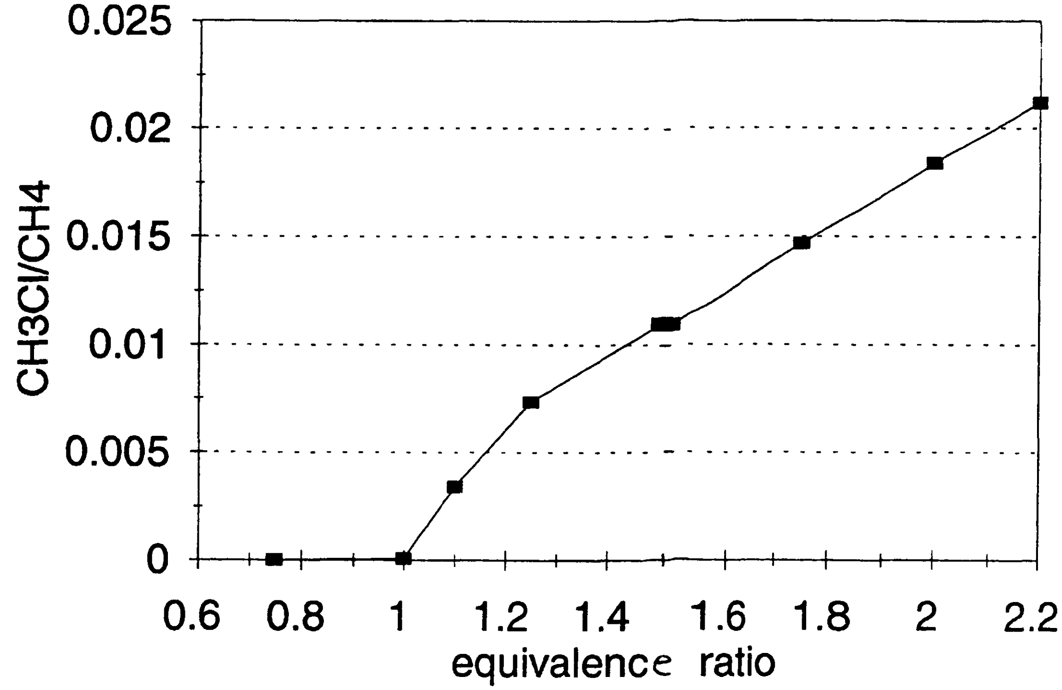


Figure 4.4. Molar ratio versus equivalence ratio (CH_3Cl/CH_4)

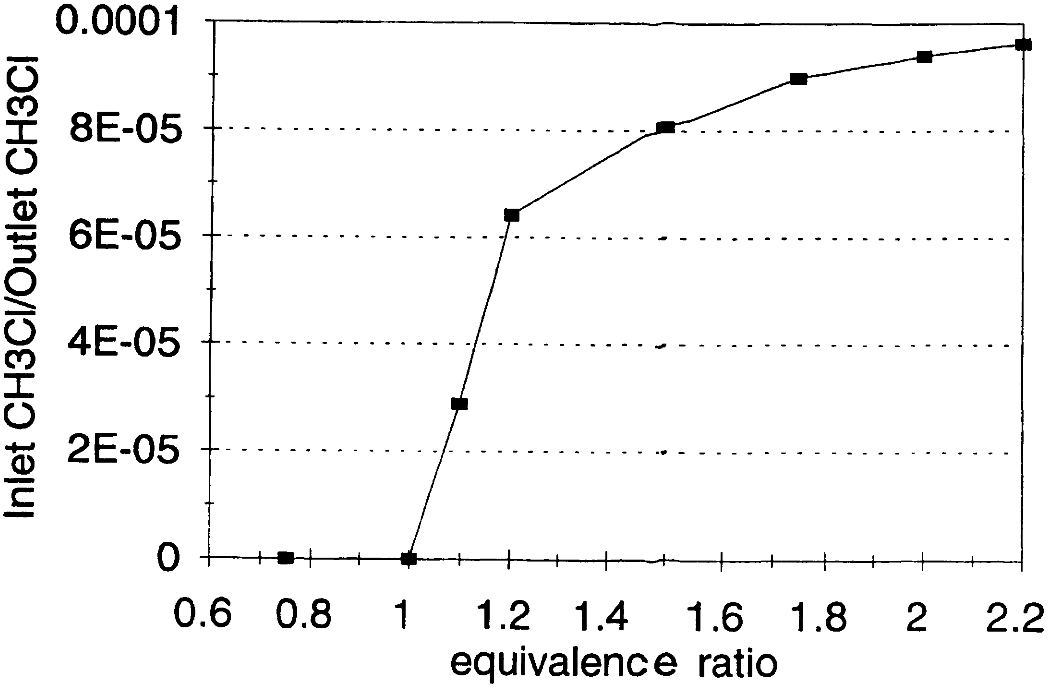


Figure 4.5. Molar ratio versus equivalence ratio (CH_3Cl_{in}/CH_3Cl_{out})

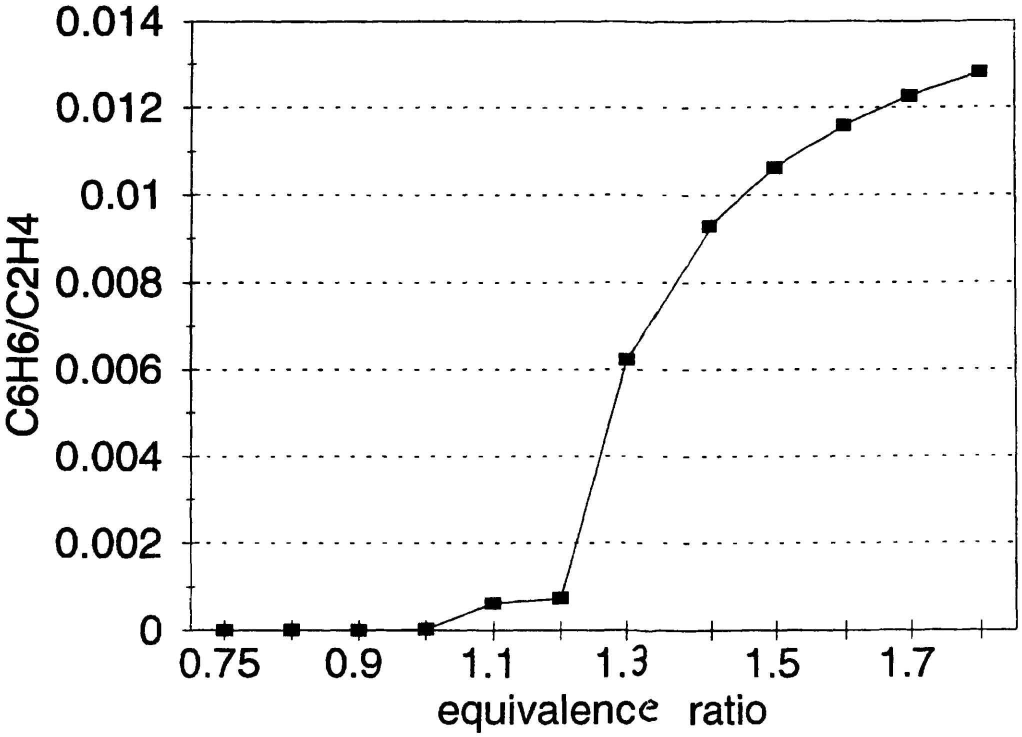


Figure 4.6. Molar ratio versus equivalence ratio (C_6H_6/C_2H_4)

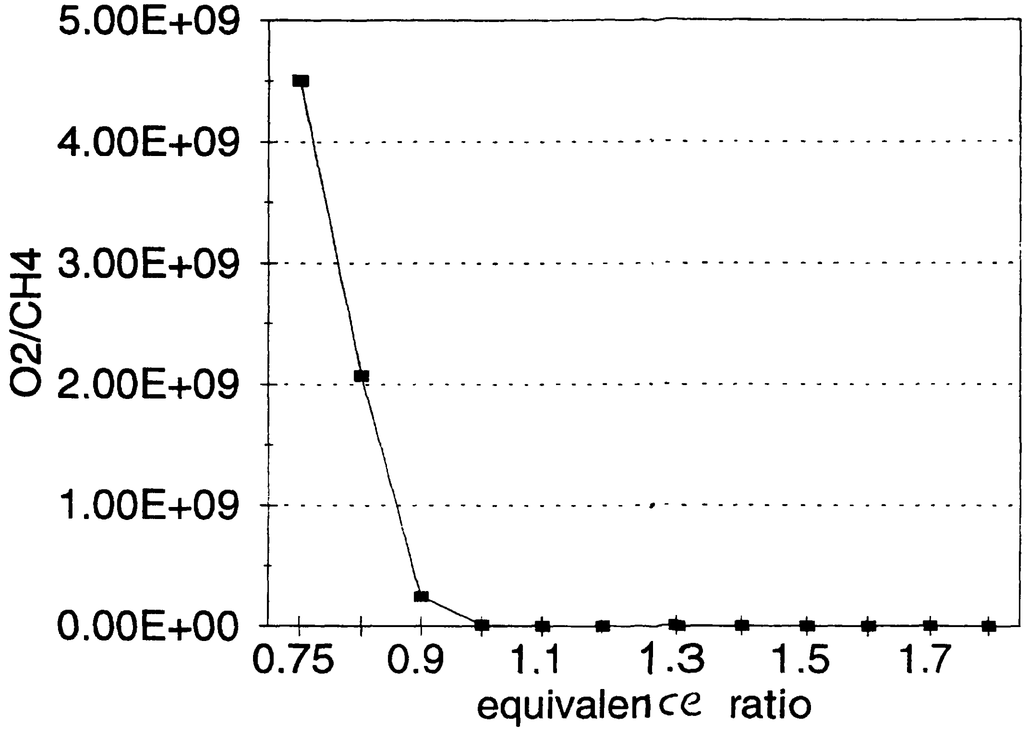


Figure 4.7. Molar ratio versus equivalence ratio (O_2/CH_4)

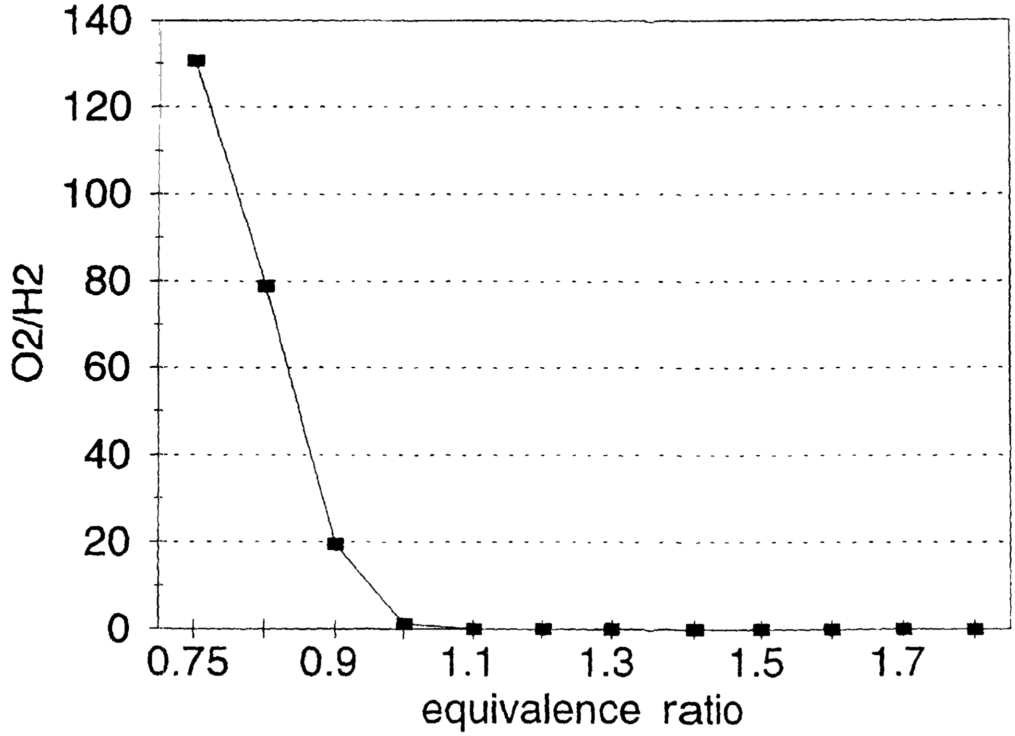


Figure 4.8. Molar ratio versus equivalence ratio (O_2/H_2)

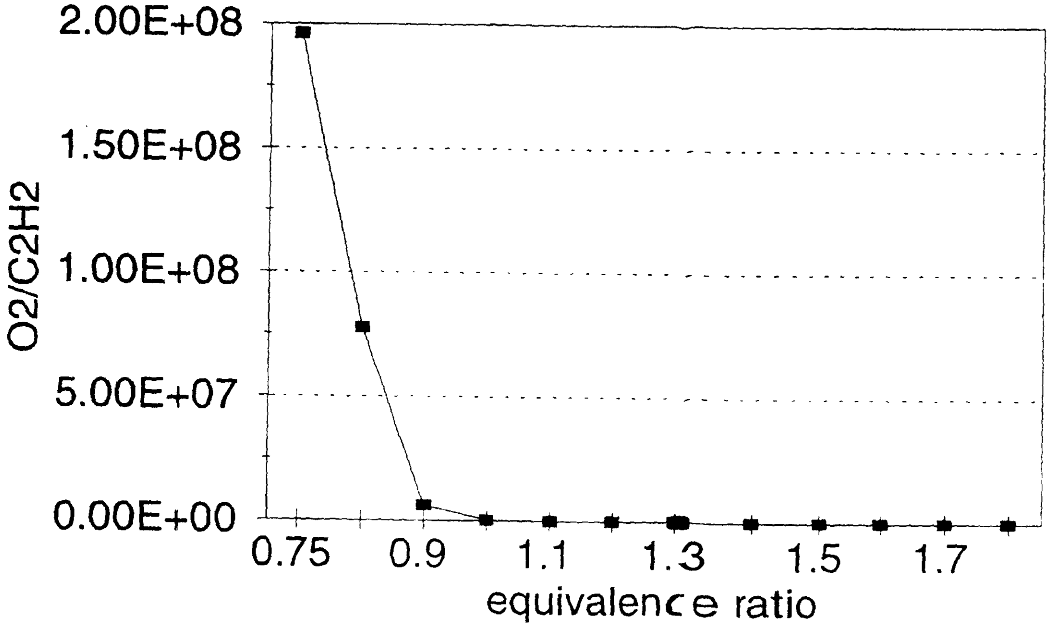


Figure 4.9. Molar ratio versus equivalence ratio (O_2/C_2H_2)

Chapter Five

5. Theory of the Staged Combustion Process

Combustion process in hazardous waste incinerator generally consists of combustion in primary combustion chamber followed by secondary chamber. In this work, the primary and the secondary combustion chamber are characterized as PSR and PFR respectively. In this work, conventional and staged combustion process are named after the number of stage in the secondary combustion chamber. Staged combustion means it has at least more than two stages in the secondary combustion chamber. Sensitivity analysis are performed for understanding of chemical kinetics.

5.1. Chemistry in the Staged Combustion Process

The background in terms of chemistry for staged combustion process is that it provide the fuel in starved-air condition into the primary combustion chamber. Most of the Hazardous Waste Incinerators are operated under fuel-lean condition to avoid the formation of PIC at the end of secondary combustion chamber. Instead of fuel-lean, operating under fuel-rich condition makes the concentration of Cl and Cl_2, to be exact, both the $Cl/(Cl+Cl_2+HCl)$ and $Cl_2/(Cl+Cl_2+HCl)$ ratios considerably lower than those of the fuel-lean condition. Fuel-rich condition generates substantially higher concentration of H radicals than fuel-lean condition. Those H radicals reform HCl in conjunction with Cl atoms when the temperature of the flue gas drops. The reformation of HCl from Cl atoms prevents the potential reformation of Cl_2 from Cl atoms, which will subsequently leads to the formation of dioxin in gas phase. However, providing the rich fuel into the primary combustion chamber requires extra O_2 injection into the flue gas in the secondary combustion chamber. The O_2 injection will be discussed in detail later in chapter 6 when the stage by stage approach is presented.

In recalling that the H radicals play a important role in preventing the formation of Cl_2 from Cl atoms, extra steam or water injection were performed in this work for two major reasons; 1) to drop the temperature of the flue gas coming out of PSR to prevent further formation of Cl_2 during the last burning stage of the process, 2) by providing extra H radicals to form more HCl from Cl atoms instead of letting Cl atoms to form Cl_2. In chemistry point of view, the role of the H_2O can be described as shifting the following reaction to the right;

$$Cl + H_2O \text{<---->} HCl + OH \qquad (5.1)$$

Consequently, OH radicals will help the CO burn out which indicates the efficiency of the incinerator.

5.2. Background Calculations

By using the EQUIL FORTRAN code developed at National Sandia Laboratory, the equilibrium state concentration were calculated for all the species in the C_1/C_2 Hydrocarbon and chlorocarbon reaction mechanism. Figure 5.1 is the plot of $Cl/(Cl+Cl_2+HCl)$ and $Cl_2/(Cl+Cl_2+HCl)$ ratios versus equivalence ratio (ϕ) at the equilibrium temperature of 1800K. It shows that as the equivalence ratio increases, the $Cl/(Cl+Cl_2+HCl)$ and $Cl_2/(Cl+Cl_2+HCl)$ ratios decrease. Especially, the considerable drop in ratios occurs as the condition goes from fuel-lean to fuel-rich. It validates the chemistry discussed in section 5.1. Figure 5.2 shows the instant jump of HCl ratio at fuel-rich condition.

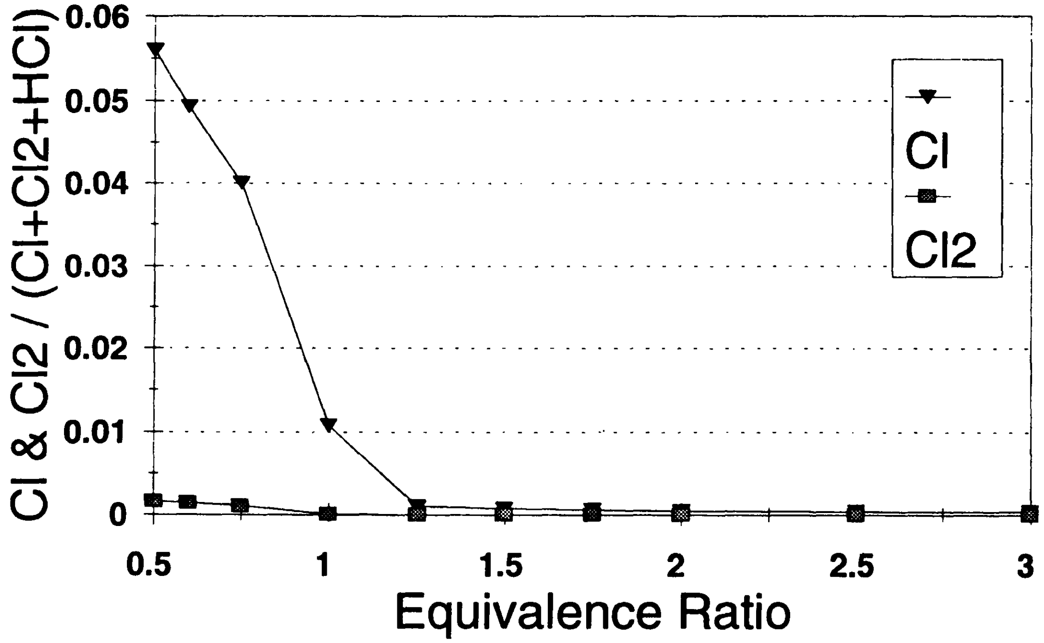


Figure 5.1. Molar ratio versus equivalence ratio (Cl & Cl_2/(Cl+Cl_2+HCl)) (T=1800K, equilibrium state)

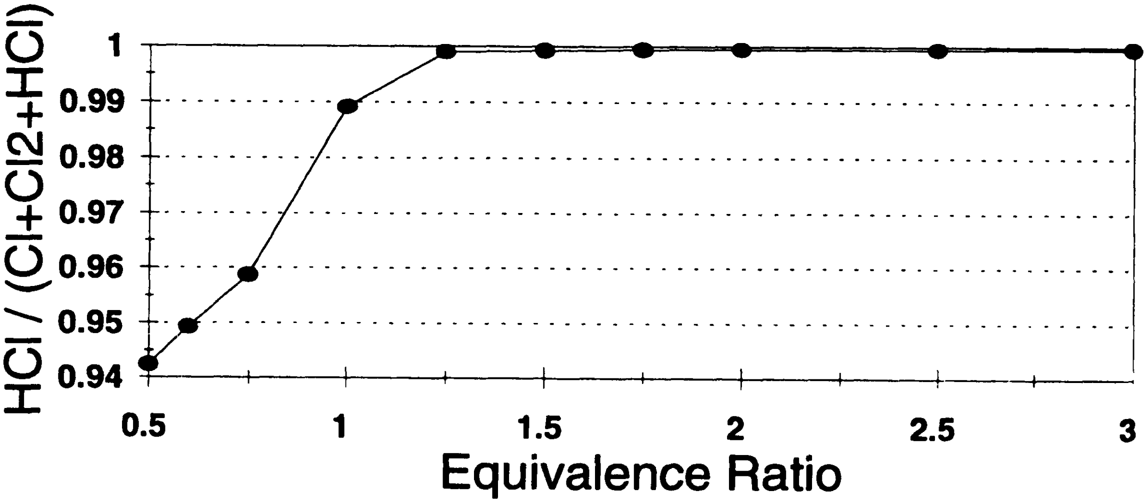


Figure 5.2. Molar ratio versus equivalence ratio (HCl/(Cl+Cl_2+HCl)) (T=1800K, equilibrium state)

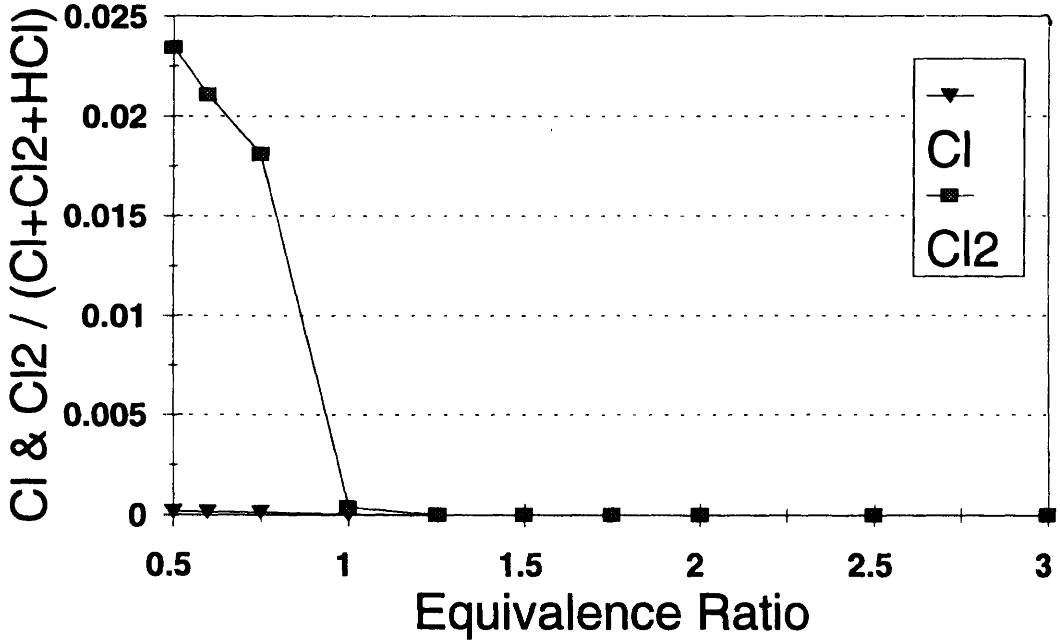


Figure 5.3. Molar ratio versus equivalence ratio (Cl & Cl_2/(Cl+Cl_2+HCl))
(T is cooled from 1800K to 373K, during 3.e-02 second)

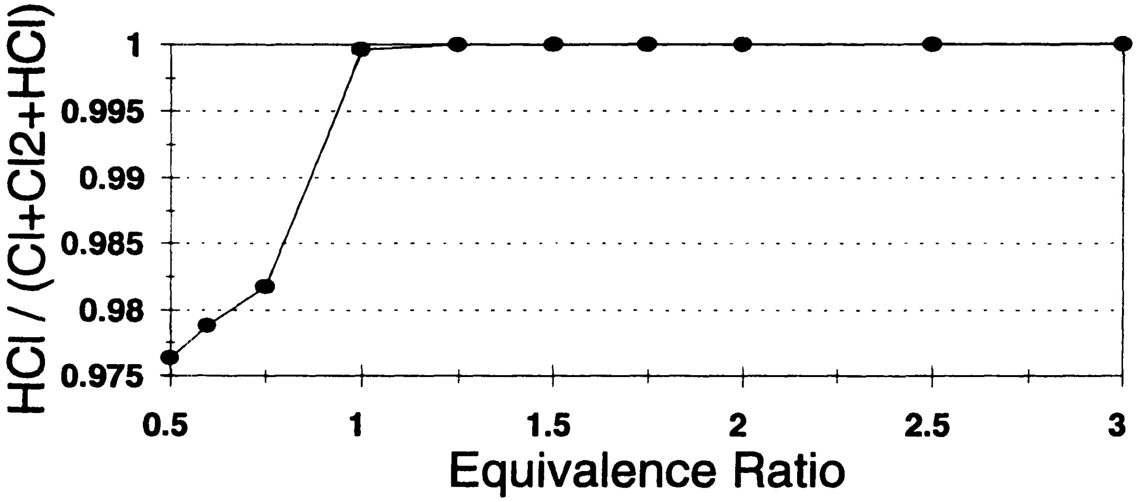


Figure 5.4. Molar ratio versus equivalence ratio (HCl/(Cl+Cl_2+HCl))
(T is cooled from 1800K to 373K, during 3.e-02 second)

Figure 5.1 and 5.2 indicate the clear advantage in surprising the Cl and Cl_2 by employing the starved-air fuel. Figure 5.3 and 5.4 are the plots of Cl & $Cl_2/(Cl+Cl_2+HCl)$ and $HCl/(Cl+Cl_2+HCl)$ ratios versus equivalence ratio when the gases are cooled down from 1800K to 373K during 3.e-02 seconds. Cooling of the flue gas is simulated by using SENKIN model. Between the fuel-lean and fuel-rich conditions, especially $Cl_2/(Cl+Cl_2+HCl)$ and $HCl/(Cl+Cl_2+HCl)$ ratios drop dramatically. Figure 5.5 shows the Cl & $Cl_2/(Cl+Cl_2+HCl)$ ratios versus various starting (equilibrium) temperatures from which the flue gases are cooled down to 373K during 3.e-02 seconds. The equilibrium ratio is set to 0.75 to simulate the fuel condition after the extra O_2 injection. Figure 5.6 is the same plot as Figure 5.5 except for replacing the ratio with $HCl/(Cl+Cl_2+HCl)$. Both Figures indicate the desirable O2 injection temperature at which the Cl_2 can be prevented from reformation. Figure 5.7 and 5.8 also support the results of Figure 5.5 and 5.6. Keeping in mind the fact that there are no point between right above 1000K and right below 1200K, more points of temperature should be examined for the above range of $1000K < T < 1200K$.

5.3. Cooling Rate

As discussed in chapter 3, the cooling rate or the cooling itself of the flue gas has a major effect on the Cl_2 concentration. In fuel-rich condition dropping the flue gas temperature cause the decreasing in Cl_2 concentration, while in fuel-lean condition it increases the ratio. The faster the cooling occurs the less Cl_2 concentration it gets in fuel-rich condition. This work on the cooling rate is to find the direction of approaching, not to find any exact cooling rate to be applied in the staged combustion process. The cooling rate should be picked after considering the optimal reactor volume also.

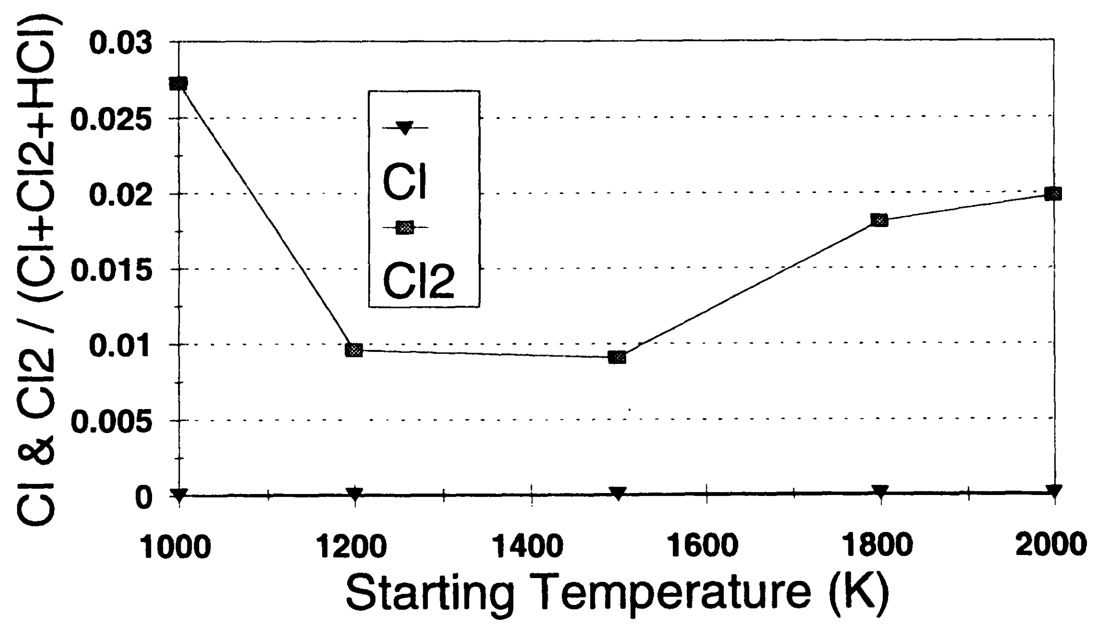


Figure 5.5. Molar ratio versus starting T of cooling (Cl & $Cl_2/(Cl+Cl_2+HCl)$) (ϕ=0.75, residence time=3.e-02 second)

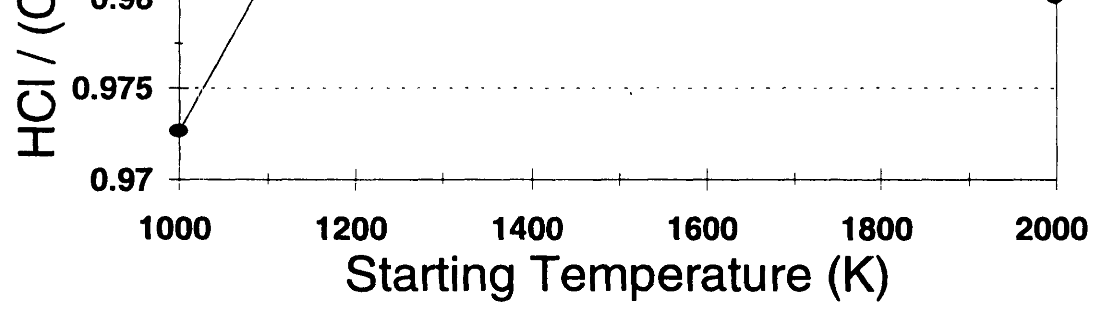


Figure 5.6. Molar ratio versus starting T of cooling ($HCl/(Cl+Cl_2+HCl)$) (ϕ=0.75, residence time=3.e-02 second)

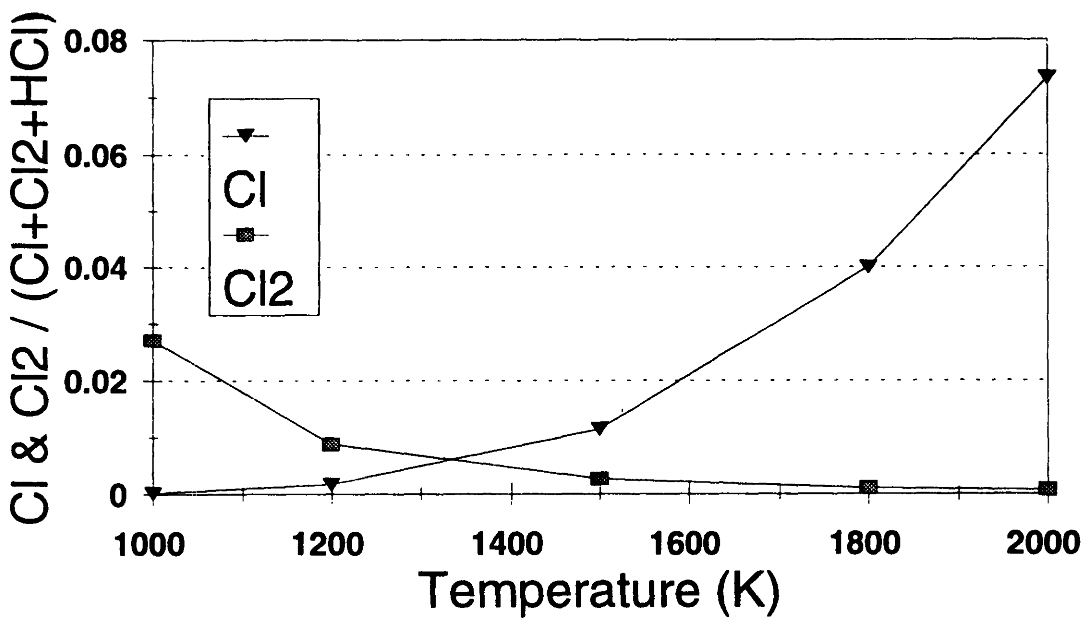


Figure 5.7. Molar ratio versus temperature (Cl & $Cl_2/(Cl+Cl_2+HCl)$) (ϕ=0.75, equilibrium state)

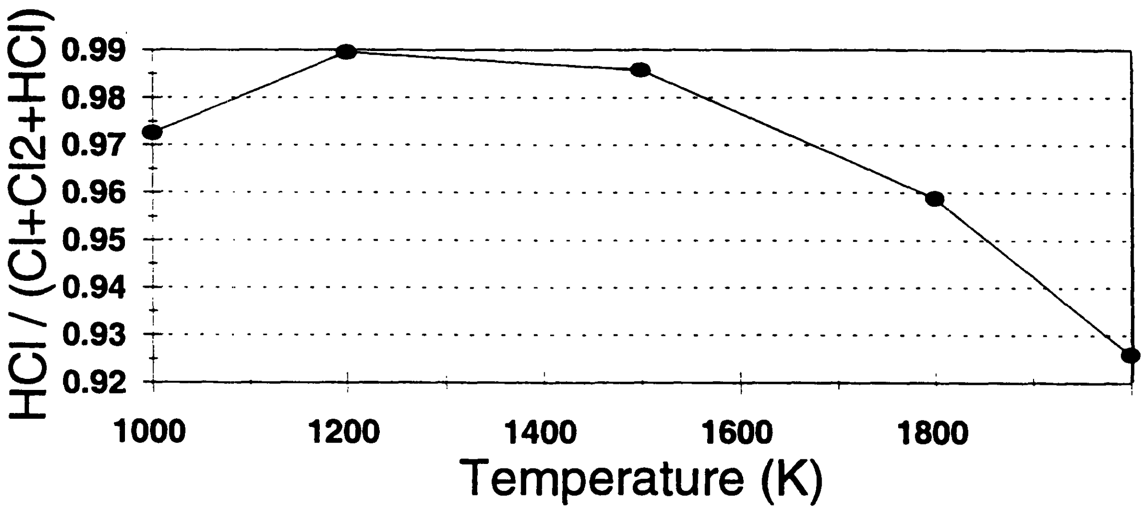


Figure 5.8. Molar ratio versus temperature ($HCl/(Cl+Cl_2+HCl)$) (ϕ=0.75, equilibrium state)

Figure 5.9 and 5.10 show that the plots of the cooling rate versus Cl, Cl_2 and HCl over $Cl+Cl_2+HCl$ in fuel-lean (ϕ=0.75) condition. The flue gas is cooled down from 1800K to 373K during various residence times. As the plots indicate, the results are desirable when the cooling occurs during the residence time of over 1.e-01 seconds. The same results are presented in Figure 5.11 and 5.12, for the case of fuel-rich (ϕ=3.0) condition, respectively.

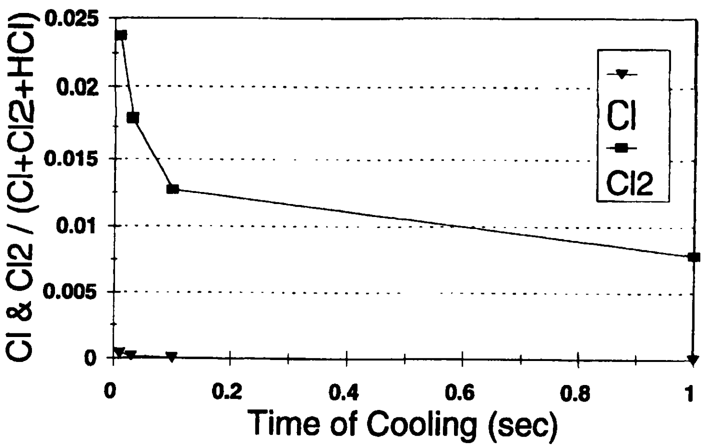


Figure 5.9. Molar ratio versus time of cooling (Cl & $Cl_2/(Cl+Cl_2+HCl)$)
(T is cooled down from 1800K to 373K, ϕ=0.75)

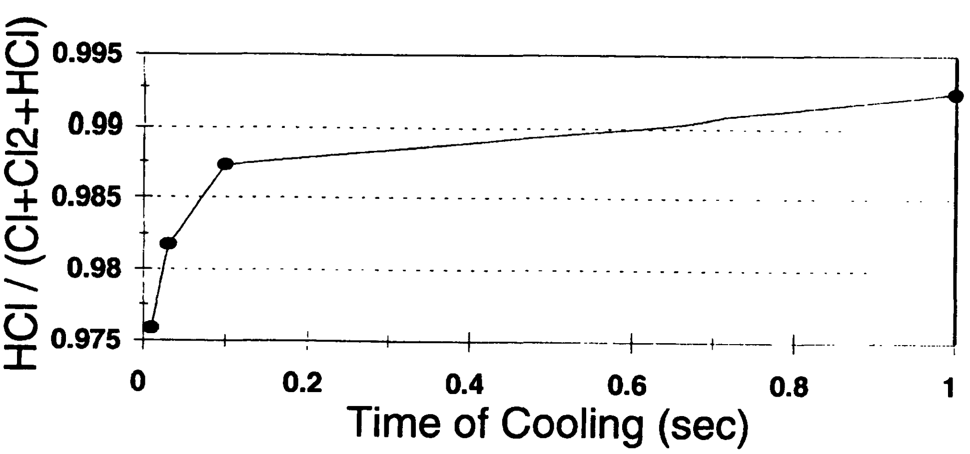


Figure 5.10. Molar ratio versus time of cooling ($HCl/(Cl+Cl_2+HCl)$)
(T is cooled down from 1800K to 373K, ϕ=0.75)

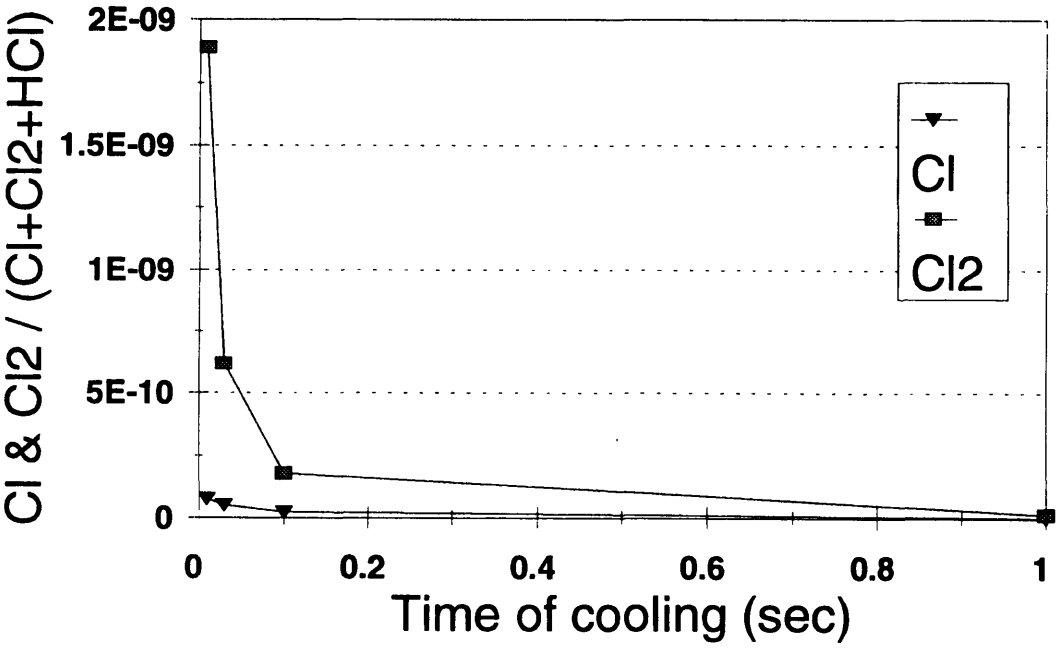


Figure 5.11. Molar ratio versus time of cooling (Cl & $Cl_2/(Cl+Cl_2+HCl)$)
(T is cooled down from 1800K to 373K, ϕ=3.0)

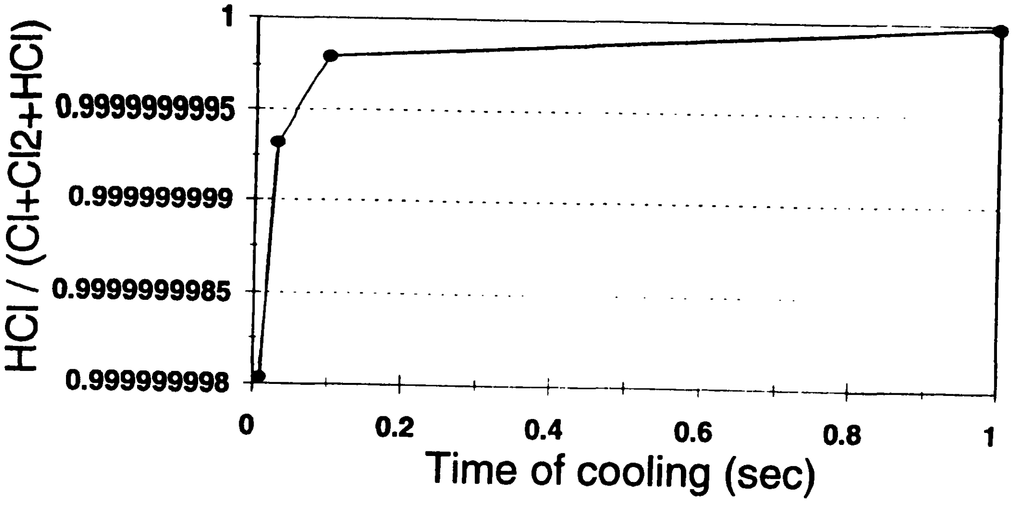


Figure 5.12. Molar ratio versus time of cooling ($HCl/(Cl+Cl_2+HCl)$)
(T is cooled down from 1800K to 373K, ϕ=3.0)

5.4. Effect of Steam (or Water) Injection

Effects of steam (or water) injection into the flue gas are carefully examined. The steam is injected at the same temperature as that of the flue gas at the equilibrium state. The steam (or water) injection causes the temperature drop of the flue gas. Heat is allowed to transfer through the reactor wall because the only way to inject steam in SENKIN model is injecting at the temperature of the flue gas. Since the extra O_2 is going to be injected in later stage, steam and the fixed amount of are injected together into the flue gas for the purpose of background calculation. Figure 5.13, 5.14 show that the comparison in $Cl/(Cl+Cl_2+HCl)$ and $Cl_2/(Cl+Cl_2+HCl)$ ratios for the case of; 1) no injection, 2) $O_2:H_2O(g) = 1:0$, 3) $O_2:H_2O(g) = 1:1$, 4) $O_2:H_2O(g) = 1:2$, 5) $O_2:H_2O(g) = 1:3$, 6) $O_2:H_2O(g) = 1:4$. The results show the more steam injected the less Cl and Cl_2 are founded. In Figure 5.15, the efficiencies in terms of CO/CO_2 ratios are plotted for the various amount of H2O(g) injections. For the case of water injection, since the models only deal with the homogeneous gas phase, the results are expected to be very similar to those of the case of steam injection by matching the cooling rate of the flue gas in both cases.

The work presented in this chapter is only for qualitative explanation of the starting point of staged combustion process concept, not to find any optimal equivalence ratio, temperature or cooling rate. Application of the above results will be presented in detail at the chapter 6 when the whole line of staged combustion process is discussed.

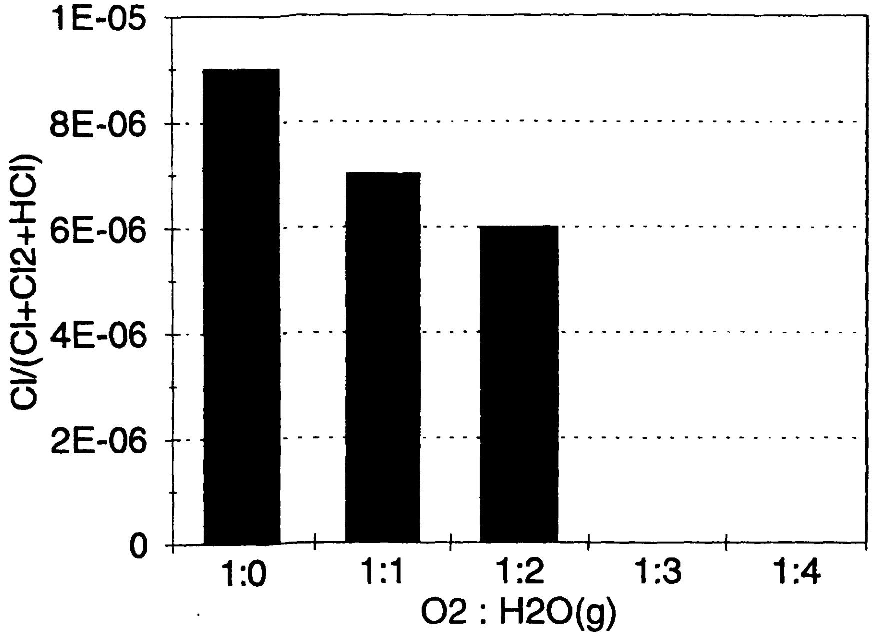


Figure 5.13. $Cl/(Cl+Cl_2+HCl)$ molar ratio versus (O2 injected:H2O(g) injected)

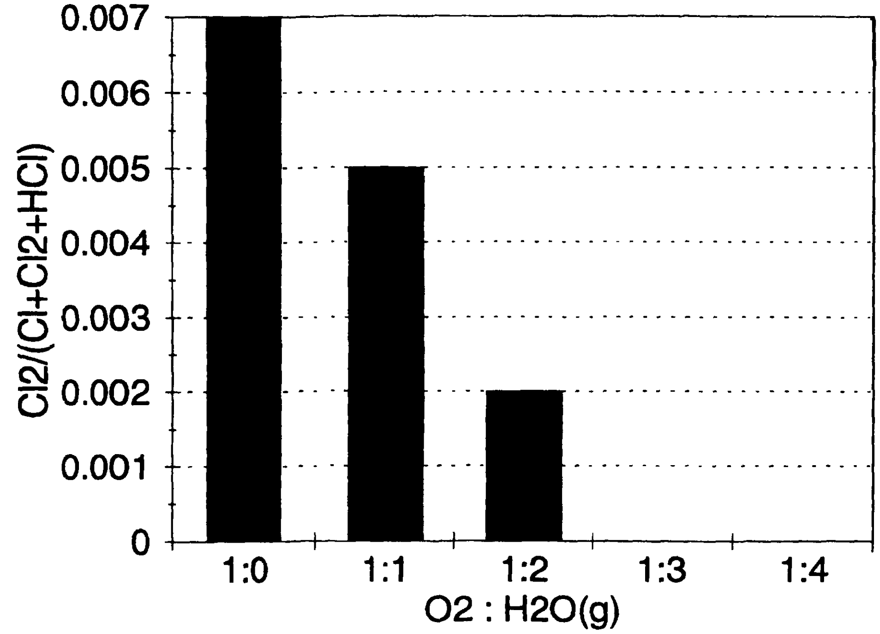


Figure 5.14. $Cl_2/(Cl+Cl_2+HCl)$ molar ratio versus (O2 injected:H2O(g) injected)

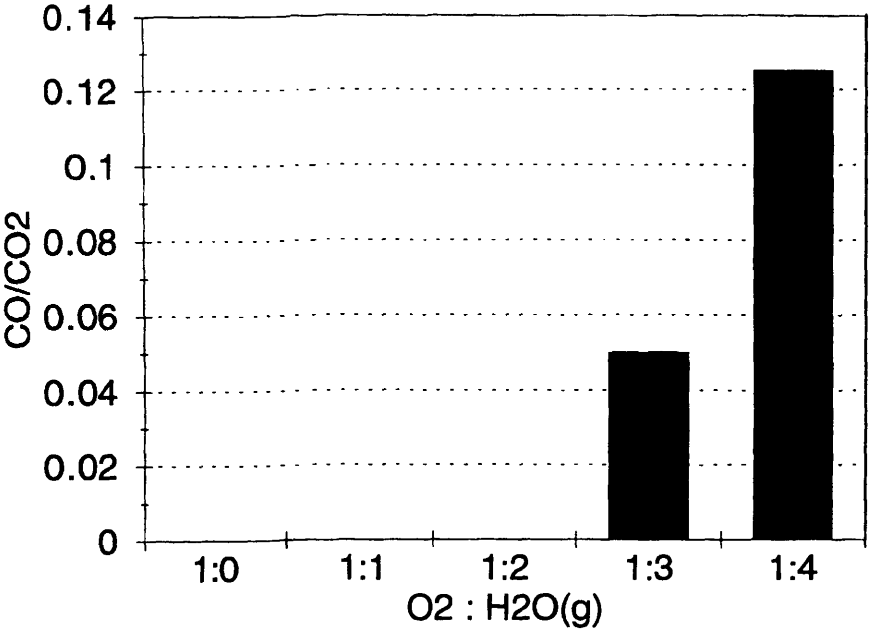


Figure 5.15. CO/CO$_2$ molar ratio versus (O2 injected:H2O(g) injected)

Chapter Six

6. Staged Combustion Process

Recalling the results discussed at the chapter 5, the staged combustion process in this work basically consists of stages as following; 1) burning of the rich fuel in the primary combustion chamber, 2) injection of steam into the flue gas in secondary combustion chamber, 3) cooling of the flue gas, 4) injection of the extra O_2 into the flue gas, 5) cooling of the flue gas to the exit gas temperature. The basic approach for this job should be finding the appropriate; 1) equilibrium ratio for the fuel in primary combustion chamber, 2) amount of steam which should be injected, 3) cooling rate of the flue gas, 4) temperature that the gas should be dropped to, in other words, the O2 injection temperature, 5) cooling rate of the flue gas to the temperature of exit gas. The final result is presented in the form of the temperature window that finds the optimal operating temperature in staged combustion chamber. Comparison of the results between the staged combustion and conventional combustion processes is presented at the end of this chapter.

6.1. First Stage

The first stage of the staged combustion process is the burning of the rich fuel in the primary combustion chamber. The basis for operating the primary chamber in fuel-rich condition is the result of the equilibrium calculation which is discussed in chapter 5. The abundant content of H radicals in fuel-rich condition successfully prevent the Cl atoms from reforming the Cl_2 molecules.

The ratios of Cl and Cl_2 over $Cl+Cl_2+HCl$ are calculated for adiabatic PSR, since previous work described in chapter 5 is for the equilibrium state only, at the conditions of; 1) various equivalence ratios, 2) gas inlet temperature of 400K, which is matched to that of experiment previously done at MIT, 3) residence time of 1.e-02 seconds, 4) Cl/C ratio of 0.1, and 5) reactor volume of 250 cm^3. The purpose of this work is to find the basis for choosing the right equivalence ratio for the first stage. Table 6.1 shows that the higher the equilibrium ratio, the lower the Cl and Cl_2 over $Cl+Cl_2+HCl$ ratio at this given condition.

Table 6.1. Cl and Cl_2 over $Cl+Cl_2+HCl$ ratio versus equivalence ratio

Equivalence Ratio	Cl	Cl_2	HCl	$Cl/(Cl+Cl_2+HCl)$	$Cl_2/(Cl+Cl_2+HCl)$
0.75	2.88E-07	9.78E-05	0.00968	2.9161934603E-05	0.019805813917695
1	1.29E-09	1.33E-07	0.0129	9.9997928027E-08	2.06197277948E-05
1.05	5.53E-13	5.74E-10	0.0134	4.1268653179E-11	8.56716344479E-08
1.1	6.92E-12	1.43E-10	0.0138	5.0144926472E-10	2.07246372413E-08
1.15	5.1E-12	6.28E-11	0.0143	3.5664335338E-10	8.78321670294E-09
1.2	3.52E-12	3.45E-11	0.0147	2.3945578113E-10	4.69387752786E-09
1.25	2.57E-12	2.16E-11	0.0151	1.7019867498E-10	2.86092714365E-09
1.3	1.97E-12	1.48E-11	0.0155	1.2709677393E-10	1.90967741547E-09
1.35	1.57E-12	1.08E-11	0.016	9.8124999858E-11	1.34999999805E-09
1.4	1.28E-12	8.1E-12	0.0163	7.8527607278E-11	9.93865029609E-10
1.45	1.07E-12	6.37E-12	0.0167	6.4071856234E-11	7.62874250866E-10
1.5	9.11E-13	5.15E-12	0.0171	5.3274853766E-11	6.02339180892E-10

Based on the above results, the equivalence ratio of the fuel gas is chosen as 1.1; 1) because of not much difference equivalence ratio of over 1.0, 2) to reduce the potential formation of PIC, 3) to match to feasible experimental condition, and 4) to prevent the reformation of Cl_2 caused by injection of too much amount of O_2 at once in later stage. Cl/C=0.2 is chosen to examine the advantage of staged combustion process on suppressing Cl_2 concentration in more severe condition.

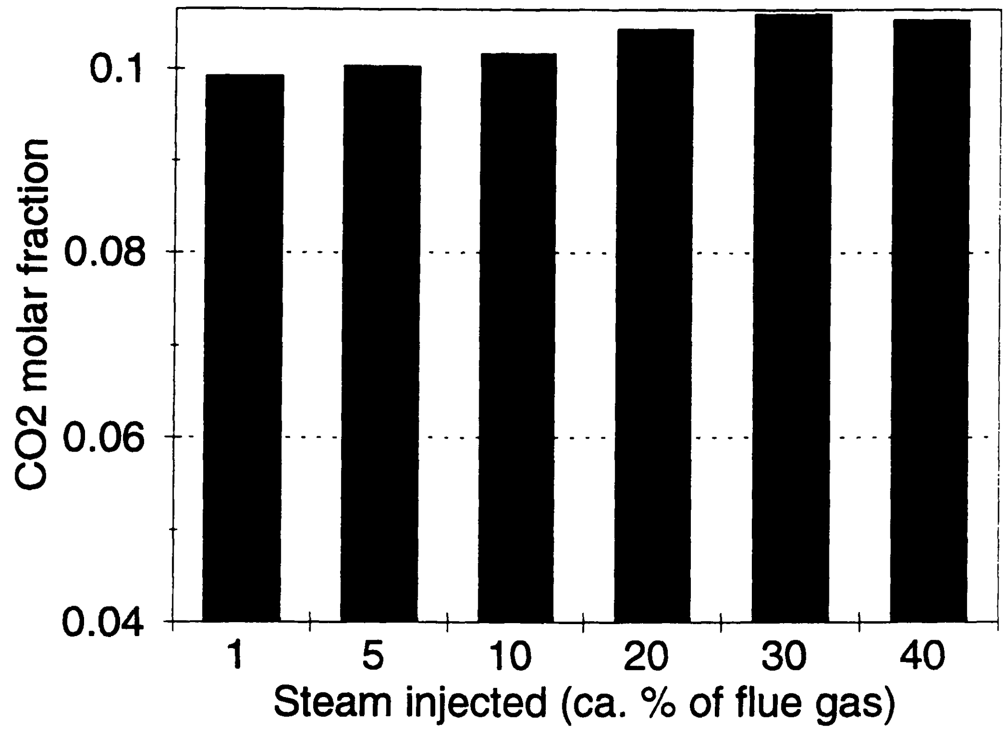


Figure 6.1. Molar fraction versus amount of steam injected (CO_2)

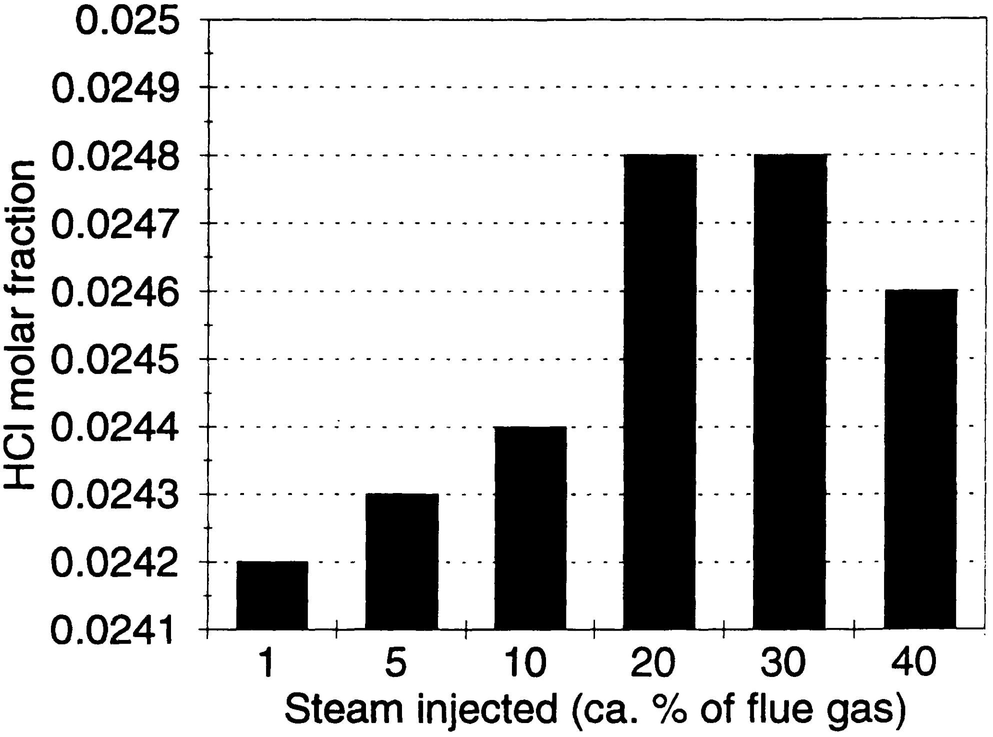


Figure 6.2. Molar fraction versus amount of steam injected (HCl)

6.2. Second Stage

The second stage is where the steam is injected into the flue gas out of PSR. The steam injection causes the flue gas temperature drop to that of extra O_2 injection. The amount of steam to be injected is carefully examined by comparing the molar fraction of CO_2 and HCl for the various amount of injected steam (Figure 6.1 and 6.2). The steam is injected at the temperature of 2387.5K, the temperature of flue gas coming out of PSR with residence time of 1.e-02 seconds. After the steam is injected residence time is 1.5e-02 seconds. The values 1, 5, 10, 20, 30, 40 of x-axis are, respectively, 1%, 5%, 10%, 20%, 30%, 40% of mass of the initial fuel gas. Both figures show that when the steam is injected in the amount of 30% of the mass of the initial fuel gas, the best results are expected. The temperature drop of the flue gas is expected to occur by; 1) steam injection, and 2) the heat transfer through the wall from the flue gas to the cooling water (283.15K). The final temperature of the second stage is discussed in next section because it should be decided for the optimal O_2 injection.

6.3. Third and Fourth Stages

The extra O_2 injection occurs at the third stage in the form of air. Finding the optimal temperature for the O_2 injection is important because at that temperature, the O_2 injection should; 1) prevent the reformation of Cl_2 molecules, 2) increase the efficiency of the incinerator by increasing the $CO_2/(CO+CO_2)$ ratio. The appropriate method for finding of this optimal O_2 injection temperature is development of "temperature window". At previously described condition, various temperatures within the range of 1000K to 2000K are examined to be the optimal O_2 injection temperature. With those candidate temperatures, the rest of the stages should be followed before any optimal O_2 injection temperature is selected. Though the temperatures between 1000K and 2000K with 50K interval were examined, the result from chapter 5 indicate that the O_2 injection temperature should be within the range of $1000K < T < 1500K$. The injection amount of

O_2 and N_2 (since the O_2 is injected in forms of air) to make the flue gas fuel-lean (ϕ =0.75) for the case of initial equivalence ratio of 1.1 are 0.0606 and 0.228, respectively in terms of molar fraction. The temperature window will be presented later in this chapter. The third stage has the residence time of 1.5e-02 seconds. The temperature is constant. The reformation of Cl_2 occurs here at the various extent according to the temperature. However, the remaining PICs are burned and the $CO_2/(CO+CO_2)$ ratio, which indicates the efficiency of the incinerator, increases throughout the third and fourth stages. Figure 6.3 shows that the CO2/(CO+CO2) ratio at both before and after the O_2 injection.

The fourth stage is where the flue gas is burned for 1.5e-02 seconds. In this stage, the phenomena occurred in third stage continue.

6.4. Final Stage

In the final stage, the temperature of the flue gas is dropped to the approximate exit gas temperature (400K). The residence time is 1 second. The major concern here is the reformation of Cl_2 molecules from the Cl atoms. The equivalence ratio is already changed from 1.1 to 0.75 at the third stage by injecting the extra O_2. As discussed in Section 5.1, when the fuel-lean gas is cooled down, the Cl atoms reform Cl_2 molecules. Furthermore, even the existing HCl provides the Cl atoms to be used in the reformation of Cl_2. Temperature window for the optimal O_2 injection in staged combustion process for the case of 30% steam injection is presented in Figure 6.3. Figure 6.4 and 6.5 are the temperature windows for the case of 10%, 20% steam injection. Figure 6.3, 6.4, 6.5 indicate the optimal O_2 injection temperature for all three cases in terms of both $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratios should be within the range of $1100K < T < 1200K$. However, a different O_2 injection temperature can be chosen according to which specific species should be produced considerably less than the other. Also, after the staged combustion process, the $CO/(CO+CO_2)$ ratio (indicator of incinerator efficiency) can be decreased even at the 400K by using catalyst or any other post process treatment. Actually, the main reason for using staged combustion process is suppressing Cl_2 to prevent the potential formation of dioxin in gas phase, it is recommended to choose 1000K, which is the optimal O_2 injection temperature in suppressing the Cl_2.

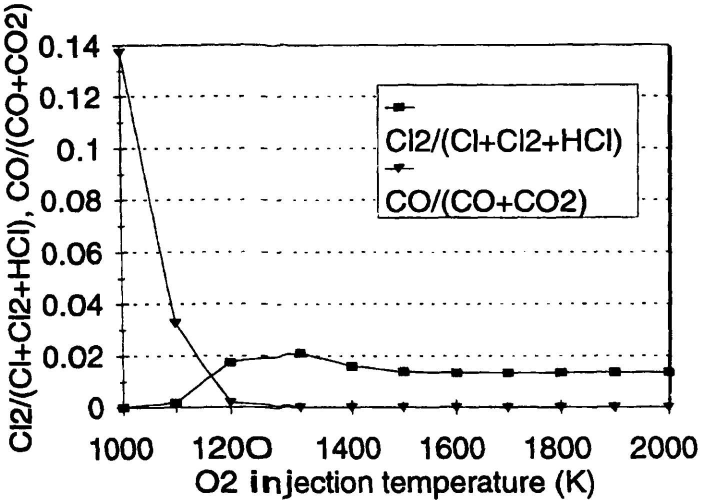


Figure 6.3. $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratio versus O_2 injection temperature (H_2O 10%)

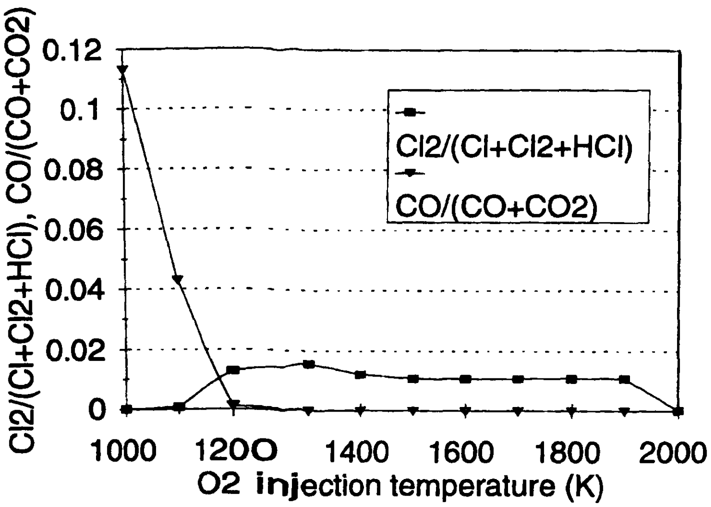


Figure 6.4. $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratio versus O_2 injection temperature (H_2O 20%)

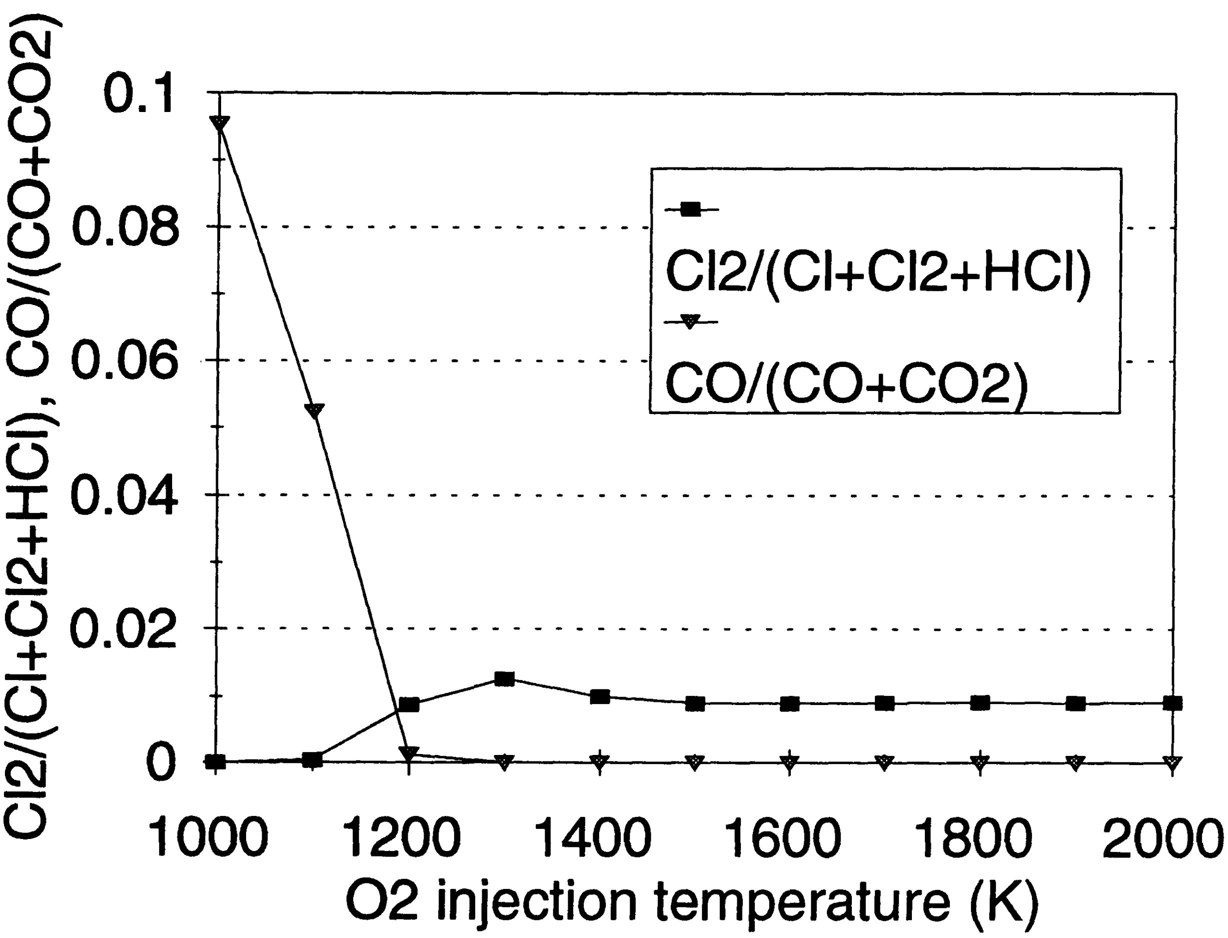


Figure 6.5. $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratio versus O_2 injection temperature (H_2O 30%)

6.5. Comparison with Conventional Process

Table 6.2, 6.3, 6.4 show the $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratios at various O_2 injection temperatures for the case of steam injection of 10%, 20%, 30% of mass of initial flue gas, respectively. The same ratios of the simulated conventional incineration process are shown in all three tables. The fuel injected into the PSR is equivalence ratio of 0.75 and temperature of 400K. The residence time is 2.e-02 seconds. The temperature of gas coming out of PSR is 2091.4K. Then this gas is burned at SENKIN for the residence time of 4.e-02 seconds. During 1 second, the flue gas is finally cooled down to 400K. The residence times at PSR, SENKIN, quenching process are matched to those of staged combustion process previously discussed throughout the chapter 6.

Table 6.2. $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratio versus O_2 injection temperature (H_2O=10%)

H_2O (ca. 10%)	$Cl_2/(Cl+Cl_2+HCl)$	$CO/(CO+CO_2)$
1000	8.21427896684E-07	0.1372093023
1100	0.001761597181248	0.0327054201
1200	0.017543603163696	0.0019729783
1300	0.021206868928150	0.0001408578
1400	0.016162789744359	8.913215E-06
1500	0.013852805721444	3.549120E-06
1600	0.013541696459372	3.429549E-06
1700	0.013541696459372	3.510380E-06
1800	0.013656840939240	3.579664E-06
1900	0.013771958541736	3.660495E-06
2000	0.013737005614561	3.695136E-06
Conventional Process	0.021029426694319	7.290335E-06

Table 6.3. $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratio versus O_2 injection temperature (H_2O=20%)

H_2O (ca. 20%)	$Cl_2/(Cl+Cl_2+HCl)$	$CO/(CO+CO_2)$
1000	2.23684160492E-07	0.1130591724
1100	0.000709174134458	0.0429212044
1200	0.012903017693263	0.0012608921
1300	0.015671291424501	5.792503E-05
1400	0.012138225985359	4.181568E-06
1500	0.010733040825642	2.442449E-06
1600	0.010674122932051	2.429662E-06
1700	0.010733033885998	2.493600E-06
1800	0.010860943078961	2.544751E-06
1900	0.010791179752150	2.583114E-06
2000	0.000109789856986	2.618129E-06
Conventional Process	0.021029426694319	7.290335E-06

Table 6.4. $Cl_2/(Cl+Cl_2+HCl)$ and $CO/(CO+CO_2)$ ratio versus O_2 injection temperature (H_2O=30%)

H_2O (ca. 30%)	$Cl_2/(Cl+Cl_2+HCl)$	$CO/(CO+CO_2)$
1000	8.99999919000E-08	0.0953924193
1100	0.000354484225441	0.0523516237
1200	0.008779227215604	0.0011971665
1300	0.012554440780773	3.664201E-05
1400	0.010040827986475	2.887021E-06
1500	0.009059855919979	1.944052E-06
1600	0.009059849507406	1.966523E-06
1700	0.009135455616794	2.008364E-06
1800	0.009200107287405	2.055940E-06
1900	0.009135449197064	2.081001E-06
2000	0.009200100776489	2.122901E-06
Conventional Process	0.021029426694319	7.290335E-06

Table 6.2, 6.3, 6.4 are the data for the plots presented in Figure 6.3, 6.4, 6.5. If the sole purpose of the staged combustion process is suppressing the Cl_2, which is true for most cases, O_2 injection temperature of 1000K should be chosen for all three cases (10%, 20%, 30% of steam injection). In that cases, the advantage over employing conventional combustion process in Cl_2 reductions are 99.9961(%), 99.9989(%), 99.9996(%), which are very impressive results. The possibly unburned species can be treated by using catalysts or any other appropriate method. Since the main purpose of employing staged combustion process for this work is preventing the formation of Cl_2 and dioxin, the practical use of this process is very promising despite of need in improving the $CO/(CO+CO_2)$ ratio.

Chapter Seven

7. Summary and Conclusions

Results from the Rayleigh scattering diagnostics have indicated the existence of mixing constraints in the PFR. When CH_3Cl is injected near the inlet of the PFR such that it is not completely mixed with the baseline flow of hot products from the TJSC, products of incomplete combustion are formed that clearly indicate mixing controlled PIC formation. These products include aromatics, chlorinated aromatics, and higher molecular weight species which are formed under pyrolytic conditions. Detection of these species can be used as a diagnosis of mixing failure in the PFR. Also, PDFs generated by Rayleigh scattering diagnostics in cold flow experiments provide the evolution of turbulent mixing in the PFR and can be used as the basis for construction of the PDF of the equivalence ratio of a flue gas in the PFR. After getting the right PDF, prediction of products spectrum from PFR can be possible. Numerical modeling was applied to simulate various failure modes keeping perfect mixing conditions in the PFR. The results can be compared to those of the PFR, and any difference between the PFR and the numerical modeling can be interpreted as mixing failure, since the only difference in operating conditions is the degree of mixing. The methodology used in the prediction of products spectrum for the PFR can be applied to any selected incinerator by investigating the evolution of turbulent mixing for that particular system. One can diagnose any problem, which eventually causes the formation of PICs, in the Hazardous Waste Incinerators by relating the selected PICs and a specific failure mode; not only the mixing failure mode but also every possible failure mode. To reach this point, it is necessary to perform as many experiments as possible at off optimal conditions. The current work introduced in this paper can be very useful in terms of saving money and time and also minimizing the PICs in hazardous waste incinerators.

Chapter 2 presents the background of numerical modeling of experimental facility at MIT, which again the pilot scale device of real incinerator. The primary chamber was modeled using PSR FORTRAN model and the secondary combustion chamber was modeled by SENKIN FORTRAN model. The background theory of both models were presented with their basic equations. The sample of input file for PSR model was introduced and the necessary keywords were also described.

In chapter 3, the results of application of models were discussed. The cooling rate has great effect on the extent of formation of certain species. The slower the cooling rate the less the formation. Since the degree of temperature drop was constant, it is believed that the reason for this result is because of longer residence time. General assumption about the residence time was proved to be right, which is the longer the residence time the better the combustion. Also, in terms of temperature, as the temperature increases more CH_3Cl reacted away. The work described in chapter 4 were intended to suggest various usage of the models (PSR and SENKIN). Since the models can be used with any kind of chemical kinetic mechanisms, the potential in using these models are unlimited.

In chapter 4, another chemical mechanism which includes pure hydrocarbon aromatics was introduced. There are 18 of reactions for the benzene. A brief discussion of experimental work were presented. As discussed above in this chapter, the plots of Rayleigh scattering measurements clearly indicate the evidence of mixing failure in plug flow reactor. Stable species concentration measurements show the results that there are certain species only can be found in fuel-rich case or condition with mixing constraints. Based on the results of experimental work, the failure diagnosis theory was introduced. Although the failure in the waste incinerator can be caused by many reason, this research is limited for the failure mode caused by mixing problem. The failure diagnosis was developed by employing two method; 1) detection of particular species, 2) comparison of the selected molar ratios of species. The detection of CH_3Cl in operating the incinerator at fuel-lean condition, which is common for real waste incinerators, indicates that there is a mixing failure in the reactor. In that case, CH_3Cl is believed to slip off the cold reactor wall being not reacted with other species. Also, detection of benzene indicates the existence of localized fuel-rich pockets. Several plots of selected molar ratios of species were presented so that the same ratios can be compared. Since the ratios show strong non-linear behavior over equivalence ratio, especially between fuel-lean and fuel-rich condition, any mixing failure can be detected by locating their points on the plots presented. Although the prediction method was not validated. The theory of prediction method gives a promising future in practical use. Using the Rayleigh scattering measurements, the averaged character of mixing in certain incinerator can be found in forms of PDF. Based on the PDF, the final concentration of species of interest can be predicted.

In chapter 5 and 6, staged combustion process was discussed. The motivation of developing staged combustion process was to suppress the Cl_2 concentration, since the Cl_2 eventually forms dioxin in gas phase. Chemistry suggests the fuel-rich condition at the primary combustion chamber and extra O_2 injection at lower temperature. The Cl_2 concentration is considerably less in fuel-rich condition than in fuel-lean condition, when the flue gas is cooled down. In fuel-lean condition, Cl_2 concentration increases as the temperature drops. Examination of cooling rate suggests slow rate of cooling for suppressing Cl_2. However, for the purpose of matching the conditions to those of experimental work, order of magnitude of cooling time were 1.e-02 seconds. Steam injection was proved to have a great effect on suppressing Cl_2. The first stage of the staged combustion process is where the initial fuel is injected into the PSR at fuel-rich condition. As the chemistry discussed above indicates, abundant H radicals in starved-air fuel prevent the Cl atoms from forming the Cl_2, especially when the flue gas is cooled down in second stage. The cooling of the flue gas is performed by injecting steam into the flue gas and allowing the heat to be transferred through the reactor wall. The steam injection has a great effect on suppressing Cl_2. The final temperature of flue gas coming out of second stage is the optimal O_2 injection temperature. The O_2 is injected to change the condition of the flue gas from fuel-rich to fuel-lean throughout the third and fourth stages. The results show that for the cases of steam injection of 10%, 20% and 30% of mass of the initial flue gas, the O_2 injection temperature should be in the range of $1100K < T < 1200K$ in terms of suppressing Cl_2 reformation and increasing $CO/(CO+CO_2)$ ratio. However, recalling the fact that the main reason of applying staged combustion process is keeping the Cl_2 concentration at its lowest point possible, the optimal O_2 injection temperature should be near 1000K. In these cases, the advantage of using staged combustion process in terms of reducing Cl_2 over conventional combustion process are all over 99.9%. Although more research should be done for the increase of incinerator efficiency, by increasing the $CO/(CO+CO_2)$, the practical use of the staged combustion process are very promising in terms of suppressing Cl_2. And these lead to some of the suggestions on the future research.

Recommendation

Finally, I would like to make a few recommendations to anyone interested in continuing this research or pursuing similar research.

First, more vigorous work should be done for the failure diagnosis. The more data is available, the more accurate failure diagnosis. Development of failure diagnosis for not only mixing but also temperature, residence time and other parameters and their interactions. In terms of using the numerical models, complete and reliable chemical kinetic mechanism should be developed especially for the aromatic compounds. The validations of failure diagnosis and the prediction theory by applying to the results of experiments are recommended. The prediction theory needs more accurate and efficient way to characterize the mixing behavior of the incinerator interested. Although the temperature PDF (Probability Density Function) from Rayleigh scattering measurement can be a good starting point, more reliable relation between temperature PDF and equivalence ratio PDF should be evaluated.

Second, for the staged combustion process, effect of the steam injection on formation of other PICs should be examined more. Also, finding the way of increasing the incinerator efficiency is recommended. Conversion of CO to CO_2 by catalysts may be one of the answers.

References

Baldyaga, J. and Bourne, J.R., A fluid-mechanical approach to turbulent mixing and chemical reaction. Part I. Inadequacies of available methods. Chem. Eng. Commun., vol. 28, pp. 231-241, 1984a.

Baldyaga, J. and Bourne, J.R., Afluid-mechanical approach to turbulent mixing and chemical reaction. Part II. Micro-mixing in light of turbulence theory. Chem. Eng. Commun., vol. 28, pp. 243-258, 1984b.

Barat, R.B., Characterization of the Mixing/Chemistry Interaction in a Toroidal Jet Stirred Combustor, Ph.D. Thesis, Department of Chemical Engineering, Massachusetts Institute of Technology, Prof. A.F. Sarofim, advisor, 1990.

Barat, R.B., Sarofim A.F., Longwell, J.P., and Bozzelli, J.W., Inhibition of Fuel Lean Ethylene/Air Flame in a Jet Stirred Combustor by Methyl Chloride: Experimental and Mechanistic Analyses. Combustion Science and Technology, vol. 74, pp. 361-378, 1990.

Barat, R.B., Smith, S.P., Sarofim, A.F., Longwell, J.P., and Bar-Ziv, E., Laser Rayleigh Scattering for Flame Thermometry in a Toroidal Jet Stirred Combustor, Applied Optics, vol. 30, no. 12, pp. 3003-3010, July 20, 1991.

Batchelor, G.K., Small-scale variation of convected quantities like temperature on turbulent fluid. Part 1. General discussion and the case of small conductivity. J. Fluid Mechanics, vol. 5, pp. 113-133, 1959.

Benson, S.W., Thermochemical Kinetics, Second Edition, J.Wiley and Sons, New York, 1976

Bird, R.B., Stewart, W.E., and Lightfoot, E.N., Transport Phenomena, John Wiley and Sons, 1960.

Bose, D., and Senkan, S.M., Combustion Science and Technology, Vol. 35, p. 187, 1983

Broadwell, J.E., and Breidenthal, R.E., A simple model of mixing and chemical reaction in a turbulent shear layer. J. Fluid Mechanics, vol. 125, pp. 397-410, 1982.

Broadwell, J.E., and Mungal, M.G., Molecular mixing and chemical reactions in turbulent shear layers. 22nd Symp. (Intl.) on Combustion, The Combustion Institute, pp. 579-587, 1988.

Brouwer, J., Longwell, J.P., Sarofim, A.F., Barat, R.B., and Bozzelli, J.W., Chlorocarbon-Induced Incomplete Combustion in a Jet-Stirred Reactor, Combustion Science and Technology, vol. 85, no. 1-6, p. 87, 1992.

Brouwer, J., The Effects of Chlorine Chemistry and Mixing on Combustion Efficiency and Temperature: Implications for Products of Incomplete Combustion, PH.D. Thesis, MIT Department of Mechanical Engineering, Professor A.F. Sarofim, advisor, 1993.

Caracotsios, M., and Stewart, W.E., Sensitivity analysis of initial value problems including ODE's and algebraic equations, Computers and Chemical Engineering, Vol. 9, No. 4, pp. 359-365, 1985.

Chang, W.D., and Senkan, S.M., (1989). Detailed Chemical Kinetic Modeling of Fuel Rich C_2HCl_3/Ar Flames, Environmental Science and Technology, vol. 23, no. 4, pp. 442-450, 1989.

Chomiak, J., Combustion: A study in Theory, Fact and Application, Abacus Press, Gordon and Breach Science Publishers, New York, 1990.

Curl, R.L., Dispersed phase mixing. I: Theory and effects in simple reactors, AIChE Journal, vol. 9, pp. 175-181, 1963.

Dean, A.M., Prediction of Pressure and Temperature Effects Upon Radical Addition and Recombination Reactions, J. Physical Chemistry, vol. 89, p. 4600, 1985.

Evangelista, J.J., Skinnar, R., and Katz, S., The effect of imperfect mixing on stirred combustion reactors, 12th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, p. 901, 1968.

Fisher, E.M., and Koshland, C.P., Numerical simulation of the thermal destruction of some chlorinated C_1 and C_2 hydrocarbons, J. Air and Waste Management Assoc., vol. 40, no. 10, p. 1384, 1990.

Fisher, E.M., Koshland, C.P., Hall, M.J., Sawyer, R.F., and Lucas, D., Experimental and numerical study of the thermal destruction of C_2H_5Cl, 23rd Symposium (International) on Combustion, The Combustion Institute, pp. 895-901, 1990.

Flagan, R.C., and Appleton, J.P., A stochastic model of turbulent mixing with chemical reaction: Nitric oxide formation in a plug-flow burner, Massachusetts Institute of Technology, Fluid Mechanics Laboratory, Publication No. 73-10, 1973.

Glarborg, P., Kee, R.J., Grcar, J.F., and Miller, J.A., PSR: A FORTRAN program for modeling well-stirred reactors, Sandia National Laboratories, Livermore, CA, Sandia Report SAND86-8209, 1991.

Glarborg, P., Kee, R.J., Grcar, J.F., and Miller, J.A., PSR: A FORTRAN program for Modeling Well-Stirred Reactors, Sandia National Laboratories, Albuquerque, NM, Sandia Report SAND86-8209, 1986.

Hesketh, R.P., and Davidson, J.F., Combustion of Methane and Propane in an Incipiently Fluidized Bed, Combustion and Flame, vol. 85, pp. 449-467, 1991.

Hinze, J.O., Turbulence, 2nd edition, McGraw-Hill, 1975.

Ho, W.P., Barat, R.B., and Bozzelli, J.W., Thermal reactions of CH_2Cl_2 in H_2/O_2 mixtures: Implications for chlorine inhibition of CO conversion to CO_2. Combustion and Flames, vol. 88, pp. 265-295, 1992.

Johnson, C., Numerical Solution of Partial Differential Equations by the Finite Element Method, Cambridge University Press, Cambridge, 1987.

Karra, S.B., Gutman, D., and Senkan, S.M., A detailed chemical kinetic mechanism for the oxidative pyrolysis of CH_3Cl, Combustion Science and Technology, vol. 60, pp. 45-62, 1988.

Kee, R.J., Rupley, F.M., and Miller, J.A., CHEMKIN-II: A FORTRAN chemical kinetics package for the analysis of gas phase chemical kinetics, Sandia National Laboratories, Livermore, CA, Sandia Report SAND89-8009, 1991.

Koshland, C.P., Lee, S., and Lucas, D., Enhanced destruction of CH3Cl in Postflame combustion gases, Combustion and Flame, vol. 92, pp. 106-114, 1993.

Kridiotis, A.C., The Effect of Imperfect Micromixing on Chemical Reaction in the CO/H2-Air System, Ph.D. Thesis, MIT Department of Chemical Engineering, Professor J.P. Longwell, advisor, 1986.

Lee, K.C., Hansen, J.L., and Macauley, D.C., Predictive model of the time-temperature requirements for thermal destruction of dilute organic vapors, presented at 72nd Annual Meeting of APCA, Cincinnati, 1979.

Lee, K.C., Morgan, N., Hansen, J.L., and Whipple, G.M., Revised model for the prediction of time-temperature requirements for thermal destruction of dilute organic vapors and its usage for predicting compound destructability, presented at 75th Annual Meeting of APCA, New Orleans, 1982.

Lutz, A.E., Kee, R.J., and Miller, J.A., SENKIN: A FORTRAN Program for Predicting Homogeneous Gas Phase Chemical Kinetics with Sensitivity Analysis, Sandia National Laboratories, Albuqurque, NM, Sandia Report SAND87-8248, 1987.

Lyon, R. 23rd Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, p. 903, 1990.

Lyon, R., Apparatus and method for incineration for toxic organic compound, U.S. Patent 4,974,530.

Marr, J.A., PAH Chemistry in a Jet-Stirred/Plug Flow Reactor System, Ph.D. Thesis, MIT Department of Chemical Engineering, Professor J.B. Howard, advisor, 1993.

McMurtry, P.A., and Givi, P., Direct numerical simulations of mixing and reaction in a non-premixed homogeneous turbulent flow. Combustion and Flame, vol. 77, pp. 171-185, 1989.

Nenniger, J.E., Kridiotis, A., Chomiak, J., Longwell, J.P., and Sarofim, A.F., Characterization of a Toroidal Well Stirred Reactor. 20th Symposium (International) on Combustion, The Combustion Institute, p. 473, 1984.

Petzold, L.R., A description of DASSL: a differential/algebraic syatem solver, Sandia National Laboratories, Sandia Report SAND82-8637, 1982.

Pope, S.B., PDF methods for turbulent reactive flows. Prog. Energy Combustion Sci., vol. 11, pp. 119-192, 1985.

Pratt, D.T., Mixing and chemical reaction in continuous combustion. Prog. Energy Combustion Sci., vol. 1, pp. 73-86, 1976.

Reynolds, W.C., The element potential method for chemical equilibrium analysis: Implementation in the interactive program STANJAN, Department of Mechanical Engineering, Stanford University, 1986.

Ritter, E., and Bozzelli, J.W., (1989). THERM: Thermodynamic Property Estimation Computer Code for Use with Detailed Kinetic Mechanisms. Central States Meeting of the Combustion Institute, Dearborn, MI, May 1989.

Russel, J., Seetula, J., Gutman, D., Senkan, S.M., and Melius, C.F., Experimental and Theoretical Study of the Kinetics and Thermochemistry of Chlorinated Methyl Radicals with Molecular Oxygen. 2nd International Conference on Chemical Kinetics, National Institute of Standards and Technology, Gaithersburg, MD, July 24-27, 1989.

Senkan, S.M., Detailed chemical kinetic modeling: Chemical reaction engineering of the future, Advances in Chemical Engineering, vol. 18, p. 95, 1992.

Taylor, P.H., and Dellinger, B., Development of thermal stability based index of hazardous waste incinerability, Incineration Research Branch, US-EPA (HWERL), Dr. C.C. Lee, program manager, 1988.

Taylor, P.H., and Dellinger, B., and Lee, C.C., Development of thermal stability based ranking of hazardous organic compound incinerability, Environmental Science and Technology, vol. 22, p. 438, 1988.

Tennekes, H., and Lumley, J.L., A First Course in Turbulence, Massachusetts Institute of Technology Press, 1972.

Tirey, D.A., Taylor, P.H., Kasner, J., and Dellinger, B., Gas phase formation of chlorinated aromatic compounds from the pyrolysis of tetrachloroethylene, Combustion Science and Technology, 1990.

Tsang, W., Mechanisms for the formation and destruction of chlorinated organic products of incomplete combustion, Combustion Science and Technolgy, vol. 74, pp. 99-116, 1990.

Tsang, W., Waste Management, vol. 10, pp. 217-225, 1990.

Vaughn, C.B., Sun, W.H., Howard, J.B., and Longwell, J.P., Measurement and Modeling of Light Hydrocarbons in Rich C2H4 Combustion in a Jet-Stirred Reactor, Combustion and Flame, vol. 84, pp. 38-46, 1991.

Wetbrook, C.K., Inhibition of hydrocarbon oxidation in laminar flames and detonations by halogenated compounds, 19th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, p. 127, 1982.

Westmoreland, P.R., Howard, J.B., Longwell, J.P., and Dean A.M., Prediction of Rate Constants for Combustion and Pyrolysis Reactions by Bimolecular QRRK. AIChE Journal., vol. 32, no. 12, 1986.

Williams, G.C., Hottel, H.C., and Morgan, A.C., The combustion of methane in a jet-mixed reactor, 12th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, p. 913, 1968.

Williams, F.A., Combustion Theory, Second Edition, Benjamin/Cummings Press, 1985.

Appendix A

The post-SENKIN program named SENOUT is presented here for those who want to perform a sensitivity analysis. Sensitivity analysis is very helpful understanding the chemical kinetics. The actual sensitivity analysis can be done by placing keyword SENS at the top of the SENKIN input file. After running SENKIN, the sensitivity data will be written under the file name SAVE in binary form. Program SENOUT will open the SAVE file and transfer the data to the readable form which the user desires.

PROGRAM SENSOUT

```
c-------------------------------------------------------------------
c  Post-plotting for SENKIN calculations with CHEMKIN II subroutines.
c  Keyword input to select plots of temperature, pressure,
c  mole fractions, production rates, heat release rates,
c  degree of disequilibrium, entropy production, and
c  normalized sensitivity coefficients. Program is based on
c  code from Sandia of the same name.
c  Originally developed at MIT by Thomas J. Mckinnon
c  notes:
c  mv   = no. species + 1  = kk + 1
c  mpar  = no. reactions + 1 = ii + 1
c  mpars = ii  (if sensitivity coefficients exist)
c  mt   = max. no. time datasets to be used in plot
c  mdim2 = max (mv, mpar)
c
c  array structure:
c  s(k,j) = mass fraction of k-th species at j-th time
c  sensj(k,i) = sensitivity coefficient of k-th species
c            to the l-th reaction pre-exponential
c  other arrays are work arrays
c
c-------------------------------------------------------------------
      IMPLICIT INTEGER*4 (I-N)
      IMPLICIT DOUBLE PRECISION (A-H,O-Z)
c-------------------------------------------------------------------
      PARAMETER (MT=100,MV=70,MDIM2=301,MPAR=301,MPARS=300)
      DIMENSION  SENS(MV,MPARS,MT)
      DIMENSION  TIM(MT), YMF(MDIM2,MT), XMF(MT,MDIM2), XT(MV),
     1        T(MT), P(MT), H(MV), WT(MV),
     2        RA(MPAR), RE(MPAR), RB(MPAR),
     3        SUMRT(MT), CIK(MPAR),
     4        QF(MPAR), Q(MPAR), QR(MPAR),
     5        LWANT(10),
     6        IWMOLS(MV), IWCONT(MV), IWSENS(MV), IWCI(20),
```

```
     7    SENSJ(MV,MPARS), SENT(MT,MPARS)
      REAL*4 XPLOT(MT),YPLOT(MT,MDIM2),YMN(MDIM2),YMX(MDIM2)
      REAL*4 CI(20),YMIN,YMAX,YCUT,YMXMN,YMNMX,CUTOFF(10)
      REAL*4 YMXK,YMNK
      DIMENSION IEXMA(MDIM2)
c-----------------------------------------------------------------
      PARAMETER (LENIWK=10000,LENWK=10000)
      COMMON /WRK/ IWORK(LENIWK),WORK(LENWK)
c-----------------------------------------------------------------
      PARAMETER (LENCWK=100)
      CHARACTER CWORK(LENCWK)*16
c-----------------------------------------------------------------
      CHARACTER*30 FILNAM
      CHARACTER*16 CHEM
      CHARACTER*40 REAC,NAME(MDIM2)
      LOGICAL LWANT, LSENS, IPLOT(MDIM2), LTSENS, KERR
c-----------------------------------------------------------------
      COMMON /SPECNAM/ CHEM(MV),REAC(MPARS)
c-----------------------------------------------------------------
      DATA LINKCK/15/, LOUT/6/, LSAVE/16/, LIN/5/
      DATA JJ/0/
      DATA LTSENS /.FALSE./
      DATA (LWANT(I),I=1,10) /10* .FALSE./
      DATA (IPLOT(I),I=1,MDIM2) /301* .TRUE./
      DATA TIMMAX, TIMMIN /2* 0./
      DATA KERR /.FALSE./
c-----------------------------------------------------------------
      NTIM = MT
C
C  READ IN DATA FROM INTERPRETER
      OPEN(UNIT=LINKCK,STATUS='OLD',FORM='UNFORMATTED',FILE='cklink')
C
C  WRITE HEADER
      WRITE(LOUT,*) ' '
      WRITE(LOUT,*) ' '
      WRITE(LOUT,'(A30)') 'SENKIN Post-Plotting Routine '
      WRITE(LOUT,*) ' '
      WRITE(LOUT,*) ' '
C
C  GET SENKIN RECORD FILENAME
      WRITE(LOUT,1000)
1000  FORMAT(2X,'Enter binary filename (def: save:)',$)
      READ(LIN,'(A)') FILNAM
      IF (FILNAM .EQ. ' ') FILNAM = 'save'
      FILNAM = 'save'
      OPEN(UNIT=LSAVE,FILE=FILNAM,STATUS='OLD',FORM='UNFORMATTED',
     1   ERR=10)
      WRITE(LOUT,'(2X,A,A)') 'Reading file ', FILNAM
      WRITE(LOUT,*) ' '
      GO TO 15
10    CONTINUE
      WRITE(LOUT,'(2X,A,A)') 'Stop, cannot open file ', FILNAM
      STOP
15    CONTINUE
```

```
C
C   SETUP CHEMKIN
      CALL CKINIT(LENIWK,LENWK,LENCWK,LINKCK,LOUT,IWORK,
      1         WORK,CWORK)
      CALL CKINDX(IWORK,WORK,MM,KK,II,NFIT)
      CALL CKRP(IWORK,WORK,RU,RUC,PATM)
      CALL CKABE(IWORK,WORK,RA,RB,RE)
      CALL CKWT(IWORK,WORK,WT)
C
C
C   CHECK FOR DIMENSIONING ERRORS
      IF ((KK+1).GT.MV) THEN
        WRITE(LOUT,*) '*********************************************'
        WRITE(LOUT,*) 'STOP: Too many species for dimension.'
        WRITE(LOUT,*) 'Maximum Number of species = ',MV
        WRITE(LOUT,*) '*********************************************'
        STOP
      ENDIF
C
C   READ SOLUTION FROM UNIT LSAVE
      READ(LSAVE) LSENS
      READ(LSAVE) NATJ,KSPEC,IREAC
C
C   CHECK FOR DIMENSIONING ERRORS
      IF (KSPEC .NE. KK) THEN
        WRITE(LOUT,*) '*********************************************'
        WRITE(LOUT,*) 'STOP: Data and linking files not compatible.'
        WRITE(LOUT,*) 'Wrong number of species.'
        WRITE(LOUT,*) 'Data file has ', KSPEC
        WRITE(LOUT,*) 'Link file has ', KK
        WRITE(LOUT,*) '*********************************************'
        STOP
      ENDIF
      IF (IREAC .NE. II) THEN
        WRITE(LOUT,*) '*********************************************'
        WRITE(LOUT,*) 'STOP: Data and linking files not compatible.'
        WRITE(LOUT,*) 'Wrong number of reactions.'
        WRITE(LOUT,*) 'Data file has ', IREAC
        WRITE(LOUT,*) 'Link file has ', II
        WRITE(LOUT,*) '*********************************************'
        STOP
      ENDIF
      IF (LSENS) THEN
       IF (II .GT. MPARS) THEN
         WRITE(LOUT,*) '*********************************************'
         WRITE(LOUT,*) 'STOP: Too many reactions for dimension.'
         WRITE(LOUT,*) 'Maximum No. of reactions =', MPAR
         WRITE(LOUT,*) '*********************************************'
         STOP
       ENDIF
      ENDIF
C
C   READ IN SPECIES NAMES AND REACTION NAMES
      CALL CKSYMS(CWORK, LOUT, CHEM, KERR )
```

```
      IF( KERR ) WRITE(LOUT, *) 'ERROR: Species name read error'
      DO 20 I=1,II
        CALL CKSYMR(I, LOUT, IWORK, WORK, CWORK, LNREAC,
     1        REAC(I), KERR)
        IF( KERR ) WRITE(LOUT, *)
     1        'ERROR: Reaction name read error'
20    CONTINUE
      IF( KERR ) STOP
C
C     READ KEYWORD INPUT
      CALL REDKEY(LIN,LOUT,LWANT,KK,
     1   KMTOT,KCTOT,KSTOT,IWMOLS,IWCONT,IWSENS,
     2   TIMMIN,TIMMAX,DELTIM,CUTOFF,NTIM)
C
C     IF SENSITIVITY IS DESIRED, CHECK TO SEE IF IT WAS RUN
      IF (LWANT(7).AND.(.NOT.LSENS)) WRITE(LOUT,'(/,1X,A,/)')
      1 ' Sorry, sensitivity coefficients are not available.'
      WRITE(LOUT,'(/,1X,A,/)') ' Reading data.'
C
C     LOOP OVER DATASETS
      IF (LSENS) THEN
       IF (NATJ.EQ.KSPEC) THEN
         KSKIP = 0
         LTSENS = .FALSE.
       ELSE
         KSKIP = 1
         LTSENS = .TRUE.
       ENDIF
C      READ SENSITIVITY COEFFICIENTS
       JMAX=0
       DO 50 J=1,NTIM
C      READ DATA
45       READ(LSAVE,END=90) TIM(J),P(J),T(J),(YMF(K,J),K=1,KK)
         READ(LSAVE) (( SENSJ(L,I),L=1,NATJ),I=1,II)
         IF (JMAX.EQ.0) THEN
C      READ IN INITIAL CONDITIONS
          CI(1)=T(J)
          CI(2)=P(J)
          ICOUNT=0
          CALL CKYTX(YMF(1,J),IWORK,WORK,XT(1))
          DO 30 K=1,KK
            IF (XT(K).GT.0.0) THEN
              ICOUNT=ICOUNT+1
              CI(ICOUNT+2)=XT(K)
              IWCI(ICOUNT+2)=K
            ENDIF
            IF (ICOUNT.EQ.18) THEN
              WRITE(LOUT,*)
     1            'Initial condition space exceeded; too'
              WRITE(LOUT,*) 'many species (maximum = 18)'
              GOTO 35
            ENDIF
30        CONTINUE
35        CONTINUE
```

```
      ENDIF
      DO 55 I=1,II
        IF (LTSENS) SENT(I,J) = SENSJ(1,I)
        DO 60 K=1,KK
          SENS(K,I,J)=SENSJ(K+KSKIP,I)
60        CONTINUE
55      CONTINUE
C    CHECK FOR SAVING THE DATA POINT
      JMAX = JMAX + 1
      IF (TIM(J).LT.TIMMIN) GOTO 45
      TSTEP = TIM(J) - TIM(J-1)
      IF ( (J.GT.1) .AND. (TSTEP.LT.DELTIM) ) GOTO 45
      JJ = JJ + 1
      IF (TIM(J).GE.TIMMAX) GOTO 90
50    CONTINUE
C
    ELSE
C    NO SENSITIVITY COEFFICIENTS TO READ
     JMAX=0
     DO 80 J = 1, NTIM
65      READ(LSAVE,END=90) TIM(J),P(J),T(J),(YMF(K,J),K=1,KK)
       IF (JMAX.EQ.0) THEN
C      READ IN INITIAL CONDITIONS
         CI(1)=T(J)
         CI(2)=P(J)
         ICOUNT=0
         CALL CKYTX(YMF(1,J),IWORK,WORK,XT(K))
         DO 70 K=1,KK
           IF (XT(K).GT.0.0) THEN
             ICOUNT=ICOUNT+1
             CI(ICOUNT+2)=XT(K)
             IWCI(ICOUNT+2)=K
           ENDIF
           IF (ICOUNT.EQ.18) THEN
             WRITE(LOUT,*)
     1             'Initial condition space exceeded; too'
             WRITE(LOUT,*) 'many species (maximum = 18)'
             GOTO 75
           ENDIF
70         CONTINUE
75         CONTINUE
       ENDIF
C
C    CHECK FOR SAVING THE DATA POINT
      JMAX = JMAX + 1
      IF (TIM(J).LT.TIMMIN) GOTO 65
      TSTEP = TIM(J) - TIM(J-1)
      IF ( (J.GT.1) .AND. (TSTEP.LT.DELTIM) ) GOTO 65
      JJ = JJ + 1
      IF (TIM(J).GE.TIMMAX) GOTO 90
80    CONTINUE
C
    ENDIF
C
```

```
C  DONE READING DATA
C
90  CONTINUE
    IF (TIM(JJ).GT.TIMMAX) JJ = JJ - 1
    WRITE (LOUT,*) 'Finished reading data.'
    WRITE (LOUT,'(A,I4)')
   1 ' Number of time datasets read = ', JMAX
    WRITE (LOUT,'(A,I4)') ' Number kept for plots = ', JJ
    NPLT = (JJ / 2) + 1
C
    DO 95 J = 1, JJ
C      SETUP ABCISSA FOR PLOTS
      XPLOT(J)=TIM(J)
C      CONVERT TO MOLE FRACTIONS AND STEP TIME ARRAY FOR PLOTTING
      CALL CKYTX(YMF(1,J),IWORK,WORK,XT)
      DO 93 K=1,KK
        XMF(J,K) = XT(K)
93      CONTINUE
95   CONTINUE
C
C
C  OUTPUT PROPLOT FILES USING PROGRAPH
C
c-------------------------------------------------------------------
c  Prograph creates proplot command files for a given set of data.
c  Multiple curves can be plotted on a single graph (sensitivity
c  and mols). Prograph uses the insert option to include the data
c  sets in the command files. This saves space and makes the command
c  files easily editable.
c
c  Synopsis:
c
c  CALL PROGRAPH(NSTEP,KGRAPH,KSPEC,NAME,KTYPE,X,Y,YMAX,YMIN,IPLOT)
c
c  NSTEP = number of x,y pairs to be plotted
c  KGRAPH = number of curves to be plotted on single graph
c  KSPEC = code which indicates species for graph (KTYPE = 3,4 or 7)
c  NAME = name of curves cont and sens plots
c  KTYPE = code which indicates graph (essentially LWANT)
c      X = vector of x values (dimension NSTEP)
c      Y = vector of y values (dimension NSTEP by KGRAPH)
c  YMAX = maximum value in y vector
c  YMIN = minimum value in y vector
c   IPLOT = logical vector indicating plot (yes/no) (dimension KGRAPH)
c
c-------------------------------------------------------------------
C
    IF (LWANT(1)) THEN
C  WRITE TEMP VS. TIME IN FILE TEMP.OUT
      DO 110 J=1,JJ
        YPLOT(J,1) = T(J)
110    CONTINUE
      CALL MINMAX(YPLOT(1,1),JJ,YMIN,YMAX,IPK)
      CALL FLOPEN(CI(1),IWCI(1),ICOUNT,0,1)
```

```
      CALL PROGRAPH(JJ,1,0,NAME(1),1,
     1      XPLOT(1),YPLOT(1,1),YMAX,YMIN,IDUM,IPLOT(1))
      CALL FLCLSE(1)
      WRITE(LOUT,*) 'Wrote temperature output file'
      DO 115 J=1,JJ
        YPLOT(J,1)=0.0
115   CONTINUE
      ENDIF
C
      IF (LWANT(2)) THEN
C     WRITE OUPUT FILE FOR PRESSURE VS. TIME
      DO 120 J=1,JJ
        YPLOT(J,1) = P(J)
120   CONTINUE
      CALL MINMAX(YPLOT(1,1),JJ,YMIN,YMAX,IPK)
      CALL FLOPEN(CI(1),IWCI(1),ICOUNT,0,2)
      CALL PROGRAPH(JJ,1,0,NAME(1),2,
     1      XPLOT(1),YPLOT(1,1),YMAX,YMIN,IDUM,IPLOT(1))
      CALL FLCLSE(2)
      WRITE(LOUT,*) 'Wrote pressure output file'
      WRITE(LOUT,*) ' '
      DO 125 J=1,JJ
        YPLOT(J,1)=0.0
125   CONTINUE
      ENDIF
C
      IF (LWANT(3)) THEN
C     WRITE OUTPUT FILE FOR MOLE FRACTIONS VS TIME
      DO 130 K=1,KMTOT
        DO 132 J=1,JJ
          YPLOT(J,1) = XMF(J,IWMOLS(K))
132     CONTINUE
        CALL MINMAX(YPLOT(1,1),JJ,YMIN,YMAX,IPK)
        CALL FLOPEN(CI(1),IWCI(1),ICOUNT,IWMOLS(K),3)
        CALL PROGRAPH(JJ,1,IWMOLS(K),NAME(1),3,
     1      XPLOT(1),YPLOT(1,1),YMAX,YMIN,IDUM,IPLOT(1))
        CALL FLCLSE(3)
130   CONTINUE
      WRITE(LOUT,*) 'Wrote species mols output files.'
      DO 135 J=1,JJ
        YPLOT(J,1)=0.0
135   CONTINUE
      ENDIF
C
      IF (LWANT(10)) THEN
C     WRITE OUPUT FILE FOR ALL LOG OF MOLES VS. TIME
      DO 1010 K=1,KK
        NAME(K)=CHEM(K)
        DO 1020 J=1,JJ
          YPLOT(J,K) = XMF(J,K)
1020    CONTINUE
        CALL MINMAX(YPLOT(1,K),JJ,YMN(K),YMX(K),IEXMA(K))
1010  CONTINUE
      YMIN = 1.0E-6
```

```
      CALL MINMAX(YMX(1),KK,YMXMN,YMAX,IPK)
      DO 1015 I=1,KK
        IF (YMX(I).LT.YMIN) THEN
          IPLOT(I) = .FALSE.
        ENDIF
1015  CONTINUE
      CALL FLOPEN(CI(1),IWCI(1),ICOUNT,0,10)
      CALL PROGRAPH(JJ,KK,0,NAME(1),10,
   1      XPLOT(1),YPLOT(1,1),YMAX,YMIN,IEXMA(1),IPLOT(1))
      CALL FLCLSE(10)
      WRITE(LOUT,*) 'Wrote log moles output file'
      DO 1030 K=1,KK
        IPLOT(I)=.TRUE.
        DO 1030 J=1,JJ
          YPLOT(J,K)=0.0
1030    CONTINUE
     ENDIF
C
C
C
     IF (LWANT(4)) THEN
C    WRITE OUTPUT FILES FOR CONTRIBUTION PLOTS
      DO 140 K=1,KCTOT
       KSPEC=IWCONT(K)
       DO 142 J=1,JJ
         DO 143 L=1,KK
           XT(L)=YMF(L,J)
143      CONTINUE
         CALL CKQYP(P(J),T(J),XT(1),IWORK,WORK,Q(1))
         CALL CKCONT(KSPEC,Q(1),IWORK,WORK,CIK(1))
         SUMRT(J) = 0.0
         DO 144 I=1,II
           YPLOT(J,I) = CIK(I)
           SUMRT(J)=SUMRT(J)+CIK(I)
           IF (J.EQ.1) THEN
             NAME(I) = REAC(I)
           ENDIF
144      CONTINUE
         YPLOT(J,II+1) = SUMRT(J)
142    CONTINUE
       DO 145 I=1,II+1
         CALL MINMAX(YPLOT(1,I),JJ,YMN(I),YMX(I),IEXMA(I))
145    CONTINUE
       NAME(II+1) = 'SUMMATION'
       CALL MINMAX(YMN(1),II+1,YMIN,YMNMX,IPK)
       CALL MINMAX(YMX(1),II+1,YMXMN,YMAX,IPK)
       DO 146 I=1,II
         IF ( ABS(YMN(I)) .LT. ABS(YMX(I)) ) THEN
           YMX(I) = ABS(YMX(I))
         ELSE
           YMX(I) = ABS(YMN(I))
         ENDIF
146    CONTINUE
       IF ( ABS(YMIN) .LT. ABS(YMAX) ) THEN
```

```
            YCUT=ABS(YMAX)*CUTOFF(4)
          ELSE
            YCUT=ABS(YMIN)*CUTOFF(4)
          ENDIF
          DO 147 I=1,II
            IF (YMX(I).LT.YCUT) THEN
              IPLOT(I) = .FALSE.
            ENDIF
147       CONTINUE
          CALL FLOPEN(CI(1),IWCI(1),ICOUNT,IWCONT(K),4)
          CALL PROGRAPH(JJ,II+1,IWCONT(K),NAME(1),4,
     1         XPLOT(1),YPLOT(1,1),YMAX,YMIN,IEXMA(1),IPLOT(1))
          CALL FLCLSE(4)
          DO 148 I=1,II+1
            IPLOT(I)=.TRUE.
            DO 148 J=1,JJ
              YPLOT(J,I)=0.0
148         CONTINUE
140       CONTINUE
        WRITE(LOUT,*) 'Wrote contribution plot output files.'
      ENDIF
C
      IF (LWANT(5)) THEN
C     WRITE OUPUT FILE FOR HEAT RELEASE VS. TIME
        DO 152 J=1,JJ
          SUMRT(J) = 0.0
          DO 151 K=1,KK
            XT(K)=YMF(K,J)
151       CONTINUE
          CALL CKQYP(P(J),T(J),XT(1),IWORK,WORK,Q(1))
          CALL CKHMS(T(J),IWORK,WORK,H(1))
          DO 153 I=1,II
            DO 154 K=1,KK
              CALL CKCONT(K,Q(1),IWORK,WORK,CIK(1))
              YPLOT(J,I) = YPLOT(J,I)+CIK(I)*H(K)
154         CONTINUE
            SUMRT(J) = SUMRT(J) + YPLOT(J,I)
            IF (J.EQ.1) NAME(I) = REAC(I)
153       CONTINUE
          YPLOT(J,II+1) = SUMRT(J)
152     CONTINUE
        NAME(II+1) = 'SUMMATION'
        DO 155 I=1,II+1
          CALL MINMAX(YPLOT(1,I),JJ,YMN(I),YMX(I),IEXMA(I))
155     CONTINUE
        CALL MINMAX(YMN(1),II+1,YMIN,YMNMX,IPK)
        CALL MINMAX(YMX(1),II+1,YMXMN,YMAX,IPK)
        DO 156 I=1,II+1
          IF ( ABS(YMN(I)) .LT. ABS(YMX(I)) ) THEN
            YMX(I)=ABS(YMX(I))
          ELSE
            YMX(I)=ABS(YMN(I))
          ENDIF
156     CONTINUE
```

```
      IF ( ABS(YMIN) .LT. ABS(YMAX) ) THEN
        YCUT=ABS(YMAX)*CUTOFF(5)
      ELSE
        YCUT=ABS(YMIN)*CUTOFF(5)
      ENDIF
      DO 157 I=1,II
        IF (YMX(I).LT.YCUT) THEN
          IPLOT(I) = .FALSE.
        ENDIF
157     CONTINUE
      CALL FLOPEN(CI(1),IWCI(1),ICOUNT,0,5)
      CALL PROGRAPH(JJ,II+1,0,NAME(1),5,
     1       XPLOT(1),YPLOT(1,1),YMAX,YMIN,IEXMA(1),IPLOT(1))
      CALL FLCLSE(5)
      WRITE(LOUT,*) 'Wrote heat release output file.'
      DO 158 I=1,II+1
        IPLOT(I)=.TRUE.
        DO 158 J=1,JJ
          YPLOT(J,I)=0.0
158     CONTINUE
C
    ENDIF
C
    IF (.NOT. LSENS) GO TO 9900
C   SENSITIVITY PLOTS
C
    IF (LWANT(6)) THEN
C   PLOT SENSITIVITY OF TEMPERATURE
      IF (NATJ.EQ.KSPEC) THEN
        WRITE(LOUT,'(/,1X,A,/)')
     1  ' Sorry, temperature sensitivity not run.'
        GO TO 700
      ENDIF
      DO 162 I = 1, II
        DO 163 J = 1, JJ
C         Sensitivity normalization
C           YPLOT(J,I) = SENT(I,J)*RA(I)/(T(J)+1.0D-8)
          YPLOT(J,I) = SENT(I,J)/(T(J)+1.0D-8)
163       CONTINUE
        NAME(I)=REAC(I)
        CALL MINMAX(YPLOT(1,I),JJ,YMN(I),YMX(I),IEXMA(I))
162     CONTINUE
      CALL MINMAX(YMN(1),II,YMIN,YMNMX,IPK)
      CALL MINMAX(YMX(1),II,YMXMN,YMAX,IPK)
      DO 164 I=1,II
        IF ( ABS(YMN(I)) .LT. ABS(YMX(I)) ) THEN
          YMX(I)=ABS(YMX(I))
        ELSE
          YMX(I)=ABS(YMN(I))
        ENDIF
164     CONTINUE
      IF ( ABS(YMIN) .LT. ABS(YMAX) ) THEN
        YCUT=ABS(YMAX)*CUTOFF(6)
      ELSE
```

```
         YCUT=ABS(YMIN)*CUTOFF(6)
       ENDIF
       DO 166 I=1,II
         IF (YMX(I).LT.YCUT) THEN
           IPLOT(I) = .FALSE.
         ENDIF
166    CONTINUE
       CALL FLOPEN(CI(1),IWCI(1),ICOUNT,0,6)
       CALL PROGRAPH(JJ,II,0,NAME(1),6,
   1          XPLOT(1),YPLOT(1,1),YMAX,YMIN,IEXMA(1),IPLOT(1))
       CALL FLCLSE(6)
       WRITE(LOUT,*) 'Wrote temperature sensitivity output file.'
       DO 168 I=1,II+1
         IPLOT(I)=.TRUE.
         DO 168 J=1,JJ
           YPLOT(J,I)=0.0
168    CONTINUE
     ENDIF
C
700  CONTINUE
C
     IF (LWANT(7)) THEN
C    PLOT SENSITIVITY OF SPECIES FRACTIONS
       DO 170 K=1,KSTOT
         MSPEC=IWSENS(K)
         DO 1705 J=1,JJ
           YPLOT(J,1)=YMF(MSPEC,J)
1705     CONTINUE
         CALL MINMAX(YPLOT(1,1),JJ,YMNK,YMXK,IMAX)
         DO  171 I = 1, II
           DO 172 J = 1, JJ
C        Sensitiviy normalization
C              YPLOT(J,I) = SENS(MSPEC,I,J)*RA(I)/YMXK
             YPLOT(J,I) = SENS(MSPEC,I,J)/YMXK
172          CONTINUE
           NAME(I)=REAC(I)
           CALL MINMAX(YPLOT(1,I),JJ,YMN(I),YMX(I),IEXMA(I))
171        CONTINUE
         CALL MINMAX(YMN(1),II,YMIN,YMNMX,IPK)
         CALL MINMAX(YMX(1),II,YMXMN,YMAX,IPK)
         DO 174 I=1,II
           IF ( ABS(YMN(I)) .LT. ABS(YMX(I)) ) THEN
             YMX(I)=ABS(YMX(I))
           ELSE
             YMX(I)=ABS(YMN(I))
           ENDIF
174        CONTINUE
         IF ( ABS(YMIN) .LT. ABS(YMAX) ) THEN
           YCUT=ABS(YMAX)*CUTOFF(7)
         ELSE
           YCUT=ABS(YMIN)*CUTOFF(7)
         ENDIF
         DO 176 I=1,II
         IF (YMX(I).LT.YCUT) THEN
```

```
            IPLOT(I) = .FALSE.
          ENDIF
 176        CONTINUE
          CALL FLOPEN(CI(1),IWCI(1),ICOUNT,MSPEC,7)
          CALL PROGRAPH(JJ,II,MSPEC,NAME(1),7,
     1         XPLOT(1),YPLOT(1,1),YMAX,YMIN,IEXMA(1),IPLOT(1))
          CALL FLCLSE(7)
          DO 178 I=1,II+1
            IPLOT(I)=.TRUE.
            DO 178 J=1,JJ
              YPLOT(J,I)=0.0
 178        CONTINUE
 170      CONTINUE
        WRITE(LOUT,*) 'Wrote sensitivity plots output files.'
C
      ENDIF
C
 9900 CONTINUE
C
      IF (LWANT(8).OR.LWANT(9)) THEN
C     CALCULATE DEGREE OF DISEQUILIBRIUM AND ENTROPY
        DO 180 J=1,JJ
          DO 180 I=1,II
            XMF(J,I)=0.0
 180      CONTINUE
        JACT=1
        DO 181 J=1,JJ
          SUMRT(J)=0.0
          DO 1815 K=1,KK
            XT(K)=YMF(K,J)
 1815       CONTINUE
          CALL CKQFQR(P(J),T(J),XT(1),IWORK,WORK,QF(1),QR(1))
          DO 182 I=1,II
            IF ( (QF(I).EQ.0.0) .OR. (QR(I).EQ.0.0) ) THEN
              SUMRT(1)=0.0
              GO TO 181
            ENDIF
            XMF(JACT,I)=DLOG(QF(I)/QR(I))
            YPLOT(JACT,I)=XMF(JACT,I)
            XMF(JACT,I)=(QF(I)-QR(I))*XMF(JACT,I)
            SUMRT(JACT)=SUMRT(JACT)+XMF(JACT,I)
 182        CONTINUE
          XPLOT(JACT)=TIM(J)
          JACT=JACT+1
 181      CONTINUE
        JACT=JACT-1
      ENDIF
C
      IF (LWANT(8)) THEN
C     PLOT DEGREE OF DISEQUILIBRIUM
        DO 184 I=1,II
          NAME(I)=REAC(I)
          CALL MINMAX(YPLOT(1,I),JACT,YMN(I),YMX(I),IEXMA(I))
 184      CONTINUE
```

```
      CALL MINMAX(YMN(1),II,YMIN,YMNMX,IPK)
      CALL MINMAX(YMX(1),II,YMXMN,YMAX,IPK)
      DO 185 I=1,II
        IF ( ABS(YMN(I)) .LT. ABS(YMX(I)) ) THEN
          YMX(I)=ABS(YMX(I))
        ELSE
          YMX(I)=ABS(YMN(I))
        ENDIF
185   CONTINUE
      IF ( ABS(YMIN) .LT. ABS(YMAX) ) THEN
        YCUT=ABS(YMAX)*CUTOFF(8)
      ELSE
        YCUT=ABS(YMIN)*CUTOFF(8)
      ENDIF
      DO 186 I=1,II
        IF (YMX(I).LT.YCUT) THEN
          IPLOT(I) = .FALSE.
        ENDIF
186   CONTINUE
      CALL FLOPEN(CI(1),IWCI(1),ICOUNT,0,8)
      CALL PROGRAPH(JACT,II,0,NAME(1),8,
    1         XPLOT(1),YPLOT(1,1),YMAX,YMIN,IEXMA(1),IPLOT(1))
      CALL FLCLSE(8)
      WRITE(LOUT,*) 'Wrote degree of disequilibrium output file.'
      DO 188 I=1,II+1
        IPLOT(I)=.TRUE.
        DO 188 J=1,JJ
          YPLOT(J,I)=0.0
188   CONTINUE
    ENDIF
C
    IF (LWANT(9)) THEN
C   PLOT ENTROPY PRODUCTION
      DO 194 I=1,II
        DO 195 J=1,JACT
          YPLOT(J,I)=XMF(J,I)
          IF (I.EQ.1) YPLOT(J,II+1)=SUMRT(J)
195     CONTINUE
        NAME(I)=REAC(I)
194   CONTINUE
      DO 196 I=1,II+1
        CALL MINMAX(YPLOT(1,I),JACT,YMN(I),YMX(I),IEXMA(I))
196   CONTINUE
      NAME(II+1)='SUMMATION'
      CALL MINMAX(YMN(1),II+1,YMIN,YMNMX,IPK)
      CALL MINMAX(YMX(1),II+1,YMXMN,YMAX,IPK)
      DO 197 I=1,II
        IF ( ABS(YMN(I)) .LT. ABS(YMX(I)) ) THEN
          YMX(I)=ABS(YMX(I))
        ELSE
          YMX(I)=ABS(YMN(I))
        ENDIF
197   CONTINUE
      IF ( ABS(YMIN) .LT. ABS(YMAX) ) THEN
```

```
          YCUT=ABS(YMAX)*CUTOFF(9)
        ELSE
          YCUT=ABS(YMIN)*CUTOFF(9)
        ENDIF
        DO 198 I=1,II
          IF (YMX(I).LT.YCUT) THEN
            IPLOT(I) = .FALSE.
          ENDIF
198     CONTINUE
        CALL FLOPEN(CI(1),IWCI(1),ICOUNT,0,9)
        CALL PROGRAPH(JACT,II+1,0,NAME(1),9,
     1        XPLOT(1),YPLOT(1,1),YMAX,YMIN,IEXMA(1),IPLOT(1))
        CALL FLCLSE(9)
        WRITE(LOUT,*) 'Wrote entropy production output file.'
C
      ENDIF
C
C  ALL PLOTTING COMPLETED
C
C  WRITE FINAL MESSAGE
      WRITE(LOUT,*) ' '
      WRITE(LOUT,*) '******** SENSOUT finished ********'
C
      STOP
      END
C
C
c*********************************************************************
C
      SUBROUTINE CKQFQR (P, T, Y, IWORK, WORK, QF, QR)
c--------------------------------------------------------------------
      IMPLICIT REAL*8 (A-H,O-Z)
      IMPLICIT INTEGER*4 (I-N)
c--------------------------------------------------------------------
C
C     THIS SUBROUTINE RETURNS THE MOLAR PRODUCTION RATES
C     OF THE SPECIES GIVEN THE PRESSURE, TEMPERATURE AND MASS
C     FRACTIONS. REFERENCE EQUATION (II.5.2).
C
C    INPUT
C     P     - PRESSURE.
C               CGS UNITS - DYNES/CM**2.
C     T     - TEMPERATURE.
C               CGS UNITS - K
C     Y     - ARRAY OF MASS FRACTIONS OF THE KK SPECIES.
C               CGS UNITS - NONE.
C               DIMENSION Y(*) AT LEAST KK.
C     IWORK  - ARRAY OF INTEGER INTERNAL WORK SPACE. THE IWORK ARRAY
C             IS INITIALIZED BY THE CALL TO SUBROUTINE CKINIT.
C               DIMENSION IWORK(*) AT LEAST LENIWK. SEE CKINIT FOR
C               DETAILS ON THE REQUIRED LENGTH OF IWORK.
C     WORK   - ARRAY OF REAL INTERNAL WORK SPACE. THE WORK ARRAY IS
C             INITIALIZED BY THE CALL TO SUBROUTINE CKINIT.
C               DIMENSION WORK(*) AT LEAST LENWK. SEE CKINIT FOR
```

```
C             DETAILS ON THE REQUIRED LENGTH OF WORK.
C
C   OUTPUT
C     QF   - ARRAY OF FORWARD RATE OF PROGRESS FOR THE
C           II REACTIONS
C             CGS UNITS - MOLES/(CM**3*SEC).
C             DIMENSION QF(*) AT LEAST II.
C     QR   - ARRAY OF REVERSE RATE OF PROGRESS FOR THE
C           II REACTIONS
C             CGS UNITS - MOLES/(CM**3*SEC).
C             DIMENSION QR(*) AT LEAST II.
c---------------------------------------------------------------------
      DIMENSION Y(1), IWORK(1), WORK(1), QF(1), QR(1)
C
C*****fall off
C     COMMON /CKSTRT/ NMM, NKK, NII, NMAXSP, NMAXTB, NLENEL, NLNSYM,
C    1 NTHCF, NCP1, NCP2, NCP2T2, IMH, IKH, INC, IPH, ICH, INU, INK,
C    2 INS, ITB, IRV, INN, INT, NAW, NWT, NWL, NTL, NTH, NTM, NAA,
C    3 NAI, NFP, NRA, NRB, NRE, NRU, NRC, NPA, NK1, NK2, NK3, NK4
C*****END fall off
C
C       THE FOLLOWING IS FOR THE PRODUCTION VERSION OF CHEMKIN
C
C*****production chemkin
      COMMON /CKSTRT/ NMM, NKK, NII, NMAXSP, NMAXTB, NLENEL, NLNSYM,
     1 NTHCF, NCP1, NCP2, NCP2T2, IMH, IKH, INC, IPH, ICH, INU, INK,
     2 INS, ITB, IRV, INN, INT, NAW, NWT, NWL, NTL, NTH, NTM, NAA,
     3 NAI, NRA, NRB, NRE, NRU, NRC, NPA, NK1, NK2, NK3, NK4
C*****END production chemkin
C
      CALL CKYTCP (P, T, Y, IWORK, WORK, WORK(NK1))
      CALL CKQQFR (NII, NKK, NMAXSP, NMAXTB, NCP2, T, WORK(NK1),
     1            IWORK(INU), IWORK(INK), IWORK(INS), IWORK(ITB),
     2            IWORK(IRV), IWORK(INN), IWORK(INT), WORK(NTM),
     3            WORK(NAA), WORK(NAI), WORK(NRA), WORK(NRB),
     4            WORK(NRE), WORK(NRU), WORK(NRC), WORK(NPA),
     5            WORK(NK2), QF, QR)
C
      RETURN
      END
C
c************************************************************************
      SUBROUTINE CKQQFR (II, KK, MAXSP, MAXTB, NCP2, T, C,
     1             NU, NUNK, NUSUMK, ITHB, IREV, NNEG, NKTB,
     2             TMID, A, AIK, RA, RB, RE, RU, RUC, PATM,
     3             SMH, QF, QR)
C--------------------------------------------------------------------
      IMPLICIT REAL*8 (A-H,O-Z)
      IMPLICIT INTEGER*4 (I-N)
C--------------------------------------------------------------------
      DIMENSION C(KK),SMH(KK),TMID(KK)
      DIMENSION NU(MAXSP,II),NUNK(MAXSP,II),AIK(MAXTB,II),NKTB(MAXTB,II)
      DIMENSION NUSUMK(II),ITHB(II),IREV(II),RA(II),RB(II),RE(II)
      DIMENSION NNEG(II)
```

```
    DIMENSION QR(II), QF(II)
    DIMENSION A(NCP2,2,KK)
    DIMENSION TN(10)
    DIMENSION N1(2),N2(2),PD(2)
C
    COMMON /CKMACH/ SMALL,BIG,EXPARG,UROUND
C
C
C  EVALUATE THERMODYNAMIC PROPERTIES
C
C
    CTOT = 0.0
    DO 150 K =1,KK
     CTOT = CTOT + C(K)
150  CONTINUE
C
    NCP1 = NCP2 - 1
    NTHCF = NCP2 - 2
    ALOGT = LOG(T)
    TN(1) = ALOGT - 1.0
    DO 200 N = 2,NTHCF
     TN(N) = T**(N-1) / FLOAT((N-1)*N)
200  CONTINUE
    DO 300 K = 1,KK
     L = 1
     IF (T.GT.TMID(K)) L = 2
     SUM = 0.0
     DO 250 N = 1,NTHCF
      SUM = SUM + A(N,L,K)*TN(N)
250   CONTINUE
     SMH(K) = SUM + A(NCP2,L,K) - A(NCP1,L,K)/T
300  CONTINUE
    RTR = 1.0/(RUC*T)
    PFAC = PATM/(RU*T)
C
C        PROCESS EACH REACTION
C
    DO 1500 I = 1,II
     N1(1) = 1
     N2(1) = NNEG(I)
     N1(2) = NNEG(I) + 1
     N2(2) = IABS(IREV(I))
C        EQUILIBRIUM CONSTANTS
     NN = IABS(IREV(I))
     SUMSMH = 0.0
     DO 600 N = 1,NN
      NC = NU(N,I)
      NK = NUNK(N,I)
      SUMSMH = SUMSMH + FLOAT(NC)*SMH(NK)
600   CONTINUE
     SUMSMH = MIN (SUMSMH,EXPARG)
     EQKP = EXP(SUMSMH)
     IF (NUSUMK(I). NE. 0) THEN
      PFN = PFAC**NUSUMK(I)
```

```
          IF (PFN.GT.1.0 .AND. SUMSMH.EQ.EXPARG) THEN
            EQKC = BIG
          ELSE
            EQKC = EQKP*PFN
          ENDIF
        ELSE
          EQKC = EQKP
        ENDIF
C
C         SET THE EQUILIBRIUM CONSTANT IF IRTASK = 3
C
      RKF = RA(I) * EXP(RB(I)*ALOGT - RE(I)*RTR)
      IF (IREV(I).LT.0) THEN
        RKR = 0.0
      ELSE
        RKR = RKF / MAX(EQKC, SMALL)
      ENDIF
C
C          FORWARD AND REVERSE CONCENTRATION PRODUCTS
C                 PD(1) = FORWARD PRODUCT
C                 PD(2) = REVERSE PRODUCT
C
      PD(1) = 1.0
      PD(2) = 1.0
      DO 900 J = 1,2
        NS = N1(J)
        NF = N2(J)
        DO 900 N = NS,NF
          NK = NUNK(N,I)
          NC = IABS(NU(N,I))
          PD(J) = PD(J)*C(NK)**NC
900     CONTINUE
      PF = PD(1)
      PR = PD(2)
C
C        CONCENTRATION OF THE EFFECTIVE THIRD BODY
C
      NT = ITHB(I)
      IF (NT .EQ. 0) THEN
        CTB = CTOT
      ELSE IF (NT .LT. 0) THEN
        CTB = 1.0
      ELSE
        DO 950 N = 1,NT
          NK = NKTB(N,I)
          CTB = CTB + (AIK(N,I) - 1.0)*C(NK)
950       CONTINUE
      ENDIF
C
      QF(I) = (RKF*PF) * CTB
      QR(I) = (RKR*PR) * CTB
C
1500    CONTINUE
C
```

```
      RETURN
      END
c*********************************************************************
      SUBROUTINE MINMAX(V,N,VMIN,VMAX,IPK)
c-------------------------------------------------------------------
c   Returns min and max values of vector, and index
c   of the peak absolute value.
c-------------------------------------------------------------------
      IMPLICIT REAL*4 (A-H,O-Z)
      IMPLICIT INTEGER*4 (I-N)
c-------------------------------------------------------------------
C
      DIMENSION V(*)
      IPK = 1
      VMAX = V(1)
      VMIN = V(1)
      VPK  = VMAX
      DO 100 J = 2, N
        VMIN = MIN(V(J),VMIN)
        VMAX = MAX(V(J),VMAX)
        AMIN = ABS(VMIN)
        AMAX = ABS(VMAX)
        IF (AMIN.GT.VPK) THEN
          VPK = AMIN
          IPK = J
        ELSEIF (AMAX.GT.VPK) THEN
          VPK = AMAX
          IPK = J
        ENDIF
  100 CONTINUE
C
      RETURN
      END
C
C-------------------------------------------------------------------
C
      SUBROUTINE REDKEY(LIN,LOUT,LWANT,KK,
     1  KMTOT,KCTOT,KSTOT,IWMOLS,IWCONT,IWSENS,
     2  TIMMIN,TIMMAX,DELTIM,CUTOFF,NTIM)
C
C-------------------------------------------------------------------
c   This subroutine reads in commands which determine which plots
c   are to be constructed and what time window is desired.
C-------------------------------------------------------------------
      IMPLICIT REAL*8 (A-H,O-Z)
      IMPLICIT INTEGER*4 (I-N)
C-------------------------------------------------------------------
      DIMENSION IWMOLS(*),IWCONT(*),IWSENS(*)
      DIMENSION VALUE(5),LWANT(10)
      REAL*4 CUTOFF(10)
c-------------------------------------------------------------------
      CHARACTER*4 KEYWRD
      CHARACTER*1 ANS
      CHARACTER*76 LINE
```

```
      CHARACTER*16 CHEM
      CHARACTER*40 REAC
      LOGICAL LWANT,KERR,ISERR,IXERR,KMIN,KMAX,KDEL,ICUT(10)
c-----------------------------------------------------------------
      PARAMETER(MV=70,MPARS=300)
      COMMON /SPECNAM/ CHEM(MV),REAC(MPARS)
c-----------------------------------------------------------------
      DATA KERR /.FALSE./, ISERR /.FALSE./, IXERR /.FALSE./
      DATA KMIN /.FALSE./ KMAX /.FALSE./ KDEL /.FALSE./
      DATA NCHAR /76/, KWANT/0/
      DATA KMOLS /0/, KCONT /0/, KSENS /0/
      DATA (ICUT(I),I=1,10) /10* .FALSE./
C-----------------------------------------------------------------
C
C  ISSUE A PROMPT
C
80  CONTINUE
      WRITE(LOUT,*) 'Enter Keywords: '
      WRITE(LOUT,*)
     1    '   TMIN, TMAX, DELT, TEMP, PRES, MOLS, MLOG, CONT,'
      WRITE(LOUT,*)
     1    '   HEAT, SENT, SENS, DSEQ, ENTP, ALL, END or HELP.'
      WRITE(LOUT,*) ' '
C
C  READ NEXT INPUT LINE
C
90  CONTINUE
      LINE = ' '
      WRITE(LOUT,*) 'Keyword input: '
      READ(LIN,1000) KEYWRD,LINE
1000 FORMAT(A4,A)
C
C  CHECK FOR COMMENT
      IF (KEYWRD(1:1) .EQ. '.' .OR. KEYWRD(1:1) .EQ. '/' .OR.
     1  KEYWRD(1:1) .EQ. '!' ) GO TO 90
C
C  CHECK TO SEE IF ALL OPTIONS ARE DESIRED
      IF (KEYWRD .EQ. 'ALL ') THEN
        DO 10 L=1,9
          LWANT(L) = .TRUE.
10      CONTINUE
        KMOLS = KK
        KCONT = KK
        KSENS = KK
        DO 20 K=1,KK
          IWMOLS(K) = K
          IWCONT(K) = K
          IWSENS(K) = K
20      CONTINUE
        GO TO 90
C
C  ALL OTHER OPTIONS
      ELSE IF (KEYWRD.EQ.'TEMP') THEN
        LWANT(1) = .TRUE.
```

```
      GO TO 90
C
    ELSE IF (KEYWRD.EQ.'PRES') THEN
      LWANT(2) = .TRUE.
      GO TO 90
C
    ELSE IF (KEYWRD.EQ.'MOLS') THEN
      LWANT(3) = .TRUE.
C     READ IN WHICH SPECIES FOR MOLS PLOT
      CALL MFMSNUM (LINE, 0, LOUT, CHEM, KK, KSPEC, NVAL,
    1           VALUE, ISERR, IXERR)
      IF (ISERR) THEN
        CALL ERRPR (KERR, KEYWRD, LOUT)
      ELSE
        KMOLS = KMOLS + 1
        IWMOLS(KMOLS) = KSPEC
      ENDIF
      GO TO 90
C
    ELSE IF (KEYWRD.EQ.'MLOG') THEN
      LWANT(10) = .TRUE.
      GO TO 90
C
    ELSE IF (KEYWRD.EQ.'CONT') THEN
      LWANT(4) = .TRUE.
      CALL MFMSNUM (LINE, 1, LOUT, CHEM, KK, KSPEC, NVAL,
    1           VALUE, ISERR, IXERR)
      IF (ISERR) THEN
        CALL ERRPR (KERR, KEYWRD, LOUT)
      ELSE
        KCONT = KCONT + 1
        IWCONT(KCONT) = KSPEC
        IF (IXERR) THEN
          ICUT(4)=.FALSE.
        ELSE
          ICUT(4)=.TRUE.
          CUTOFF(4)=VALUE(1)
        ENDIF
      ENDIF
      GO TO 90
C
    ELSE IF (KEYWRD.EQ.'HEAT') THEN
      LWANT(5) = .TRUE.
      CALL MFMXNUM (LINE, 1, LOUT, NVAL, VALUE, IXERR)
      IF (IXERR) THEN
        ICUT(5)=.FALSE.
      ELSE
        ICUT(5)=.TRUE.
        CUTOFF(5)=VALUE(1)
      ENDIF
      GO TO 90
C
    ELSE IF (KEYWRD.EQ.'SENT') THEN
      LWANT(6) = .TRUE.
```

```
        CALL MFMXNUM (LINE, 1, LOUT, NVAL, VALUE, IXERR)
        IF (IXERR) THEN
          ICUT(6)=.FALSE.
        ELSE
          ICUT(6)=.TRUE.
          CUTOFF(6)=VALUE(1)
        ENDIF
        GO TO 90
C
      ELSE IF (KEYWRD.EQ.'SENS') THEN
        LWANT(7) =.TRUE.
C       READ IN WHICH SPECIES FOR SENSITIVITY PLOT
        CALL MFMSNUM (LINE, 1, LOUT, CHEM, KK, KSPEC, NVAL,
     1             VALUE, ISERR, IXERR)
        IF (ISERR) THEN
          CALL ERRPR (KERR, KEYWRD, LOUT)
        ELSE
          KSENS = KSENS + 1
          IWSENS(KSENS) = KSPEC
          IF (IXERR) THEN
            ICUT(7)=.FALSE.
          ELSE
            ICUT(7)=.TRUE.
            CUTOFF(7)=VALUE(1)
          ENDIF
        ENDIF
        GO TO 90
C
      ELSE IF (KEYWRD.EQ.'DSEQ') THEN
        LWANT(8) = .TRUE.
        CALL MFMXNUM (LINE, 1, LOUT, NVAL, VALUE, IXERR)
        IF (IXERR) THEN
          ICUT(8)=.FALSE.
        ELSE
          ICUT(8)=.TRUE.
          CUTOFF(8)=VALUE(1)
        ENDIF
        GO TO 90
C
      ELSE IF (KEYWRD.EQ.'ENTP') THEN
        LWANT(9) = .TRUE.
        CALL MFMXNUM (LINE, 1, LOUT, NVAL, VALUE, IXERR)
        IF (IXERR) THEN
          ICUT(9)=.FALSE.
        ELSE
          ICUT(9)=.TRUE.
          CUTOFF(9)=VALUE(1)
        ENDIF
        GO TO 90
C
      ELSE IF (KEYWRD.EQ.'TMIN') THEN
C       READ IN START TIME
        CALL MFMXNUM (LINE, 1, LOUT, NVAL, VALUE, IXERR)
        IF (IXERR) THEN
```

```
          CALL ERRPR (KERR, KEYWRD, LOUT)
        ELSE
          TIMMIN = VALUE(1)
          KMIN = .TRUE.
        ENDIF
        GO TO 90
C
      ELSE IF (KEYWRD.EQ.'TMAX') THEN
C       READ IN END TIME
        CALL MFMXNUM (LINE, 1, LOUT, NVAL, VALUE, IXERR)
        IF (IXERR) THEN
          CALL ERRPR (KERR, KEYWRD, LOUT)
        ELSE
          TIMMAX = VALUE(1)
          KMAX = .TRUE.
        ENDIF
        GO TO 90
C
      ELSE IF (KEYWRD.EQ.'DELT') THEN
C       READ IN TIME STEP
        CALL MFMXNUM (LINE, 1, LOUT, NVAL, VALUE, IXERR)
        IF (IXERR) THEN
          CALL ERRPR (KERR, KEYWRD, LOUT)
        ELSE
          DELTIM = VALUE(1)
          KDEL = .TRUE.
        ENDIF
        GO TO 90
C
      ELSE IF (KEYWRD.EQ.'END ') THEN
        GO TO 6000
C
      ELSE IF (KEYWRD.EQ.'HELP') THEN
       WRITE(LOUT,*) ' '
       WRITE(LOUT,*)
     1' Keywords must be uppercase characters. Cut-off values are '
       WRITE(LOUT,*)
     1' specified after the keyword for HEAT, SENT, DSEQ, and ENTP '
       WRITE(LOUT,*)
     1' and after the species name for CONT and SENS (def=0.05).'
       WRITE(LOUT,*) ' Keyword inputs are as follows:'
       WRITE(LOUT,*)
     1' TMIN  # -- Minimum of time range desired (sec). Default=0.'
       WRITE (LOUT,*)
     1' TMAX  # -- Maximum of time range desired (sec). No default.'
       WRITE(LOUT,*)
     1' DELT  # -- Time step desired for output (sec).'
       WRITE(LOUT,*)
     1'           Default is time step used by ODE solver.'
       WRITE(LOUT,*) ' TEMP -- Plot of temperature vs time.'
       WRITE(LOUT,*) ' PRES -- Pressure vs time.'
       WRITE(LOUT,*) ' MOLS  X -- Mole fractions for species X.'
       WRITE(LOUT,*)
     1' MLOG -- Mole fractions for all species (log).'
```

```
      WRITE(LOUT,*) ' CONT -- Species contribution factors.'
      WRITE(LOUT,*) ' HEAT -- Heat release rates of reactions.'
      WRITE(LOUT,*) ' DSEQ -- Degree of disequilibrium of reactions.'
      WRITE(LOUT,*) ' ENTP -- Entropy contribution factors.'
      WRITE(LOUT,*) ' SENT',
     1'-- Sensitivity coefficients for temperature.'
      WRITE(LOUT,*)
     1' SENS  X -- Sensitivity coefficients for the species X.'
      WRITE(LOUT,*)
     1' ALL  -- All of the above plots. Sensitivities and contribution'
      WRITE(LOUT,*)
     1'        and mole plots for all species. Note: Time information'
      WRITE(LOUT,*)
     1'        must still be specified!'
      WRITE(LOUT,*) ' END  -- Indicates the last input.'
      WRITE(LOUT,*) ' '
      WRITE(LOUT,777)
777   FORMAT(2X,'Hit [RETURN] to continue: ',$)
      READ(LIN,'(A)') ANS
      WRITE(LOUT,*) ' '
      GO TO 80
     ENDIF
C
C   END OF KEYWORDS
C
C   TO GET HERE, AN INVALID KEYWORD WAS READ
     WRITE (LOUT,*) ' Error, illegal keyword.'
C
C   GO BACK UP AND READ THE NEXT LINE
     GO TO 90
C
C   DONE READING CARDS
C
6000 CONTINUE
C
C   CHECK TIME RANGE
     IF (KMIN) THEN
       IF (TIMMAX.LE.0.0) THEN
         WRITE(LOUT,*) 'STOP: Maximum time must be > 0.'
         KERR =.TRUE.
       ENDIF
     ELSE
       TIMMIN = 0.0
     ENDIF
C
     IF (KMAX) THEN
       IF (TIMMAX.LE.TIMMIN) THEN
         WRITE(LOUT,*) 'STOP: Maximum time < minimum time.'
         KERR =.TRUE.
       ENDIF
     ELSE
c     WRITE(LOUT,1011)
c1011   FORMAT(2X,'Enter now: ',$)
c     READ(LIN,*) TIMMAX
```

```
c       KMAX = .TRUE.
c       GOTO 6000
        WRITE(LOUT,*) 'Maximum time not specified!'
        KERR = .TRUE.
      ENDIF
C
      IF (KDEL) THEN
        DELMAX = TIMMAX - TIMMIN
        IF (DELTIM.GE.DELMAX) THEN
          WRITE(LOUT,*) 'STOP: Maximum time step exceeded.'
          KERR = .TRUE.
        ENDIF
      ELSE
        DELTIM = (TIMMAX-TIMMIN) / FLOAT(NTIM)
      ENDIF
C
      IF (.NOT.KERR) THEN
C     SPECIES FOR MOLS PLOT
      IF (LWANT(3)) THEN
       KMTOT = KMOLS
       WRITE(LOUT,*) 'Species for mols plots are:'
       DO 6005 K=1,KMTOT
         KMOLS = IWMOLS(K)
         WRITE(LOUT,'(2X,I3,4X,A16)') K,CHEM(KMOLS)
6005    CONTINUE
      ENDIF
C
C     SPECIES FOR CONTRIBUTION PLOT
      IF (LWANT(4)) THEN
       KCTOT = KCONT
       WRITE(LOUT,*) 'Species for contribution plots are:'
       DO 6010 K=1,KCTOT
         KCONT = IWCONT(K)
         WRITE(LOUT,'(2X,I3,4X,A16)') K,CHEM(KCONT)
6010    CONTINUE
      ENDIF
C
C     SPECIES FOR SENSITIVITY PLOT
      IF (LWANT(7)) THEN
       KSTOT = KSENS
       WRITE(LOUT,*) 'Species for sensitivity plots are:'
       DO 6015 K=1,KSTOT
         KSENS = IWSENS(K)
         WRITE(LOUT,'(2X,I3,4X,A16)') K,CHEM(KSENS)
6015    CONTINUE
      ENDIF
C
C     SET CUTOFF VALUES
C     Note that only array positions 4,5,6,7,8,9 are needed
      DO 7000 I=4,9
        IF (.NOT.ICUT(I)) THEN
          CUTOFF(I)=0.05
        ENDIF
7000  CONTINUE
```

```
C
      ELSE
C     STOP IF ERRORS ENCOUNTERED
      STOP 'SENSOUT ERROR'
      ENDIF
996   FORMAT(6X,'Error: Too few parameters specified')
997   FORMAT(6X,'Error: No species specified. ')
998   FORMAT(6X,'Error: Illegal character specified')
999   FORMAT(6X,'Error: Too many parameters specified')
C
      RETURN
      END
C
C-----------------------------------------------------------
C
      SUBROUTINE ERRPR (KERR, KEYWRD, LOUT)
      LOGICAL KERR
      CHARACTER *4 KEYWRD
      KERR =.TRUE.
      WRITE (LOUT, '(2X,A,A,A,/)')
     1 ' Error reading data for keyword ', KEYWRD,'.'
      STOP 'FATAL INPUT ERROR'
      END
C
C-------------------------------------------------------------
C
      SUBROUTINE MFMSNUM (LINE, NEXP, LOUT, KRAY, NN, KNUM, NVAL,
     1                RVAL, KERR, IERR)
C
c
c  Modified version of cksnum which allows seperate error flags
c  for parsing of substring and numbers. MFM 9/92
c
C  START PROLOGUE
C
C  SUBROUTINE MFMSNUM (LINE, NEXP, LOUT, KRAY, NN, KNUM, NVAL,
C                RVAL, KERR, IERR)
C     This subroutine is called to parse a character string, LINE,
C     that is composed of several blank-delimited substrings.
C     It is expected that the first substring in LINE is also an
C     entry in a reference array of character strings, KRAY(*), in
C     which case the index position in KRAY(*) is returned as KNUM,
C     otherwise an error flag is returned.  The substrings following
C     the first are expected to represent numbers, and are converted
C     to elements of the array RVAL(*).  If NEXP substrings are not
C     found an error flag will be returned.  This allows format-free
C     input of combined alpha-numeric data.  For example, after
C     reading a line containing a species name followed by several
C     numerical values, the subroutine might be called to find
C     a Chemkin species index and convert the other substrings to
C     real values:
C
C     input:  LINE    = "N2  1.2"
C             NEXP    = 1, the number of values expected
```

```
C         LOUT   = 6, a logical unit number on which to write
C                diagnostic messages.
C         KRAY(*) = "H2" "O2" "N2" "H" "O" "N" "OH" "H2O" "NO"
C         NN     = 9, the number of entries in KRAY(*)
C    output: KNUM   = 3, the index number of the substring in
C                KRAY(*) which corresponds to the first
C                substring in LINE
C         NVAL   = 1, the number of values found in LINE
C                following the first substring
C         RVAL(*) = 1.200E+00, the substring converted to a number
C         KERR   = .FALSE.
C         IERR   = .FALSE.
C  INPUT
C    LINE  - A character string.
C             Data type - CHARACTER*80
C    NEXP  - Number of real values to be found in character string.
C          If NEXP is negative, then ABS(NEXP) values are
C          expected.  However, it is not an error condition,
C          if less values are found.
C             Data type - integer scalar
C    LOUT  - Output unit for printed diagnostics.
C             Data type - integer scalar
C    KRAY  - Array of character strings.
C             Data type - CHARACTER*(*)
C    NN    - Total number of character strings in KRAY.
C             Data type - integer scalar
C
C  OUTPUT
C    KNUM  - Index number of character string in array which
C          corresponds to the first substring in LINE.
C             Data type - integer scalar
C    NVAL  - Number of real values found in LINE.
C             Data type - integer scalar
C    RVAL  - Array of real values found in LINE.
C             Data type - real array
C             Dimension RVAL(*) at least NEXP
C    KERR  - Error flag corresponding to error finding match
C          in substring parsing will result in KERR = .TRUE.
C             Data type - logical
C    IERR  - Error flag; syntax or dimensioning error,
C          corresponding string not found, or total of
C          values found is not the number of values expected,
C          in parsing after substring (XNUM call)
C          will result in IERR = .TRUE.
C             Data type - logical
C
C  END PROLOGUE
C    A '!' will comment out a line, or remainder of the line.
C
C*****double precision
      IMPLICIT DOUBLE PRECISION (A-H, O-Z), INTEGER (I-N)
C*****END double precision
C*****single precision
C       IMPLICIT REAL (A-H, O-Z), INTEGER (I-N)
```

```
C*****END single precision
C
      CHARACTER LINE*(*), KRAY(*)*(*), ISTR*80
      DIMENSION RVAL(*)
      LOGICAL KERR, IERR
C
      NVAL = 0
      KERR = .FALSE.
      IERR = .FALSE.
      ILEN = MIN (IPPLEN(LINE), ILASCH(LINE))
      IF (ILEN .LE. 0) RETURN
C
      I1 = IFIRCH(LINE(:ILEN))
      I3 = INDEX(LINE(I1:ILEN),' ')
      IF (I3 .EQ. 0) I3 = ILEN - I1 + 1
      I2 = I1 + I3
      ISTR = ' '
      ISTR = LINE(I1:I2-1)
C
      CALL CKCOMP (ISTR, KRAY, NN, KNUM)
      IF (KNUM.EQ.0) THEN
        LT = MAX (ILASCH(ISTR), 1)
        WRITE (LOUT,'(A)')
     1  ' Error in MFMSNUM...'//ISTR(:LT)//' not found...'
        KERR = .TRUE.
      ENDIF
C
      ISTR = ' '
      ISTR = LINE(I2:ILEN)
      IF (NEXP .NE. 0)
     1    CALL MFMXNUM (ISTR, NEXP, LOUT, NVAL, RVAL, IERR)
C
      RETURN
      END
C---------------------------------------------------------------------C
C
      SUBROUTINE MFMXNUM (LINE, NEXP, LOUT, NVAL, RVAL, KERR)
C
C  START PROLOGUE
c
c  Modified to return KERR = .TRUE. when ILEN < 0; MFM 9/92
C
C  SUBROUTINE MFMXNUM (LINE, NEXP, LOUT, NVAL, RVAL, KERR)
C     This subroutine is called to parse a character string, LINE,
C     that is composed of several blank-delimited substrings.
C     Each substring is expected to represent a number, which
C     is converted to entries in the array of real numbers, RVAL(*).
C     NEXP is the number of values expected, and NVAL is the
C     number of values found.  This allows format-free input of
C     numerical data.  For example:
C
C     input:  LINE    = " 0.170E+14 0 47780.0"
C             NEXP    = 3, the number of values requested
C             LOUT    = 6, a logical unit number on which to write
```

```
C               diagnostic messages.
C   output: NVAL    = 3, the number of values found
C           RVAL(*) = 1.700E+13, 0.000E+00, 4.778E+04
C           KERR    = .FALSE.
C
C INPUT
C   LINE  - A character string.
C                Data type - CHARACTER*80
C   NEXP  - Number of real values to be found in character string.
C           If NEXP is negative, then ABS(NEXP) values are
C           expected.  However, it is not an error condition,
C           if less values are found.
C                Data type - integer scalar
C   LOUT  - Output unit for printed diagnostics.
C                Data type - integer scalar
C
C OUTPUT
C   NVAL  - Number of real values found in character string.
C                Data type - integer scalar
C   RVAL  - Array of real values found.
C                Data type - real array
C                Dimension RVAL(*) at least NEXP
C   KERR  - Error flag;  syntax or dimensioning error results
C           in KERR = .TRUE.
C                Data type - logical
C
C END PROLOGUE
C
C   A '!' will comment out a line, or remainder of the line.
C
C*****double precision
      IMPLICIT DOUBLE PRECISION (A-H, O-Z), INTEGER (I-N)
C*****END double precision
C*****single precision
C       IMPLICIT REAL (A-H, O-Z), INTEGER (I-N)
C*****END single precision
C
      CHARACTER LINE*(*), ITEMP*80
      DIMENSION RVAL(*), RTEMP(80)
      LOGICAL KERR
C
C----------Find Comment String (! signifies comment)
C
      ILEN = IPPLEN(LINE)
      NVAL = 0
      KERR = .FALSE.
C
C  This test has been modified to return KERR = .TRUE.
      IF (ILEN .LE. 0) THEN
        KERR = .TRUE.
        RETURN
      ENDIF
      IF (ILEN .GT. 80) THEN
        WRITE (LOUT,*)    ' Error in MFMXNUM...line length > 80 '
```

```
          WRITE (LOUT,'(A)') LINE
          KERR = .TRUE.
          RETURN
        ENDIF
C
        ITEMP = LINE(:ILEN)
        IF (NEXP .LT. 0) THEN
          CALL IPPARR (ITEMP, -1, NEXP, RTEMP, NVAL, IERR, LOUT)
        ELSE
          CALL IPPARR (ITEMP, -1, -NEXP, RTEMP, NVAL, IERR, LOUT)
          IF (IERR .EQ. 1) THEN
            WRITE (LOUT, *)   ' Syntax errors in MFMXNUM...'
            WRITE (LOUT,'(A)') LINE
            KERR = .TRUE.
          ELSEIF (NVAL .NE. NEXP) THEN
            WRITE (LOUT,*) ' Error in MFMXNUM...'
            WRITE (LOUT,'(A)') LINE
            KERR = .TRUE.
            WRITE (LOUT,*) NEXP,' values expected, ',
     1                 NVAL,' values found.'
          ENDIF
        ENDIF
        IF (NVAL .LE. ABS(NEXP)) THEN
          DO 20 N = 1, NVAL
            RVAL(N) = RTEMP(N)
   20     CONTINUE
        ENDIF
C
        RETURN
        END
C
c*********************************************************************
        SUBROUTINE PROGRAPH(NSTEP,KGRAPH,KSPEC,NAME,KTYPE,
     1                XPLT,YPLT,YMAX,YMIN,IEXMA,IPLOT)
c-----------------------------------------------------------------
c   Prograph creates proplot command files for a given set of data.
c   Multiple curves can be plotted on a single graph (sensitivity
c   and mols). Prograph uses the insert option to include the data
c   sets in the command files. This saves space and makes the command
c   files easily editable.
c
c   Synopsis:
c
c                                                                    CALL
PROGRAPH(NSTEP,KGRAPH,IWSPEC,NAME,KTYPE,XPLT,YPLT,YMAX,YMIN,IPLOT)
c
c    NSTEP = number of x,y pairs to be plotted
c   KGRAPH = number of curves to be plotted on single graph
c    KSPEC = code which indicates species for graph (KTYPE=3,4 or 7)
c     NAME = label of each curve
c    KTYPE = code which indicates graph (essentially LWANT)
c        X = vector of x values (dimension NSTEP)
c        Y = vector of y values (dimension NSTEP by KGRAPH)
c     YMAX = maximum value in y vector
```

```
c   YMIN = minimum value in y vector
c  IEXMA = array of extrema indicies of curves
c  IPLOT = logical vector indicating whether to plot (dimension KGRAPH)
c
c----------------------------------------------------------------
    IMPLICIT REAL*4 (A-H,O-Z)
    IMPLICIT INTEGER*4 (I-N)
c----------------------------------------------------------------
    PARAMETER(NKK=70,NII=300)
    LOGICAL RESCLE
    CHARACTER*6 NUM(20),LNUM
    CHARACTER*16 CHEM
    CHARACTER*40 REAC
    CHARACTER*40 TTITLE(10),LTITLE(10)
    CHARACTER*40 BTITLE1,BTITLE2
    CHARACTER*42 RNAME,LNAME
    LOGICAL IPLOT
    COMMON /SPECNAM/ CHEM(NKK),REAC(NII)
c----------------------------------------------------------------
    PARAMETER (MT=100,MDIM2=301)
    DIMENSION XPLT(MT),YPLT(MT,MDIM2)
    DIMENSION IEXMA(MT),IPLOT(MT),L(10),NL(3)
    CHARACTER*40 NAME(MDIM2)
c----------------------------------------------------------------
    DATA L(1) /21/,L(2) /22/, L(3) /23/, L(4) /24/, L(5) /25/
    DATA L(6) /26/, L(7) /27/, L(8) /28/, L(9) /29/, L(10) /30/
c----------------------------------------------------------------
    DATA TTITLE(1) /'"Temperature Time History"          '/
    DATA TTITLE(2) /'"Pressure Time History"             '/
    DATA TTITLE(3) /'"Species Time History"              '/
    DATA TTITLE(4) /'"Species Contributions Plot"        '/
    DATA TTITLE(5) /'"Heat Release Contributions Plot"   '/
    DATA TTITLE(6) /'"Temperature Sensitivity Plot"      '/
    DATA TTITLE(7) /'"Species Sensitivity Plot"          '/
    DATA TTITLE(8) /'"Disequilibrium Contribution Plots"  '/
    DATA TTITLE(9) /'"Entropy Production Contribution Plots"'/
    DATA TTITLE(10) /'"Species Mole Fractions Time History " '/
c----------------------------------------------------------------
    DATA LTITLE(1) /'"T [K]"                             '/
    DATA LTITLE(2) /'"P [atm]"                           '/
    DATA LTITLE(3) /'"X"                                 '/
    DATA LTITLE(4) /'"Contribution Factor [mole/cmb3e sec]" '/
    DATA LTITLE(5) /'"Heat Release [erg/gm sec]"         '/
    DATA LTITLE(6) /'"Sensitivity"                       '/
    DATA LTITLE(7) /'"Sensitivity"                       '/
    DATA LTITLE(8) /'"log(RRbFe/RRbBe)"                  '/
    DATA LTITLE(9) /'"(RRbFe - RRbBe) log(RRbFe/RRbBe)"   '/
    DATA LTITLE(10) /'"Log X"                            '/
c----------------------------------------------------------------
    DATA BTITLE1  /'"Time [msec]"                        '/
    DATA BTITLE2  /'"Time [sec]"                         '/
c----------------------------------------------------------------
    DATA NUM(1)  /'" 1"'/
    DATA NUM(2)  /'" 2"'/
```

```
      DATA NUM(3)  /'" 3"'/
      DATA NUM(4)  /'" 4"'/
      DATA NUM(5)  /'" 5"'/
      DATA NUM(6)  /'" 6"'/
      DATA NUM(7)  /'" 7"'/
      DATA NUM(8)  /'" 8"'/
      DATA NUM(9)  /'" 9"'/
      DATA NUM(10) /'"10"'/
      DATA NUM(11) /'"11"'/
      DATA NUM(12) /'"12"'/
      DATA NUM(13) /'"13"'/
      DATA NUM(14) /'"14"'/
      DATA NUM(15) /'"15"'/
c-----------------------------------------------------------------------
      DATA TTX /5.75/
c-----------------------------------------------------------------------
C
C  SET COUNTER
      KABS=0
C  CHECK FOR NUMBER OF CURVES PER GRAPH
      IF (KGRAPH.GT.15) THEN
        NTIMES=INT(KGRAPH/15+0.5)
      ELSE
        NTIMES=1
      ENDIF
C
C  SET OUTPUT UNIT
      LOUT=L(KTYPE)
C
C  WRITE PROPLOT COMMANDS
        DO 10 N=1,NTIMES
          KCNT=0
          IF (N.GT.1) THEN
C         START NEW PAGE
            WRITE(LOUT,*) ' '
            WRITE(LOUT,*) 'new'
            WRITE(LOUT,*) ' '
          ENDIF
C         SET SIZE OF WINDOW FOR MULTI-CURVE GRAPHS
          IF (KGRAPH.GT.1) THEN
            WRITE(LOUT,1100) 'set window x ',2.0,8.0
            WRITE(LOUT,1100) 'set box size ', 0.24, 0.20
            NL(1) = INT(NSTEP/4)
            NL(3) = INT(NSTEP*3/4)
            TTX=4.75
          ENDIF
C         WRITE TITLES
          WRITE(LOUT,1000) 'title top    ',TTITLE(KTYPE)
          IF ((KTYPE.EQ.3).OR.(KTYPE.EQ.4).OR.(KTYPE.EQ.7)) THEN
            CALL CONCAT('"',CHEM(KSPEC),RNAME)
            CALL CONCAT(RNAME,'"',LNAME)
            WRITE(LOUT,1050) 'legend justify center size=2.5',
     1                  TTX,7.15,LNAME
          ENDIF
```

```
      WRITE(LOUT,1000) 'title left   ',LTITLE(KTYPE)
      IF (KTYPE.EQ.4) THEN
       WRITE(LOUT,*) 'case "                    + +"'
      ELSEIF (KTYPE.EQ.8) THEN
       WRITE(LOUT,*) 'case "     - -  - - "'
      ELSEIF (KTYPE.EQ.9) THEN
       WRITE(LOUT,*) 'case  "  - -    - -      - -  - - "'
      ENDIF
      IF (XPLT(NSTEP).GT.1.0E-2) THEN
       RESCLE=.FALSE.
       WRITE(LOUT,1000) 'title bottom ',BTITLE2
c      WRITE(LOUT,*) 'set labels bottom format exp'
      ELSE
       RESCLE=.TRUE.
       DO 12 I=1,NSTEP
         XPLT(I)=1.0E6*XPLT(I)
12      CONTINUE
       WRITE(LOUT,1000) 'title bottom ',BTITLE1
       WRITE(LOUT,*) 'case "    G"'
      ENDIF
      WRITE(LOUT,*) ' '
      IF ((KTYPE.NE.1).AND.(KTYPE.NE.2)) THEN
       IF ( (ABS(YMAX).GT.1000).OR.(ABS(YMAX).LT.1.0E-3) ) THEN
         WRITE(LOUT,*) 'set labels left format exp'
       ENDIF
      ENDIF
      IF (KTYPE.EQ.10) THEN
       WRITE(LOUT,*) 'set scale y log'
      ENDIF
C     SET LIMITS OF GRAPH
      IF (YMIN.GT.0.0) THEN
        YMIN=0.9*YMIN
      ELSE
        YMIN=1.1*YMIN
      ENDIF
      IF (YMAX.GT.0.0) THEN
        YMAX=1.1*YMAX
      ELSE
        YMAX=0.9*YMAX
      ENDIF
      WRITE(LOUT,1100) 'set limits y ',YMIN,YMAX
      WRITE(LOUT,*) ' '
C    WRITE DATA
15      CONTINUE
      KABS=KABS+1
      KCNT=KCNT+1
      IF (KCNT.EQ.16) THEN
        KABS = KABS-1
        GOTO 500
      ENDIF
      IF (KABS.GT.KGRAPH) GOTO 800
C     CHECK PLOT OPTION
      IF (.NOT.IPLOT(KABS)) THEN
        KCNT=KCNT-1
```

```
          GOTO 15
        ELSE
          DO 20 J=1,NSTEP
            WRITE(LOUT,1200) XPLT(J),YPLT(J,KABS)
20         CONTINUE
          WRITE(LOUT,*) ' '
          WRITE(LOUT,*) 'join linear'
          WRITE(LOUT,*) ' '
C         LABEL CURVES
          IF (KGRAPH.GT.1) THEN
            NL(2)=IEXMA(KABS)
            DO 30 I=1,3
              IF ( (YPLT(NL(I),KABS).GT.YMIN) .AND.
     1            (YPLT(NL(I),KABS).LT.YMAX) ) THEN
              WRITE(LOUT,1150) 'box         ',
     1                   XPLT(NL(I)),YPLT(NL(I),KABS)
              IF( KCNT.LT.10 ) THEN
              WRITE(LOUT,1300) XPLT(NL(I)),YPLT(NL(I),KABS),
     1                   KCNT
              WRITE(LOUT,1301)
              ELSE
                WRITE(LOUT,1305) XPLT(NL(I)),
     1                   YPLT(NL(I),KABS),KCNT
                WRITE(LOUT,1306)
              ENDIF
              ENDIF
30           CONTINUE
C            WRITE NAMES OF CURVES ON RIGHT HAND SIDE
            YL = 7.0 - KCNT*0.25
            XLNUM = 8.25
            XLNAM = 8.35
            CALL CONCAT("",NAME(KABS),LNAME)
            CALL CONCAT(LNAME,"",RNAME)
            CALL LJUST(RNAME,LNAME)
            WRITE(LOUT,1400) XLNUM,YL,NUM(KCNT)
            WRITE(LOUT,1401) XLNAM,YL,LNAME
            WRITE(LOUT,*) ' '
          ENDIF
        ENDIF
C       PLOT NEXT CURVE
        GOTO 15
C
C       START NEW PAGE
500       CONTINUE
C
10     CONTINUE
C
C   DONE PLOTTING
800  CONTINUE
C
C   RESET TIME SCALE IF NECESSARY
   IF (RESCLE) THEN
     DO 812 I=1,NSTEP
       XPLT(I)=1.0E-6*XPLT(I)
```

```
812    CONTINUE
   ENDIF
C
C  FORMAT STATEMENTS
1000 FORMAT(2X,A13,2X,A40)
1050 FORMAT(2X,A30,2X,1E12.5,2X,1E12.5,2X,A)
1100 FORMAT(2X,A13,1E12.5,2X,1E12.5)
1150 FORMAT(2X,A13,1E12.5,2X,1E12.5,' data ')
1200 FORMAT(2X,1E12.5,4X,1E12.5)
1300 FORMAT(2X,'legend size=1.5 justify left ',1E12.5,2X,
   1      1E12.5,' data ',2X,'''44',1I1,'''')
1301 FORMAT(2X,'case',2X,'''HV ''')
1305 FORMAT(2X,'legend size=1.5 justify left ',1E12.5,2X,
   1      1E12.5,' data ',2X,'''444',1I2,'''')
1306 FORMAT(2X,'case',2X,'''HHV  ''')
1400 FORMAT(2X,'legend size=2 justify right ',1E12.5,2X,1E12.5,2X,A)
1401 FORMAT(2X,'legend size=2 ',1E12.5,2X,1E12.5,2X,A)
C
   RETURN
   END
C
C
c*********************************************************************
   SUBROUTINE FLOPEN(CI,IWCI,ICNT,KSPEC,KTYPE)
c---------------------------------------------------------------------
c    Opens output files and writes header
     CI = initial condition vector
c    IWCI = initial condition species index
c    ICNT = number of nozero initial species concentrations
c    KSPEC = species for which the graph made (KTYPE = 3,4 or 7)
c    KTYPE = type of graph
c---------------------------------------------------------------------
   IMPLICIT REAL*4 (A-H,O-Z)
   IMPLICIT INTEGER*4 (I-N)
c---------------------------------------------------------------------
   DIMENSION CI(*),IWCI(*)
   CHARACTER*7 FILSUF
   CHARACTER*8 FILNAM(10)
   CHARACTER*16 CHEM
   CHARACTER*24 FNAME
   CHARACTER*40 REAC
c---------------------------------------------------------------------
   PARAMETER (NKK=70,NII=300)
   COMMON /SPECNAM/ CHEM(NKK),REAC(NII)
c---------------------------------------------------------------------
   DIMENSION L(10)
   DATA L(1) /21/,L(2) /22/, L(3) /23/, L(4) /24/, L(5) /25/
   DATA L(6) /26/, L(7) /27/, L(8) /28/, L(9) /29/, L(10) /30/
   DATA FILNAM(1) /'temp.plt'/, FILNAM(2) /'pres.plt'/
   DATA FILNAM(5) /'heat.plt'/, FILNAM(6) /'tsen.plt'/
   DATA FILNAM(8) /'dseq.plt'/, FILNAM(9) /'entp.plt'/
   DATA FILNAM(10) /'mlog.plt'/
c---------------------------------------------------------------------
C
```

```
      IF ( (KTYPE.EQ.3) .OR. (KTYPE.EQ.4) .OR. (KTYPE.EQ.7) ) THEN
C   OPEN FILE NAMED AFTER SPECIES
        IF (KTYPE.EQ.3) FILSUF = 'mol.plt'
        IF (KTYPE.EQ.4) FILSUF = 'con.plt'
        IF (KTYPE.EQ.7) FILSUF = 'sen.plt'
        CALL CONCAT(CHEM(KSPEC),FILSUF,FNAME)
      ELSE
        FILSUF = '      '
        CALL CONCAT(FILNAM(KTYPE),FILSUF,FNAME)
      ENDIF
C   OPEN ONE OUTPUT FILE AND WRITE HEADER
      OPEN(UNIT=L(KTYPE),FILE=FNAME,STATUS='UNKNOWN')
      WRITE(L(KTYPE),*) '%'
      WRITE(L(KTYPE),*) 'Initial Conditions of SENKIN Run'
      WRITE(L(KTYPE),1000) ' T(0) [K] ',CI(1)
      WRITE(L(KTYPE),1000) 'P(0) [Pa] ',CI(2)
      WRITE(L(KTYPE),*) 'Mole Fractions'
      DO 10 I=1,ICNT
        ISPEC=IWCI(I+2)
        WRITE(L(KTYPE),1000) CHEM(ISPEC),CI(I+2)
10    CONTINUE
      WRITE(L(KTYPE),*) '%'
      WRITE(L(KTYPE),*) ' '
1000  FORMAT(2X,A10,1PE10.3)
C
C
      RETURN
      END
C
C
C*********************************************************************
      SUBROUTINE FLCLSE(KTYPE)
c----------------------------------------------------------------------
c   Closes output files
c----------------------------------------------------------------------
      IMPLICIT INTEGER*4 (I-N)
c----------------------------------------------------------------------
      DIMENSION L(10)
c----------------------------------------------------------------------
      DATA L(1) /21/,L(2) /22/, L(3) /23/, L(4) /24/, L(5) /25/
      DATA L(6) /26/, L(7) /27/, L(8) /28/, L(9) /29/, L(10) /30/
c----------------------------------------------------------------------
C
      CLOSE (L(KTYPE))
C
C
      RETURN
      END
C
C
      subroutine upcase(c)
      character*1 c
      int= ichar(c)
      if ((int.ge.97).and.(int.le.122)) int= int-32
```

```
      c= char(int)
      return
      end
c************************************************************************
      subroutine ljust(s1,s2)
      character*(*) s1,s2
      l1=len(s1)
      do 10 i=1,l1
        i1= i
        if(s1(i:i).ne.' ') goto 15
10    continue
15    continue
      s2= s1(i1:l1)
      return
      end
c************************************************************************
      subroutine concat(s1,s2,s3)
      character*(*) s1,s2,s3
      do 10 i=len(s1),1,-1
        l1= i
        if(s1(i:i).ne.' ') goto 15
10    continue
15    continue
      s3= s1(1:l1)//s2
      return
      end
```

---

*The above FORTRAN code should be compiled and linked with CKLIB.F which can be obtained from Sandia National Laboratory with free of charge.

Appendix B

The reaction mechanism set discussed in chapter 4 is presented below. There are 323 reactions and 162 species.

Reactions considered	**A**	**b**	**E**
1. C*CC+H=H2+C*CC.	175000	2.5	2492
2. C*CC+H=NC3H7	1.33E+59	-13.9	24900
3. C*CC+H=CH3+C2H4	7.4E+40	-7.8	25780
4. NC3H7=CH3+C2H4	4.55E+53	-12.3	50590
5. C*CC+C*CC.=CYC5H8+CH3	4.68E+64	-15.8	50120
6. C*CC+C*CC.=CCYC5H8	1.52E+72	-19	40900
7. C*CC+C*CC.=CCYC5H8R	20000000	0	0
8. CPDC*C+H=CPDCRC	1E+12	0	0
9. CPDCRC=C6H6+CH3	100000000	0	0
10. CY13PD5.+C*CC=C6H5CH3+CH3	4.83E+15	-1	41410
11. CY13PD5.+C*CC=CPDIC3H6R	9.97	1.8	-3010
12. CPDRIC3H6=C6H5CH3+CH3	1.74E+14	-1.3	8180
13. CPDIC3H6R+H2=CPDRIC3H6+H2	7E+13	0	6870
14. CPDIC3H7+H=CPDIC3H6R+H2	105000000	1.5	7416
15. CPDIC3H7+H=CPDRIC3H6+H2	100000000	1.5	7400
16. CPEBICHD=IND+H2	100000000	0	0
17. C6H6+C*CC.=H+CPEBICHD	2E+10	0	0
18. CYC5H7+C*CC*CC=CPEBCHENC+H	100	0	0
19. CY13PD5.+C*CC=CPDC*C+CH3	1.54E+11	0	28740
20. C*CCCC.+H=C*CCC.+CH3	130000000	0	0
21. CYC5H8+H=CYC5H9	3.47E+17	-1.5	3880
22. CYC5H8+H=C*CCCC.	835000	2.1	7050
23. CYC5H8+H=C*CC.+C2H4	1.21E-02	4.7	13440
24. CYC5H8=CYC5H7+H	5E+15	0	84170
25. CYC5H7+H2=CYC5H8+H	108000	2.4	19000
26. C*COH+H=COC+H	1.19E-01	3.9	18570
27. C*COH+H=CH3+CH2O	4.57E-01	3.8	18430

Reactions considered	A	b	E
28. C*COH+H=CH2CH2OH	3.69E+14	-0.2	3020
29. C*CC+OH=COC+CH3	4.14E+11	0.3	22450
30. C*CC+OH=C*COH+CH3	2E+12	0	0
31. C*CC+OH=IC3H6OH	6.03E+16	-1	1910
32. C2H4+OH=COC+H	1.4E-01	3.6	18530
33. C2H4+OH=CH3+CH2O	2E+12	0	950
34. C2H4+OH=CH2CH2OH	3E+13	-0.2	400
35. CY13PD+H=C*CC*C.+CH2	100000	0	0
36. CH2+O2=CO+H2O	2.24E+22	-3.3	2865
37. CH2+H2=CH3+H	300000000	0	0
38. CH2+OH=CH2O+H	1.8E+13	0	0
39. CH2+O=CH2O	1.2E+14	0	0
40. NTSOBENZ=C6H5+NO	3E+15	0	54000
41. NTBENZ=C6H5+NO2	4.41E+16	0	72310
42. NO2+PHENOXYP=ONOCHDONE	42500000	0	-17600
43. NO2+PHENOXYP=NO+O.CHDONE	9.34E+12	0	-298
44. O.CHDONE=H+C6H4O2	5.32E+10	0	5550
45. C6H6+NO2=C6H5+HNO2	3E+13	0	33000
46. NO2+CY13PD5.=CPDON*O	1.98E+10	0	-16200
47. NO2+CY13PD5.=CYC5H5O.+NO	2.35E+13	0	4340
48. NO2+H2=H2+NO+O	1.18E+16	0	65900
49. OH+NO2=HO2+NO	1.82E+13	0	6676
50. O+NO2=O2+NO	3.92E+12	0	-238
51. H+NO2=OH+NO	1.32E+14	0	182
52. OCH3PHOH+CY13PD5.=CY13PD+OCH3PHO.	2.5E+12	0	24000
53. OCH3PHOH+CH3=CH4+OCH3PHO.	1.7E+11	0	5500
54. OCH3PHOH+H=OH+C6H5CH3	7.09E+12	0	5390
55. OCH3PHOH+H=C6H5OH+CH3	1.65E+13	0	9530
56. OCH3PHOH=H+OCH3PHO.	2.67E+16	0	86500
57. OMECHDKO+CH3=CH4+OCH3PHO.	2.5E+11	0	9200
58. OCH3PHO.+CH3CY24PD=OCH3PHOH+CYC5H4CH3	2.5E+12	0	13000
59. OCH3PHO.=CO+CYC5H4CH3	1.5E+13	0	48300
60. PCH3PHOH+H=C6H5OH+CH3	3.32E+13	0	9520

Reactions considered	**A**	**b**	**E**
61. PMECHDKO+CH3=CH4+PCH3PHO.	2.5E+11	0	9200
62. PCH3PHO.+CH3CY24PD=PCH3PHOH+CYC5H4CH3	2.5E+12	0	13000
63. PHOCH3+H=C6H5OH+CH3	7.1E+12	0	5390
64. PHOCH3+H=PHOC.H2+H2	1.32E+12	0	3890
65. PHOCH3=CH3+C6H5O.	2.52E+15	0	63300
66. PHOCH3+CH3=PHOC.H2+CH4	5E+11	0	10500
67. PHOCH3+CH3=CHD.MEOME	10600000	0	-269
68. PHOCH3+CH3=CH3O.+C6H5CH3	1.21E+12	0	10800
69. PHOCH3+H=CHD.OCH3	1.85E+10	0	-3190
70. PHOCH3+H=C6H6+CH3O.	4.77E+13	0	10800
71. PHOC.H2=C6H5CHO+H	3E+12	0	26900
72. PHOC.H2=C6H5+CH2O	2E+13	0	30560
73. C6H5CH3+H=C6H6+CH3	4.17E+13	0	11000
74. C6H5OH+OH=C6H5O.+H2O	6E+12	0	0
75. C6H5OH+O2=C6H5O.+HO2	1E+13	0	32949
76. C6H5OH+C6H5=C6H6+C6H5O.	1E+13	0	6064
77. C6H5OH+C*CC*C.=C6H5O.+C*CC*C	1E+13	0	2000
78. C6H5OH+C*CC.=C6H5O.+C*CC	1E+13	0	2000
79. C6H5OH+C#CC.=C6H5O.+CC#C	1E+13	0	2000
80. C6H5+OH=C6H5OH	1.59E+13	0	0
81. C6H5OH+CH3=CH4+C6H5O.	2.88E+11	0	5500
82. C6H5OH+H=C6H6+OH	3.44E+13	0	9420
83. C6H5OH+CY13PD5.=CY13PD+C6H5O.	2.5E+12	0	22490
84. C6H5OH+H=H2+C6H5O.	1.15E+14	0	12390
85. C6H5OH+H=H2+PHENOXYP	1.15E+14	0	12399
86. C6H5OH=H+C6H5O.	2.67E+16	0	88840
87. C6H5O.=PHENOXYP	263000000	0	-1780
88. PHENOXYP=BICYC6H5O	3.06E+13	0	47000
89. BICYC6H5O=CYC5H5C.O	302000000	0	-1620
90. CYC5H5C.O=CO+CY13PD5.	225000000	0	-1750
91. PHENOXYP+H=CHDKO	1.32E+13	0	-5660
92. PHENOXYP+H=C6H5OH	2E+15	0	4440
93. PHENOXYP+CH3=PMECHDKO	1.08E+13	0	0

Reactions considered	**A**	**b**	**E**
94. PHENOXYP+CH3=OMECHDKO	7.36E+12	0	-584
95. PHENOXYP+CH3=OCH3PHOH	7.88E+13	0	10400
96. PHENOXYP+O=C6H4O2+H	1.7E+14	0	0
97. C6H5O.=BICYC6H5O	3.54E+13	0	50500
98. CPDOOH=CYC5H5O.+OH	3.07E+18	-1.1	44330
99. C6H5O.+PHOCH3=PHOC.H2+C6H5OH	4.15E+11	0	16060
100. C6H5O.+CHDKO=C6H5OH+C6H5O.	1E+13	0	14000
101. CYC5H5O.=CYPDONE+H	545000000	0	3140
102. C6H6+H=C6H5+H2	2E+13	0	18600
103. C6H6+H=CYC6H7	1.6E+12	0	-2120
104. C6H6+H=BICYC6H7	2.75E+10	0	7370
105. C6H6+H=CH2CY24PD	2.26E+14	0	14100
106. C6H6=C6H5+H	1.67E+16	0	111500
107. C6H6+H=LINC6H7	1.22E+22	-1.9	31200
108. C6H6+H=CYC5H4CH3	2.39E+27	-3.9	29200
109. C6H6+O=C6H5O.+H	6.32E+14	-0.4	5640
110. C6H6+O=C6H5OH	39100	1.6	17190
111. C6H6+OH=C6H5+H2O	1.4E+13	0	4490
112. C6H6+O2=C6H5+HO2	6.31E+13	0	67832
113. CYC6H7=CYC5H4CH3	5E+12	0	38100
114. CYC6H7=CH2CY24PD	5.5E+10	0	23500
115. CYC6H7+H=C*CC*C+C2H2	6.5E+13	0	0
116. LINC6H7=C*CC*C.+C2H2	5.5E+14	0	41000
117. C6H5+HO2=C6H5O.+OH	8E+11	0	0
118. CYPDONE+H=CO+C*CC*C.	3.61E+14	0.3	13550
119. C6H5+CYPDONE=DCHD.+CO	2.5E+12	0	7000
120. DCHD.=NAPH+H	311000000	0	-2070
121. C6H5+O2=C6H5O.+O	2.6E+13	0	6160
122. C6H5+O2=C6H4O2+H	7.9E+11	0	0
123. C6H5+O=CY13PD5.+CO	5.25E+14	-0.2	710
124. CH3CY24PD+PHENOXYP=CYC5H4CH3+CHDKO	6E+12	0	18000
125. CH3CY24PD+C6H5O.=C6H5OH+CYC5H4CH3	3E+12	0	13000
126. CH3CY24PD+CH3=CH4+CYC5H4CH3	2.5E+11	0	5000

Reactions considered	**A**	**b**	**E**
127. CH3CY24PD+CH3=CH4+CH2CY24PD	2.5E+11	0	6000
128. CH3CY24PD+H=H2+CH2CY24PD	1.2E+14	0	8000
129. CH2CY24PD=H+CYC5H4CH2	7.48E+11	0	19700
130. CYC5H4CH3=H+CYC5H4CH2	7.48E+12	0	46800
131. CYC5H4CH3+H=CY13PD5.+CH3	8E+13	0	0
132. CYC5H4CH3+H2=CH3CY24PD+H	2E+13	0	46000
133. CY13PD=CY13PD5.+H	5.96E+14	0	75100
134. CY13PD+H=H2+CY13PD5.	1300000	2.4	4471
135. CY13PD+H=CYC5H7	2E+12	0	0
136. CY13PD+H=C*CC*CC.	549000000	0	0
137. CY13PD+H=C*CC.C*C	3.17E+10	0	0
138. CY13PD+O=CY13PD5.+OH	2.2E+12	0	0
139. CY13PD+O=HCO+C*CC*C.	5.51E+16	0	32800
140. CY13PD+O=C*CC*CCO	5.25E+12	0	1450
141. CY13PD+OH=CY13PD5.+H2O	6E+12	0	0
142. CY13PD+O2=CY13PD5.+HO2	2E+12	0	37410
143. CY13PD+OH=C2H3+C*CC*O	8.02E+33	-5.7	25120
144. CY13PD+HO2=CY13PD5.+H2O2	4E+12	0	18000
145. CY13PD+CH3=CH4+CY13PD5.	1.8E-01	4.0	0
146. CY13PD+C2H3=CY13PD5.+C2H4	1.2E-01	4.0	0
147. CY13PD+C*CC.=C*CC+CY13PD5.	6E+12	0	6000
148. CY13PD+C*CC*C.=C*CC*C+CY13PD5.	3E+12	0	1000
149. CY13PD5.+O=C*CC*C.+CO	5.28E+12	0.1	10
150. CY13PD5.+O=CYPDONE+H	2.72E+13	-0.2	210
151. CY13PD5.+O=CYC5ODE.	2.32E+16	-1.5	1240
152. CY13PD5.+O=CYC5H5O.	1.96E+24	-4.5	2630
153. CY13PD5.+OH=CYC5H5OH	1.24E+14	-0.6	0
154. CY13PD5.+O2=CO+C*OCC*C.	1.11E-01	3.8	19010
155. CY13PD5.+O2=C.OC*CCCO	1.28E+19	-2.1	20360
156. CY13PD5.+O2=COC*CC.CO	8.38E+24	-3.8	19950
157. CY13PD5.+O2=CPDOO.	4.33E+33	-6.3	10420
158. CY13PD5.+HO2=CYC5H5O.+OH	2.08E+20	-1.4	13680
159. CY13PD5.+HO2=CPDOOH	5.73E+29	-5.1	4800

Reactions considered	**A**	**b**	**E**
160. CY13PD5.+CH3=CH3CY24PD	5.05E+13	0	-149
161. CY13PD5.+CY13PD5.=H2+NAPH	3E+10	0	0
162. CYC5H7+O2=C*OCCC.CO	8E+24	-3.8	20000
163. C*OCCC.CO+O2=C*OCCC*O+HCO2.	300000000	0	0
164. CYC5H7+OH=CY13PD+H2O	2.42E+13	0	0
165. C*CC.C*C=C*CC*CC.	283000000	0	-1750
166. C*CC*CC.+OH=C*CC*CCOH	1.51E+13	0	0
167. C*CC*CCOH+H=C*CC*C+CH2OH	1E+13	0	0
168. C*CC*CC.+H2=H+C*CC*CC	1.02E+12	0	25200
169. C*CC*CC.+H=C*CC*CC	4.14E+14	0	-119
170. C*CC*CC.+H=C*CC*C.+CH3	3.17E+18	0	35800
171. C*CC.C*C+O2=PTD2OO.	3.46E+12	0	0
172. C*CC.C*C+O2=C*CC*O+C2H3O.	93500000	0	0
173. C*CC*CC+H=C*CC.CC	1.03E+13	0	0
174. C*CC*CC+H=C*CC*C+CH3	7E+12	0	1300
175. COC*CC.CO+H=COC*CCCO	1E+14	0	0
176. COC*CC.CO+OH=LC5H6O3	2.89E+13	-0.6	0
177. COC*CC.CO=C.OC*CCCO	2.18E+11	0	12200
178. COC*CC.CO+O2=HCOHCO+C*OC.C*O	309000000	0	0
179. C*CC*O+O=OH+C*C.C*O	1.4E+12	0	0
180. C*CC*O+OH=H2O+C*C.C*O	3E+12	0	0
181. C*CC*O+H=H2+C*C.C*O	2.7E+11	0	0
182. C*CC*O+H=C*CC.*O+H2	5.4E+11	0	0
183. C*CC*O+O=C*CC.*O+OH	2E+12	0	0
184. C*CC*O+OH=C*CC.*O+H2O	8.6E+12	0	0
185. C*CC*O+HO2=C*CC.*O+H2O2	1.98E+12	0	9800
186. C*CC*O+O=COC.+HCO	3E+13	0	0
187. C*CC*O+O=C2H3+HCO2.	3E+13	0	0
188. C*CC*O+H=C2H4+HCO	1.33E+12	0	0
189. C.*CCO=HCO+C2H2	3.16E+13	0	4000
190. C*C.C*O+O2=C*C*O+HCO2.	200000000	0	0
191. C*CC.*O+O2=COC.+CO2	2E+10	0	0
192. C*OCC.C*O+O2=C*OCC*O+HCO2.	238000000	0	0

Reactions considered	**A**	**b**	**E**
193. C*OCC*O+O=COC.+HCO2.	6E+12	0	0
194. C*OCC.C*O=C*CC*O+HCO	509000	0	0
195. C*OCC.C*O=C*OCC*CO.	337000000	0	0
196. C.OC*CCCO+O2=C*OCC*CO.+CO2	1.32E+11	0	0
197. C.OC*CCCO+O2=BDONEOO.	3.44E+12	0	0
198. C.OC*CCCO+O=CO2+COCC*C.	1.5E+14	0	0
199. C*OCC*C.+O2=C*CC*O+HCO2.	680000000	0	0
200. C*OCC*C.+O2=C*CC.OOCO	572000000	0	0
201. C*OCC*C.+O2=COCC*COO.	3.59E+12	0	0
202. C*OC.C*O+O2=HCOHCO+HCO2.	20400000	0	0
203. C*CC*CC.+O2=C*CC*CO.+CH2O	200000000	0	0
204. C*CC*COH+H=H2+C*CC*CO.	4E+13	0	6000
205. C*CC*COH+H=C*CC*C+OH	200000000	0	0
206. CYC5H4OH=CYPDONE+H	1E+13	0	47450
207. CYC5H5OH+H=H2+CYC5H4OH	3.15E+12	0	0
208. CYC5H5OH+H=CYC5H5O.+H2	4E+13	0	6094
209. CYC5H5OH+O=OH+CYC5H4OH	4.17E+11	0	0
210. CYC5H5OH+O=CYC5H5O.+OH	1E+13	0	4683
211. CYC5H5OH+OH=H2O+CYC5H4OH	3.98E+12	0	0
212. CYC5H5OH+OH=CYC5H5O.+H2O	1E+13	0	1697
213. CYC5H5OH+HO2=H2O2+CYC5H4OH	1E+11	0	0
214. CYC5H5OH+HO2=CYC5H5O.+H2O2	1E+13	0	15800
215. CYC5H5O.=C*CC*C.+CO	4.53E+36	-7.9	31170
216. C*CC*CCO+H=C.OC*CC*C+H2	1E+13	0	0
217. C.OC*CC*C=C*CC*C.+CO	1E+14	0	21000
218. CC*CCO+H=CC*CC.O+H2	1E+13	0	0
219. C*CC*C=C2H3+C2H3	3.98E+19	-1	98150
220. C*CC*C+OH=C*CC.+CH2O	1E+12	0	0
221. C*CC#C+H=C*CC*C.	5.5E+12	0	2400
222. C*CC#C+O=C.*C*O+C2H3	5E+13	0	0
223. C*CC*C.+C2H4=C*CC*C+C2H3	6.31E+11	0	7800
224. C*CC*C.+O2=C*CC*O+HCO	6.38E+12	0	0
225. C*CC*C.+O2=CH2O+C.*CCO	7.89E+17	-2	300

Reactions considered	**A**	**b**	**E**
226. C*CC*C.+O2=H+COC*CCO	6.57E+20	-3	1160
227. C*CC*C.+H2=H+C*CC*C	1.02E+12	0	10000
228. C*CC*C.+H=C*CC*C	2.64E+14	0	-403
229. C*CC*C.+H=C2H3+C2H3	2.29E+17	0	25400
230. C*CC*C.=C2H2+C2H3	1E+14	0	43890
231. C*CC.+C2H2=CY13PD+H	2.95E+32	-5.8	25733
232. CC*C.+CO=CC*CC.O	6.98E+11	0	5000
233. C*CC.=C*C*C+H	2.63E+13	0	59785
234. C*CC.+H=C2H3+CH3	6.74E-12	8.1	9390
235. C*CC.+H=C*CC	3.33E+15	-0.6	1800
236. C*CC=CC*C.+H	7.59E+14	0	101271
237. C*C*C=CC#C	1.48E+13	0	60395
238. C*C*C+H=C#CC.+H2	330000	2.5	3000
239. C*C*C+O=CO+C2H4	7.8E+12	0	1602
240. C*C*C+O=C#CC.+OH	1E+13	0	3000
241. CC#C+O=C#CC.+OH	1E+13	0	3000
242. CH3OC.*O=CO2+CH3	8E+14	0	6000
243. C2H6+CH3=C2H5+CH4	5.48E-01	4.0	8280
244. C2H6+CH3O.=C2H5+CH3OH	2.41E+11	0	7090
245. C2H6+H=C2H5+H2	144000000	1.5	7416
246. C2H6=C2H5+H	1.26E+16	0	98000
247. C2H5+CH2O=HCO+C2H6	6E-02	4.0	4600
248. C2H5+O2=C2H4+HO2	3E+20	-2.9	6761
249. C2H5=C2H4+H	3.8E+43	-9.5	51000
250. C2H3O.=COC.	328000000	0	-926
251. C2H3O.=C*C*O+H	3E+13	0	20000
252. C2H4+C2H3=C*CC*C+H	5E+11	0	7304
253. CH3CO+CH3=C2C*O	2.4E+13	0	0
254. CH3CO+C6H5O.=CH3COOPH	1E+12	0	0
255. COC.+O2=CH2O+HCO2.	242000000	0	0
256. C.*C*O+O2=CO2+HCO	4E+12	0	0
257. C*C*O+OH=HCO+CH2O	2.8E+13	0	0
258. C*C*O+OH=H2O+C.*C*O	7.24E+12	0	1400

Reactions considered	**A**	**b**	**E**
259. C*C*O+O=OH+C.*C*O	8E+12	0	6500
260. C*C*O+H=H2+C.*C*O	1E+13	0	9000
261. C2H3+CH2O=HCO+C2H4	1.2E-01	4.0	3600
262. C2H3+CO=C*CC.*O	1.51E+11	0	4809
263. C2H3+O2=C2H3O.+O	5E+12	0	0
264. C2H3+O2=CH2O+HCO	2.53E+26	-4.3	5320
265. C2H3+O2=COC.+O	2.03E+13	-0.1	4210
266. C2H3+O2=C2H2+HO2	4.5E+20	-2.8	4670
267. C2H3+OH=C2H2+H2O	3.01E+13	0	0
268. C2H3+H2=H+C2H4	30200	2.6	8541
269. C2H3=C2H2+H	2E+14	0	38740
270. HCOHCO=HCO+HCO	9.01E+14	0	64100
271. HCOHCO+OH=H2O+HCOC.*O	343000000	1.2	-447
272. HCOHCO+O=OH+HCOC.*O	4.16E+11	0.6	2762
273. HCOHCO+H=H2+HCOC.*O	2.29E+10	1.1	3279
274. HCOC.*O+O2=HCO2.+CO2	2.12E+10	0	0
275. HCO2.+O=OH+CO2	6E+12	0	0
276. HCO2.+OH=H2O+CO2	6E+12	0	0
277. HCO2.=CO2+H	1.75E+12	0.3	32920
278. CH3O.+CO=CH3OC.*O	1.6E+13	0	11800
279. CH3O.=CH2O+H	1.6E+14	0	25100
280. CH2OH+H2=CH2O+H+H2	1.67E+24	-2.5	34190
281. CH2O+H=HCO+H2	440000	2.5	2000
282. CH2O+H2=H+H2+HCO	1.2E+41	-6.9	96558
283. CH2O+OH=HCO+H2O	343000000	1.2	-447
284. CH2O+O=HCO+OH	1.8E+13	0	3080
285. CH2O=CO+H2	4.52E+15	0	35295
286. C2H2+HO2=C*C*O+OH	603000000	0	7948
287. H2O2+OH=H2O+HO2	1.75E+12	0	318
288. H2O2+H=HO2+H2	440000	2.5	2000
289. H2O2=OH+OH	1.97E+12	0	44400
290. CH3+CH2O=CH4+HCO	1.8E-01	4.0	3600
291. CH3+CH3=C2H6	1.13E+12	0	-4270

Reactions considered	A	b	E
292. CH3+CH3=H+C2H5	4.51E+13	0	15900
293. CH3+CO+H2=CH3CO+H2	1.2E+23	-2.8	7600
294. CH3+O2=CH3O.+O	4.42E+17	-0.9	30820
295. CH3+O2=CH2O+OH	1.13E+12	-0.2	15560
296. CH3+OH=CH2OH+H	1.09E+11	0.4	-708
297. CH3+H2=CH4+H	39800	2.2	6399
298. CH3+O=CH2O+H	8.43E+13	0	0
299. CH3+H=CH4	8.09E+36	-7.2	9200
300. HO2+HO2=O2+H2O2	2E+12	0	0
301. HO2+OH=H2O+O2	1.45E+16	-1	0
302. HO2+O=O2+OH	2E+13	0	0
303. HO2+H=OH+OH	1.5E+14	0	1008
304. HO2+H=H2+O2	2.51E+13	0	700
305. H2O+O=OH+OH	460000000	1.3	17100
306. HCO+O2=CO+HO2	3.31E+12	0	0
307. HCO+O2=CO2+OH	6.29E+11	0	0
308. HCO+OH=CO+H2O	1E+14	0	0
309. HCO+O=CO2+H	3E+13	0	0
310. HCO+H=H2+CO	9.04E+13	0	0
311. HCO+H2=H+CO+H2	1.87E+17	-1	17000
312. CO+HO2=CO2+OH	1.5E+14	0	23688
313. CO+O2=CO2+O	2.51E+12	0	47690
314. CO+OH=CO2+H	4400000	1.5	-717
315. CO+O+H2=CO2+H2	6.17E+14	0	3000
316. O2+H+H2=HO2+H2	2.9E+17	-0.7	0
317. OH+H+H2=H2O+H2	2.2E+22	-2	0
318. H2+OH=H2O+H	100000000	1.6	3300
319. H2+O=H+OH	11000	2.8	5920
320. O+OH=O2+H	1.45E+13	0	700
321. O+O+H2=O2+H2	1E+17	-1	0
322. O+H+H2=OH+H2	4.71E+18	-1	0
323. H+H+H2=H2+H2	6.53E+17	-1	0

*developed by Joseph W. Bozzelli at NJIT.

*for the nomenclature of the species contact either author or NJIT.

*since 1) the above reaction mechanism set is not published and 2) the work was concentrated on only a few species, the author feels that there is no need for presenting the complete nomenclature here.