Prediction of Species Concentration and Temperature Profile in Methanol Oxygen and Argon Flame

by

Mohammed Yaqub

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

MECHANICAL ENGINEERING

December, 1990

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This thesis, written by

MOHAMMED YAQUB

under the direction of his thesis committee, and approved by all the members, has been presented to and accepted by the Dean, College of Graduate Studies, in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN MECHANICAL ENGINEERING

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Dean College of Graduate Studies

Date : 13-5-91

This thesis is dedicated

To

My beloved mother, brothers and sisters

for the sacrifices they made to educate me

ACKNOWLEDGEMENT

Praise and gratitude be to Allah Almighty, with whose gracious help it was possible to accomplish this work. Acknowledgement is due to King Fahd University of Petroleum and Minerals for extending all facilities and providing financial support.

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LIST OF SYMBOLS

A_i : pre-exponential factor in the rate constant of the i^{th} reaction

a_{nk} : coefficients to fits of thermodynamic data

A : cross sectional area of the burner

c_p : constant pressure heat capacity of the mixture

c_{pk} : specific heat at constant pressure of the k^{th} species

c^0_{pk} : standard state specific heat at constant pressure of the k^{th} species

E_i : activation energy in the rate constant of the i^{th} reaction

H^0_k : standard state enthalpy of the k^{th} species

h_k : specific enthalpy of the k^{th} species

i : reaction index

I : total number of reactions

k : species index

k_{fi} : forward rate constant of the i^{th} reaction

k_{ri} : reverse rate constant of the i^{th} reaction

K : total number of species

K_{ci} : equilibrium constant in concentration units for the i^{th} reaction

K_{pi} : equilibrium constant in pressure units for the i^{th} reaction

N : number of coefficients in polynomial fits to c_p^0/R

p : pressure

q_i : rate of progress of the i^{th} reaction

R : universal gas constant

s_k^0 : standard state specific entropy of the k^{th} species

t : time coordinate for reaction

T : temperature

u : velocity of the fluid mixture

V_k : diffusion velocity of the k^{the} species

$\overline{W}$: mean molecular weight of the mixture

W_k : molecular weight of the k^{th} species

x_k : chemical symbol for the k^{th} species

X : spatial coordinate

X_k : mole fraction of k_{th} species

$[X_k]$: molar concentration of k^{th} species

Y_k : mass fraction of the k^{th} species

Greek Symbols

α_{ki} : enhanced third body efficiencies of the k^{th} species in the i^{th} reaction

β_i : temperature exponent in the rate constant of the i^{th} reaction

ρ : mass density

ν_{ki} : stoichiometric coefficients of the k^{th} species in the i^{th} reaction

ν'_{ki} : stoichiometric coefficients of the k^{th} reactant species in the i^{th} reaction

ν''_{ki} : stoichiometric coefficients of the k^{th} product species in the i^{th} reaction

$\dot{\omega}_k$: molar rate of production by chemical reaction of the k^{th} species per unit volume

φ : Equivalence ratio

THESIS ABSTRACT

NAME OF STUDENT	*: MOHAMMED YAQUB*
TITLE OF STUDY	*: Prediction of Species and Temperature Profile in Methanol, Oxygen and Argon Flame.*
MAJOR FIELD	*: Mechanical Engineering*
DATE OF DEGREE	*: December, 1990*

A chemical kinetic model is developed to predict the adiabatic flame temperature and the species concentration profiles for the methanol / oxygen /argon flames. The Modelling is carried out for atmospheric pressure and sub-atmospheric pressure (0.167 atmosphere) and for the equivalence ratio ranging from 0.6 to 1.5.

The reaction mechanism for the modelling is used as given by Thomas and Dryer in 1989. It contains 84 elementary reactions and 25 stable and unstable species. The concentration profiles of the stable and unstable species are computed as a function of distance over the burner and a comparison is made between the calculated and the experimental concentration profiles. As the reaction zone is very narrow in the case of atmospheric pressure flame, the comparison is made in the post flame zone only for the species CO_2, CO, H_2 *and* H_2O. *For low pressure flames, the comparisons are made for every point and a good quantitative and qualitative agreement is observed between the computed and the experimental concentration profiles in reaction zone. The Study shows a difference between the computed and the experimental concentrations for the post flame zone at low pressure and it may occur due to the diffusion effect which is neglected in this modelling work. A sharp concentration gradient for* CO *after the peak value at equivalence ratio 1.0 also suggests that the molecular diffusion may effect the profile.*

This modelling work is useful to analyse the methanol as an alternate fuel and provides an understanding of the combustion phenomena and exhaust emission of methanol.

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Dhahran , Saudi Arabia

December 1990

ملخص الرسالة

اسم الطالب : **محمد يعقوب**

عنوان الرسالة : تخمين لأصناف ودرجة حرارة اللهب لكل من الميثانول والأوكسجين والأرجون

مجال التخصص : هندسة ميكانيكية

تاريخ الدرجة العلمية : ديسمبر ١٩٩٠م

لقد تم فى هذا البحث تطوير نموذج حركية كيميائية لتخمين درجة اللهب الانعزالية وأصناف التركيز لكل من لهب الميثانول /الأوكسجين / الأرجون . كما تم تشكيل هذا النموذج عند ظروف الضغط الجوي والضغط الجوي المنخفض (0.167 ضغط جوى) وبنسبة تكافؤ من 0.6 إلى 1.5/ إستعمل ميكانزم التفاعل لهذا النوع كما اعطى من طرف آلية Dryerو Thomas فى 1989. ويحتوى هذا الميكانزم على 84 تفاعل اولى و 25 نوعاً مستقراً وغير مستقر . كما حسبت قطوع التركيز لكل من الأنواع المستقرة والغير مستقرة كدالة للمسافة فوق الحارق وتم عمل مقارنة مع قطوع التركيز الناتجة بالحساب مع تلك الموجودة بالتجارب . نظراً لان منطقة التفاعل ضيقة جداً عندما يكون اللهب عند الضغط الجوي ، فقد قورنت قيم تركيز كل من CO_2,Co,H_2,H_2O عند السنة اللهب فقط . أما بالنسبة للهب ذي الضغط المنفخض فقد تمت المقارنة لكل نقطة وقد لوحظ توافق نوعى وكمى جيد بين منحنيات تغير قيم التركيز المحسوبة والتجريبية ، للمركبات المذكورة ، فى منطقة التفاعل . ولقد أظهرت الدراسة اختلافاً بين قيم التركيزات المحسوبة والتركيزات المقاسة تجريبياً لمنطقة لسان اللهب عند الضغط المنخفض ويمكن ان يعزى ذلك الى تأثير عملية الانتشار والذي تم اهماله خلال هذا البحث .ولقد لوحظ ميل حاد لتركيز CO بعد النهاية العظمى عند نسبة تكافؤ 1.0التى تقترح أن الأنتشار الجزيئى يمكن ان يؤثر على القطاع . يستعمل هذا النموذج لتحليل الميثانول كوقود بديل والذي يعطينا توضيحاً لظاهرة الأحتراق وإخراج العادم المنبعث من الميثانول .

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران - المملكة العربية السعودية

ديسمبر ١٩٩٠م

CHAPTER 1

INTRODUCTION

1-1 Combustion Modelling and its Applications

Numerical modelling is becoming an important tool in explaining the behavior of large and complex systems. Modelling is used in such widely diverse fields as reaction kinetics, combustion, air pollution, weather prediction, atmospheric phenomena, operations research, population biology, reactor physics, and quantum mechanics. A model is defined as a functional relationship or relationships among various quantities involved in a physical process. The relationships may be expressed in the form of algebraic, differential, or integral equations, which need not necessarily possess an explicit analytical solution. In chemical kinetics mechanistic models involving elementary chemical reactions may be described (neglecting fluid mechanics) by a set of coupled nonlinear first-order ordinary differential equations (ODE's). The accumulation of developments in the areas of solution techniques, detailed experimental data, and computer capability has made feasible and desirable a general, broadly applicable computational solution of the chemical kinetic and fluid dynamic equations describing a laminar, steady, one-dimensional flame.

The objectives of the modelling of a flame are

1. To simulate combustion processes and to develop predictive capability for combustion behavior under various conditions.
2. To help in interpreting and understanding observed combustion phenomenon.
3. To substitute for difficult or expensive experiments.
4. To guide the design of combustion experiments.

The results obtained from modelling of a combustion reaction may be utilized in several areas, such as:

1. Combustion effect:
   - Formation of pollutants such as NO_x, CO and SO_x.
   - Formation of particulates such as soot, coke.
   - Methods of comparison and temperature control of exhaust.
2. Fire prevention and safety, and
3. Designing of combustion systems for:
   - I.C. Engines
   - Furnaces in coal fired power plants.
   - Rockets, air crafts, ships etc.

In this study, the selected fuel for modelling is methanol. Current concern over the dwindling global oil reserves has instigated research in alternative fuels. Also the pollutants from both mobile and stationary sources will be subjected to more stringent regulations. During the nineteenth century methanol was widely used as a fuel for heating, lightning and cooking until it was replaced by kerosene. Methanol now is recognized as an important alternate fuel candidate. It can be used to replace conventional fuels in a variety of combustion systems. The advantages and disadvantages of methanol in comparison with conventional fuel are given briefly in Sections 1.4 and 1.5.

1-2 Stoichiometry of Oxidation

The stoichiometric equations for combustion of methanol (CH_3OH) with oxygen and air are

$$CH_3OH + 1.5\,O_2 = CO_2 + 2\,H_2O \qquad (1.1)$$

$$CH_3OH + 1.5\,(O_2 + 3.76\,N_2) = CO_2 + 2\,H_2O + 5.64\,N_2 \qquad (1.2)$$

The relative mole ratios of the reactants and products, and the respective mass ratios of the reactions are given in Table 1.1 for methanol oxidation in oxygen and air.

The combustion of gasoline (Isooctane) with oxygen is:

$$C_8H_{18} + 12.5\,O_2 = 8\,CO_2 + 9\,H_2O \qquad (1.3)$$

In comparison, the water molecules in the product of gasoline is higher than

TABLE 1.1

Stoichiometric Oxidation Quantities for Methanol

	Oxygen		Air	
	Moles	Kg	Moles	Kg
Fuel	1.0	1.000	1.0	1.0
Oxidant	1.5	1.498	7.295	6.549
Reactants	2.5	2.498	8.295	7.549
Products	3.0	2.498	8.795	7.549
%Increase of moles	20.0	-	6.00	-

that of methanol. Fristrom and Westenberg [1] observed that H_2O promoted the oxidation of CO through the sequence

$$O + H_2O \rightarrow 2\,OH$$

$$OH + CO \rightarrow CO_2 + H$$

CO reaction with O atom is slow. Thermal NO is formed by the Zeldovich reactions

$$O + N_2 \rightarrow NO + N$$

$$N + O_2 \rightarrow NO + O$$

NO is not produced by OH attacking N_2. Thus, H_2O promotes CO oxidation and inhibits NO formation by converting O into OH radicals. This results in a reduction of formation of nitrogen oxides (NO_x) in the exhaust.

1-3 Reaction Mechanism

The combustion process described by the equation 1.1 does not represent the every step of the reaction. Nevertheless, it tells the overall picture of the reaction. In fact, a combustion process is so complex that a set of reactions is needed to explain the true behavior of the phenomenon. This set of reactions which consists of several elementary reactions containing stable and unstable species involved in the combustion process with Arrhenius rate constants is called the reaction mechanism. It provides the description of the elementary reaction steps to convert the input fuel and oxidizer to final products. Two mechanisms are available in literature for combustion of methanol and are discussed in chapter 2.

1-4 Advantages of Methanol

The advantages of methanol which make it a more favorable fuel than gasoline are:

1. A higher octane number which results in reduced tendency to knock in internal combustion engines.
2. A leaner misfire limit for flame, stable combustion and improved fuel efficiency.
3. A higher flame speed.
4. Greater stability for safer storage and transport because of its relatively high heat of vaporization, flash point and autoignition temperature.
5. The methanol fires can be extinguished with water because of the miscibility of methanol in water.
6. From its simple molecular structure, it can be concluded that pollutant generation from methanol combustion with oxygen should be limited to formaldehyde, carbon monoxide, unburned fuel, and possibly some simple hydrocarbons hence it has an ability to reduce the exhaust emissions.

1-5 Disadvantages of Methanol

The major disadvantages of using methanol as an automotive fuel are:

1. Its heat of combustion per unit volume is half that of isooctane which means a vehicle burning methanol would need a larger fuel tank to carry the same amount of potential energy as isooctane.
2. Its heat of vaporization is higher than isooctane which means sufficient heat is needed to vaporize methanol in the internal combustion engines.
3. Methanol is a strong solvent and softens many of the plastics or rubbers that are often used as gaskets and floats in conventional hydrocarbon fuel systems. This solvent action of methanol may damage the automotive components not designed to use methanol requiring the use of solvent resistant materials.
4. Corrosive action may result inside the engine because of the miscibility between methanol and water from local atmospheric moisture.
5. Vapor pressure characteristics of methanol may increase difficulty of cold start.

1-6 Objective of this Study

A lot of work has been done on methanol fuel characteristics, its production, its usage in I.C engines and other power appliances. But for designing purpose and from the pollution point of view, a complete knowledge of the combustion of fuel is required. Very little work has been done on this aspect of methanol.

In 1981, Abualhamayel [2] measured the temperature profile and stable species concentrations experimentally for $CH_3OH/O_2/Ar$ flames at various equivalence ratios and at two different pressures. These results are the basis of comparison for this modelling. The reaction mechanism is used as given by Thomas & Dryer [3] in 1989 which is actually the modification of the mechanism given by Westbrook & Dryer [4] in 1979. Before using the mechanism, a comparison is made between the two mechanisms. The computational results are compared with the experimental results and the discrepancies between experimental and computational results are discussed if observed.

CHAPTER 2

LITERATURE REVIEW

Research is being carried out on methanol in many aspects, such as its usage for I.C engines and other power generating machines, combustion characteristics (flame speed etc), and emissions etc.

Though Hagen [5] reported that methanol is not a good fuel for diesel engines but nowadays this statement has been proved false. A number of techniques by which alcohols can by used as fuels in diesel engines, in spite of the fact that alcohols in their neat form have properties much better suited to spark ignition engines, Ecklund et al., [6].

Fanick and Smith [7] discussed the methods for improving the safety aspects of methanol. It has been concluded that some additives should be added to methanol for safety. Following are the some of the recommended abilities of the additives.

1. Flame from combustion of methanol is essentially invisible in day light. In the case of accidental fire it is very difficult to detect and extinguish. Therefore an additive is needed to insure that methanol burns with a visible flame.

2. Reduce the potential for skin contact.
3. Give the fuel an unpleasant taste causing expectoration of any methanol accidentally taken into the mouth.
4. act as an emetic.
5. Produce an easily detectable odor.

Tsao and Li [8] made a performance comparison of gasoline water and gasoline methanol emulsions for a spark ignition engine.

It has been concluded that,

1. Based on test results, a commercial single cylinder, four stroke engine can be operated smoothly and stably with water/methanol gasoline mixtures at 2000 RPM.
2. Emissions of Hydrocarbon and Carbonmonooxide have been found to increase by 22 and 42% for the 10% volume and 15% volume water, gasoline fuels respectively in comparison with the base fuel which is gasoline. The 30% volume methanol-gasoline fuel displayed a reduction of 3% in unburned hydrocarbon emissions in comparison with base fuel.

As methanol can theoretically be dissociated into a 2/1 molar mixture of Hydrogen (H_2) and carbenmonooxide (CO) above room temperature, Brinkman and Stebar [9] studied experimentally the effect of dissociation of methanol prior to the ignition.

Dissociated methanol was suggested as a productive method for utilization of waste exhaust heat, because the heating value of dissociated methanol was 14% greater than that of methanol vapor (20% greater than liquid methanol).

An important area of research for a fuel is its emission. A detailed kinetic reaction mechanism is needed to analyze the exhaust. The result should be confirmed with the experimental study for the validity of the reaction mechanism. A very small work has been done on this aspect for methanol.

In 1979 Westbrook and Dryer [4] presented a reaction mechanism for methanol known as WD79 mechanism. The mechanism is given in Appendix I. It is composed of 84 elementary reactions and forward rate parameters. It is valid 1000-2800 K temperatures, 1-5 atmosphere pressures, and 0.05-3.0 equivalence ratios. Since that time WD79 mechanism has been used to study a wide variety of applications by many authors.

Westbrook and Dryer [10] is used the mechanism for prediction of laminar methanol flame properties. A one dimensional time dependent model is used to study the propagation of laminar methanol air flame. Solutions are used to study the dependence of laminar flame speed and flame structure on pressure, equivalence ratio, and unburned-gas temperature. The computed flame properties are compared with available experimental data. It has been concluded that at low pressures, flame speed and species concentration profiles vary only slightly with changes in pressure, but at high pressures, this variation is considerably larger.

After that the mechanism has been used either directly (Schoenung & Hanson, [11]; Leppared, [12]; Koda & Tanaka, [13]), or with a few modifications (Cathonnet et al., [14]; Westbrook, [15]; Andersson et al., [16]; Olsson et al., [17] and [18]), flame inhibition by *HBr* Westbrook, [19], flame quenching by walls Westbrook et al., [20].

The mechanism is also used by Olsson & Smooke [21] with some alternations in rate constants predicted by Warnatz [22] for modelling a premixed laminar formaldehyde flame.

In 1989 ,Thomas and Dryer [3] reported some new observations on methanol oxidation chemistry and revised the WD79 mechanism. Forward and reverse rate constants have been given separately and third bodies efficiencies have been mentioned. The mechanism with forward and reverse rate parameters is given in Table 2.2. New experiments were conducted in a turbulent flow reactor and data was collected for methanol oxidation at equivalence ratios in the range of 0.6 - 1.6 at atmospheric pressure. The results are compared with the computed results by using both the WD79 and the revised mechanism.

TABLE 2.1

REVISED METHANOL OXIDATION MECHANISM [3]. FORWARD AND REVERSE RATE PARAMETERS.

A in cm^3-mole-sec. units   *Ea in Cal/mole.*   *T in $^\circ K$*
$k = AT^n exp(-Ea/RT)$

SN	REACTIONS	Forward Rates Parameters			Reverse Rates Parameters		
		A	n	Ea	A	n	Ea
M1	$CH_3OH = CH_3 + OH$	5.40E15	00.00	00.917E5	5.63E11	00.40	-0.708E03
M2	$CH_3OH + O_2 = CH_2OH + HO_2$	2.05E13	00.00	00.449E5	1.06E13	-0.51	-0.150E04
M3	$CH_3OH + OH = CH_2OH + H_2O$	6.62E04	02.53	-0.959E3	8.92E03	02.53	00.218E5
M4	$CH_3OH + O = CH_2OH + OH$	3.88E05	02.50	00.308E4	4.96E03	02.50	00.877E4
M5	$CH_3OH + H = CH_2OH + H_2$	4.00E13	00.00	00.609E4	1.14E12	00.00	00.136E5
M6	$CH_3OH + H = CH_3 + H_2O$	6.45E11	00.00	00.530E4	5.85E07	00.78	00.314E5
M7	$CH_3OH + CH_3 = CH_2OH + CH_4$	4.15E01	03.17	00.717E4	2.43E02	02.94	00.161E5
M8	$CH_3OH + HO_2 = CH_2OH + H_2O_2$	3.98E13	00.00	00.194E5	3.13E15	-0.90	00.107E5
M9	$CH_2OH + M = CH_2O + H + M$	1.85E24	-2.50	00.342E5	1.06E23	-1.99	00.590E4

Table continued on next page...

Table (2.1) continued.

		Forward Rates Parameters			Reverse Rates Parameters		
SN	REACTIONS	A	n	Ea	A	n	Ea
M10	$CH_2OH+O_2=CH_2O+HO_2$	1.00E14	00.00	00.500E4	3.26E12	00.61	00.258E5
M11	$CH_4=CH_3+H$	8.51E14	00.00	00.104E6	7.42E12	00.00	-0.119E4
M12	$CH_4+H=CH_3+H_2$	2.25E04	03.00	00.875E4	6.72E02	03.00	00.771E4
M13	$CH_4+OH=CH_3+H_2O$	1.93E05	02.40	00.210E4	2.73E04	02.40	00.162E5
M14	$CH_4+O=CH_3+OH$	1.02E09	01.50	00.860E4	1.38E07	01.50	00.571E4
M15	$CH_4+HO_2=CH_3+H_2O2$	1.81E11	00.00	00.186E5	2.43E12	-0.66	00.100E4
M16	$CH_3+HO_2=CH_3O+OH$	2.00E13	00.00	00.00000	1.01E14	00.00	00.243E5
M17	$CH_3+OH=CH_2OH+H$	6.67E10	00.40	-0.707E3	5.78E14	-0.60	-0.377E4
M18	$CH_3+O=CH_2O+H$	7.83E13	00.00	00.00000	3.82E15	-0.15	00.702E5
M19	$CH_3+O_2=CH_3O+O$	1.99E18	-1.57	00.292E5	6.15E09	-1.83	00.108E4

Table continued on next page...

Table (2.1) continued.

		Forward Rates Parameters			Reverse Rates Parameters		
SN	REACTIONS	A	n	Ea	A	n	Ea
M20	$CH_2O+CH_3=CH_4+HCO$	5.54E03	02.81	00.586E4	1.65E03	03.05	00.204E5
M21	$CH_3+HCO=CH_4+CO$	1.20E14	00.00	00.00000	5.42E15	00.45	00.994E5
M22	$CH_3+HO_2=CH_4+O_2$	3.61E12	00.00	00.00000	4.08E13	00.00	00.553E5
M23	$CH_3O+M=CH_2O+H+M$	1.20E25	-2.70	00.306E5	7.18E23	-2.58	00.103E5
M24	$CH_3O+O_2=CH_2O+HO_2$	6.62E10	00.00	00.260E4	2.24E09	00.22	00.314E5
M25	$CH_2O+M=HCO+H+M$	1.05E32	-4.10	00.925E5	1.74E30	-4.10	00.245E4
M26	$CH_2O+OH=HCO+H_2O$	3.43E09	01.18	-0.447E3	1.38E08	01.43	00.282E5
M27	$CH_2O+H=HCO+H_2$	2.19E08	01.77	00.300E4	1.91E06	02.01	00.165E5
M28	$CH_2O+O=HCO+OH$	1.81E13	00.00	00.308E4	8.22E10	00.22	00.148E5
M29	$CH_2O+HO_2=HCO+H_2O_2$	1.99E12	00.00	00.117E5	7.96E12	-0.42	00.865E4

Table continued on next page...

Table (2.1) continued.

		Forward Rates Parameters			Reverse Rates Parameters		
SN	REACTIONS	A	n	Ea	A	n	Ea
M30	$HCO+OH=CO+H_2O$	3.01E13	00.00	0000.000	1.88E13	00.45	00.104E6
M31	$HCO+M=H+CO+M$	2.16E15	-0.11	00.203E4	1.56E15	-0.04	00.533E4
M32	$HCO+H=CO+H_2$	1.20E14	00.00	00.00000	1.64E13	00.45	00.884E5
M33	$HCO+O=CO+OH$	3.01E13	00.00	00.00000	2.15E12	00.43	00.866E5
M34	$HCO+HO_2-CO_2+OH+H$	0.00E13	00.00	00.00000	No Reverse Reaction		
M35	$HCO+O_2=CO+HO_2$	5.12E13	00.00	00.169E4	2.10E13	00.17	00.358E5
M36	$CO+OH=CO_2+H$	1.50E07	01.30	-0.765E3	2.54E13	00.17	00.250E5
M37	$CO+HO_2=CO_2+OH$	1.51E14	00.00	00.236E5	1.69E17	-0.52	00.847E5
M38	$CO_2+M=CO+O+M$	6.65E18	-0.78	00.123E6	4.00E13	00.00	-0.454E4
M39	$CO_2+O=CO+O_2$	1.60E16	-0.78	00.563E5	2.53E12	00.00	00.746E5

Table continued on next page...

Table (2.1) continued.

		Forward Rates Parameters			Reverse Rates Parameters		
SN	REACTIONS	A	n	Ea	A	n	Ea
M40	$H+O_2=O+OH$	1.97E14	00.00	00.165E5	7.37E11	00.36	-0.609E3
M41	$H_2+O=H+OH$	5.08E04	02.67	00.629E4	2.64E04	02.65	00.446E4
M42	$H_2O+O=OH+OH$	2.21E09	01.40	00.166E5	2.11E08	01.40	-0.396E3
M43	$H_2O+H=H_2+OH$	1.02E09	01.51	00.186E5	2.16E08	01.51	00.343E4
M44	$H_2O_2+OH=H_2O+HO_2$	7.00E12	00.00	00.143E4	7.03E10	00.67	00.331E5
M45	$H_2O+M=H+OH+M$	1.96E22	-1.62	00.119E6	2.25E22	-2.00	00.00000
M46	$HO_2+M=H+O_2+M$	2.46E15	00.00	00.482E5	2.00E15	00.00	-0.999E3
M47	$HO_2+O=OH+O_2$	1.81E13	00.00	-0.397E3	3.11E12	00.26	00.520E5
M48	$HO_2+H=OH+OH$	1.69E14	00.00	00.873E3	1.08E11	00.61	00.362E5
M49	$HO_2+H=H_2+O_2$	6.63E13	00.00	00.212E4	2.19E13	00.28	00.564E5

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Table (2.1) continued.

SN	REACTIONS	Forward Rates Parameters			Reverse Rates Parameters		
		A	n	Ea	A	n	Ea
M50	$HO_2+OH=H_2O+O_2$	1.45E16	-1.00	00.00000	2.18E16	-0.72	00.694E5
M51	$H_2O_2+O_2=HO_2+HO_2$	1.51E15	-0.39	00.387E5	1.00E13	00.00	00.979E3
M52	$H_2O_2+M=OH+OH+M$	1.20E17	00.00	00.455E5	9.00E11	00.90	-0.606E4
M53	$HO_2+H_2=H_2O_2+H$	1.41E11	00.66	00.245E5	4.82E13	00.00	00.794E4
M54	$OH+M=O+H+M$	4.66E17	-0.65	00.102E6	4.72E18	-1.00	00.00000
M55	$O_2+M=O+O+M$	1.58E17	-0.50	00.119E6	6.17E15	-0.50	00.00000
M56	$H_2+M=H+H+M$	4.58E19	-1.40	00.104E6	2.45E20	-1.77	00.959E3
M57	$C_2H_6=CH_3+CH_3$	2.17E22	-1.79	00.910E5	6.19E15	-0.91	00.705E3
M58	$C_2H_6+CH_3=C_2H_5+CH_4$	5.50E-1	04.00	00.827E4	1.55E-3	04.65	00.127E5
M59	$C_2H_6+H=C_2H_5+H_2$	5.54E02	03.50	00.516E4	4.63E-2	04.16	00.858E4

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Table (2.1) continued.

		Forward Rates Parameters			Reverse Rates Parameters		
SN	REACTIONS	A	n	Ea	A	n	Ea
M60	$C_2H_6+OH=C_2H_5+H_2O$	8.85E09	01.04	00.181E4	3.36E06	01.70	00.204E5
M61	$C_2H_6+O=C_2H_5+OH$	1.20E12	00.60	00.731E4	5.23E07	01.42	00.890E4
M62	$C_2H_5=C_2H_4+H$	1.23E09	01.19	00.372E5	2.00E09	01.19	00.642E3
M63	$C_2H_5+O_2=C_2H_4+HO_2$	8.43E11	00.00	00.387E4	9.35E12	-0.22	00.169E5
M64	$C_2H_5+C_2H_3=C_2+H_4+C_2H_4$	4.82E11	00.00	00.00000	3.12E15	-0.49	00.717E5
M65	$C_2H_4+O=CH_3+HCO$	1.32E08	01.55	00.427E3	9.98E03	02.19	00.265E5
M66	$C_2H_4=C_2H_2+H_2$	6.39E12	00.44	00.887E5	1.63E11	00.44	00.468E5
M67	$C_2H_4+H=C_2H_3+H_2$	1.32E06	02.53	00.122E5	7.59E02	03.07	00.785E4
M68	$C_2H_4+OH=C_2H_3+H_2O$	1.57E04	02.75	00.417E4	4.08E01	03.30	00.150E5
M69	$C_2H_4+O=CH_2O+CH_2$	2.50E13	00.00	00.500E4	1.05E09	00.82	00.115E5

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Table (2.1) continued.

SN	REACTIONS	Forward Rates Parameters			Reverse Rates Parameters		
		A	n	Ea	A	n	Ea
M70	$C_2H_3+M=C_2H_{2+}H+M$	4.18E29	-3.97	00.431E5	9.47E31	-4.70	00.587E4
M71	$C_2H_2+M=C_2H+H+M$	6.66E30	-3.70	00.127E6	9.03E27	-3.29	-0.469E4
M72	$C_2H_2+O_2=HCO+HCO$	4.00E12	00.00	00.280E5	4.45E07	00.92	00.608E5
M73	$C_2H_2+H=C_2H+H_2$	6.02E13	00.00	00.222E5	1.53E10	00.79	-0.614E4
M74	$C_2H_2+OH=C_2H+H_2O$	1.45E04	02.68	00.120E5	1.67E01	03.47	-0.118E4
M75	$C_2H_2+O=C_2H+OH$	3.20E15	-0.60	00.170E5	4.20E11	00.17	-0.132E5
M76	$C_2H_2+O=CH_{2+}CO$	1.75E13	00.00	00.318E4	4.17E07	01.33	00.498E5
M77	$C_2H+O_2=HCO+CO$	2.41E12	00.00	00.00000	1.43E10	00.59	00.150E6
M78	$C_2H+O=CO+CH$	1.81E13	00.00	00.00000	4.11E10	00.67	00.775E5
M79	$CH_2+O_2=CO+OH+H$	1.57E13	00.00	00.00000	No Reverse Reaction		

Table continued on next page...

Table (2.1) continued.

		Forward Rates Parameters			Reverse Rates Parameters		
SN	REACTIONS	A	n	Ea	A	n	Ea
M80	$CH_2+O=CO+H+H$	1.05E13	00.00	00.00000	No Reverse Reaction		
M81	$CH_2+H=CH+H_2$	9.64E13	00.00	00.00000	2.38E13	00.12	00.240E4
M82	$CH_2+OH=CH_2O+H$	2.41E13	00.00	00.00000	4.64E17	-0.56	00.781E6
M83	$CH+O_2=CO+OH$	1.35E11	00.67	00.257E5	2.51E10	01.02	00.184E6
M84	$CH+O_2=HCO+O$	1.00E13	00.00	00.00000	2.61E13	-0.08	00.721E5

$[M] = 1.0[N_2] + 5.0[CH_3OH] + 2.5[H_2] + 16.0[H_2O] + 1.9[CO]$
$+ 3.8[CO_2] + 16.0[CH_4] + 1.0[ALL\ OTHER\ SPECIES]$

Experimental Studies

The earliest studies done on methanol were on combustion and was conducted by Hinshelwood [23] in 1930. Pressure-time curves were used to study the kinetics of the reactions. It has been concluded that the oxidation reaction occurred by a chain mechanism and that the rate of reaction mainly depends upon the concentration of methanol (not oxygen).

In 1956, Bell & Tipper [24] studied methanol oxidation in a static reactor. In the mechanism, they concluded HO_2 as a chain propagating radical while the chain termination was suggested by the walls.

In 1955, Wiser & Hill [26] used the tube method of Gerstein [25] to determine the flame velocities of methanol and methane with air. For methanol, the flame velocity and adiabatic flame temperature was reported as 44.7 cm/sec and 2023 K respectively.

In 1956 Henderson & Hill [27] found the burning velocity for stoichiometric CH_3OH/Air mixture to be 47.2 cm/sec. The burning velocities and temperatures for a series of CH_3OH/O_2 flames with variant N_2 content were reported by De Wilde & Van Tiggleden [28] in 1968. Activation energy and reaction orders of 43-47 kcal/mole and unity were derived.

In 1978, Akrich et al., [29], studied the subatmospheric pressure flat flame combustion of methanol-air at various equivalence ratios. The chemical product species were found to be CO_2, CO, CH_3OH, H_2, and H_2O. The temperature distribution was reported. Overall rates for stable species were deduced from the mass and species conservation equations.

In 1981 Abualhamayel [2] studied the structure of laminar premixed flames of methane and methanol. Ar gas was used as a diluent. The experiments were conducted at two different pressures and at three equivalence ratios. Species concentrations and flames temperature profiles were observed.

Present study is motivated by this work. A numerical model is developed with the help of the reaction mechanism and the results are compared with the experimental studies available from [2].

CHAPTER 3

PREMIXED FLAME EQUATIONS & NUMERICAL SOLUTION METHOD

The equations governing steady, isobaric, quasi-one-dimensional flame propagation may be written as follows [30-31].

(i) Continuity equation,

$$M = \rho\, u\, A \tag{3.1}$$

(ii) Energy conservation equation,

$$M\frac{dT}{dx} - \frac{1}{c_p}\frac{d}{dx}\left(\lambda A\frac{dT}{dx}\right) + \frac{A}{c_p}\sum_{k=1}^{K}(\rho Y_k V_k)c_{pk}\frac{dT}{dx} + \frac{A}{c_p}\sum_{k=1}^{K}h_k\dot{\omega}_k W_k = 0 \tag{3.2}$$

(iii) Mass conservation equation for a specie,

$$M\frac{dY_k}{dx} + \frac{d}{dx}(\rho A Y_k V_k) - A\dot{\omega}_k W_k = 0 \qquad (k = 1,\dots,K) \tag{3.3}$$

(iv) Equation of state,

$$P = \frac{\rho R T}{\overline{W}} \tag{3.4}$$

In these equations x denotes the spatial coordinate; $\dot{M}$ the mass flow rate (which is independent of x),T, the temperature; Y_k the mass fraction of the kth species (there are K species); p, the pressure; u, the velocity of the fluid mixture; ρ, the mass density; W_k, the molecular weight of the kth species; $\overline{W}$, the mean molecular weight of the mixture; R, the universal gas constant; λ, the thermal conductivity of the mixture; c_p, the constant pressure heat capacity of the mixture; c_{pk}, the constant pressure heat capacity of the kth species; $\dot{\omega}_k$, the molar rate of production by chemical reaction of the kth species per unit volume; h_k, the specific enthalpy of the kth species; V_k, the diffusion velocity of the kth species; and A, the cross-sectional area of the stream tube encompassing the flame. By default, the stream tube area is taken to be constant and equal to unity.

For the numerical solution of the above equations, the following assumptions are made.

1. Model is 1-Dimensional.
2. Flame is adiabatic i.e no heat can be conducted, convected or radiated to the surrounding.
3. Diffusion of mass and conduction of heat are neglected and only convection is considered as a transport mechanism. This is true for reaction zone in which reaction mechanism is valid.

These assumptions omit the second and third term from the Energy conservation equation and second term from the mass conservation equation. Also by substituting the value of M form continuity equation into Energy and Species conservation equations, equations 3.2 & 3.3 become,

(i) Energy conservation equation,

$$\frac{dT}{dt} = -\frac{1}{\rho c_p}\sum_{k=1}^{K} h_k \dot{\omega}_k W_k \tag{3.5}$$

(ii) Mass conservation for a specie,

$$\frac{dY_k}{dt} = \frac{\dot{\omega}_k W_k}{\rho} \qquad (k=1,\ldots,K) \tag{3.6}$$

The variables appeared in equations 3.5 & 3.6 are explained in the following section [31].

3-1 Mean Molecular Weight ($\overline{W}$)

The mean molecular weight $\overline{W}$ is defined variously as

$$\overline{W} = \frac{1}{\sum_{k=1}^{K} \frac{Y_k}{W_k}} \tag{3.7}$$

$$\overline{W} = \sum_{k=1}^{K} X_k W_k \tag{3.8}$$

$$\overline{W} = \frac{\sum_{k=1}^{K} [X_k] W_k}{\sum_{k=1}^{K} [X_k]} \tag{3.9}$$

3-2 Density of mixture (ρ)

The density of mixture can be obtained from equation of state (3.4) as follows.

$$\rho = \frac{P\overline{W}}{RT} \tag{3.10}$$

3-3 Thermodynamic Properties

Thermodynamic properties are taken to be in the form of polynomial fits to the specific heat at constant pressure.

$$\frac{C^0_{Pk}}{R} = \sum_{n=1}^{N} a_{nk} T^{n-1} \tag{3.11}$$

The superscript 0 refers to the standard state one atmosphere. For perfect gases, however, the heat capacities are independent of pressure; the standard state values are the actual values. Other thermodynamic properties are given in terms of the fits to C^0_p. First, the enthalpy is given by

$$\frac{H^0_k}{R} = \int_0^T C^0_{P_k} dT \tag{3.12}$$

so that

$$\frac{H^0_k}{R} = \frac{\sum_{n=1}^{N} a_{nk} T^{n-1}}{n} + \frac{a_{N+1,k}}{T} \tag{3.13}$$

Where the constant of integration, $a_{N+1,k} \times R$ is the standard formation enthalpy at 0 K. Additionally, the standard state entropy is written as

$$\frac{S^0_k}{R} = \int_0^T \frac{C^0_{P_k}}{T} dT \tag{3.14}$$

so that

$$\frac{S^0_k}{R} = a_{1k} \ln T + \sum_{n=2}^{N} \frac{a_{nk} T^{(n-1)}}{(n-1)} + a_{N+2,k} \tag{3.15}$$

Where the constant of integration, $a_{N+2,k} \times R$, is the standard formation entropy at 0 K.

For the present work, the data for the polynomial fit is taken from the JANNAF TABLE [32]. In this case seven coefficients are needed for two temperature ranges. These fits are given in the following form:

$$C^0_{P_k} = a_{1k} + a_{2k} T + a_{3k} T^2 + a_{4k} T^3 + a_{5k} T^4 \tag{3.16}$$

$$H^0_k = a_{1k} + \frac{a_{2k}}{2} T + \frac{a_{3k}}{3} T^2 + \frac{a_{4k}}{4} T^3 + \frac{a_{5k}}{5} T^4 + \frac{a_{6k}}{T} \tag{3.17}$$

$$S^0_k = a_{1k} \ln T + a_{2k} T + \frac{a_{3k}}{2} T^2 + \frac{a_{4k}}{3} T^3 + \frac{a_{5k}}{4} T^4 + a_{7k} \qquad (3.18)$$

Other thermodynamic properties are easily given in terms of C^0,H^0, and S^0.

3-4 Chemical Rate Expressions

The net chemical production rate $\dot{\omega}_k$ of each species results from a competition between all the chemical reactions involving that species. We presume that each reaction proceeds according to the law of mass action. The details of the chemical reaction equations and the thermochemical properties are described in the following section.

Consider I elementary reversible (or irreversible) reactions involving chemical species which can be represented in the general form given below,

$$\sum_{k=1}^{K} \nu'_{ki} \chi_k \rightarrow \sum_{k=1}^{K} \nu''_{ki} \chi_k \qquad (i=1,\ldots,I) \qquad (3.19)$$

The stoichiometric coefficients ν_{ki} are integers and χ_k is the chemical symbol for the k^{th} species. Normally a reaction involves three or four species; hence the ν_{ki} matrix is quite sparse for a large set of reactions.

The production rate $\dot{\omega}_k$ of the k^{th} species can be written as a summation of the rate of progress variables for all reactions involving the k^{th} species:

$$\dot{\omega}_k = \sum_{i=1}^{I} \nu_{ki} q_i \qquad (k=1,...,K) \tag{3.20}$$

where

$$\nu_{ki} = (\nu''_{ki} - \nu'_{ki}) \tag{3.21}$$

The rate of progress variable, q_i, for the i^{th} reaction is given by the difference of the forward rates minus the reverse rates as

$$q_i = k_{f_i} \prod_{k=1}^{K} [X_k]^{\nu'_{ki}} - k_{r_i} \prod_{k=1}^{K} [X_k]^{\nu''_{ki}} \tag{3.22}$$

where $[X_k]$ is the molar concentration of the k^{th} species and k_{f_i} and k_{r_i} are the forward and reverse rate constants of the i^{th} reaction. The forward rate constants for the I reactions are assumed to have the following Arrhenius temperature dependence:

$$k_{f_i} = A_i T_i^{\beta} \exp\left[- \frac{E_i}{R_c T} \right] \tag{3.23}$$

where the pre-exponential factor A_i , the temperature exponent β_i , and the activation energy E_i usually come from experiment. For all reactions the parameters in Eq. (3.23) are required input to the CHEMKIN package [31] for each reaction.

If the parameters appeared in equation (3.23) are not given for the reverse reaction, then the the reverse rate constants k_{r_i} are related to the forward rate constants through the equilibrium constants as

$$k_{r_i} = \frac{k_{f_i}}{K_{c_i}} \tag{3.24}$$

Although K_{c_i} is given in concentration units, the equilibrium constants K_{p_i} are obtained with the relationship

$$K_{c_i} = K_{p_i}\left(\frac{P_{atm}}{R\,T}\right)^{\sum_{k=1}^{K}\nu_{ki}} \tag{3.25}$$

where P_{atm} denotes atmospheric pressure. The equilibrium constants K_{p_i} are obtained with the relationship

$$K_{p_i} = \exp\left(\frac{\Delta S^{\circ}_{i}}{R} - \frac{\Delta H^{\circ}_{i}}{R\,T}\right) \tag{3.26}$$

The Δ refers to the change that occurs in passing completely from reactants to products by the i^{th} reaction. More specifically

$$\frac{\Delta S^{\circ}_{i}}{R} = \sum_{k=1}^{K} \nu_{ki} \frac{S^{\circ}_{k}}{R} \tag{3.27}$$

$$\frac{\Delta H^{\circ}_{i}}{R\,T} = \sum_{k=1}^{K} \nu_{ki} \frac{H^{\circ}_{k}}{R\,T} \tag{3.28}$$

Where S^0 and H^0 can be calculated from equations 3.17 & 3.18.

3-5 Three Body Reactions

In some reactions a third body is required for the reaction to proceed. This is often the case in dissociation or recombination reactions. When a third body is needed, the rate of progress variable is different from the Eq 3.22 by the first factor in the equation below.

$$qi = \left(\sum_{k=1}^{K} \alpha_{ki}[X_k]\right)\left(k_{f_i}\prod_{k=1}^{K}[X_k]^{\nu'_{ki}} - k_{ri}\prod_{k=1}^{K}[X_k]^{\nu''_{ki}}\right) \tag{3.29}$$

All species contribute equally as third bodies, then all $\alpha_{ki,}$ = 1 and the first factor is the total concentration of the mixture.

$$\sum_{k=1}^{K}[X_k] = \frac{P}{RT} \tag{3.30}$$

However, it is often the case that some species act more efficiently as third bodies than do others. The $\alpha_{ki,}$ coefficients are then used to specify the increased efficiency of the k^{th} species in the i^{th} reaction. Note also that if a species is to be excluded from acting as a third body, then $\alpha_{ki} = 0$ for that species. Any α_{ki} which differ from 1 must be input to the CHEMKIN INTERPRETER.

3-6 Numerical Solution Method

The CHEMKIN [31] (Kee et al.) general purpose chemical kinetics computer program developed at the Sandia Laboratories, Livermore, California is used in this study. As discussed in previous section, the model used is one-dimensional and adiabatic, and involved only convection as the mechanism of transport. Diffusion of heat and mass are also neglected. In the absence of diffusion effects, mass, momentum and energy conservation equations reduce to initial value problems. The model, therefore, involves the specification of an initial mixture composition and temperature, followed by direct integration of the conservation equations until the adiabatic flame temperatures are reached. The same procedure was used by Selim M.Senkan [33] for chemical kinetic modelling of $C_2HCl_3 / N_2 / O_2$ flame. The LSODE program [34] developed at the Lawrence Livermore Laboratory Livermore, California was used to integrate the conservation equations and found to be highly reliable for the solution of very wide range of stiff initial value problem. The more details of CHEMKIN and LSODE are presented in Appendix II.

3-7 Initial Conditions

Initial conditions e.g, initial concentration of the species, initial temperature of the reaction zone and pressure are the input in the program. A detail chemical reaction mechanism with Arrhenius rate constant is also needed as the input.

CHAPTER 4

RESULTS & DISCUSSIONS

4-1 Comparison of the Mechanisms

A Comparison between the two mechanisms listed in Appendix I and Table 2.2 is presented in this section. This is carried out for the following reasons.

1. To make the decision that which mechanism should be used for this modelling purpose.
2. To check the validity and the working capacity of the CHEMKIN package as it is being used for the first time at KFUPM mainframe.

The comparisons are made for three different initial conditions given in Table 4.1 [3]. The predicted profiles for temperature and methanol (CH_3OH), oxygen (O_2), hydrogen (H_2), form aldehydes (CH_2O), carbonmonooxide (CO), carbondioxide (CO_2), and, water (H_2O) are plotted through Figures 4.1 to 4.3. Nitrogen is used as a diluent and it is assumed to be inert for the study.

The major difference between the prediction of the two mechanisms is the reaction time. For the revised mechanism, the reaction time is shorter than the WD79 mechanism. This is due to the rate of the several important reactions have been increased. For example, the rate of reaction No 10 is increased by 160 times, reaction 9 by 170 times and reaction 35 by 180 times. A brief comparison

TABLE 4.1

(a) Initial Conditions for Comparison of the Mechanisms [3]

Equivalence Ratio	Initial Temp(K)	Initial Mole Percentage		
		CH_3OH	O_2	N_2
0.6	1027	0.779	1.980	97.2404
1.2	1030	0.943	1.160	97.8964
1.6	1034	1.010	0.961	98.0284

TABLE 4.1

(b) Initial Mole Fractions of Minor Species [3]

$H_2,HO_2,H_2O_2,H_2O,CO,CH_2O$	10^{-06}
$H,OH,CO_2,CH_2OH,CH_4,CH_3$	10^{-09}
O,CH_3OH,HCO,C_2H_6	10^{-20}
CH_2,CH,C_2H	10^{-30}

between the two mechanisms is given in the following sections. A detailed comparison between the two mechanism and with the experimental results is given in Thomas and Dryer [3], where it was concluded that the existing model, WD79, has errors which can be minimize by updating the model with more recent data.

For Equivalence ratio 0.6 and for WD79 mechanism, rapid reaction starts after 50 msec and completes in about 250 msec, Figure 4.1 (a), while for the revised mechanism it starts after 20 msec and completes in 80 msec Figure 4.1 (b). The final temperature and the equilibrium concentrations for the fuel, oxidizer and other species are nearly the same. However peak concentration of CO is 50 % higher in case of WD79 mechanism. Due to equivalence ratio less than 1, the fuel is depleted fully and oxygen remains in the final equilibrium products.

For the flame at Equivalence ratio 1.0, the rapid reaction starts just before 50 msec in the WD79 mechanism and after 10 msec in the revised mechanism. The reaction completes about after 220 msec and 80 msec in the WD79 mechanism and revised mechanism respectively, Figure 4.2 (a) and (b). The equilibrium concentration of CO_2 and H_2 are 20 % higher in the revised mechanism while CO is 50 % less. The peak concentrations of H_2 is also 30 % higher in the revised mechanism. As the fuel and oxidizer are in exact proportion, no fuel or oxidizer is predicted in equilibrium state i.e all fuel is

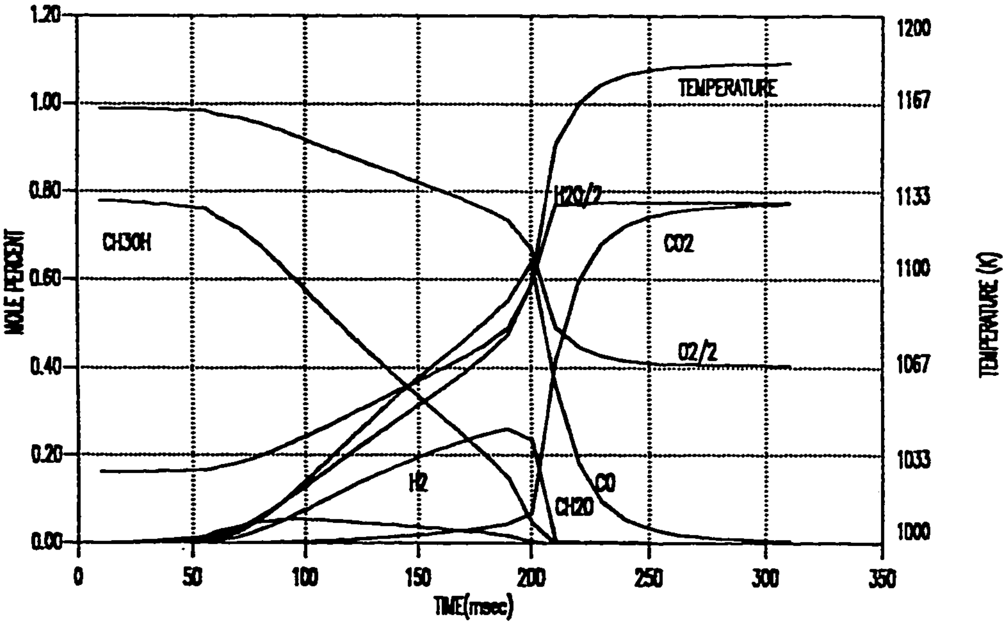

Fig. 4.1(a) Temperature and Stable Species Concentration profiles. Predicted by WD79 Mechanism (Equivalence Ratio = 0.6).

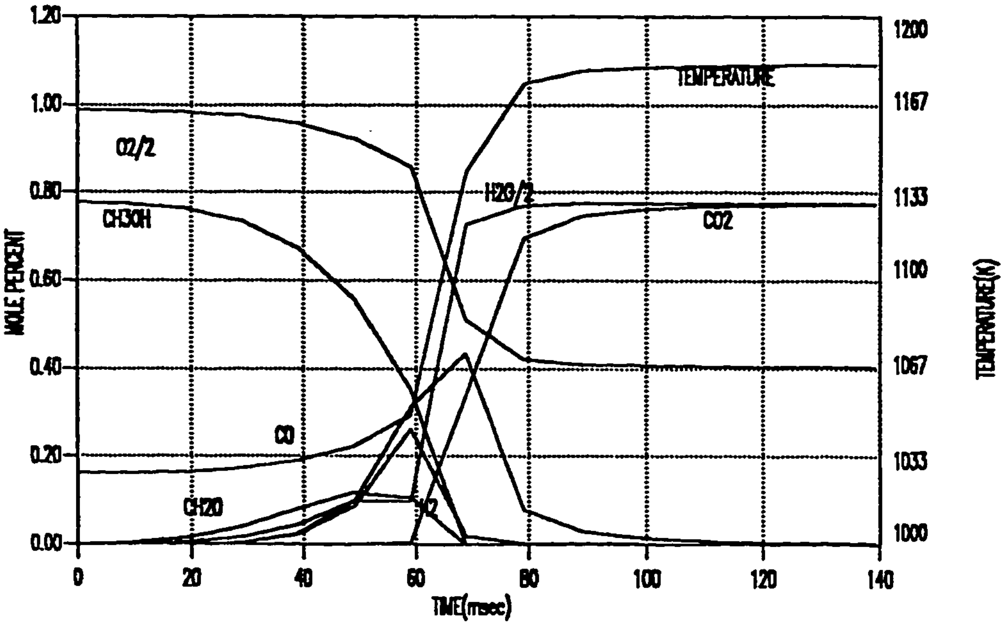

Fig. 4.1(b) Temperature and Stable Species Concentration profiles. Predicted by Revised Mechanism (Equivalence Ratio = 0.6).

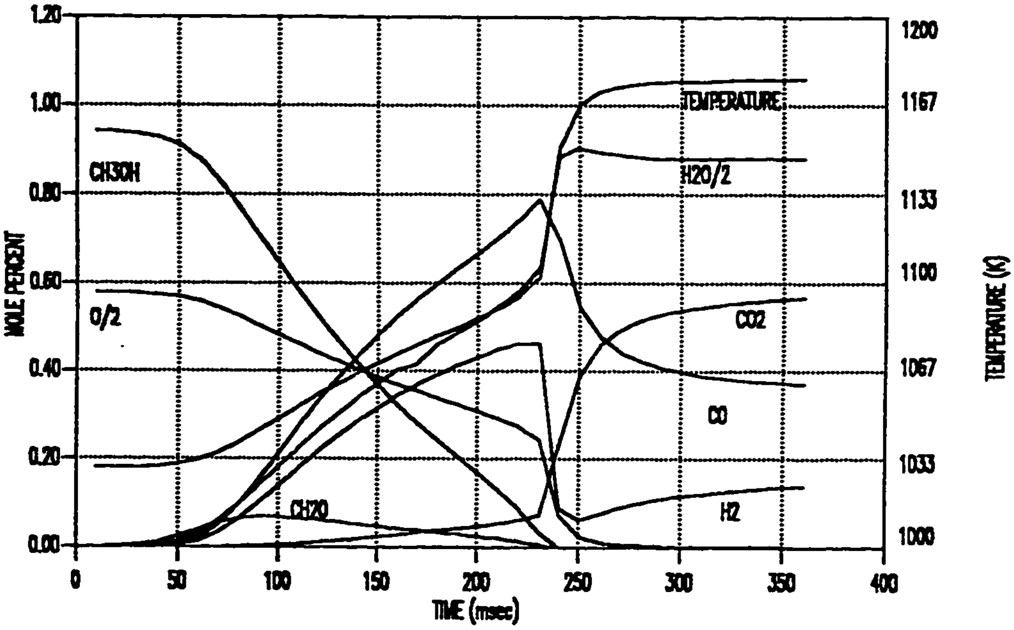

Fig. 4.2(a) Temperature and Stable Species Concentration profiles. Predicted by WD79 Mechanism (Equivalence Ratio = 1.0).

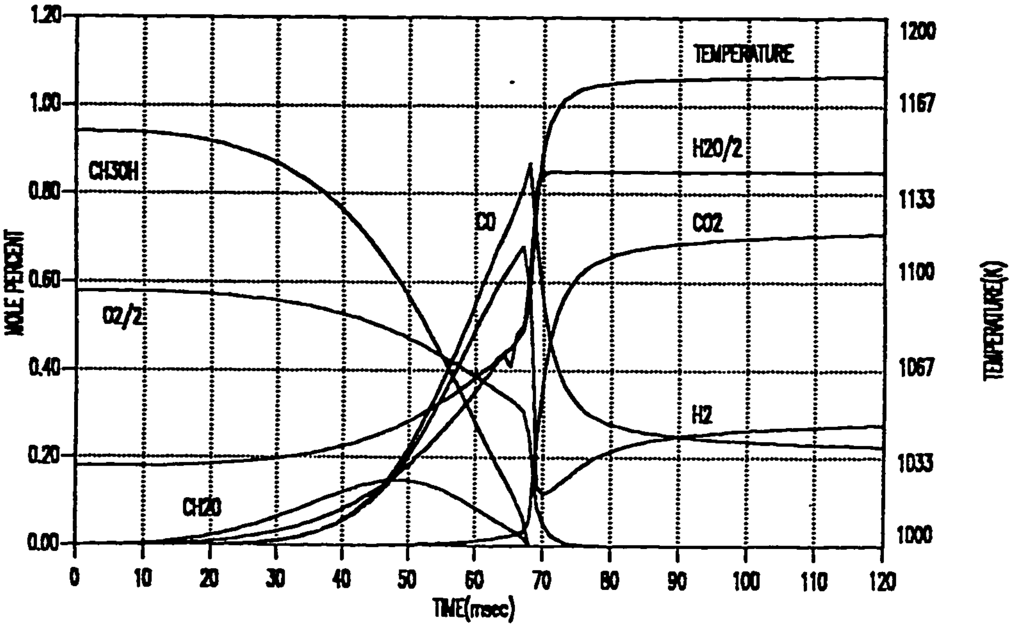

Fig. 4.2(b) Temperature and Stable Species Concentration profiles. Predicted by Revised Mechanism (Equivalence Ratio = 1.0).

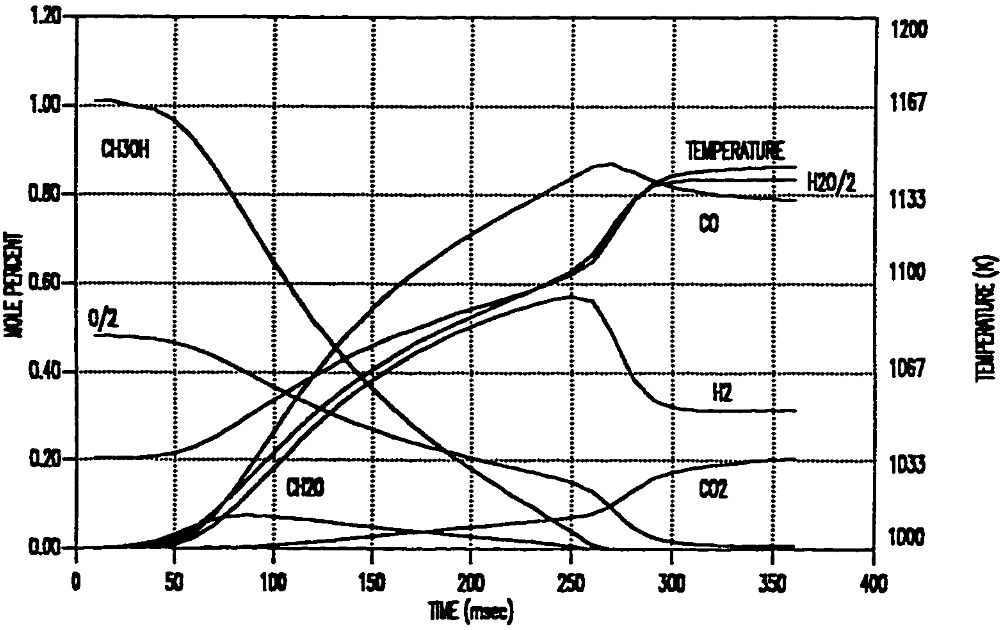

Fig. 4.3(a) Temperature and Stable Species Concentration profiles. Predicted by WD79 Mechanism (Equivalence Ratio = 1.6).

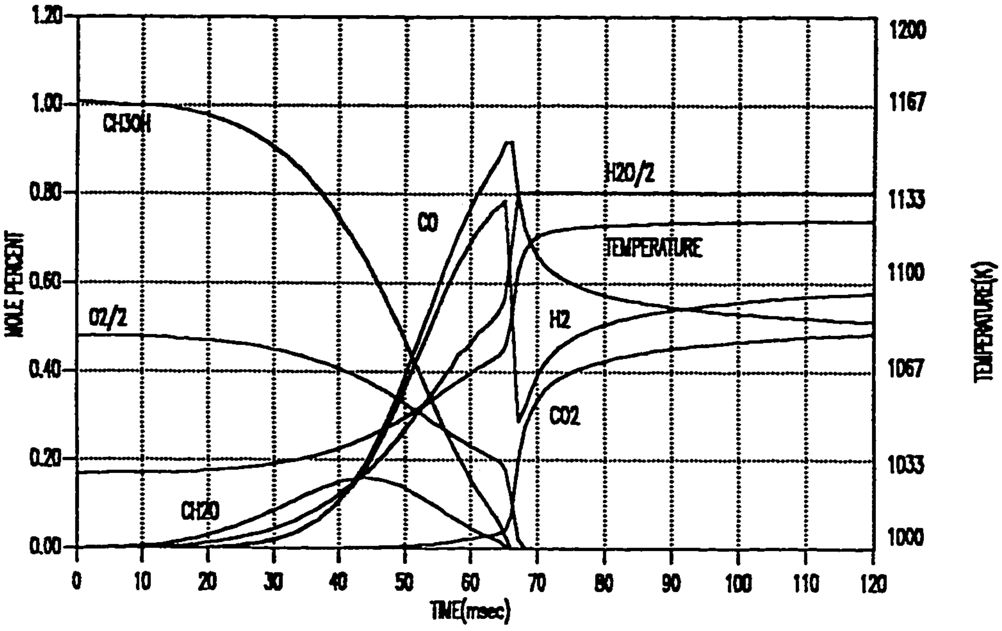

Fig. 4.3(b) Temperature and Stable Species Concentration profiles. Predicted by Revised Mechanism (Equivalence Ratio = 1.6).

consumed with oxidizer.

For the flame at Equivalence ratio 1.6, the duration of the reaction predicted between 50 msec to 300 msec by the WD79 mechanism, Figure 4.3 (a), while in the revised mechanism, the duration is between 10 msec to 90 msec Figure 4.3 (b). The final temperature is almost the same. Fuel is depleted fully in both mechanisms although the equivalence ratio is 1.6. It might be due to dissociation of CO_2 into CO and O_2. Dissociated oxygen helps the fuel to burn completely. A higher concentration of CO (0.8%) and less concentration of CO_2 (0.2%) in post flame zone is also an indication of this justification.

4-2 Conclusion from Comparisons

1. The revised mechanism predicts the concentration profile closer to the profiles obtained by the experimental study. If the experimental temperature profile is imposed on the model, the results are even more closer, showed by Thomas and Dryer [3]. They have concluded that the revised mechanism is more reliable for modelling the flame. For this reason, the revised mechanism is used in this modelling work.
2. The results plotted in Figures 4.1 to 4.3 are in good agreement with [3] and hence concluded that the CHEMKIN package can be used for this modelling work on mainframe available at KFUPM.

4-3 Initial Conditions for CH_3OH / O_2 / Ar Flame

The exhaust of Methanol/Oxygen flame is predicted at different equivalence ratios. Argon is used as a diluent. The mole ratios of Ar / O_2 is taken as 3.0. It is because of the experimental data available from Abualhamayel [2]. Diluent gas is used to reduce the adiabatic flame temperature and to increase the reaction time. It helps to analyze the reaction zone and the species and temperature profiles more deeply. Initial conditions for fuel, oxidizer and diluent are given in Table 4.2 for each study.

Initial temperature is taken as 1000 K which is the lower limit for the validity of the mechanism. The modelling is done for 10 equivalence ratios starting from 0.6 to 1.5 with an interval of 0.1. Out of 26 species only a few important stable and unstable species are plotted and discussed. The plotted stable species are $CH_3OH, O_2, H_2O, CO_2, CO, H_2$ and unstable species are $CH_2O, OH, H, O, H_2O_2, HO_2$. These are plotted in Figures 4.4 to 4.13.

4-4 Reaction Time

The reaction zone is supposed to be started when the rapid changes in temperature and species concentration are observed. In this study it is about the 5% change of the initial temperature. The reaction ends when the temperature stabilized, the corresponding time is characterized here as the final time.

As the equivalence ratio increases, the starting time of reaction (or reaction

TABLE 4.2

Initial Conditions for Modelling Calculations [2]

$A_r/O_2 = 3.0$

Study	Equivalence Ratio	Initial Temp(K)	Initial Mole Percentage		
			CH_3OH	O_2	A_r
a	0.6	1000	9.09	22.73	68.18
b	0.7	1000	10.45	22.39	67.16
c	0.8	1000	11.76	22.06	66.18
d	0.9	1000	13.04	21.77	65.19
e	1.0	1000	14.29	21.43	64.28
f	1.1	1000	15.49	21.13	63.38
g	1.2	1000	16.67	20.83	62.50
h	1.3	1000	17.81	20.55	61.64
i	1.4	1000	18.92	20.25	60.83
j	1.5	1000	20.00	20.00	60.00

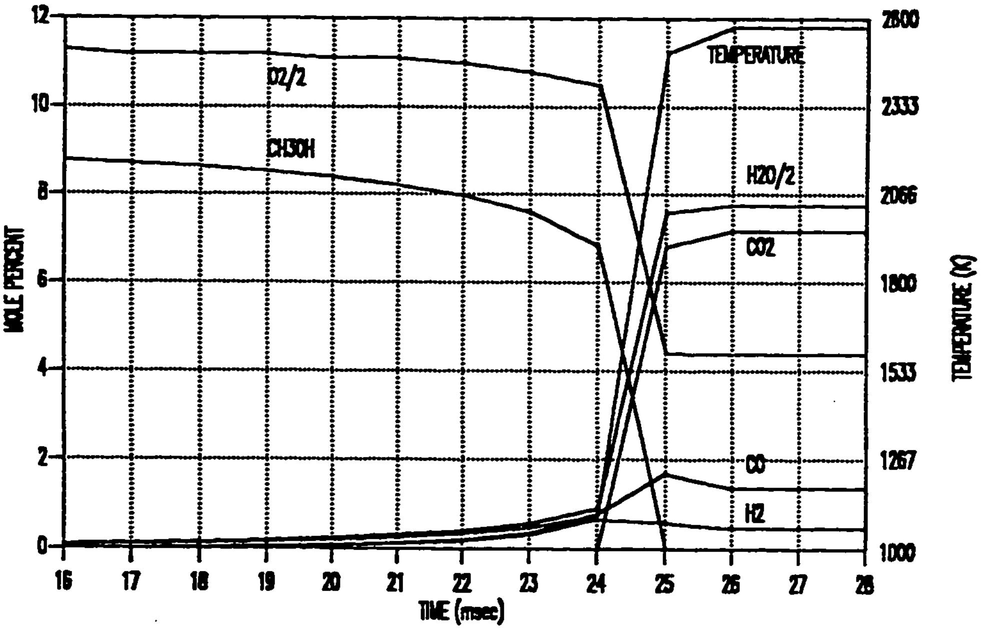

Fig. 4.4(a) Temperature and Stable Species Concentration profiles. (Equivalence Ratio = 0.6).

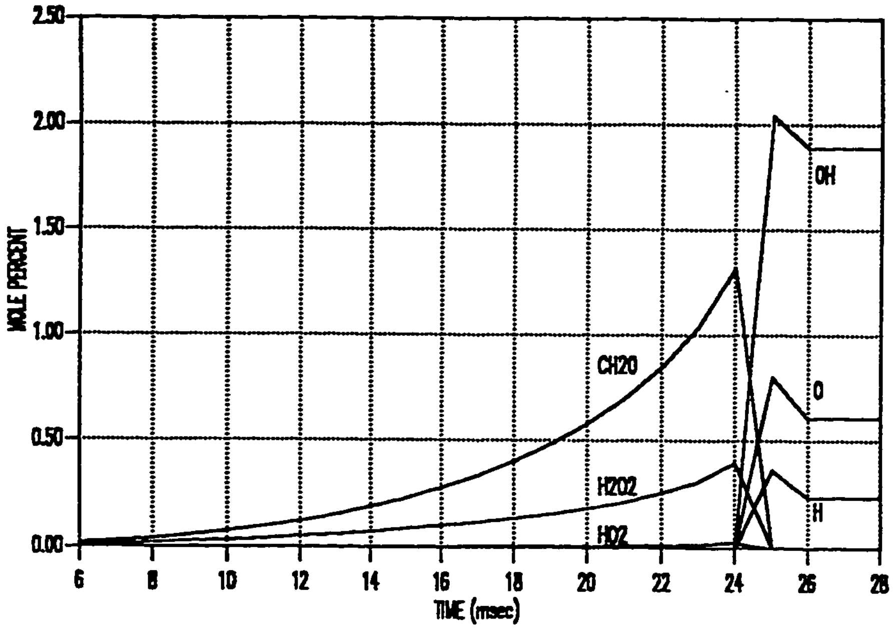

Fig. 4.4(b) Unstable Species Concentration profiles. (Equivalence Ratio = 0.6).

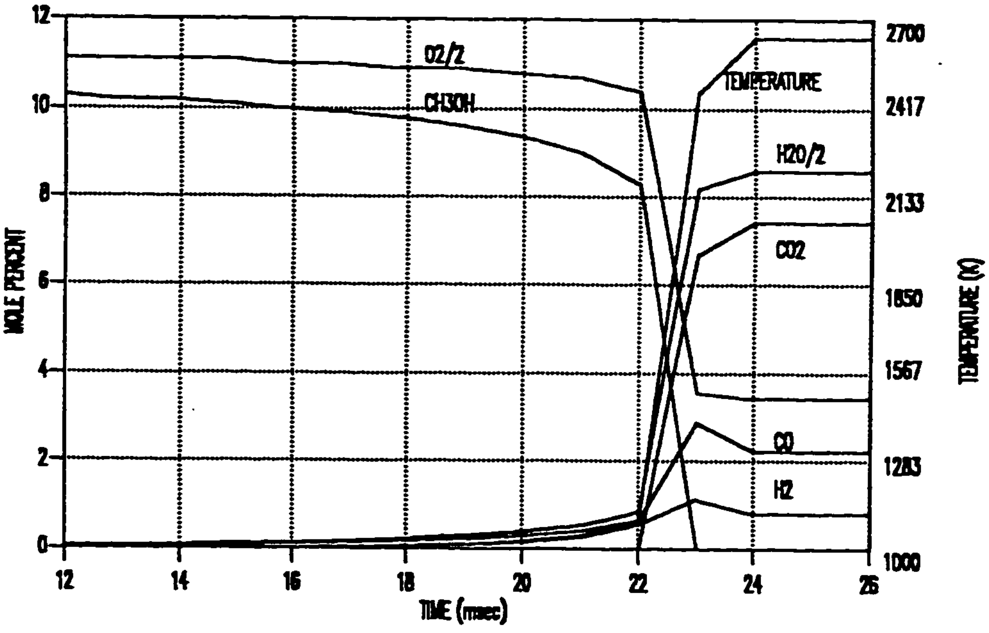

Fig. 4.5(a) Temperature and Stable Species Concentration profiles. (Equivalence Ratio = 0.7).

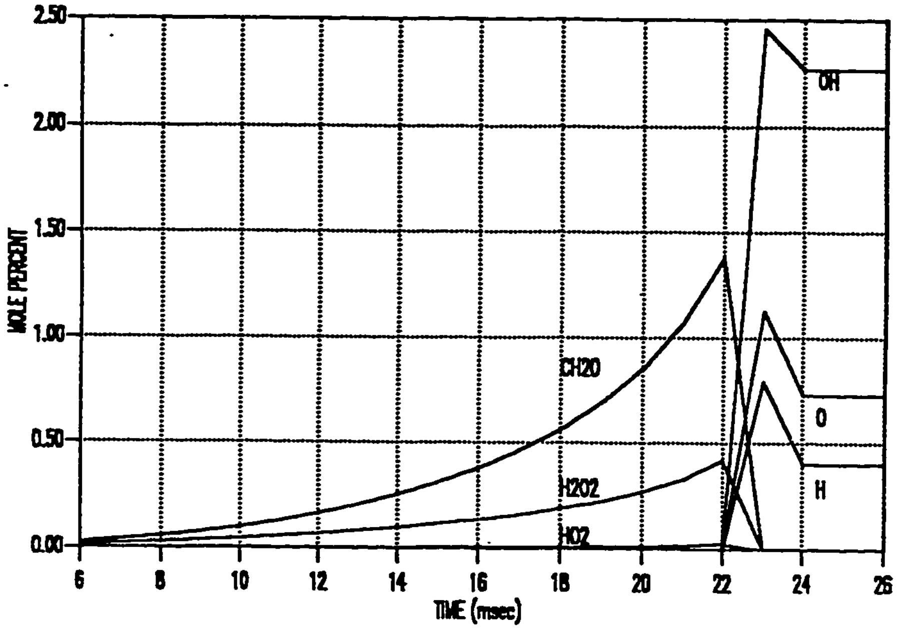

Fig. 4.5(b) Unstable Species Concentration profiles. (Equivalence Ratio = 0.7).

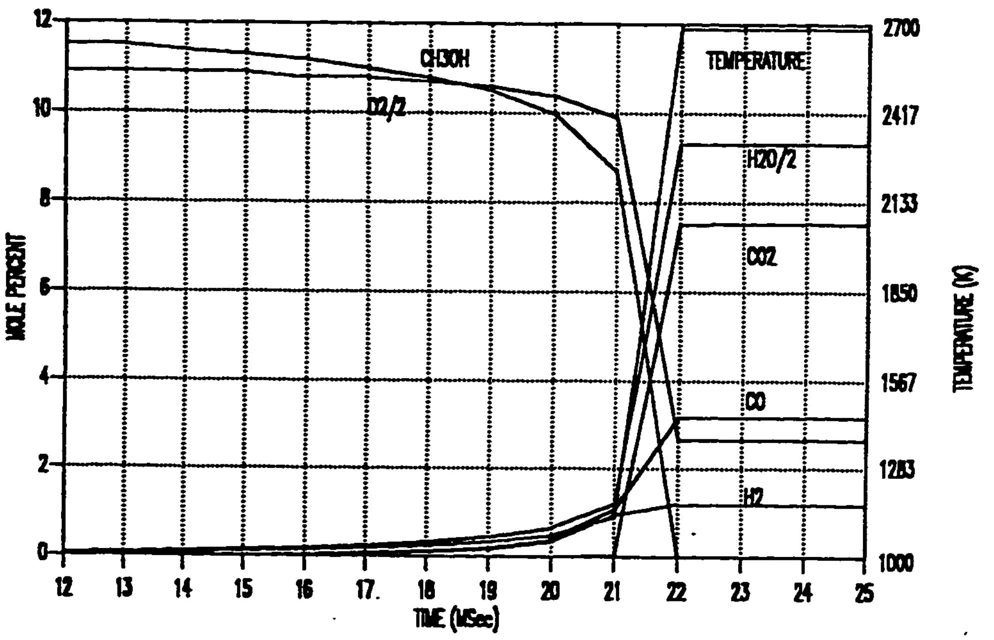

Fig. 4.6(a) Temperature and Stable Species Concentration profiles. (Equivalence Ratio = 0.8).

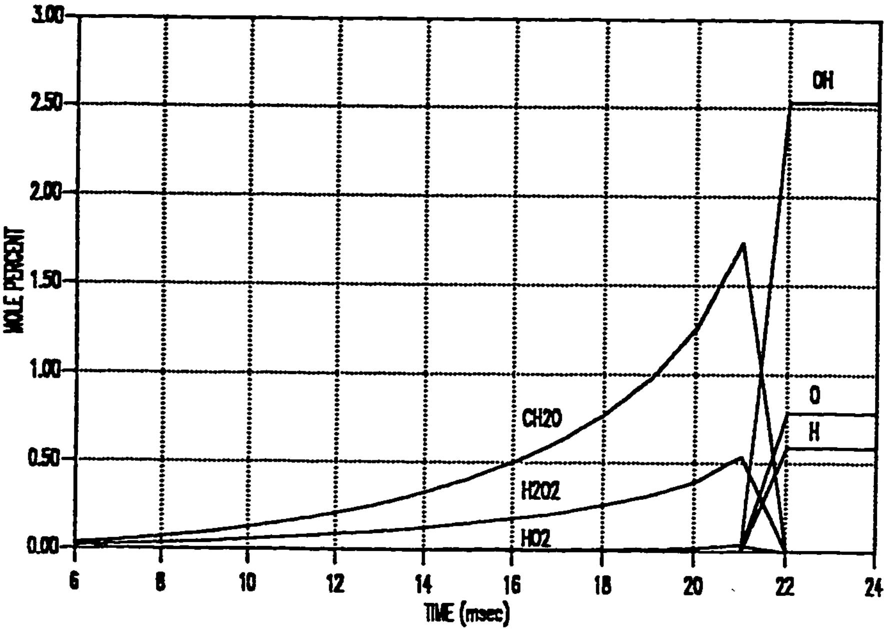

Fig. 4.6(b) Unstable Species Concentration profiles. (Equivalence Ratio = 0.8).

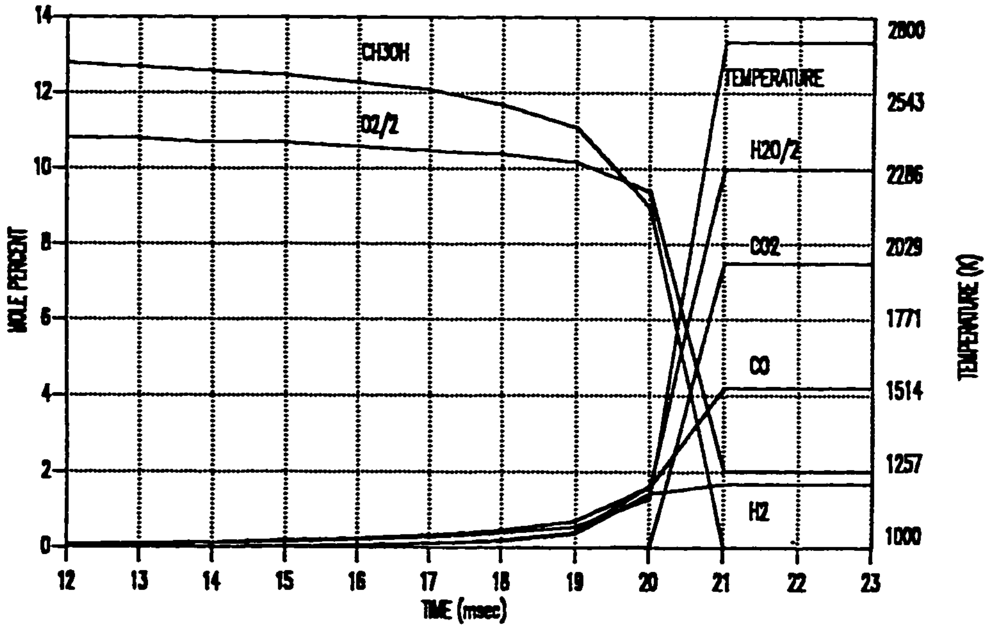

Fig. 4.7(a) Temperature and Stable Species Concentration profiles.
(Equivalence Ratio = 0.9).

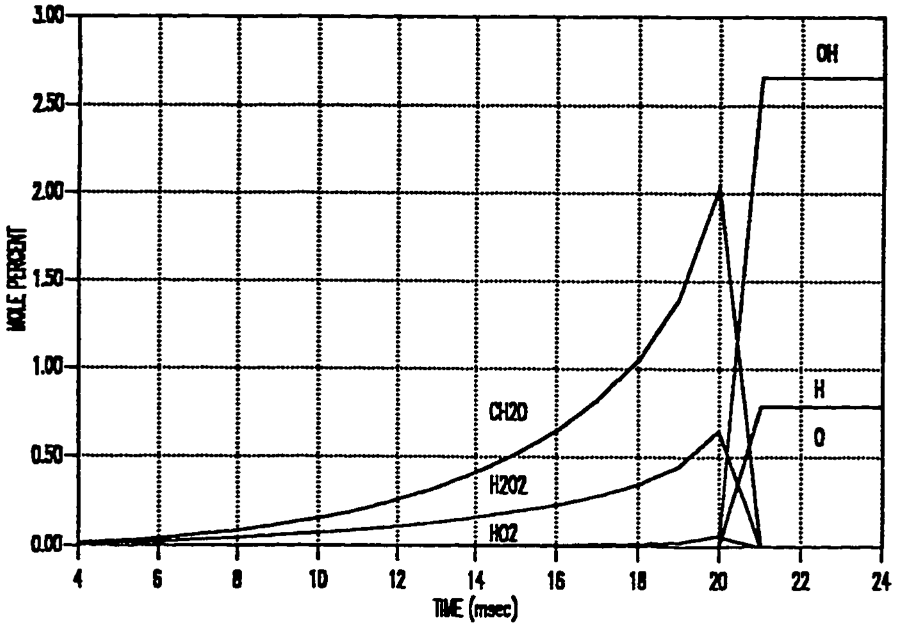

Fig. 4.7(b) Unstable Species Concentration profiles.
(Equivalence Ratio = 0.9).

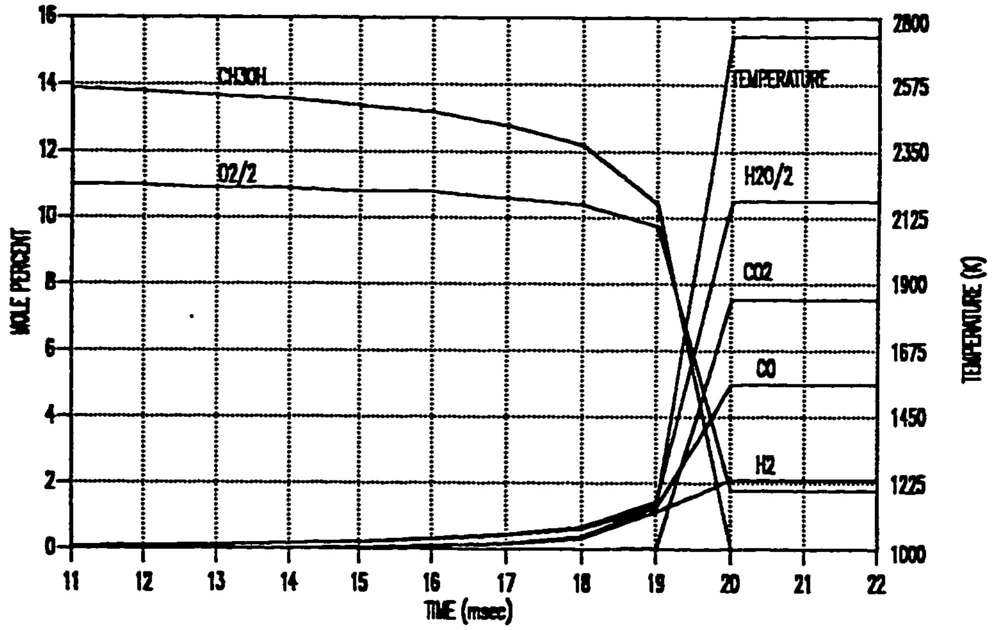

Fig. 4.8(a) Temperature and Stable Species Concentration profiles. (Equivalence Ratio = 1.0).

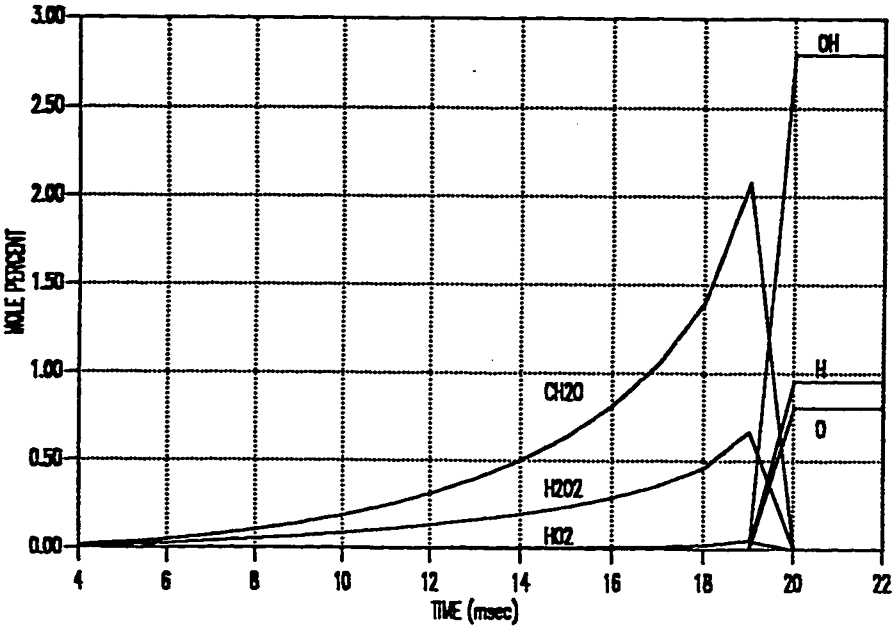

Fig. 4.8(b) Unstable Species Concentration profiles. (Equivalence Ratio = 1.0).

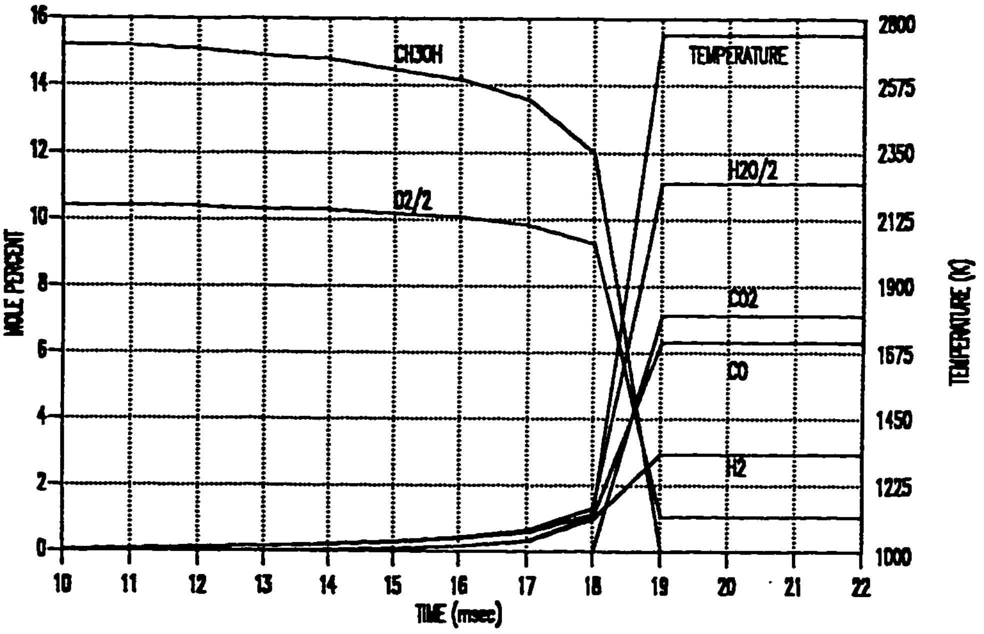

Fig. 4.9(a) Temperature and Stable Species Concentration profiles. (Equivalence Ratio = 1.1).

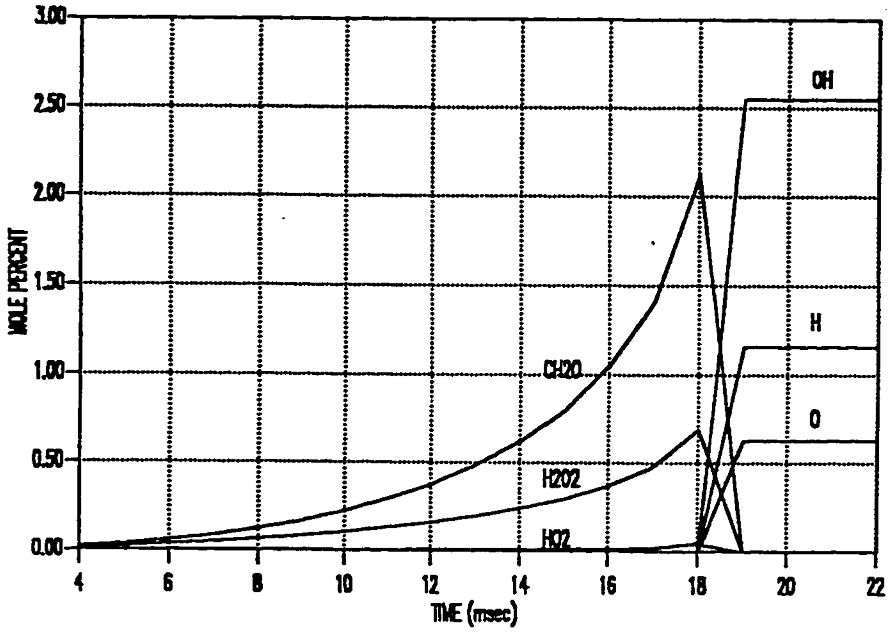

Fig. 4.9(b) Unstable Species Concentration profiles. (Equivalence Ratio = 1.1).

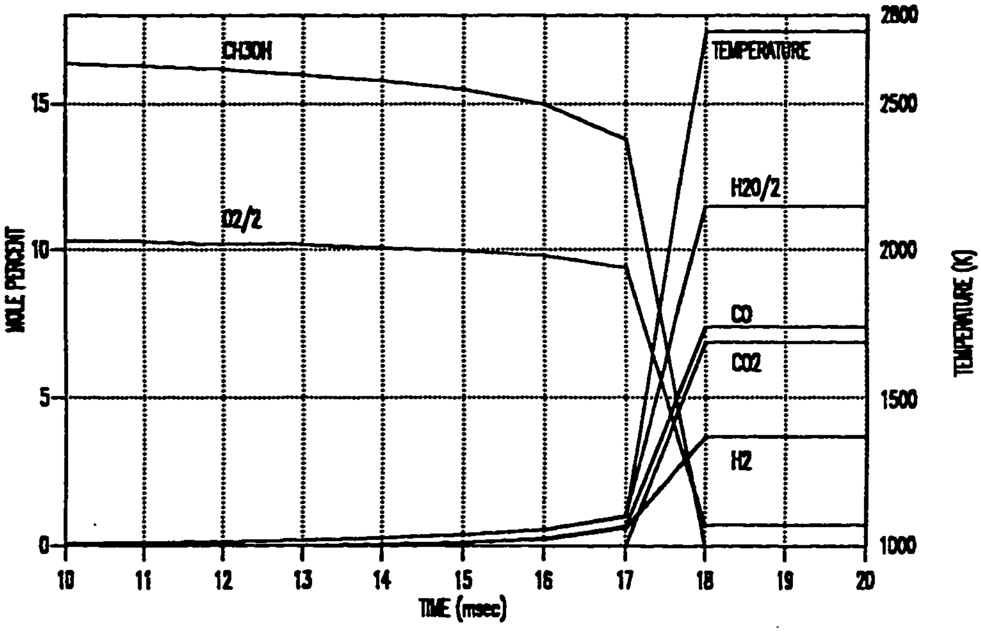

Fig. 4.10(a) Temperature and Stable Species Concentration profiles. (Equivalence Ratio = 1.2).

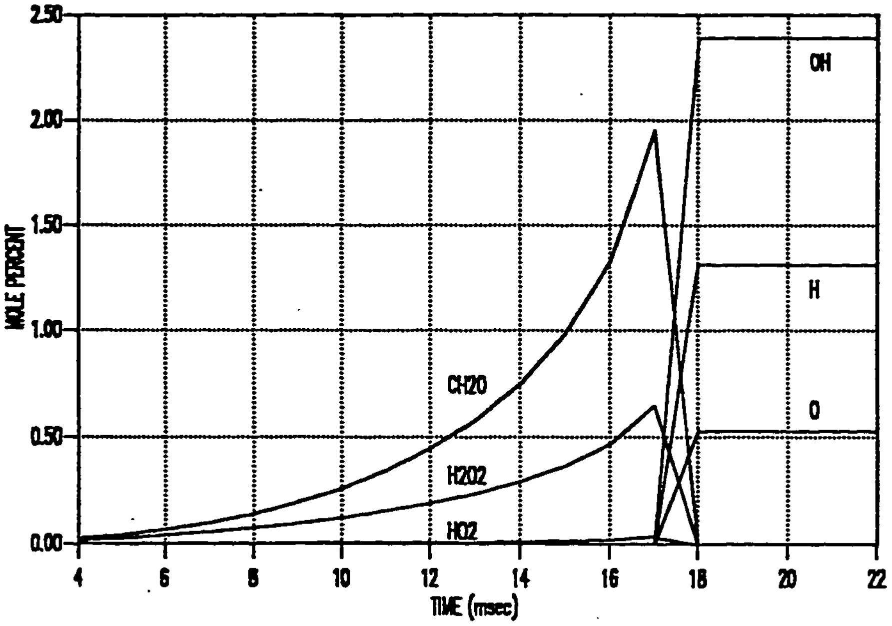

Fig. 4.10(b) Unstable Species Concentration profiles. (Equivalence Ratio = 1.2).

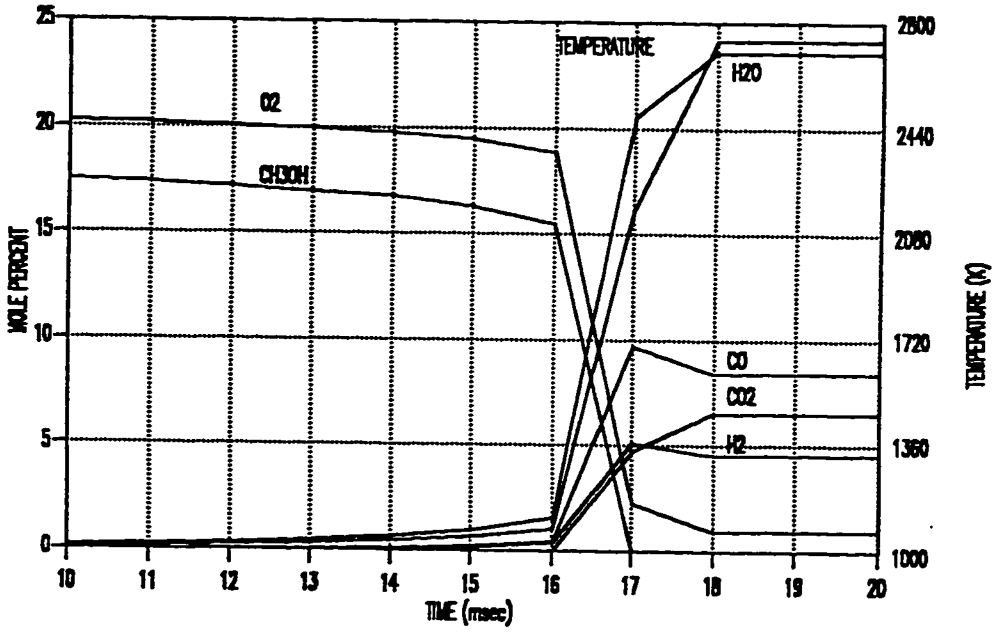

Fig. 4.11(a) Temperature and Stable Species Concentration profiles. (Equivalence Ratio = 1.3).

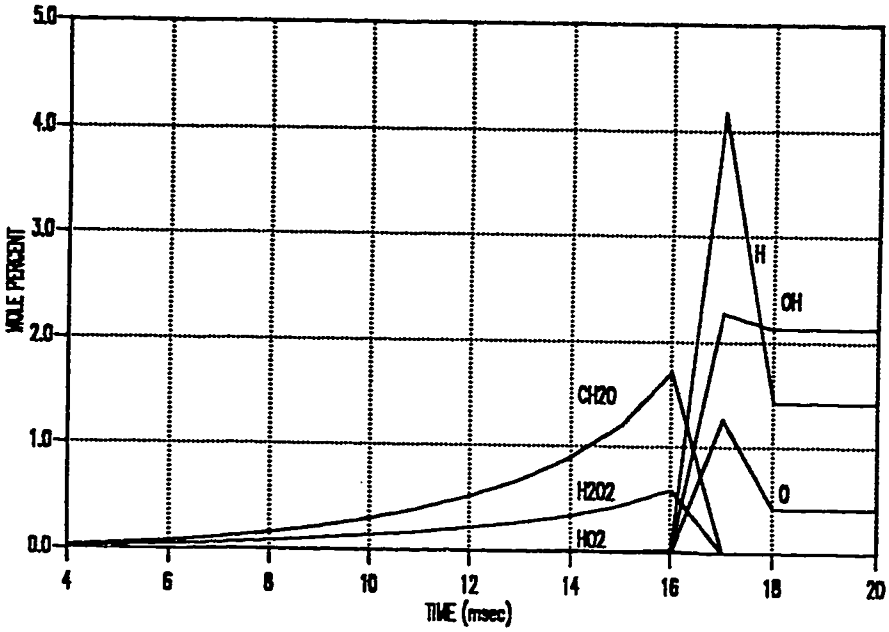

Fig. 4.11(b) Unstable Species Concentration profiles. (Equivalence Ratio = 1.3).

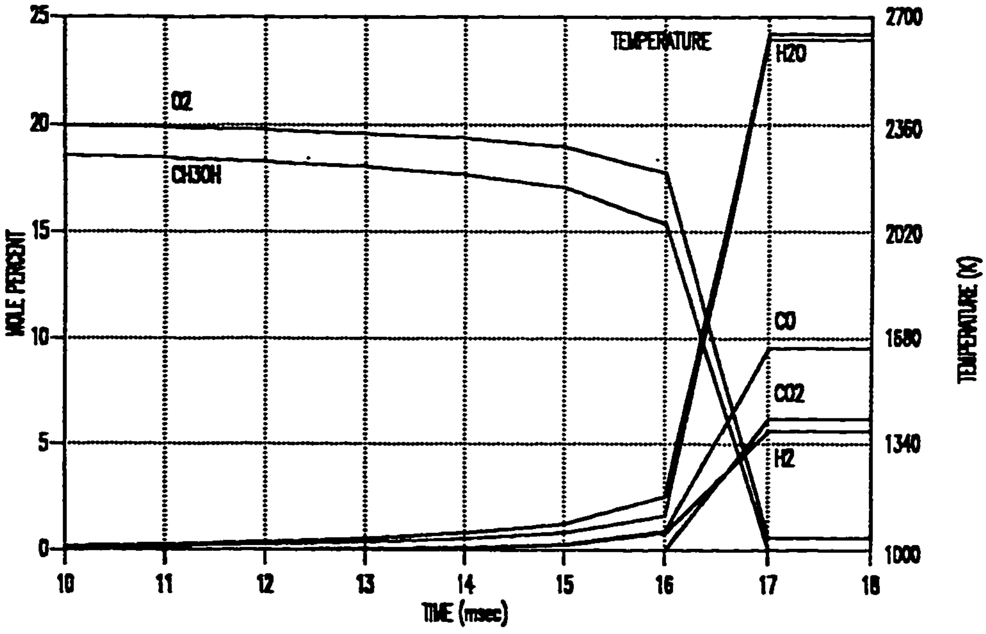

Fig. 4.12(a) Temperature and Stable Species Concentration profiles. (Equivalence Ratio = 1.4).

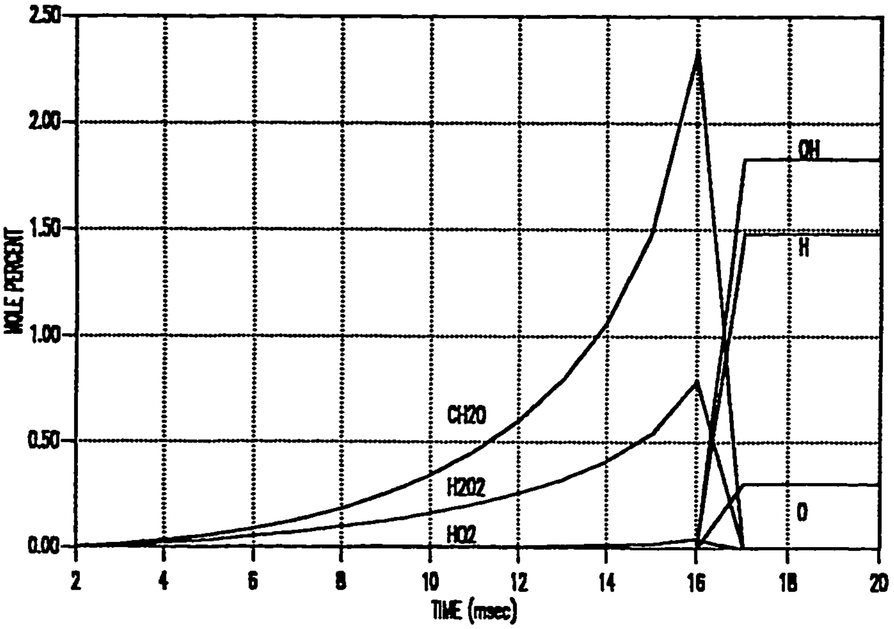

Fig. 4.12(b) Unstable Species Concentration profiles. (Equivalence Ratio = 1.4).

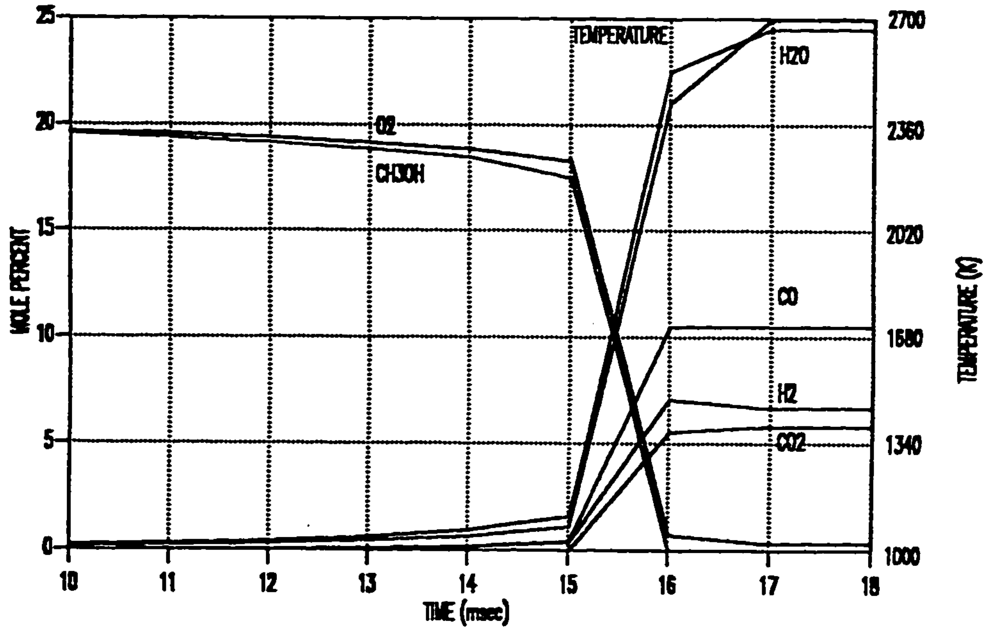

Fig. 4.13(a) Temperature and Stable Species Concentration profiles. (Equivalence Ratio = 1.5).

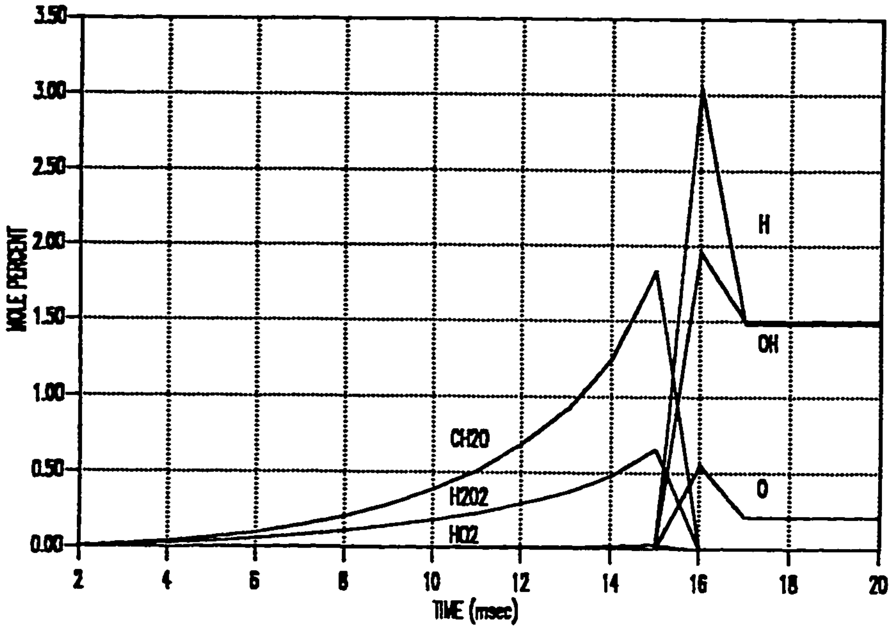

Fig. 4.13(b) Unstable Species Concentration profiles. (Equivalence Ratio = 1.5).

zone) decreases. This is due to more fuel available at higher equivalence ratios. Reaction completes early for the mixture around stoichiometric mixture and takes more time for mixtures either too lean or too rich. Table 4.3 shows the starting and final times of the reaction and the reaction times for each study. The times verses equivalence ratios are plotted in Figure 4.14.

4-5 Adiabatic Flame Temperature

In Table 4.3, adiabatic flame temperature is also tabulated along with the reaction time. It is obvious that this temperature is not the exact flame temperature but higher than the actual flame temperature. It is because of the assumptions made in the modelling. The conduction and the diffusion terms are neglected. Also heat transfer from the flame to the surrounding is not taken into the account. The temperature has plotted in Figure 4-15. The temperature is maximum at slightly richer side of the mixture which is in agreement with the conventional theory. It is because of the excess fuel present in the initial mixture. The O_2 from dissociation of CO_2 enables this excess fuel to burn and hence temperature increases. But for the more richer fuel, incomplete combustion takes place which produces CO and reduces temperature. Either too lean or too rich side, the temperature is lower due to the less fuel in lean side and more fuel in richer side.

It is possible for the user to supply its own temperature profile in the program. In this case a temperature profile obtained from the experiments can

TABLE 4.3

Reaction Time and Adiabatic Flame Temeparature

Equivalence Ratio	Reaction Starts at (msec)	Reaction Ends at (msec)	Reaction Time (msec)	Adiabatic Flame Temperature (K)
0.6	24	26	2	2573
0.7	22	24	2	2939
0.8	21	22	1	2685
0.9	20	21	1	2716
1.0	19	20	1	2738
1.1	18	19	1	2744
1.2	17	18	1	2746
1.3	16	18	2	2738
1.4	16	17	1	2722
1.5	15	17	2	2697

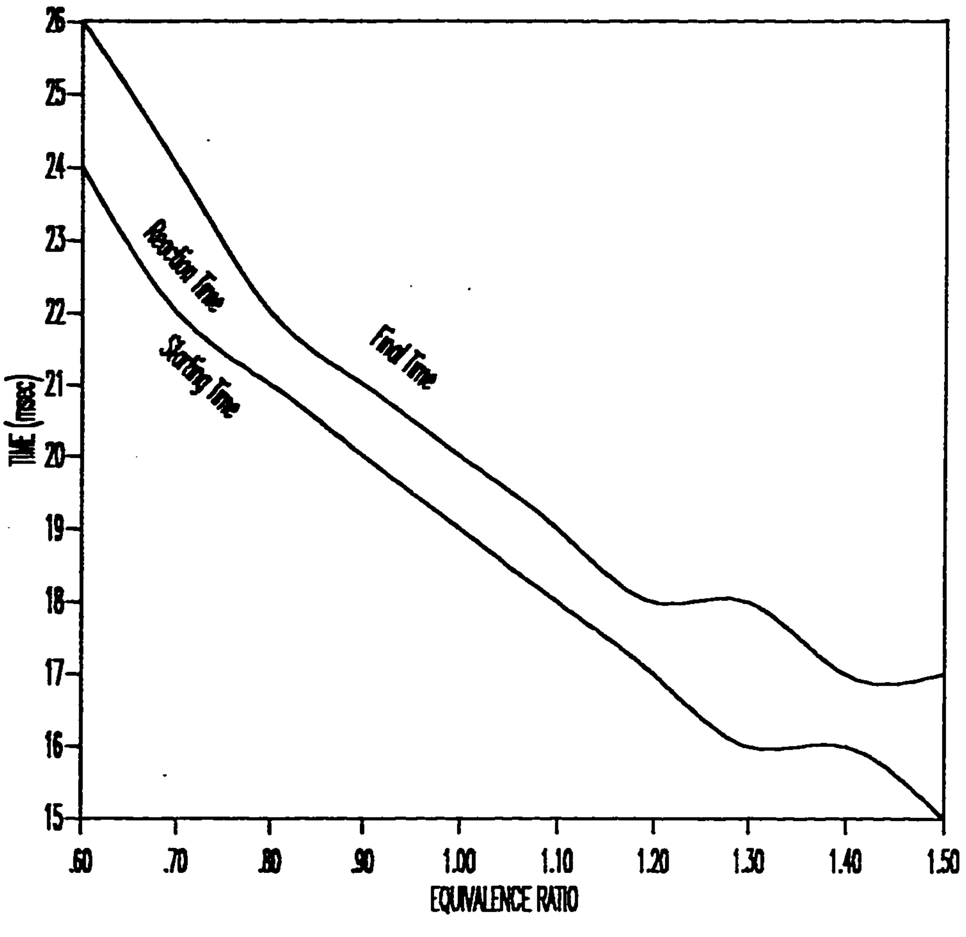

Fig. 4.14 Variation of Varoius Reaction Times With Respect to Equivalence Ratio.

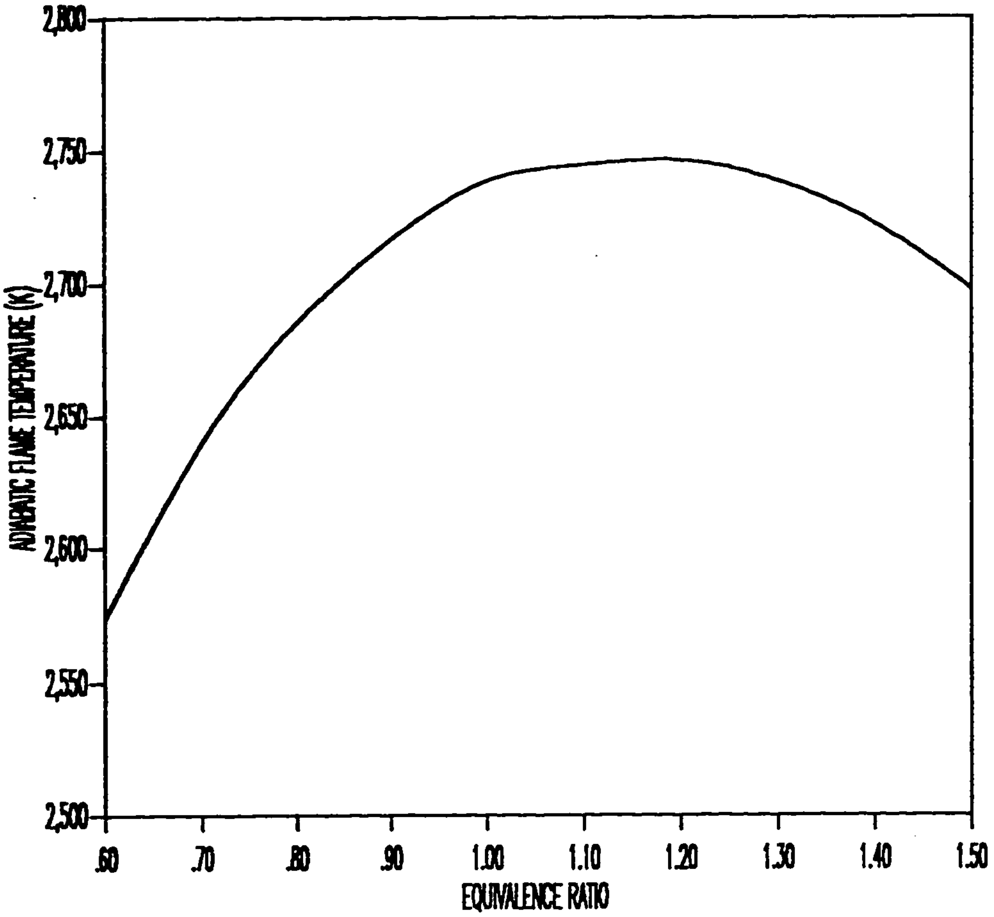

Fig. 4.15 Variation of Adiabatic Flame Temperature With Respect to Equivalence Ratio.

be a input to the program. Then the prediction of the species will be done on the basis of the experimental temperature and the more accurate prediction of the species profiles are possible. However, by using the adiabatic flame temperature profile, the behavior of the stable species predicted is almost the same as in the case of experimental temperature profile for the low temperature ranges. This has been done in proceeding sections.

4-6 STABLE SPECIES

4-6.1 CH_3OH (Fuel)

The fuel decay proceeds through several stages. Initially, the fuel is attacked by both OH and HO_2 in the chain branching process.

$$CH_3OH + OH = CH_2OH + H_2O \tag{M3}$$

$$CH_2OH + O_2 = CH_2O + HO_2 \tag{M10}$$

$$CH_3OH + HO_2 = CH_2OH + H_2O_2 \tag{M8}$$

$$H_2O_2 + M = OH + OH + M \tag{M52}$$

The other important reactions which are responsible for the depletion of the fuel are M4 to M7 in Table 2.1. For the lean mixture, all the fuel is depleted as the excess oxygen is present and no fuel is predicted in the equilibrium mixture. For the rich mixture also, all the fuel is depleted inspite of lack of oxygen supplied initially. Extra oxygen is obtained from the dissociation of CO_2 at high temperature which helps fuel to deplete fully.

$$CO_2 + M = CO + O + M \tag{M28}$$

$$O + O + M = O_2 + M \tag{M-55}$$

4-6.2 O_2 (Oxidizer)

The residual quantity of oxidizer reduces with an increase of the equivalence ratio in lean mixtures which is obvious. Even for the equivalence mixture, the residual oxygen is predicted because of the dissociation of CO_2. For the rich mixture, the temperature decreases and the dissociation of CO_2 also decreases, therefore, the oxygen concentration decreases with an increase of the equivalence ratio.

4-6.3 CO

The concentration of CO varies for both lean and rich mixture almost linearly with the equivalence ratio. In the lean side, production of CO is less because all the fuel is oxidized due to the excess of oxygen and hence combustion is completed. The CO produced in this region is due to the dissociation reaction M28. The concentration of CO in lean region is lower than that in the richer region. In the richer side, lack of oxygen in the initial mixture is responsible for the incomplete combustion hence production of CO. The curve is almost a straight line which represents the rate of change of CO concentration with equivalence ratio is almost a constant.

4-6.4 CO_2

Generally in methanol combustion reactions, production of CO starts initially. As the temperature increases, this CO oxidizes and form CO_2. Hence the production of CO_2 starts after some time. As the production of CO_2 starts, concentration of CO starts decreasing. This can be shown in Figure 4.4. But if the flame temperature is high enough to sustain the dissociation reaction, the CO and CO_2 attain an equilibrium value which is the case for the stoichiometric mixture and its neighborhood. For high equivalence ratios like 1.3, the temperature drops and CO concentration drops up to some extent after getting a peak and hence CO_2 increases. But for the very high equivalence ratios, incomplete combustion is responsible for high production of CO and hence production of CO_2 decreases for richer mixture. The variations of CO, CO_2 and O_2 with respect to the equivalence ratio are plotted in Figure 4.16.

As a summary we can say that the concentration of CO_2 is higher at lean side due to almost complete combustion and also increases with equivalence ratio. At rich side, it decreases with equivalence ratio due to incomplete combustion and also has a lower value in comparison with the lean side.

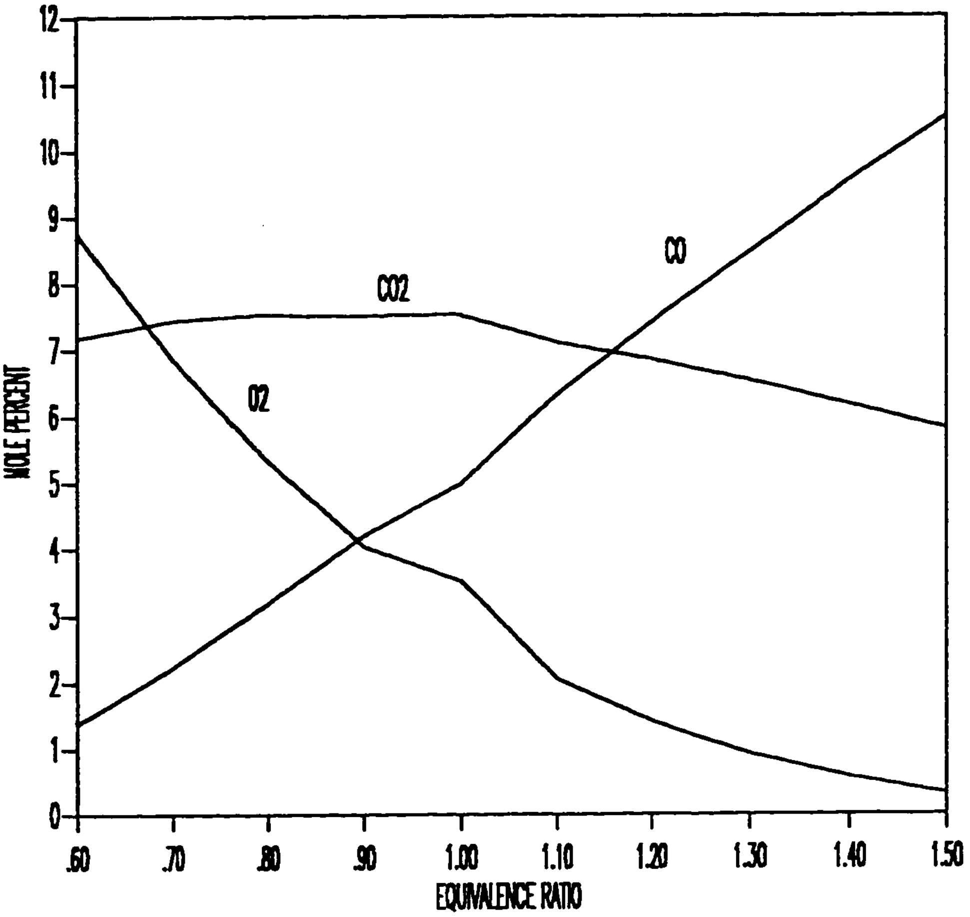

Fig. 4.16 Variation of CO, CO_2 and O_2 With Respect to Equivalence Ratio.

4-6.5 H_2

The production of hydrogen starts at the early stage of the combustion process (Fig 4.4(a) to 4.13(b)) for all equivalence ratios. Its concentration increases with equivalence ratio. It is higher at the rich side and lower towards the lean side. For low equivalence ratio, the hydrogen concentration drops after getting a peak value but for higher values of equivalence ratios, it attains a peak value and does not reduce due to high flame temperature. The variation of H_2 with respect to equivalence ratio is shown in Figure 4.17.

4-6.6 H_2O

Water is the product almost from all the combustion processes. Its concentration depends on the initial fuel concentration (equivalence ratio). It is obvious that its concentration increases with the equivalence ratio because of the more fuel available to burn and convert into water and CO or CO_2.

Water has large contribution in the exhaust which is shown in Figure 4.18. For the cases analyzed in this study, its mole percent varies from 14 to 26.

4-7 Unstable Species

Intermediates or unstable species are formed during chain branching reactions and then swept away by chain termination reactions. The behavior of the some of the intermediate are plotted through Figures 4.4(b) to 4.13(b). These are CH_2O, H_2O_2, HO_2 OH, O and H. CH_2O, H_2O_2 and HO_2 start growing with

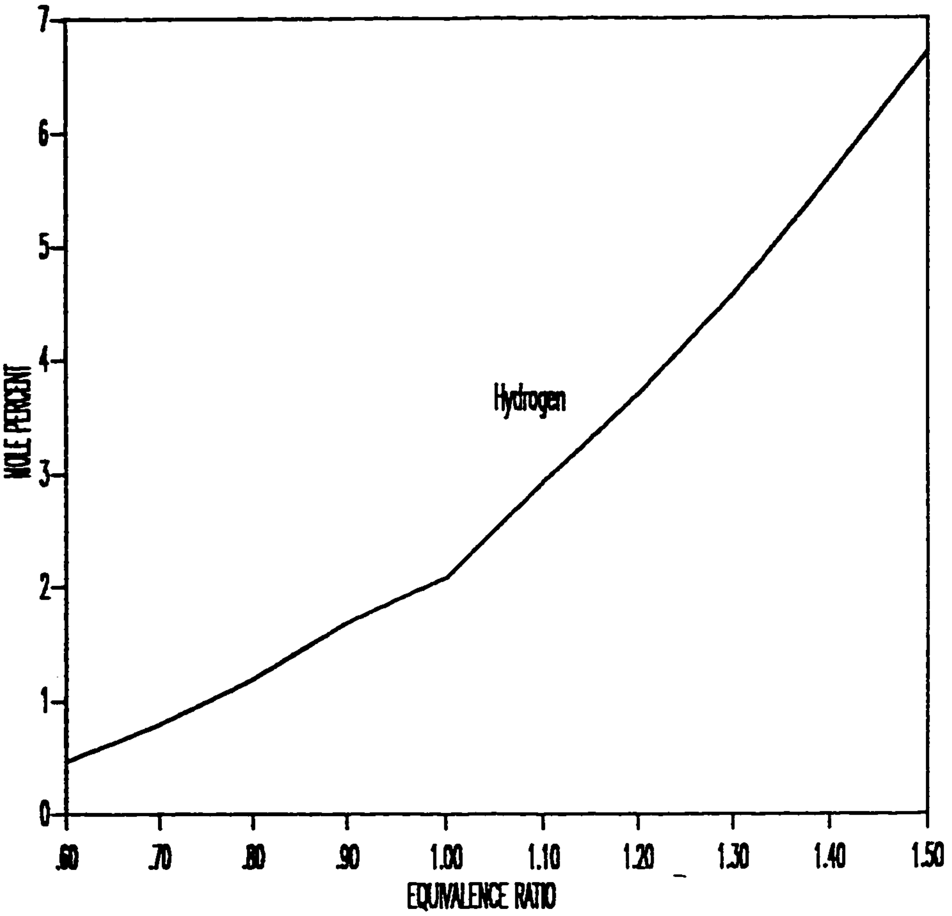

Fig. 4.17 Variation of H_2 With Respect to Equivalence Ratio.

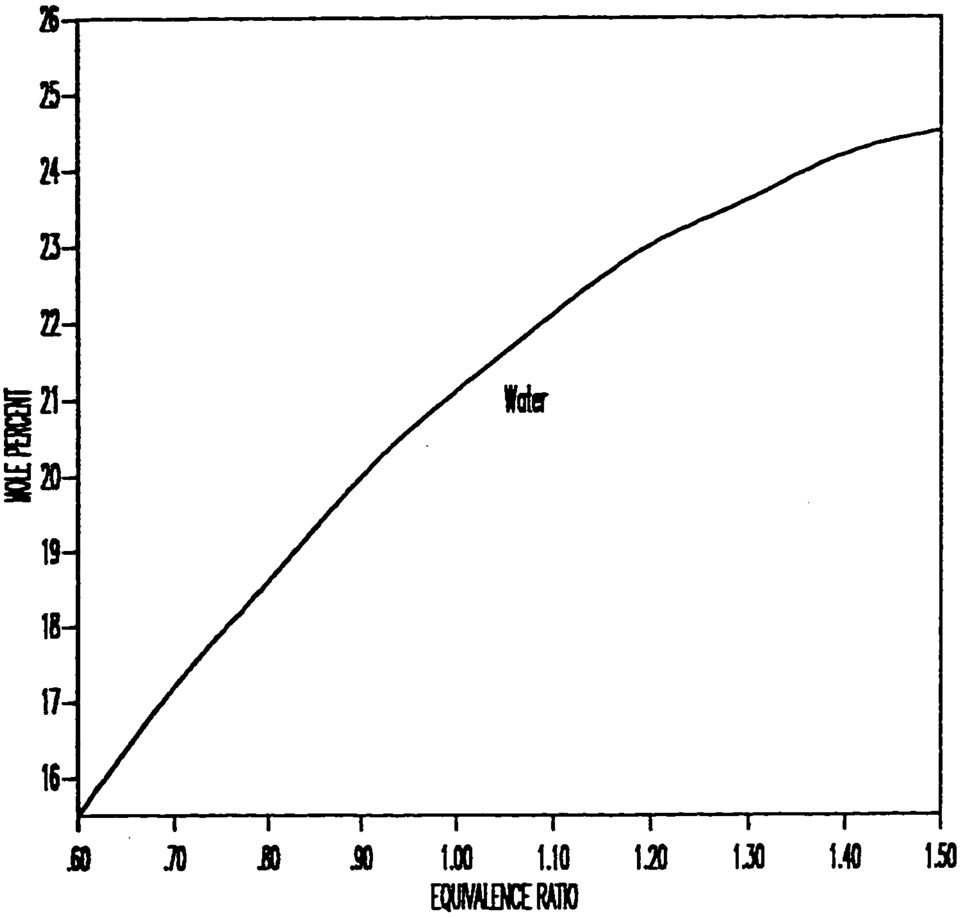

Fig 4.18 Variation of H_2O With Respect to Equivalence Ratio.

the initiation of the reaction and get peak values before the highest temperature reaches. They are consumed to form stable species and vanished at the time when the highest temperature is achieved.

OH, O and H starts growing when the decay of CH_2O, H_2O_2 and HO_2 started. For the low temperatures (equivalence ratios either too low or too high), these intermediates go up to peak values and then drop when the highest temperatures reach. But the temperatures are not low enough to avoid the dissociation of water, oxygen and hydrogen fully, therefore these radicals do not consume fully and are predicted in the final equilibrium mixture.

For the equivalence ratio around 1, the temperature of the flame is very high and dissociation of water, hydrogen and oxygen become dominant. Hence the concentration of these intermediates do not decay after getting peak values.

4-8 Comparisons

4-8.1 Atmospheric Pressure Flames

In the previous section, the modelling was done on the basis of adiabatic flame temperature. The equilibrium concentrations of species were calculated at different time after the flame started first by developing an adiabatic temperature profile by using the assumptions given in chapter 3. These results may deviate from the actual values because of the temperature is higher than the actual one, nevertheless the trend of the profile for stable species with respect to time is almost the same. To compare the modelling results, one can use the temperature profile from the experiment and supply it as an input to the program. The species profile obtained thus are comparable with the experimental results. This is done in this section. The experimental temperature values for equivalence ratios 0.9, 1.0 and 1.1 are taken from Abualhamayel [2] and a polynomial is fitted for every data set. These polynomials are given in appendix III. The diameter of the burner and the volumetric flow rate are tabulated in Table 4.4 which is also taken from the same reference. These are used later to model the flame at different distances. At atmospheric pressure, the flame is attached to the burner and most of the reaction is taken place within the burner. Therefore the variation of temperature in the experimental data is very low and hence, a wide range of concentration for any species can not be obtained at this pressure. Only the equilibrium results are possible to get because of the high initial temperature. These results are tabulated in Table 4.5 and compared with Abualhamayel [2] from where the experimental temperature values are taken. The results are plotted in Figures 4.19 and 4.20.

For equivalence ratios 0.9 and 1.0, the predicted mole fractions of water are not very far from the experimental one. The difference is about 12%.. But for 1.1, difference is high and it is 35%. The same is for CO_2. CO does not predicted at equilibrium state from both, modelling and experimental results.

TABLE 4.4 Experimental Conditions [2]

Equivalence Ratio	Pressure Atmosphere	Flow Rate Liter/min	Burner Dia cm	Velocity cm/Sec
0.9	1.0	3.69	4.6	3.76
1.0	1.0	3.43	4.6	3.44
1.1	1.0	3.15	4.6	3.16
0.9	0.167	30.78	4.6	30.87
1.0	0.167	28.11	4.6	20.20
1.1	0.167	25.92	4.6	25.99

TABLE 4.5 Comparison With Experimental Results in Post Flame Zone

Pressure = 1.0 atm.

Equivalence Ratio	CO_2		CO		H_2		H_2O	
	Ref [2]	Model	Ref [2]	Model	Ref [2]	Model	Ref [2]	Model
0.9	0.122	0.145	0.00	0.00	4.00×10^{-7}	6.15×10^{-4}	0.244	0.275
1.0	0.132	0.160	0.00	0.00	1.20×10^{-6}	1.45×10^{-3}	0.264	0.300
1.1	0.122	0.177	0.00	0.00	2.07×10^{-2}	2.00×10^{-3}	0.260	0.350

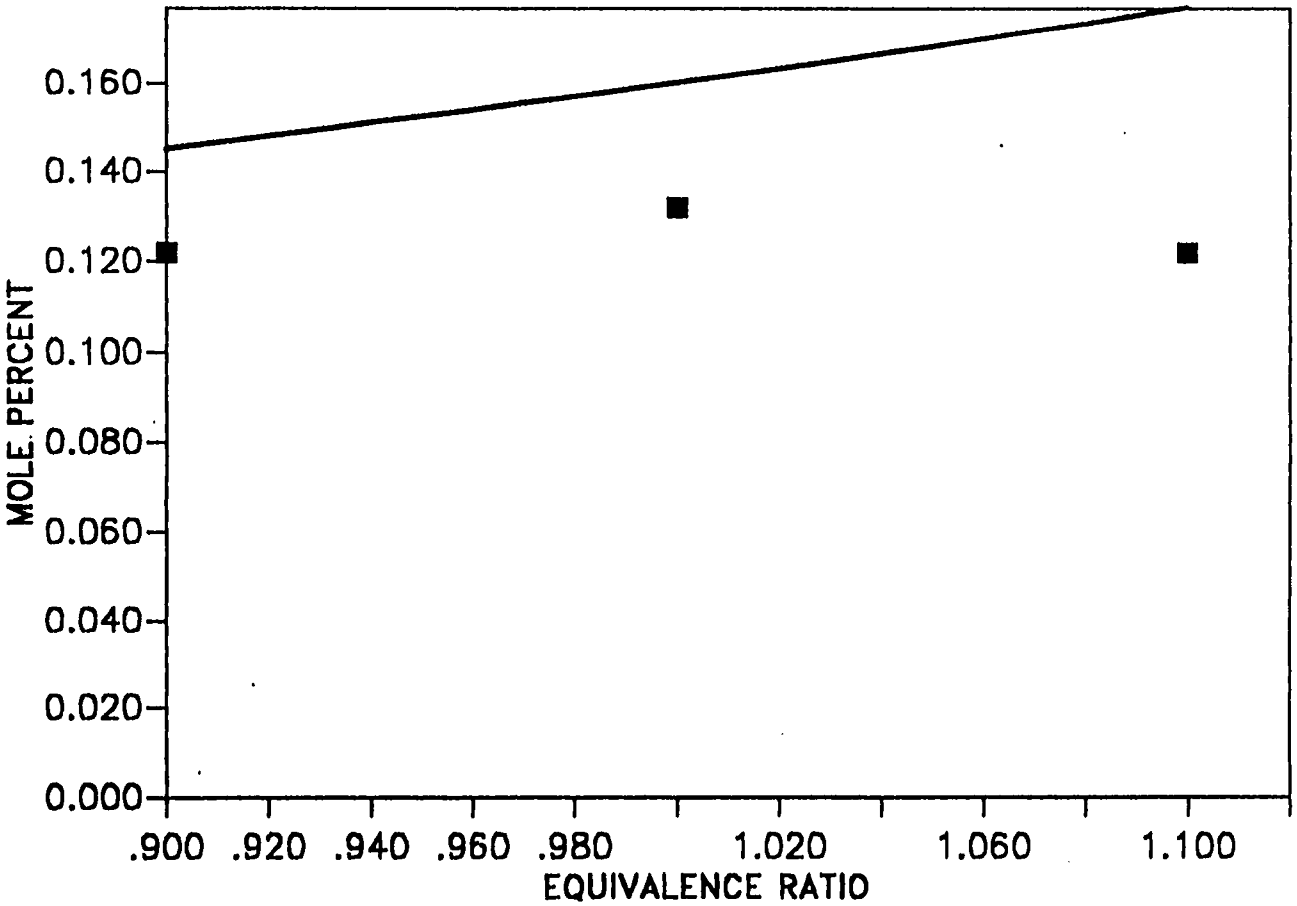

Fig. 4.19 Comparion of predicted and experimental mole percent of CO_2 in post flame zone;Pressure = 1.0 Atmosphere.

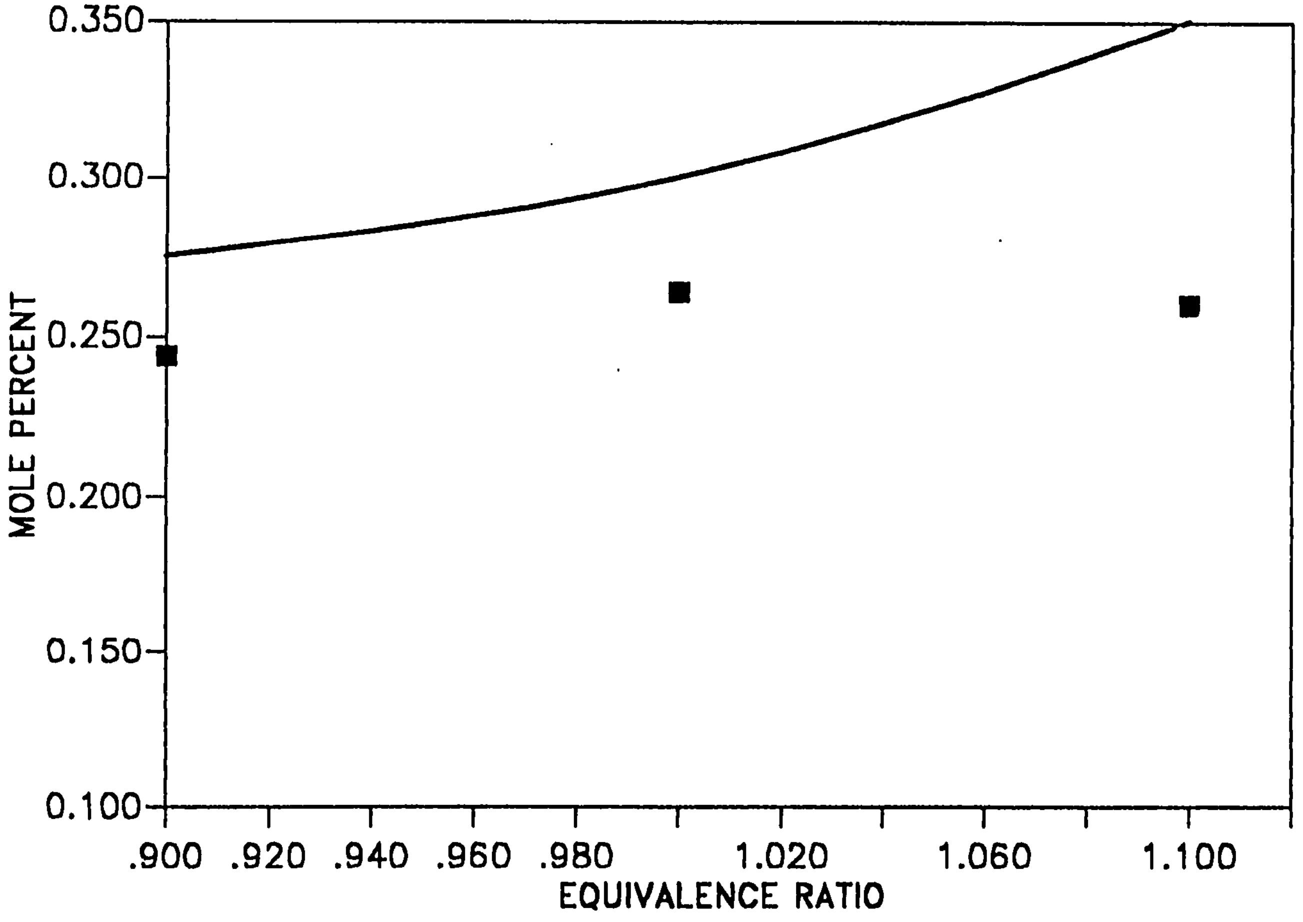

Fig. 4.20 Comparion of predicted and experimental mole percent of H_2O in post flame zone;Pressure = 1.0 Atmosphere.

The mole fraction of H_2 is also approximately zero for both the studies except equivalence ratio 1.1, where it seems that the difference is quite high. but this can be possible because of the tolerances allowed in the program ($10^{-4} \times H_2$ *Concentration*). Because the predicted mole fractions is very low, even a small tolerance can create a big percentage of error.

4-8.2 Low Pressure Flames (0.167 Atmosphere)

At low pressure, the reaction zone increases and the flame rises above the burner higher than as in the atmosphere pressure case. Therefore it is possible to measure the species concentration and temperature at every point more accurately. This is why the predicted results are comparable at each point at this pressure. The comparison is made for few important species for which the experimental data is available from [2] and are plotted through Figures 4.21 to 4.32. These comparisons are made for three equivalence ratios 0.9, 1.0 and 1.1. The fitted polynomials for the experimental data are given in Appendix III. The predicted results are shown by continuous lines while the experimental data points are represented by the small square blocks.

The prediction of CO_2 matches with the experimental data points with both quantitatively and qualitatively for all the three equivalence ratios.

The prediction of CO concentration does not match with the experimental data expect for the peak concentration at equivalence ratio equal to 1.0. A sharp concentration gradients predicted in the model and the poorer agreement of

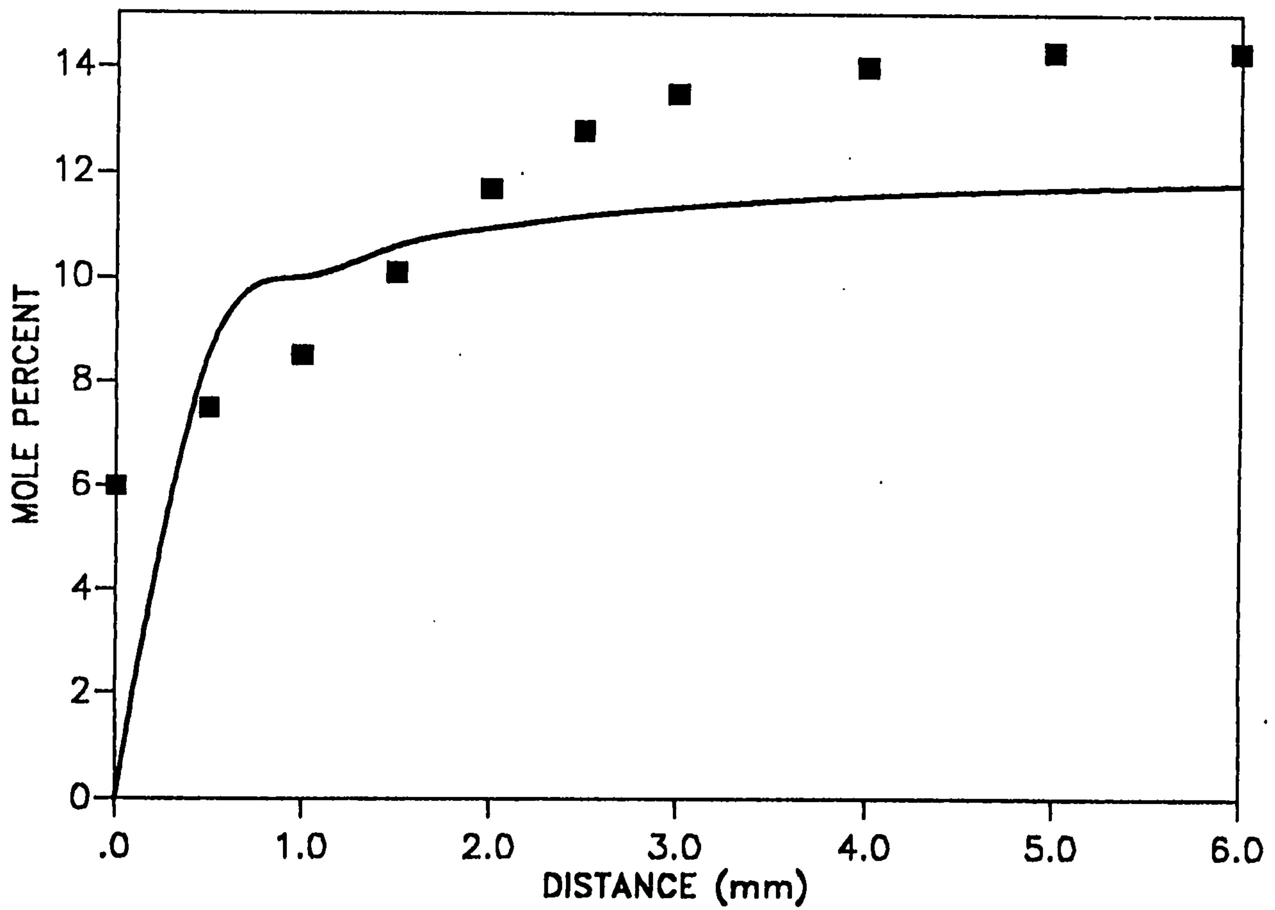

Fig. 4.21 Comparion of predicted and experimental mole percent of CO_2
Equivalence Ratio = 0.9; Pressure = 0.167 Atmosphere.

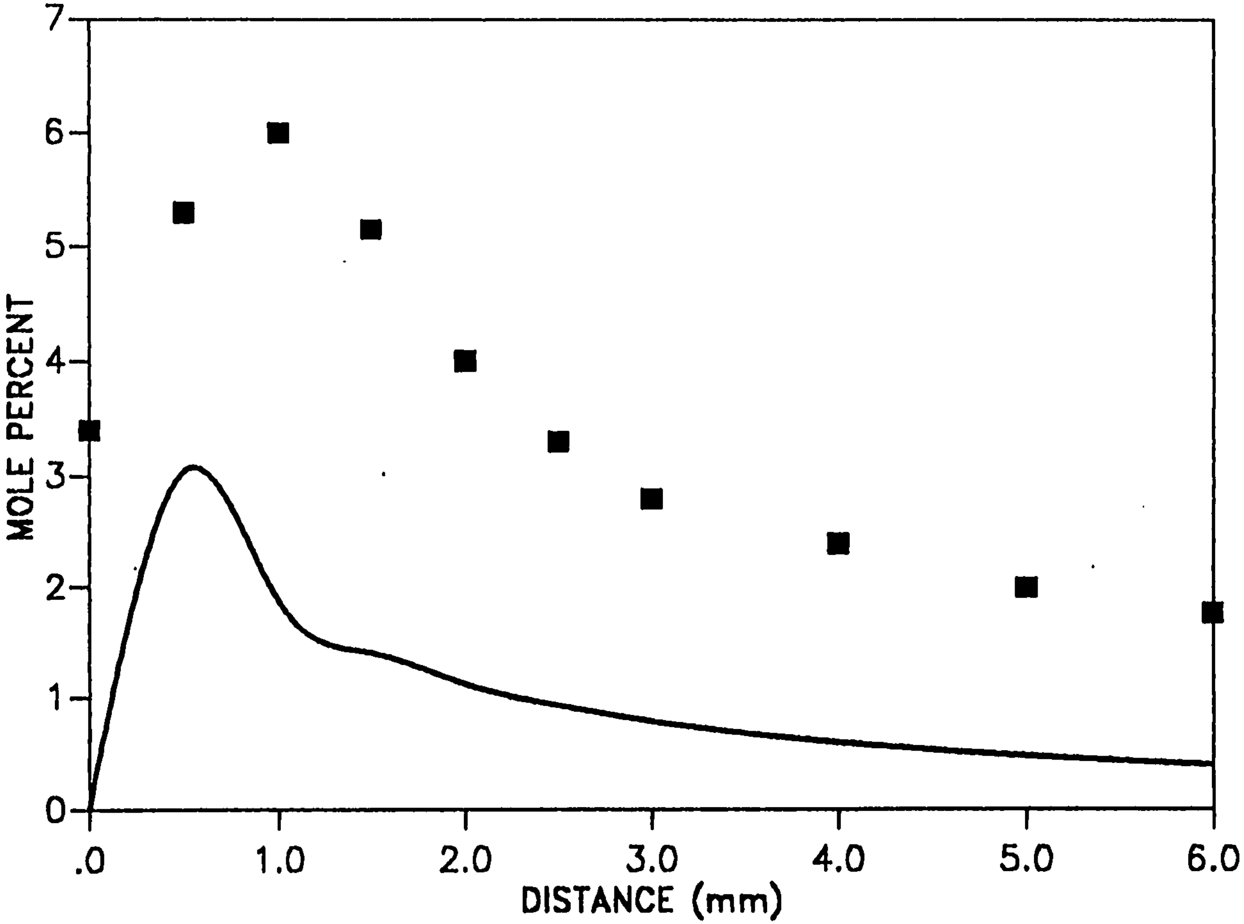

Fig. 4.22 Comparion of predicted and experimental mole percent of CO
Equivalence Ratio = 0.9; Pressure = 0.167 Atmosphere.

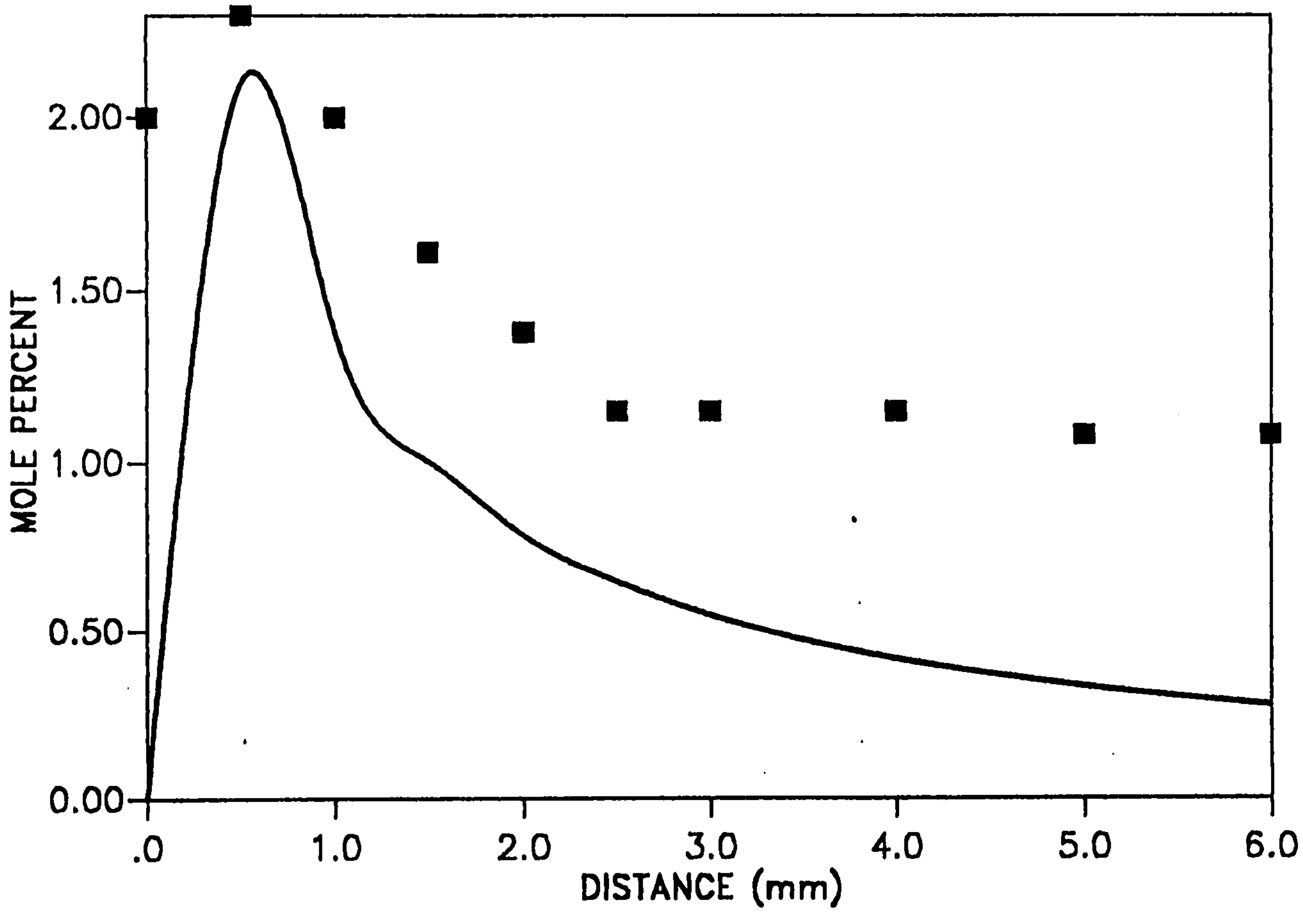

Fig. 4.23 Comparion of predicted and experimental mole percent of H_2
Equivalence Ratio = 0.9; Pressure = 0.167 Atmosphere.

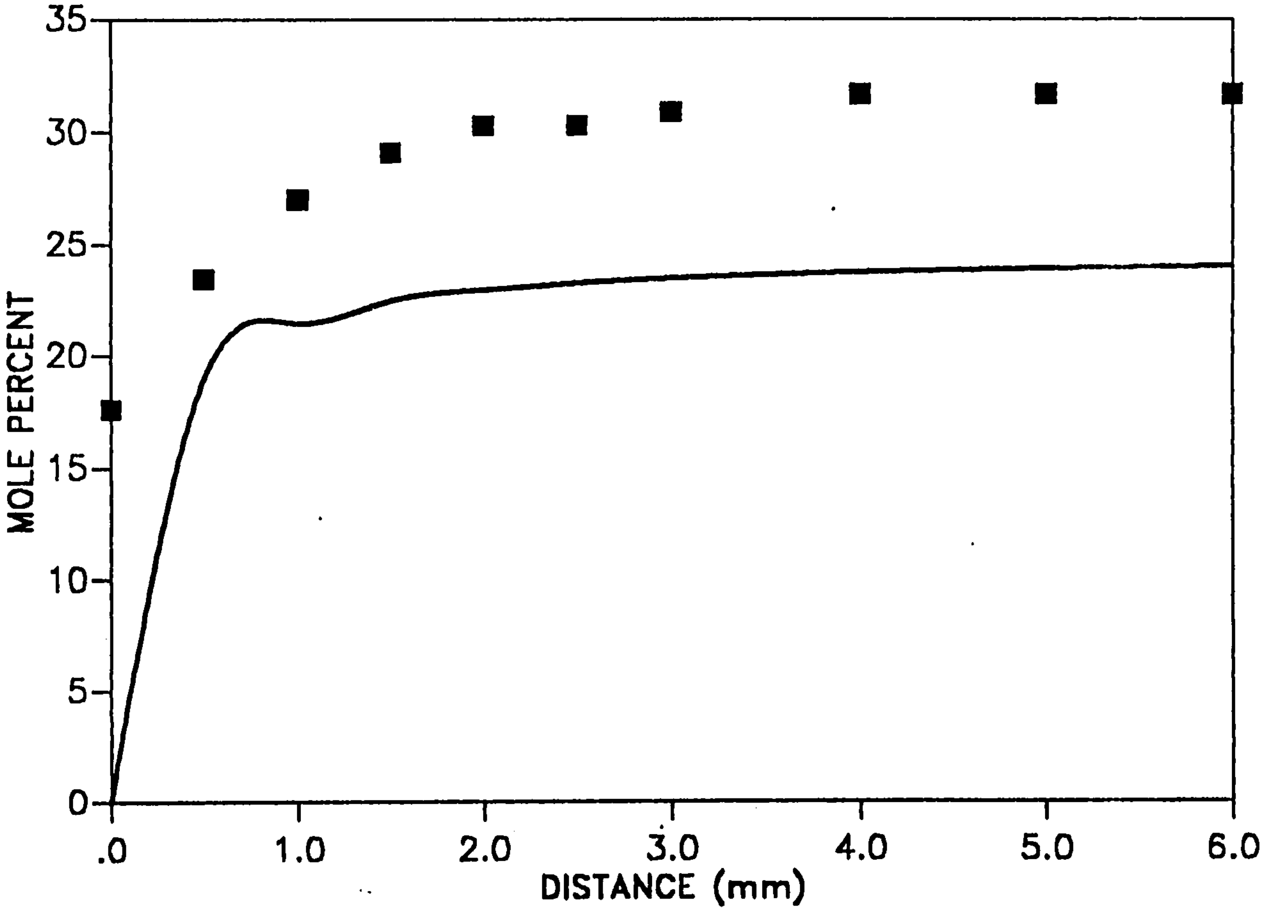

Fig. 4.24 Comparion of predicted and experimental mole percent of H_2O
Equivalence Ratio = 0.9; Pressure = 0.167 Atmosphere.

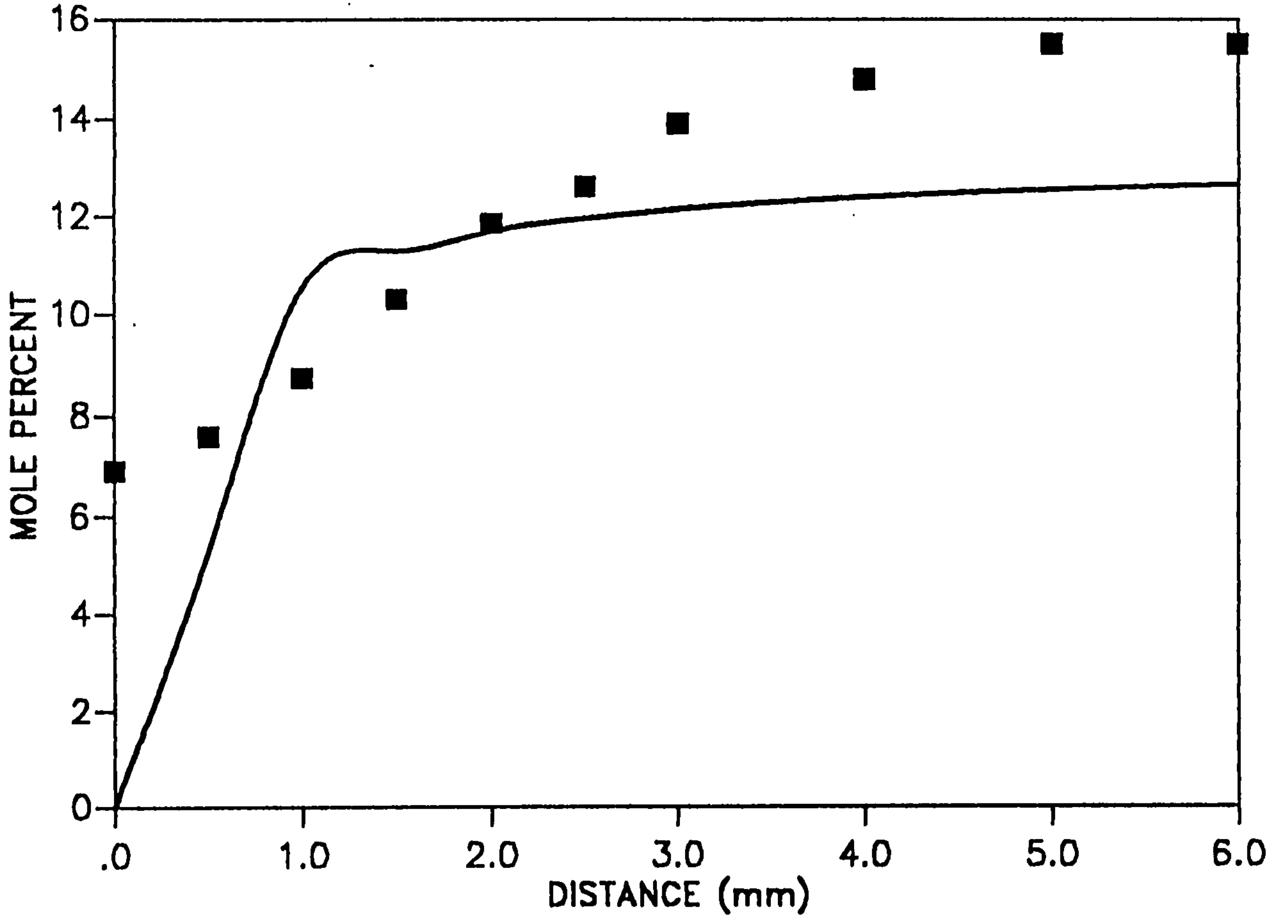

Fig. 4.25 Comparion of predicted and experimental mole percent of CO_2
Equivalence Ratio = 1.0; Pressure = 0.167 Atmosphere.

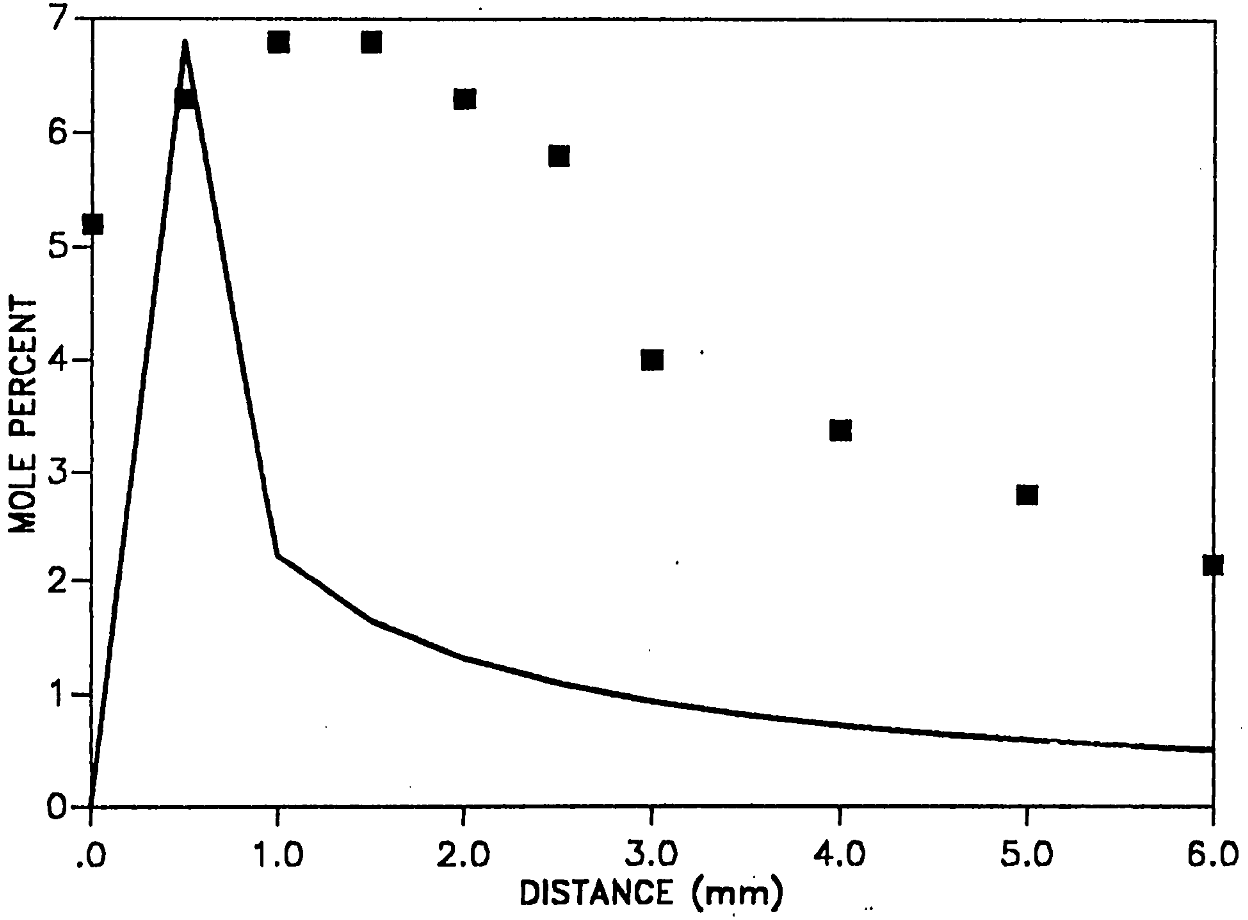

Fig. 4.26 Comparion of predicted and experimental mole percent of CO
Equivalence Ratio = 1.0; Pressure = 0.167 Atmosphere.

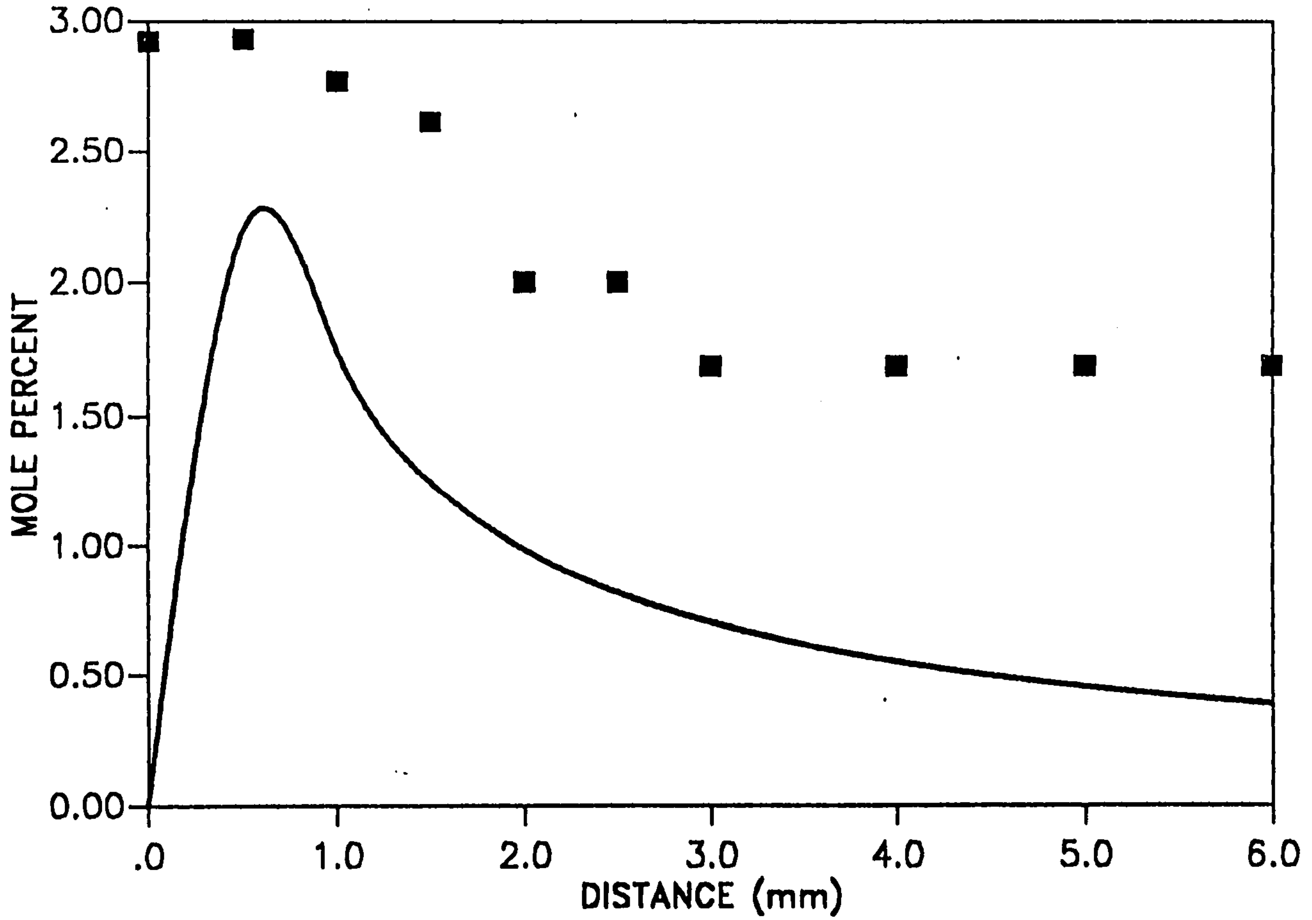

Fig. 4.27 Comparion of predicted and experimental mole percent of H_2
Equivalence Ratio = 1.0; Pressure = 0.167 Atmosphere.

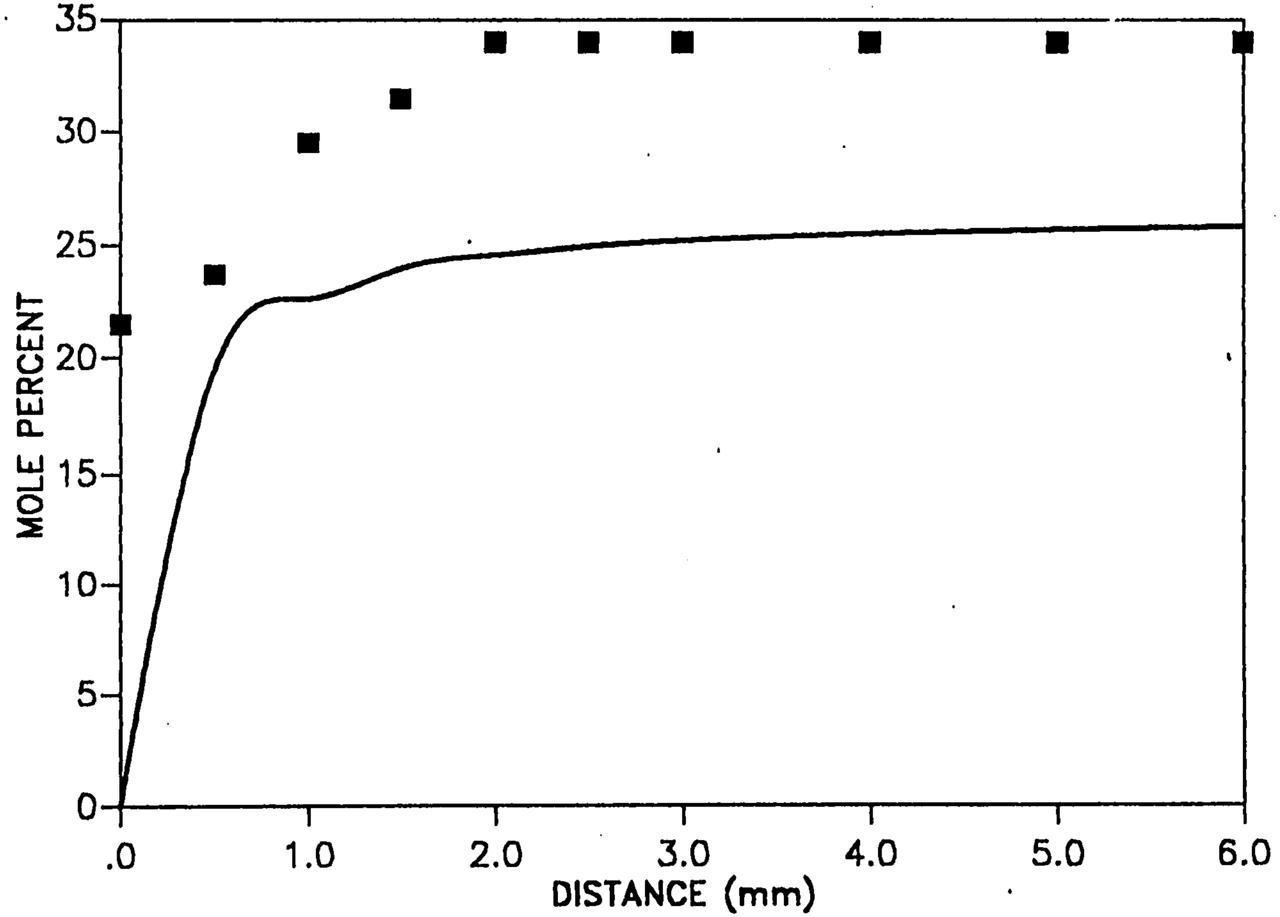

Fig. 4.28 Comparion of predicted and experimental mole percent of H_2O
Equivalence Ratio = 1.0; Pressure = 0.167 Atmosphere.

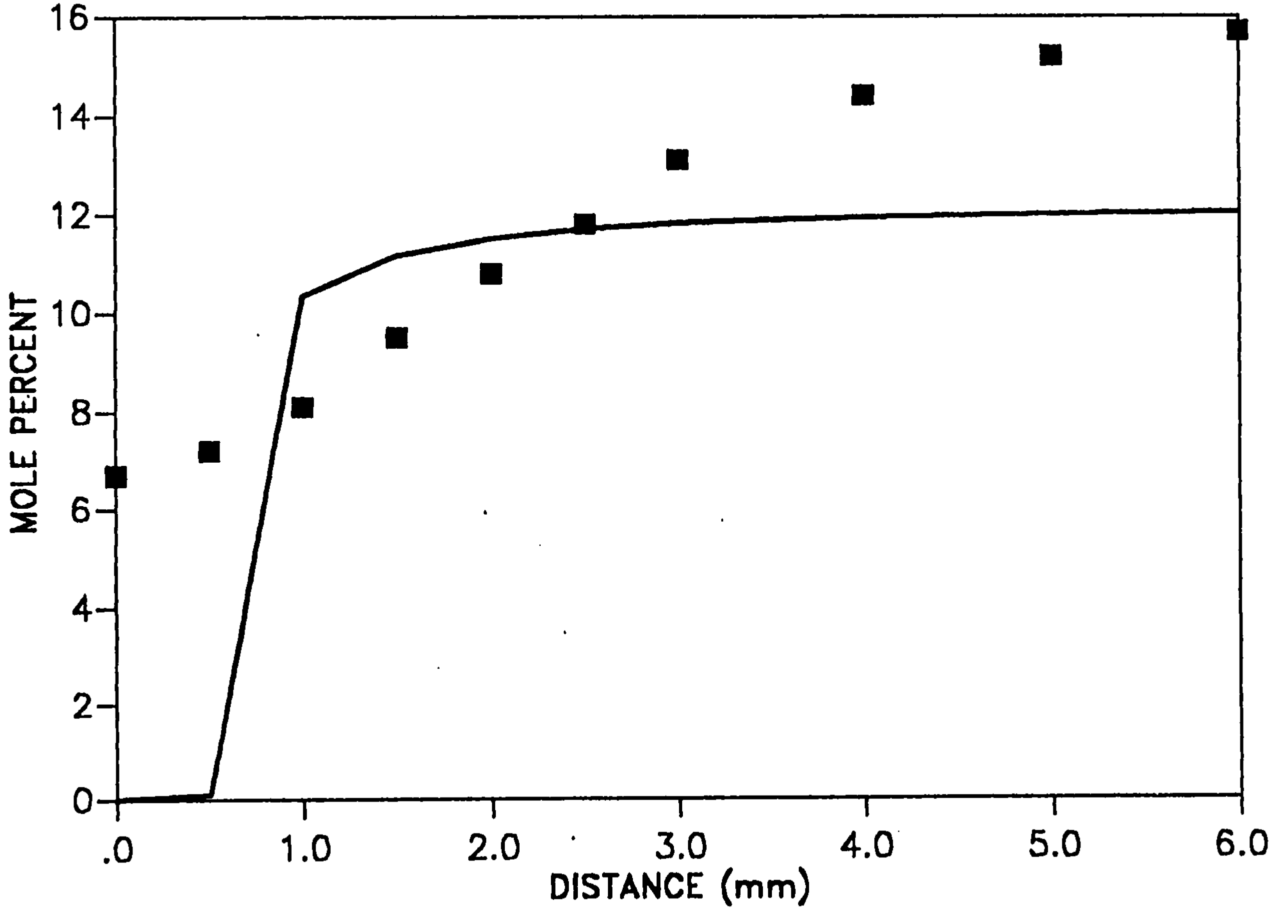

Fig. 4.29 Comparion of predicted and experimental mole percent of CO_2
Equivalence Ratio = 1.1; Pressure = 0.167 Atmosphere.

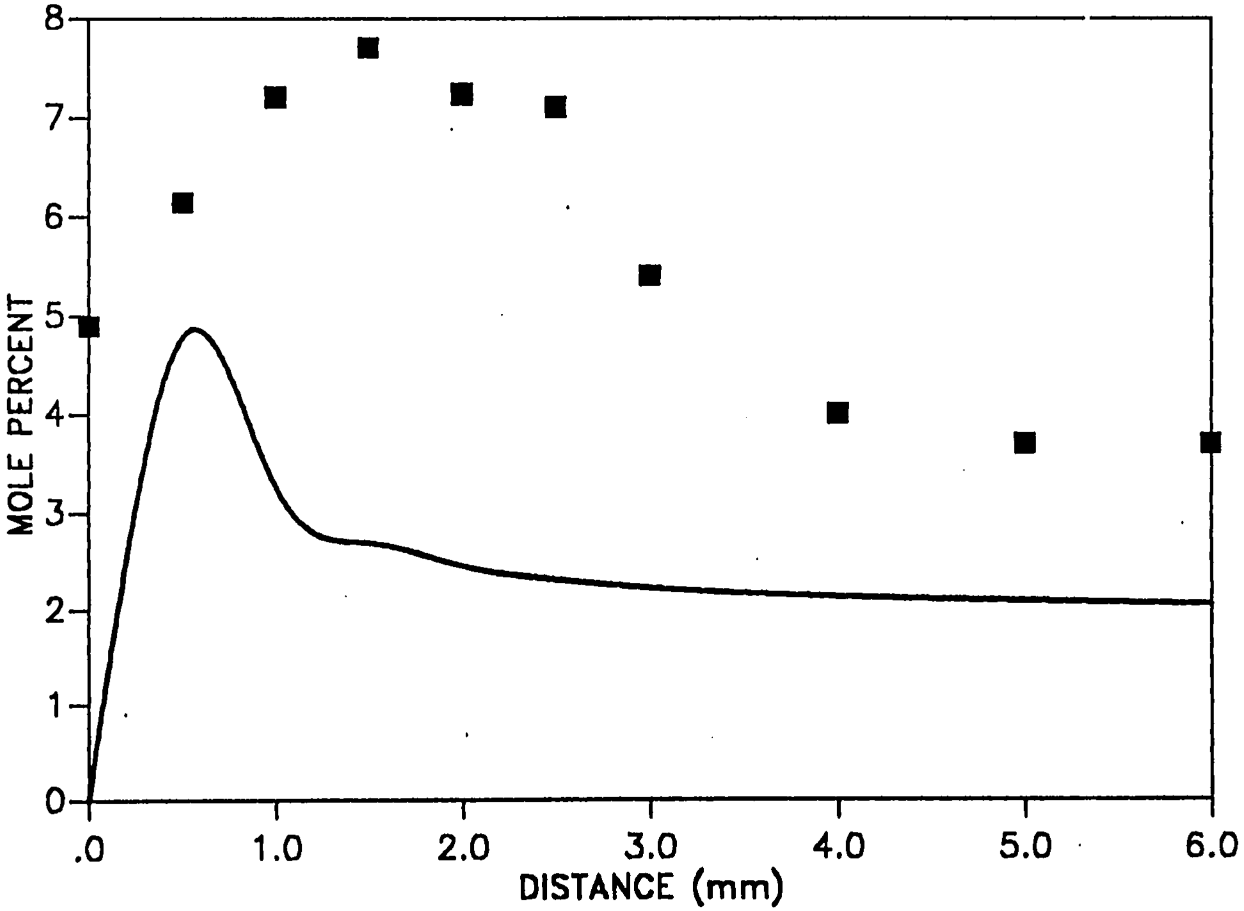

Fig. 4.30 Comparion of predicted and experimental mole percent of CO Equivalence Ratio = 1.1; Pressure = 0.167 Atmosphere.

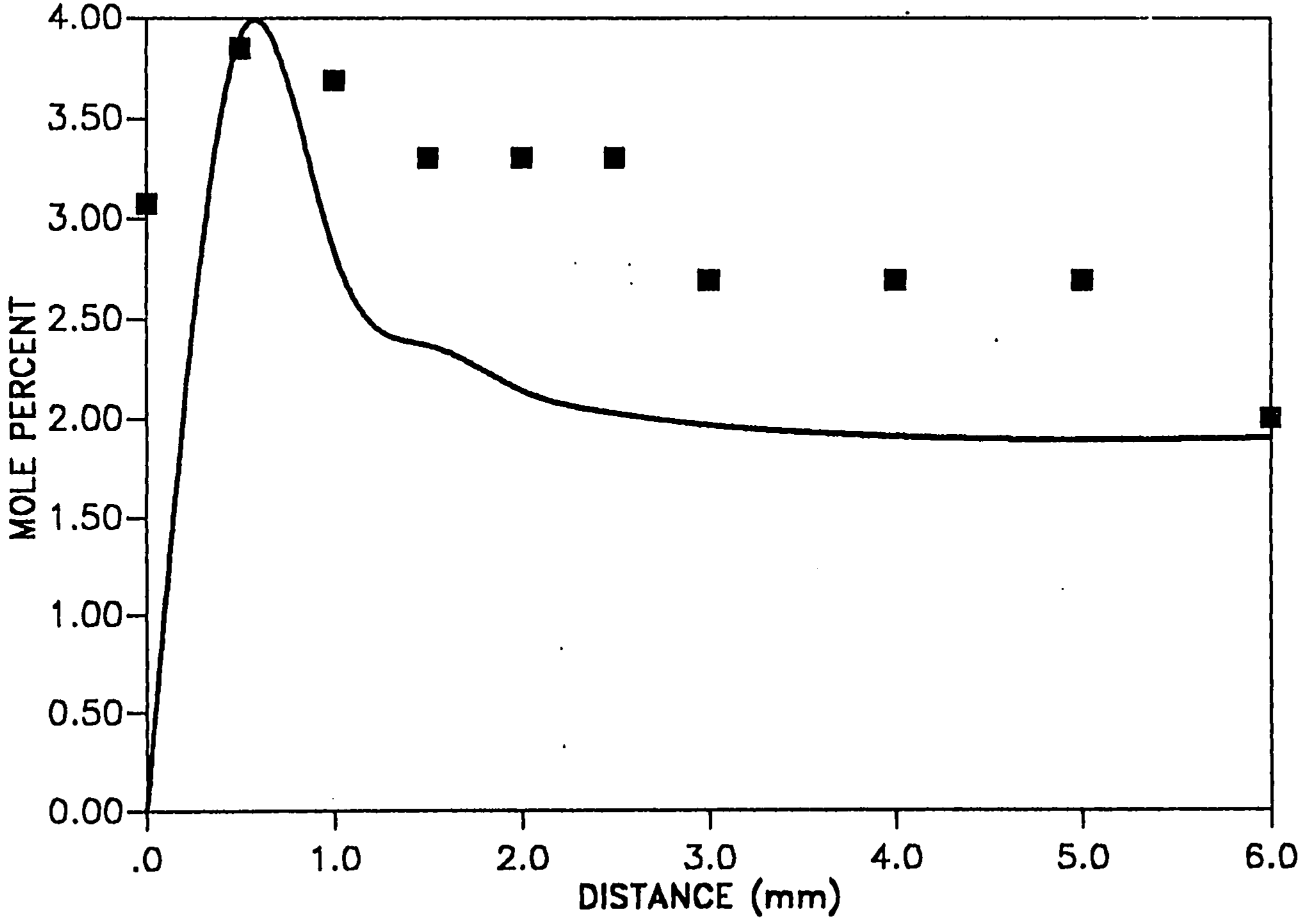

Fig. 4.31 Comparion of predicted and experimental mole percent of H_2 Equivalence Ratio = 1.1; Pressure = 0.167 Atmosphere.

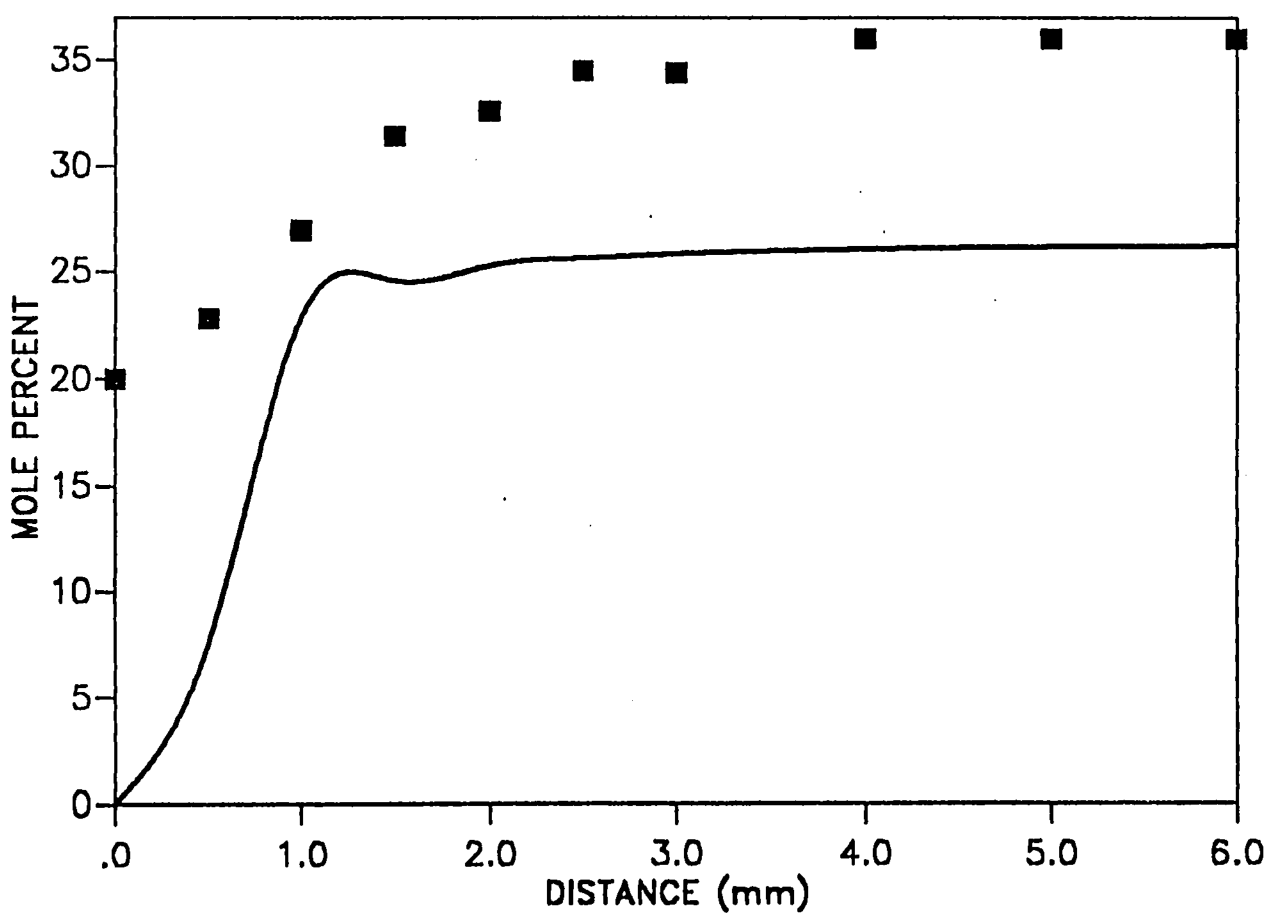

Fig. 4.32 Comparion of predicted and experimental mole percent of H_2O
Equivalence Ratio = 1.1; Pressure = 0.167 Atmosphere.

model and experiment after the *CO* peak suggest that molecular diffusion may affect the species profiles. If these experimental data are to be modeled accurately, diffusion may need to be included in the calculations. However, the conclusions of the current study, drawn from a general comparison between model and experiment up to the *CO* peak, are still valid.

The prediction of hydrogen at equivalence ratio 0.9 is not very far from the experimental results for the earlier stage of the combustion. For the peak concentration, the difference is only 9%. The results differ in the post flame zone and difference increases with the distance. Initially, in post flame zone, the difference is about 30% but at the last point it reaches up to as high as 70%. It is because of the the diffusion term is neglected in this model which is dominant in post flame zone. Though for the equivalence ratio 1.0, the hydrogen is under predicted but it follows the same trend as the experimental data follows. The prediction of the peak and equilibrium concentrations for hydrogen at equivalence ratio 1.1 is almost the same as measured from the experimental run.

The curves for water concentration is very near to experimental data points for all the equivalence ratios in the reaction zone. The difference is not more than 20%. The difference in the post flame zone is observed which is about 25% for the first two stoichiometric ratios but for equivalence ratio 1.1, the results are very close.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5-1 Conclusions

Species concentration and the adiabatic flame temperature profiles are predicted in this modelling for methanol, oxygen and argon flame. Two detail mechanisms are available for the combustion of methanol in literatures. One is known as WD79 mechanism which is developed by Westbrook and Dryer [4] in 1979. The other is the new mechanism which is actually the revision of the WD79 mechanism given by Thomas and Dryer [3]. A comparison of the two mechanisms is made in Section 4-1. The revised mechanism predicts that the reaction completes earlier in comparison with the prediction of WD79 mechanism. It is due to the rate constants of several important elementary reactions have been increased which was reported by many scientist in literature after experimental studies.

The results obtained from the two mechanisms are compared with the experimental results by Thomas and Dryer [3]. The temperature profile from the experimental study is the input for both the mechanisms. It has been proved that the new mechanism predicts the species profile more close to the experimental profiles. For this reason, the new mechanism is used in this modelling work.

The modelling for methanol, oxygen and argon flame is done for equivalence ratios ranges 0.6 to 1.5 which is the flammability limit for the methanol. For the first study, adiabatic flame temperature is developed for each equivalence ratio. Argon is used as a diluent in this study. It is because of the data available for the flame with argon as a diluent from Abulhamayel [2].

The following conclusions have been drawn from the modelling of methanol, oxygen and argon flame.

1. The combustion time for the flame is higher for too high or too lean mixtures as compare with the stoichiometric mixture and its neighborhood (Fig. 4.14).
2. Adiabatic flame temperature peaks at richer side ($\varphi = 1.2$) and has an increasing trend in the lean side of mixture and decreasing trend in rich side of mixture with respect to equivalence ratio which is in agreement with the work available in literatures (Fig. 4.15).
3. The concentration of *CO* increases with equivalence ratio. The rate of increase is almost a constant for both lean and rich side (Fig. 4.16).
4. Fuel is not predicted at equilibrium state for both lean and rich mixtures [Fig. 4.4 (a) to Fig. 4.13 (a)].
5. The concentration of oxygen is predicted for both lean and rich mixture.

For rich mixture, it is obtained from the dissociation of CO_2 [Fig. 4.4 (a) to Fig. 4.13 (a)].

6. The concentration of carbon dioxide increases for lean mixture and decreases for rich mixtures with equivalence ratio (Fig. 4.16).

7. The concentration of hydrogen increases with equivalence ratio for both lean and rich mixtures. The rate of increase of H_2 is higher at rich side (Fig. 4.17).

8. The concentration of water in equilibrium mixture increases for both lean and rich mixture with equivalence ratio (Fig. 4.18).

9. Concentration profiles of unstable species are also predicted. In the neighborhood of stoichiometric mixtures, where the flame temperature is very high, the equilibrium concentration of the intermediates are very high. But for the two lean or too rich mixtures, their concentrations decay after getting a peak value [Fig. 4.4 (b) to 4.13 (b)].

5-2 Recommendations for future work

1. The mechanism analysed in this study is the revision of WD79 mechanism. An independent mechanism is needed for the combustion of methanol. This can be done by an extensive literature survey and performing experiments for the combustion of methanol at different equivalence ratios.

2. In practical applications, fuel burns with air. Therefore, experiments should be performed in the presence of air and the effect of nitrogen should be observed.

3. Modelling should be done by considering nitrogen as a diluent gas, for the reason given above, and the reactions involving oxidation of nitrogen should be considered with the reaction mechanism of oxidation of methanol.

4. Modelling should be done by considering the conduction and diffusion terms which are neglected in this modelling work.

5. As the hydrocarbon fuels are depleting, a mixture of methane and methanol is now an interesting fuel to model. Hence it is recommended to model the mixture of the methane and methanol by developing a reaction mechanism.

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7.APPENDIX I

W.D.79 METHANOL OXIDATION MECHANISM [4].
FORWARD RATE PARAMETERS.

A in cm^3*-mole-sec. units Ea in Cal/mole. T in °K*

$k = AT^n exp(-Ea/RT)$

SN	REACTIONS	A	n	Ea
1	$CH_3OH+M=CH_3+OH+M$	3.16E18	00.00	08.000E4
2	$CH_3OH+O_2=CH_2OH+HO_2$	3.98E13	00.00	05.090E4
3	$CH_3OH+OH=CH_2OH+H_2O$	3.98E12	00.00	02.000E3
4	$CH_3OH+O=CH_2OH+OH$	1.58E12	00.00	02.300E3
5	$CH_3OH+H=CH_2OH+H_2$	3.16E13	00.00	07.000E3
6	$CH_3OH+H=CH_3+H_2O$	5.00E12	00.00	05.300E3
7	$CH_3OH+CH_3=CH_2OH+CH_4$	2.00E11	00.00	09.800E3
8	$CH_3OH+HO_2=CH_2OH+H_2O_2$	6.30E12	00.00	01.940E4
9	$CH_2OH+M=CH_2O+H+M$	2.50E13	00.00	02.900E4
10	$CH_2OH+O_2=CH_2O+HO_2$	1.00E12	00.00	06.050E3
11	$CH_4+M=CH_3+H+M$	1.26E17	00.00	08.840E4
12	$CH_4+H=CH_3+H_2$	1.26E14	00.00	01.190E4
13	$CH_4+OH=CH_3+H_2O$	3.16E03	03.08	02.000E3
14	$CH_4+O=CH_3+OH$	1.58E13	00.00	09.200E3
15	$CH_4+HO_2=CH_3+H_2O2$	2.00E13	00.00	01.800E4
16	$CH_3+HO_2=CH_3O+OH$	1.58E13	00.00	00.00000
17	$CH_3+OH=CH_2O+H_2$	3.98E12	00.00	00.00000
18	$CH_3+O=CH_2O+H$	1.24E14	00.00	02.000E3
19	$CH_3+O_2=CH_3O+O$	2.50E13	00.00	02.900E4
20	$CH_2O+CH_3=CH_4+HCO$	1.00E10	00.50	06.000E3
21	$CH_3+HCO=CH_4+CO$	3.16E11	00.50	00.00000
22	$CH_3+HO_2=CH_4+O_2$	1.00E12	00.00	04.000E2
23	$CH_3O+M=CH_2O+H+M$	5.00E13	00.00	02.100E4
24	$CH_3O+O_2=CH_2O+HO_2$	1.00E12	00.00	06.000E3
25	$CH_2O+M=HCO+H+M$	5.00E16	00.00	07.200E4
26	$CH_2O+OH=HCO+H_2O$	5.00E14	00.00	06.300E3
27	$CH_2O+H=HCO+H_2$	3.98E13	00.00	03.800E3
28	$CH_2O+O=HCO+OH$	5.00E13	00.00	04.600E3
29	$CH_2O+HO_2=HCO+H_2O_2$	1.00E12	00.00	08.000E3
30	$HCO+OH=CO+H_2O$	1.00E14	00.00	00.00000
31	$HCO+M=H+CO+M$	1.58E14	00.00	01.900E4
32	$HCO+H=CO+H_2$	2.00E14	00.00	00.00000
33	$HCO+O=CO+OH$	1.00E14	00.00	00.00000

SN	REACTIONS	A	n	Ea
34	$HCO+HO_2=CH_2O+O_2$	1.00E14	00.00	03.000E3
35	$HCO+O_2=CO+HO_2$	3.16E12	00.00	07.000E3
36	$CO+OH=CO_2+H$	1.26E07	01.30	-8.000E2
37	$CO+HO_2=CO_2+OH$	1.00E14	00.00	02.300E4
38	$CO+O+M=CO_2+M$	6.30E15	00.00	04.100E3
39	$CO_2+O=CO+O_2$	2.50E12	00.00	04.380E4
40	$H+O_2=O+OH$	2.00E14	00.00	01.680E4
41	$H_2+O=H+OH$	2.00E10	00.00	08.900E3
42	$H_2O+O=OH+OH$	3.16E13	00.00	01.846E4
43	$H_2O+H=H_2+OH$	1.00E14	00.00	02.030E4
44	$H_2O_2+OH=H_2O+HO_2$	1.00E13	00.00	01.800E3
45	$H_2O+M=H+OH+M$	2.00E16	00.00	01.051E5
46	$H+O_2+M=HO_2+M$	1.58E15	00.00	-1.000E3
47	$HO_2+O=OH+O_2$	5.00E13	00.00	01.000E3
48	$HO_2+H=OH+OH$	2.50E14	00.00	01.900E3
49	$HO_2+H=H_2+O_2$	2.50E13	00.00	07.000E2
50	$HO_2+OH=H_2O+O_2$	5.00E13	00.00	01.000E3
51	$H_2O_2+O_2=HO_2+HO_2$	3.98E13	00.00	04.260E4
52	$H_2O_2+M=OH+OH+M$	1.26E17	00.00	04.550E4
53	$H_2O_2+H=HO_2+H_2$	1.58E12	00.00	03.894E3
54	$O+H+M=OH+M$	1.00E16	00.00	00.00000
55	$O_2+M=O+O+M$	5.00E15	00.00	01.150E5
56	$H_2+M=H+H+M$	2.00E14	01.00	09.600E4
57	$C_2H_6=CH_3+CH_3$	2.50E19	-1.00	08.830E4
58	$C_2H_6+CH_3=C_2H_5+CH_4$	-0.5000	04.00	08.300E3
59	$C_2H_6+H=C_2H_5+H_2$	5.01E02	03.50	05.200E3
60	$C_2H_6+OH=C_2H_5+H_2O$	6.31E13	00.00	02.400E3
61	$C_2H_6+O=C_2H_5+OH$	2.50E13	00.00	06.400E3
62	$C_2H_5=C_2H_4+H$	3.98E13	00.00	03.800E4
63	$C_2H_5+O_2=C_2H_4+HO_2$	1.00E12	00.00	05.000E3
64	$C_2H_5+C_2H_3=C_2+H_4+C_2H_4$	3.16E18	00.00	03.560E4
65	$C_2H_4+O=CH_{3+}HCO$	1.00E13	00.00	01.100E3
66	$C_2H_4+M=C_2H_{3+}H+M$	3.98E17	00.00	09.820E4
67	$C_2H_4+H=C_2H_3+H_2$	6.31E13	00.00	06.000E3
68	$C_2H_4+OH=C_2H_{3+}H_2O$	1.00E14	00.00	03.500E3
69	$C_2H_4+O=CH_2O+CH_2$	2.50E13	00.00	05.000E3
70	$C_2H_3+M=C_2H_{2+}H+M$	3.16E16	00.00	04.050E4

SN	REACTIONS	A	n	Ea
71	$C_2H_2+M=C_2H+H+M$	1.00E14	00.00	01.140E5
72	$C_2H_2+O_2=HCO+HCO$	3.98E12	00.00	02.800E4
73	$C_2H_2+H=C_2H+H_2$	2.00E14	00.00	01.900E4
74	$C_2H_2+OH=C_2H+H_2O$	6.30E12	00.00	07.008E3
75	$C_2H_2+O=C_2H+OH$	3.16E16	-0.60	01.700E4
76	$C_2H_2+O=CH_2+CO$	6.30E13	00.00	04.000E3
77	$C_2H+O_2=HCO+CO$	1.00E13	00.00	07.000E3
78	$C_2H+O=CO+CH$	5.00E13	00.00	00.00000
79	$CH_2+O_2=HCO+OH$	1.00E14	00.00	03.700E3
80	$CH_2+O=CH+OH$	2.00E11	00.68	02.500E4
81	$CH_2+H=CH+H_2$	2.50E11	00.67	02.570E4
82	$CH_2+OH=CH+H_2O$	2.50E11	00.67	02.571E4
83	$CH+O_2=CO+OH$	1.26E11	00.67	02.570E4
84	$CH+O_2=HCO+O$	1.00E13	00.00	00.00000

All third bodies are equally effecient.

8.APPENDIX II

CHEMKIN

CHEMKIN is a package of FORTRAN programs which are designed to facilitate a chemist's interaction with the computer in modelling chemical kinetics. The modelling process requires that the chemist formulate an applicable reaction mechanism with rate constants and that he formulate and solve an appropriate system of governing equations.

The package is comprised of the following two major components.

1. INTERPRETER
2. GAS PHASE SUBROUTINE LIBRARY

The first step for using the package is to execute the Interpreter. The CHEMKIN Interpreter first reads (Unit 5) user-supplied information about the species and chemical reactions for a particular reaction mechanism. It then extracts further information about the species 'thermodynamic properties' from a data base (Unit 21). This information is stored on the CHEMKIN Linking File (Unit 25); a file that is needed by the CHEMKIN subroutine library, which will be accessed by the CHEMKIN program. In addition, the CHEMKIN Interpreter requires an additional binary scratch file on Unit 23.

The results from the interpreter is the linking file (unit 25) which is written in the machine language. This file contains all the information of a specie and reaction like, thermodynamic constants, Arrhenius rate coefficients and third body enhancement of the specie in third body reaction. The linking file is used by main program along with the CHEMKIN subroutine library and LSODE (Ordinary Differential Equation Solver).

The Gas Phase Subroutine Library is a collection of about 200 modular FORTRAN subroutines which may be called to return equation of state variables, thermodynamic properties, chemical production rates, derivatives of equation of state variables, derivatives of thermodynamic properties, derivatives of chemical production rates, and sensitivity parameters.

The second step is to write a main program (CHEMKIN program) which calls the necessary subroutines of gas-phase subroutine library. Linking file (unit 25), out put from the interpreter is the input to the main program. These CHEMKIN subroutines must be initialized before use and the CHEMKIN program makes the appropriate initialization calls. The purpose of the initialization is to read the Linking Files and set up the internal working and storage space required by all subroutines in the library. Main program opens all appropriate files, allocates the working storage, and calls the CHEMKIN subroutines and the differential equation solver LSODE. LSODE is independent of the main program. Any initial value problem can be solved by the solver. The user has to defined the parameters given in the solver. User may set the tolerances on its own choice. The solver gives the solution of the ODE after successive internal calculated by itself. The main program prints the solution in a file (unit 6) and save in unit 7 after successive interval supplied by the user. The solver (LSODE) prints the error massages, if the solution is not found. It may happene due to high accuracy demanded by the user or convergence of the solution does not reach or due to floating point errors. For these cases, the solver tries to find the solution five times and if does not find, prints an error massage in LOUT (unit 6) in the form of flags defined in the manual. A schematic representation for the solution techniques is given in Figure A.1.

Therefore, to solve a flame problem the user must be able to set up a command procedure that allows for the execution of several preprocessor programs, the access to several data bases, the loading of subroutines from several libraries, and the passing of files from one process to another.

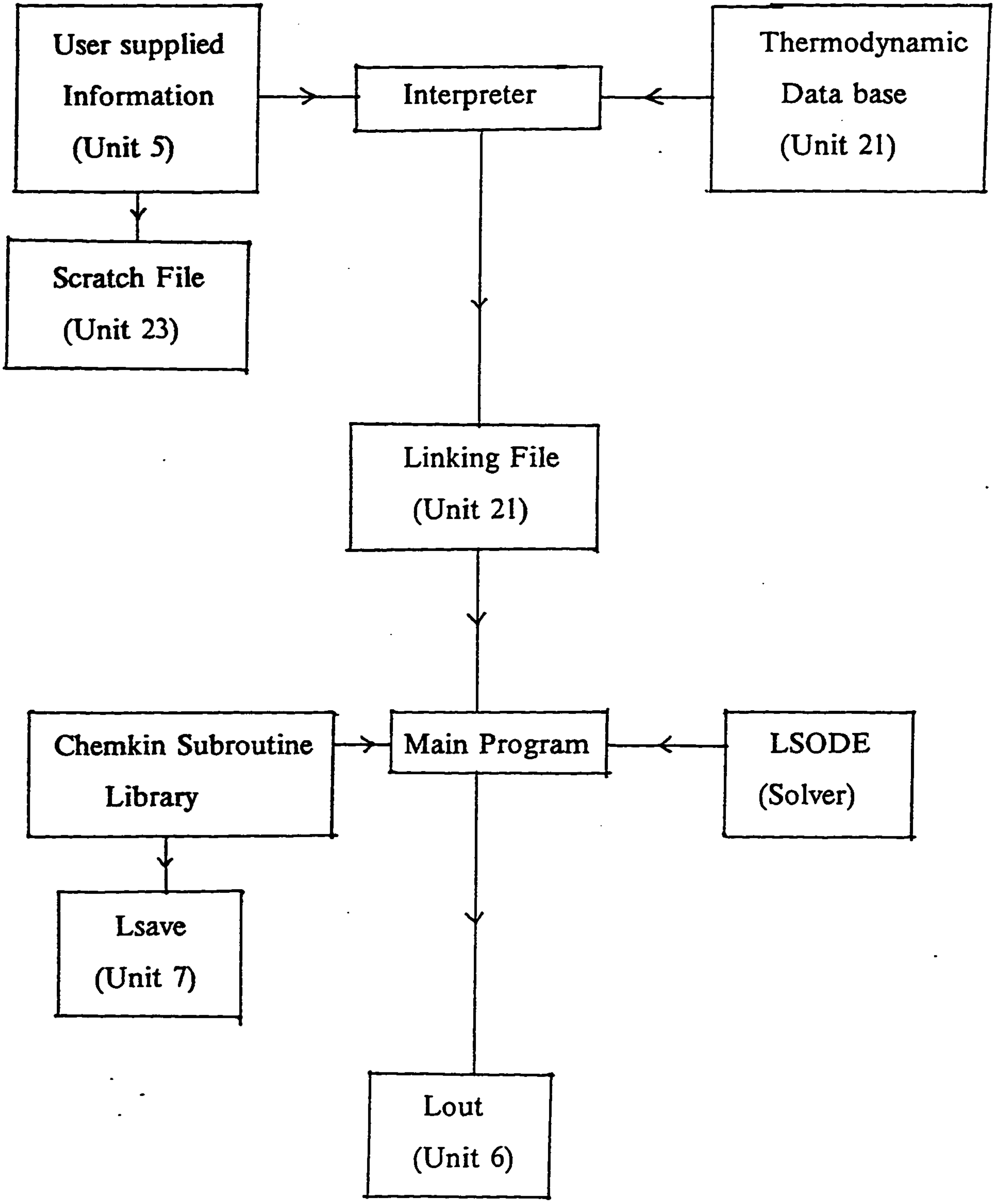

Fig. A.1 Schematic representation for the solution technique.

9. APPENDIX III

Sample Calculations for curve fitting in experimental temperature data

$$\text{Diameter of the burner} = 4.6 \text{ cm}$$

$$\text{Area of the burner} = \frac{\pi}{4}(4.6)^2\, cm^2$$

$$= 16.62\, cm^2$$

Area of the burner is constant and used for all equivalence ratios.

$$\text{Velocity of the mixture} = \frac{\textit{Volume flow rate}}{\textit{Area of the burner}}$$

For

$$\text{Equivalence ratio} = 0.9$$

$$\text{Pressure(in atmosphere)} = 1.0$$

$$\text{Velocity of the mixture} = \frac{3.69 \times 1000}{60 \times 16.62}$$

$$= 3.76 \text{ cm/sec.}$$

In the governing equations, the independent variable is time. Therefore next is to find out the time of reaction corresponding to the different locations given in reference [2].

$$Time = \frac{Distance}{Velocity}$$

Temperatures were measured up to 6 mm height of the flame at an interval of 0.5 mm. Note that the time for the flame for reaching a particular location is different for every equivalence ratio because of the different flow rate (or velocity). For the flame considered, the distance, time and temperature are given as follows.

Distance(mm)	Time(s)	Temperaure(K)
0.0	0.0000	1375.5
0.5	0.0133	1396.2
1.0	0.0266	1375.5
1.5	0.0399	1379.2
2.0	0.0532	1320.1
2.5	0.0665	1241.5
3.0	0.0798	1190.6
3.5	0.0931	1183.0
4.0	0.1064	1175.5
4.5	0.1197	1167.9
5.0	0.1329	1160.4
5.5	0.1463	1149.1
6.0	0.1596	1141.5

A fourth order polynomial is fitted in the data with the help of plotsys package available at K.F.U.P.M. mainframe. The order of the polynomial is so selected that it matches with the experimental data as close as possible.

The fitted polynomial is

$$T = -4704100R^4 + 204790R^3 + 36598R^2 - 2757R + 1211.3$$

Where R = Time - 0.0797

The same procedure is adopted for the rest of the equivalence ratios and pressure. The distance time and temperatures for each case are tabulated in Table A.1 and A.2 and the fitted polynomial are given as follows.

Pressure = 1.0 Atmosphere.

Equivalence Ratio	Polynomial
1.0	$T = -2.17\times10^{10}R^7 - 1.54\times10^{9}R^6 - 2.21\times10^{8}R^5$ $+ 1.31\times10^{7}R^4 + 6.23\times10^{5}R^3 - 23632R^2$ $- 1592.2R + 1307.4$ R = Time - 0.07812
1.1	$T = -3.85\times10^{8}R^6 + 3.41\times10^{7}R^5 + 2.21\times10^{6}R^4$ $- 1.17\times10^{5}R^3 + 7239.0R^2 - 1937.6R + 1232.2$ R = Time - 0.08070

Pressure = 0.167 Atomsphere.

0.9	$T = -3.53\times10^{13}R^6 + 4.26\times10^{11}R^5 - 4.16\times10^{9}R^4$ $+ 4.46\times10^{7}R^3 - 97024R^2 - 1217.7R + 1523.4$ R = Time - 0.00972
1.0	$T = 9.95\times10^{12}R^6 + 3.69\times10^{11}R^5 - 8.93\times10^{9}R^4$ $+ 3.89\times10^{7}R^3 + 74144R^2 - 1523.6R + 1479.7$ R = Time - 0.01064
1.1	$T = 2.58\times10^{13}R^6 + 1.64\times10^{11}R^5 - 9.88\times10^{9}R^4$ $+ 3.36\times10^{7}R^3 + 1.11\times10^{2}R^2 - 733.77R + 1441.7$ R = Time - 0.01154

Table A.1 Distance, Time and Temperature of the Flame

Pressure = 1.0 Atmosphere.

φ	Distance(mm)	Time(s)	Temperaure(K)
1.0	0.0	0.00000	1384.8
	0.5	0.01453	1404.0
	1.0	0.02907	1357.6
	2.0	0.05812	1327.3
	3.0	0.08718	1291.5
	4.0	0.11624	1254.6
	5.0	0.14530	1238.8
	6.0	0.17436	1224.2
1.1	0.0	0.00000	1366.7
	0.5	0.01582	1396.2
	1.0	0.03164	1347.0
	1.5	0.04746	1324.2
	2.0	0.06328	1236.4
	2.5	0.07910	1284.8
	3.0	0.09492	1172.7
	4.0	0.12656	1169.1
	5.0	0.15820	1160.6
	6.0	0.18984	1146.1

Table A.2 Distance, Time and Temperature of the Flame

Pressure = 0.167 Atmosphere.

φ	Distance(mm)	Time(s)	Temperaure(K)
0.9	0.0	0.00000	1381.2
	0.5	0.00162	1460.6
	1.0	0.00324	1500.0
	1.5	0.00486	1518.2
	2.0	0.00648	1524.2
	2.5	0.00810	1524.2
	3.0	0.00972	1524.2
	3.5	0.01134	1521.2
	4.0	0.01296	1519.4
	4.5	0.01458	1518.8
	5.0	0.01620	1518.2
	5.5	0.01782	1518.2
	6.0	0.01944	1513.3
1.0	0.0	0.00000	1307.7
	0.5	0.00177	1400.0
	1.0	0.00355	1453.8
	1.5	0.00532	1476.9
	2.0	0.00709	1480.8
	2.5	0.00887	1480.8
	3.0	0.01064	1480.8
	3.5	0.01241	1480.8
	4.0	0.01418	1473.1
	4.5	0.01596	1473.1
	5.0	0.01773	1473.1
	5.5	0.01950	1469.2
	6.0	0.02128	1469.2
1.1	0.0	0.00000	1265.4
	0.5	0.00192	1350.0
	1.0	0.00385	1406.9
	1.5	0.00577	1430.8
	2.0	0.00770	1442.3
	2.5	0.00962	1442.3
	3.0	0.01154	1442.3
	3.5	0.01347	1442.3
	4.0	0.01539	1438.5
	4.5	0.01731	1438.5
	5.0	0.01924	1434.6
	5.5	0.02116	1423.1
	6.0	0.02309	1419.2