

2007

Modeling study of impact of water on CO, PAH and NOx emissions from combustion of surrogate fuel

Abdulaziz H. Elsinawi
University of Dayton

Follow this and additional works at: https://ecommons.udayton.edu/graduate_theses

Recommended Citation

Elsinawi, Abdulaziz H., "Modeling study of impact of water on CO, PAH and NOx emissions from combustion of surrogate fuel" (2007). *Graduate Theses and Dissertations*. 2521.
https://ecommons.udayton.edu/graduate_theses/2521

This Dissertation is brought to you for free and open access by the Theses and Dissertations at eCommons. It has been accepted for inclusion in Graduate Theses and Dissertations by an authorized administrator of eCommons. For more information, please contact mschlange1@udayton.edu, ecommons@udayton.edu.

**MODELING STUDY OF IMPACT OF WATER ON CO, PAH
AND NO_x EMISSIONS FROM COMBUSTION
OF SURROGATE FUEL**

Dissertation

Submitted to

The School of Engineering of the

UNIVERSITY OF DAYTON

In partial fulfillment of the Requirement for

The Degree

Doctor of Philosophy in Materials Engineering

by

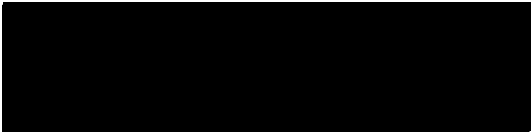
Abdulaziz H. Elsinawi

**UNIVERSITY OF DAYTON
Dayton, Ohio
USA**

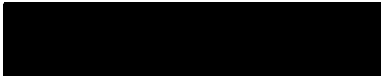
December 2007

MODELING STUDY OF IMPACT OF WATER ON CO, PAH AND NO_x EMISSIONS FROM COMBUSTION OF SURROGATE FUEL


APPROVED BY:



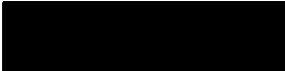
Sukh S. Sidhu, Ph.D.
Advisory Committee Chairman
Associate Professor, Mechanical and
Aerospace Engineering Department
Distinguished Research Scientist
UDRI Environmental Science and
Engineering




Philip H. Taylor, Ph.D.
Committee Member
Associate Professor, Group
Leader and Distinguished
Research Scientist, UDRI
Environmental Science and
Engineering



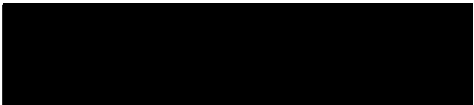
James Snide, Ph.D.
Committee Member
Professor Emeritus
Materials Engineering Department



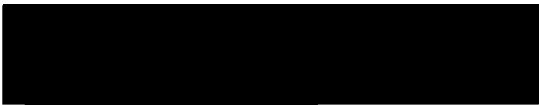
Atif Abueida, Ph.D.
Committee Member
Associate Professor
Department of Mathematics



Takahiro Yamada, Ph.D.
Committee Member
Research Scientist
UDRI Environmental Science and
Engineering



Malcolm W. Daniels, Ph.D.
Associate Dean
School of Engineering



Joseph E. Saliba, Ph.D., P.E.
Dean, School of Engineering

ABSTRACT

MODELING STUDY OF IMPACT OF WATER ON CO, PAH AND NO_x EMISSIONS FROM COMBUSTION OF SURROGATE FUEL

by

Abdulaziz H. Elsinawi

University of Dayton

2007

Advisor: Sukh S. Sidhu, Ph.D.

Methods for reducing emissions are required to meet the new and increasingly stringent emission regulations for diesel engines. Water-emulsified fuel is one of the few promising emission reduction techniques with the potential to simultaneously reduce NO_x and soot in diesel engines. Even though a better understanding could be obtained by modeling the processes involved, little effort has been directed toward modeling the combustion of water-in-fuel emulsion. This dissertation provides a better understanding of the effects of the presence of water in fuel in the form of emulsion on spray combustion and pollutant emissions, namely NO_x, soot, and carbon monoxide by modeling the relevant processes and focusing on the variables behind the emission reduction and performance. The modeling study was performed using the commercially available software package CFD-ACE+ to simulate spray combustion at conditions relevant to diesel engines. Surrogate fuel (80% n-heptane and 20% toluene) was used instead of the conventional diesel fuel because the detailed kinetic and thermodynamic

data needed for modeling is available for this surrogate fuel but not available for diesel. An emulsified fuel with 3, 5, 8 and 15% water by volume was used as an engine feed for each separate run and the results are compared with that of the dry surrogate fuel with 0% water. The modeling results are also validated against experimental data for 2-stroke diesel engines available in the literature [1].

The modeling results show that water had a significant effect on reducing engine operating temperature, NO_x and the formation of soot precursors. However, the reduction of NO_x and soot formation is at the expense of an increase in carbon monoxide (CO) emissions and elongated ignition delay time, which is disadvantageous for the steady running of diesel engines.

DEDICATION

I dedicate this work to the memory of my loving Parents:

My mother: Miriam H. Alalawi (1936 -2000)

My Father: Husein A. Elsinawi (1930- 2005)

They were the inspiration in my life to pursue higher education and in many ways helped instill in me a lifelong passion to learn.. They were always there to listen or advise and were truly interested in all that I did. I love you both and miss you deeply.

ACKNOWLEDGMENTS

All praises goes to Almighty God for guidance, health and strength.

I wish to express my gratitude to everyone who contributed to making this work a reality.

The first person to single out and acknowledge is my advisor, Dr. Sukh S. Sidhu, for the guidance, steadfast support, patience, and encouragement that he has given to me throughout my graduate studies and during the completion of this dissertation. He is a talented and passionate scientist.

I extend special and sincere thanks to Prof. Eylon the department chair of materials engineering for his support and encouragement.

A very special thanks goes to Dr. Philip Taylor for his technical expertise, advice, friendship and humor. It was under his tutelage that I developed a focus and became interested in environmental studies. Without this motivation and encouragement, I would not have considered a graduate degree in engineering. I doubt that I will ever be able to fully convey my appreciation, but I owe him my eternal gratitude.

My sincere appreciation goes to Dr. Takahiro Yamada who provided me with direction, advice and technical support and became more of a friend than a mentor or teacher.

I would also like to thank Dr. Atif Abueida, who served as a member of my committee and whose advice and valuable suggestions significantly improved the quality of my work.

I am also extremely grateful to Professor Dr. James Snide for being a member of my committee and for his input and interest in this research.

I gratefully acknowledge the Dayton Area Graduate Studies Institute (DAGSI) for the scholarship they gave me to pursue my graduate studies.

I must reserve my deepest thanks to my family for their support, encouragement, time and love that I received from my wife Hala, my daughters Heba and Hadeel, my sons Waseem, Mohammad, Amro and Hussien, who during these years gave me the strength to succeed. Thanks for putting up with me; I could not have done without you.

Thanks also to my mother, father, brothers and sisters. You've always supported me and loved me no matter what.

My deepest thanks goes to our wonderful friends Mr. Norman Gosselin and his wife Darlene Gosselin for standing behind me and my family and being supportive and kind.

I thank God and pray that I will somehow find the wisdom to put what I've learned to use for the betterment of all living things and nature.

TABLE OF CONTENTS

CHAPTER		PAGE
	ABSTRACT	iii
	ACKNOWLEDGEMENTS	vi
	LIST OF ILLUSTRATIONS	x
	LIST OF TABLES	xvi
	LIST OF ABBREVIATIONS	xvii
	OBJECTIVES	xix
I	INTRODUCTION	1
	1.1 Background.....	1
	1.2 Diesel Exhaust Gases.....	2
	1.3 Effects on Humans.....	4
	1.4 Motivation and Problem Statement	5
II	BACKGROUND OF EMISSION FORMATION.....	9
	2.1 Diesel Combustion Overview.....	9
	2.2 Polycyclic Aromatic Hydrocarbons.....	16
	2.3 Oxides of Nitrogen-NO _x	21
	2.3.1 Thermal NO	21
	2.3.2 Prompt NO; reaction of N ₂ with hydrocarbon fraction	26
	2.3.3 Fuel-NO; oxidation of fuel-bound nitrogen compound.....	28
III	EMISSION REDUCTION TECHNIQUES.....	29
	3.1 Emission Reduction Overview	29

CHAPTER		PAGE
	3.1.1 Pre-treatment.....	29
	3.1.2 Internal Measures (Primary Methods)	31
	3.1.3 After-Treatment (Secondary Methods).....	32
IV	LITERATURE REVIEW OF WATER-DIESEL EMULSION MODELING	33
	4.1 Introduction and Approach.....	33
	4.2 Literature Review of Water-diesel Emulsion Modeling.....	36
V	CHEMKIN MODELING OF FUEL COMBUSTION	41
VI	CFD MODEL APPROACH AND THEORY	73
	6.1 Introduction.....	73
	6.2 Spray Module Theory	73
	6.3 Droplet Heat and Mass Transfer.....	74
	6.4 Turbulent κ - ϵ Model.....	76
	6.5 Chemistry/Reaction Model.....	77
	6.6 Physical Model	79
	6.7 CFD Combustion Analysis Software	79
	6.8 Model Setup.....	80
	6.9 Boundary Conditions and Input Values.....	83
VII	MODELING RESULTS AND DISCUSSION	86
VIII	CONCLUSION AND FUTURE RECOMMENDATIONS.....	126
	8.1 Conclusions	126
	8.2 Future Recommendations	129
	APPENDIX	130
	REFERENCES	163

LIST OF ILLUSTRATIONS

Figure		Page
2.1	Exhaust compositions for complete combustion of surrogate fuel under fuel-lean conditions	11
2.2	Diesel spray combustion during the quasi-steady combustion phase	12
2.3	Temporal sequences of autoignition and the premixed combustion phase	12
2.4	Variation of SI engine CO emissions with air/fuel ratio	14
2.5	Experimental temperature, pressure and C/O-ratio dependence of the final soot volume fraction and soot yield (fraction of C appearing as soot)	15
2.6	Mechanistic model for formation of soot from aromatic and aliphatic compounds	16
2.7	A schematic diagram illustrating kinetic pathways of multi-ring aromatic formation that leads to PAH growth.....	17
2.8	Schematic reaction path leading to soot formation	19
2.9	Variation in soot volume fraction F_v , particle number density N , particle size d and soot hydrogen/carbon H/C ratio with time in a flame	20
2.10	Characteristic NO formation time, initial NO formation rate and NO equilibrium concentration as given by Eqs. 2.9, 2.11 and 2.13. $[O_2]_e = 4.2 \mu\text{mol}/\text{cm}^3$, $[N_2]_e = 0.43 \text{ millimol}/\text{cm}^3$ ($\phi \approx 1$). $p = 50 \text{ bar}$	24
2.11	Calculated NO formation as functions of temperature and air excess ratio (λ).....	24
2.12	Reaction rate coefficients for thermal NO (k_{1f}) and three-body reaction (k_{5f}) as shown in (Eq. 2.14)	26

Figure		Page
3.1	Fuel oil droplet and emulsified fuel droplet size and distribution	31
3.2	NO _x tradeoff with other emission components	32
5.1	Calculated temperature for air/ (80% n-heptane+20% toluene) mixtures of different fuel/air-equivalence ratios. Pressure = 39 bar	44
5.2	Major species and OH for auto-ignition and combustion of (80% n-Heptane+20% Toluene), Fuel/air-equivalence ratio ($\phi = 2$)	44
5.3	Mole fraction of carbon monoxide at different equivalence ratios	45
5.4	Formation of HCHO from the combustion of surrogate fuel (80% n-heptane and 20% toluene) at different equivalence ratios.....	46
5.5	Formation of soot precursor C ₃ H ₃ from the combustion of surrogate fuel (80% n-heptane and 20% toluene) at different equivalence ratios	47
5.6	Mole fraction of surrogate fuel (80% n-heptane and 20% toluene)	48
5.7	Mole fractions of CO and soot precursor C ₃ H ₃ change with equivalence ratios	49
5.8	Calculated temperatures for water (80% n-heptane and 20% toluene) in surrogate emulsified mixtures at fuel/air-equivalence ratio, $\phi=0.8$	50
5.9	Calculated temperatures for 0, 3, 5, 8, and 15% water (80% n-heptane and 20% toluene) in surrogate emulsified mixtures at fuel/air-equivalence ratio, $\phi=2$	51
5.10	Maximum model temperature change at different water-in-fuel percentage for fuel lean and fuel rich conditions where $\phi = 0.8$ and 2	52
5.11	Concentration change of OH radicals with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel. $\phi=0.8$	54
5.12	Concentration change of OH radicals with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel. $\phi=2$	55
5.13	Carbon monoxide formation change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel, $\phi=0.8$	57

Figure		Page
5.14	Carbon monoxide formation change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel, $\phi=2$	59
5.15	Formation path of the first aromatic ring via the combination of two propargyl (C_3H_3) radicals	59
5.16	Concentration of C_3H_3 precursors change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel, at $\phi=0.8$	61
5.17	Concentration of C_3H_3 precursors change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel, at $\phi=2$	62
5.18	PAH growth initiated by aromatic combination of two benzene rings	63
5.19	Reaction mechanisms for the oxidation of naphthalene with OH radicals.....	65
5.20	Benzene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.	66
5.21	Naphthalene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel	66
5.22	Phenanthrene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel	67
5.23	Chrysene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.	67
5.24	Benzene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.	68
5.25	Naphthalene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel	69
5.26	Phenanthrene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel	69
5.27	Chrysene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.	70
5.28	NO formation during the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion at $\phi=0.8$ for 0, 3, 5, 8 and 15% water in fuel	71

Figure		Page
5.29	NO formation during the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion at $\phi=2.0$ for 0, 3, 5, 8 and 15% water in fuel	72
6.1	Dimensions and characteristics of 2-stroke diesel engine used in the model	81
6.2	Generated axisymmetric structured grid of the 2-stroke diesel engine cylinder used in the model.....	82
6.3	Angle view of the generated axisymmetric structured grid of the 2-stroke diesel engine used in the model	82
7.1	Temperature profile at the combustion of surrogate fuel (80% n-heptane and 20% Toluene)/water emulsion of 0, 3, 5, 8 and 15% water content.....	89
7.2	Experimental temperature profile from the combustion of n-heptane/water emulsion with 0, 10 and 20% of water.....	90
7.3	In-cylinder engine pressure change, P [atm], versus crank angle, $^{\circ}\text{CA}$, at combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion with 0, 3, 5, 8 and 15% water contents...	91
7.4	Engine torque output versus engine speed using water-diesel emulsions	93
7.5	Engine power output versus engine speed using diesel-water emulsions	93
7.6	Concentration profiles of O radicals from the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% water in fuel.....	96
7.7	NO_x concentration during the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% water content.....	97
7.8	Sensitivity of NO for the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% of water content based on rate of formation/consumption of the most significant reactions	97
7.9	Percent NO_x reduction for the combustion of emulsified fuel at 3, 5, 8 and 15% water in fuel compared to that of neat fuel of 0% water	98
7.10	NO concentration during the combustion of n-heptane/water emulsion of 0, 10, and 20% of water content	99

Figure		Page
7.11	Experimental exhaust [NO _x] change with the real engine power....	101
7.12	Concentration profiles of OH radicals from the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% water in fuel.....	102
7.13	Concentration profiles of H radicals from the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% water in fuel.....	107
7.14	Concentration change of C ₂ H ₂ with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.	107
7.15	Concentration change of C ₂ H ₂ with temperature from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.....	108
7.16	Concentration change of C ₃ H ₃ with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15 % water in fuel	108
7.17	Concentration change of C ₃ H ₃ with temperature from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.....	109
7.18	Sensitivity of C ₂ H ₂ for the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% of water content based on rate of formation/consumption of the most significant reactions.....	111
7.19	Sensitivity of C ₃ H ₃ for the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% of water content based on rate of formation/consumption of the most significant reactions.....	111
7.20	Benzene (A1) concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel	113
7.21	Naphthalene (A2) concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.....	114
7.22	Phenanthrene (A3) concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.....	114
7.23	Chrysene (A4) concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.....	115

Figure		Page
7.24	Proposed reaction mechanism for the oxidation of phenanthrene and naphthalene using hydroxyl radicals.....	116
7.25	Sensitivity of PAHs for the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% of water content based on rate of formation/consumption of the most significant reactions	118
7.26	Soot fraction time profile during the combustion of n-heptane/ water emulsion with 0, 10, and 20% of water content	119
7.27	Carbon monoxide formation change with time from the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% water in fuel.....	120
7.28	Sensitivity of CO for the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% of water content based on rate of formation/consumption of the most significant reactions	121
7.29	Experimental change of exhaust [CO] with real engine power.....	122
7.30	CO emission as a function of water fraction (W/F %) in MDO (marine diesel oil) and IFO (intermediate fuel oil) at different engine loads	122
7.31	Ignition delay profile in degree crank angle (°CA) change for each run at the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% water in fuel.....	124
7.32	Ignition lag in degree crank angle (°CA) change at the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% water in fuel.....	124
7.33	Ignition delay with respect to the W/O (Water/Oil) ratio.....	125

LIST OF TABLES

Table		Page
1.1	Compositions of light-duty diesel engine exhaust.....	3
2.1	Critical fuel/air-equivalence ratio for different fuels premixed with air	14
5.1	Initial gas composition for the CHEMKIN computations.....	42
5.2	Maximum model temperature values at different water in fuel percentage for both fuel lean and fuel rich conditions where $\phi = 0.8$ and 2	51
6.1	Diesel engine model parameters.....	79
6.2	Parameters of the grid geometry.....	83
6.3	Boundary condition parameters used in the simulation.....	83
6.4	Properties of n-heptane fuel.....	84
6.5	Properties of toluene fuel.....	84
7.1	Peak temperature in [K] and peak time in milliseconds for 0, 3, 5, 8 and 15% water-fuel emulsion	89
7.2	Maximum peak pressure values and the corresponding crank angle values for 0, 3, 5, 8 and 15% water in fuel combustion	92

LIST OF ABBREVIATIONS

BDC	Bottom Dead Center
BSFC	Brake Specific Fuel Consumption
CI	Compression-Ignited
CFD	Computational Fluid Dynamics
CPU	Computer Processing Unit
DI	Direct Injection
EGR	Exhaust Gas Recirculation
EPA	Environmental Protection Agency (USA)
HAM	Humid Air Motor
HC	Total Hydrocarbons
IDI	Indirect Injection
ICE	Internal Combustion Engine
IEA	International Energy Agency
IFO	Intermediate Fuel Oil
IMEP	Indicated Mean Effective Pressure
LNG	Liquid Natural Gas
LPG	Liquid Petroleum Gas
MDO	Marine Diesel Oil

NO _x	Nitrogen Oxide
OECD	Organization for Economic Cooperation and Development
NTP	Non Thermal Plasma
PAH	Poly Aromatic Hydrocarbon
PaSR ₂	Partially Stirred Reactor
PLIF	Planar Laser-Induced Fluorescence
PM	Particulate Matter
POC	Persistent Organic Compounds
POP	Persistent Organic Pollutants
SAE	Society of Automotive Engineers
SCR	Selective Catalytic Reduction
SFC	Specific Fuel Consumption
SI	Spark Ignition
SINL	Spatially Integrated Natural Luminosity
SOF	Soluble Organic Fraction
SOI	Start Of Injection
TDC	Top Dead Center
VOC	Volatile Organic Compounds
WEO	World Energy Outlook
WHO	World Health Organization
W/O	Water-Oil Ratio
UNFCCC	United Nations Framework Convention on Climate Change

OBJECTIVES

The main objective of this modeling study was to investigate and understand the impact of the addition of 3, 5, 8 and 15% water on diesel engine emissions. This investigation was performed to accomplish the following specific objectives:

- To test the effect of water addition to fuel on the diesel engine operating conditions, specifically temperature, pressure and ignition delay which directly influence the engine efficiency and emission formation.
- To investigate the influence of water on the formation of nitrogen oxide (thermal NO_x) and carbon monoxide pollutants with the increasing water content of the emulsion.
- To present the impact of water addition on soot precursors formation such as C_2H_2 and C_3H_3 in addition to some of the PAHs namely benzene, naphthalene, phenanthrene and chrysene precursors.
- To test the hypothesis whether water addition to fuel has a physical, chemical or both effects on the engine emission by studying the OH concentration change in the combustion process.

To achieve these goals:

- Numerical computations were conducted using the computational fluid dynamic code CFD-ACE+ software package 2002 [95], in which the

governing mass, momentum, and energy conservation equations were solved in a Lagrangian frame through a discrete phase generated grid of a 2-stroke diesel engine cylinder.

- Chemkin code [82] was used as an alternative method to study the influence of water addition to surrogate fuel on emission formation and validate the modeling results of the CFD code
- Results were compared and validated against experimental data from studies conducted in literature [1, 45, 63, 66].

CHAPTER I

INTRODUCTION

1.1 Background

Diesel fuel is a very complex mixture of thousands of individual compounds, most with carbon numbers between 10 and 22. These compounds are mostly paraffinic (C_nH_{2n+2}), olefinic (C_nH_{2n}), naphthenic (cycloalkanes) (C_nH_{2n}), or aromatic (C_nH_{2n-6}) hydrocarbons. These four classes of hydrocarbons have different chemical and physical properties, so the different relative proportions of the three classes is one of the factors that make one diesel fuel different from another [2]. The average chemical formula for common diesel fuel is $C_{12}H_{26}$, ranging from approximately $C_{10}H_{22}$ to $C_{15}H_{32}$. At room temperature, diesel fuels are generally moderately volatile, slightly viscous, flammable, brown liquids with a kerosene-like odor. The boiling point range is usually between 140 and 385°C, and density is between 0.87 and 1.0 g/cm³ at 20°C [2].

The water solubility of diesel fuel varies. The aqueous solubility of crude and fuel oils in the environment is clearly dependent on the salinity of the water and the age of the oil slick. It is the same order of magnitude as the solubility of fuel oils: at room temperature, 0.37-0.53 mg/liter in sea water and 0.7-11 mg/liter in tap water [2]. Diesel fuels are widely used for transportation purposes. The more volatile fuels with low viscosity are required for high-speed engines and the heavier grades for railroad and ship diesel engines. Diesel fuels are used in stationary engines and boilers, as well as

reciprocating engines, gas turbines, pipeline pumps, gas compressors, steam processing units in electric power plants, burner installations, and industrial space and water heating facilities. Diesel fuel is produced commercially in various qualities with regard to volatility, aromaticity, cetane number, and sulfur content. The composition of diesel fuel, which influences the type and amount of compounds emitted in the exhaust, has not changed greatly during the last few decades, although the cetane number has been slightly increased, resulting in better ignition.

1.2 Diesel Exhaust Gases

Diesel engine exhaust emissions contain hundreds of chemical compounds that are emitted partly in the gaseous phase and partly in the particulate phase of the exhaust. The major gaseous products of combustion are carbon dioxide, nitrogen oxides, oxygen, nitrogen, and water vapor; carbon monoxide, sulfur dioxide, and hydrocarbons and their derivatives are also present. Benzene and toluene are present in the lower weight percent range in the gaseous part of the hydrocarbon fraction. Other gaseous exhaust components are low-relative-molecular-mass polycyclic aromatic hydrocarbons (PAHs). Some of the compositions of diesel exhaust gas are shown in Table 1.1 [3, 4]. A main characteristic of diesel exhaust is the release of particles at a rate about 20 times greater than that from gasoline-fueled vehicles. The particles are composed of elemental carbon, organic compounds adsorbed from fuel and lubricating oil, sulfates from fuel sulfur, and traces of metallic components. Most of the total particulate matter appears to occur in the sub-micrometer range, between 0.01 and 0.5 μm . Agglomeration may occur during aging, up to a maximal diameter of 30 μm . The emitted particles have a large surface area. Organic

compounds generally contribute 10 to 30% of the total particulate matter, but poorly-designed and -maintained engines may result in as much as 90% organic compounds.

Higher-relative-molecular-mass, oxygenated and nitro-PAHs occur at concentrations of parts per million in this fraction [4]. Combustion products originating from fuel and lubricating oil additives or from corrosion inhibitors may also occur. For example, nitrate-based cetane improvers are assumed to form nitro-PAHs.

Diesel engine exhausts are emitted mainly from motor vehicles, stationary, railway locomotive, and ship diesel engines. The emissions from diesel motor vehicles have been well described, but the individual results are often not comparable due to differences in parameters such as driving cycle, engine type, and fuel composition. The individual components are emitted in the following quantities: carbon dioxide, about 1 kg/km; carbon monoxide, nitrogen oxides, total gaseous hydrocarbons, and particulate matter, 0.1-20 g/km; and aliphatic compounds, alcohols, aldehydes, light aromatics, and PAHs, micrograms per kilometer [4, 5].

Table 1.1: Compositions of light-duty diesel engine exhaust. Adapted from [3, 4].

Component	Concentration (% by weight)
Carbon dioxide	7.1
Water vapor	2.6
Oxygen	15.0
Nitrogen	75.2
Carbon monoxide	0.03
Hydrocarbons	0.0007
Nitrogen oxides	0.03
Hydrogen	0.002
Sulfur dioxide	0.01
Sulfates	0.00016
Aldehydes	0.0014
Ammonia	0.00005
Particulates	0.006

In principle, there is no difference between the quality and quantity of exhaust emissions from light- and heavy-duty engines, although heavy-duty vehicles release larger amounts of particulate matter. Exhaust emissions depend on driving cycle, engine conditions, and fuel composition, sulfur content, aromaticity, volatility and adjustment of the engine play a major role [4, 5].

The release of particulate matter increases with decreasing air/fuel ratio, increasing load, and increasing temperature. More particulates are released from older, intensively used engines than from new, low-mileage engines, probably due to their increased consumption of lubricating oil. The emission of particles from light-duty diesel vehicles is also correlated with the sulfur content of the fuel.

Increasing fuel aromaticity also increases particle emissions. PAHs and oxygenated PAHs from diesel and spark-ignition engines are qualitatively similar. Oxygenated and nitrated PAHs are emitted in the low microgram per kilometer range. PAHs emissions increase with increasing load and temperature and with the age of the engine, probably due to increased consumption of lubricating oil. The aromaticity and volatility of the fuel are directly correlated with the emission of PAHs. Malfunction of engine devices, especially the fuel injection system, increases the emission of the main exhaust components.

1.3 Effects on Humans

In general, diesel exhaust contributes to air pollution. Although the role of diesel particles cannot be singled out in acute or chronic studies, they may be partly responsible for a range of health effects associated with air pollution. The symptoms seen after acute and chronic exposure to diesel exhaust have been described in studies and anecdotal reports

of occupationally exposed subjects [3-5]. Acute exposure to diesel exhaust has been associated with irritation of the ocular and nasal mucous membranes, and an increased frequency of respiratory symptoms has been observed in occupational cohorts. No consistent short-term effect on pulmonary functions has been found, but asthma attacks have been reported [4]. The relationship between cancers of the lung and bladder and occupational exposure to diesel exhaust have been evaluated in a number of epidemiological studies [5]. The most relevant studies with regard to lung cancer are those focusing on railroad workers, bus garage workers, and stevedores, all of whom have definite exposure to diesel exhaust and report an increased risk for lung cancer.

An assessment made by the U.S. Environmental Protection Agency (EPA), suggests that possible health hazards associated with long-term exposure to diesel engine exhaust are likely to cause a lung cancer hazard to humans, as well as damage to the lung in other ways depending on exposure [5]. Short-term, acute exposure can cause irritation and inflammatory symptoms of a transient nature, these being highly variable across the population.

An estimation of increased mortality due to cancer showed that somewhere between 6 and 60 deaths per 100,000 individuals are caused by air pollution in densely populated areas [5]. Several investigations performed by the World Health Organization (WHO) have also concluded that there is a risk of increased mortality as a consequence of increasing particulate emissions.

1.4 Motivation and Problem Statement

Worldwide global warming created by the increase in CO₂ emission via fossil fuel consumption is a serious concern with respect to climate changes. In addition, control of

pollutant emissions is a major focus in the design of modern combustion systems. The major task for combustion engineers to pursue is, therefore, to achieve low pollutant emissions as well as reduced fuel consumption.

Exhaust emission from diesel engines is a serious problem. However; according to the International Energy Agency (IEA) [6], 90% of the world's primary energy comes from combustion of fossil fuels, coal, oil and natural gas. The transportation sector is a major consumer of fossil fuel and additional efforts to cut emissions from road vehicles and airplanes are very important. Further growth of diesel engines in the light-duty and heavy-duty vehicular market has continued to focus attention on emissions reduction technology and the health risks of diesel exhaust. Market penetration of light-duty diesels has the potential for a significant impact on CO₂ emissions and a reduction in demand for imported crude oil due to offsets in overall global warming or thermal efficiency [7, 9].

Although significant advances have been made during the past few years in reducing diesel engine emissions, the new stringent emission standards and legislation and the challenge to protect society, animals and nature against air pollution necessitates further research and development to comply with the new regulations and reduce diesel engine emissions.

The basic engineering methods used by engine manufacturers to control emissions involve combustor design modifications [7, 9], optimization of the in-cylinder operating parameters, and exhaust after-treatment techniques. However, redesigning a combustor would be a viable option only for future engine design since retrofit costs would apply in this case. Also, optimizing the in-cylinder operating parameters by doing some

combustor modifications or changing operating conditions would very often result in reduced particle emissions and increased NO_x [8].

Exhaust after-treatment technologies for lean burn systems such as diesels in transportation applications are still in the development phases. Development and application of catalytic exhaust after-treatment technologies are hampered by the inherently high sulfur content in currently-available diesel fuel. The high aromatic and sulfur content of currently-available diesel fuel also influences both NO_x and PM emissions [8]. For turbine engines, the use of after-treatment devices such as particle traps may not be practical as they would increase the engine weight and reduce performance. The industry expects to enable after-treatment technologies so that heavy-duty engines can meet 2007 and later emission regulations [9, 12] following significant new 2006 legislation regarding sulfur content of diesel fuel (<15 ppm).

Fuel reformulation by altering the physical or chemical composition of fuel has been used as a pollution control technique and continues to be considered as one of the more preferred avenues for realigning emissions in the future. The technology includes increasing fuel efficiency, wider use of alternative fuels and the use of fuel additives to improve fuel quality.

One promising method to enhance this technology is the use of water emulsified diesel which can economically and environmentally accomplish the goals. This method is one effective solution to improve combustion, reduce fuel consumption and reduce emissions without the enormous costs associated with engine modifications. In this regard, emulsified water-diesel fuel is attractive, offering future economic and strategic alternatives to fuel oil consumption. There is a wide range of applications with the

potential of utilizing water-in-oil emulsified fuel in liquid-fueled combustors for pollutant reduction and enhanced fuel economy.

The present study focuses on two aspects of emulsified water-diesel fuel utilization in diesel engines: first, the effect on engine operating conditions, mainly combustion temperature, pressure, and ignition delay; and second, further benefits of emulsified water-diesel fuel on emissions reduction of NO_x , soot, and carbon monoxide.

CHAPTER II

BACKGROUND OF EMISSION FORMATION

2.1 Diesel Combustion Overview

Combustion is a rapid or slow oxidation generating heat, or both light and heat. For engine combustion, only rapid oxidation is considered. The oxidizer is air with varying degrees of oxygenated combustion products. The gas exchange process is not perfect and some residuals from one cycle will participate in the next. Moreover, the concentrations of combustion products increase during the combustion event. The first oxidation can be considered to occur in almost pure air, but the burnout process definitely occurs in a mixture of unused air and combustion products. According to Heywood [10], dry air consists of 20.95% O₂, 78.09% N₂, 9300 ppm argon and 300 ppm CO₂. However, the immense consumption of fossil fuels raises the CO₂ concentration of the globe as a whole to approximately 370 ppm [11, 12]. This is a 23% increase since 1973, the year of Heywood's reference. In combustion, oxygen is the active component and the inlet air can thus be treated as composed of 20.95% oxygen and 79.05% nitrogen. The molar ratio between oxygen and nitrogen is thus:

$$\frac{1 - 0.2095}{0.2095} = 3.773 \quad (2.1)$$

The commercially-available diesel fuel is a very complex mixture of different hydrocarbons including alkanes, alkenes, alkynes and aromatics. However, for treatment of the composition of reactants (fuel and air), only an empirical formula of the hydrocarbon mixture is needed. A stoichiometric mixture ($\lambda = 1$, $\phi = 1$) has just enough oxygen to fully combust the fuel. The air excess factor λ is defined as:

$$\lambda = \frac{(F/A)_s}{(F/A)_{actual}} \quad (2.2)$$

where $(F/A)_s$ is the mass-based fuel/air ratio for a stoichiometric mixture. The fuel/air-equivalence ratio is defined as the reciprocal of the air excess factor:

$$\phi = \frac{(F/A)_{actual}}{(F/A)_s} = \lambda^{-1} \quad (2.3)$$

A diesel engine is normally operated with overall air in excess (i.e. $\phi < 1$, $\lambda > 1$).

Based on n carbon atoms, the global combustion reaction of a generic hydrocarbon of the form C_nH_b can thus be written (assuming complete combustion):

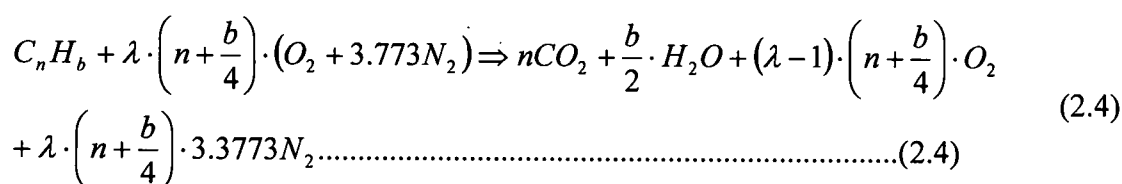


Figure 2.1 shows the exhaust compositions calculated using Equation (2.4).

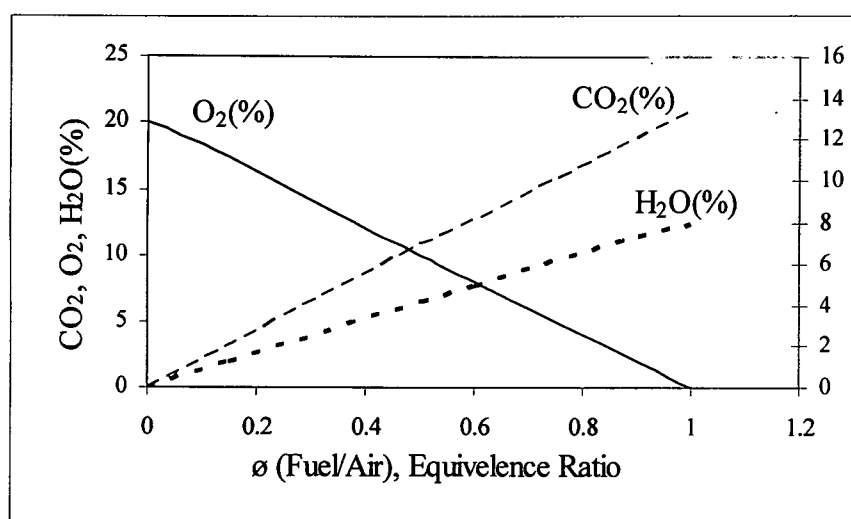


Figure 2.1. Exhaust compositions for complete combustion of surrogate fuel under fuel-lean conditions.

The exhaust concentrations vary in a close to linear fashion with fuel/air equivalence ratio. However, in practice the combustion is not fully complete and carbon monoxide, soot and unburned and partially-burned hydrocarbons are found in the exhaust gas. The exact concentration of exhaust species cannot be determined from an element balance like Equation (2.4) [10, 13].

According to Dec [14], Siebers and Higgins [15, 16], Higgins and Siebers [17] and Flynn *et al.* [18] diesel spray combustion essentially is a two-stage process. Air is entrained into the spray upstream of the flame lift-off location as shown in Figure 2.2. This creates a fuel-rich mixture that burns downstream of the liquid core and this constitutes the first combustion step. Figures 2.2 and 2.3 depict the quasi-steady combustion phase and autoignition during injection.

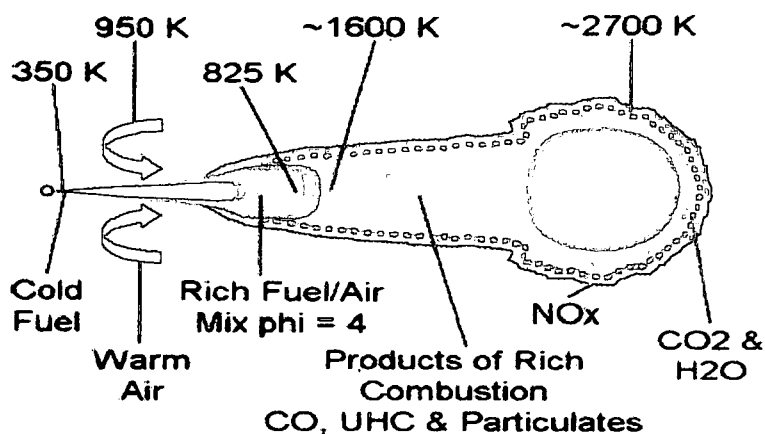


Figure 2.2. Diesel spray combustion during the quasi-steady combustion phase according to Flynn *et al.* [18], as adapted from Dec *et al.* [14].

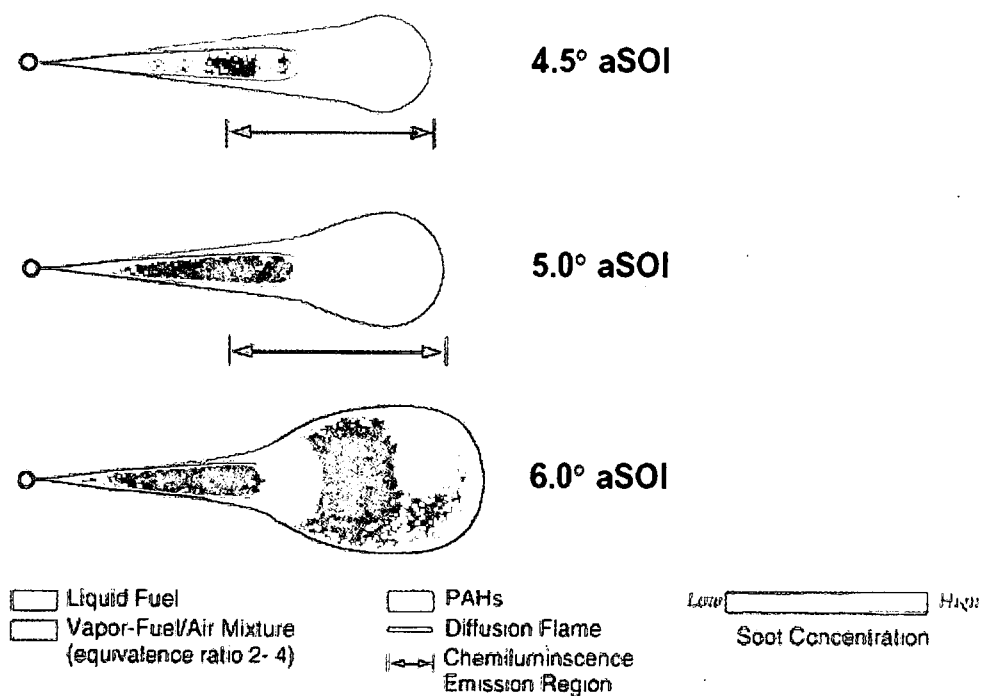


Figure 2.3 Temporal sequences of autoignition and the premixed combustion phase according to the conceptual model of Dec [14].

The premixed burn that follows the ignition delay is also generally fuel-rich as shown in Figure 2.3. Also, the premixed combustion phase can therefore be considered the first stage of fuel oxidation, similar to the reactions in the premixed zone during the quasi-steady combustion phase. The fuel-rich products of the premixed burn are quickly confined by a luminous diffusion flame that continues the fuel oxidation from the first stage of combustion. Thus, the second stage combustion takes place at the periphery of the turbulent reacting jet where the fuel-rich combustion products from the first stage of combustion meet the surrounding oxygen. Most of the formation of CO and soot precursors occurs in the first "premixed" combustion stage. The amount of CO formed at fuel-rich conditions cannot be calculated from an element balance alone [10]; additional assumptions regarding the product composition must be made. For reasonably fuel-rich mixtures, $\lambda < 1.4$ or $\phi > 1$, equilibrium for the water-gas reaction provides the following reaction:



However, for diesel combustion this approach is of little value since the first combustion step is usually very fuel rich so that not only are CO_2 and H_2 found in the products, but also soot precursors such as C_2H_2 , C_2H_4 , C_3H_3 [10, 12, 22]. Nonetheless, it can be helpful to recognize how the concentration of CO changes with the fuel/air-equivalence ratio for a premixed system. Figure 2.4 shows how the CO-concentration in the exhaust of an SI-engine varies with air excess ratio.

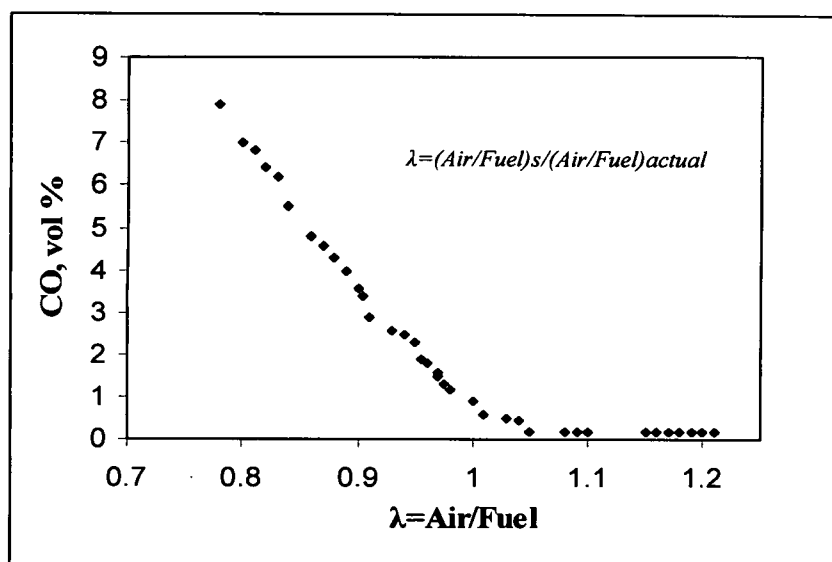


Figure 2.4. Variation of SI engine CO emissions with air/fuel ratio from Heywood [10].

It is interesting to note from Figure 2.4 that the CO level increases almost linearly with fuel/air-equivalence ratio for rich mixtures. On the other hand, soot requires significantly richer conditions before it starts to form. Glassman [19, 20] reported the critical fuel/air-equivalence ratios for different fuels, which is considered to be the ratio at which soot begins to form. A selection is listed in Table 2.1.

Table 2.1. Critical fuel/air-equivalence ratio for different fuels premixed with air, from Glassman [19, 20].

Ethane	1.69	Propane	1.65
n-pentane	1.47	n-heptane	1.55
Ethene	1.86	n-hexane	1.53
IsoOctane	1.58	Ethyne	2.03
Cyclohexane	1.65	Benzene	1.49
Toluene	1.39	Methyl Napthalene	1.12

Although not a complete list, Table 2.1 indicates that a hydrocarbon fuel must be combusted under fairly fuel-rich conditions to initiate soot formation. The C/O ratio of the reacting mixture can be helpful when considering soot formation. Heywood [10]

reports that the critical C/O ratio is 0.5 to 0.8 depending on fuel type. The soot yield increases rapidly with increasing C/O ratio beyond the critical value. This is illustrated in Figure 2.5, which shows the relation between combustion temperature and final soot volume fraction and soot yield.

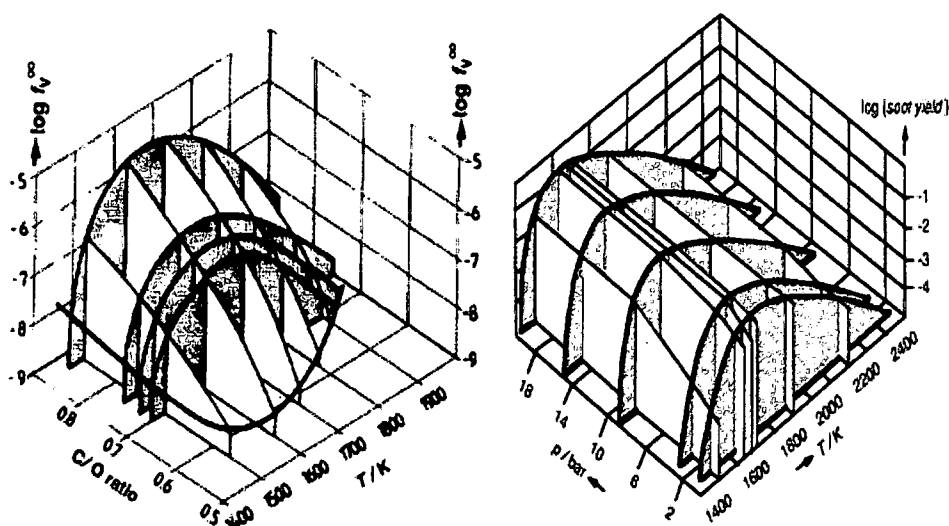


Figure 2.5. Experimental temperature, pressure and C/O ratio dependence of the final soot volume fraction and soot yield (fraction of C appearing as soot), adopted from Warnatz *et al* [21].

It is clear from Figure 2.5 that the final soot volume fraction is very sensitive to the C/O ratio. Therefore, the production of soot is expected to increase faster than the production of CO when the fuel/air-equivalence ratio increases beyond a critical value, which would clarify the maximum soot yield found for temperatures around 1700 K. This is close to the reported temperature in the interior of the reacting diesel spray which is considered as a pyrolytic, not oxidative regime as shown in Figure 2.2.

2.2 Polycyclic Aromatic Hydrocarbons

The formation of a soot particle is indeed very complex and despite decades of study, there is still no consensus regarding the formation of the soot nuclei. According to Heywood [10], two different pathways are active during diesel combustion. At low temperatures (<1700 K) only aromatics or highly unsaturated hydrocarbons of high molecular weight are very effective at forming solid carbon, because the aromatics can take a direct route to form soot. This is illustrated in Figure 2.6.

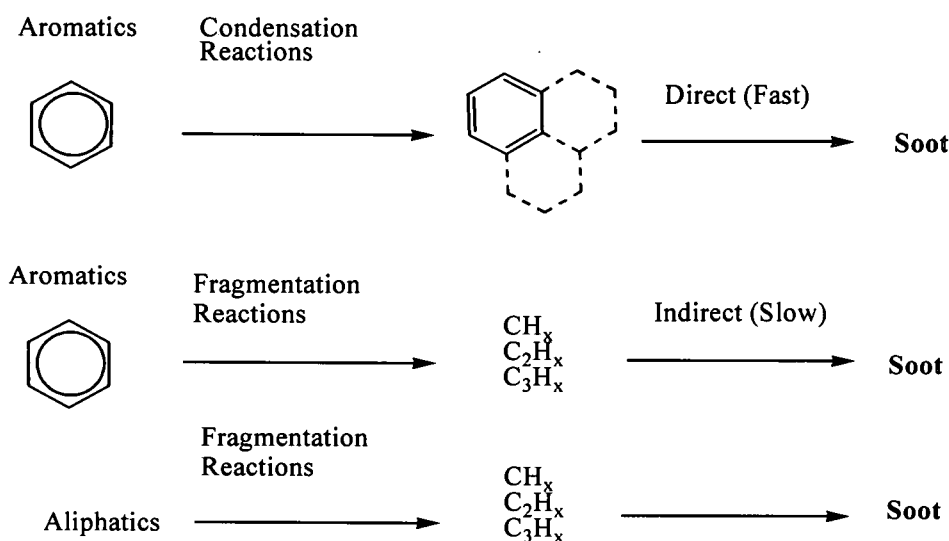


Figure 2.6. Mechanistic model for the formation of soot from aromatic and aliphatic compounds, From Heywood [10].

The mechanism of PAHs growth occurs through the replication of the H abstraction and acetylene addition (HACA) sequence or through kinetic pathways involving resonantly stabilized free radicals [22, 23]. Figure 2.7 presents a schematic diagram illustrating the kinetic pathways for larger aromatic formation. Route **a** shows the sequence of steps involving hydrogen abstraction and acetylene addition to benzene

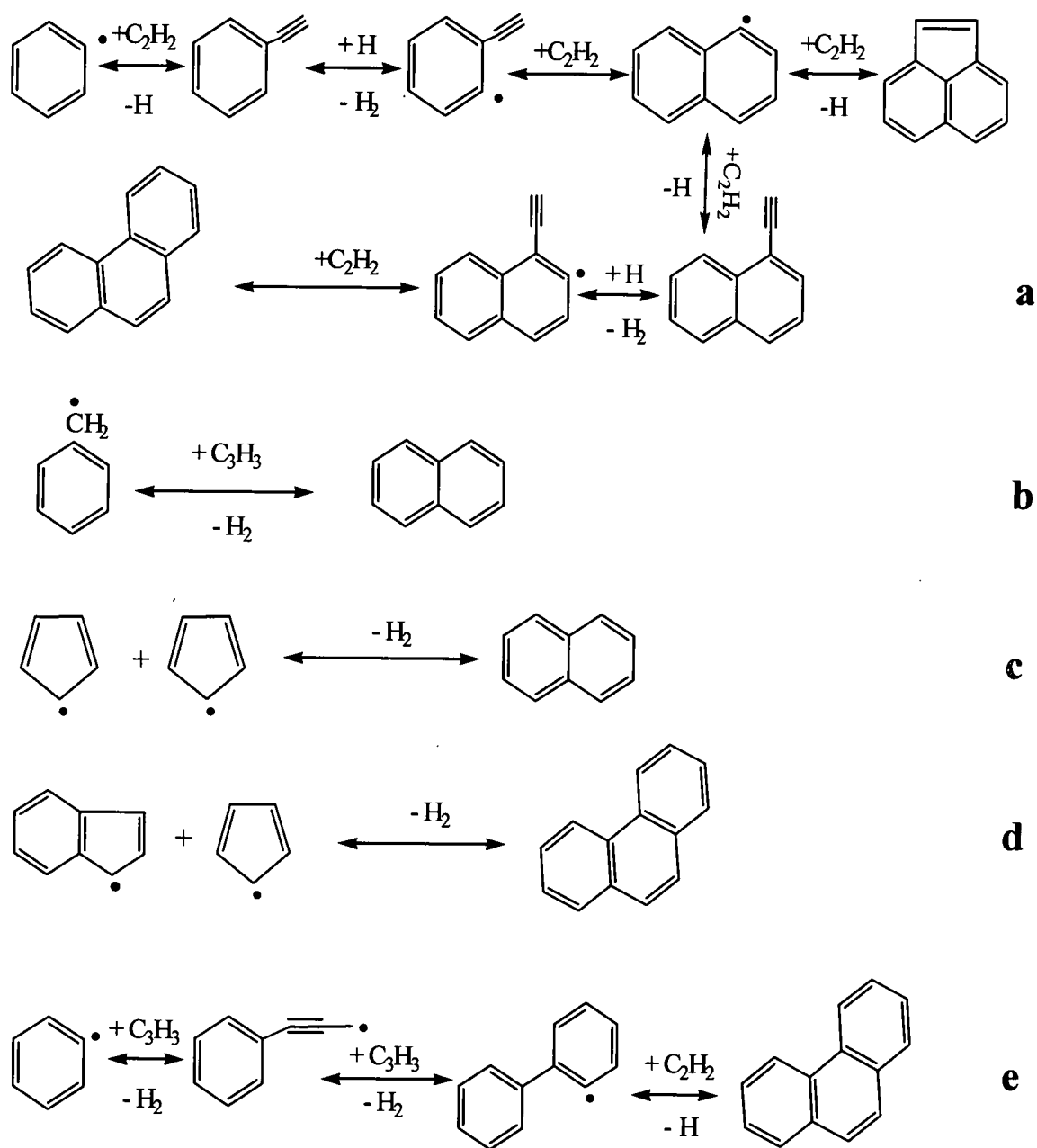


Figure 2.7. Schematic diagram illustrating kinetic pathways of multi-ring aromatic formation that lead to PAH growth [23].

with the subsequent cyclization to form larger aromatics (HACA mechanism), proposed by Frenklach and Warnatz [24]. Routes **b** and **c** were proposed by Colket and Seery [25] in which route **b** involves the resonantly-stabilized radical mechanisms that comprise the benzyl and propargyl radical combination leading to naphthalene production, and route **c** involves the self-combination of cyclopentadienyl radical to form naphthalene which could be added to indenyl radicals through route **d** to form phenanthrene as suggested by Castaldi *et al* [27] and Marinov *et al* [26]. Cyclopentadienyl and indenyl radicals are formed by benzene and naphthalene oxidation, respectively. The last route in Figure 2.7 (route **e**), which was suggested by D'Anna and Violi [22] considers the sequential addition of propargyl radicals to phenyl, leading to biphenyl and subsequent cyclization to phenanthrene by acetylene addition.

At temperatures above 1800 K, all hydrocarbon fuels can produce soot if burned sufficiently rich. The mechanism is then a less direct route via molecule fragmentation and dehydrogenation that produces soot precursors like acetylene. These soot precursors then form PAHs that grow by further addition of unsaturated fuel fragments combined with dehydrogenation. The formation of particle-like structures begins with conglomeration of molecules. This particle inception takes place at molecular masses between 500 and 2000 μm [21]. The further particle growth is a result of surface growth and coagulation. The process is illustrated in Figure 2.8.

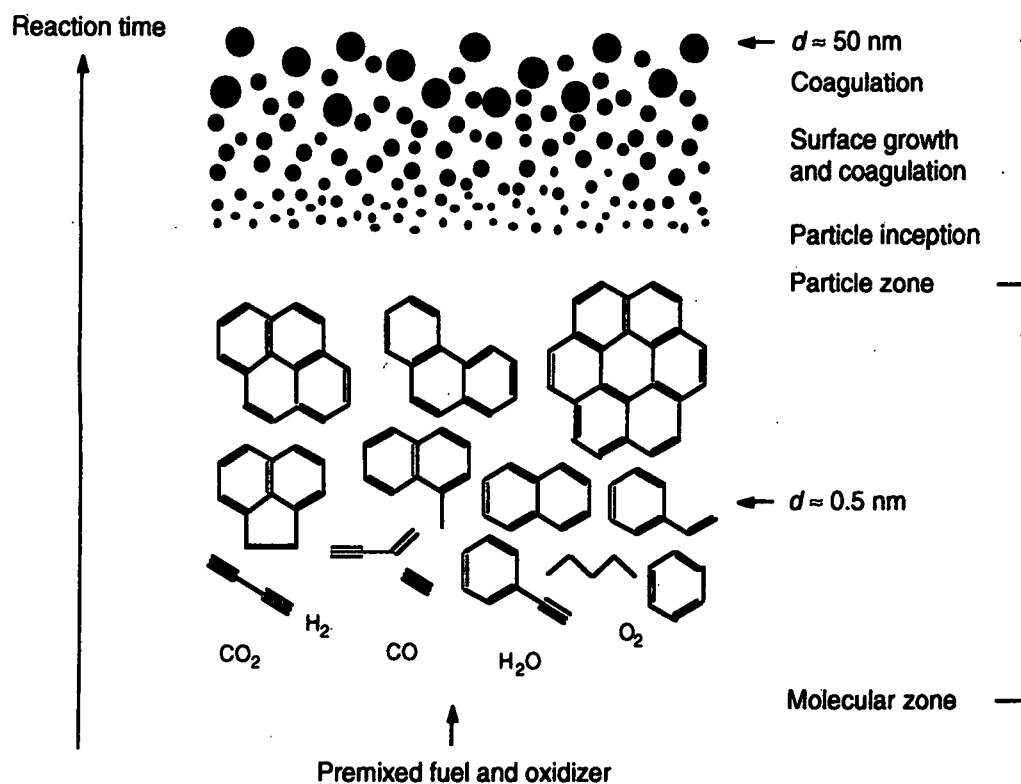


Figure 2.8. Schematic reaction path leading to soot formation, from Warnatz *et al.* [21].

Several studies [10, 19, 28] show that the number of soot particles during rich combustion first reaches a maximum and then rapidly decreases. The average soot particle diameter increases throughout the main combustion event. The agglomeration of numerous small particles into larger particles is illustrated in Figure 2.9.

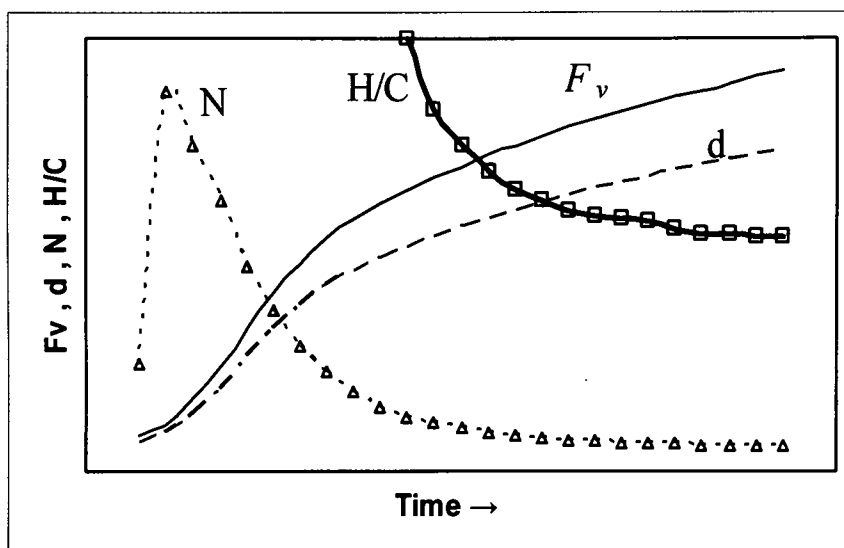


Figure 2.9. Variation in soot volume fraction F_v , particle number density N , particle size d and soot hydrogen/carbon H/C ratio with time in a flame, from Heywood [10].

It is important to realize that as oxygen is present in the combustion chamber of a diesel engine, the process of soot formation and growth can be terminated at any time if the soot particle meets oxygen and/or OH radicals [28, 29]. By dumping experiments, Pipho *et al.* [30] investigated the in-cylinder soot histories for different injection timings and piston bowl shapes. In addition to the increasing soot particle size, they found that the total mass of soot peaked a 10 of TDC where afterwards it decreased towards the final exhaust value. For the entrant piston investigated, the peak value of soot was 9.5 times higher than the exhaust level. This, in combination with the steadily increasing soot diameter, shows that most of the soot particles oxidize and the exhausted soot consists of soot that was able to escape combustion for some reason.

Heywood [10] points out that the soot particle size is important for the relative soot oxidation rate. Soot oxidation is essentially a surface phenomenon and the

volume/surface ratio increases with particle size. Thus, the combination of soot particle growth and delayed exposure to the oxidizing atmosphere facilitated by sheltered regions in the combustion chamber represents the ideal conditions for the creation of engine-out soot. So far, soot formation is considered as an effect of the first rich premixed combustion stage in the two-stage combustion proposed by Dec [14].

2.3. Oxides of Nitrogen – NO_x

NO_x is a mixture of nitric oxide (NO) and nitrogen dioxide (NO_2). It may also include other oxides of nitrogen, such as N_2O , NO_3 , N_2O_4 , and N_2O_5 . However, these additional nitrogen oxide species are insignificant in the emissions of internal combustion engines and readily react and convert to NO and NO_2 . The formation of NO can be explained by three different mechanisms [31-34]:

- (1) Thermal NO, or the Extended Zeldovich mechanism, in which O, OH, and N_2 are in equilibrium concentrations
- (2) Prompt NO ; Other mechanisms with NO formation rates above that predicted by the Extended Zeldovich mechanism, including Fenimore CN and HCN pathways [32], N_2O -intermediate route, and “Super-equilibrium” concentrations of O and OH in combination with the Extended Zeldovich mechanism.
- (3) Fuel-NO mechanism, in which fuel-bound nitrogen is oxidized to NO.

2.3.1 Thermal NO

The primary pathway for NO formation is oxidation of atmospheric molecular nitrogen (N_2) through the thermal or extended Zeldovich mechanism. It is generally accepted that reactions shown in reactions (2.6) – (2.8) govern the formation of NO in

combustion engines [10, 28, 32, 34, 35]. Together, they are dubbed the Zeldovich mechanism.



Reactions (2.6) through (2.8) are considered responsible for thermal NO. They are considered "Thermal" because reaction (2.6) has very high activation energy for the "right bound" NO formation reaction. Heywood [10] shows that the initial formation rate can be simplified to:

$$\frac{d[\text{NO}]}{dt} = \frac{6.0 \times 10^{16}}{\sqrt{T}} e^{-69090/T} \sqrt{[\text{O}_2]_e [\text{N}_2]_e} \quad \text{mol/cm}^3 \cdot \text{s} \quad (2.9)$$

where 'e' denotes equilibrium concentration at temperature T in Kelvin. Equation (2.9) was derived by considering equilibrium for the reaction



Further, Heywood [10] calculates a characteristic time for the NO formation process from

$$\tau_{\text{NO}} = \frac{[\text{NO}]_e}{d[\text{NO}]/dt} = \frac{8.0 \times 10^{-16} T e^{58300/T}}{\sqrt{P}} \quad (2.11)$$

where P is given in atm units. This was done by considering equilibrium for the reaction



which has equilibrium constant as follows:

$$K_{\text{NO}} = 20.3 e^{-21650/T}, \quad \text{appears in the following relationship}$$

$$[\text{NO}]_e = \sqrt{K_{\text{NO}} [\text{O}_2]_e [\text{N}_2]_e} \quad (2.13)$$

The strong temperature dependence for NO formation is exemplified in Figure 2.10 which shows results from calculations using Equations 2.9, 2.11 and 2.13. The formation rate is much more dependent on the temperature level than the equilibrium concentration.

It has been reported that only a small fraction of the flames have a temperature higher than 2500 K [36-38]. Judging from the quite long characteristic NO formation time for temperatures below 2500 K, we should expect the total amount of NO formed in a diesel engine to be dependent on the time spent at high temperature. The residence time is roughly inversely proportional to the engine speed, which explains why it is more difficult to achieve low specific NO_x emission with larger, low-speed engines than for small, high-speed automotive engines. In fact, the regulated maximum specific NO_x level from huge engines decreases with the rated speed of the engine [39]. Müller and Zillmer [40] developed a two-zone model to describe NO and soot formation in diesel engines. They showed how the concentration of NO increases with time for different conditions. Figure 2.11 illustrates some of their results.

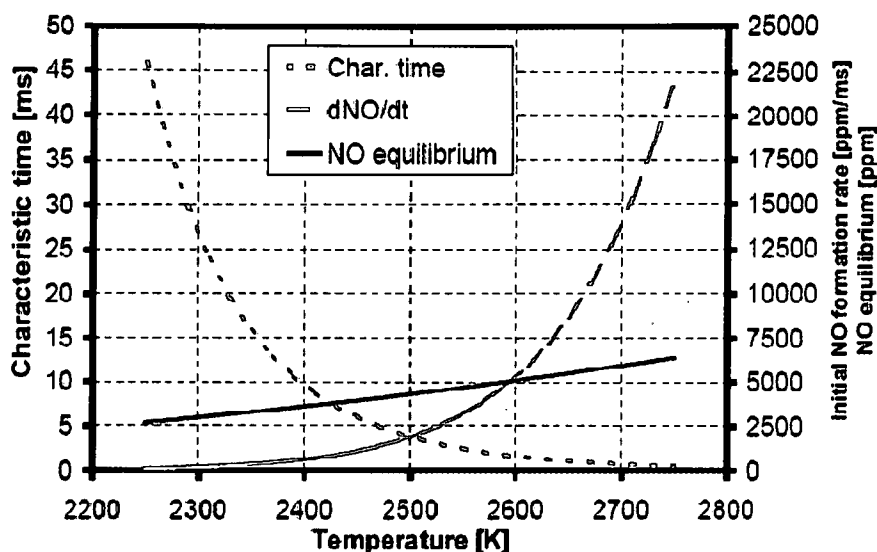


Figure 2.10. Characteristic NO formation time, initial NO formation rate, and NO equilibrium concentration as given by Eqs. 2.9, 2.11 and 2.13. $[O_2]_e = 4.2 \mu\text{mol}/\text{cm}^3$, $[N_2]_e = 0.43 \text{ millimol}/\text{cm}^3$ ($\phi \approx 1$). $p = 50 \text{ bar}$, from Müller *et al* [40].

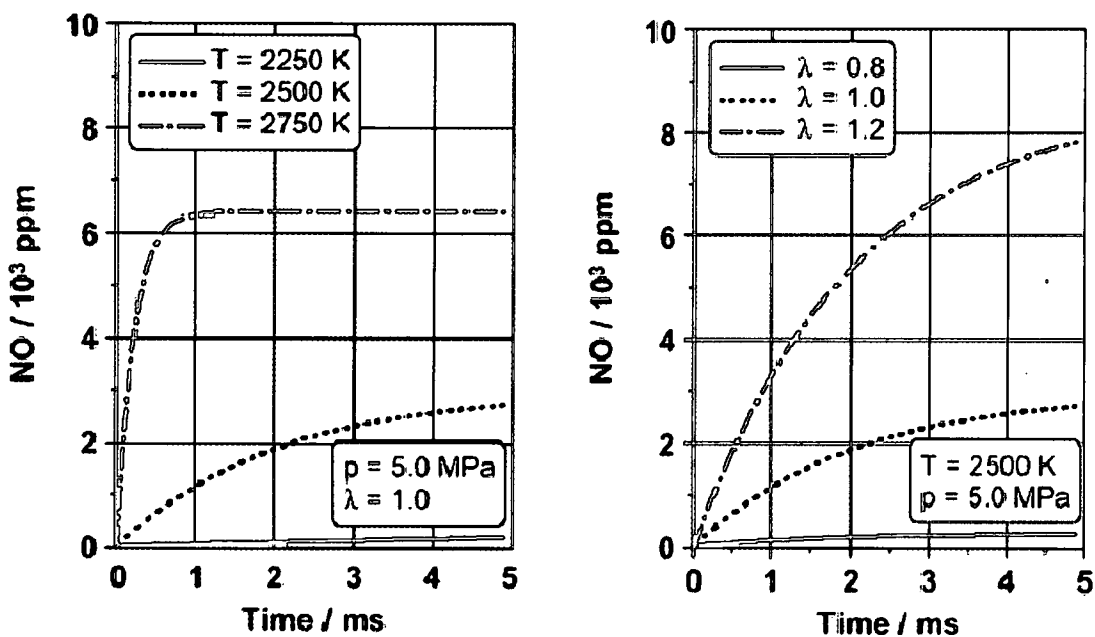


Figure 2.11. Calculated NO formation as functions of temperature and air excess ratio(λ), from Müller *et al.* [40].

The large influence of temperature on NO formation is clear from the left chart in Figure 2.11. During the 5 ms time span plotted, equilibrium is obtained only for the highest temperature considered, 2750 K. Fortunately, this high temperature is encountered in very limited regions of the combustion chamber [37, 38, 41]. The right chart in Figure 2.11 shows the influence of air excess ratio (λ) on the NO formation. NO formation is clearly favored by lean, hot conditions. Dec and Canaan [42] found that NO formation occurs on the lean side of the diffusion flame. This is in agreement with the right chart of Figure 2.11. It can be concluded that the total amount of thermal NO formed is dependent on the following parameters: (a) the temperature in the high temperature regions, (b) the time spent at high temperature, (c) the volume of the high temperature regions, and (d) the local air (fuel/air-equivalence) ratio.

In addition to the thermal NO contribution to the engine-out NO considered, there are additional pathways. Mellor *et al.* [43] suggest that under high-pressure conditions found in engines, nitrous oxide (N_2O) is formed from the O attack on the N_2 molecules via the three-body reaction:



Further, they show that this reaction is faster than the Zeldovich mechanism for temperatures below 2400 K. This is illustrated in Figure 2.12.

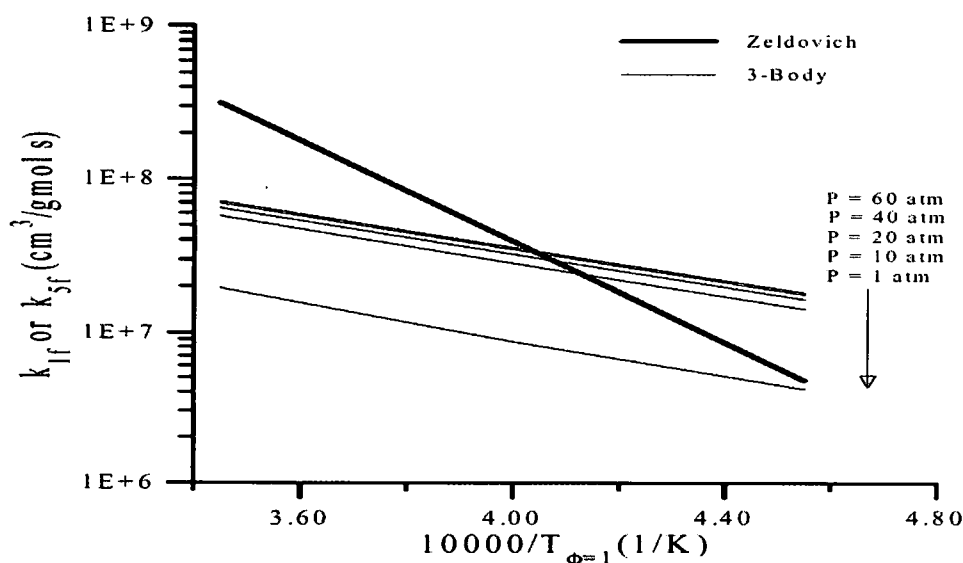


Figure 2.12. Reaction rate coefficients for thermal NO (k_{lf}) and three-body reaction (k_{3f}) as shown in (Eq 2.14), from Mellor *et al.* [43].

This nitrous oxide is then reduced into NO via

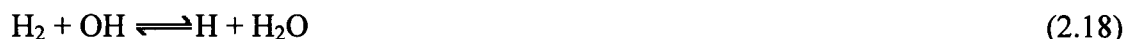


Mellor *et al.* [43] proposed that this N_2O mechanism contributes significantly to the engine-out NO and refer to research on lean premixed combustion for engines.

2.3.2 Prompt-NO; reaction of N_2 with hydrocarbon fractions

Prompt-NO is characteristic of a hydrocarbon flame and is produced by hydrocarbon radicals attacking N_2 near the injector (flame). Various arguments have been proposed to explain the rapid formation of these anomalous quantities of NO. In early studies [31, 44], it was suggested that the mechanism of formation of Prompt-NO is explained by a modified Zeldovich mechanism with no assumption of local equilibrium of the O atoms; however, it must be assumed that there is a high concentration of O atoms, so this suggestion was rejected. Some research postulates that in lean and near-

stoichiometric flames, the rapid formation of anomalous quantities of NO are caused by an overshoot of radical concentrations (O, OH) above the equilibrium values, which in turn has the effect of enhancing thermal NO. A simple approach to the radical species involved is given by the pool of radicals formed in the following set of reactions [45], which are locally equilibrated:



O and OH radicals would thereafter enter the mechanism of thermal NO formation.

Accurate values of the temperature and radical concentrations used in calculations of the thermal NO mechanism yielded results that were closer to experimental values. N_2O has been suggested to play an important role in the low temperature ($<1,225^\circ\text{C}$) combustion of lean CO-air mixtures, as radical concentration overshoots cannot explain the increase of NO formation. The following mechanism was proposed [37]:



However, kinetic modeling demonstrates that N_2O does not play a significant role at high temperatures, and such are the conditions in internal combustion engines and other combustion hardware.

2.3.3 Fuel-NO; oxidation of fuel-bound nitrogen compounds

Fuel-bound nitrogen is another source of combustion NO emissions [34]. If the fuel contains considerable amounts of nitrogen, then fuel NO_x becomes significant. However, normal diesel fuel contains very little nitrogen, not more than 28 ppm nitrogen by weight [34, 35, 46]. Therefore, fuel NO_x is insignificant and not considered.

CHAPTER III

EMISSION REDUCTION TECHNIQUES

3.1 Emission Reduction Overview

Emission control technologies [47] can be divided into three basic categories: pre-treatment, internal measures, and after-treatment. Pre-treatment methods are concentrated on lowering the adiabatic flame and/or combustion temperature by treatment or use of alternative fuels. Internal measures or primary methods alter the engine configuration to, in some form or another, alter the combustion process. After-treatment or secondary methods are fitted externally to the engine and applied directly to the combustion gases.

3.1.1 Pre-treatment

Pre-treatment methods generally fall within three categories: (A) de-nitration of fuel, (B) use of alternative fuels, and (C) water addition to fuel (water emulsification).

A. De-nitration of Fuel

Most of the fuel-bound nitrogen becomes NO_x . For each 0.1% nitrogen in the fuel, 0.6 g/kWh of NO_x is produced. Diesel fuels normally have 0.1% N, while residual fuel oil has a nominal value of 0.3 - 0.4% [48]. Therefore, by removing some of the nitrogen from the fuel, some NO_x will be eliminated from the combustion gases. Unfortunately, there is no practical method available within reach of industry to remove nitrogen from the fuel.

B. Use of Alternative Fuels

Two alternative fuels are currently under investigation for use in automotive or stationary diesel engines: methanol and liquid petroleum gas (LPG). Methanol has been the subject of much research over the last few years [47]. Since methanol does not contain sulfur, SO_x is completely eliminated from emissions. By combining methanol and exhaust gas recirculation (EGR), NO_x can be reduced as much as 50%. However, methanol has poor ignition qualities and is corrosive in nature. The absence of sulfur means that the lubricity of this fuel is very low. Additionally, the use of methanol would require modification to the engine injection system. Methanol is more expensive than distillate and would also incur additional modification costs to fuel storage tanks and the need for leak detection systems. There would also be large-scale logistic problems associated with storing and obtaining this type of fuel in some international ports.

The use of LNG and LPG, on the other hand, is well advanced and in place at many generating power plants. LNG is also low in sulfur and, combined with the use of pilot injection, can reduce engine NO_x emissions by 60%. Nevertheless, the major problem of storage on ships without LNG engines would constitute a significant problem, which has yet to be overcome.

C. Water Addition to Fuel (Water Emulsification)

Automotive manufacturers are trying to find ways to reduce pollutant emissions and improve the fuel conversion efficiency of internal combustion engines [49-51]. One promising method may be the use of water emulsified diesel which could economically accomplish both of these goals. Emulsion of the fuel involves adding water to produce a new kind of fuel that has characteristics different from both consistent water and fuel.

Figure 3.1 shows the two different fuel oil droplets, one before adding water and one after water was added. This emulsified fuel is expected to improve combustion characteristics and reduce emission later.

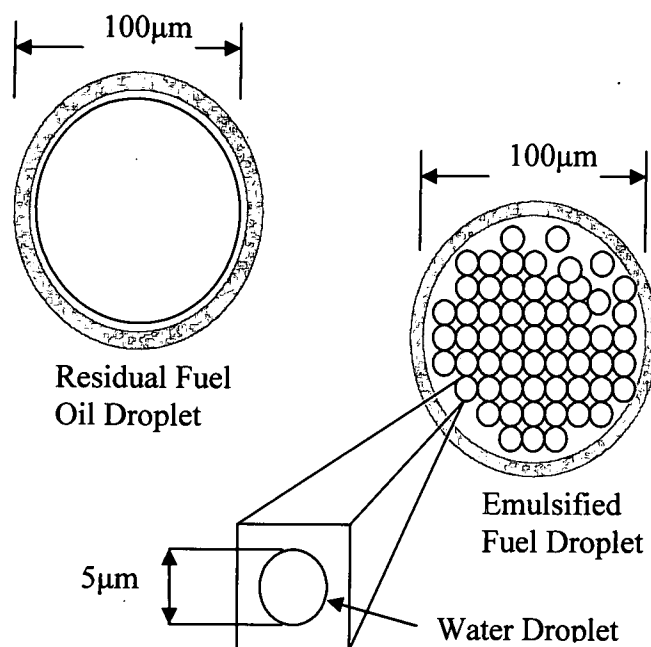


Figure 3.1. Fuel oil droplet and emulsified fuel droplet size and distribution [52].

3.1.2 Internal Measures (Primary Methods)

Primary methods involve changes to the combustion process within the engine and fall under five main categories [53]: (A) modification of combustion instruments/engines, (B) modification of scavenge/charging air, (C) water injection, (D) exhaust gas re-circulation, and (E) humid air motor. There are tradeoffs with improving NO_x emissions on other kind of emissions such as particulate matter and carbon monoxide (CO), as shown in Figure 3.2 [54].

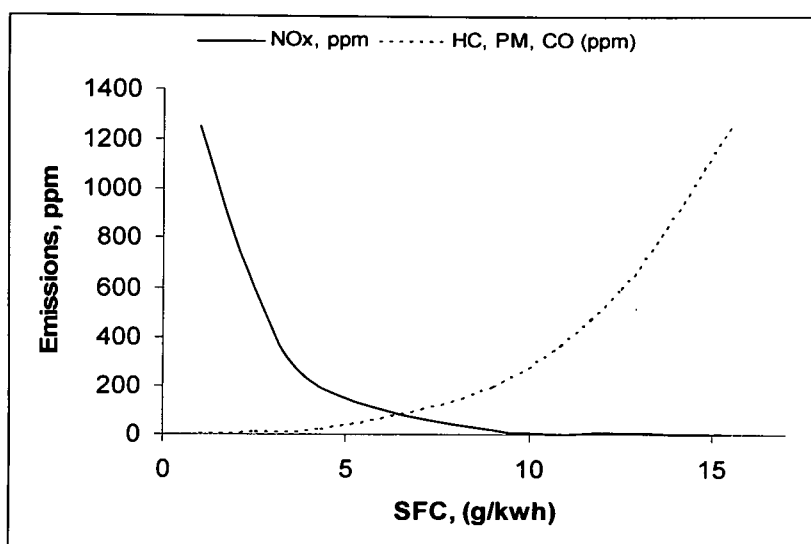


Figure 3.2 NO_x tradeoff with other emission components [54].

3.1.3 After-Treatment (Secondary Methods)

Secondary or after-treatment methods are centered on treating the engine exhaust gas itself, either by re-burning the exhaust gas or passing it through a catalyst or plasma system [55]. There has been much development in selective catalytic reduction (SCR) and non-thermal plasma (NTP) systems over the last few years. Secondary methods require a step change in capital cost, maintenance and through-life costs over primary methods [53, 55]. Three-way catalysts, such as those used on spark ignition engines, cannot be used, as diesel engines are non-stoichiometric.

CHAPTER IV

LITERATURE REVIEW OF WATER-DIESEL EMULSION MODELING

4.1 Introduction and Approach

The development of internal combustion (IC) engines has followed a dual strategy over the years:

- Improvement of engine performance and
- Reduction of pollutant emissions.

Various attempts focused on engine tuning, modifications, alternative fuels, alternative fuel compositions, and different exhaust gas after-treatments have been attempted. Many of these steps could be used in future engine design and have a positive influence on the main part of emissions, but some are not practical solutions for the existing diesel engines and may contribute to increases in other harmful emissions. For example, the addition of ethanol to diesel fuel may increase aldehyde emissions, some of which are considered to be carcinogenic [5, 17]. Also, continuously regenerating diesel particle filters (DPF) lower particulate emissions, but are also suspected to increase emissions of NO₂ to the atmosphere.

It is important to improve the quality of the fuel and lubricant in order to achieve the above-mentioned strategy. Some of the chemical improvements in the fuels and lubricants used in heavy-duty diesel engines consist of numerous technologies designed

to meet the required levels of environmental compatibility (economy, emissions, noise) and market requirements (reliability, lifetime, price, etc.).

Several conventional and unconventional techniques have proved to be powerful tools to improve diesel engine emissions, especially NO_x and soot emissions. Among these approaches, the addition of water to diesel fuel and its addition to gasoline as a modified fuel for spark-ignited engines has a long history [56].

The interest in water-in-diesel emulsions derives from the fact that water in the form of droplets exerts positive effects on the fuel combustion. Water-in-oil emulsions have been formulated and evaluated for most types of fuels, ranging from light hydrocarbons to triglycerides [50, 57-59]. However, the main interest in the concept lies in water-in-diesel emulsions.

Water may be added to the fuel in several ways:

- Continuously into the air stream via a single point using a humid air motor [16].
- Fumigation through intake valves via a multi-point system [60, 61].
- Injected directly into the cylinder through a separate nozzle, or introduced to fuel within the injection nozzle when fuel injection does not take place [49].
- Stratified fuel-water injection [62], or
- Through the preparation of stabilized water/fuel emulsion.

Adding water into the air stream using a humid air motor is an alternative to water injection currently being investigated by some diesel engine manufacturers [16, 63]. In this process, water is evaporated into the relatively hot scavenging air, which flows to the engine through the inlet air manifold. This technique may be suitable for older and stationary engines, but extra costs and modifications may be needed.

Fumigation is where liquid water is injected into the intake manifold upstream of the intake valve. The fumigation technique has been used in direct injection diesel applications (DI), but suffers from the drawback that the liquid water in the combustion chamber is typically located in areas where it is less effective at reducing emissions. Therefore, fumigation requires approximately twice the liquid volume for the same reduction in engine-out emissions when compared to other injection techniques [60, 61]. Additionally, liquid water present after combustion can contaminate the oil and increase engine wear.

Water injection involves adding water directly into the cylinders during combustion through a special injector [49, 50], whereas separate pumps and tanks for the fuel and water are needed along with modifications to the fuel delivery lines and injectors. Potential drawbacks are higher engine costs and corrosion problems.

Stratification of water in fuel has also been investigated [62]. This technique involves injecting water using the same injector used for fuel. Although this eliminates the need for an additional water injector, it requires more complex electronic fuel injection equipment to control the fuel/water injection, which means higher cost.

Among these techniques, the emulsified fuel with a stabilizing agent is the simplest and most practical, because it doesn't require additional equipment or system modifications and there are no extra costs associated [57, 64]. As an alternative to separate storage of the oil and water, emulsifying agents that resulted in a reduced rate of oil/water separation have been developed, allowing "premixed" emulsified oils to maintain their properties for extended periods of time when properly stored. This approach eliminates the need for additional handling and mixing equipment, and utilizes

existing fuel handling systems, thereby reducing the cost of use. Current emulsifying agents are much more effective at inhibiting phase separation, allowing emulsified fuels to be effectively used in a variety of applications [57, 64].

The main reason for the increased interest in incorporating water in diesel instead of gasoline is that the high combustion temperature and the high pressure that exist in diesel engines are particularly suitable for the concept. This was found experimentally [58] and verified by theory [65] years ago.

This study examines the effects of combusting a mixture of diesel fuel and water at various water ratios of 3, 5, 8 and 15% by volume on the nitrogen oxides emission, carbon monoxide, and soot precursors formation in addition to the effect on engine operating conditions, mainly combustion temperature and ignition delay of a compression ignition diesel engine.

4.2 Literature Review of Water-diesel Emulsion Modeling

Several basic studies on the evaporation and combustion of isolated drops and burning sprays of emulsions have appeared in the literature [66, 67]. Also, many investigations on the use of emulsions in practical combustors have been reported. These studies have shown that the benefits of emulsification are greater with heavier fuels such as residual oils and particulate emission, and flame radiation is generally reduced by emulsification of fuel [68, 69]. However, the CO, NO, and hydrocarbon emissions and the thermal efficiency of combustion devices do not always improve when fuels are emulsified with water.

The effects of single- and multi-point water addition systems on the NO_x and soot emissions of a vehicular heavy-duty diesel engine have been investigated by Samec and

Cernej [60, 70]. They concluded that both systems (single- and multi-point) showed practically the same beneficial influence on NO_x emission reduction, but had a rather poor effect on soot emission. However, the results of several other investigations performed recently using water-fuel emulsion [63, 71] concluded that more promising effects on NO_x and soot reduction may be expected.

Few experimental investigations of water-diesel emulsion combustion in diesel engines have been made to show some of the benefits of water addition to the diesel fuel on the reduction of pollutant emission, specific fuel consumption, thermal loading, and maximum combustion pressure [57, 72]. Those investigations could not offer, however, a more detailed explanation of some of the specific physical and chemical effects of the combustion processes.

Very few experimental studies have been made on the effect of water in the form of water-in-diesel emulsion on the formation of polycyclic aromatic hydrocarbons, some of which are known to be mutagenic [73]. Emulsion fuels were found to give lower amounts of PAHs in the flame, as well as reduced atmospheric emissions. No attempts have been made to model these experimental results and explain the theory behind this reduction.

Schlitt and Exner [74] have compared water-in-diesel emulsions with humidified intake air; such as water in the form of aerosol. It was found that both systems reduced the NO_x level compared to traditional diesel fuel. Only the emulsion was effective in also reducing the soot level. The water level in the studies on diesel emulsions varies. Most authors use water content of 5 to 10%, but water use at higher percentages needs to be

thoroughly investigated. It has been claimed that the optimum water content for NO_x and PM reduction is between 10 and 20% [86]

Samec *et al.* [45] studied the effect of 10 and 20% water-in-diesel on emission levels of NO_x , hydrocarbons and soot, as well as on the specific fuel consumption. The values obtained, relative to the values for neat diesel, show considerable reduction in both hydrocarbons and soot at 10% water. The NO_x reduction seems to be more water dependent. A 20 % level is needed to obtain a significant effect, whereas the 20% water level did not significantly reduce NO_x that had been reported to be high in earlier work [75]. This discrepancy in results should be carefully reviewed and interpreted .

Several experimental investigations were carried out on industrial furnaces and external combustion systems [68, 76], diesel engines [59, 77] and gas turbines [69, 78]. All of these investigations demonstrated the beneficial effects of using emulsified fuels; however, variations between the results from one set of experiments to another were indicated. These variations make it necessary to model the combustion of emulsified fuels and relate the modeling to the practical combustion system to be used as an attempt to predict the possible improvement that can be expected.

Many researchers concentrated on the secondary atomization phenomena and emulsified fuel penetration concept. Zhou and Thorp [79, 80] have presented both theoretical and experimental studies on the differences between pure fuel and emulsified fuel atomization and discussed the effect of emulsified fuel atomization on fuel combustion. They measured the spray tip penetration and spray angle of emulsion spray in a noncombusting bomb that simulated the combustion chamber of a marine diesel engine (Ruston 6APC) by using a high-speed camera with a micro-lens. Compared with

the pure fuel spray, the emulsified fuel has a longer spray tip penetration and wider spray angle. For the emulsion fuel with water content of 5 to 20%, the tip penetration increases as the water percentage increases. The number of countable droplets of emulsion fuel was much greater than that for pure fuel, indicating that the emulsion fuel spray possesses a larger total surface area. In addition, mathematical models for the prediction of spray tip penetration and spray angle were proposed.

A literature review indicates that one of the beneficial aspects of applying emulsion fuels to combustion systems may be the change in fuel properties which leads to enhanced atomization characteristics.

Little attention has been paid in the past to modeling the combustion of emulsified fuels. Most of the work was directed toward modeling the behavior of an emulsion droplet when heated to predict whether the conditions needed for the micro-explosion phenomenon to occur would or would not be established [65, 81]. The ability to predict whether micro-explosions will or will not occur, and when during the droplet lifetime they are likely to take place, though of great value, is not sufficient for an understanding of the effects of the presence of water in the fuel on soot and gaseous products formed during spray combustion.

The approach described here aims at providing a computational fluid dynamics (CFD) model for emulsion spray combustion of different water-in-fuel ratios on emission reduction and engine operating conditions. The modeling procedure conducted used the CFD-ACE⁺ code applied to a 2-stroke diesel engine and the fuel used is a surrogate fuel consisting of 80% n-heptane and 20% toluene which represents that of conventional diesel fuel.

Results from testing diesel fuel with varying ratios of water will be presented and discussed in the following chapters. The data shows significant soot and NO_x emission reduction in the fuel, but little increase in carbon monoxide. These results are correlated with a thermodynamic first law analysis to estimate the adiabatic flame temperature of the standard fuel and fuel-water emulsion cases. Results indicate that thermal NO_x is indeed reduced by quenching and flame temperature suppression, confirming reports in the literature. Recommendations are given for further studies, including improving the fuel-water emulsion and considerations for long-term testing.

CHAPTER V

CHEMKIN MODELING OF FUEL COMBUSTION

CHEMKIN [82] is a software tool for solving complex chemical kinetics problems. It is used worldwide in the microelectronics, automotive, combustion, and chemical processing industries. It was originally developed at Sandia National Laboratories and is now developed at Reaction Design. CHEMKIN solves thousands of reaction combinations to develop a comprehensive understanding of a particular process, which might involve multiple chemical species, concentration ranges, and gas temperatures. The computational capabilities of CHEMKIN allow for a complex chemical reaction to be studied in detail, including intermediate compounds and trace compounds.

One important driver for the development and use of CHEMKIN is the reduction of pollutants such as NO_x . One limitation of CHEMKIN is that it assumes the reaction vessel has a relatively simple geometry, whereas this is not always the case. For that reason, Computational Fluid Dynamics tools CFD programs are better able to account for geometric complexity, at the expense of being more limited in their treatment of the underlying chemistry of the reactive process being studied.

The CHEMKIN modeling code[82] was used in this study as an alternative method to model the combustion of a mixture of surrogate fuel consists of 80% n-heptane and 20% toluene (by volume), which was selected to be the fuel for this model, and water

at different ratios of 3, 5, 8 and 15% H₂O (by volume). The analysis was carried out using the PaSR model approach. PaSR addresses the interaction between chemical reactions and turbulence. One of the basic characteristics of PaSR is that the thermo-chemical properties inside a PaSR, which are assumed to be spatially homogeneous, but are imperfectly mixed at the molecular level. The reactive fluids are not completely diffused into each other at the molecular level, but their mean values are uniform throughout the reactor by turbulent stirring. Thus, PaSR may be used as a stand-alone model for studying turbulent combustion or other reactor systems where mass transport may be a rate-limiting factor.

CHEMKIN computation was performed using 393 species [83], including NO_x and soot precursors species, and 1,925 reactions [83]. The computations were initiated at 900 K and 39 bar with air as the oxidizer and surrogate mixture as the fuel. The temperature and pressure values were chosen to fit the actual parameters of the real engine [1]. The fuel/air equivalence ratios studied were 0.8, 1, 2, 3, and 5. This enabled an exploration of how the product composition changed with the amount of fuel from lean and stoichiometric ($\phi \leq 1$) to fuel rich ($\phi > 1$) combustion. Table 5.1 shows the initial composition for the five runs.

Table 5.1. Initial gas composition for the CHEMKIN computations

ϕ Mole Fraction[%]	0.8	1	2	3	5
n-heptane, C ₇ H ₁₆	0.8823	1.1005	2.1685	3.202	5.191
Toluene, C ₇ H ₈	0.3027	0.3795	0.7475	1.102	1.787
Oxygen, O ₂	20.705	20.651	20.345	20.054	19.495
Nitrogen, N ₂	78.110	77.869	76.739	75.642	73.527

The temperature histories are plotted in Figure 5.1. First, it can be observed that the final combustion temperature decreases with increasing fuel/air-equivalence ratio. The ignition characteristics also change with fuel/air-equivalence ratio. It is a pronounced two-stage process for the lean and low equivalent ratios cases [14-18], as discussed in Chapter II and shown in Figures 2.2 and 2.3, but for the richest conditions it is more likely a single-step ignition followed by slower completion of the rich combustion. The ignition delay decreases monotonically with increasing fuel/air equivalence ratio. This might appear unusual, but can be explained by the higher concentration of fuel that speeds up the formation of H, O and OH.

These three species are important for the chain-branching reactions leading up to autoignition [9, 10, 84]. Information about ignition delay acquired from these computations is very important. In diesel spray combustion, the temperature increases as the mixture is leaned out by entrained hot ambient air, thus acting in the opposite direction compared to the influence of mixture strength alone. Figure 5.2 exemplifies how the chemical reactions proceed for a fuel/air-equivalence ratio of 2.

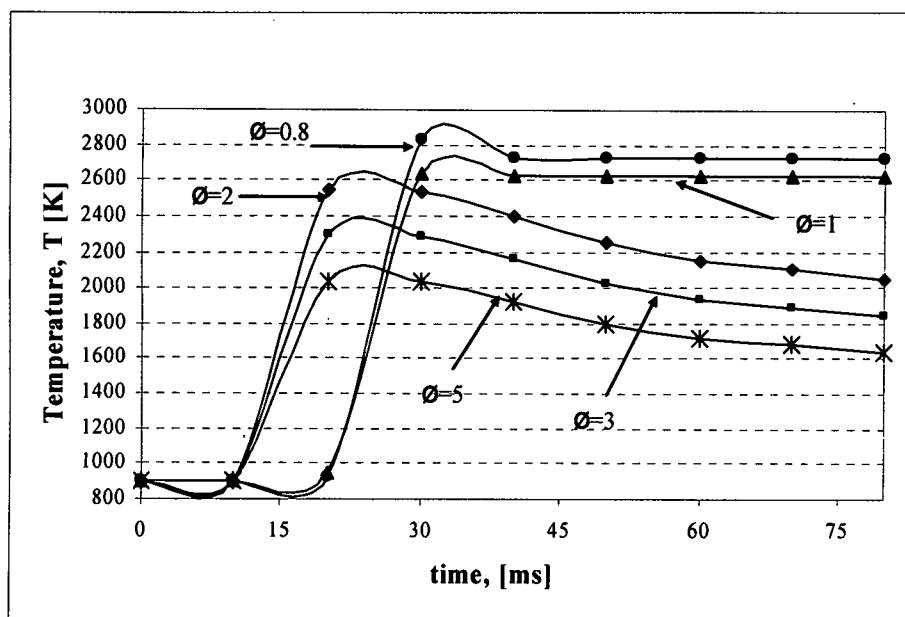


Figure 5.1. Calculated temperature for air/ (80% n-heptane+20% toluene) mixtures of different fuel/air-equivalence ratios. Pressure = 39 bar.

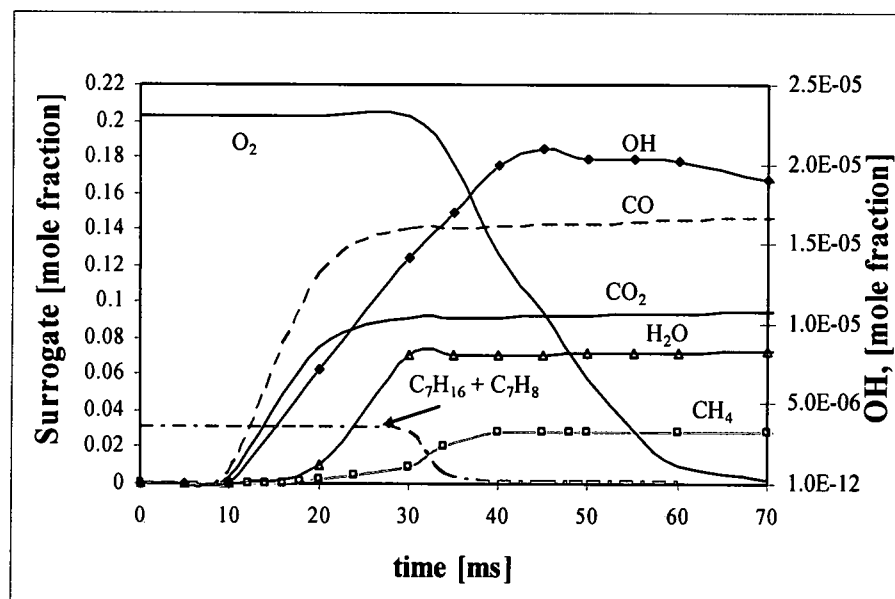


Figure 5.2. Major species and OH for auto-ignition and combustion of (80% n-heptane+20% toluene), Fuel/air-equivalence ratio($\phi = 2$).

Shown in Figure 5.2 are the major species during the combustion: C_7H_{16} , C_7H_8 and O_2 as reactants, CO , H_2O , CH_4 and CO_2 . OH is plotted since it plays an important role during autoignition and combustion. The amount of carbon dioxide is small since there is an oxygen deficit at fuel-rich conditions. From an emissions point of view, it can be interesting to evaluate how the amounts of CO and soot precursors change with fuel/air-equivalence ratio. The time-histories for CO are shown in Figure 5.3.

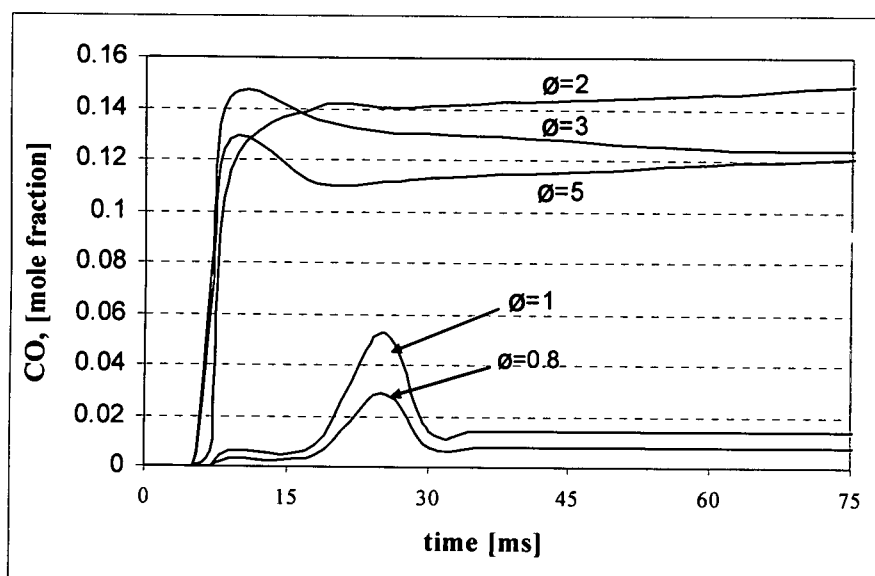


Figure 5.3. Mole fraction of CO at different equivalence ratios.

As expected, the lowest CO level is found for lean and stoichiometric conditions at $\phi = 0.8$ and 1 . This is in relatively good agreement with Figure 2.4 [10]. The temperature is, however, high and dissociation of CO_2 keeps the CO level higher than would be expected at normal exhaust temperature. It can be interesting to note the peak at 24 ms for $\phi = 0.8$ and 1 which coincides with the beginning of the final fuel breakdown and maximum heat-release. This shows that CO is an important intermediate species during lean and stoichiometric combustion. The final CO level is much higher for the rich

combustion cases. The highest CO level among the mixture strengths considered is found for a fuel/air equivalence ratio of 2. Richer mixtures have somewhat lower CO levels. This can be explained by considering that CO has to compete for oxygen with partially oxidized hydrocarbons. This is shown in Figure 5.4.

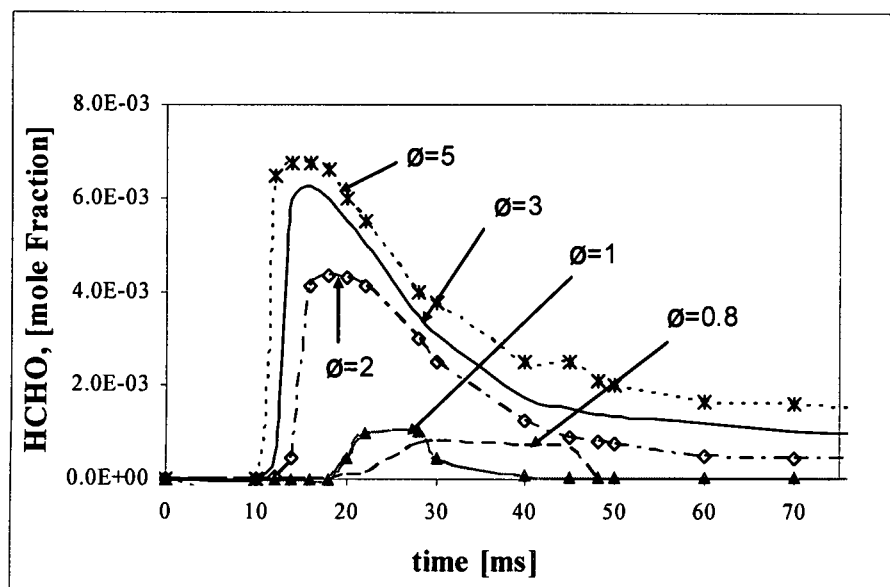


Figure 5.4. Formation of HCHO from the combustion of surrogate fuel (80% n-heptane and 20% toluene) at different equivalence ratios.

It is clear that combustion at all fuel/equivalence ratios creates partially oxidized hydrocarbons that are effectively further oxidized for $\phi = 0.8$ and $\phi = 1$. Partially-oxidized hydrocarbons, such as HCHO, are therefore absent or appear at a very low percentage in the products. For $\phi=2$ to 5 there is an increasing amount of partially-oxidized hydrocarbons in the products, and it is expected that aldehydes would be included as discussed by Neumann *et al.* [56].

To evaluate the soot-forming tendency of the product mixture, it is useful to examine the fraction of soot precursors' formation during the combustion process. Flynn *et al.* [18] considered ethyne (acetylene C_2H_2), ethene (C_2H_4) and propargyl (C_3H_3) to be

the most significant soot precursors. Acetylene (C_2H_2) is formed in large quantities during fuel-rich combustion and is considered one of the important precursors in the PAHs formation reactions. Propargyl (C_3H_3) is the most important, since two such molecules can form the first ring (benzene, C_6H_6) after recombination and rearrangement to an aliphatic C_6H_6 [10]. Figure 5.5 shows how the mole fraction of soot precursor C_3H_3 evolved for the different cases.

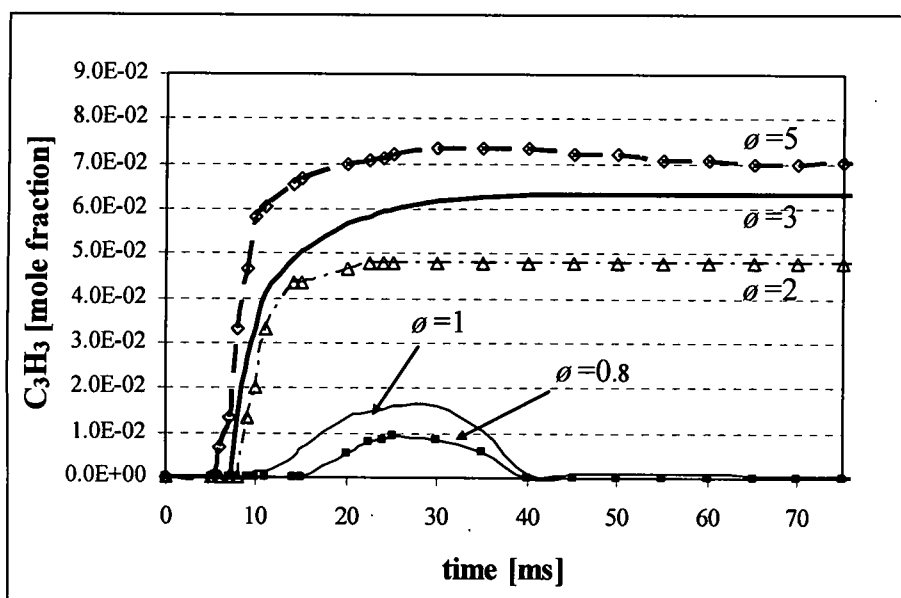


Figure 5.5. Formation of soot precursor C_3H_3 from the combustion of surrogate fuel (80% n-heptane and 20% toluene) at different equivalence ratios.

At lean and stoichiometric condition where $\phi \leq 1$, soot precursors are completely reduced or vanished. The paramount difference between $\phi=1$ and $\phi=2$ is clear. The mole fraction of C_3H_3 for the cases $\phi=2$ and $\phi=3$ at 75 ms, is 4.85×10^{-2} and 6.3×10^{-2} , respectively. So at $\phi=3$, the mole fraction of C_3H_3 is 1.3 times higher than that for the $\phi=2$, which means that the mole fraction of soot precursors increases with fuel/air-equivalence ratio; however, for $\phi=2$ and 3 the steps are not as great as between $\phi=1$ and

2. This suggests that soot formation is most sensitive to changes in fuel/air equivalence ratios between 1 and 2 and that the soot formation does not increase much when the fuel/air equivalence ratio is raised beyond 3. Calculations show that an increasing amount of fuel remains unoxidized at increasing fuel/air equivalence ratios, as illustrated in Figure 5.6.

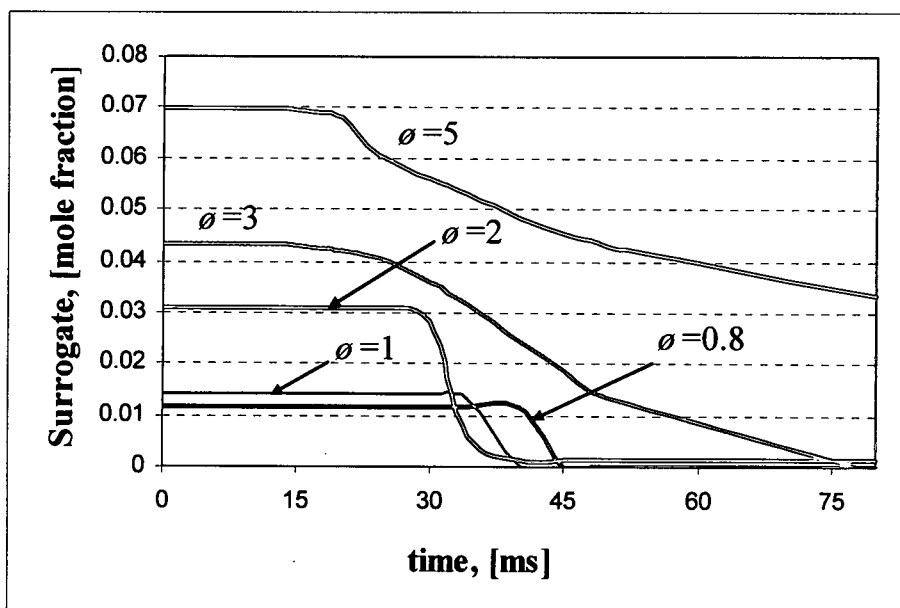


Figure 5.6. Mole fraction of surrogate fuel (80% n-heptane and 20% toluene).

For the two lowest fuel/air-equivalence ratios, the fuel is completely consumed during the second ignition step. The $\phi=3$ and $\phi=5$ cases show trace amounts of surrogate fuel after the main combustion has occurred. Only the richest case has significant amounts of intact fuel left after the main combustion. It is clear that the direct route to soot particle formation becomes more important for increasing fuel/air equivalence ratios.

Figures 5.7 summarizes the results for CO and soot precursor formation. It can be concluded that dependence on the fuel/air-equivalence ratio differs for CO and soot

precursor formation. Specifically, it can be noted that concentration of soot precursors increases in the range $\phi = 2$ -5 while the concentration of CO decreases.

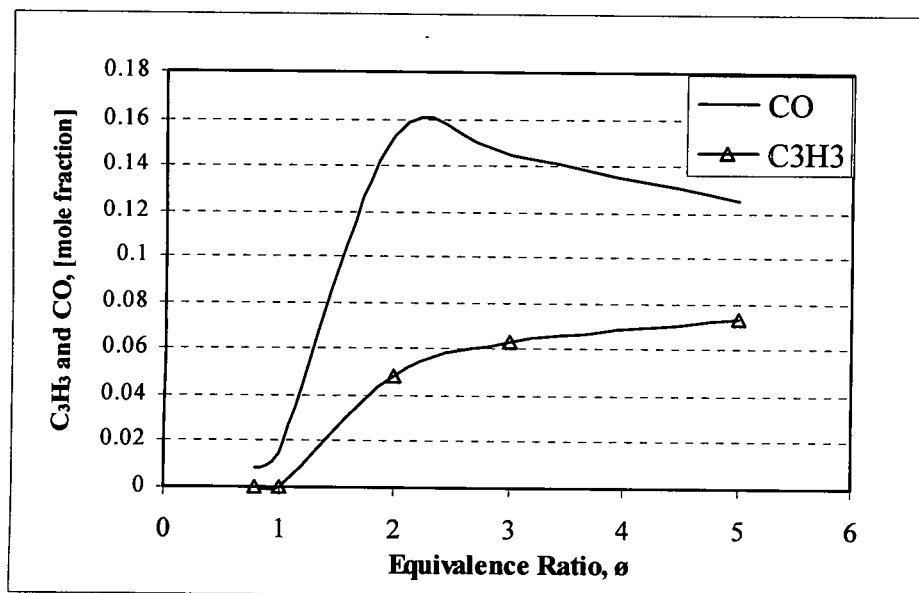


Figure 5.7. Mole fractions of CO and soot precursor C₃H₃ change with equivalence ratios.

It is interesting to see that the maximum CO gain is found for $\phi=2$ and then noticeably decreases for richer combustion conditions. The soot precursors gain a little peak at $\phi=2$ and then show a relatively slow increase at richer combustion conditions. Modeling of heptane by Curran *et al.* [85] showed that the production of soot precursors drops to an insignificant level when the equivalence ratio is below two in the fuel/air mixture.

Adding water to surrogate fuel (80% n-heptane and 20% toluene) has a significant effect on changing the combustion behavior inside the PaSR reactor. Four different ratios (3, 5, 8 and 15%) of water (by volume) were added to fuel in the form of emulsion at two

different air/fuel equivalence ratios (0.8 and 2). Those ratios were chosen to study the effect of water on the fuel-lean and fuel-rich combustion conditions. The real diesel engine only runs on under fuel-lean conditions, so it is just a matter of curiosity to know how water can affect this assumed situation.

Figures 5.8 and 5.9 present the temperature profiles of both conditions after adding 3, 5, 8 and 15% water to fuel. It is clear from these figures that the addition of water can eventually reduce the combustion temperature over the time range of the combustion process. Compared to neat surrogate fuel, the peak temperature decreases with the increasing water content.

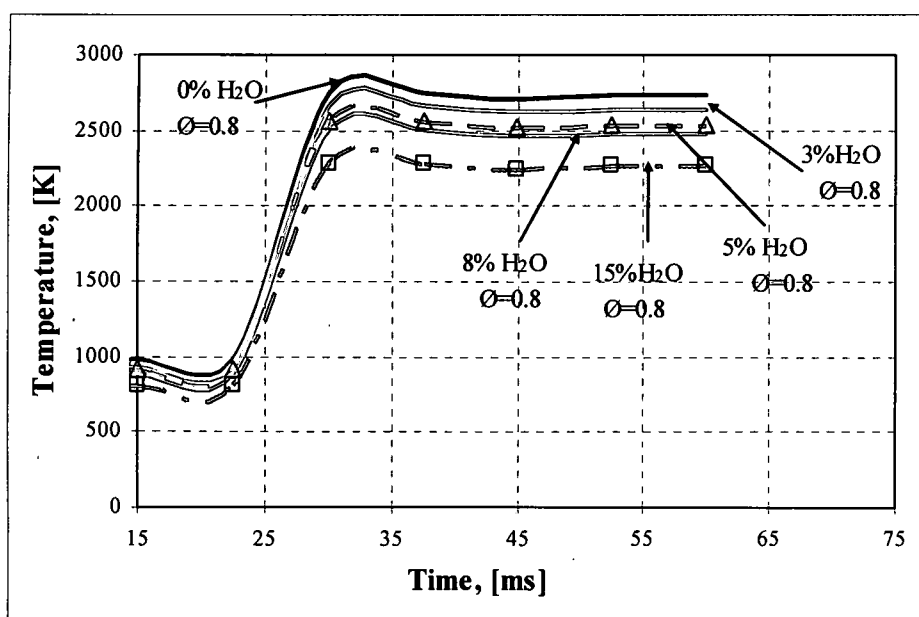


Figure 5.8. Calculated temperatures for water (80% n-heptane and 20% toluene) in surrogate emulsified mixtures at fuel/air-equivalence ratio, $\Phi=0.8$.

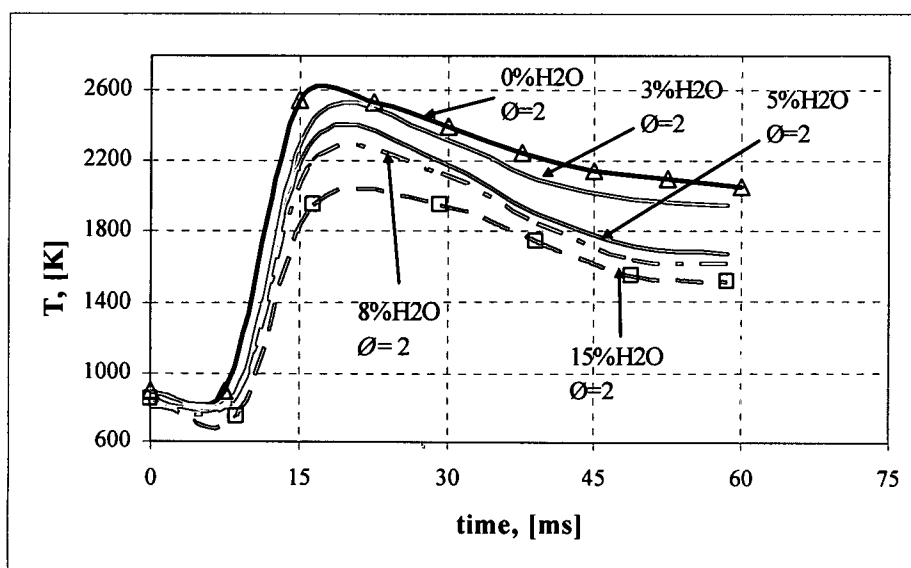


Figure 5.9. Calculated temperatures for 0, 3, 5, 8, and 15% water (80% n-heptane and 20% toluene) in surrogate emulsified mixtures at fuel/air-equivalence ratio, $\phi=2$.

Table 5.2 shows the maximum peak temperatures during the combustion of different surrogate emulsions at $\phi=0.8$ and 2. The values from this table were plotted in Figure 5.10 to closely express the effect on combustion temperature of adding water to fuel. This figure clarifies the temperature drop for both cases (fuel lean $\phi=0.8$ and rich $\phi=2$ conditions) at different water percentage. The 15% water in fuel shows the largest temperature drop, which suggests a major change in the combustion environment of the PaSR model.

Table 5.2. Maximum model temperature values at different water in fuel percentages for both fuel-lean and fuel-rich conditions where $\phi = 0.8$ and 2.

Equivalence Ratio	$\phi = 0.8$					$\phi = 2$				
H ₂ O	0%	3%	5%	8%	15%	0%	3%	5%	8%	15%
Maximum Temperature, K	2750	2670	2560	2550	2280	2550	2450	2350	2200	1950

The temperature drop that occurs after adding water to fuel is explained by the heat loss taken from the process to evaporate water and also the increased specific heat of the combustion gases due to the percent of water vapor involved [16].

Comparably, the effect of adding water to fuel in the case of the fuel-rich condition at $\phi=2$ is not different from that of the fuel-lean condition at $\phi=0.8$. However, the originally lower temperature at the fuel-rich condition reflects a clear change in temperature profile by suppressing ignition and lowering maximum temperature from 2550 K to 1950 K at 15% water added to fuel in the fuel-rich condition and from 2750 K to 2280 K for 15% water added to fuel in fuel-lean condition.

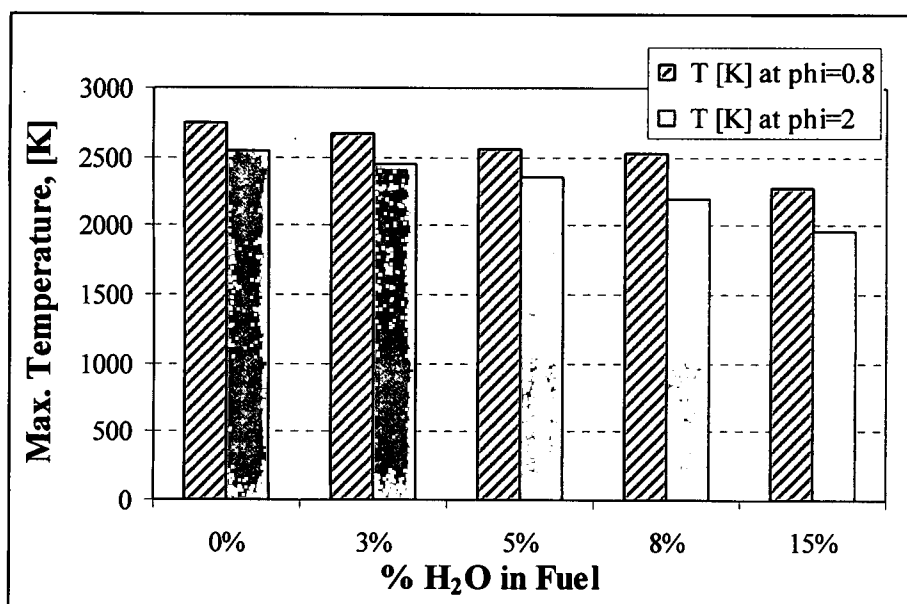


Figure 5.10. Maximum model temperature at different water-in-fuel percentages for fuel-lean and fuel-rich conditions where $\phi = 0.8$ and 2.

Compared to pure fuel, it can be observed that the maximum combustion temperature decreases with the addition of water. Also, higher ignition delay times can be observed when water is added to fuel due to lower combustion temperature. Ignition

delay times increase monotonically with the increasing water percentage in fuel due to the change in ignition characteristics that occurs after addition of water.

The effect of adding water to fuel is quite obvious from the change of OH concentration which increases with the increasing amount of water. OH is plotted since it plays an important role during autoignition and combustion [86]. Bartok and Sarofim [86] say that OH is most likely to dominate soot oxidation under fuel-rich and stoichiometric conditions even in the presence of large concentrations of O₂. Under lean conditions, soot is oxidized by OH and O₂. According to Haynes and Wagner [87], about 10 to 20 % of all collisions of OH with soot are effective in gasifying a carbon atom.

Figures 5.11 and 5.12 show how the OH production changes with the amount of water added to fuel. It is obvious from Figure 5.11 that the OH concentration increases with the increasing amount of water in fuel for the fuel-lean condition ($\phi=0.8$).

Also, Figure 5.11 shows that the effect of adding water to fuel results in increased concentrations of OH to a narrow maximum peak value, which then falls down to a nearly constant lower value over the specific time range. Adding more water to fuel did not show significant increases in OH concentration compared to that between 5% water and base fuel with 0% water. This is possibly related to the imperfect turbulent mixing and temperature reduction inside the PaSR reactor at higher water-in-fuel ratio which affects autoignition and OH concentration [88].

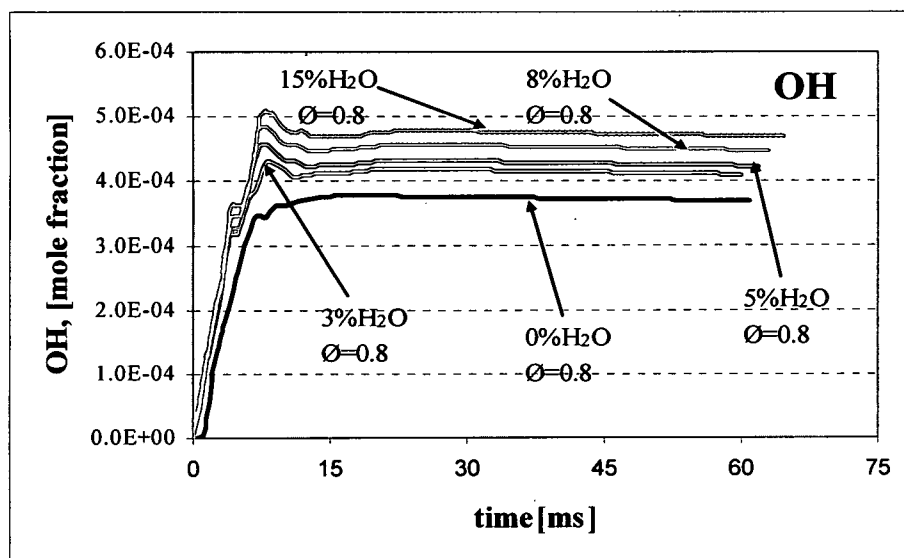


Figure 5.11. Concentration change of OH radicals with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel. $\phi=0.8$.

In their experimental study, Markides and coworkers [88], which depends on measuring the OH chemiluminescences from certain spots in the reactor, concluded that at the fuel-rich condition ($\phi=2$), the concentration of OH decreases as the fuel ratio increases. They suggested that the combustion reactions are not simply kinetically controlled because of the nonlinear Arrhenius plots they obtained, and that the turbulence inside the reactor can delay autoignition, which further suggests the effect of mixing on autoignition.

Figure 5.12 shows the change of OH concentration at fuel-rich condition ($\phi=2$) with percent water added to fuel over a certain time period. The addition of 3 and 5% water to fuel shows an increase in the OH production to a higher value than that of regular fuel; however, when 8 and 15% water was added, the results were contrary and the production of OH noticeably decreased, which reflects the intensive dependence of

OH formation on air/fuel equivalence ratio, water-in-fuel ratio, and the combustion environment inside the PaSR. More water in fuel means lower combustion temperature and lower production of OH radicals. It is also clear that the ignition delay increases with the increasing amount of water added to the fuel and predicts higher values at fuel-rich conditions with higher amount of water in fuel.

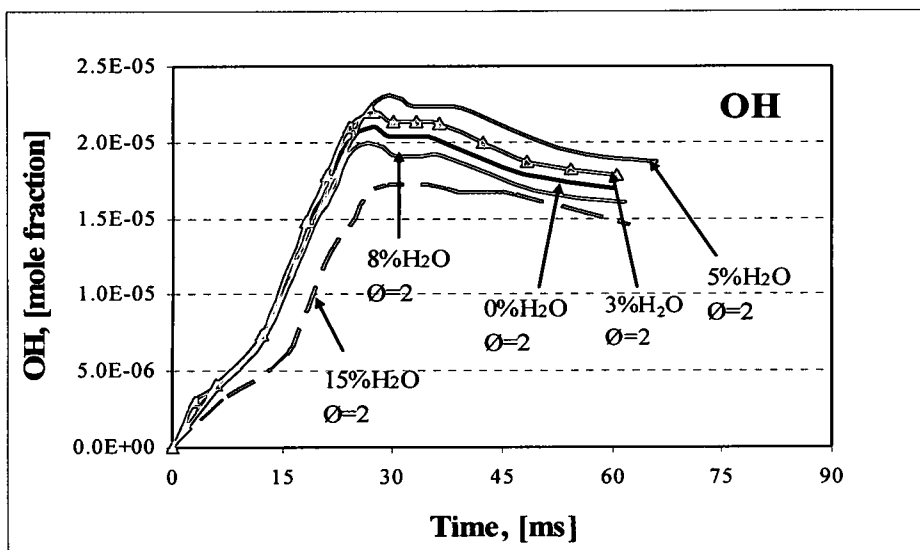
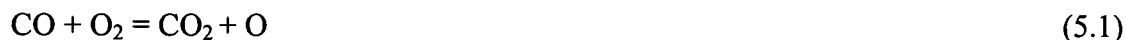
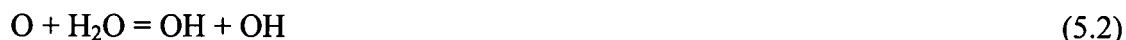


Figure 5.12. Concentration change of OH radicals with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel. $\phi=2$.

Carbon monoxide (CO) is considered to be one of the major species that could be formed during the combustion process. The mechanism of CO oxidation with hydrogen-containing compounds such as water is usually called wet oxidation. According to Glassman [89], the CO oxidation rate substantially increases with the increasing amount of hydrogen-containing compounds (H₂O) and decreases with temperature. In his proposed mechanism, Glassman [89] shows that the effect of adding small quantities of H₂O on the CO oxidation rate was significant. The water-catalyzed reaction proceeds in the following manner:



where $k = 2.500\text{E}+12 \, T^{0.0} \exp(-47800.0 \text{ cal/mol} / RT) \text{ cm}^3/\text{mols} [90]$



where $k = 4.76\text{E}+7 \, T^{1.2} \exp(-70 \text{ cal/mol} / RT) \text{ cm}^3/\text{mols} [90]$



Reaction (5.1) is a chain initiating step, but it is slow and does not contribute significantly to the production of CO_2 . Reaction (5.3) is a chain propagating step, yielding H radicals which react with O_2 to produce OH and O by the chain branching step (5.4). The OH radicals that are formed participate in reaction (5.3) and the O radicals formed participate in reaction (5.2). It was shown Figures 5.11 and 5.12 that OH concentration increases with the increasing water content at fuel-lean conditions and decreases above 5% H_2O for fuel rich conditions. This means that CO formation should decrease with the increasing amount of water in fuel. The formation profile of CO at fuel-lean condition ($\phi=0.8$) (illustrated in Figure 5.13) with the percentage of water added to fuel shows that the concentration of CO increases sharply at the beginning as increasing amounts of water are added to the fuel to a maximum peak point and then decreases to a lower value where it remains constant over the entire time range. Thus, more CO is produced by the oxidation reactions of soot precursors with OH radicals from which CO formation is essential. In addition, CO will compete with the other compounds in the process (soot precursors and N_2) to react with OH radicals and oxygen to form carbon dioxide which may control the amount of CO that can be oxidized to form CO_2 . Consequently, the effect of temperature is important in suppressing the oxidation reactions of CO and N_2 to form

CO₂ and NO_x. Adams and coworkers [91] revealed that CO oxidizes rapidly at high temperatures in the presence of oxygen, but does not oxidize as well at the cooler temperatures in turbulent conditions and since adding water to fuel in the form of emulsion reduces the temperature as shown in Figures 5.8 and 5.9, the oxidation reaction of CO to CO₂ is expected to be lower. Equation (5.5) expresses the relationship between the CO oxidation rate and temperature which increases with the increase in temperature, hence lowering CO concentration.

$$\frac{d[CO]}{dt} = (6.52 \times 10^6) [CO] [H_2O]^{0.5} [O_2]^{0.25} \exp\left\{-\frac{15,968}{RT}\right\},$$

for $T > 1150 \text{ K}$ [91]

(5.5)

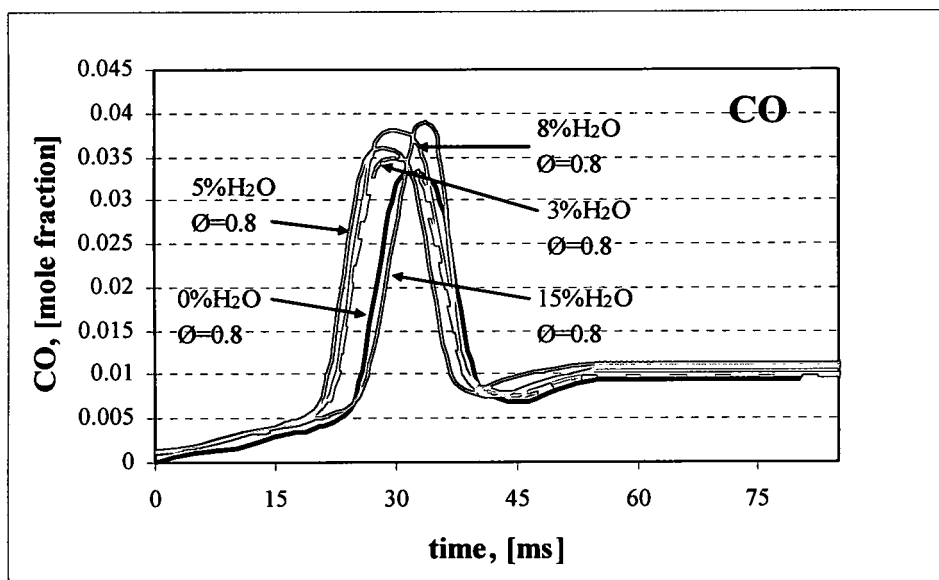


Figure 5.13. Carbon monoxide formation change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel, $\phi=0.8$.

Since CO is an important intermediate species during lean and stoichiometric combustion, as predicted from Figure 5.3, the formation level of CO is much higher at fuel-rich combustion conditions; the highest CO formation level is found for a fuel/air equivalence ratio of 2. Therefore, adding water to fuel at this level is expected to affect the CO formation in a different way than under lean and stoichiometric conditions.

Figure 5.14 presents this change when 3, 5, 8 and 15% water is added to fuel. It is clear that CO level increases with the increasing amount of water added to fuel which is similar to the trend at the fuel-lean condition; however, the variation of CO level at the fuel-rich condition increases sharply at the beginning and then continues to increase monotonically after the maximum peak point in the early combustion stage. The oxygen deficits in the fuel-rich and low temperature condition created after adding water to fuel play an important role in increasing the CO formation level during the combustion of emulsified fuel at the fuel-rich condition because it substantially reduces the oxidation of CO to CO₂.

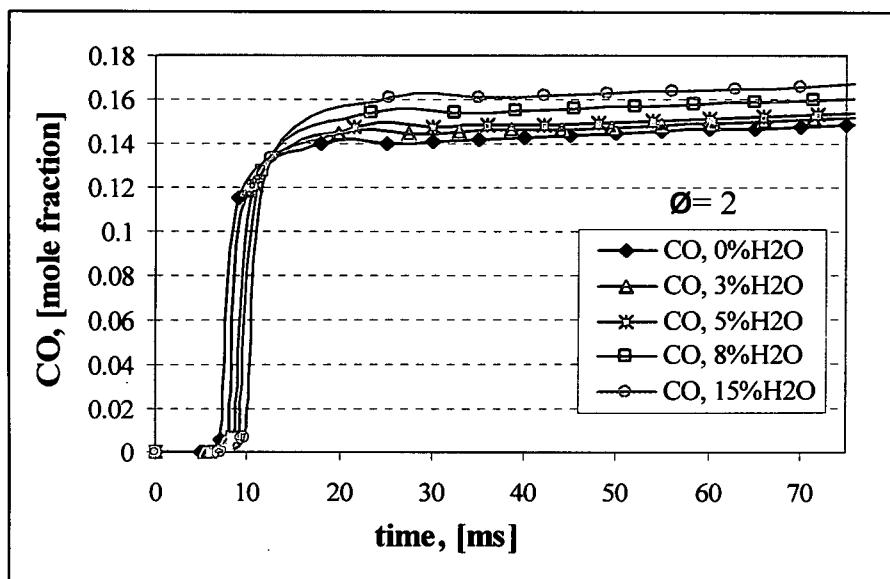


Figure 5.14. Carbon monoxide formation change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel, $\phi=2$.

As discussed earlier, C_3H_3 is considered to be one of the most important precursors of PAHs since two molecules of C_3H_3 can form the first benzene ring (C_6H_6) after recombination and rearrangement to an aliphatic C_6H_6 [10, 92] as shown in the mechanism illustrated in Figure 5.16.

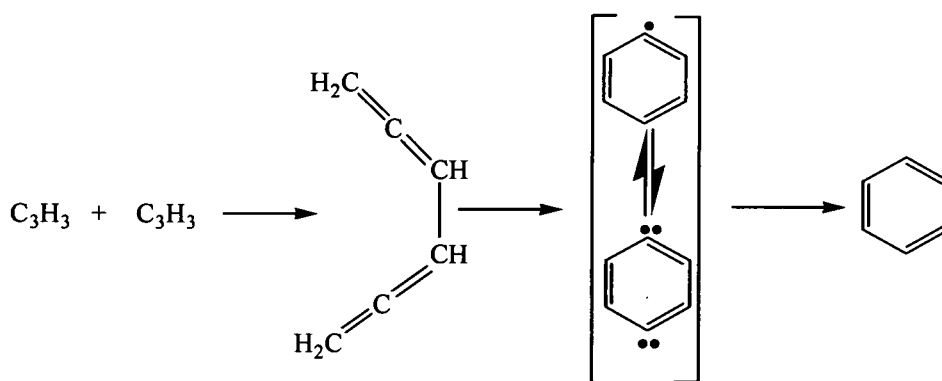


Figure 5.15. Formation path of the first aromatic ring via the combination of two propargyl (C_3H_3) radicals, from Miller *et al.* [93].

The effect of adding water to fuel in the form of emulsion creates many different changes in the combustion process inside the PaSR reactor. Those changes affected mainly the combustion temperature and the formation of many other species such as CO, OH, NO_x and soot precursor species. The latter are formed in a rich, premixed reaction zone that initiates the soot-generating reactions discussed in Chapter II [10, 19]. The concentration of soot precursor species available to produce soot is strongly dependent on the amount of oxygen available in the mixture. When sufficient oxygen is available, soot precursor species react with molecular oxygen or oxygen-containing radicals (OH, O, etc.) and eventually produce CO rather than aromatics and soot. Thus, this kind of reaction is considered to be another way to increase the CO formation level.

Figures 5.16 and 5.17 present the effect of adding 3, 5, 8 and 15% water to fuel on the formation of soot precursor C₃H₃ at different air/fuel equivalence ratios ($\phi=0.8, 2$). As shown in Figure 5.16, the formation of C₃H₃ at $\phi=0.8$ decreases when 3 and 5% water is added to fuel; however, when adding more water (8 and 15% water) to fuel, the formation of propargyl species noticeably increased. As a result, the formation level of soot precursors inside the PasR reactor are very sensitive to water content. Temperature reduction and the slight reduction in the formation of OH radicals as illustrated in Figures 5.11 and 5.12 can cause an increase in soot precursors when more water is added to fuel.

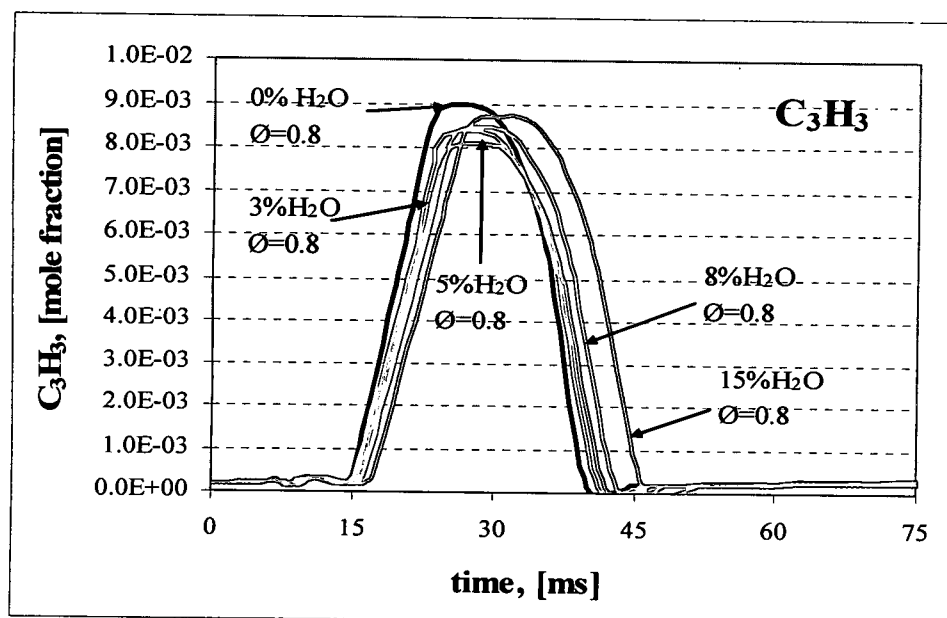


Figure 5.16 Concentration of C_3H_3 precursors change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel, at $\phi=0.8$.

Figure 5.17 shows the change of C_3H_3 with water content in fuel under fuel-rich ($\phi=2$) conditions. It is clear that C_3H_3 formation increases with increasing amounts of water in fuel, as expected, because in addition to a significant amount of fuel that always remains un-oxidized at higher fuel/air equivalence ratios as shown in Figure 5.6, soot precursors including C_3H_3 have higher concentration at this air/fuel equivalence ratio ($\phi=2$) than that of the fuel-lean cases ($\phi=0.8$), as illustrated in Figure 5.5. Modeling results shown in Figures 5.1, 5.5 and 5.8 clarify the trend of C_3H_3 formation illustrated in Figure 5.17 which expresses the effect of fuel-rich combustion on generating a suitable environment for soot precursors' formation at lower temperatures.

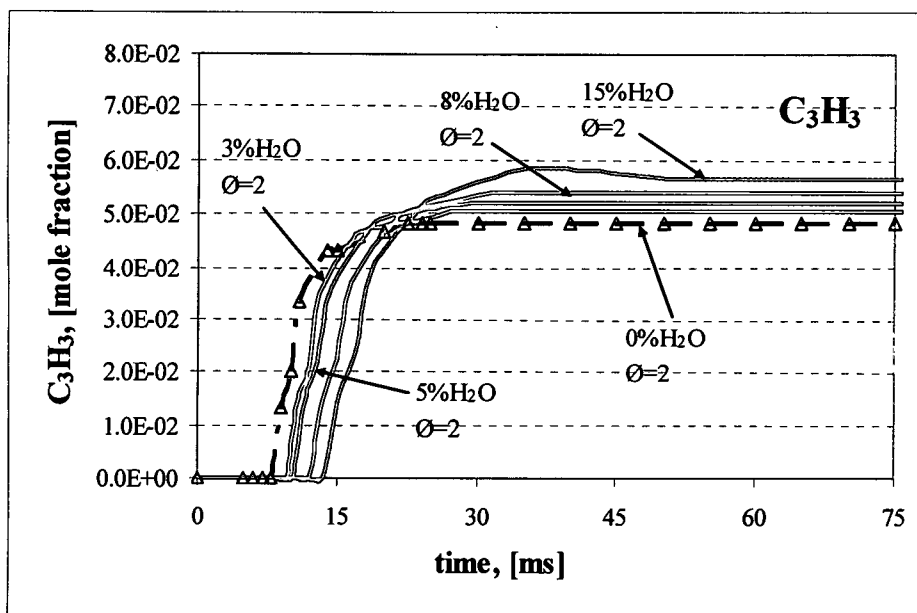


Figure 5.17 Concentration of C_3H_3 precursors change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water-in-fuel, at $\phi=2$.

Diesel fuel contains a variety of different hydrocarbons, among which aromatics are important for smoke emissions. Aromatics are significant contributors to the formation of soot particles in the combustion process as discussed in Chapter II and illustrated in Figures 2.6 and 2.7. The chemical kinetic mechanism predicts a too-slow formation of PAH at low temperature. The growth of larger aromatic species follows essentially the HACA (H-Abstraction- C_2H_2 -Addition) mechanism. The HACA mechanism, as discussed in Chapter II, assumes a sequential two-step process for the aromatic ring formation: H-abstraction, which activates the aromatic molecules, followed by acetylene addition, which promotes continued molecular growth and cyclization of PAH, as shown in Figure 2.7 [23].

When starting with a surrogate fuel (80% n-heptane and 20% toluene) that

contains an aromatic, a “direct combination” of the intact aromatic rings becomes important. For example, in the case of high temperature pyrolysis of benzene, the reactions shown in Figure 5.18 dominated the initial stages of PAH growth [92]. However, as the reaction progressed, the initial benzene molecules decompose, forming acetylene. As the concentration of acetylene approaches that of benzene, shortly after the initial reaction period, the PAH growth switches to the HACA mechanism.

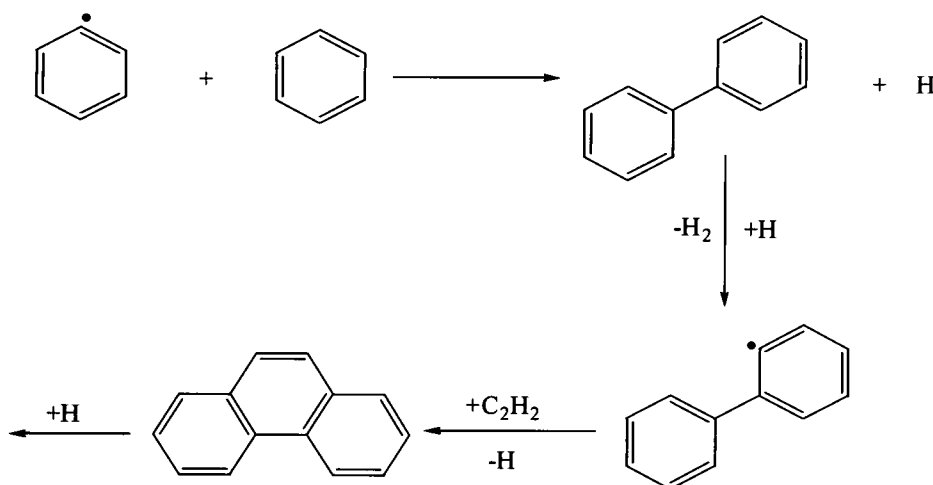


Figure 5.18 PAH growth initiated by aromatic combination of two benzene rings [92].

To understand the effect of adding water to surrogate fuel in the PaSR combustion model, Figures 5.20 through 5.23 are plotted for different PAH compounds at 3, 5, 8 and 15% water in fuel. The figures depict that formation of benzene, naphthalene, phenanthrene and chrysene has a tendency to decrease at fuel-lean conditions when water is added to fuel, but it decreases slowly with the increasing amount of water in fuel. Thus, the 15% water-in-fuel case has the highest concentration of PAH precursors among the other percentages of water in fuel, but it is still lower than the concentration of the base fuel; whereas, the lowest concentration is found for 5% water in fuel.

It is important to know that the surrogate fuel used in this study consists of 80% n-heptane and 20% toluene with an aromatic content similar to conventional diesel fuel. Toluene is an aromatic which, in addition to the benzene rings formed from a combination of propargyl compounds, can play an important role in PAHs and soot formation, as illustrated in Figures 5.15 and 5.18. Water plays a significant role in oxidizing soot precursors either through the reactions of propargyl precursors with OH radicals before they can form the benzene rings, as shown in Reaction (5.5), or the oxidation of the PAH precursors formed from toluene with OH radicals, as shown in Figure 5.19. More explanation about these oxidation reactions is provided in Chapter VII.



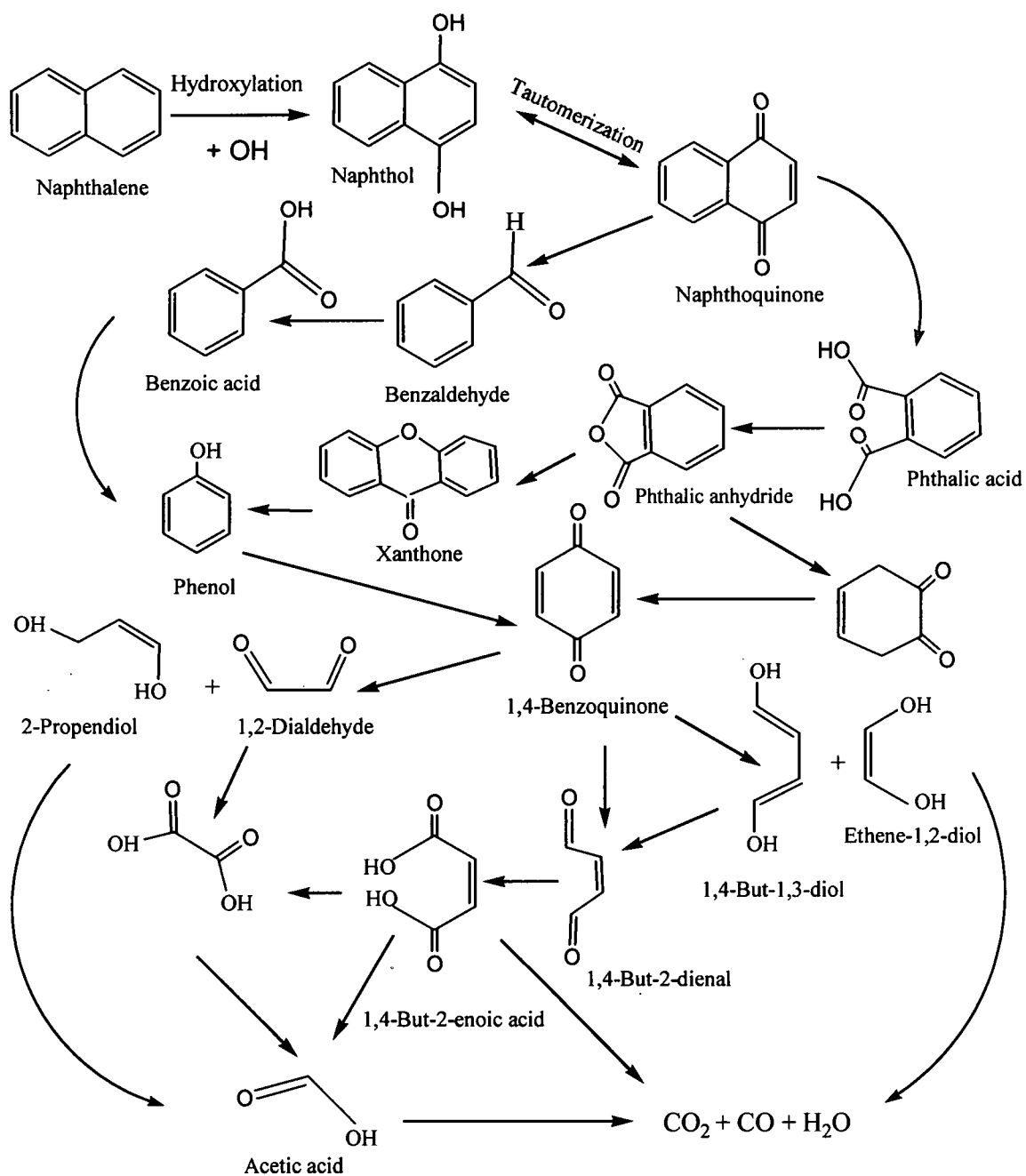


Figure 5.19 Reaction mechanisms for the oxidation of naphthalene with OH radicals, from Onwudili, *et. al* [94].

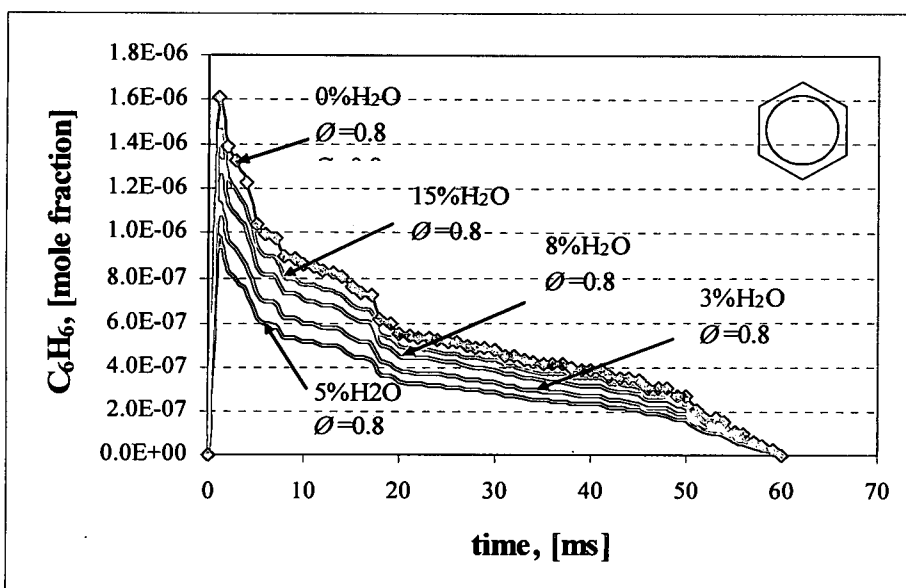


Figure 5.20 Benzene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

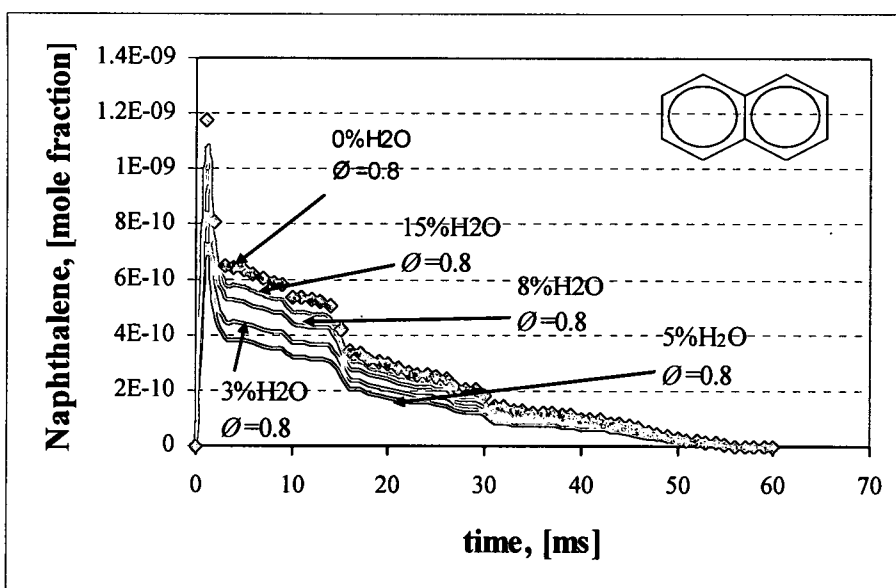


Figure 5.21 Naphthalene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

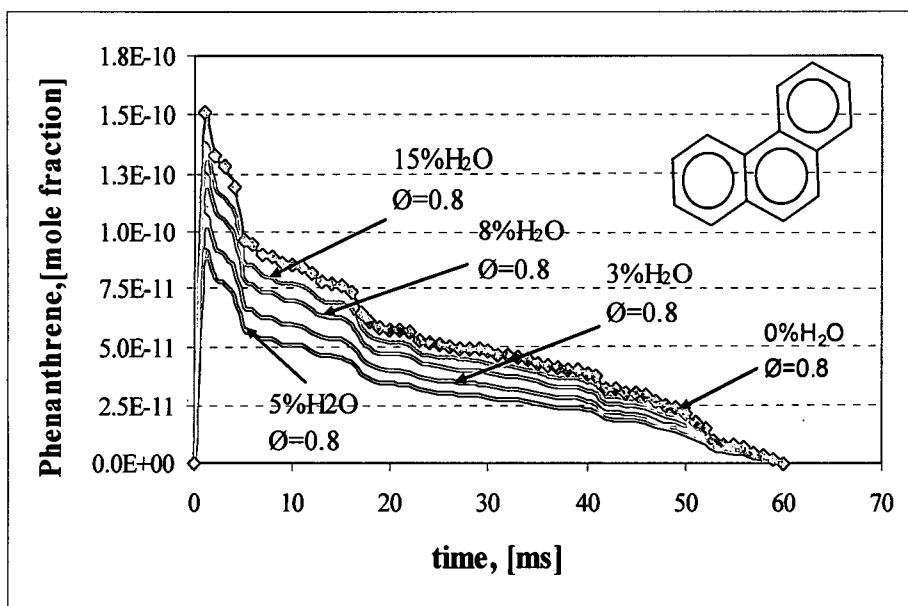


Figure 5.22 Phenanthrene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

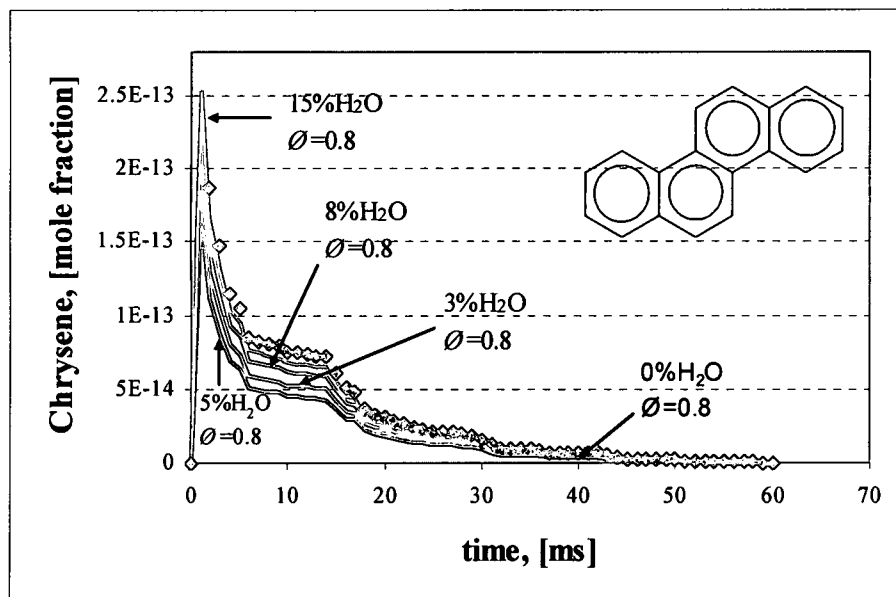


Figure 5.23 Chrysene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

As the fuel becomes more fuel-rich, the peak PaSR model temperature decreases, soot precursors formation and the amount of un-burned fuel increases, as shown in Figures 5.1, 5.5, and 5.6. This emphasizes the tendency of aromatic compounds to form soot particles at low temperature and fuel-rich combustion conditions.

Adding water to surrogate fuel at fuel-rich conditions results in further decreases in temperature as shown in Figure 5.9. The model shows a decrease in the formation of soot precursors as shown in Figures 5.24 through 5.27. This reduction is significant for 5% water in fuel, which shows the lowest value; however, it starts to increase slowly with the increasing amount of water in fuel up to 8% water, after which the formation rate starts to increase to the highest value at 15% water in fuel. Thus, it is clear that at fuel-rich conditions, more water in fuel (15% and above) may inversely affect the production rate of soot precursors.

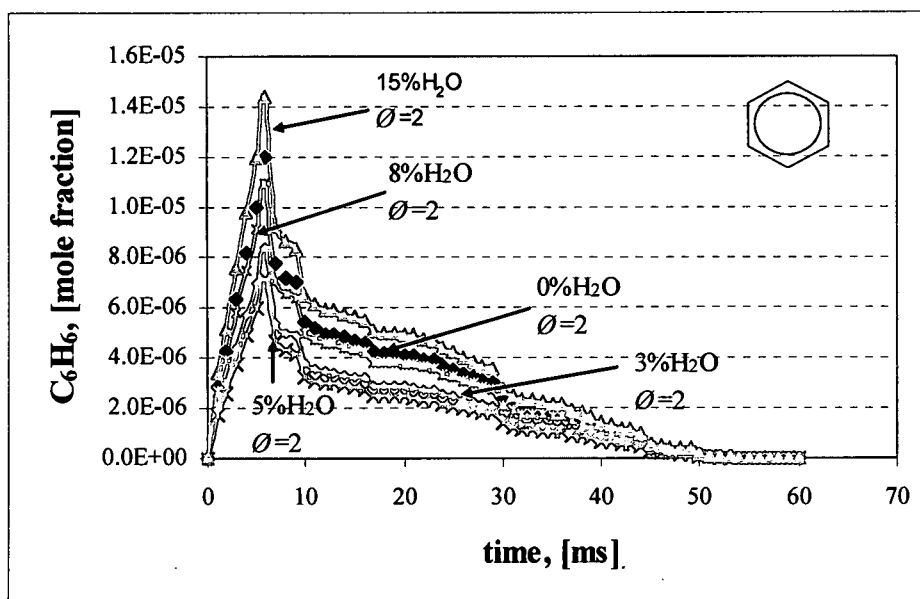


Figure 5.24 Benzene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

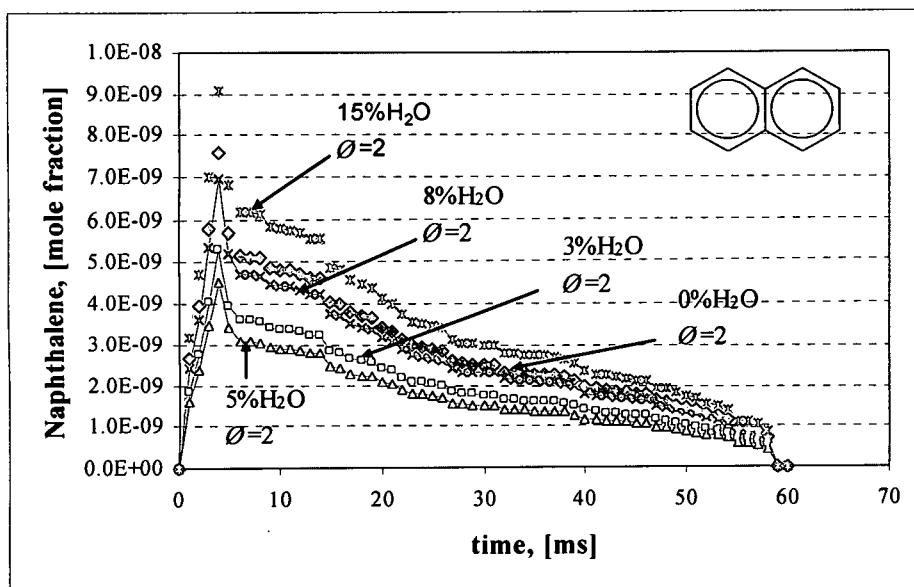


Figure 5.25 Naphthalene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

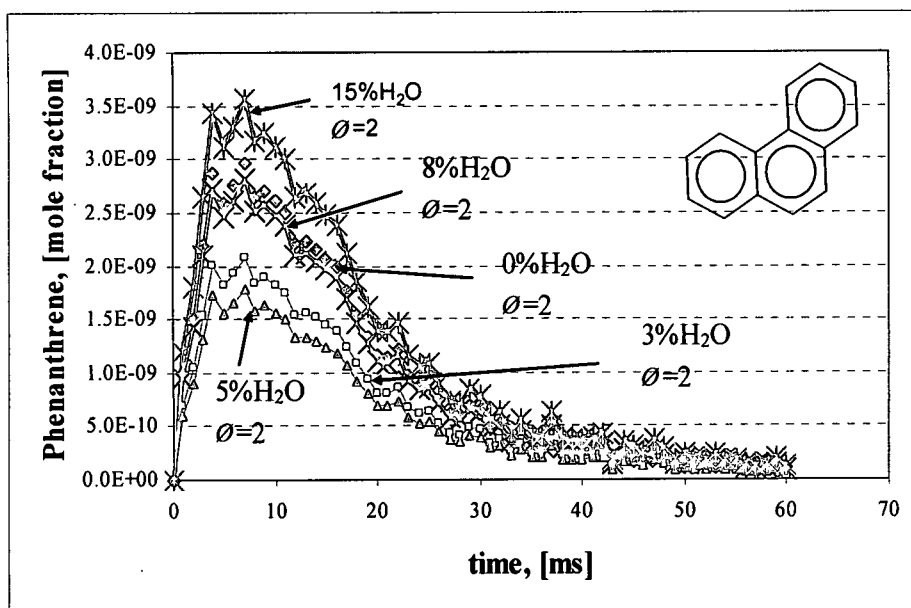


Figure 5.26 Phenanthrene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

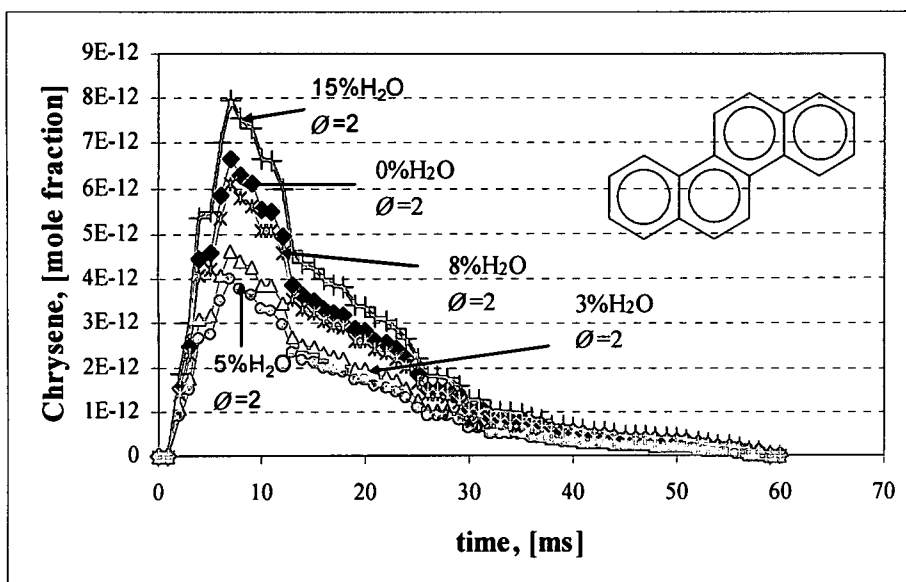


Figure 5.27 Chrysene concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

The effect on the NO_x formation of adding water to fuel is presented in Figures 5.28 and 5.29. These figures represent the trend of NO_x formation inside the PaSR reactor, with 3, 5, 8 and 15% water added to fuel at fuel-lean and fuel-rich conditions where $\phi = 0.8$ and 2, respectively. Both Figures 5.28 and 5.29 show a decrease in NO_x formation with the increasing amount of water; however, at fuel-lean conditions, NO_x formation is higher than at fuel-rich condition for many reasons. First, at fuel-rich conditions, the overall combustion temperature is lower than at fuel-lean conditions for both neat and emulsified fuel as shown in Figures 5.1, 5.8 and 5.9. Since this has a negatively effect on the formation rate of NO_x, a higher temperature is favored for NO_x formation. Secondly, an oxygen deficit at fuel-rich conditions makes the nitrogen molecules compete with the hydrocarbon molecules in the combustion region to form NO_x. NO_x then has less

opportunity to react with oxygen at this lower temperature. The imperfect mixing condition inside the PaSR reactor is an important factor to NO_x reduction because it reduces the opportunity of nitrogen molecules to collide with oxygen or hydroxyl radicals and form NO_x . Also, it can be noticed from Figures 5.28 and 5.29 that adding more water to fuel ($>5\%$) does not lead to significant reduction in the level of NO_x formation, which means that NO_x formation can be reduced by adding water to fuel up to a certain level. Additional discussions of NO_x reduction using emulsified fuel are provided in Chapter VII.

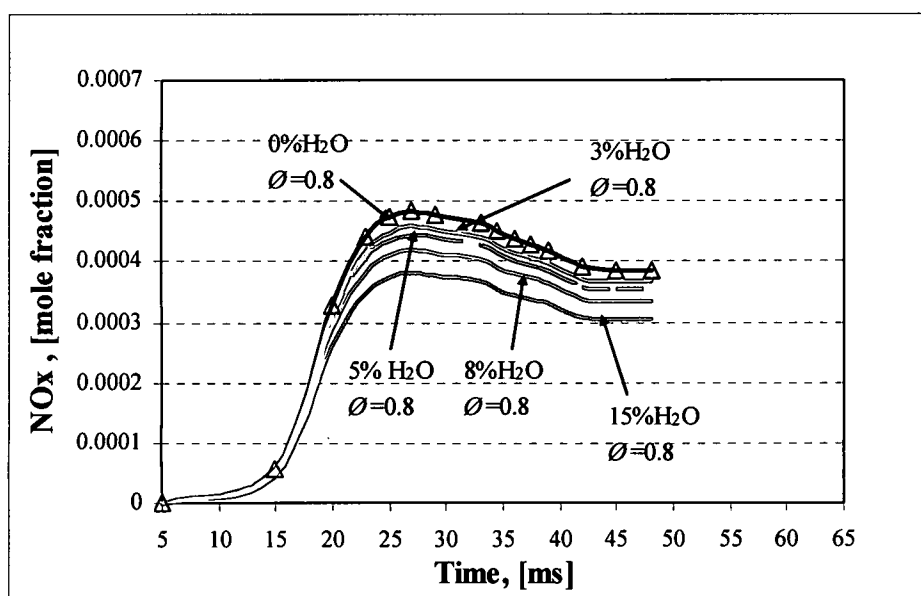


Figure 5.28 NO formation during the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion at $\phi=0.8$ for 0, 3, 5, 8 and 15% water in fuel.

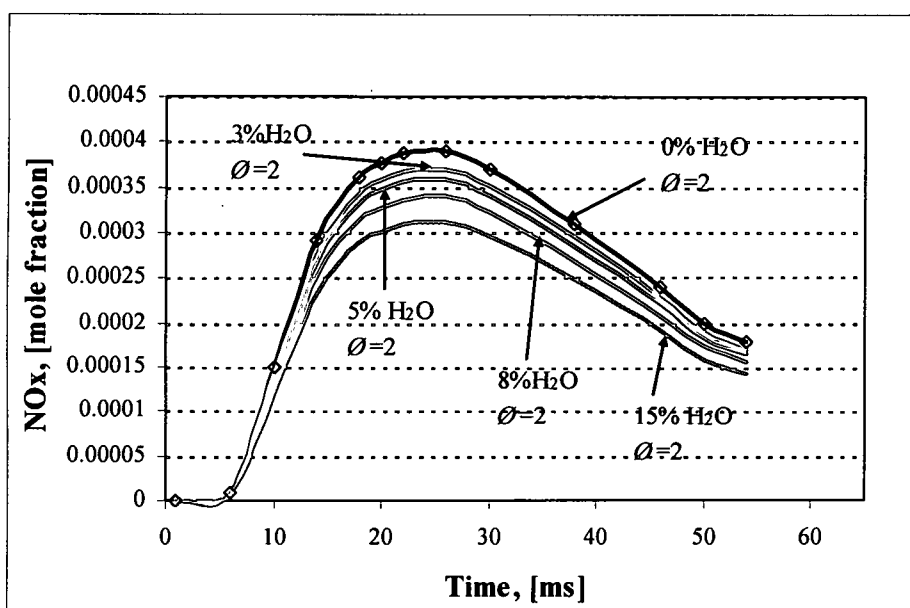


Figure 5.29 NO formation during the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion at $\phi=2.0$ for 0, 3, 5, 8 and 15% water in fuel.

CHAPTER VI

CFD MODEL APPROACH AND THEORY

6.1 Introduction

The spray module used in this work is the discrete phase model that tracks fuel particles through a calculation domain. Tracking is achieved by solving the governing mass, momentum, and energy conservation equations in a Lagrangian frame of reference through the computational fluid dynamic code CFD-ACE+ [95]. The discrete phase is allowed to exchange mass, momentum, and energy with the continuous phase (surrounding ambient fluid). The model was set up to account for one-way (continuous to discrete phase) and two-way coupling between the phases. Each particle or parcel tracked by the model represents the behavior of a large number of droplets. The number density associated with each parcel is determined from the mass flow rate condition.

6.2 Spray Module Theory [15, 96- 99].

In the spray module, the Lagrangian spray equations are integrated by the solver for the fluid parcels over the global time step period. Sub-cycling is used if the time step (global time step for transient sprays) is large compared to the droplet/particle relaxation time.

The equation for the droplet motion can be written as:

$$m_d \frac{dv}{dt} = C_D \rho (U - v) |U - v| \frac{A_d}{2} + m_d g + S m \quad (6.1)$$

where m_d is the mass of the droplet and $v = ui + vj + wk$ its velocity vector; u , v and w are the Cartesian velocity components; C_D is the drag coefficient; ρ , U and p are the density, velocity and pressure of the surrounding gas, respectively; A_d is the droplet frontal area and V_d is the droplet volume. For a spherical droplet, $A_d = \pi d^2/4$ and $V_d = \pi d^3/6$ where d is the droplet diameter. The gravity vector is represented by (g) . Equation 6.1 accounts for the acceleration/deceleration of the droplet due to combined effects of drag with gas and body forces such as gravity. Additional mass sources, Sm , can be added to this equation by selecting the option for user-defined mass source in the spray equation. The drag coefficient, C_D , for the droplet is a function of the local Reynolds number, which is evaluated as

$$R_e = \rho \frac{|U - v|d}{\mu} \quad (6.2)$$

where μ is the dynamic viscosity of the gas.

6.3 Droplet Heat and Mass Transfer

As the droplet moves through the surrounding medium, it absorbs latent heat and evaporates. The rate of evaporation is modeled as:

$$\dot{m}_{ev} = 2\pi d \rho \Gamma_m Sh \ln(1 + B_m) \quad (6.3)$$

where Sh is the Sherwood number, Γ_m is the mass diffusion coefficient for the gas, and B_m is known as the Spalding number. Let Y_v and Y_∞ be the vapor mass fractions at the droplet surface and in the free stream, respectively. In this model Y_v is calculated by equating the surface partial pressure with the liquid saturation pressure.

$$Y_v = \frac{M_d}{M} \frac{p_{sat}}{p} \quad (6.4)$$

where M_d is the droplet molecular weight while M is the mixture molecular weight. The Spalding and Sherwood numbers are obtained from the following expressions:

$$B_m = \frac{Y_v - Y_\infty}{1 - Y_v} \quad (6.5)$$

$$Sh = 1 + 0.3 Re^{0.5} Sc^{0.333} \quad (6.6)$$

where Sc is the Schmidt number. Since $m_d = \rho d \pi d^3 / 6$, the mass conservation equation for the droplet is rewritten in terms of its diameter:

$$\frac{d(d)}{dt} = \frac{4 \rho \Gamma_m Sh \ln(1 + B_m)}{\rho_d d} \quad (6.7)$$

The energy equation for the droplet is written as:

$$m_d C_d \frac{dT_d}{dt} = \pi d^2 \dot{q} - \dot{m}_{ev} L \quad (6.8)$$

where \dot{q} is the sensible heat transferred to the droplet and T_d is the droplet temperature. L is the latent heat of vaporization for the droplet fluid and C_d is the specific heat of the droplet. The sensible heat transfer is calculated as:

$$\dot{q} = \frac{2K(T_g - T_d)Nu \ln(1 + B_m)}{dB_m} \quad (6.9)$$

where K and T_g are the thermal conductivity and temperature of the gas, respectively. The Nusselt number, Nu , is obtained from the following correlation:

$$Nu = 1 + 0.3 Re^{0.5} Pr^{0.333} \quad (6.10)$$

$$Pr = \frac{\nu}{\alpha} = \frac{C_p \mu}{k}$$

where P_r is the Prandtl number, ν is the kinematic viscosity, $\nu = \mu/\rho$ and α is the thermal diffusivity, $\alpha = k/(\rho C_p)$.

Substituting the above expressions into Equation (6.8), the energy equation rewritten as:

$$\frac{dT_d}{dt} = \frac{T_g - T_d}{\theta} - \frac{Q_L}{\theta} \quad (6.11)$$

$$Q_L = \frac{LSh\rho DB_m}{NuK} \quad (6.12)$$

$$\theta = \frac{\rho_d d^2 C_d B_m}{12KNu \ln(1 + B_m)} \quad (6.13)$$

6.4 Turbulent k - ϵ Model

The parameter k refers to the turbulent kinetic energy and ϵ refers to the dissipation rate.

Almost all the models in the CFD-ACE+ code involve solving two extra transport equations: one for the turbulent kinetic energy, k , and the other for the rate of dissipation, ϵ .

In this model, the turbulent viscosity is expressed as:

$$\nu_t = \frac{C_\mu k^2}{\epsilon} \quad (6.14)$$

The transport equations for k is,

$$\frac{\partial}{\partial t}(\rho k) + \frac{\partial}{\partial x_j}(\rho u_j k) = \rho P - \rho \epsilon + \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_t}{\sigma_k} \right) \frac{\partial k}{\partial x_j} \right] \quad (6.15)$$

and the transport equations for ε is,

$$\frac{\partial}{\partial t}(\rho\varepsilon) + \frac{\partial}{\partial x_j}(\rho u_j \varepsilon) = C_{\varepsilon_1} \frac{\rho P \varepsilon}{k} - C_{\varepsilon_2} \frac{\rho \varepsilon^2}{k} + \frac{\partial}{\partial x_j} \left[\left(\mu + \frac{\mu_t}{\sigma_\varepsilon} \right) \frac{\partial \varepsilon}{\partial x_j} \right] \quad (6.16)$$

with the production term P defined as:

$$P = \nu_t \left(\frac{\partial u_i}{\partial x_j} + \frac{\partial u_j}{\partial x_i} - \frac{2}{3} \frac{\partial u_m}{\partial x_m} \delta_{ij} \right) \frac{\partial u_i}{\partial x_j} - \frac{2}{3} k \frac{\partial u_m}{\partial x_m} \quad (6.17)$$

The five constants used in this model are:

$$C_\mu = 0.09, C_{\varepsilon_1} = 1.44, C_{\varepsilon_2} = 1.92, \sigma_k = 1.0, \sigma_\varepsilon = 1.3.$$

The standard k - ε model is a high Reynolds model and is intended to be used in the regions where viscous effects dominate.

6.5 Chemistry/Reaction Model

The built-in Finite-Rate Model is used in this approach because it is the only model in CFD-ACE+ package that enables the user to specify any number of reaction steps each of which proceed at a finite rate. Also, there are no restrictions on the number of reactant species involved in the main reaction model. The data for the reactions involved are taken from the Chemkin format database of n-heptane kinetics, thermo, and transport data. The model can be briefly described as follows.

This finite-rate model allows for specification of single or multiple reaction steps of N_{rxn} chemical reactions involving N_{sp} species to model the process as shown in Equation (6.18).

$$\sum_{i=1}^{N_{sp}} \nu'_{ij} \beta_i = \sum_{i=1}^{N_{sp}} \nu''_{ij} \beta_i, \quad j = 1, \dots, N_{rxn} \quad (6.18)$$

where β_i is the chemical symbol for species i , and ν'_{ij} and ν''_{ij} are the forward and reverse

stoichiometric coefficients for the i^{th} species in the j^{th} reaction. Transport equations are solved for the mass fraction of N_{sp} species. The transport equation for species i is:

$$\frac{\partial}{\partial t}(\rho Y_i) + \frac{\partial}{\partial x_j}(\rho u_j Y_i) = \frac{\partial}{\partial x_j} J_{ij} + M_i \omega_i \quad (6.19)$$

The molar production rate (ω_i) of species i , is given in Equation (6.20).

$$\omega_i = \sum_{j=1}^{N_{\text{re}}} \nu_{ij} q_j \quad (6.20)$$

where q_j is the rate-of-progress variable for the j^{th} reaction, which can be generally expressed as follows:

$$q_j = (k_f)_j \prod_{i=1}^{N_{\text{sp}}} c_i^{\alpha_{ij}'} - (k_r)_j \prod_{i=1}^{N_{\text{sp}}} c_i^{\alpha_{ij}''} \quad (6.21)$$

where $(k_f)_j$ and $(k_r)_j$ are temperature-dependent forward and reverse rate coefficients, c_i is the molar concentration of species i . α_{ij}' and α_{ij}'' are constants and, for elementary reactions, they are equal to ν_{ij}' and ν_{ij}'' respectively.

The molar concentration of species i , c_i , is defined as the number of moles of the i^{th} species per unit volume. It is related to Y_i as:

$$c_i = \frac{\rho Y_i}{M_i} \quad (6.22)$$

The source term $(S_i)^{n+1}$ shown in Equation (6.23) is linearized to improve convergence

$$(S_i)^{n+1} = M_i \omega_i^n + M_i \sum_{j=1}^{N_{\text{re}}} \left(\frac{\partial \omega_i}{\partial Y_j} \right)^n (Y_j^{n+1} - Y_j^n) \quad (6.23)$$

where the indices n and $n+1$ denote the iteration at which the corresponding quantity is evaluated.

6.6 Physical Model

The diesel engine model used in this study represents the actual Detroit Diesel 4-71N two-stroke diesel engine used by Canfield [1] in his experimental study of water/fuel emulsion combustion. Engine parameters are shown in Table 6.1.

Table 6.1 Diesel engine model parameters [1]

Engine Characteristics	Engine Dimensions
Engine type	Detroit Diesel 4-71N-2 stroke
Combustion chamber type	Direct injection
Fuel injector, N90	2.286 mm (0.090 in)
Cylinder volume	71 in ³ (1163.5 cm ³)
Number of cylinders	4
Displacement	4,653.9 cm ³ (284 in ³)
Bore	107.95 mm(4.25in)
Stroke	127 mm(5in)
Compression ratio	18.71:1
Rated power at 2100 rpm	110.4 Kw
Power factor	0.8
Max electric power output	72
Air box pressure	34.1 kPa(10.1Hg)
Air inlet restriction	2.86 kPa
Exhaust back pressure	13.5 kPa (4.0 Hg)
Compression pressure	3900 kPa(565psi)(39bar)
Recommended injection timing	3.708 cm(1.460in)

6.7 CFD Combustion Analysis Software

CFD calculations were performed with commercial CFD-ACE+ flow analysis software [95], a set of computer programs for multi-physics computational analysis. The programs provide an integrated geometry, grid generation module, and a graphical user interface for preparation of the model called CFD-GEOM, a computational solver for performing the simulation called CFD-GUI, and a program to examine and analyze the simulation results called CFD-VIEW. CFD-ACE+ is primarily used for low-speed flows

(Mach < 2.5) and is capable of simulating a diverse range of fluid flow and chemical reactions [95].

6.8 Model Setup

CFD is a numerical tool used to describe the motion of a fluid flow in a region. It is necessary to translate and develop the physical model in a numerical language to be able to submit it to the solver for computation purposes. The computational theory and governing equations necessary to numerically compute combustive flows were discussed earlier. The geometry and modulation of the problem were designed according to the characteristics and dimensions of the proposed 2-stroke diesel engine cylinder used in this study and illustrated in Figure 6.1.

Figures 6.2 and 6.3 show the grid generated using the CFD package GEOM. CFD-GEOM, as mentioned before, is a pre-processor package that allows to a geometrical field setup in which the fluid flow and the combustion reaction takes place. This involves the CAD-like specifying of points and joining of lines for both the object to be studied and the entire domain [95], after which the entire area grid model should be generated to form the computational domain. This step is important to divide the whole volume into discrete control volumes or cells to be able to trace the movement of fluid parcels from one control cell to another. For step-by-step instructions on how to build a model in CFD-GEOM, refer to the manual supplied with the CFD package [95].

A two-dimensional structured axisymmetric grid is generated and used for this model as shown in Figures 6.1 and 6.2. The grid parameters, size, and the number of cells are specified in Table 6.2. More cells mean greater accuracy but also longer

computational time. The number of cells may also have an impact on the stability of the simulation, so that a tradeoff between accuracy, stability and run time is always required.

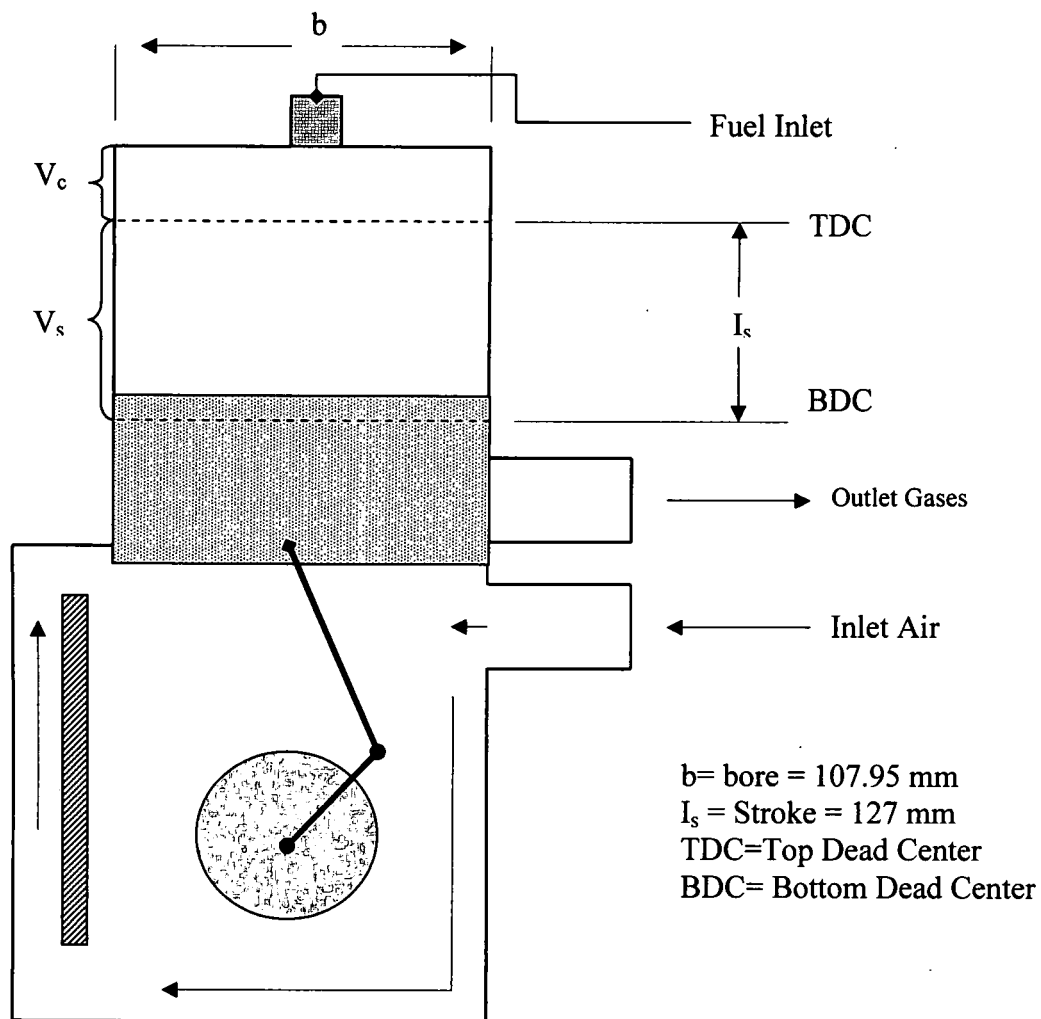


Figure 6.1 Dimensions and characteristics of 2-stroke diesel engine used in the model.

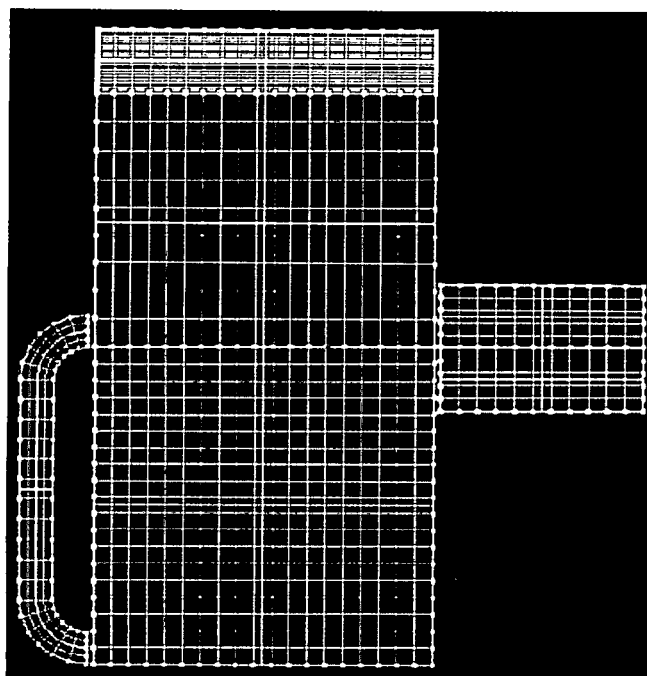


Figure 6.2 Generated axisymmetric structured grid of the 2-stroke diesel engine cylinder used in the model.

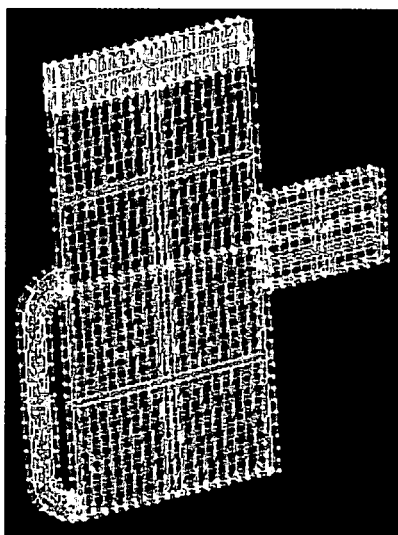


Figure 6.3 Angle view of the generated axisymmetric structured grid of the 2-stroke diesel engine cylinder used in the model.

Table 6.2 Parameters of the grid geometry.

Structure	Quantity
Cells	21900
Nodes	37920

6.9 Boundary Conditions and Input Values

Initial and boundary data is listed in Table 6.3. This data is taken from the actual parameters of the physical engine used by Canfield [1]. Surrogate fuel properties of 80% n-heptane and 20% toluene are used in this model. Instead of the real marine diesel, n-heptane and toluene were used in this computation because the kinetics mechanism is available for n-heptane and toluene but not for marine diesel that Canfield used [1]. Also, it represents the conventional diesel fuel due to n-heptane, which makes 80% of the surrogate fuel and has a cetane number similar to that of diesel fuel. Tables 6.4 and 6.5 show the properties of n-heptane and toluene respectively.

Table 6.3 Boundary condition parameters used in the simulation [1, 7, 100].

Bore [mm]	107.95
Intake port height from the BDC [mm]	20
Nozzle hole diameter [μm]	113
Intake pressure [bar]	39
Compression ratio	18.71
Stroke [mm]	127
Squish [cm]	0.513
Engine speed [RPM]	2100
Inlet fuel flow [gr/s]	1.2
Inlet air flow [gr/s]	11.4
Amount of recirculated exhaust gas EGR%	0
Diesel particle diameter [μm]	0.02
Droplet diameter [μm]	100
Ambient temperature [K]	300
Ambient pressure [kPa]	100
Equivalence ratio (ϕ)	0.8
Spray velocity (m/s)	200

Table 6.4 Properties of n-heptane fuel [2].

Molecular Formula	C_7H_{16} / $CH_3(CH_2)_5CH_3$
Molecular mass	100.2
Boiling point	98°C (371°K)
Melting point	-91°C (182°K)
Specific gravity	0.684
Solubility in water	none
Relative vapor Density (Air=1)	3.46
Vapour Pressure at (20 °C)	4.6 kPa
Flash Point	-4°C (269°K)
Auto-ignition temperature	285°C (558°K)
Cetane number	52-56

Table 6.5 Properties of toluene fuel [2].

Molecular Formula	$C_6H_5CH_3$
Molecular mass	92.14
Boiling point	111°C (384°K)
Melting point	-94.5 °C (178.5°K)
Specific gravity	0.865
Solubility in water	Nearly insoluble
Relative vapor Density (Air=1)	3.14
Vapour Pressure at (20°C)	2.93 kPa
Flash Point	4°C (277°K)
Auto-ignition temperature	480°C (753°K)
Cetane number	-5 to 18.3

The model simulation started by assigning the boundary conditions in Table 6.3 to the generated grid model and saved as DTF file which can then be read by the solver. Fuel and air are introduced into the combustion chamber according to the parameters in Tables 6.3, 6.4 and 6.5. Fuel is injected as liquid spray, resulting in a two-phase CFD problem. Engine spray simulation started by submitting the model parameters to the solver after activating the turbulent, chemistry, heat, and spray models discussed before. The first step of the modeling procedure was to determine the baseline data by running

the system using pure surrogate fuel (80% n-heptane + 20% toluene) without adding any water. The second step started by adding different amounts of water (3, 5, 8 and 15% by volume) to the surrogate fuel, after which data were collected and plotted for each individual case as shown in Chapter VII.

CHAPTER VII

MODELING RESULTS AND DISCUSSION

This modeling study was conducted to investigate and understand the influence of the addition of water to fuel on the formation of combustion pollutants, namely NO_x , CO and PAHs formation. To accomplish this task, the CFD modeling technique [95] was applied on a suggested 2-stroke diesel engine cylinder with surrogate fuel consisting of 80% n-heptane and 20% toluene as a substitute for the conventional diesel fuel. Water was added to surrogate fuel in four different portions 3, 5, 8 and 15% (by volume) at 39 atm pressure and the equivalence ratio was constant at 0.8 to be consistent with the real diesel engine operating conditions [1], (see Table 6.1). Data were collected and plotted over a certain run time between (0 and 75 ms) for five runs, one of them for neat surrogate fuel without water and four with water.

Very little efforts have been devoted to modeling the combustion of water-fuel emulsion. The lack of experimental data also makes it difficult to validate the results of this CFD modeling study. Therefore, the CHEMKIN modeling code [82] was used as an alternative method to model the combustion of the same emulsified and surrogate fuel to compare and validate the results with data from the literature.

It has been hypothesized that the combustion of emulsion is potentially useful for relieving the difficulty in solving problems related to clean environments and effective utilization of energy. It may help to extend the range of the fuel resources and improve

the utilization of low quality fuel. Emulsion also has the potential to be fire resistant so that upon spillage and incendiary ignition, the initial fireball extinguishes itself.

The modeling results show that the corresponding amounts of water added to fuel caused many different changes to the combustion process inside the engine. The participation of water in the evaporation process is expected to lower the droplet combustion temperature due to the high heat of vaporization of water (43.99 KJ/mol) [101] compared to that of surrogate fuel (36.87 KJ/mol), which is calculated from the average heat of vaporization of n-heptane, (36.57 KJ/mol), and that of toluene, (38.06 KJ/mol) according to their ratios in surrogate fuel [101]. Thus, by lowering the heat content of the emulsified fuel due to the addition of water, the energy output per mass of total fuel can be lowered. Figure 7.1 presents the impact of water addition to fuel on the combustion temperature inside the engine cylinder which noticeably decreases with the increasing amount of water added to fuel. The temperature profile of the base fuel (0% water) shows a gradual increase in temperature to a maximum peak point of ~3075 K then starts to decrease to a lower temperature where it remains constant throughout the engine stroke. When water blended fuel is introduced into the engine cylinder, a reduction in temperature is noticed. This reduction starts at the moment the emulsified fuel is injected and increases with the increasing amount of water in fuel, so the lowest temperature is found for the fuel that contains 15% water. Table 7.1 gives the values of the highest peak temperatures achieved with the relevant time for each kind of water-fuel emulsion. It is noticed from this table that the time needed for maximum peak temperature increases with the increasing amounts of water in fuel, which means the liquid persists for a longer period and travels further into the domain before ignition. This

could be explained by the phenomena of ignition lag which is discussed in Chapter II and presented at the end of Chapter VII. Hence, more water in fuel means more energy is needed to evaporate the mixture droplet and this energy is taken from the system which reduces the temperature and makes the droplet travel longer before ignition. It had been postulated that peak temperatures in the domain are reduced by two localized phenomena [16]. First, vaporization of liquid water decreases the internal energy proportionally to the vaporization enthalpy of the liquid water. Secondly, higher concentrations of water vapor increase the specific heat capacity of the gas.

The modeling results are validated against the experimental work in literature, especially that of Samec *et al* [45] which illustrates the temperature reduction with the increasing water content as seen in Figure 7.2. Compared to their results, the modeling results of this study depict higher peak values but lower temperatures, as shown in Figures 7.1 and 7.2, due to differences in combustion system, design, fuels and water percentages used. Although the fuel used by Samec *et al* [45] was pure n-heptane without toluene and the water percentages were 10 and 20%, their results show a similar trend and predict the same tendency to decrease temperature when water is added to fuel.

The alternative modeling results of the PaSR model shown in Figure 5. 9 for fuel-lean combustion at $\phi=0.8$ predict similar results within the same combustion cycle, hence temperature decreases with the increasing amount of water added to fuel. Therefore, regardless of the combustion system used or the type of the model applied, temperature reduction occurs when water is added to the fuel. The PaSR model results show lower peak temperature and nearly different time-temperature profile but it predicts a similar trend.

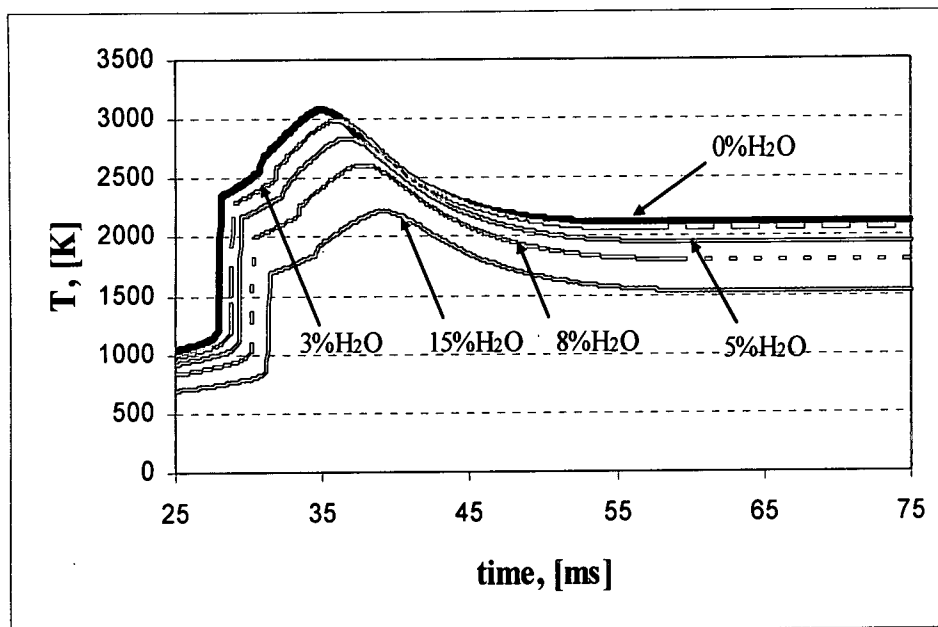


Figure 7.1 Temperature profile at the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15 % water content.

Table 7.1 Peak temperature in [K] and peak time in milliseconds for 0, 3, 5, 8 and 15% water-fuel emulsion.

Parameters	0% Water	3% Water	5% Water	8% Water	15% Water
Peak t, ms	35	36	37	38	39
Peak T, [K]	3075	2983	2833	2607	2216

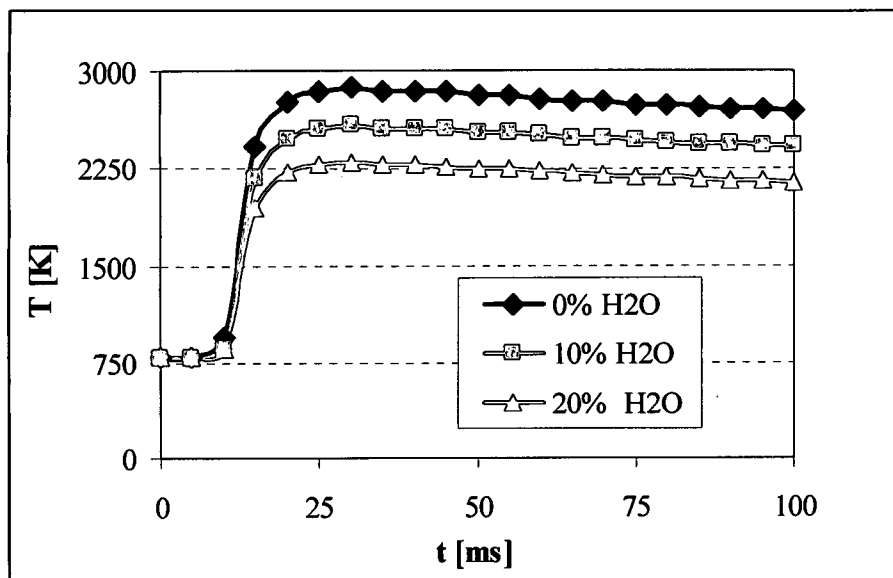


Figure 7.2 Experimental temperature profile from the combustion of n-heptane/water emulsion with 0, 10 and 20% of water [from Samec *et. al* 45].

The engine in-cylinder pressure versus crank angle was plotted in Figure 7.3 to show the impact of water-in-fuel content on the pressure change, which increases with the increasing amount of water. It is known from literature and experimental work of others [66, 102-107] that the pressure performance curve is the most important data necessary to analyze the power output and combustion process. Compared to that of base fuel, the pressure curves of water-emulsified fuel have higher peak values than that of the base fuel and the highest peak value is shown for the 15% water-in-fuel condition. Wang and coworkers [102] postulated that, after the ignition of water-fuel emulsion, water vapor pressure works on piston instead of part fuel and acts exclusively in a manner similar to a steam engine. Once ignition occurs, the effect of steam pressure will be more effective with more water in fuel and the power output will increase to some

extent due to the increased work output with the increasing in-cylinder pressure. So the peak pressure gain resulted from the combustion of the emulsified fuel, shown in Figure 7.3, is caused by the addition of water to fuel and it increases with the increasing percentage of water in fuel.

The effect of the strictly-called steam engine can be considered as an important reason behind the improvement of fuel economy in diesel engines [102] which could be experimentally studied in a future work by measuring the BSFC [10] of a real engine that shows the rate of fuel or emulsified fuel consumption per engine power output (kW). Table 7.2 shows the pressure rise at the peak values after adding different amounts of water in fuel which predicts the relationship between water content and pressure.

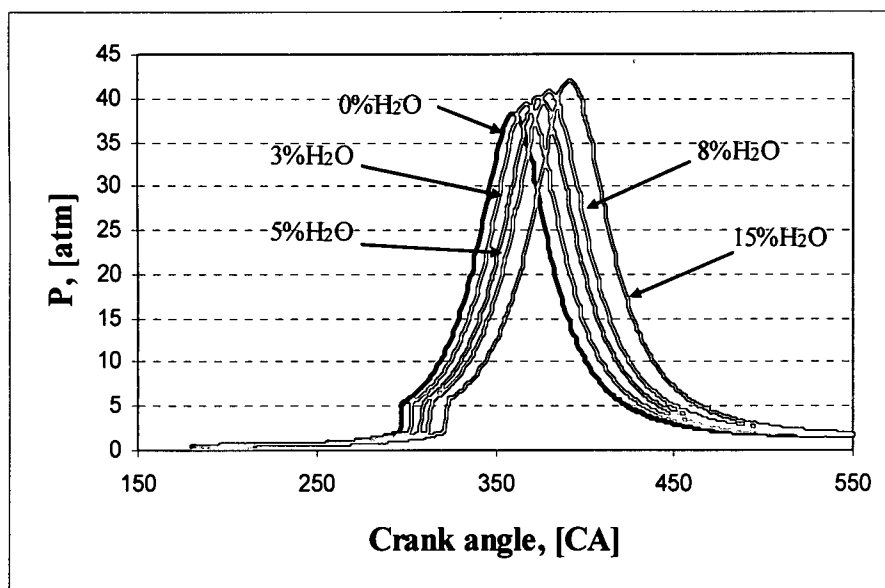


Figure 7.3 In-cylinder engine pressure change, P [atm], versus crank angle, $^{\circ}\text{CA}$, at combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion with 0, 3, 5, 8 and 15% water content.

Table 7.2 The maximum peak pressure values and the corresponding crank angle values for 0, 3, 5, 8 and 15% water in fuel combustion.

% Water in Fuel	0%	3%	5%	8%	15%
Crank angle, [°CA]	360	367	374	380	392
Peak Pressure,[atm]	38.33	39.48	40.27	40.87	42.09

Bedford *et al* [49] and Wang *et al* [102] theoretically believed and experimentally proved that water in fuel results in better mixing between fuel and air in the combustion chamber of diesel engines. Their theory was attributed to an additional momentum input from the increased density of the water vapor of emulsified fuel and higher exposed fuel surface area to air, which leads to larger air entrainment ability and improved mixing between fuel and intake air. Once better mixing and wider distribution is achieved in the combustion chamber, a complete combustion and rapid heat release process could be achieved, resulting in significant improvement in combustion performance, power output, and fuel consumption control.

Experimental work performed by Abu-Zaid [108] validates the predicted high pressure results upon using different ratios of water in fuel as shown in Figure 7.3. His work clearly shows (see Figures 7.4 and 7.5) that the addition of water in the form of emulsion increases engine torque and improves engine efficiency by increasing the power output over the entire engine speed range. The engine torque and power output increase as the water percentage in the emulsion increases.

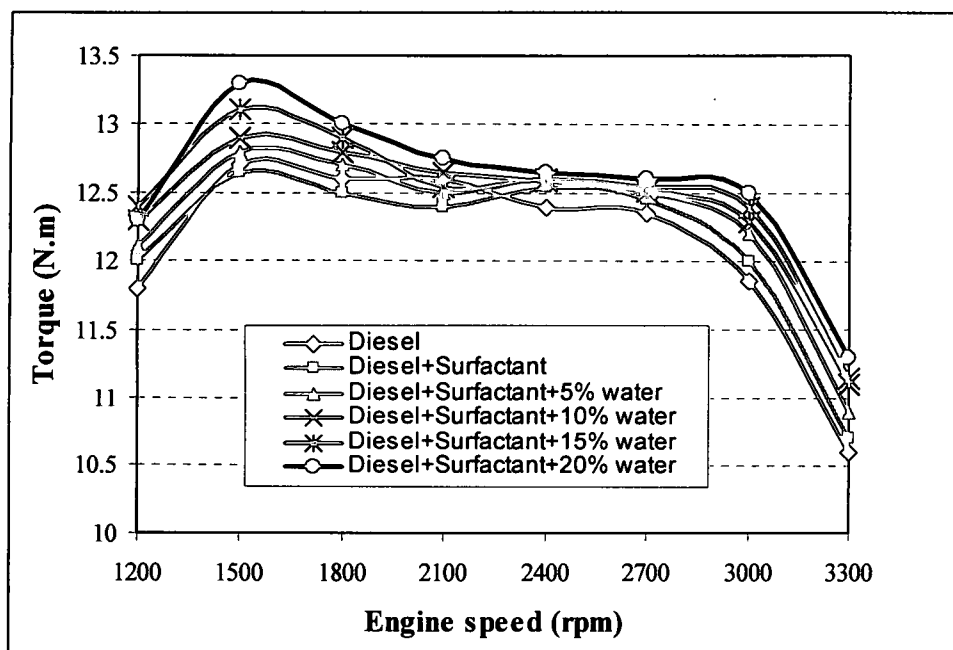


Figure 7.4 Engine torque output versus engine speed using water-diesel emulsions [108].

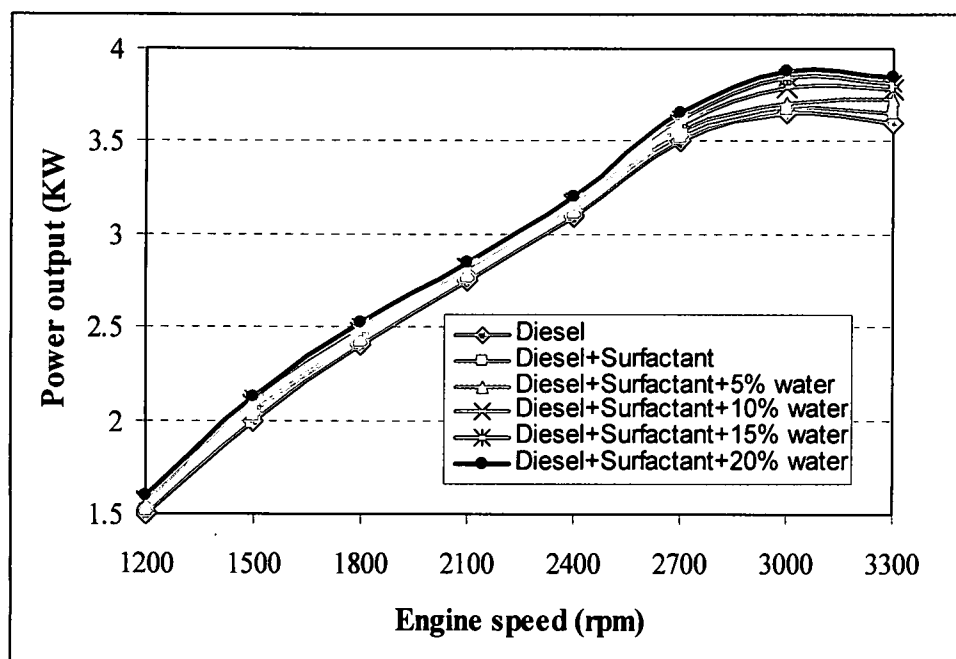


Figure 7.5 Engine power output versus engine speed using diesel-water emulsions [108].

Emulsions have both physical and chemical effects on combustion. When a pure water droplet is heated externally, the maximum temperature will be at the droplet surface and will increase until it approaches the boiling temperature [109]. At that point, a fraction of the additional input energy will be conducted to the droplet interior. As at the water-air interface, the phase transformation of liquid to vapor is favored thermodynamically and most of the additional input energy will be dissipated as latent heat of vaporization. Internal vapor bubble nucleation and growth involve the formation of new gas-liquid interfaces, which require energy to overcome compressive surface tension forces and external pressure. If this energy (superheat) is too low, collapse of the vapor bubble nucleus is favored thermodynamically and internal boiling is unlikely to occur. Internal or nucleate boiling is characterized by a sudden rapid phase change, and as thermodynamically continued growth of a vapor bubble nuclei that exceeded a critical size is favored, spontaneous phase transformation occurs.

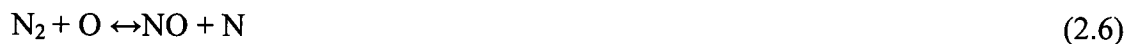
Theoretical analysis on the combustion of emulsion droplets predicts that water emulsification causes a significant increase in the water vapor concentration within the hot fuel-rich region between the flame front and the droplet surface, a drastic decrease in the flame size, and a slight decrease in the flame temperature [65]. Since the rate of chemical reactions is a strong exponential function of temperature, these results imply that with increased water emulsification both the intensity and the volume of the chemical reactions in the flame zone decrease exponentially [52]. As a result, the decreased flame zone directly influences thermal NO_x formation during the chemical reaction rate reduction for Zeldovich mechanism reactions [35], as described before in Chapter II and shown in Reactions (2.6), (2.7) and (2.8). The temperature dependence of

the thermal NO formation rate (shown in Eq. 2.9) can be seen to decrease with decreasing temperature:

$$\frac{d[NO]}{dt} = \frac{6.0 \times 10^{16}}{\sqrt{T}} e^{-69090/T} \sqrt{[O_2]_e [N_2]_e} \quad (2.9)$$

In addition to the thermal NO reactions that take place in a few tens of microseconds, the residence time of the combusted gases inside the engine cylinder is very low and total amount of NO formed in a diesel engine is expected to be dependent on the time spent at high temperature [39].

Additionally, the NO concentration may be reduced by reducing the concentration of O atoms as shown in Figure 7.6. This could predict a decrease in O concentration level with the increase of water content in fuel due to its consumption in the formation of OH radicals by many reactions such as the following overall reactions [45]:



These reactions indicate the very high dependence of NO formation on the O atom concentration which is mainly affected by combustion temperature.

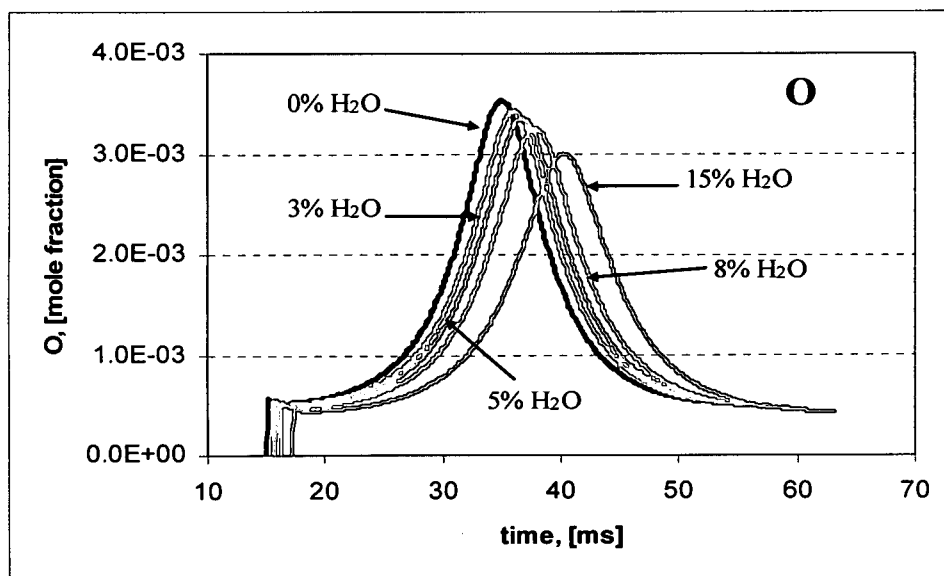


Figure 7.6 Concentration profiles of O radicals from the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

Figures 7.7 and 7.8 show the overall history of NO formation and the rate sensitivity analysis of the most important reactions that dominate NO formation during the emulsion combustion of water/fuel mixtures. These figures show that NO_x formation decreases as the amount of water added to the fuel increases. The NO species production rate, which has a positive value in the sensitivity column graph (see Figure 7.8), decreases with increases in the amount of water in fuel and the NO consumption rate, which has a negative value, increases with increasing water content in fuel. Thus, the decrease of NO_x formation and the increase of consumption of NO reflects the thermal effect on the NO formation reactions which controls the overall NO_x as well as the chemical effect represented by the O reduction (see Figure 7.6).

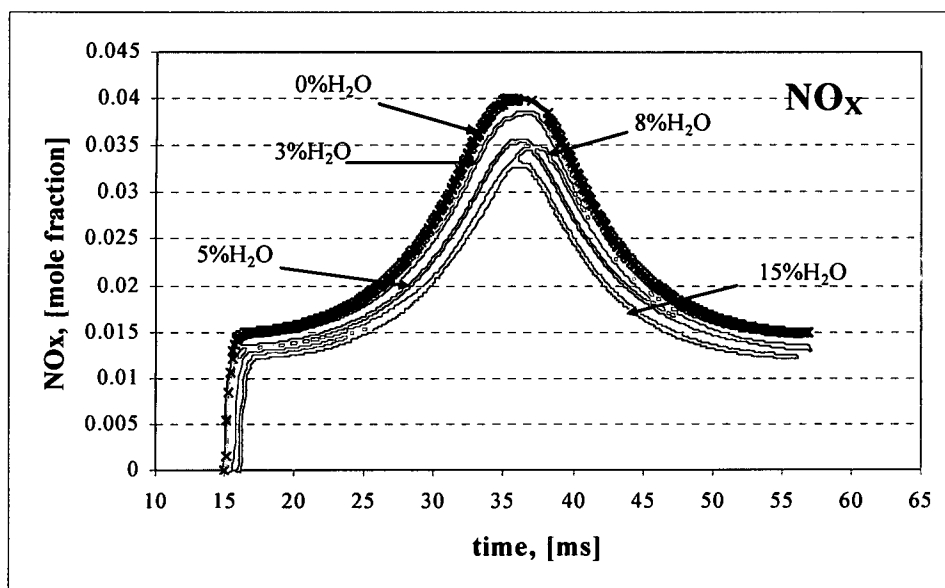


Figure 7.7 NO_x concentration during the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% of water content.

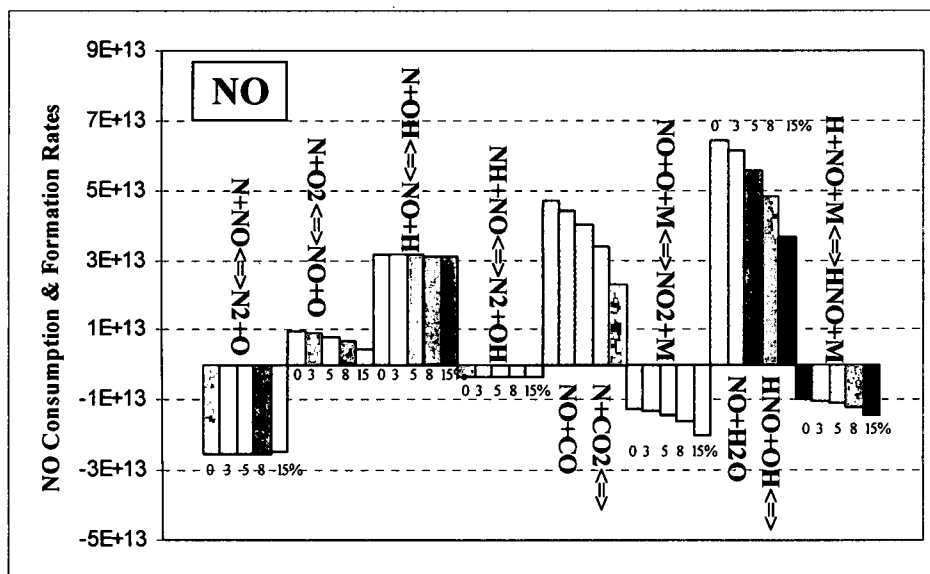


Figure 7.8 Sensitivity of NO for the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% of water content based on rate of formation/consumption of the most significant reactions.

The percentage reduction is illustrated in Figure 7.9 and varies between ~4 % up to ~17% relative to the amount of water added to fuel. The highest NO_x reduction value is found for the 15% water in fuel; however, it can be seen from Figure 7.9 that the difference between the percentage reduction of NO_x for 3 and 5% of water in fuel is more than that between 5 and 8% or 5 and 15% water in fuel. This means that the addition of 8 and 15% water to fuel did not reduce as much in the formation of NO_x as the 5% water in fuel, so more water in fuel does not have an additional impact on NO_x formation reduction.

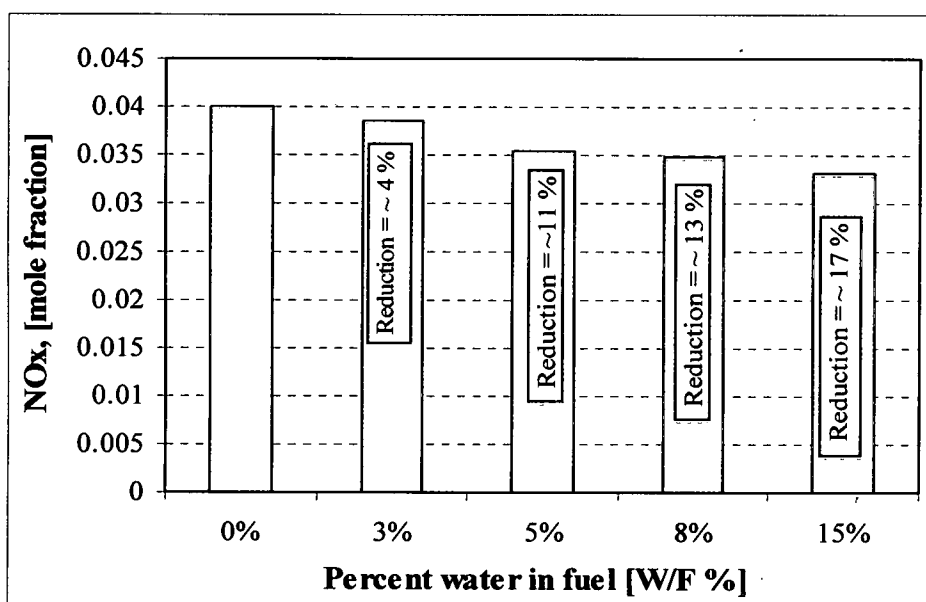


Figure 7.9 Percent NO_x reduction for the combustion of emulsified fuel at 3, 5, 8 and 15% water in fuel compared to that of neat fuel of 0% water.

The trend of NO_x formation reduction by adding water to fuel in the form of emulsion is validated against the alternative CHEMKIN PaSR modeling results shown in Figure 5.29. It is also validated by the work of Samec *et al* [45] presented in Figure 7.10. Both results depict that the formation of NO_x decreases as the water content increases.

However, NO_x formation is not much affected by adding more water to fuel and the reduction of NO_x at 8 and 5% water does not show significant change from that of 5% water in fuel.

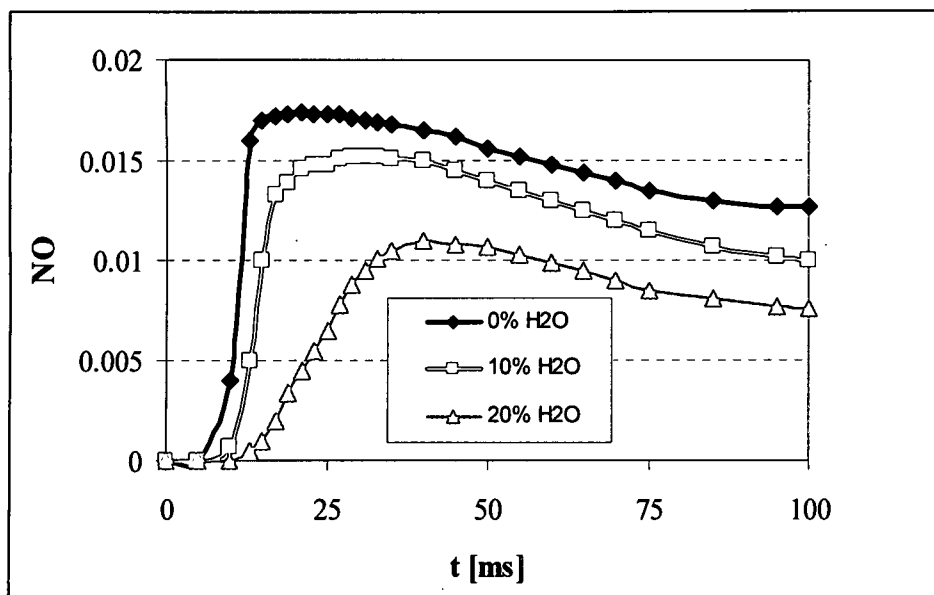


Figure 7.10 NO concentration during the combustion of n-heptane/water emulsion of 0, 10, and 20% of water content [from Samec *et al* 45].

Compared to the work of Samec *et al.* [45], the CFD model results presented in Figure 7.7 show a sharp increase in NO formation up to higher peak values followed by a sharp decrease at the end of the combustion cycle, which predicts similar trend of decreasing thermal NO formation with the increased amount of water in fuel but with a different NO formation profile. In contrast to the work of Samec *et al.* [45] more water in fuel (> 5 %) did not show significant impact on NO_x formation level as shown from Figures 7.7 and 7.8 whereas Samec *et al* [45] found that the addition of 20% water to fuel could reduce NO_x formation level by a factor of 3 which differ from our findings. These differences could be due to differences in modeling approach and type of fuel used. It is interesting to

note that the CHEMKIN PaSR model results (see Figure 5.29) at fuel lean condition agree well with Samec *et al* [45] results. That means that thermal NO formation through the PaSR model, which doesn't exactly represent the real engine compartment, is not sensitive to the type of fuel used, but there is evidence showing the effect of water percentage on the NO formation reduction at different water percentages as shown in Figure 5.29.

The modeling results of NO_x formation were also validated against the experimental data of Canfield [1] as shown in Figure 7.11. Canfield used the engine power output as a reference to the NO_x emission measurement in the exhaust. Canfield found that NO_x formation decreased with the increasing amount of water in fuel, but adding more than 30% water to fuel did not result in further reduction in NO_x formation. The data collected by Canfield was for the exhaust NO_x yield and was plotted against different reference axis (engine power output) which is practically possible for the case of his real engine experiment but not possible for the modeling approach of this work which focused on the in-cylinder combustion process. The modeling results of this work also predict a reduction in NO_x formation with the addition of water which is consistent with the results of Canfield.

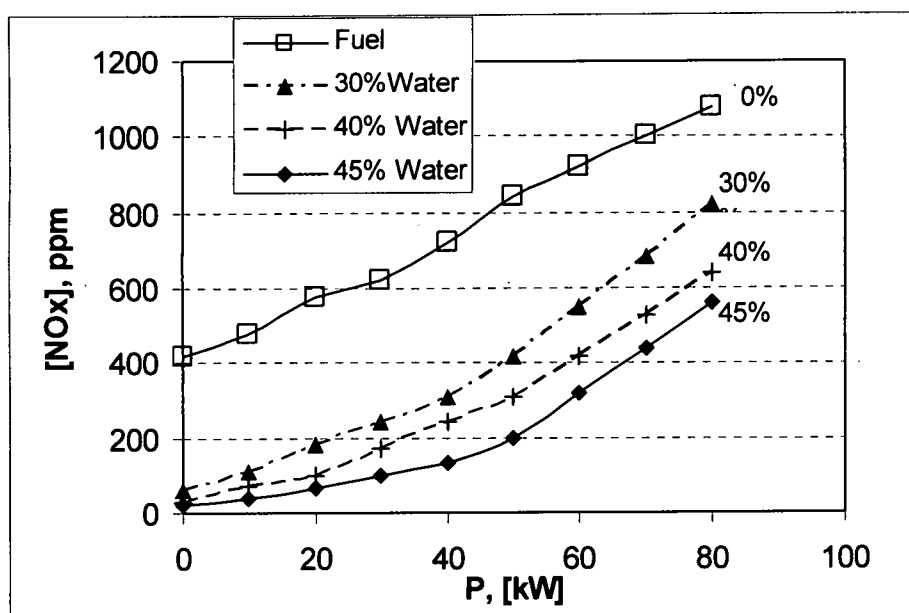


Figure 7.11 Experimental exhaust $[\text{NO}_x]$ change with the real engine power [1].

The chemical composition of fuel changes with the addition of water, resulting in the formation of higher OH radicals during combustion, as shown in Reactions (7.3) and (7.4). Figure 7.12 shows the change in the concentration of OH radicals by the addition of water to fuel. The OH concentration increases with the increasing amount of water in fuel which is consistent with the CHEMKIN modeling results.

Figure 7.12 predicts the change of OH concentration over the time range of the engine cycle which is expressed in milliseconds. The effect of adding water to fuel is quite obvious from the increase in the concentration of OH radicals with the increase in amount of water added to fuel. The maximum peak point then starts to decrease rapidly to a lower concentration value where it remains nearly constant.

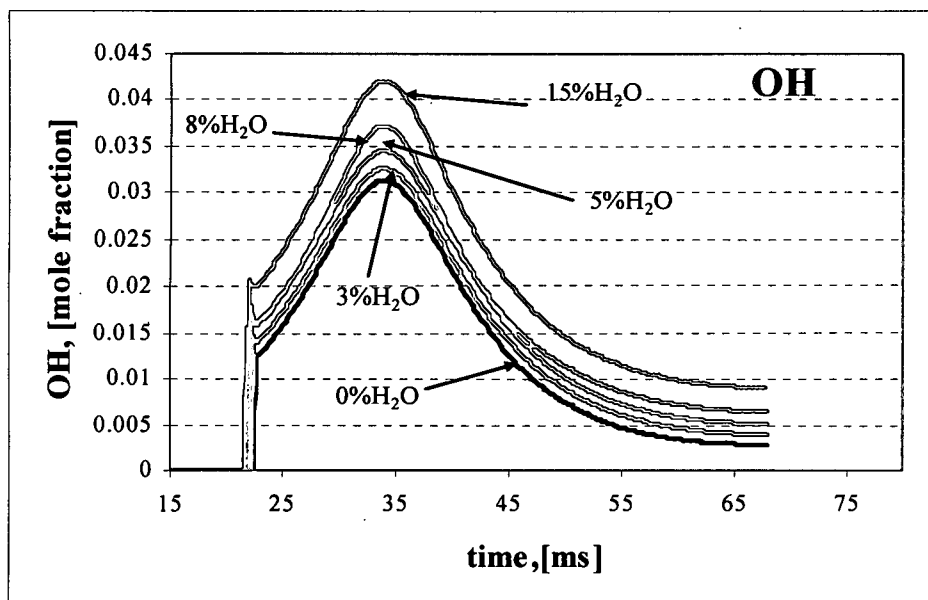


Figure 7.12 Concentration profiles of OH radicals from the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

Compared to the CHEMKIN modeling results illustrated in Figure 5.12 for the fuel-lean combustion case ($\phi=0.8$), which is also the overall equivalence ratio at which the diesel engine normally runs, the CFD modeling results show a higher level of OH radical formation (see Figure 7.12). Both models show increasing OH concentration with the increasing amount of water in fuel; however, the PaSR modeling results show a different profile and lower OH formation than the CFD model. This difference is due to different combustion systems used in both models which are expected to give different results as suggested by Bedford *et al* [49] and Park *et al* [66].

A significant drop in the OH concentration level is expected during the combustion process due to OH consumption through hydrocarbon and soot oxidation by reactions similar to ones shown below [90, 110]:



In addition to the above reactions, OH is also consumed during NO formation through Reaction (7.8) [41], which predicts the possible reaction between OH radicals and N so that not much nitrogen can react with oxygen to form more NO_x.



OH radicals play an important role in soot oxidation, especially at higher temperatures, because they become the leading oxidants of soot precursors, whereas oxygen in its molecular form is consumed by the flame [41] as shown in Figure 7.6. Soot precursor species are formed in a rich premixed reaction zone that initiates the soot-generating reactions as discussed in Chapter II [10, 19, 110]. The amount of soot precursor species available to produce soot is strongly dependent on the amount of oxygen available in the mixture. However, when sufficient oxygen is available, soot precursor species react with molecular oxygen or oxygen-containing radicals (OH, O etc.) and eventually produce CO rather than aromatics and soot. This is seen in the case of the soot precursor species acetylene reactions (7.6) and (7.7) where C₂H and CH₂CO eventually lead to CO. When insufficient oxygen is available, soot precursor species alternatively react with themselves and with the other hydrocarbon species to form polyaromatics and soot.

Figures 7.14 through 7.17 show the overall history of the formation of some soot precursors during the combustion process of neat surrogate and emulsified fuel with 3, 5, 8 and 15% water (by volume). It is known from the mechanism suggested by Frenklach

and Vollenweider *et al* [24, 54] that the addition of acetylene (C_2H_2) to C_4 -hydrocarbons followed by cyclization can form the first aromatic ring as shown below:



Also, Miller and coworkers [111] proposed that propargyl-propargyl recombination followed by multiple isomerization involving H-atom shifts and cyclization leads to phenyl and subsequently to benzene ring as follows:



These reactions illustrate the role of C_2H_2 and C_3H_3 in forming the benzene ring to start the molecular growth process to larger PAHs and eventually to soot particles [22, 24].

Thus, by reducing C_2H_2 and C_3H_3 concentration in the gas phase reaction, the formation and growth process of PAHs and soot particles could be reduced. Figures 7.14 and 7.16 show that the addition of water has a significant impact on the formation of C_2H_2 and C_3H_3 . The addition of 3% water in fuel doesn't show a significant decrease in the formation level of soot precursors but the addition of 5% water has a major impact on lowering the concentration of C_2H_2 and C_3H_3 components. The further addition of water to fuel (>5 %) increases the formation of soot precursors to levels higher than for 5% water but are still lower than for 3% water and the base surrogate fuel. The CHEMKIN modeling results using the PaSR model (see Figure 5.14) for fuel-lean combustion conditions ($\phi=0.8$) predict results similar to those of the CFD model. In conclusion, the addition of water to fuel has the same impact on the soot precursor (C_2H_2 and C_3H_3) formation levels regardless of the type of combustion system used.

Very few studies have been reported on the influence of water vapor addition on soot formation [35, 37]. Based on the work in flames, two possible effects have been hypothesized by which addition of water vapor can affect soot formation: a thermal effect and a chemical effect. The thermal effect is due to the large heat capacity of water vapor, which reduces the flame temperature. The addition of water vapor lowers the flame temperature, as shown in Figure 7.1, and causes a reduction in soot precursor formation as shown in Figures 7.15 and 7.17 which predict that the formation of C_2H_2 and C_3H_3 decreases with increasing amounts of water added to fuel. The addition of 5% water in fuel has the maximum effect in inhibiting C_2H_2 and C_3H_3 formation whereas the addition of 3% water in fuel results in an insignificant decrease in C_2H_2 and C_3H_3 levels compared to the base fuel.

The chemical effect was attributed to changes in the radical pool (O, OH, H) by the presence of water vapor as shown in Figures 7.6, 7.12 and 7.13. Water vapor enhances formation of hydroxyl radicals through the reaction



and OH may subsequently attack the soot precursors and limit the soot formation. Also, H formation increases with the increasing water content (see Figure 7.13) due to the reactions of hydroxyl radicals with soot precursors and carbon monoxide as shown from reactions (7.9), (7.11), (7.15), (7.16), (7.17) and (5.3). The reaction of H with H_2O competes with reaction of H with the parent fuel (RH),



The relative importance of the two H-consuming steps depends on their rate constants and the fuel and water vapor concentration but the effect of adding water was concluded

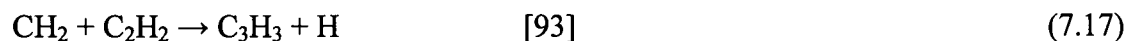
to be predominantly thermal, with little contribution from a chemical effect on the soot precursors [35]. It was acknowledged through experimental work on flames that even a low concentration of OH could have an effect on the soot formation process [35], whereas relatively high concentrations of water vapor are needed to affect soot formation [37].

Reaction analysis indicates that the influence of the water vapor on acetylene conversion is a result of an increased hydroxyl formation from water. Hydroxyl is, as mentioned earlier, was produced from the reaction of water vapor with H radicals.

Acetylene is subsequently oxidized by reaction with hydroxyl through the reactions:



Both reactions produce H radicals, which may contribute to further enhancement of hydroxyl formation from water vapor. Reduction of the acetylene concentration results in a decreased formation of propargyl radicals as shown from Reaction (7.17). This subsequently leads to a reduction in benzene formation, since propargyl radicals are the dominant precursor for benzene ring formation [22, 24].



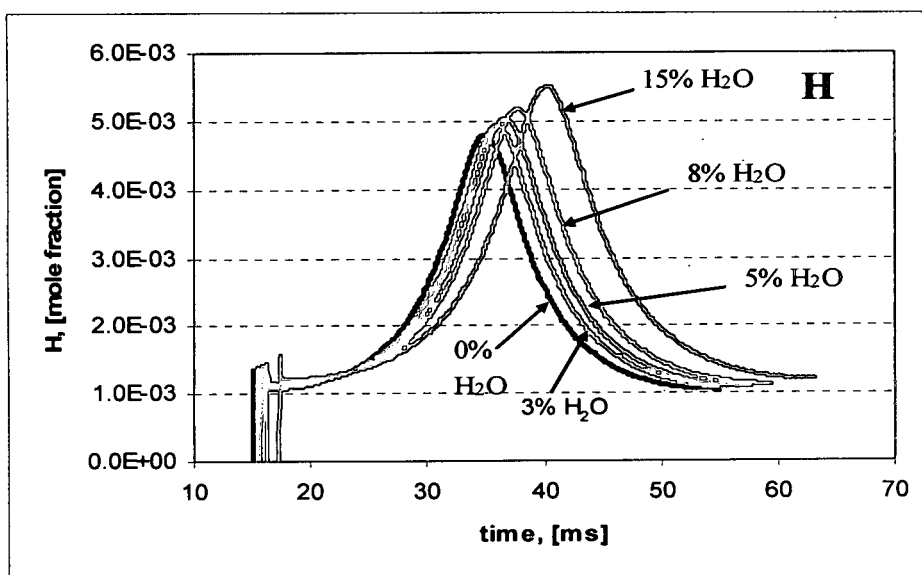


Figure 7.13 Concentration profiles of H radicals from the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

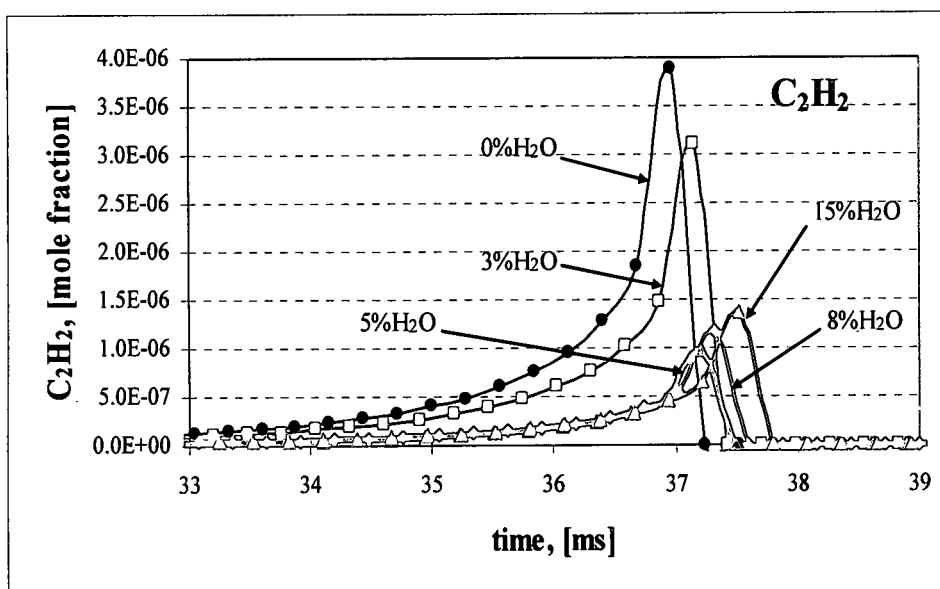


Figure 7.14 Concentration change of C₂H₂ with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

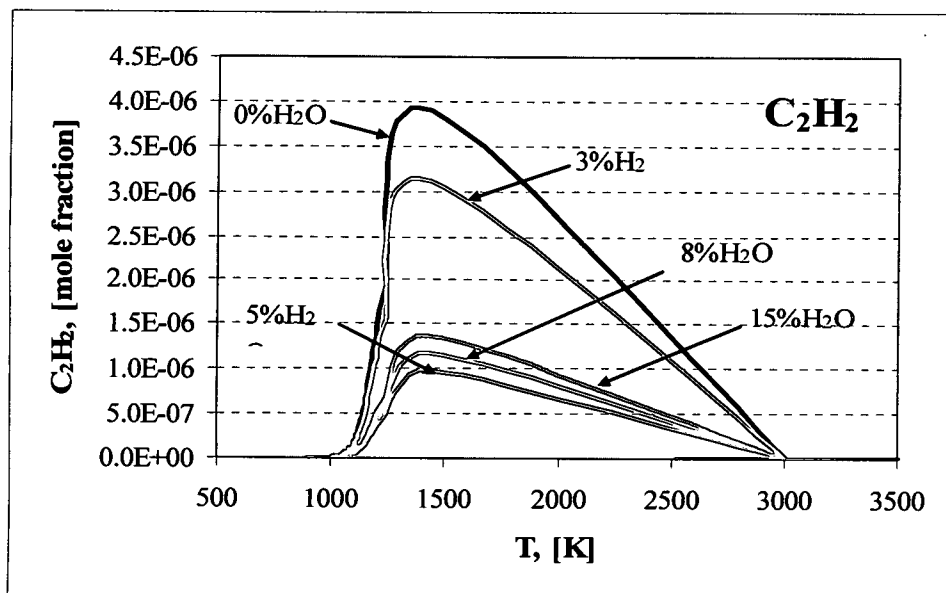


Figure 7.15 Concentration change of C_2H_2 with temperature from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

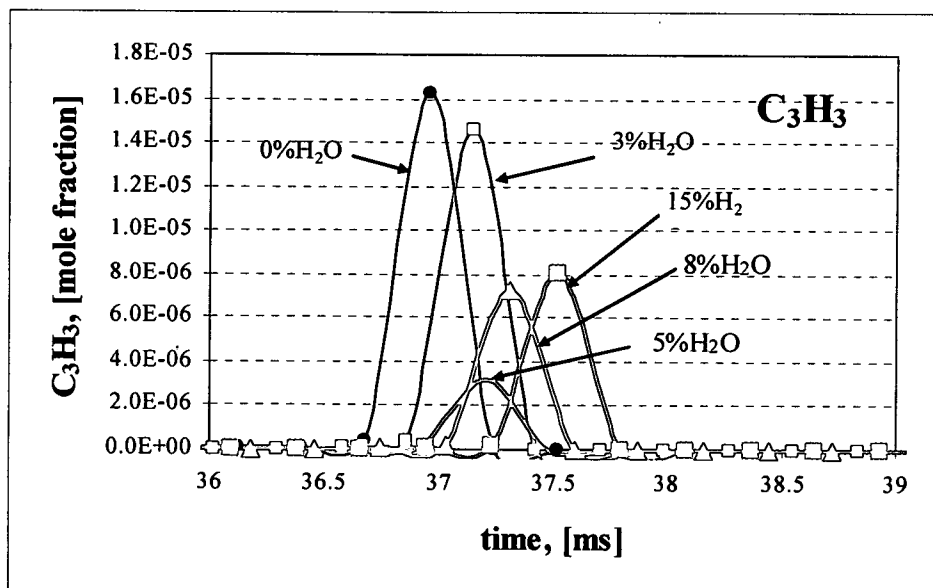


Figure 7.16 Concentration change of C_3H_3 with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

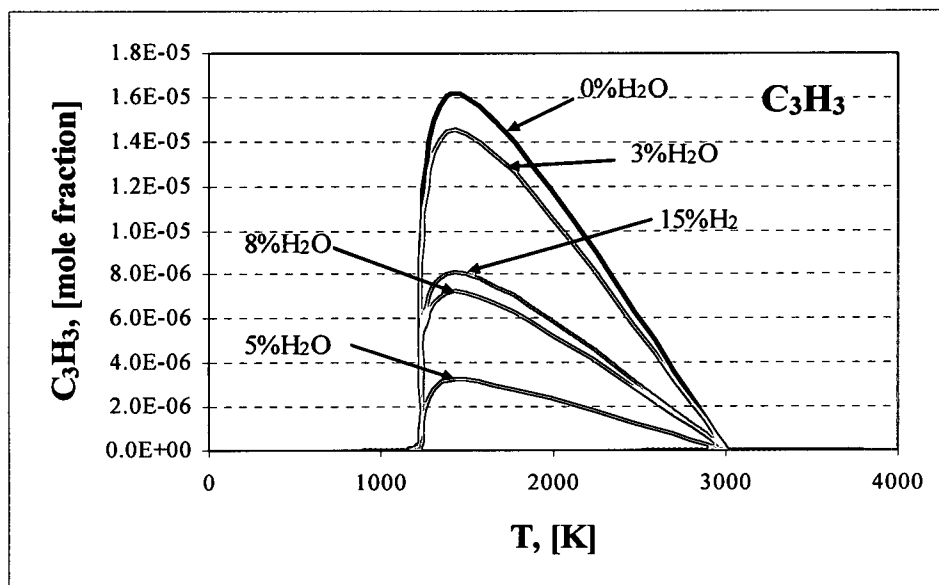


Figure 7.17 Concentration change of C_3H_3 with temperature from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

Besides benzene ring formation, D'Anna and coworkers [22] proposed that other compounds may serve as precursors in the growth process to larger PAHs without passing through the benzene ring intermediate. Suppressing the formation of those compounds by introducing more OH radicals in the combustion region through the addition of water to fuel is one way to minimize the growth of PAHs and consequently soot. The enhanced oxidation of soot precursors by increasing OH radicals is a significant pathway to reduce the soot formed in the gas phase. The mechanistic model for soot formation from aromatic and aliphatic compounds suggested by Heywood [10] and discussed in Chapter II reveals that as oxygen and OH are present in the combustion chamber of a diesel engine, the growth of the soot formation process can be terminated at any instance due to the oxidation of soot particles with oxygen and/or OH radicals [28, 29]. Figures 7.18 and 7.19 present the sensitivity analysis of the rates of the

production/consumption reactions of C_2H_2 and C_3H_3 . These figures show that the positive values of the formation reactions decrease with the increasing amount of water added to fuel and the negative values, which represent the consumption rates of C_2H_2 and C_3H_3 , decrease as well. This decrease means the addition of water to fuel hinders the formation rate of soot precursors but decreases the consumption rate, which clarifies the reasons behind the increasing concentration of soot precursors as water amount increases.

Therefore, the thermal and chemical effects of adding water to fuel can be understood from the rate of formation and consumption of the reactions shown in Figures 7.18 and 7.19. Also, the enrichment of water vapor due to the evaporation of water added in the fuel-rich region in the vicinity of the droplet surface deep inside the flame along with the simultaneous temperature reduction result in the reduction of soot formation in the gas phase [10]. According to Mueller *et al.* [112], the amount of spatially integrated natural luminosity (SINL) emitted from a cloud of radiating soot particles depends on many factors, including concentration, temperature, and the optical properties of the soot particles.

Figures 7.20 through 7.23 show the significant reduction of some cyclic aromatic compounds with one to four rings (A1, A2, A3, and A4) at the combustion of surrogate fuel/water emulsion with the addition of 3, 5, 8 and 15% water to fuel. It had been observed that the remarkable decrease in the peak level of soot formation was caused by the addition of 5% of water to fuel; however, the peak level increases slightly when water content is increased from 5 to 15%.

As discussed in Chapters II and V, soot precursors of PAHs formed in a rich, premixed reaction zone where they initiate soot-generating reactions [10, 19, 110]. The concentration of soot precursor species available to produce soot is strongly dependent on the amount of oxygen available in the mixture. When sufficient oxygen is available, soot precursor species react with molecular oxygen or oxygen-containing radicals (OH, O, etc.) and eventually produce CO rather than aromatics and soot.

The addition of water can play a significant role in oxidizing soot precursors, either by the reaction OH radicals with propargyl precursors before they can form the benzene ring, as discussed earlier, or by the oxidation of the PAH precursors formed from aromatic rings as shown in Figures 5.20 and 7.24.

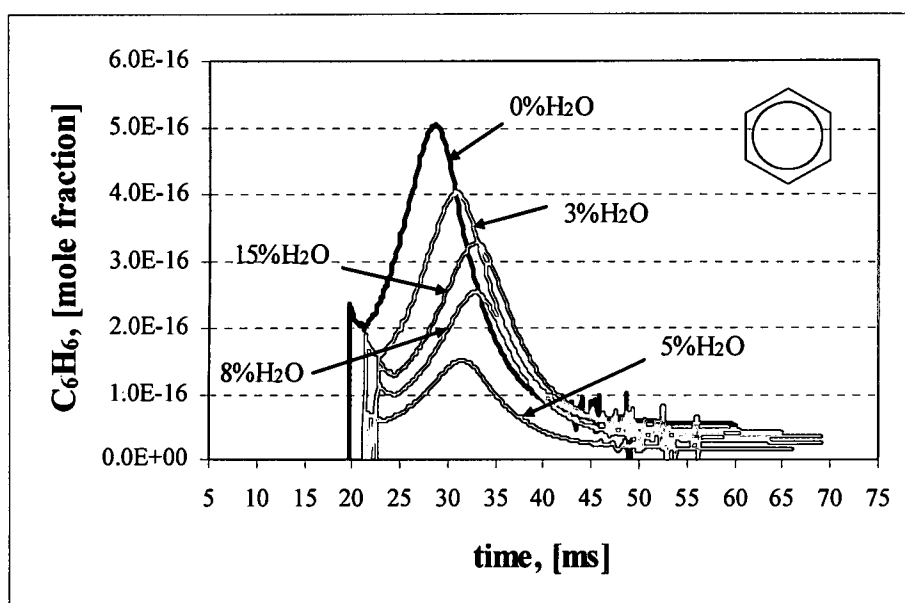


Figure 7.20 Benzene (A1) concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

Figure 7.24 clearly shows the effect of water addition on the oxidation of PAHs (phenanthrene and naphthalene). The PAH oxidation proceeded via hydroxylation by hydroxy radicals. Figure 7.24 also shows that decarbonylation and decarboxylation of the carbonyl compounds, including aromatic acids, leads to an increase in the concentration of CO_2 and CO in the gas phase. A further increase in the oxidant concentration not only enhances the oxidative decomposition of the phenanthrene molecule but also converts most of the intermediate compounds to CO_2 and smaller organic intermediates like benzoic acid, phenol and benzaldehyde.

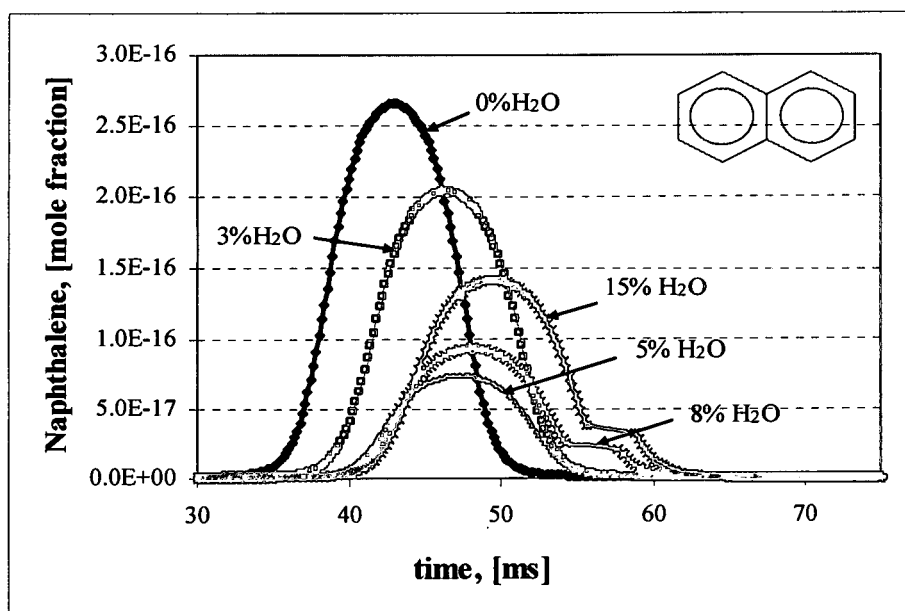


Figure 7.21 Naphthalene (A2) concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

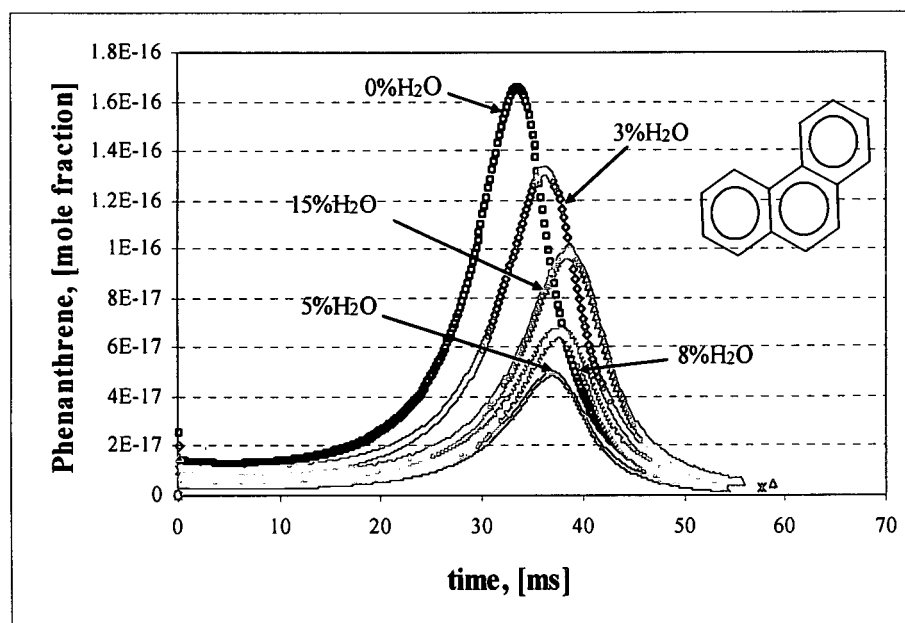


Figure 7.22 Phenanthrene (A3) concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

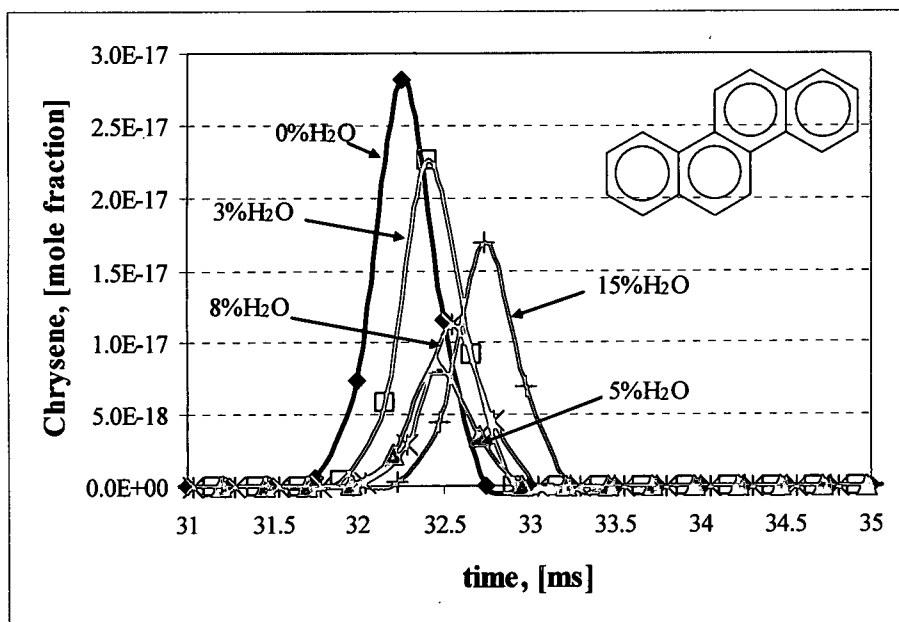


Figure 7.23 Chrysene (A4) concentration change with time from the combustion of surrogate fuel/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

The oxidation process was initiated by the attack of hydroxyl groups at several positions on one of the aromatic rings. Phenanthrene readily undergoes certain addition reactions at the (K-region) 9-, 10-positions [113] and hence was possibly hydroxylated at these positions leading to the formation of 9-, 10-quinone [114]. With increasing temperature and/or reaction time, the loss of CO from the quinones led to open-ring products such as naphthalic anhydride, etc. Larson *et al.* [115] suggested the possibility of forming anthraquinone from phenanthrene or phenanthrenequinone during the wet air oxidation of phenanthrene. Increasing the oxidant concentration resulted in increasing degradation of naphthalene and the formation of CO₂, CO and water.



Figure 7.24 Proposed reaction mechanism for the oxidation of phenanthrene and naphthalene using hydroxyl radicals [from Onwudili *et al* 94].

The sensitivity analysis of some of the reaction rates depicted in Figure 7.25 indicates that the formation rates of benzene, naphthalene, phenanthrene and chrysene decreases as increasing amounts of water are added to fuel which support the findings illustrated in Figures 7.20 through 7.23 where the PAH concentration decreases with the increasing amount of water and the consumption rates of the same species show non-linear decrease with the increasing amount of water as well, which reflects the effect of adding more water to fuel on the oxidation reaction rates of the PAH with OH radicals. Hence the reaction rates decrease with the increased amount of water added to fuel due to the decreased combustion temperature. Similar to that of C_2H_2 and C_3H_3 shown in Figures 7.14 and 7.16, the PAH precursors (see Figures 7.20 through 7.23) show remarkable level decrease when 5% water is added to fuel; however the peak level increases slightly when water content is increased from 5 to 15% which can be understood from the sensitivity analysis shown in Figure 7.25 where the consumption rates of the reactions between PAH precursors and OH radicals decrease with the increasing amount of water in fuel.

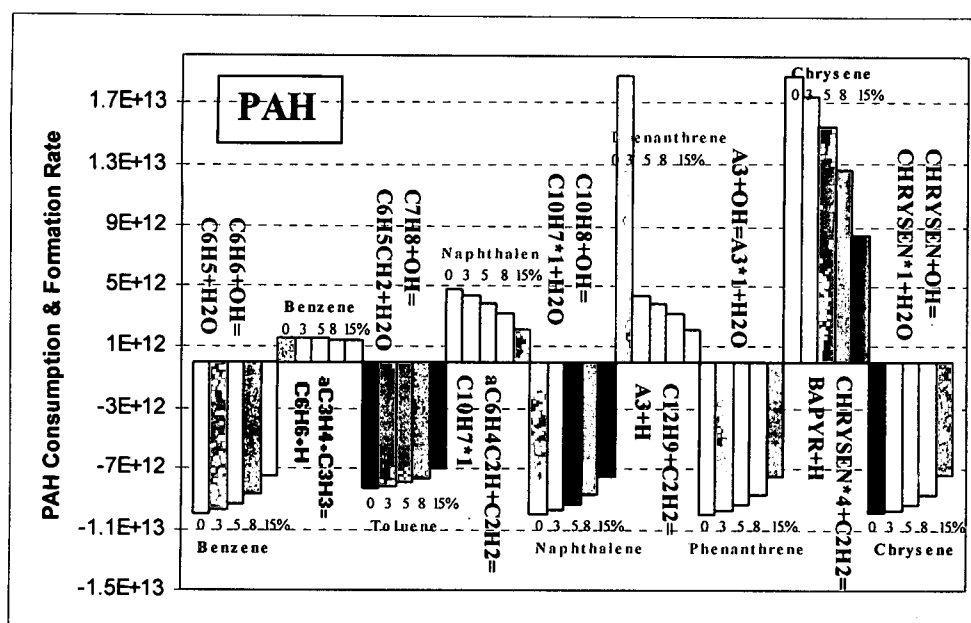


Figure 7.25 Sensitivity of PAHs for the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% of water content based on rate of formation/consumption of the most significant reactions.

The modeling results of this work were validated against the work performed by Samec and coworkers [45]. Their experimental and numerical studies showed that the addition of 10 and 20% water to n-heptane reduces the overall soot formation by 35 to 60% (see Figure 7.26). Their results are not consistent with the results obtained in this modeling study because the soot precursor formation increased when water content was increased above 5% water as shown in Figures 7.14 through 7.23. This suggests that soot formation will also increase at higher percentage of water in fuel. The results obtained using the CHEMKIN PaSR model, as shown in Figures 5.21 through 5.24, also support the findings of the CFD model.

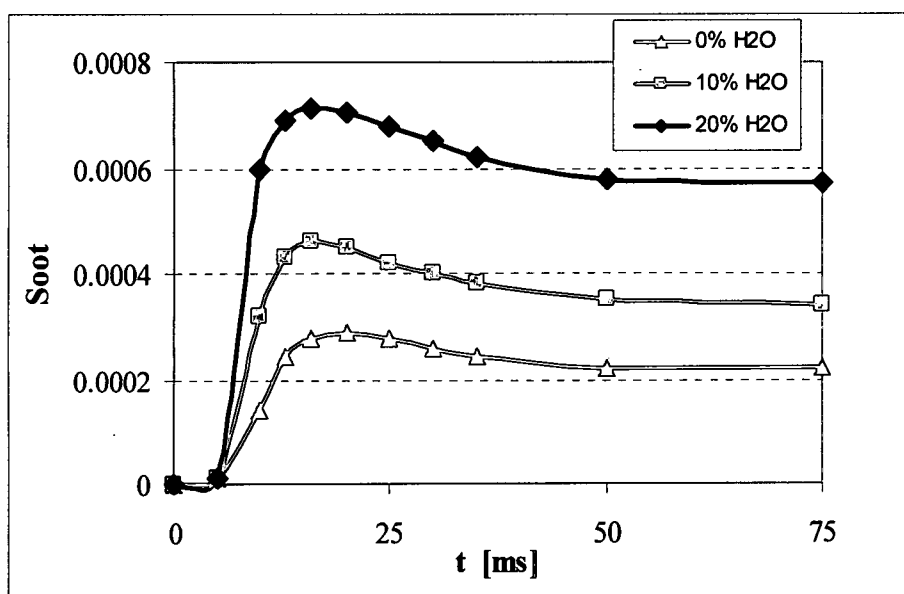


Figure 7.26 Soot fraction time profile during the combustion of n-heptane/water emulsion with 0, 10, and 20% of water content [from Samec *et al*, 45].

The modeling analysis conducted in this work shows that the formation of CO increased with the increasing amount of water added to fuel as shown in Figure 7.27. It is clear from this figure that the formation of CO increases sharply at the beginning to a maximum, and then decreases a little and remains constant over the full engine stroke. The key difference is that with dry fuel or base fuel (0% water), a substantial amount of CO oxidation occurs during the travel through the engine cylinder, but the addition of water reduces the average temperature along the cylinder to a level where CO oxidation is substantially reduced. This increases the CO concentration, so compared to that of the base fuel, the CO profile shows higher values with the increasing amount of water added to fuel and the 15% water in fuel shows the highest CO concentration.

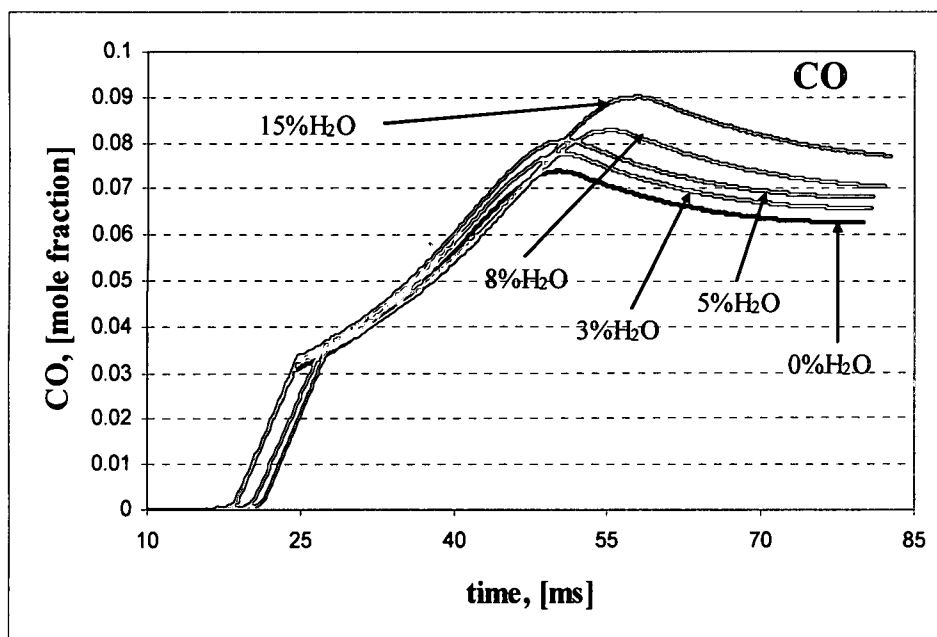


Figure 7.27 Carbon monoxide formation change with time from the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

The step-by-step hydroxylation, oxidation and decarbonylation of each aromatic ring, as shown in Figure 7.24, also contributes to the high concentration of CO. The reaction products show that direct oxidation to CO₂ might be difficult without the opening of an aromatic ring. Hence, the formation of CO₂ possibly resulted from oxidation of CO. Decarboxylation of aromatic compounds and oxidation of other oxygenated aliphatic compounds such as acetaldehyde and acetone along with PAH oxidation are all considered to be sources for increasing CO formation.

The sensitivity analysis of the formation/consumption reaction rates shown in Figure 7.28 predict that the major oxidation reaction rates of CO with OH, O, and O₂ decrease with the increasing amount of water added to fuel due to the decreased temperature and eventually increase the concentration level of CO. Also, the formation

rates of CO increase with the increasing amount of water in fuel due to the reduction of O formation level (see figure 7.6) which is essential in the conversion of CO to CO₂ also due to the oxidation of PAHs and other soot precursors with OH radicals which increase the concentration level of CO as well.

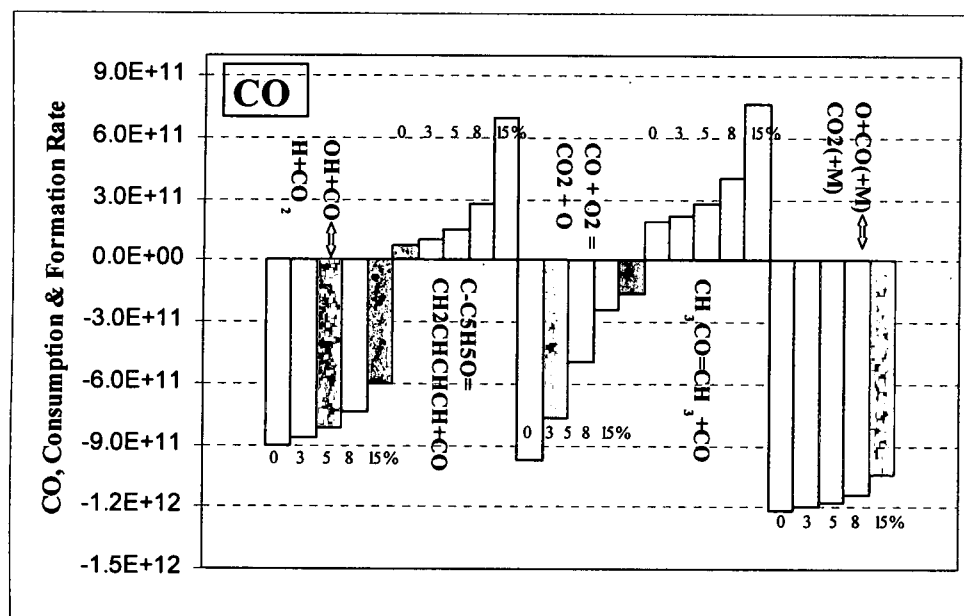


Figure 7.28 Sensitivity of CO for the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% of water content based on rate of formation/consumption of the most significant reactions.

This trend of increasing CO level with the addition of water to fuel was validated against the experimental results of Canfield [1] (see Figure 7.29) which also show an increase of CO formation with the increase of water percentage in fuel. Radloff and Gautier [63] did similar experimental work and their results also show an increase in CO emission with the increase in percent water in fuel at different engine loads (see Figure 7.30). Also, the PaSR modeling results presented in Chapter V predicted similar effects of the addition of water on CO formation. Hence, both Figures 5.14 and 7.27 indicate that

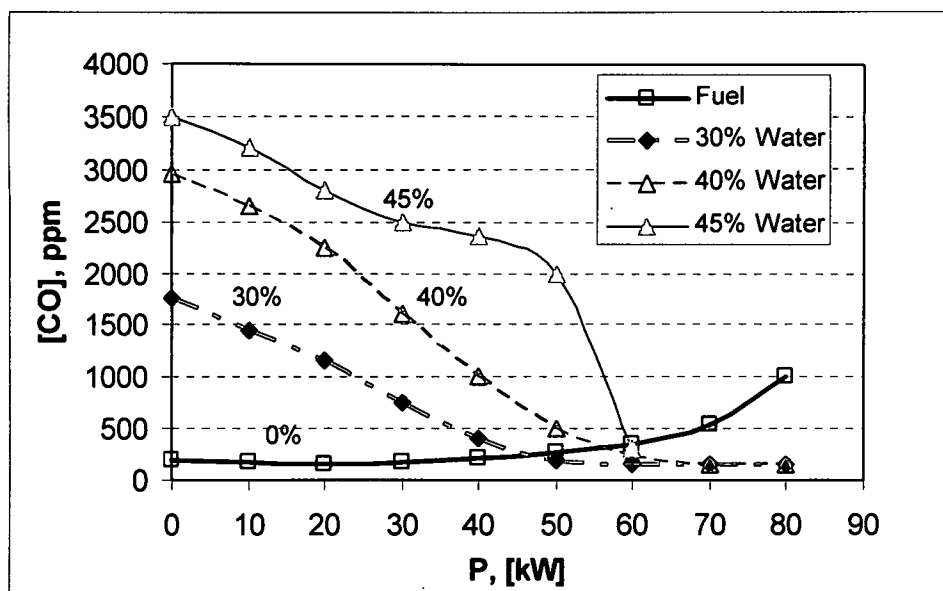


Figure 7.29 Experimental change of exhaust [CO] with real engine power, from Canfield [1].

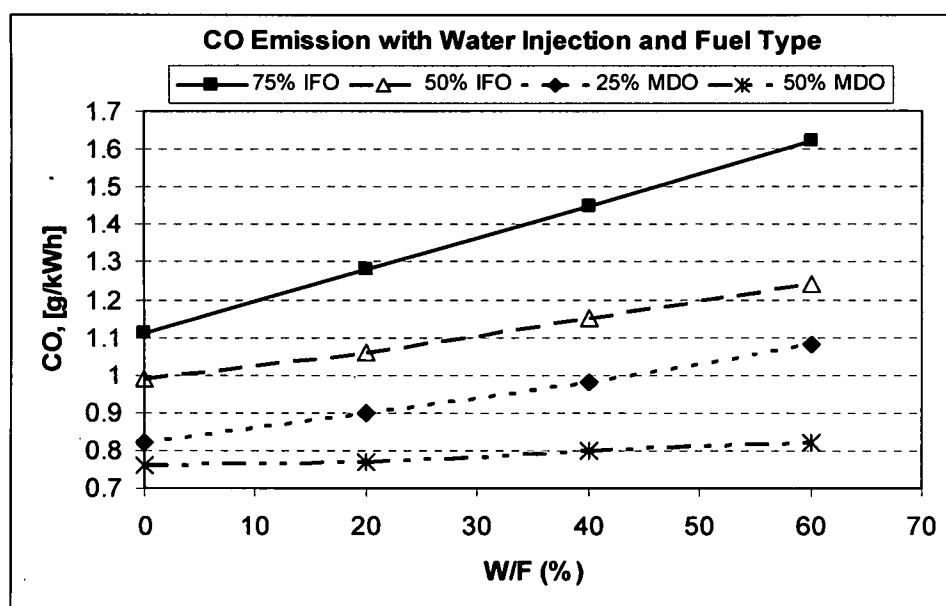


Figure 7.30 CO emission as a function of water fraction (W/F %) in MDO (marine diesel oil) and IFO (intermediate fuel oil) at different engine loads [63].

the CO formation increases with the increasing amount of water added to fuel under fuel lean conditions ($\phi=0.8$). Regardless of the combustion system used, the addition of water to fuel increases CO formation via thermal and chemical effects, namely, temperature reduction and an increase in OH concentration.

CO predictions from this study are consistent with the experimental results of Canfield [1] and Radloff and Gautier [63]. This agreement is clearly shown in the trend where CO formation increases with the increasing amount of water added to fuel.

The water content ratio has a remarkable effect on fuel ignition timing. It can be seen from Figures 7.31 and 7.32 that more water in fuel will lead to a longer ignition delay. For example, the addition of 5% water to fuel produced an ignition lag of 4 degrees of crank angles from the regular ignition timing. Also, the addition of more water to fuel resulted in lags of 7 and 12 degrees crank angle for 8 and 15% water added.

The longer ignition delay can accumulate more oil vapor in the chamber [16, 102], which is one of the disadvantages of adding water to fuel. As mentioned earlier, the calories consumed by evaporation of the injected fuel, together with the increase in the water content ratio, lower the gas temperature in the combustion chamber. Consequently, this drop of the in-cylinder gas temperature due to the increase in the water content ratio increases the ignition lag.

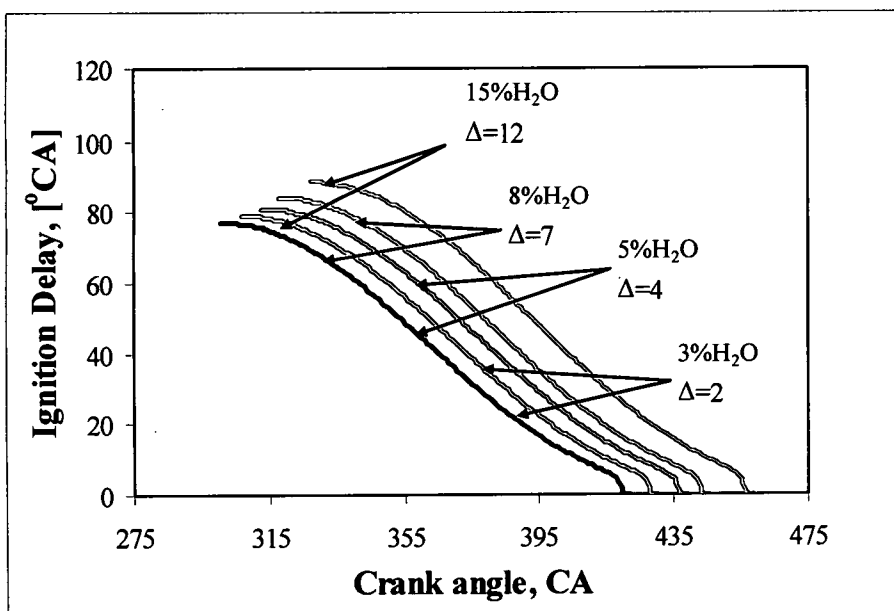


Figure 7.31 Ignition delay profile in degree crank angle (°CA) change for each run at the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

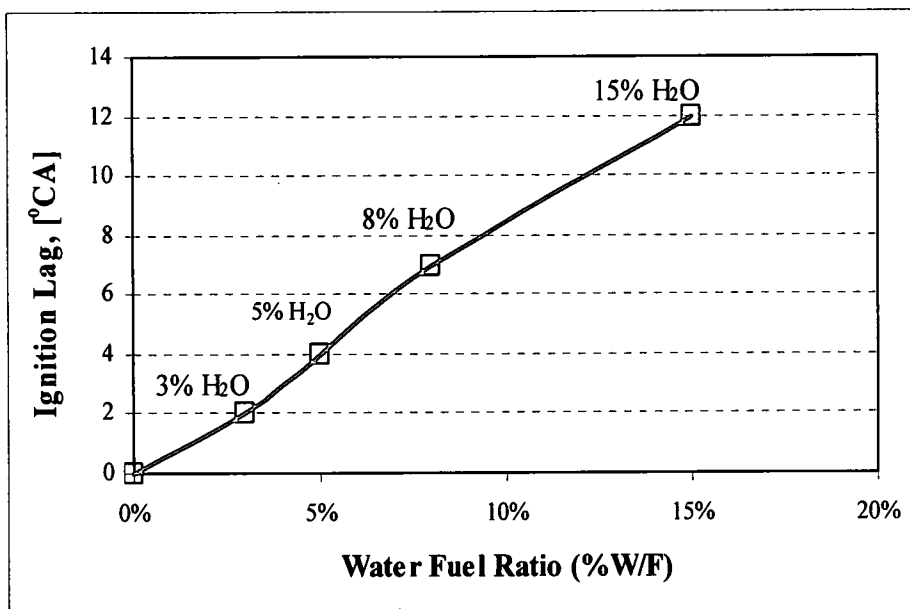


Figure 7.32 Ignition lag in degree crank angle (°CA) change at the combustion of surrogate fuel (80% n-heptane and 20% toluene)/water emulsion of 0, 3, 5, 8 and 15% water in fuel.

The ignition lag calculations were validated against the experimental results of Park *et al.* [66], (see Figure 7.33). Park and coworkers [66] studied the ignition delay for different percentages of water injected with fuel at different crank angles and found that the ignition delay of the mixture increases with the increasing amounts of water in fuel which is consistent with the findings of this study.

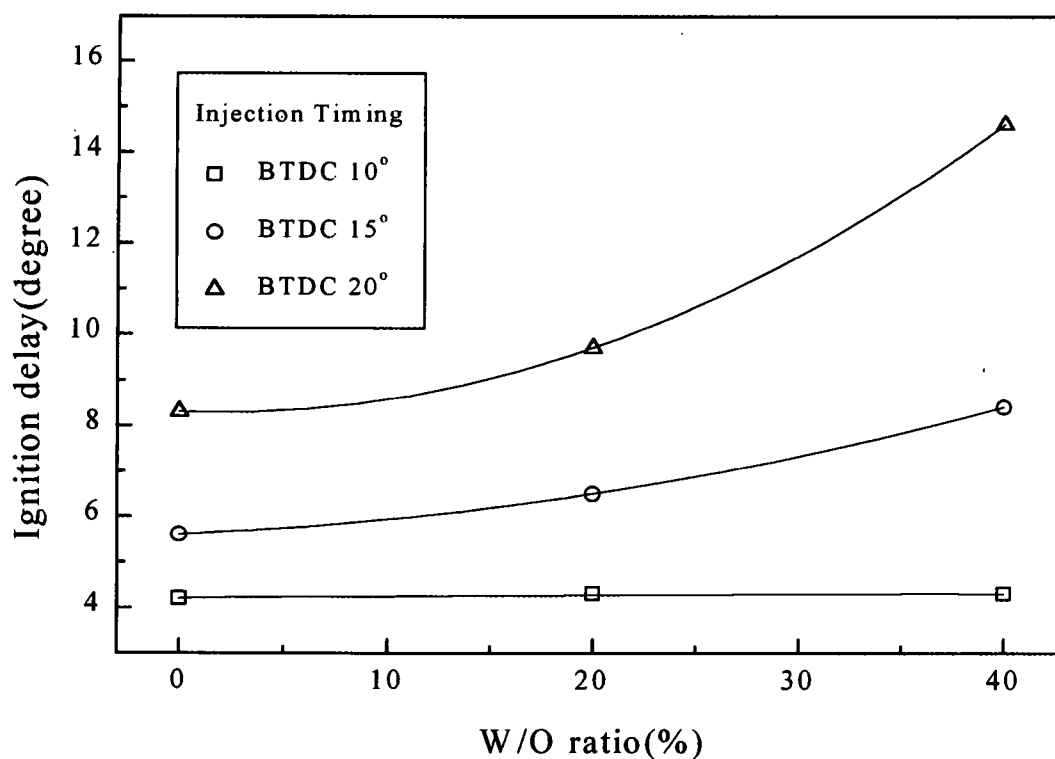


Figure 7.33 Ignition delay with respect to the W/O (Water/Oil) ratio [66].

CHAPTER VIII

CONCLUSION AND RECOMMENDATIONS FOR FUTURE RESEARCH

8.1 Conclusions

CFD-ACE+/CFRD simulation tools provide an opportunity to understand complex internal processes in the cylinders of internal combustion engines as well as predict emission levels of different pollutants. A consequent application of these innovative tools will accelerate research and development tasks, reduce costs, and significantly reduce environmentally harmful engine emissions. This modeling study of a large, 2-stroke diesel engine has provided a comprehensive understanding of the effect of water on combustion performance. The overall effects of water addition on combustion and pollutants emissions can be summarized as follows.

Adding water to fuel in the form of emulsion reduces the combustion peak temperature in proportion to the amount of water added to fuel. Hence, more water in fuel means more energy is needed to evaporate the mixture droplets and this energy is taken from the system which reduces the temperature. The vaporization of liquid water decreases the internal energy proportionally to the vaporization enthalpy of the liquid water and increases the specific heat capacity of the gas, which leads to lower combustion temperature. This temperature reduction was predicted by both CFD and the PaSR models. These modeling results were validated against experimental data of Samec *et al* [45] which agrees with the findings of this work.

This work proves that NO_x formation decreases as increasing amounts of water are added to fuel. The percentage reduction is related to the amount of water added to fuel. The rate of chemical reactions is a strong exponential function of temperature, which implies that with increased water emulsification, both the intensity and the volume of the chemical reactions in the flame zone decrease exponentially. This result directly influences thermal NO_x formation by reducing chemical reaction rates of Zeldovich mechanism reactions [35]. Additionally, the reduction in NO concentration could be due to reduction in the concentration of O atoms due to its consumption in the formation of OH radicals. Water-emulsified fuel has both physical and chemical effects that reduce NO_x formation; but after certain level, the addition of water does not lead to further reduction in NO_x .

The reduction of NO_x could be at the expense of an increase in carbon monoxide which is a significant environmental threat. The modeling analysis conducted in this work revealed that the CO formation increased as increasing amounts of water were added to fuel. The addition of water reduces the average temperature along the cylinder to a level where CO oxidation is substantially reduced, increasing the concentration of CO. Also, PAH oxidation with OH radicals, enhanced by the addition of water to fuel, is considered to be one source of increasing CO concentration. The 15% water in fuel shows the highest CO concentration.

A remarkable decrease in the peak value of the concentration of soot precursors was found after adding 5% water; however, the peak value decreased slightly when the amount of water was increased from 5 to 15%, which means that an extra amount of water in fuel can inversely affect soot formation levels. Two possible effects have been

hypothesized by which the addition of water vapor can affect soot formation: a thermal effect and a chemical effect [35, 36]. The thermal effect is due to the reduction in the flame temperature which results in a reduction in the formation level of soot precursors. The chemical effect is attributed to changes in the radical pool due to the presence of water vapor which enhances formation of hydroxyl radicals and OH may subsequently attack the soot precursors and hence suppress their formation.

An elongated ignition delay occurs when the temperature of the gas in the combustion chamber is reduced due to an increase in the water content ratio. This longer ignition delay can accumulate more oil vapor in the chamber [16, 53, 102] and is one of the disadvantages of adding water to fuel for the steady running of diesel engines.

The engine in-cylinder pressure profile shows the impact of water-in-fuel content on the pressure change which increases with the increasing amount of water due to water vapor pressure. The water vapor pressure works on piston instead and behaves similar to a steam engine - once the ignition occurs, the effect of steam pressure will be more effective with more water in the fuel. Thus, water emulsification has the potential to significantly improve and increase the power output.

Water-emulsified fuel (up to 5% water) can be successfully used to reduce heavy-duty diesel engine exhaust pollutant emissions, especially NO_x and soot. This unconventional technique to reduce NO_x and soot emissions in diesel exhaust is suitable for use on vehicular diesel engines for special purposes, primarily in urban areas or on stationary engines when they have to satisfy ultra-low emission standards.

8.2 Recommendations For Future Research

- Study the influences of emulsion parameters such as water and surfactant contents on the stability variation and microstructure of emulsified fuel with time. Conduct additional studies on the internal phase droplet size distribution by investigating the Sauter mean diameter of the droplet group.
- Perform further studies on the combustion stability and engine performance after using water-in-fuel emulsion which creates a combustion delay phenomena.
- The size of the water drops in the emulsion such as the degree of dispersion of the water is probably an important factor for the emissions. This issue does not seem to have been studied in a systematic way for diesel fuels.
- Conduct experimental studies on the effect of water-on-diesel emulsion on fuel consumption economy to estimate the saving rate in gallons per mile and determine the BSFC at different water percentages.

APPENDIX

MODEL CHEMKIN 'N-HEPTANE' MECHANISM [83]

!nc7h16 and c7h8 mechanism [83]

! Curran, H. J., Pitz, W. J., and Westbrook, C. K., 2002

! UCRL-WEB-204236

ELEMENTS

C H O N AR

END

SPECIES

H2	H	O	O2	OH	H2O	HO2	H2O2
C	CH	CH2	CH2*	CH3	CH4	CO	CO2
HCO	CH2O	CH2OH	CH3O	CH3OH	C2H	C2H2	C2H3
C2H4	C2H5	C2H6	HCCO	CH2CO	HCCOH		

AR N2

CH2CHO C3H3 CH3CHO C3H2 C4H2 C5H2(L) C5H3 C5H3(L) C5H4 C5H4(L)

C6H2 C6H C6H3 C6H4 C4H BENZYNE C6H5(L) C6H813 C6H814 C6H4OH !

C6H5OCH3 C6H5OC6H5 CH2CHCCH HCCHCCH H2CCCCCH C6H5 C6H6 C6H5O CH2CHCHCH

CH2CHCCH2 H2C4O CH2CHCHCH2 !CH3OH !CH2CHO

C-C5H5 C-C5H5O C-C5H6 C6H5OH C-C5H4OH C-C5H4O C5H5(L) !

C4H10 pC4H9 sC4H9 C4H8-1 C4H8-2 I-C4H7 C4H71-3 C4H72 C3H6 ac3H5 pC3H5!C4H7

SC3H5 CH2CHCHO pC3H4 ac3H4 CH3CO C6H5CH2 C6H5CH3 CH2CHCO CH3CHCO !CH3CHO

CHOCHO C3H8 iC3H7 nC3H7 CH3CHCCH2 CH3CCCH2 CH3CHCHCHO CH2CHCHCHO

C4H612 C4H6-2 CH3CHCHCO C6H5C2H5 C10H10 C10H9 C6H4C2H3 C6H4C2H C6H5C2H3 C6H5C2H

C6H3O3 C10H7O-1 C10H7O-2 C10H7OH-1 C10H7OH-2 INDENE INDENE*

A2CH2-1 A2CH2-2 A2CH3-1 A2CH3-2 C6H5CHO C6H5CO HOC6H4CH3 C6H5CH2OH

C10H8 C10H7*1 C10H7*2 A2T1 A2T2 A21C6H4 A22C6H4 A2C2H-1 !C10H7CCH

A2C2H-2 A2VINP A2C2H3-2 A2C2H-2*1 A2C2H-1*2 A2C2H-2*3 !C10H6CCH

BIPHEN BIPHENH A2R5 A2R5*1 A2R5*3 A2R5*4 A2R5*5 HA2R5 A2R5H2 A2R5T

A2R5YNE1 A2R5YNE3 A2R5YNE4 A2R5YNE5 A2R5YN4*5 A2R5YN5*4 A2R5R5

A3 A3*1 A3*2 A3*4 A3*9 !phnthryl-1 phnthryl-9 A3*S2 A3L A3L*1 A3L*2

A3L*9 A3R5 A3R5*7 A3R5*10 A3LR5 A2R5YN3*4 A2R5YN4*3 A3LR5*S

CHRYSEN CHRYSEN*1 CHRYSEN*4 CHRYSEN*5 A3C2H-1 A3C2H-1*P A3C2H-2

A3LC2H-2P A3C2H-2*S bz(a)ndene bz(a)ndnyl A4 A4*1 A4*4 A4*12

A4L A4L*S A3LC2H-1 A3LC2H-1P A3LC2H-2 A3LC2H-2S A3CH2R A3CH2 A3CH3

CH3indene CH3indenyl CH3phnthrn FLUORENE BENZNAF BENZNAF*P C17H12

BENZYL BENZYL* A2C6H5-2 FLTHN FLUORANTHENE A2R5YN1*2 FLTHN*7 FLTHN*1 FLTHN*3

CPCDFLT CPCDFLT*S BGHIFR BGHIFR*S COR1 BGHIF BGHIF- PYRENE PYRENE*1 PYRENE*2

PYRENE*4 !PYRENE*1 !PYRENE*S1 !PYRENE*S2 !PYRENE*P !PYRYNEP

PYC2H-1 PYC2H-2 PYC2H-4 PYC2H-1*P PYC2H-2*S PYC2H-4*S CPCDPYR CPCDPYR*S DPCPDFG

PERYLEN PERYLEN*S OC6H4O2 PC6H4O2 C6H3O2 ! mitOC6H4O C6H5CH !

OC6H4CH3 CH3C6H4CH3 CH3CHCCH CH3CH2CCH CH3C6H4CH2 CH3C6H4C2H3 CH3C6H4C2H5

C-2*4C6H6O C-C5H7 I-C5H8 I-C5H7 C10H7C2H5 C6H5CCO C6H5CHCH C6H5CCH2 fluoryl

H2CCCCCH2 CHCHCHO HCCCHO HCCCO phnthroxy-1 phnthroxy-9 phnthrol-1 phnthrol-9

biphenyl fulvene fulvenyl ch3cy24pd ch3cy24pd1 ch3dcy24pd cyc6h7 C12H9

FLTHNCH2 FLTHNCH3 FLTHNCH2 BGHIFCH2 BGHIFCH3 BGHIFCH2 BBFLUOR !+

BBFLUOR*S BKFLUOR BAPYR BAPYR*S ANTHAN ANTHAN*S BEPYREN BEPYREN*S !+

BGHIFER BGHIFER*S1 CPBPER CORONEN INPYR COR COR- CORCH3 CORCH2

COR1- COR2 COR2- COR3 COR3- COR4 COR4- !+

HB C3H4CY CH3OCH3 CH3OCH2 CH3COCH3 C2H5CHO C2H5CO C6H5C3H2 C5H91-3

C5H10-1 C3H5O C6H13-1 C6H12-1 C6H111-3 nc7H16 !C6H11 1-c6h11-3 !C5H11-1

! *****

cor- corC2H !-

corC2H* corC2H)2 cor1- cor2 cor1 cor1C2H cor2C2H cor2- ova1 corCH3 corCH3*

PYRENECH3 PYRENECH3* BAPYRC6H5 BAPYRC6)2 BAPYRC6)2* BAPYRC6)3 BAPYRC6)3* BAPYRC6)4

BAPYRC6)4* CHRYSENC6H5 CHRYSENC6)2 CHRYSENC6)2* A3C6H5

! *****

! N-species

CH3NO2 CH3ONO CH2NO2 N2O4 NO3 CH3NO N2O3 CH3ONO2 HNO2 HNO3

N NH

NH2 NH3 NNH NO NO2 N2O HNO CN

HCN H2CN HCNN HCNO HOCN HNCO NCO

!

! *****

! Pyridine-species

PYRIDINE PYRROLE HCCCN C2N2 !C4H4=CH2CHCCH !C3H4P=pC3H4
 CH3CN H2CCHCN CVA BIPY C5H4NOH PYRLNE NACROLEIN !CH2(S) in Pyridine mechsims = CH2*
 HCCCHN !C4H3 !NC4H3=n-C4H3=HCCCHCCH in main mechanism

!*****

!CH2CN !CH2CH2CN !CH3CHCN -no reactions in pyridine mechanism for this specie
 ! therefore thermo data was not included

A-C5H4N C4H4CN A-C4H4CN C5H4NO PYRLYL NC4H4CO C4H4NCO C2H2NCO C3H3CO C3H3O NCC3H4CO
 HNACROLEIN OCNC4H4O C5H5NO
 END

!

REACTIONS

2O+M<=>O2+M	1.200E+17	-1.000	.00
H2/ 2.40/ H2O/15.40/ CH4/ 2.00/ CO/ 1.75/ CO2/ 3.60/ C2H6/ 3.00/ AR/ .83/			
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/			
O+H+M<=>OH+M	5.000E+17	-1.000	.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/			
O+H2<=>H+OH	3.870E+04	2.700	6260.00
O+HO2<=>OH+O2	2.000E+13	.000	.00
O+H2O2<=>OH+HO2	9.630E+06	2.000	4000.00
O+CH<=>H+CO	5.700E+13	.000	.00
O+CH2<=>H+HCO	8.000E+13	.000	.00
O+CH2* <=> H2+CO	1.500E+13	.000	.00
O+CH2* <=> H+HCO	1.500E+13	.000	.00
O+CH3<=>H+CH2O	5.060E+13	.000	.00
O+CH4<=>OH+CH3	1.020E+09	1.500	8600.00
O+CO(+M) <=> CO2(+M)	1.800E+10	.000	2385.00
LOW / 6.020E+14 .000 3000.00/			
H2/2.00/ O2/6.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/3.50/ C2H6/3.00/ AR/ .50/			
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/			
O+HCO<=>OH+CO	3.000E+13	.000	.00
O+HCO<=>H+CO2	3.000E+13	.000	.00
O+CH2O<=>OH+HCO	3.900E+13	.000	3540.00
O+CH2OH<=>OH+CH2O	1.000E+13	.000	.00
O+CH3O<=>OH+CH2O	1.000E+13	.000	.00
O+CH3OH<=>OH+CH2OH	3.880E+05	2.500	3100.00
O+CH3OH<=>OH+CH3O	1.300E+05	2.500	5000.00
O+C2H<=>CH+CO	5.000E+13	.000	.00
O+C2H2<=>H+HCCO	1.350E+07	2.000	1900.00
O+C2H2<=>OH+C2H	4.600E+19	-1.410	28950.00
O+C2H2<=>CO+CH2	6.940E+06	2.000	1900.00
O+C2H3<=>H+CH2CO	3.000E+13	.000	.00
O+C2H4<=>CH3+HCO	2.500E+07	1.830	220.00
O+C2H5<=>CH3+CH2O	2.240E+13	.000	.00
O+C2H6<=>OH+C2H5	8.980E+07	1.920	5690.00
O+HCCO<=>H+2CO	1.000E+14	.000	.00
O+CH2CO<=>OH+HCCO	1.000E+13	.000	8000.00
O+CH2CO<=>CH2+CO2	1.750E+12	.000	1350.00
O2+CO<=>O+CO2	2.500E+12	.000	47800.00
O2+CH2O<=>HO2+HCO	1.000E+14	.000	40000.00
H+O2+M<=>HO2+M	2.800E+18	-.860	.00
O2/ .00/ H2O/ .00/ CO/ .75/ CO2/1.50/ C2H6/1.50/ N2/ .00/ AR/ .00/			
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/			
H+2O2<=>HO2+O2	2.080E+19	-1.240	.00
H+O2+H2O<=>HO2+H2O	11.26E+18	-.760	.00
H+O2+N2<=>HO2+N2	2.600E+19	-1.240	.00
H+O2+AR<=>HO2+AR	7.000E+17	-.800	.00
H+O2<=>O+OH	2.650E+16	-.6707	17041.00
2H+M<=>H2+M	1.000E+18	-1.000	.00
H2/ .00/ H2O/ .00/ CH4/2.00/ CO2/ .00/ C2H6/3.00/ AR/ .63/			
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/			
2H+H2<=>2H2	9.000E+16	-.600	.00
2H+H2O<=>H2+H2O	6.000E+19	-1.250	.00
2H+CO2<=>H2+CO2	5.500E+20	-2.000	.00
H+OH+M<=>H2O+M	2.200E+22	-2.000	.00
H2/ .73/ H2O/3.65/ CH4/2.00/ C2H6/3.00/ AR/ .38/			
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/			
H+HO2<=>O+H2O	3.970E+12	.000	671.00
H+HO2<=>O2+H2	7.750E+13	.000	1068.00
H+HO2<=>2OH	0.420E+14	.000	635.00
H+H2O2<=>HO2+H2	1.210E+07	2.000	5200.00
H+H2O2<=>OH+H2O	1.000E+13	.000	3600.00
H+CH<=>C+H2	1.650E+14	.000	.00
H+CH2(+M) <=> CH3(+M)	6.000E+14	.000	.00
LOW / 1.040E+26 -2.760 1600.00/			
TROE/ .5620 91.00 5836.00 8552.00/			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/			
H+CH2* <=> CH+H2	3.000E+13	.000	.00
H+CH3(+M) <=> CH4(+M)	13.90E+15	-.534	536.00
LOW / 2.620E+33 -4.760 2440.00/			
TROE/ .7830 74.00 2941.00 6964.00 /			
H2/2.00/ H2O/6.00/ CH4/3.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/			
H+CH4<=>CH3+H2	6.600E+08	1.620	10840.00
H+HCO(+M) <=> CH2O(+M)	1.090E+12	.480	-260.00
LOW / 2.470E+24 -2.570 425.00/			
TROE/ .7824 271.00 2755.00 6570.00 /			
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/			
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/			
H+HCO<=>H2+CO	7.340E+13	.000	.00

! k_opt=2*ko

! k_opt=1.73*ko

! k_opt=0.5*ko


```

H+CH2O(+M)<=>CH2OH(+M)
LOW / 1.270E+32 -4.820 6530.00/
TROE/ .7187 103.00 1291.00 4160.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
H+CH2O(+M)<=>CH3O(+M)
LOW / 2.200E+30 -4.800 5560.00/
TROE/ .7580 94.00 1555.00 4200.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
H+CH2O<=>HCO+H2
LOW / 4.360E+31 -4.650 5080.00/
TROE/ .600 100.00 90000.0 10000.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
H+CH2OH(+M)<=>CH3OH(+M)
LOW / 4.660E+41 -7.440 14080.0/
TROE/ .700 100.00 90000.0 10000.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
H+CH2OH<=>H2+CH2O
H+CH2OH<=>OH+CH3
H+CH2OH<=>CH2*+H2O
H+CH3O(+M)<=>CH3OH(+M)
LOW / 4.660E+41 -7.440 14080.0/
TROE/ .700 100.00 90000.0 10000.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
H+CH3O<=>H+CH2OH
H+CH3O<=>H2+CH2O
H+CH3O<=>OH+CH3
H+CH3O<=>CH2*+H2O
H+CH3OH<=>CH2OH+H2
H+CH3OH<=>CH3O+H2
H+C2H(+M)<=>C2H2(+M)
LOW / 3.750E+33 -4.800 1900.00/
TROE/ .6464 132.00 1315.00 5566.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
H+C2H2(+M)<=>C2H3(+M)
LOW / 3.800E+40 -7.270 7220.00/
TROE/ .7507 98.50 1302.00 4167.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
H+C2H3(+M)<=>C2H4(+M)
LOW / 1.400E+30 -3.860 3320.00/
TROE/ .7820 207.50 2663.00 6095.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
H+C2H3<=>H2+C2H2
H+C2H4(+M)<=>C2H5(+M)
LOW / 0.600E+42 -7.620 6970.00/
TROE/ .9753 210.00 984.00 4374.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
H+C2H4<=>C2H3+H2
H+C2H5(+M)<=>C2H6(+M)
LOW / 1.990E+41 -7.080 6685.00/
TROE/ .8422 125.00 2219.00 6882.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
H+C2H5<=>H2+C2H4
H+C2H6<=>C2H5+H2
H+HCCO<=>CH2*+CO
H+CH2CO<=>HCCO+H2
H+CH2CO<=>CH3+CO
H+HCCOH<=>H+CH2CO
H2+CO(+M)<=>CH2O(+M)
LOW / 5.070E+27 -3.420 84350.00/
TROE/ .9320 197.00 1540.00 10300.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
OH+H2<=>H+H2O
2OH(+M)<=>H2O2(+M)
LOW / 2.300E+18 -.900 -1700.00/
TROE/ .7346 94.00 1756.00 5182.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
2OH<=>O+H2O
OH+HO2<=>O2+H2O
DUPLICATE
OH+H2O2<=>HO2+H2O
DUPLICATE
OH+H2O2<=>HO2+H2O
DUPLICATE
OH+C<=>H+CO
OH+CH<=>H+HCO
OH+CH2<=>H+CH2O
OH+CH2<=>CH+H2O
OH+CH2*<=>H+CH2O
OH+CH3(+M)<=>CH3OH(+M)
LOW / 4.000E+36 -5.920 3140.00/
TROE/ .4120 195.0 5900.00 6394.00/
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
OH+CH3<=>CH2+H2O

```

OH+CH3<=>CH2*+H2O	6.440E+17	-1.340	1417.00	
OH+CH4<=>CH3+H2O	1.000E+08	1.600	3120.00	
OH+CO<=>H+CO2	4.760E+07	1.228	70.00	
OH+HCO<=>H2O+CO	5.000E+13	.000	.00	
OH+CH2O<=>HCO+H2O	3.430E+09	1.180	-447.00	
OH+CH2OH<=>H2O+CH2O	5.000E+12	.000	.00	
OH+CH3O<=>H2O+CH2O	5.000E+12	.000	.00	
OH+CH3OH<=>CH2OH+H2O	1.440E+06	2.000	-840.00	
OH+CH3OH<=>CH3O+H2O	6.300E+06	2.000	1500.00	
OH+C2H<=>H+HCCO	2.000E+13	.000	.00	
OH+C2H2<=>H+CH2CO	2.180E-04	4.500	-1000.00	
OH+C2H2<=>H+HCCOH	5.040E+05	2.300	13500.00	
OH+C2H2<=>C2H+H2O	3.370E+07	2.000	14000.00	
OH+C2H2<=>CH3+CO	4.830E-04	4.000	-2000.00	
OH+C2H3<=>H2O+C2H2	5.000E+12	.000	.00	
OH+C2H4<=>C2H3+H2O	1.800E+06	2.000	2500.00	! k_opt=0.5*ko
OH+C2H6<=>C2H5+H2O	3.540E+06	2.120	870.00	
OH+CH2CO<=>HCCO+H2O	7.500E+12	.000	2000.00	
2HO2<=>O2+H2O2	1.300E+11	.000	-1630.00	
DUPLICATE				
2HO2<=>O2+H2O2	4.200E+14	.000	12000.00	
DUPLICATE				
HO2+CH2<=>OH+CH2O	2.000E+13	.000	.00	
HO2+CH3<=>O2+CH4	1.000E+12	.000	.00	
HO2+CH3<=>OH+CH3O	2.870E+13	.000	.00	! k_opt=0.76*ko
HO2+CO<=>OH+CO2	1.500E+14	.000	23600.00	
HO2+CH2O<=>HCO+H2O2	5.600E+06	2.000	12000.00	
C+O2<=>O+CO	5.800E+13	.000	576.00	
C+CH2<=>H+C2H	5.000E+13	.000	.00	
C+CH3<=>H+C2H2	5.000E+13	.000	.00	
CH+O2<=>O+HCO	6.710E+13	.000	.00	
CH+H2<=>H+CH2	1.080E+14	.000	3110.00	
CH+H2O<=>H+CH2O	5.710E+12	.000	-755.00	
CH+CH2<=>H+C2H2	4.000E+13	.000	.00	
CH+CH3<=>H+C2H3	3.000E+13	.000	.00	
CH+CH4<=>H+C2H4	6.000E+13	.000	.00	
CH+CO(+M)<=>HCCO(+M)	5.000E+13	.000	.00	
LOW / 2.690E+28 -3.740 1936.00/				
TROE/ .5757 237.00 1652.00 5069.00 /				
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/				
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/				
CH+CO2<=>HCO+CO	1.900E+14	.000	15792.00	
CH+CH2O<=>H+CH2CO	9.460E+13	.000	-515.00	
CH+HCCO<=>CO+C2H2	5.000E+13	.000	.00	
CH2+O2<=>OH+H+CO	5.000E+12	.000	1500.00	
CH2+H2<=>H+CH3	5.000E+05	2.000	7230.00	
2CH2<=>H2+C2H2	1.600E+15	.000	11944.00	
CH2+CH3<=>H+C2H4	4.000E+13	.000	.00	
CH2+CH4<=>2CH3	2.460E+06	2.000	8270.00	
CH2+CO(+M)<=>CH2CO(+M)	8.100E+11	.500	4510.00	
LOW / 2.690E+33 -5.110 7095.00/				
TROE/ .5907 275.00 1226.00 5185.00 /				
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/				
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/				
CH2+HCCO<=>C2H3+CO	3.000E+13	.000	.00	
CH2*+N2<=>CH2+N2	1.500E+13	.000	600.00	
CH2*+AR<=>CH2+AR	9.000E+12	.000	600.00	
CH2*+O2<=>H+OH+CO	2.800E+13	.000	.00	
CH2*+O2<=>CO+H2O	1.200E+13	.000	.00	
CH2*+H2<=>CH3+H	7.000E+13	.000	.00	
CH2*+H2O(+M)<=>CH3OH(+M)	4.820E+17	-1.160	1145.00	
LOW / 1.880E+38 -6.360 5040.00/				
TROE/ .6027 208.00 3922.00 10180.0 /				
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/				
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/				
CH2*+H2O<=>CH2+H2O	3.000E+13	.000	.00	
CH2*+CH3<=>H+C2H4	1.200E+13	.000	-570.00	
CH2*+CH4<=>2CH3	1.600E+13	.000	-570.00	
CH2*+CO<=>CH2+CO	9.000E+12	.000	.00	
CH2*+CO2<=>CH2+CO2	7.000E+12	.000	.00	
CH2*+CO2<=>CO+CH2O	1.400E+13	.000	.00	
CH2*+C2H6<=>CH3+C2H5	4.000E+13	.000	-550.00	
CH3+O2<=>O+CH3O	3.560E+13	.000	30480.00	
CH3+O2<=>OH+CH2O	2.310E+12	.000	20315.00	
CH3+H2O2<=>HO2+CH4	2.450E+04	2.470	5180.00	
2CH3(+M)<=>C2H6(+M)	6.770E+16	-1.180	654.00	
LOW / 3.400E+41 -7.030 2762.00/				
TROE/ .6190 73.20 1180.00 9999.00 /				
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/				
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/				
2CH3<=>H+C2H5	6.840E+12	.100	10600.00	
CH3+HCO<=>CH4+CO	2.648E+13	.000	.00	
CH3+CH2O<=>HCO+CH4	3.320E+03	2.810	5860.00	
CH3+CH3OH<=>CH2OH+CH4	3.000E+07	1.500	9940.00	
CH3+CH3OH<=>CH3O+CH4	1.000E+07	1.500	9940.00	
CH3+C2H4<=>C2H3+CH4	2.270E+05	2.000	9200.00	
CH3+C2H6<=>C2H5+CH4	6.140E+06	1.740	10450.00	
HCO+H2O<=>H+CO+H2O	1.500E+18	-1.000	17000.00	
HCO+M<=>H+CO+M	1.870E+17	-1.000	17000.00	
H2/2.00/ H2O/ .00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/				
HCO+O2<=>HO2+CO	13.45E+12	.000	400.00	
CH2OH+O2<=>HO2+CH2O	1.800E+13	.000	900.00	

```

CH3O+O2<=>HO2+CH2O      4.280E-13      7.600      -3530.00
C2H+O2<=>HCO+CO          1.000E+13      .000      -755.00
C2H+H2<=>H+C2H2          5.680E+10      0.900      1993.00
C2H3+O2<=>HCO+CH2O      4.580E+16      -1.390      1015.00
C2H4(+M)<=>H2+C2H2(+M)    8.000E+12      .440      86770.00
  LOW / 1.580E+51      -9.300      97800.00/
  TROE/ .7345      180.00      1035.00      5417.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
C2H5+O2<=>HO2+C2H4      8.400E+11      .000      3875.00
HCCO+O2<=>OH+2CO        3.200E+12      .000      854.00
2HCCO<=>2CO+C2H2        1.000E+13      .000      .00
O+C2H3<=>H+H2+CO        3.370E+13      .000      .00
O+C2H4<=>H+CH2CHO        3.350E+06      1.830      220.00      ! k_opt=0.5*ko
O+C2H5<=>H+CH3CHO        1.096E+14      .000      .00
OH+HO2<=>O2+H2O         0.500E+16      .000      17330.00
  DUPLICATE
OH+CH3<=>H2+CH2O         8.000E+09      .500      -1755.00
CH+H2(+M)<=>CH3(+M)      1.970E+12      .430      -370.00
  LOW/ 4.820E+25      -2.80      590.0 /
  TROE/ .578      122.0      2535.0      9365.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
CH2+O2<=>2H+CO2          5.800E+12      .000      1500.00
CH2+O2<=>O+CH2O          2.400E+12      .000      1500.00
CH2+CH2<=>2H+C2H2        2.000E+14      .000      10989.00
CH2*+H2O=>H2+CH2O       6.820E+10      .250      -935.00
C2H3+O2<=>O+CH2CHO      1.212E+11      .290      11.00      ! k_opt=0.4*ko
C2H3+O2<=>HO2+C2H2      1.337E+06      1.610      -384.00
O+CH3CHO<=>OH+CH2CHO     2.920E+12      .000      1808.00
O+CH3CHO<=>OH+CH3+CO     2.920E+12      .000      1808.00
O2+CH3CHO<=>HO2+CH3+CO   3.010E+13      .000      39150.00
H+CH3CHO<=>CH2CHO+H2     2.050E+09      1.160      2405.00
H+CH3CHO<=>CH3+H2+CO     2.050E+09      1.160      2405.00
OH+CH3CHO<=>CH3+H2O+CO   2.343E+10      0.730      -1113.00
HO2+CH3CHO<=>CH3+H2O2+CO 3.010E+12      .000      11923.00
CH3+CH3CHO<=>CH3+CH4+CO   2.720E+06      1.770      5920.00
H+CH2CO(+M)<=>CH2CHO(+M)  4.865E+11      0.422      -1755.00
  LOW/ 1.012E+42      -7.63      3854.0/
  TROE/ 0.465      201.0      1773.0      5333.0 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
C2H4/3.0/ pC3H4/4.0/ C3H6/4.0/ C3H8/4.0/
O+CH2CHO<=>H+CH2+CO2     1.500E+14      .000      .00
O2+CH2CHO<=>OH+CO+CH2O   1.810E+10      .000      .00
O2+CH2CHO<=>OH+2HCO       2.350E+10      .000      .00
H+CH2CHO<=>CH3+HCO        2.200E+13      .000      .00
H+CH2CHO<=>CH2CO+H2       1.100E+13      .000      .00
OH+CH2CHO<=>H2O+CH2CO     1.200E+13      .000      .00
OH+CH2CHO<=>HCO+CH2OH     3.010E+13      .000      .00
! Dimethylether (CH3OCH3): Formation and Consumption
!
CH3+CH3O=CH3OCH3         1.21E13      0.0      0.0      ! [Tsang/Hampson '86]
CH3OCH3+H=CH3OCH2+H2     1.90E13      0.0      5166.0      ! [Faubel et al. '79]
CH3OCH3+OH=CH3OCH2+H2O   6.27E12      0.0      739.0      ! [Tully/Droege '87]
CH3OCH3+O=CH3OCH2+OH     5.00E13      0.0      4571.0      ! [Herron '88]
CH3OCH3+CH3=CH3OCH2+CH4  3.55E12      0.0      11800.0      ! [Batt et al. '82]
CH3OCH2=CH3+CH2O         1.60E13      0.0      25440.0      ! [Sehested et al. 1997]
!
! Formation and Consumption of the Acetaldehyde Radical (CH2CHO)
!
CH+CH2O=CH2CHO           9.64E13      0.0      -517.0      ! [Baulch '92]
! duplicate C2H4+O=CH2CHO+H 1.21E06      2.08      0.0      ! [Baulch '92]
C3H6+O=CH2CHO+CH3        1.08E06      2.15      -795.0      ! [Tsang '91; Knyazev '92][e]
! C4H8+O=CH2CHO+C2H5      5.14E06      1.95      -596.0      ! [ko et al. '91/
!                               koda et al. '91][f]
C4H8-1+O=CH2CHO+C2H5     5.14E06      1.95      -596.0      ! [ko et al. '91/
!                               koda et al. '91][f]
CH2CHO=CH2CO+H           1.58E13      0.0      34970.0      ! [Colket et al. '75]
CH2CHO=CH3CO             1.00E13      0.0      47100.0      ! [Colket et al. '75]
!
! CH3CO Formation and Consumption
!
CH3CO=CH3+CO             8.74E42      -8.62      22424.0      ! [Tsang/Hampson '86]
CH3CO+CH3=CH3COCH3       4.04E15      -0.80      0.0      ! [Tsang/Hampson '86]
CH3CO+CH3=CH2CO+CH4      6.06E14      -0.80      0.0      ! [Hassinen et al. '90][g]
CH3CO+O=CH3+CO2          9.64E12      0.0      0.0      ! [Tsang/Hampson '86]
CH3CO+OH=CH2CO+H2O       1.21E13      0.0      0.0      ! [Tsang/Hampson '86]
CH3CO+H=CH3+HCO          3.30E13      0.0      0.0      ! [Bartels et al. '90][h]
!
! Acetaldehyde (CH3CHO) and acetone (CH3COCH3)
!
iC3H7+HO2=CH3CHO+CH3+OH  2.41E13      0.0      0.0      ! [Tsang '88]
iC3H7+O=CH3CHO+CH3        4.82E13      0.0      0.0      ! [Tsang '88]
iC3H7+O=CH3COCH3+H        4.82E13      0.0      0.0      ! [Tsang '88]
! C2H4+HO2=CH3CHO+OH      6.03E09      0.0      7949.0      ! [Tsang/Hampson '86]
! C2H5+O=CH3CHO+H         6.62E13      0.0      0.0      ! [Baulch '92]
! C2H5+O2=CH3CHO+OH       1.60E14      -1.17      10391.0      ! [Bozzelli/Dean '90, 1 atm]
! C2H3+OH=CH3CHO          3.01E13      0.0      0.0      ! [Tsang/Hampson '86]
! CH3CHO=CH3+HCO          7.00E15      0.0      81674.0      ! [Baulch '92]
! CH3CHO+H=CH3CO+H2       4.00E13      0.0      4207.0      ! [warnatz '84]
! CH3CHO+OH=CH3CO+H2O     1.00E13      0.0      0.0      ! [warnatz '84]

```

!CH3CHO+O=CH3CO+OH	5.00E12	0.0	1792.0	! [warnatz '84]
CH3CHO+CH3=CH3CO+CH4	1.99E-6	5.64	2464.0	! [Baulch '92]
CH3CHO+CH3=CH3COCH3+H	1.66E10	0.0	12398.0	! [Liu/Laidler '68]
! C3H2 propynylidene reactions				
C3H2+O=C2H+HCO	6.80E13	0.0	0.0	! [warnatz et al. 1982]
C3H2+O=C2H2+CO	1.00E14	0.0	0.0	! [Miller and Melius 1992]
!C3H2+OH=C2H2+HCO	5.00E13	0.0	0.0	! [Miller and Melius 1992]
C3H2+OH=CHCHCHO	3.01E13	0.0	0.0	! [Tsang/Hampson '86]
! H2CCCH reactions				
C3H3=C3H2+H	5.20E12	0.0	78447.0	! [Scherer et al. 2000]
!C3H3+H=C3H2+H2	5.00E13	0.0	1000.0	! [Miller and Melius 1992]
!C3H3+OH=C3H2+H2O	2.00E13	0.0	0.0	! [Pauwels et al. 1995]
C3H3+O=C3H2+OH	3.20E12	0.0	0.0	! [warnatz et al. 1982]
CH3+C2H=C3H3+H	2.41E13	0.0	0.0	! [Tsang et al. 1986]
C2H+CH2OH=C3H3+OH	1.21E13	0.0	0.0	! [Tsang 1987]
C2H+C2H5=CH3+C3H3	1.81E13	0.0	0.0	! [Tsang et al. 1986]
!C2H2+HCCO=C3H3+CO	1.10E11	0.0	3000.0	! [Miller and Melius 1992]
!C3H3+O2=CH2CO+HCO	3.00E10	0.0	2868.0	! [Miller and Melius 1992]
!CH2*+C2H2=C3H3+H	1.00E22	-2.508	4434.0	! [QRRK-HR, 1 atm][i]
!HCH+C2H2=C3H3+H	1.20E13	0.0	6600.0	! [Boehland et al. 1986]
C3H3+O=C2H+CH2O	7.17E13	0.0	0.0	! [p.w., as CH3+O]
! 2-Propynal and its radical: HCCCHO and HCCCO				
C3H3+O=HCCCHO+H	6.03E13	0.0	0.0	! [Tsang '91 for C3H5+O]
C3H2+O=HCCCHO	6.62E12	0.0	3060.0	! [Aleksandrov et al. '80 for C3H4+O]
!CHCHCHO+H=HCCCHO+H2	1.21E13	0.0	0.0	! [Baulch et al. '92 for C2H3]
!CHCHCHO+OH=HCCCHO+H2O	2.00E13	0.0	0.0	! [Miller and Melius '92 for C2H3]
!C2H+CH3CO=CH3+HCCCO	1.81E13	0.0	0.0	! [Tsang/Hampson '86 for C2H3]
!HCCCHO=C2H2+CO	8.51E14	0.0	70940.0	! [Saito et al. '90]
!HCCCHO+O=HCCCO+OH	5.68E12	0.0	1542.0	! [Singleton et al. '77 for C2H5CHO]
!HCCCHO+OH=HCCCO+H2O	1.60E13	0.0	0.0	! [Maldotti et al. '92 for C2H3CHO+OH]
!C2H+CO=HCCCO	1.51E11	0.0	4810.0	! [Tsang/Hampson '86 for C2H3+CO]
! 2-propenal (acrolein): CH2CHCHO Formation and Consumption				
C3H3+OH=CH2CHCHO	3.01E13	0.0	0.0	! [Tsang/Hampson '86 for C2H3+OH=CH3CHO]
!HCO+C2H3=CH2CHCHO	1.81E13	0.0	0.0	! [Tsang/Hampson '86]
!C3H5+O=CH2CHCHO+H	6.03E13	0.0	0.0	! [Tsang '91]
ac3H4+O=CH2CHCO+H	6.62E12	0.0	3060.0	! [Aleksandrov et al. '80]
!C2H3+CH3CO=CH3+CH2CHCO	1.81E13	0.0	0.0	! [Tsang/Hampson '86]
!CH2CHCHO+O=CH2CHCO+OH	5.68E12	0.0	1542.0	! [Singleton et al. '77 for C2H5CHO]
!CH2CHCHO+OH=CH2CHCO+H2O	1.60E13	0.0	0.0	! [Maldotti et al. '92]
CH2CHCHO+C2H5=CH2CHCO+C2H6	1.20E13	0.0	12647.0	! [McAdam/walker '87 and Tsang/Hamp. '86 for C2H5CHO]
CH2CHCHO+!C3H7=CH2CHCO+C3H8	1.02E10	0.0	6840.0	! [Szirovicza '85]
C2H3+CO=CH2CHCO	1.51E11	0.0	4810.0	! [Tsang/Hampson '86]
!???CH2CHCHO+H=CHCHCHO+H2	5.07E07	1.93	12951.0	! [Knyazev et al. 1996a for C2H4]
!?CH2CHCHO+OH=CHCHCHO+H2O	2.02E13	0.0	5955.0	! [Miller and Melius '92 for C2H4]
!?CH2CHCHO+CH3=CHCHCHO+CH4	4.16E12	0.0	11128.0	! [Baulch '92 for C2H4]
!?CHCHCHO+H=CH2CHCHO	5.36E14	0.0	982.0	! [Duran et al. '88 for C2H3+H->C2H4]
!?CHCHCHO=C2H2+HCO	2.95E12	0.0	11110.0	! [Cadman et al. '70 for C2H5CO=C2H5+CO]
! Propanal and its radical: C2H5CHO and C2H5CO				
! reactions of these species were absent in the models				
nc3H7+O=C2H5CHO+H	9.64E13	0.0	0.0	! [Tsang '88][j]
nc3H7+O2=C2H5CHO+OH	1.10E08	0.0	0.0	! [Baker et al. '71]
C2H5+HCO=C2H5CHO	1.81E13	0.0	0.0	! [Tsang/Hampson '86]
ac3H5+OH=C2H5CHO	3.01E13	0.0	0.0	! [C2H3+OH: Tsang/Hampson '86]
C2H5CHO+O=C2H5CO+OH	5.68E12	0.0	1542.0	! [Singleton et al. '77]
C2H5CHO+OH=C2H5CO+H2O	1.21E13	0.0	0.0	! [Atkinson et al. '97][k]
C2H5CHO+C2H5=C2H5CO+C2H6	1.20E13	0.0	12647.0	! [McAdam/walker '87 and Tsang/Hamp. '86]
C2H5+CO=C2H5CO	1.51E11	0.0	4809.0	! [Tsang/Hampson '86]
! C3H4: CH2=C=CH2 (allene), C3H4P (methylacetylene) and C3H4CY (cyclopropene)				
!ac3H4 pc3H4				
!ac3H4=C3H3+H	2.30E12	0.0	69684.0	! [Scherer et al. 2000]
!pc3H4=C3H3+H	1.34E12	0.0	69942.0	! [Scherer et al. 2000]
CH+C2H4=ac3H4+H	7.17E16	-0.84	1260.0	! [QRRK-HR, 1 atm][m]
CH2*+C2H2=ac3H4CY	5.34E34	-7.11	5830.0	! [QRRK-HR, 1 atm][i]
CH2*+C2H2=ac3H4	1.04E37	-7.42	6750.0	! [QRRK-HR, 1 atm][i]
CH2*+C2H2=pc3H4	3.71E37	-7.50	6850.0	! [QRRK-HR, 1 atm][i]
C3H4CY=ac3H4	1.51E14	0.0	50400.0	! [Karni et al. '88]
C3H4CY=pc3H4	7.08E13	0.0	43700.0	! [Karni et al. '88]
!ac3H4+O=CO+C2H4	1.50E13	0.0	2103.0	! [warnatz 1984]
!ac3H4+OH=HCO+C2H4	1.00E12	0.0	0.0	! [Westbrook and Dryer 1984]

```

!ac3H4+CH3=C3H3+CH4      2.00E12      0.0      7700.0 ! [Kern et al. 1991]
!pc3H4+CH3=C3H3+CH4      2.00E12      0.0      7700.0 ! [Kern et al. 1991]
!ac3H4+H=C2H2+CH3        2.00E13      0.0      2400.0 ! [Kern et al. 1991]
C2H+CH3=PC3H4            8.27E46     -10.0     46330.0 ! [QRRK-HR, 1 atm][c]
C2H3+CH2=ac3H4+H         3.00E13      0.0      0.0 ! [Miller and Melius 1992]
pc3H4+C2H=C2H2+C3H3      1.00E13      0.0      0.0 ! [Kern et al. 1991]
ac3H4+C2H=C2H2+C3H3      1.00E13      0.0      0.0 ! [Kern et al. 1991]
!ac3H4+O=CH2O+C2H2       9.00E12      0.0     1870.0 ! [Zhang and McKinnon 1995]
!ac3H4+O=HCO+C2H3        9.00E12      0.0     1870.0 ! [Zhang and McKinnon 1995]
!pc3H4+O=CH2O+C2H2       7.50E12      0.0     2102.0 ! [Zhang and McKinnon 1995]
!pc3H4+O=HCO+C2H3        7.50E12      0.0     2102.0 ! [Zhang and McKinnon 1995]
!ac3H4+OH=CH2CO+CH3      3.37E12      0.0     -304.0 ! [Zhang and McKinnon 1995]
!pc3H4+OH=CH2CO+CH3      4.28E11      0.0     -843.0 ! [Zhang and McKinnon 1995]
!ac3H4+H=C3H3+H2         3.00E7      2.0     5000.0 ! [Pauwels et al. 1995]
!ac3H4+OH=C3H3+H2O       2.00E7      2.0     1000.0 ! [Pauwels et al. 1995]
!pc3H4+H=C3H3+H2         3.00E7      2.0     5000.0 ! [Pauwels et al. 1995]
!pc3H4+OH=C3H3+H2O       2.00E7      2.0     1000.0 ! [Pauwels et al. 1995]
!CH3+C2H2=pc3H4+H        1.92E4      2.42    12892.0 ! [Diau et al. 1994][n]
!
C3H5 = H2CCCH2 : allyl radical reactions
!
CH+C2H4=ac3H5             2.42E37     -8.04    4840.0 ! [QRRK-HR, 1 atm][m]
!ac3H4+H=C3H5             1.20E11      0.69    3007.0 ! [Tsang and Walker 1992]
!C3H5+OH=ac3H4+H2O       6.03E12      0.0      0.0 ! [Tsang 1991]
ac3H5+CH2*=CH2CHCH2+H    3.01E13      0.0      0.0 ! [Tsang 1991]
C2H+ac3H5=C2H2+ac3H4     1.50E-1      0.0      0.0 ! [Tsang 1991]
C2H+ac3H5=C2H3+C3H3      2.00E01      0.0      0.0 ! [Tsang 1991]
ac3H5+C2H3=ac3H4+C2H4    2.41E12      0.0      0.0 ! [Tsang 1991]
ac3H5+C2H5=ac3H4+C2H6    9.64E11      0.0     -131.0 ! [Tsang 1991]
C2H3+CH2OH=ac3H5+OH      1.21E13      0.0      0.0 ! [Tsang 1987]
!C2H4+CH2=ac3H5+H        3.19E12      0.0     5285.4 ! [Zhang and McKinnon 1995]
CH3+C2H2=ac3H5           1.40E4      2.21    16500 ! [Diau et al. 1994][n]
C2H3+CH3=ac3H5+H        7.20E13      0.0      0.0 ! [Fahr et al. 1999]
nC3H7+H=C3H6+H2          1.81E12      0.0      0.0 ! [Tsang '88]
nC3H7+OH=C3H6+H2O        2.41E13      0.0      0.0 ! [Tsang '88]
nC3H7+CH2=C3H6+CH3        1.81E12      0.0      0.0 ! [Tsang '88]
nC3H7+CH3=C3H6+CH4        1.14E13     -0.32     0.0 ! [Tsang '88]
!nC3H7+O2=C3H6+HO2       1.00E12      0.0     5020.0 ! [Warnatz '84]
nC3H7+CH2OH=C3H6+CH3OH   4.82E11      0.0      0.0 ! [Tsang '88]
nC3H7+C2H=C3H6+C2H2      6.03E12      0.0      0.0 ! [Tsang '88]
nC3H7+C2H3=C3H6+C2H4      1.21E12      0.0      0.0 ! [Tsang '88]
nC3H7+C2H5=C3H6+C2H6      1.45E12      0.0      0.0 ! [Tsang '88]
nC3H7+ac3H5=C3H6         1.45E12      0.0     -131.0 ! [Tsang '91]
nC3H7+CH2=C2H4+C2H5       1.81E13      0.0      0.0 ! [Tsang '88]
!C3H7+C2H2=CH2CHCH2+CH3  2.77E10      0.0      6504.0 ! [Tsang '88]
nC3H7+C2H=C3H3+C2H5      1.21E13      0.0      0.0 ! [Tsang '88]
!CH3+C2H5=C3H8            3.37E13      0.0      0.0 ! [Baulch et al. '94]
!nC3H7+H2O2=C3H8+HO2     1.87E04      2.11    2571.0 ! [Tsang '88]
nC3H7+C2H3=C2H2+C3H8     1.21E12      0.0      0.0 ! [Tsang '88]
nC3H7+HCO=C3H8+CO        6.03E13      0.0      0.0 ! [Tsang '88]
nC3H7+CH2OH=C3H8+CH2O    9.64E11      0.0      0.0 ! [Tsang '88]
nC3H7+CH3O=C3H8+CH2O     2.41E13      0.0      0.0 ! [Tsang '88]
nC3H7+CH3OH=C3H8+CH2OH   3.37E01      3.17    9161.0 ! [Tsang '88]
nC3H7+CH3OH=C3H8+CH3O    1.45E01      3.10    8942.0 ! [Tsang '88]
nC3H7+CH2O=C3H8+HCO      3.01E03      2.90    5862.0 ! [Tsang '88]
nC3H7+C2H5=C3H8+C2H4     1.15E12      0.0      0.0 ! [Tsang '88]
nC3H7+C2H6=C3H8+C2H5     2.53E-1      3.82    9042.0 ! [Tsang '88]
nC3H7+nC3H7=C3H8+C3H6    1.69E12      0.0      0.0 ! [Tsang '88]
nC3H7+ac3H5=ac3H4+C3H8   7.23E11      0.0     -131.0 ! [Tsang '91]
nC3H7+C3H6=C3H8+ac3H5    2.23E00      3.50    6637.0 ! [Tsang '91]
nC3H7+C3H8=C3H8+ic3H7    8.44E-4      4.00    4726.0 ! [Tsang '88]
!C3H7+C2H5=C2H4+C3H8     1.84E13     -0.35     0.0 ! [Tsang '88]
!C3H7+C2H6=C3H8+C2H5     8.44E-1      4.20    8716.0 ! [Tsang '88]
!C3H7+CH3OH=C3H8+CH2OH   3.19E01      3.70    10532.0 ! [Tsang '88]
!C3H7+CH3OH=C3H8+CH3O    1.45E01      3.10    10333.0 ! [Tsang '88]
!C3H7+CH2O=C3H8+HCO      1.08E11      0.0     6955.0 ! [Tsang '88]
!C3H7+H=C3H8             2.00E13      0.0      0.0 ! [Warnatz '84]
!ic3H7+H2O2=C3H8+HO2     2.89E02      2.83    4048.0 ! [Tsang '88]
!C3H7+HCO=C3H8+CO        1.21E14      0.0      0.0 ! [Tsang '88]
!C3H7+CH2OH=C3H8+CH2O    2.35E12      0.0      0.0 ! [Tsang '88]
!C3H7+CH3O=C3H8+CH2O     1.21E13      0.0      0.0 ! [Tsang '88]
!C3H7+C2H3=C3H8+C2H2     1.52E14     -0.70     0.0 ! [Tsang '88]
!C3H7+nC3H7=C3H8+C3H6    5.13E13     -0.35     0.0 ! [Tsang '88]
!C3H7+ic3H7=C3H8+C3H6    2.11E14     -0.70     0.0 ! [Tsang '88]
!C3H7+ac3H5=C3H8+ac3H4   4.58E12     -0.35    -131.0 ! [Tsang '91]
2C3H2=C4H2+C2H2          2.00E13      0.0    85000.0 ! [Kern et al. 1991]
!C2H2+C2H=C4H2+H         4.23E17     -1.034   2690.0 ! [QRRK-HR, 1 atm][o]
C4H2+M=C4H+H+M           3.50E17      0.0    80065.0 ! [Frenklach and Warnatz 1987]
C4H2+C2H=C4H+C2H2        2.00E13      0.0      0.0 ! [Frenklach and Warnatz 1987]
CH2CHCCCH+C2H=C4H2+C2H3  1.00E13      0.0      0.0 ! [Frenklach and Warnatz 1987]
HCCHCCCH+H=C4H2+H2       2.50E13      0.0      0.0 ! [0.5*Miller and Melius 1992]
!
HCCHCCCH+OH=C4H2+H2O     1.50E13      0.0      0.0 ! [0.5*Miller and Melius 1992]
!
H2CCCCCH+H2=C2H2+C2H3    5.01E10      0.0    20000.0 ! [Colket 1986]
!H2CCCCCH+CH2=ac3H4+C2H  2.00E13      0.0      0.0 ! [Miller and Melius 1992]
C2H2+C2H=HCCHCCCH        2.14E35     -7.033   6040.0 ! [QRRK-HR, 1 atm][o]
!C3H3+CH=H2CCCCCH+H      7.00E13      0.0      0.0 ! [Miller and Melius 1992]
!C3H3+CH=HCCHCCCH+H      7.00E13      0.0      0.0 ! [Miller and Melius 1992]
C2H2+C2H2=HCCHCCCH+H     1.00E12      0.0    65980.0 ! [Benson 1989]
!
! C4H4 = H-CC-CHCH2 = CH2CHCCCH : vinyl acetylene reactions

```

C2H2+C2H2=CH2CHCCH	1.66E45	-9.46	58460.0	[QRRK-HR, 1 atm][p]
C2H3+C2H3=CH2CHCCH+2H	7.83E12	0.0	0.0	[Knyazev et al. 1996c]
!C2H3+C2H2=CH2CHCCH+H	4.88E15	-0.75	13180.0	[QRRK-HR, 1 atm][q]
CH2CHCCH+C2H=H2CCCCCH+C2H2	4.00E13	0.0	0.0	[Kiefer et al. 1985]
CH2CHCCH+C2H=HCCCHCCH+C2H2	4.00E13	0.0	0.0	[Kiefer et al. 1985]
!C3H3+C2H2=CH2CHCCH+H	4.00E13	0.0	0.0	[Miller and Melius 1992]
C2H3+C2H=CH2CHCCH	9.10E45	-9.118	21130.0	[QRRK-HR, 1 atm][r]
!C2H4+C2H=CH2CHCCH+H	1.21E13	0.0	0.0	[Tsang et al. 1986]
! Formation of n-C4H3				
CH2CHCCH+C2H3=C2H4+HCCCHCCH	5.00E11	0.0	16300.0	[Colket 1986]
! Formation of i-C4H3				
CH2CHCCH+C2H3=C2H4+H2CCCCCH	5.00E11	0.0	16300.0	[Colket 1986]
! C4H5 = CH2CHCHCH & CH2CHCHCH2 : Butadienyl reactions				
C2H3+C2H2=CH2CHCHCH	6.49E42	-9.77	16900	[QRRK-HR, 1 atm][q]
!CH2CHCHCH+H=CH2CHCHCH2	1.21E14	0.0	0.0	[Fahr et al. 1991 for C2H3+H]
! C4H613 (1,3-Butadiene=CH2CHCHCH2) and i-C4H7 (CH2=CHCHCH3) reactions				
!C2H3+C2H4=CH2CHCHCH2+H	2.63E15	-1.01	5950.0	[QRRK-HR, 1 atm][s]
C2H3+C2H4=I-C4H7	1.32E27	-5.58	4000.0	[QRRK-HR, 1 atm][s]
I-C4H7=CH2CHCHCH2+H	3.16E13	0.0	34800.0	[Weissman and Benson 1984]
I-C4H7+H=CH2CHCHCH2+H2	1.81E12	0.0	0.0	[Tsang 1986] for c2h5+h=c2h4+h2
I-C4H7+OH=CH2CHCHCH2+H2O	2.41E13	0.0	0.0	[Tsang 1986] for c2h5+oh=c2h4+h2o
C2H3+C2H3=CH2CHCHCH2	2.00E13	0.0	0.0	[Colket et al. 1989]
C3H6+C2H3=CH2CHCHCH2+CH3	7.23E11	0.0	5010.0	[Tsang 1991]
! 1-butyne Formation and Consumption				
C3H6+C2H=CH3CH2CCH+CH	1.21E13	0.0	0.0	[Tsang '91]
CH3CH2CCH=CH3CHCH2	2.50E13	0.0	65000.0	[Hidaka et al. 1995a]
CH3CH2CCH+O=C3H6+CO	2.00E13	0.0	1659.0	[Cvetanovic '87]
! 1,2-butadiene Formation and Consumption				
! Formation of C4H8 (1-butene)				
I-C4H7+H=C4H8-1	1.00E14	0.0	0.0	[Sillescu et al. 93 for C2H4+H]
! C5H3 (cyclopentatrienyl) reactions				
C5H4+H=C5H3+H2	1.00E06	2.50	5000.0	[Alzueta et al. 1998]
C5H4+OH=C5H3+H2O	1.00E06	2.00	0.0	[Alzueta et al. 1998]
C5H4+O=C5H3+OH	1.00E06	2.50	3000.0	[Alzueta et al. 1998]
C5H3+H=C5H4	1.00E14	0.00	0.0	[Alzueta et al. 2000]
C5H3+O2=C2H2+HCCO+CO	1.00E12	0.00	0.0	[Alzueta et al. 1998]
! C5H3(L) (1,3-pentadiyne-5-yl) & C5H2(L) (HCC-CC-CH) reactions				
C4H2+CH2=C5H3(L)+H	1.30E13	0.0	0.0	[Miller and Melius 1992]
C4H2+CH2=C5H3(L)+H	3.00E13	0.0	0.0	[Miller and Melius 1992]
C4H2+CH=C5H2(L)+H	1.00E14	0.0	0.0	[Miller and Melius 1992]
C5H3(L)+H=C5H2(L)+H2	6.03E13	0.0	15103.0	[CH3+H, Baulch et al. 1992]
! C5H4 (cyclopentatriene), also formed by p-C6H4O2 decay				
C-C5H5+H=C5H4+H2	3.23E07	2.095	15842.0	[Mebel et al. 1997, C6H6+H]
C-C5H5+OH=C5H4+H2O	2.11E13	0.0	4571.0	[Madronich/Felder 1985, C6H6+OH]
C-C5H5+O=C5H4+OH	2.00E13	0.0	14694.0	[Lindstedt/Skevis 1994, C6H6+O]
C-C5H5+CH3=C5H4+CH4	2.00E12	0.0	15060.0	[Zhang et al. 1989, C6H6+CH3]
! C5H4(L) (1,2-pentadiene-4-yne, CH2=C=CH-CCH)				
C5H5(L)+H=C5H4(L)+H2	1.81E12	0.0	0.0	[C2H5+H, Tsang/Hampson'86]
C5H5(L)+OH=C5H4(L)+H2O	2.41E13	0.0	0.0	[C2H5+OH, Tsang/Hampson'86]
C5H5(L)+CH3=C5H4(L)+CH4	1.95E13	-0.50	0.0	[C2H5+CH3, Tsang/Hampson'86]
! C5H5/C5H4H/C5H5(L) = cyclic and acyclic C5H5 reactions				
C-C5H5=C3H3+C2H2	1.98E68	-15.00	124887.0	[Moskaleva and Lin 2000]
C-C5H5=C5H5(L)	2.52E80	-18.90	129171.0	[Moskaleva and Lin 2000]
C-C5H5+O=CH2CHCHCH+CO	1.74E14	-0.38	790.0	[QRRK-HR, 1atm][t]
C-C5H5+O=C-C5H5O	7.06E04	1.03	-6960.0	[QRRK-HR, 1atm][t]
! C5H4O, C5H4OH and C5H5OH reactions				
C-C5H5O=C-C5H4O+H	2.90E32	-6.50	21220.0	[Alzueta et al. 2000]
C-C5H5O=CH2CHCHCH+CO	1.10E79	-19.62	66250.0	[Alzueta et al. 2000]
C-C5H4O+H=C-C5H4OH	2.06E31	-5.001	15560.0	[QRRK-HR, 1atm][c]
C-C5H4OH+O2=C-C5H4O+HO2	3.00E13	0.0	5000.0	[Alzueta et al. 2000]
C-C5H4O+H=CH2CHCHCH+CO	2.10E61	-13.27	40810.0	[Alzueta et al. 2000]
C-C5H4O+O=CH2CHCHCH+CO2	1.00E13	0.0	2000.0	[Alzueta et al. 2000]

C-C5H4O=2C2H2+CO 6.20E41 -7.87 98700.0 ! [Wang and Brezinsky 1998]

! C5H6 = cyclopentadiene reactions

C-C5H6+C10H7*1=C-C5H5+C10H8 1.00E-1 4.0 0.0 ! [p.w.,sim.to C5H6 + C6H5]

C-C5H6+C10H7*2=C-C5H5+C10H8 1.00E-1 4.0 0.0 ! [p.w.,sim.to C5H6 + C6H5]

C-C5H6+ac3H5=C-C5H5+C3H6 2.00E-1 4.0 0.0 ! [Zhong and Bozzelli 1998]

ac3H5+C-C5H5=C-C5H6+ac3H4 1.00E12 0.0 0.0 ! [Dean 1990]

C-C5H6+CH2CHCHCH=C-C5H5+CH2CHCHCH2 6.00E11 0.0 0.0 !vb,01BUR/DVI,/10

C-C5H6+C3H3=C-C5H5+ac3H4 1.1e11 0. 5500. !vb-add,01BAC/MAC

C-C5H6+C3H3=C-C5H5+pc3H4 1.1e11 0. 5500. !vb,01BAC/MAC

C-C5H6=C2H2+ac3H4 3.8e17 0. 104000. !vb,01BAC/MAC

! C6H2 = H-CC-CC-CC-H Triacetylene reactions

C6H2+M=C6H+H+M 5.00E16 0.0 80065.0 ! [Frenklach and warnatz 1987]

C6H2+OH=C6H+H2O 1.10E13 0.0 7002.7 ! [Frenklach and warnatz 1987]

C6H2+C2H=C6H+C2H2 2.00E13 0.0 00.0 ! [Frenklach and warnatz 1987]

C6H2+C2H=C4H+C4H2 1.00E13 0.0 00.0 ! [Frenklach and warnatz 1987]

C4H2+C2H=C6H2+H 3.15E43 -8.229 32480.0 ! [QRRK-HR, 1 atm][c]

2C3H2=C6H2+H2 2.00E13 0.0 85000.0 ! [Kern et al. 1991]

! C6H3 = HCCCCCHCH hexenediynyl reactions

C4H2+C2H=C6H3 8.30E52 -11.260 25420.0 ! [QRRK-HR, 1 atm][c]

C6H2+H=C6H3 3.13E33 -5.884 16640.0 ! [QRRK-HR, 1 atm][c]

C6H3+H=C6H2+H2 2.00E13 0.0 0.0 ! [Frenklach and warnatz 1987]

! C6H4: HCCCCCHCHCH cis-3-hexen-1,5-diyne and benzyne reactions

C6H4+H=C6H3+H2 1.50E14 0.0 10205.3 ! [Frenklach and warnatz 1987]

C6H3+H=C6H4 4.27E54 -11.829 26810.0 ! [QRRK-HR, 1 atm][c]

C6H4+OH=C6H3+H2O 7.00E13 0.0 3011.4 ! [Frenklach and warnatz 1987]

C6H4+C2H=C6H3+C2H2 2.00E13 0.0 0.0 ! [Frenklach and warnatz 1987]

HCCCHCHCH+C2H2=BENZZYNE+H 3.00E-11 6.48 6640.0 ! [Westmoreland et al. 1989]

HCCCHCHCH+C2H2=C6H4+H 2.77E-07 5.59 6020.0 ! [Westmoreland et al. 1989]

C6H4+H=C6H5(L) 6.67E56 -12.446 16840.0 ! [QRRK-HR, 1 atm][c]

! C6H5(+M)=C6H4+H(+M) 4.3e12 0.62 77300. !vb,00WAN/LAS

LOW / 1.e84 -18.87 90100./

TROE/ 0.902 696. 358. 3856./

C4H2+C2H2=C6H4 1.4e7 1.45 25410. !vb,kinf,00WAN/LAS

! C6H5 reactions

C6H5(L)+H=C6H4+H2 2.00E13 0.0 0.0 ! [Frenklach and warnatz 1987]

HCCCHCHCH+C2H2=C6H5(L) 6.17E15 -1.51 4830.0 ! [Westmoreland et al. 1989]

H2CCCCCH+C2H3=C6H5+H 6.00E12 0.0 0.0 ! [Pope and Miller 2000]

C6H5+HO2=C6H5O+OH 5.00E13 0.0 1000.0 ! [Leung and Lindstedt 1995]

C6H5(L)=C6H5 1.66E11 0.0 16350.0 ! [Dewar et al. 1987]

C6H5+CH2O=C6H6+HCO 1.75E10 0.0 0.0 ! [Yu and Lin 1993]

C6H5+H=BENZZYNE+H2 9.17E-22 10.28 6175.0 ! [Mebel et al. 2001]

C6H5=BENZZYNE+H 7.99E41 -7.22 92197.0 ! [Madden et al. 1997]

C6H5=C6H4+H 3.32E73 -16.02 127671.0 ! [Madden et al. 1997]

! C6H6 reactions

CH2CHCHCH+C2H3=C6H6+H 1.90E12 0.0 2510.0 ! [Kubitz et al. '94, in Lindstedt/Skevis '97]

ac3H4+C3H3=C6H6+H 2.20E11 0.0 2000.0 ! [Wu and Kern 1987]

CH2CHCHCH+C2H2=C6H6 4.47E11 0.0 30010.0 ! [Chanmugathas/Heicklen '86]

C6H6+O=C6H5+OH 2.00E13 0.0 14704.0 ! [Leidreiter and

C6H5+CH4=C6H6+CH3 6.00E12 0.0 12320.0 ! [Tokmakov et al. 1999]

CH3+C-C5H5=C6H6+H+H 2.e12 0. 0. !?vb, 00IKE/TRA

CH3H+C3H2=C6H5 3.e12 0. 0. !vb, 01DAN/DAL,d'anna

! C6H8 (& C6H7) chemistry:

CH2CHCHCH+C2H2=cyc6h7 7.12E21 -3.64 6260.0 ! [Westmoreland et al. 1989]

CH3+C-C5H5=cyc6h7+H 2.44E41 -7.989 39259.0 ! [Dean 1990]

cyc6h7+H=C6H6+H2 1.00E13 0.0 0.0 ! [Louw and Lucas 1973]

cyc6h7+C6H5=2C6H6 1.00E12 0.0 0.0 ! [Louw and Lucas 1973]

cyc6h7+H=C6H813 6.00E13 0.0 0.0 ! [Berho et al. 1999][ab]

cyc6h7+H=C6H814 6.00E13 0.0 0.0 ! [Berho et al. 1999][ab]

2cyc6h7=C6H813+C6H6 1.94E15 -1.0 0.0 ! [Berho et al. 1999][ac]

2cyc6h7=C6H814+C6H6 1.67E15 -1.0 0.0 ! [Berho et al. 1999][ac]

C6H813+O2=cyc6h7+HO2 8.13E11 0.0 24840.0 ! [Mulder and Louw 1985]

C6H814+H=cyc6h7+H2 2.80E13 0.0 2259.0 ! [Roy et al. 1998, for C5H6+H=C5H5+H2]

C6H813=C6H6+H2 4.70E13 0.0 61600.0 ! [Orchard and Thrush 1974]

C6H814=C6H6+H2 1.05E12 0.0 42690.0 ! [Ellis and Frey 1966]

C2H3+CH2CHCHCH=C6H813 8.53E13 -1.11 820.0 ! [Westmoreland et al. 1989]

CH2CHCHCH2+C2H2=C6H814 2.30E12 0.0 35000.0 ! [Westmoreland et al. 1989 h.p. limit]

! C6H5O phenoxy reactions

C6H5O+H=C6H5OH 3.47E29 -4.303 10230.0 ! [QRRK-HR, 1 atm][c][ad]

C6H5O=C-C5H5+CO 2.51E11 0.0 43900.0 ! [Lin and Lin 1986]

C6H5+OH=C6H5O+H 5.00E13 0.0 0.0 ! [Miller and Melius 1992]

C6H5O+O=C-C5H5+CO2 1.00E13 0.0 0.0 ! [Alzueta et al. 2000]

! C6H5OH (phenol) and hydroxyphenyl (C6H4OH) reactions

C6H5OH=C-C5H6+CO 1.00E12 0.0 60802.0 ! [Horn et al. 1998]

C6H5OH+H=C6H5O+H2 1.15E14 0.0 12400.0 ! [Emdee et al. 1992]

C6H5OH+O=C6H5O+OH 2.81E13 0.0 7352.0 ! [Emdee et al. 1992]

C6H5OH+HO2=C6H5O+H2O2 3.00E13 0.0 15000.0 ! [Bittker 1991]

```

!C6H5OH+C2H3=C2H4+C6H5O      6.00E12      0.0      0.0 ! [Emdee et al. 1992]
C6H5OH+CH2CHCHCH=CH2CHCHCH2+C6H5O 6.00E12      0.0      0.0 ! [Emdee et al. 1992]
C6H5OH+CH2CHCHCH2=CH2CHCHCH2+C6H5O 6.00E12      0.0      0.0 ! [Emdee et al. 1992]
C6H5OH+OH=H2O+C6H5O      1.39E08      1.43      -962.0 ! [Shandross et al.1996]
C6H5OH+OH=H2O+C6H4OH      1.41E13      0.00      4571.0 ! [Shandross et al.1996]
C6H5OH+H=H2+C6H4OH      1.67E14      0.00      16000.0 ! [Shandross et al.1996]
C-C5H5+CO=C6H4OH      4.48E10      -0.805      51190.0 ! [QRRK-HR, 1 atm][c]
!
! Benzoquinone (o-C6H4O2 and p-C6H4O2) reactions
!
C6H5+O2=OC6H4O2+H      3.00E13      0.0      9000.0 ! [Alzueta et al. 2000]
C6H5O+O=OC6H4O2+H      8.50E13      0.0      0.0 ! [Alzueta et al. 2000]
C6H5O+O=PC6H4O2+H      8.50E13      0.0      0.0 ! [Alzueta et al. 2000]
OC6H4O2=C-C5H4O+CO      1.00E12      0.0      40000.0 ! [Alzueta et al. 2000]
PC6H4O2=C-C5H4O+CO      3.70E11      0.0      59000.0 ! [Alzueta et al. 2000]
PC6H4O2=C5H4+CO2      3.50E12      0.0      67000.0 ! [Alzueta et al. 2000]
PC6H4O2+H=C-C5H5O+CO      2.50E13      0.0      4700.0 ! [Alzueta et al. 2000]
PC6H4O2+H=C6H3O2+H2      2.00E12      0.0      8100.0 ! [Alzueta et al. 2000]
PC6H4O2+O=C6H3O3+H      1.50E13      0.0      4530.0 ! [Alzueta et al. 2000]
PC6H4O2+O=C6H3O2+OH      1.40E13      0.0      14700.0 ! [Alzueta et al. 2000]
PC6H4O2+OH=C6H3O2+H2O      1.00E06      2.0      4000.0 ! [Alzueta et al. 2000]
C6H3O2+H=PC6H4O2      1.00E14      0.0      0.0 ! [Alzueta et al. 2000]
C6H3O2+H=2C2H2+2CO      1.00E14      0.0      0.0 ! [Alzueta et al. 1998]
C6H3O2+O=C2H2+HCCO+2CO      1.00E14      0.0      0.0 ! [Alzueta et al. 1998]
C6H3O3=C2H2+HCCO+2CO      1.00E12      0.0      50000.0 ! [Alzueta et al. 1998]
C6H3O3+H=C2H2+CH2CO+2CO      1.00E14      0.0      0.0 ! [Alzueta et al. 2000]
!
! C7H7 = C6H5CH2 BENZYL reactions
!
C6H5+CH3=C6H5CH2+H      3.61E17      -0.76      20250.0 ! [QRRK-HR, 1 atm][ae]
CH2CHCHCH+CH3=C6H5CH2      7.25E18      -2.770      -13860.0 ! [QRRK-HR, 1 atm][c]
! C7H8 = C6H5CH3 TOLUENE
!
C6H5CH3+C2H3=C6H5CH2+C2H4      3.98E12      0.0      8000.0 ! [Zhang and McKinnon 1995]
CH2CHCHCH+CH3=C6H5CH3+H      2.00E11      0.0      3700.0 ! [Kern et al. 1988]
CH2CHCHCH+PC3H4=C6H5CH3+H      3.16E11      0.0      3700.0 ! [Cole et al. 1984]
!
! HYDROXYTOLUENE (C7H8O)
!
C6H5O+CH3=HOC6H4CH3      1.00E12      0.0      0.0 ! [Lin and Lin 1986]
!
! Benzaldehyde (C6H5CHO) and benzoyl (C6H5CO)
!
C6H5CHO=C6H5CO+H      3.98E15      0.0      83660.0 ! [Grela and Colussi '86]
C6H5O+CH3=C6H5OCH3      1.21E13      0.0      0.0 ! [Tsang/Hampson '86
!                                     for CH3+CH3O]
!
C6H5+CH3O=C6H5OCH3      1.21E13      0.0      0.0 ! [Tsang/Hampson '86
!                                     for CH3+CH3O]
!
! Biphenylether (C6H5OC6H5)
!
C6H5+C6H5O=C6H5OC6H5      1.21E13      0.0      0.0 ! [Tsang/Hampson '86
!                                     for CH3+CH3O]
!
! PHENYLACETYLENE (C8H6 = C6H5C2H)and phenylcarbene (C6H5CH)
!
C6H6+C2H=C6H5C2H+H      1.00E12      0.0      0 ! [Colket 1986]
C6H5+C2H2=C6H5C2H+H      1.80E16      -0.62      17435.0 ! [Richter et al. 2001]
C6H4C2H+H=C6H5C2H      1.11E16      -0.817      690 ! [Mebel et al. 2001,
!                                     for C6H5+H=C6H6]
!
C6H5+C2H=C6H5C2H      2.54E17      -1.489      1541 ! [Zhang and McKinnon 1995]
C6H5+CH2CHCHCH=C6H5C2H+C2H3      3.20E11      0.0      1350 ! [Harris et al. 1988]
CH2CHCHCH+CH4H2=C6H5C2H+H      3.16E11      0.0      1800 ! [Cole et al. 1984]
HCCCHCH+C4H2=C6H4C2H      7.00E14      -0.86      6370.0 ! [n-C4H3+C2H2,
!                                     Westmoreland et al. 1989]
!
C6H5+C2H2=C6H5CHCH      6.70E34      -7.04      10987 ! [Richter et al. 2001]
C6H5CHCH+H=C6H5C2H+H2      9.57E14      -0.25      720 ! [QRRK-HR, 1 atm][ag]
C6H5CHCH=C6H5C2H+H      2.74E22      -4.061      37040 ! [Knyazev et al. 1996b
!                                     for C2H3=C2H2+H]
!
C6H5C2H+O=C6H5CH+CO      3.60E12      0.0      633 ! [Eichholtz et al. '94]
C6H5CH+H=C6H5CH2      1.00E13      0.0      0 ! [guess, p.w.]
C6H5CH2+H=C6H5CH+H2      6.03E13      0.0      15103 ! [Baulch et al. 1992
!                                     for CH3+H=HCH(T)+H2]
!
C6H5CH+O=C6H6+CO      1.00E13      0.0      0 ! [guess, p.w.]
C6H5CH+OH=C6H6+HCO      1.00E13      0.0      0 ! [guess, p.w.]
! STYRENE (C8H8 = C6H5C2H3 PHENYLETHYLENE)
!
C6H5+C2H3=C6H5C2H3      1.50E22      -2.601      6280 ! [QRRK-HR, 1 atm][c]
C6H5CHCH+H=C6H5C2H3      1.54E13      -0.99      -6880 ! [QRRK-HR, 1 atm][ag]
C6H5+CH2CHCHCH=C6H5C2H3+C2H      3.20E11      0.0      1900 ! [Harris et al. 1988]
C6H5+CH2CHCHCH2=C6H5C2H3+C2H3      3.20E11      0.0      1900 ! [Harris et al. 1988]
CH2CHCHCH+CH2CHCHCH=C6H5C2H3      1.50E14      0.0      38000 ! [Lundgard and Heicklen 1984]
CH2CHCHCH+CH2CHCHCH=C6H5C2H3+H      3.16E11      0.0      600 ! [Cole et al. 1984]
C6H5C2H3=C6H6+C2H2      1.58E11      0.0      58440 ! [Mueller-Markgraf/Troe 1988]
C6H5C2H3+H=C6H5CHCH+H2      5.07E07      1.93      12951 ! [Knyazev et al. 1996a,
!                                     Fahr and Stein 1988]
C6H6+C2H3=C6H5C2H3+H      7.94E11      0.0      6400 ! [Fahr and Stein 1988]
C6H5+C2H2=C6H4C2H3      1.10E41      -8.61      18152 ! [Richter et al. 2001]
C6H4C2H3+H=C6H5C2H3      1.11E16      -0.817      690 ! [Mebel et al. 2001,
!
! BIPHENYL
!
C6H5+C6H5=biphenyl      2.00E26      -3.90      6320 ! [QRRK-HR, 1 atm][ah]
C6H5+C6H6=biphenyl+H      2.22E83      -20.79      46890 ! [Park et al. 1999, 1 atm][ai]
biphenyl+H=C12H9+H2      3.23E07      2.095      15842 ! [Mebel et al. 1997,
!                                     for C6H6+H]
!
biphenyl+OH=C12H9+H2O      2.11E13      0.0      4571 ! [Madronich and Felder 1985,

```



```

!
C6H5+C3H3=C6H5C3H2+H 3.00E12 0.0 0 ! [D'Anna and Violi 1998]
C6H5C3H2+C3H3=C12H9+H 3.00E12 0.0 0 ! [D'Anna and Violi 1998] (vb,2001,k/10)
C12H9+H=biphenyl 2.50E20 -1.79 2880 ! [QRRK-HR, 1 atm][aj]
!
! Naphthalene (C10H8)
!
2C-C5H5=C10H8+2H 5.00E12 0.0 8000.0 ! [0.25 * Marinov
et al. 1998]
C6H5+HCCHCCH=C10H8 6.62E35 -6.485 15420.0 ! [QRRK-HR, 1 atm][c]
C6H5CH2+C3H3=C10H8+H+H 3.00E12 0.0 0.0 ! [D'Anna and Violi 1998],vb,2001-k/10
!A1C2H*2+C2H2=C10H7*1 4.67E06 1.787 3262.0 ! [ak]
C6H4C2H+C2H2=C10H7*1 4.67E06 1.787 3262.0 ! [ak]
C6H5+HCCHCCH=C10H7*2+H 2.43E31 -4.541 36700.0 ! [QRRK-HR, 1 atm][c]
C10H8+H=C10H7*1+H2 3.23E07 2.095 15842.0 ! [Mebel et al. 1997,
for C6H6+H]
C10H8+H=C10H7*2+H2 3.23E07 2.095 15842.0 ! [Mebel et al. 1997,
for C6H6 + H]
C10H8+OH=C10H7*1+H2O 2.11E13 0.0 4571 ! [Madronich and Felder
1985, for C6H6+OH]
C10H8+OH=C10H7*2+H2O 2.11E13 0.0 4571 ! [Madronich and Felder
1985, for C6H6+OH]
C10H8+CH3=C10H7*1+CH4 2.00E12 0.0 15060.0 ! [Zhang et al. 1989,
C6H6+CH3]
C10H8+CH3=C10H7*2+CH4 2.00E12 0.0 15060.0 ! [Zhang et al. 1989,
C6H6+CH3]
C10H7*1+H=C10H8 1.11E16 -0.817 690.0 ! [Mebel et al. 2001,
for C6H5+H=C6H6]
C10H7*1+H=A2T1+H2 9.17E-22 10.28 6175.0 ! [Mebel et al. 2001,
for C6H5+H=BENZENE+H2]
C10H7*2+H=C10H8 1.11E16 -0.817 690.0 ! [Mebel et al. 2001,
for C6H5+H=C6H6]
C10H7*2+H=A2T2+H2 9.17E-22 10.28 6175.0 ! [Mebel et al. 2001,
for C6H5+H=BENZENE+H2]
!
! Formation of A21C6H4 and A22C6H4
!
A2T1+BENZENE=A21C6H4 3.20E23 -3.22 5070.0 ! [QRRK-HR, 1 atm][al]
A2T2+BENZENE=A22C6H4 3.20E23 -3.22 5070.0 ! [QRRK-HR, 1 atm][al]
!
! Naphthol and indene
!
C10H7*1+O2=C10H7O-1+O 3.40E30 -5.10 12950.0 ! [QRRK-HR, 1 atm,
for C6H5+O2]
C10H7*1+OH=C10H7O-1+H 5.00E13 0.0 0.0 ! [Miller and Melius
1992, for C6H5+OH]
C10H7*2+O2=C10H7O-2+O 3.40E30 -5.10 12950.0 ! [QRRK-HR, 1 atm,
for C6H5+O2]
C10H7*2+OH=C10H7O-2+H 5.00E13 0.0 0.0 ! [Miller and Melius
1992, for C6H5+OH]
C10H7O-1+H=C10H7OH-1 3.47E29 -4.303 10230.0 ! [QRRK-HR, 1 atm,
for C6H5OH+H]
C10H7OH-1+H=C10H7O-1+H2 1.15E14 0.0 12400.0 ! [Emdee et al. 1992,
for C6H5OH+H]
C10H8+OH=C10H7OH-1+H 1.56E24 -3.19 16900.0 ! [QRRK-HR, 1 atm,
for C6H6+OH]
C10H7OH-1+OH=C10H7O-1+H2O 1.39E08 1.43 -962.0 ! [Shandross et al. 1996,
C6H5OH+OH]
C10H7O-2+H=C10H7OH-2 3.47E29 -4.303 10230.0 ! [QRRK-HR, 1 atm,
for C6H5OH+H]
C10H7OH-2+H=C10H7O-2+H2 1.15E14 0.0 12400.0 ! [Emdee et al. 1992,
for C6H5OH+H]
C10H8+OH=C10H7OH-2+H 1.56E24 -3.19 16900.0 ! [QRRK-HR, 1 atm,
for C6H6+OH]
C10H7OH-2+OH=C10H7O-2+H2O 1.39E08 1.43 -962.0 ! [Shandross et al. 1996,
C6H5OH+OH]
C10H7O-1=INDENE*+CO 2.51E11 0.0 43900 ! [Lin and Lin 1986,
for C6H5O]
C10H7O-2=INDENE*+CO 2.51E11 0.0 43900 ! [Lin and Lin 1986,
for C6H5O]
INDENE+H=INDENE*+H2 1.48E14 0.0 13585 ! [Knyazev et al. 1996a,
for CH4+H]
INDENE+OH=INDENE*+H2O 1.57E07 1.83 2780 ! [Baulch et al. 1992,
for CH4+OH]
INDENE+O=INDENE*+OH 6.92E08 1.56 8490 ! [Baulch et al. 1992,
for CH4+O]
INDENE*+H=INDENE 2.00E14 0.0 0.0 ! [Marinov et al. 1996]
C6H5CH2+C2H2=INDENE+H 3.20E11 0.0 7000 ! [Marinov et al. 1996]
INDENE*+O=C6H5CHCH+CO 1.00E14 0.0 0.0 ! [Marinov et al. 1996]
!
! Methyl naphthalene Formation
!
C10H7*1+CH3=A2CH2-1+H 6.30E14 0.26 27320.0 ! [QRRK-HR, 1 atm][am]
C10H7*2+CH3=A2CH2-2+H 6.30E14 0.26 27320.0 ! [QRRK-HR, 1 atm][am]
C10H7*1+CH3=A2CH3-1 1.85E32 -5.70 8890.0 ! [QRRK-HR, 1 atm][am]
C10H7*2+CH3=A2CH3-2 1.85E32 -5.70 8890.0 ! [QRRK-HR, 1 atm][am]
A2CH2-1+H=A2CH3-1 1.00E14 0.0 0.0 ! [Marinov et al. 1996]
A2CH2-2+H=A2CH3-2 1.00E14 0.0 0.0 ! [Marinov et al. 1996]
A2CH3-1+H=C10H8+CH3 1.20E13 0.0 5148. ! [Marinov et al. 1996]
A2CH3-2+H=C10H8+CH3 1.20E13 0.0 5148. ! [Marinov et al. 1996]
!
! 1-and-2-naphthylacetylene
!

```

C10H7*1+C2H2=A2C2H-1+H	9.90E-6	5.59	10748. !	[Richter et al. 2001]
C10H7*2+C2H2=A2C2H-2+H	3.89E17	-0.87	19780. !	[QRRK-HR, 1 atm][an]
A2VINP+H=A2C2H-2+H2	9.57E14	-0.25	720. !	[QRRK-HR, 1 atm, for C6H5CHCH+H]
A2VINP+H=A2C2H-1+H2	9.57E14	-0.25	720. !	vb-05/30/02-[QRRK-HR, 1 atm, for C6H5CHCH+H]
! 2-vinylnaphthalene and its radical				
C10H7*2+C2H4=A2C2H3-2+H	2.51E12	0.0	6200. !	[Fahr and Stein 1988, for C6H5+C2H4]
C10H8+C2H3=A2C2H3-2+H	7.94E11	0.0	6399. !	[Fahr and Stein 1988, for C6H6+C2H3]
C10H7*2+C2H2=A2VINP	1.16E35	-7.04	11720. !	[QRRK-HR, 1 atm][an]
A2VINP=A2C2H-2+H	2.74E22	-4.061	37040. !	[knyazev et al. 1996b for C2H3=C2H2+H]
A2VINP+H=A2C2H3-2	1.54E13	-0.99	-6880. !	[QRRK-HR, 1 atm, for C6H5CHCH+H]
! Biphenylene and Acenaphthylene				
BENZYNE+BENZYNE=BIPHEN	4.60E12	0.0	0.0 !	[Porter and Steinfeld 1968]
BIPHENH=BIPHEN+H	1.30E16	0.0	33203.0 !	[Mebel et al. 1997, for C6H7=C6H6+H]
BIPHENH+H= BIPHEN+H2	6.02E12	0.0	0.0 !	[Mebel et al. 1997, for C6H7+H=C6H6+H2]
BIPHENH=A2R5+H	1.00E13	0.0	20000.0 !	[estimate, p.w.]
C10H7*1+C2H2=A2R5+H	2.29E17	-0.976	14548 !	[Richter et al. 2001]
A2R5+H=A2R5*1+H2	3.23E07	2.095	19800 !	[Mebel et al. 1997, adjusted]
A2R5+H=A2R5*3+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997]
A2R5+H=A2R5*4+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997]
A2R5+H=A2R5*5+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997]
A2R5+OH=A2R5*1+H2O	2.10E13	0.0	8600 !	[Harris et al. 1988, adjusted]
A2R5+OH=A2R5*3+H2O	2.10E13	0.0	4600 !	[Harris et al. 1988]
A2R5+OH=A2R5*4+H2O	2.10E13	0.0	4600 !	[Harris et al. 1988]
A2R5+OH=A2R5*5+H2O	2.10E13	0.0	4600 !	[Harris et al. 1988]
A2R5*1+H=A2R5	1.26E20	-1.81	2900 !	[QRRK-HR, 1 atm]
A2R5*1+H=A2R5T+H2	1.92E-14	8.65	18600 !	[QRRK-HR, 1 atm]
A2R5*1+OH=A2R5T+H2O	1.00E13	0.0	0 !	[0.5 * Lindstedt and Skevis 1994]
A2R5*1+O=A2R5T+OH	1.00E13	0.0	0 !	[0.5 * Lindstedt and Skevis 1994]
A2R5*3+H=A2R5	7.00E19	-1.73	2790 !	[QRRK-HR, 1 atm]
A2R5*4+H=A2R5	7.00E19	-1.73	2790 !	[QRRK-HR, 1 atm]
A2R5*5+H=A2R5	7.00E19	-1.73	2790 !	[QRRK-HR, 1 atm]
! Acenaphthene				
C10H7*1+C2H4=A2R5H2+H	2.51E12	0.0	6200. !	[Fahr and Stein 1988, for C6H5+C2H4]
C10H7*1+C2H2=HA2R5	4.60E41	-9.00	15525. !	[Richter et al. 2001]
HA2R5+H=A2R5+H2	1.81E12	0.0	0. !	[Tsang et al. 1986, for C2H5+H]
HA2R5+OH=A2R5+H2O	2.41E13	0.0	0. !	[Tsang et al. 1986, for C2H5+OH]
HA2R5+H=A2R5H2	1.00E14	0.0	0. !	[Sillescu 1993, for C2H5+H=C2H6]
A2R5H2+H=HA2R5+H2	5.40E02	3.5	5210. !	[Miller and Melius 1992, for C2H6+H]
A2R5H2+OH=HA2R5+H2O	8.70E09	1.05	1810. !	[Miller and Melius 1992, for C2H6+OH]
A2R5H2=A2R5+H2	4.70E13	0.0	61600. !	[Orchard and Thrush 1973 for 1,3-cyclohexadiene=C6H6+H2]
! Ethynylacenaphthylene formation				
A2R5*1+C2H2=A2R5YNE1+H	1.51E17	-0.72	20230. !	[QRRK-HR, w/o is., 1 atm]
A2R5*3+C2H2=A2R5YNE3+H	1.51E17	-0.72	20230. !	[QRRK-HR, w/o is., 1 atm]
A2R5*4+C2H2=A2R5YNE4+H	1.51E17	-0.72	20230. !	[QRRK-HR, w/o is., 1 atm]
A2R5*5+C2H2=A2R5YNE5+H	4.43E-6	5.71	11070. !	[QRRK-HR, w/ is., 1 atm]
! Cyclopenta[fg]acenaphthalene				
A2R5*5+C2H2=A2R5R5+H	4.11E15	-0.443	14420. !	[QRRK-HR, isom., 1 atm]
! PHENANTHRENE (A3)				
C12H9+C2H2=A3+H	1.87E07	1.787	3262 !	[HP-limit for 1-C10H7+C2H2, O. Mazzyar in Richter et al. 2001]
INDENE*+C-C5H5=A3+2H	5.00E12	0.0	8000 !	[0.5*Marinov et al 1997]
!!D'Anna et al, 2000,cf,418, const3.8e12, lindstedt A increase by coeff.2				
A2C2H-2+H=A2C2H-2*1+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997, for C6H6+H]
A2C2H-2+OH=A2C2H-2*1+H2O	2.11E13	0.0	4571 !	[Madronich and Felder 1985, for C6H6+OH]
A2C2H-2*1+C2H2=A3*1	4.67E06	1.787	3262 !	[HP-limit for C10H7*1+C2H2/4]
A2C2H-1+H=A2C2H-1*2+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997, for C6H6+H]
A2C2H-1+OH=A2C2H-1*2+H2O	2.11E13	0.0	4571 !	[Madronich and Felder 1985, for C6H6+OH]
A2C2H-1*2+C2H2=A3*4	4.67E06	1.787	3262 !	[HP-limit for

! C6H5C2H+C6H5=A3+H	9.55E11	0.0	4308 ! [Park et al. 1999, for C6H5+C6H6][ao]
! A1C2H*2+C6H6=A3+H	9.55E11	0.0	4308 ! [Park et al. 1999, for C6H5+C6H6][ao]
! C6H4C2H+C6H6=A3+H	9.55E11	0.0	4308 ! [Park et al. 1999, for C6H5+C6H6][ao]
! A3+H=A3*1+H2	3.23E07	2.095	15842 ! [Mebel et al. 1997, for C6H6+H]
! A3+H=A3*2+H2	3.23E07	2.095	15842 ! [Mebel et al. 1997, for C6H6+H]
! A3+H=A3*4+H2	3.23E07	2.095	15842 ! [Mebel et al. 1997, for C6H6+H]
! A3+H=A3*9+H2	3.23E07	2.095	15842 ! [Mebel et al. 1997, for C6H6+H]
! A3+OH=A3*1+H2O	2.11E13	0.0	4571 ! [Madronich and Felder 1985, for C6H6+OH]
! A3+OH=A3*2+H2O	2.11E13	0.0	4571 ! [Madronich and Felder 1985, for C6H6+OH]
! A3+OH=A3*4+H2O	2.11E13	0.0	4571 ! [Madronich and Felder 1985, for C6H6+OH]
! A3+OH=A3*9+H2O	2.11E13	0.0	4571 ! [Madronich and Felder 1985, for C6H6+OH]
! A3*1+H=A3	2.02E15	-0.30	330 ! [QRRK-HR, 1 atm][aj]
! A3*2+H=A3	2.02E15	-0.30	330 ! [QRRK-HR, 1 atm][aj]
! A3*4+H=A3	2.02E15	-0.30	330 ! [QRRK-HR, 1 atm][aj]
! A3*9+H=A3	2.02E15	-0.30	330 ! [QRRK-HR, 1 atm][aj]
! ANTHRACENE			
! A2C2H-2+H=A2C2H-2*3+H2	3.23E07	2.095	15842 ! [Mebel et al. 1997, for C6H6+H]
! A2C2H-2+OH=A2C2H-2*3+H2O	2.11E13	0.0	4571 ! [Madronich and Felder 1985, for C6H6+OH]
! A2C2H-2*3+C2H2=A3L*1	4.67E06	1.787	3262 ! [ak]
! C10H7*2+C4H2=A3L*2	4.67E06	1.787	3262 ! [ak]
! A3L + H = A3L*1 + H2	3.23E07	2.095	15842 ! [Mebel et al. 1997, for C6H6+H]
! A3L + OH = A3L*1 + H2O	2.11E13	0.0	4571 ! [Madronich and Felder 1985, for C6H6+OH]
! A3L*1+H=A3L	2.02E15	-0.30	330 ! [QRRK-HR, 1 atm, for A3*1+H=A3]
! A3L + H = A3L*2 + H2	3.23E07	2.095	15842 ! [Mebel et al. 1997, for C6H6+H]
! A3L + OH = A3L*2 + H2O	2.11E13	0.0	4571 ! [Madronich and Felder 1985, for C6H6+OH]
! A3L*2+H=A3L	2.02E15	-0.30	330 ! [QRRK-HR, 1 atm, for A3*1+H=A3]
! A3L + H = A3L*9 + H2	3.23E07	2.095	15842 ! [Mebel et al. 1997, for C6H6+H]
! A3L + OH = A3L*9 + H2O	2.11E13	0.0	4571 ! [Madronich and Felder 1985, for C6H6+OH]
! A3L*9+H=A3L	2.02E15	-0.30	330 ! [QRRK-HR, 1 atm, for A3*1+H=A3]
! A3L=A3	7.94E12	0.0	65000 ! [Colket and Seery 1994]
! ACEPHENANTHRYLENE			
! A3*1+C2H2=A3R5+H	1.83E13	0.295	14940 ! [QRRK-HR; A3 w/ iso.]
! A3*9+C2H2=A3R5+H	1.83E13	0.295	14940 ! [O. Mazyar, HP-limit]
! A2T1+BENZYLENE=A3R5	2.64E32	-4.88	42450 ! [QRRK-HR, 1 atm]
! A2T2+BENZYLENE=A3R5	2.64E32	-4.88	42450 ! [QRRK-HR, 1 atm]
! A2R5YNE4+H=A2R5YN4*5+H2	3.23E07	2.095	15842 ! [Mebel et al. 1997]
! A2R5YNE4+OH=A2R5YN4*5+H2O	2.10E13	0.0	4600 ! [Harris et al. 1988]
! A2R5YN4*5+C2H2=A3R5*7	1.87E07	1.787	3262 ! [O. Mazyar, HP-limit]
! A3R5*7 + H = A3R5	5.00E13	0.0	0 ! [estimate, p.w.]
! A2R5YNE5+H=A2R5YN5*4+H2	3.23E07	2.095	15842 ! [Mebel et al. 1997]
! A2R5YNE5+OH=A2R5YN5*4+H2O	2.10E13	0.0	4600 ! [Harris et al. 1988]
! A2R5YN5*4+C2H2=A3R5*10	1.87E07	1.787	3262 ! [O. Mazyar, HP-limit]
! A3R5*10 + H = A3R5	5.00E13	0.0	0 ! [estimate, p.w.]
! ACEANTHRYLENE			
! A3L*1+C2H2=A3LR5+H	1.83E13	0.295	14940 ! [QRRK-HR; A3 w/ iso.]
! A3L*9+C2H2=A3LR5+H	1.87E07	1.787	3262 ! [O. Mazyar, HP-limit]
! A2T1+BENZYLENE=A3LR5	3.09E36	-6.29	42180 ! [QRRK-HR, 1 atm]
! A2T2+BENZYLENE=A3LR5	3.09E36	-6.29	42180 ! [QRRK-HR, 1 atm]
! A2R5YNE3+H=A2R5YN3*4+H2	3.23E07	2.095	15842 ! [Mebel et al. 1997]
! A2R5YNE3+OH=A2R5YN3*4+H2O	2.10E13	0.0	4600 ! [Harris et al. 1988]
! A2R5YNE4+H=A2R5YN4*3+H2	3.23E07	2.095	15842 ! [Mebel et al. 1997]
! A2R5YNE4+OH=A2R5YN4*3+H2O	2.10E13	0.0	4600 ! [Harris et al. 1988]
! A2R5YN3*4+C2H2=A3LR5*5	1.87E07	1.787	3262 ! [O. Mazyar, HP-limit]
! A2R5YN4*3+C2H2=A3LR5*5	1.87E07	1.787	3262 ! [O. Mazyar, HP-limit]
! A3LR5*5 + H = A3LR5	5.00E13	0.0	0 ! [estimate, p.w.]
! CHRYSENE			
! A3*2 + C2H2 = A3C2H-2 + H	2.08E15	-0.13	20860 ! [QRRK-HR, w/o is., A3]
! A3C2H-2 + H = A3C2H-2*S + H2	3.23E07	2.095	15842 ! [Mebel et al. 1997]
! A3C2H-2 + OH = A3C2H-2*S + H2O	2.10E13	0.0	4600 ! [Harris et al. 1988]
! A3C2H-2*S + C2H2 = CHRYSEN*1	1.87E07	1.787	3262 ! [O. Mazyar, HP-limit]
! A3*1 + C2H2 = A3C2H-1 + H	4.63E-7	6.03	11850 ! [QRRK-HR, A3, w/ is.]

A3C2H-1 + H = A3C2H-1*P + H2	3.23E07	2.095	15842	!	[Mebel et al. 1997]
A3C2H-1 + OH = A3C2H-1*P + H2O	2.10E13	0.0	4600	!	[Harris et al. 1988]
A3C2H-1*P + C2H2 = CHRYSSEN*4	1.87E07	1.787	3262	!	[O. Mazyar, HP-limit]
!					
C10H7*2+C6H5C2H=CHRYSSEN+H	8.51E11	0.0	3986	!	[Park et al. 99, HP-limit]
!					
C10H8+A1C2H*2=CHRYSSEN+H	8.51E11	0.0	3986	!	[Park et al. 99, HP-limit]
!					
C10H8+C6H4C2H=CHRYSSEN+H	8.51E11	0.0	3986	!	[Park et al. 99, HP-limit]
!					
A2C2H-1*2+C6H6=CHRYSSEN+H	8.51E11	0.0	3986	!	[Park et al. 99, HP-limit]
!					
CHRYSSEN+H=CHRYSSEN*1+H2	3.23E07	2.095	15842	!	[Mebel et al. 1997]
CHRYSSEN+H=CHRYSSEN*4+H2	3.23E07	2.095	15842	!	[Mebel et al. 1997]
CHRYSSEN+H=CHRYSSEN*5+H2	3.23E07	2.095	15842	!	[Mebel et al. 1997]
CHRYSSEN+OH=CHRYSSEN*1+H2O	2.10E13	0.0	4600	!	[Harris et al. 1988]
CHRYSSEN+OH=CHRYSSEN*4+H2O	2.10E13	0.0	4600	!	[Harris et al. 1988]
CHRYSSEN+OH=CHRYSSEN*5+H2O	2.10E13	0.0	4600	!	[Harris et al. 1988]
CHRYSSEN*1 + H = CHRYSSEN	5.00E13	0.0	0	!	[estimate, p.w.]
CHRYSSEN*4 + H = CHRYSSEN	5.00E13	0.0	0	!	[estimate, p.w.]
CHRYSSEN*5 + H = CHRYSSEN	5.00E13	0.0	0	!	[estimate, p.w.]
!					
! BENZO[a]PYRENE					
!					
CHRYSSEN*4+C2H2=BAPYR+H	1.87E07	1.787	3262	!	[O. Mazyar, HP-limit]
CHRYSSEN*5+C2H2=BAPYR+H	1.87E07	1.787	3262	!	[O. Mazyar, HP-limit]
!					
! Benzo[a]anthracene					
!					
A3L*1+C2H2=A3LC2H-1+H	4.63E-7	6.03	11850	!	[QRRK-HR, A3, w/ is.]
A3LC2H-1+H=A3LC2H-1P+H2	3.23E07	2.095	15842	!	[Mebel et al. 1997]
A3LC2H-1+OH=A3LC2H-1P+H2O	2.10E13	0.0	4600	!	[Harris et al. 1988]
A3LC2H-1P+C2H2=A4*1	1.87E07	1.787	3262	!	[O. Mazyar, HP-limit]
A3L*2+C2H2=A3LC2H-2+H	2.08E15	-0.13	20860	!	[QRRK-HR, w/o is., A3]
A3LC2H-2+H=A3LC2H-2S+H2	3.23E07	2.095	15842	!	[Mebel et al. 1997]
A3LC2H-2+OH=A3LC2H-2S+H2O	2.10E13	0.0	4600	!	[Harris et al. 1988]
A3LC2H-2S+C2H2=A4*4	1.87E07	1.787	3262	!	[O. Mazyar, HP-limit]
!					
C10H7*2+C6H5C2H=A4+H	8.51E11	0.0	3986	!	[Park et al. 1999 HP-limit]
!					
C10H8+C6H4C2H=A4+H	8.51E11	0.0	3986	!	[Park et al. 1999 HP-limit]
!					
A4+H=A4*1+H2	3.23E07	2.095	15842	!	[Mebel et al. 1997]
A4+H=A4*12+H2	3.23E07	2.095	15842	!	[Mebel et al. 1997]
A4+H=A4*4+H2	3.23E07	2.095	15842	!	[Mebel et al. 1997]
A4+OH=A4*1+H2O	2.10E13	0.0	4600	!	[Harris et al. 1988]
A4+OH=A4*12+H2O	2.10E13	0.0	4600	!	[Harris et al. 1988]
A4+OH=A4*4+H2O	2.10E13	0.0	4600	!	[Harris et al. 1988]
A4*1+H=A4	5.00E13	0.0	0	!	[estimate, p.w.]
A4*4+H=A4	5.00E13	0.0	0	!	[estimate, p.w.]
A4*12+H=A4	5.00E13	0.0	0	!	[estimate, p.w.]
!					
! NAPHTHACENE					
!					
A3LC2H-2+H=A3LC2H-2P+H2	3.23E07	2.095	15842	!	[Mebel et al. 1997]
A3LC2H-2+OH=A3LC2H-2P+H2O	2.10E13	0.0	4600	!	[Harris et al. 1988]
A3LC2H-2P+C2H2=A4L*S	1.87E07	1.787	3262	!	[O. Mazyar, HP-limit]
A4L*S+H=A4L	5.00E13	0.0	0	!	[estimate, p.w.]
!					
! Benzo[b]fluoranthene					
!					
A3*1+C6H5=BBFLUOR+H+H	5.00E12	0.0	0	!	[Marinov et al. 1996]
A3*1+C6H6=BBFLUOR+H2+H	4.00E11	0.0	4000	!	[Marinov et al. 1996]
A3*9+C6H5=BBFLUOR+H+H	5.00E12	0.0	0	!	[Marinov et al. 1996]
A3*9+C6H6=BBFLUOR+H2+H	4.00E11	0.0	4000	!	[Marinov et al. 1996]
!					
! Benzo[k]fluoranthene					
!					
C10H7*2+C10H7*1=BKFLUOR+H+H	5.00E12	0.0	0	!	[Marinov et al. 1996]
C10H8+C10H7*2=BKFLUOR+H2+H	4.00E11	0.0	4000	!	[Marinov et al. 1996]
C10H8+C10H7*1=BKFLUOR+H2+H	4.00E11	0.0	4000	!	[Marinov et al. 1996]
!					
! Indeno[1,2,3-cd]pyrene					
!					
PYRENE*1+C6H5=INPYR+H+H	5.00E12	0.0	0	!	[Marinov et al. 1996]
PYRENE*1+C6H6=INPYR+H2+H	4.00E11	0.0	4000	!	[Marinov et al. 1996]
BBFLUOR+H=BBFLUOR*S+H2	3.23E07	2.095	15842	!	[Mebel et al. 1997]
BBFLUOR+OH=BBFLUOR*S+H2O	2.10E13	0.0	4600	!	[Harris et al. 1988]
BBFLUOR*S+C2H2=INPYR+H	1.87E07	1.787	3262	!	[O. Mazyar, HP-limit]
!					
! Cyclopenta[def]phenanthrene					
!					
A3*4+CH3=A3CH2+H	5.00E13	0.0	0	!	[Marinov et al. 1996]
A3CH2+H=A3CH3	1.00E14	0.0	0	!	[Marinov et al. 1996]
A3CH3+H=A3CH2+H2	3.98E02	3.44	3120	!	[Park and Lin 1997]
A3CH3+H=A3+CH3	5.78E13	0.0	8090	!	[Park and Lin 1997]
A3CH3+OH=A3CH2+H2O	1.26E13	0.0	2583	!	[Emdee et al. 1992]
A3CH2 = A3CH2R+H	1.00E13	0.0	12000	!	[estimate, p.w.]
!					
! Benzo[a]fluorene					
!					
C10H8+C6H5CH2=BENZNAP+H	1.20E12	0.0	15940	!	[Robough and Tsang 1986]

C10H7*2+C6H5CH2=BENZNAP	1.19E13	0.0	220 !	[Yu and Lin 1994b]
BENZNAP+H=BENZNAP*P+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997]
BENZNAP+OH=BENZNAP*P+H2O	2.10E13	0.0	4600 !	[Harris et al. 1988]
BENZNAP*P=C17H12+H	1.00E13	0.0	12000 !	[estimate, p.w.]
! FLUORENE				
C6H6+C6H5CH2=BENZYLH+H	1.20E12	0.0	15940 !	[Robaugh and Tsang 1986]
C6H5+C6H5CH2=BENZYLH	1.19E13	0.0	220 !	[Yu and Lin 1994b]
BENZYLH+H=BENZYLH*H2	3.23E07	2.095	15842 !	[Mebel et al. 1997]
BENZYLH+OH=BENZYLH*H2O	2.10E13	0.0	4600 !	[Harris et al. 1988]
BENZYLH*H=FLUORENE+H	4.00E11	0.0	12000 !	[estimate, p.w.]
! 2-phenylnaphthalene				
C10H7*2+C6H5=A2C6H5-2	1.19E17	-1.16	1990 !	[QRRK-HR, 1 atm]
C10H7*2+C6H6=A2C6H5-2+H	2.22E83	-20.79	46890 !	[Park et al. 1999]
C10H8+C6H5=A2C6H5-2+H	2.22E83	-20.79	46890 !	[Park et al. 1999]
! FLUORANTHENE				
C10H7*1+C6H5=FLTHN+H+H	1.39E13	0.0	111 !	[Park and Lin 1997]
C10H7*1+C6H6=FLTHN+H+H2	8.51E11	0.0	3986 !	[Park et al. 1999]
! HP-limit				
C10H8+C6H5=FLTHN+H+H2	8.51E11	0.0	3986 !	[Park et al. 1999]
! HP-limit				
A2T1+BENZYNE=FLTHN	1.34E23	-2.76	22470 !	[QRRK-HR, 1 atm]
A2T2+BENZYNE=FLTHN	1.34E23	-2.76	22470 !	[QRRK-HR, 1 atm]
A2R5YNE1+H=A2R5YN1*2+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997]
A2R5YNE1+OH=A2R5YN1*2+H2O	2.10E13	0.0	4600 !	[Harris et al. 1988]
A2R5YN1*2+C2H2=FLTHN*7	1.87E07	1.787	3262 !	[O. Mazyar, HP-limit]
FLTHN+H=FLTHN*1+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997]
FLTHN+OH=FLTHN*1+H2O	2.10E13	0.0	4600 !	[Harris et al. 1988]
FLTHN+H=FLTHN*3+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997]
FLTHN+OH=FLTHN*3+H2O	2.10E13	0.0	4600 !	[Harris et al. 1988]
FLTHN*7+H=FLTHN	5.00E13	0.0	0 !	[estimate, p.w.]
FLTHN*1+H=FLTHN	5.00E13	0.0	0 !	[estimate, p.w.]
FLTHN*3+H=FLTHN	5.00E13	0.0	0 !	[estimate, p.w.]
! Isomerizations				
A21C6H4=FLTHN	8.51E12	0.0	62860 !	[Brouwer and Troe 1988]
A22C6H4=A3LR5	8.51E12	0.0	62860 !	[Brouwer and Troe 1988]
A3R5=FLTHN	8.51E12	0.0	62860 !	[Brouwer and Troe 1988]
A3LR5=A3R5	8.51E12	0.0	62860 !	[Brouwer and Troe 1988]
A3LR5=FLTHN	8.51E12	0.0	62860 !	[Brouwer and Troe 1988]
! cyclopenta[cd]fluoranthene, benzo[ghi]fluoranthene, ! cyclopentabenz[ghi]fluoranthene and cyclopentacorannulene				
FLTHN*3+C2H2=CPCDFLT+H	1.43E13	0.353	15790 !	[QRRK-HR, A4, 1 atm]
CPCDFLT+H=CPCDFLT*S+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997]
CPCDFLT+OH=CPCDFLT*S+H2O	2.10E13	0.0	4600 !	[Harris et al. 1988]
CPCDFLT*S+C2H2=BGHIFR+H	1.87E07	1.787	3262 !	[O. Mazyar, HP-limit]
BGHIFR+C2H2=BGHIFR+H	1.43E13	0.353	15790 !	[QRRK-HR, A4, 1 atm]
BGHIFR+H=BGHIFR*S+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997]
BGHIFR+OH=BGHIFR*S+H2O	2.10E13	0.0	4600 !	[Harris et al. 1988]
BGHIFR*S+C2H2=COR1+H	1.87E07	1.787	3262 !	[O. Mazyar, HP-limit]
! PYRENE				
A3*4+C2H2=PYRENE+H	1.87E07	1.787	3262 !	[O. Mazyar, HP-limit]
! C6H4C2H+C6H5C2H= PYRENE + H				
8.51E11	0.0	3986 !	[Park et al. 1999]	
! HP-limit				
PYRENE+H=PYRENE*1+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997]
PYRENE+OH=PYRENE*1+H2O	2.10E13	0.0	4600 !	[Harris et al. 1988]
PYRENE+H=PYRENE*2+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997]
PYRENE+OH=PYRENE*2+H2O	2.10E13	0.0	4600 !	[Harris et al. 1988]
PYRENE+H=PYRENE*4+H2	3.23E07	2.095	15842 !	[Mebel et al. 1997]
PYRENE+OH=PYRENE*4+H2O	2.10E13	0.0	4600 !	[Harris et al. 1988]
PYRENE*1+H=PYRENE	5.00E13	0.0	0 !	[estimate, p.w.]
PYRENE*2+H=PYRENE	5.00E13	0.0	0 !	[estimate, p.w.]
PYRENE*4+H=PYRENE	5.00E13	0.0	0 !	[estimate, p.w.]
! Pyrene-Oxidation				
PYRENE+OH=A3*4+CH2CO	1.30E13	0.0	10600 !	[Wang and Frenklach 1997]
PYRENE+O=A3*4+HCCO	2.20E13	0.0	4530 !	[Wang and Frenklach 1997]
PYRENE*4+O2=A3*4+2CO	2.10E12	0.0	7470 !	[Wang and Frenklach 1997]
! Ethynyl-pyrenes				
PYRENE*1+C2H2=PYC2H-1+H	7.92E-6	5.71	13330 !	[QRRK-HR, A4, w/ is.]
PYRENE*2+C2H2=PYC2H-2+H	1.25E17	-0.56	22560 !	[QRRK-HR, A4(si.= 2)]
PYRENE*4+C2H2=PYC2H-4+H	7.92E-6	5.71	13330 !	[QRRK-HR, A4, w/ is.]
! Benzo[ghi]fluoranthene				
FLTHN*1 + C2H2 = BGHIF + H	1.87E07	1.787	3262 !	[O. Mazyar, HP-limit]
FLTHN*7 + C2H2 = BGHIF + H	1.87E07	1.787	3262 !	[O. Mazyar, HP-limit]

BGHIF+ H = BGHIF- + H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
BGHIF + OH = BGHIF- + H2O	2.10E13	0.0	4600	[Harris et al. 1997]
! Cyclopenta[cd]pyrene				
PYRENE*1+C2H2=CPCDPYR+H	1.43E13	0.353	15790	[QRRK-HR, A4, 1 atm]
PYRENE*4+C2H2=CPCDPYR+H	1.43E13	0.353	15790	[QRRK-HR, A4, 1 atm]
CPCDPYR+H=CPCDPYR*S+H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
CPCDPYR+OH=CPCDPYR*S+H2O	2.10E13	0.0	4600	[Harris et al. 1988]
! Dicyclopenta[cd,fg]pyrene				
CPCDPYR*S+C2H2=DCPCDFG+H	1.43E13	0.353	15790	[QRRK-HR, A4, 1 atm]
BGHIF- + C2H2 = COR + H	1.87E07	1.787	3262	[O. Mazyar, HP-limit]
CPCDPYR*S+C2H2=COR+H	1.43E13	0.353	15790	[QRRK-HR, A4, 1 atm]
COR + H = COR- + H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
COR + OH = COR- + H2O	2.10E13	0.0	4600	[Harris et al. 1988]
!				
COR- + C2H2 = COR1 + H	1.43E13	0.353	15790	[QRRK-HR, A4, 1 atm]
COR1 + H = COR1- + H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
COR1 + OH = COR1- + H2O	2.10E13	0.0	4600	[Harris et al. 1988]
!				
COR1- + C2H2 = COR2 + H	1.87E07	1.787	3262	[O. Mazyar, HP-limit]
COR2 + H = COR2- + H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
COR2 + OH = COR2- + H2O	2.10E13	0.0	4600	[Harris et al. 1988]
!				
COR2- + C2H2 = COR3 + H	1.87E07	1.787	3262	[O. Mazyar, HP-limit]
COR3 + H = COR3- + H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
COR3 + OH = COR3- + H2O	2.10E13	0.0	4600	[Harris et al. 1988]
!				
COR3- + C2H2 = COR4 + H	1.87E07	1.787	3262	[O. Mazyar, HP-limit]
COR4 + H = COR4- + H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
COR4 + OH = COR4- + H2O	2.10E13	0.0	4600	[Harris et al. 1988]
COR4- + C2H2 = HB + H	1.87E07	1.787	3262	[O. Mazyar, HP-limit]
! Benzo[a]pyrene				
A4*1+C2H2=BAPYR+H	1.87E07	1.787	3262	[O. Mazyar, HP-limit]
A4*12+C2H2=BAPYR+H	1.87E07	1.787	3262	[O. Mazyar, HP-limit]
PYC2H-1 + H=PYC2H-1*P + H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
PYC2H-1 + OH=PYC2H-1*P + H2O	2.10E13	0.0	4600	[Harris et al. 1988]
PYC2H-2 + H = PYC2H-2*S + H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
PYC2H-2 + OH=PYC2H-2*S + H2O	2.10E13	0.0	4600	[Harris et al. 1988]
PYC2H-1*P + C2H2 = BAPYR*S	1.87E07	1.787	3262	[O. Mazyar, HP-limit]
PYC2H-2*S + C2H2 = BAPYR*S	1.87E07	1.787	3262	[O. Mazyar, HP-limit]
BAPYR*S + H = BAPYR	5.00E13	0.0	0	[estimate, p.w.]
!				
A2C2H-1*2+C6H5C2H=BAPYR+H	8.51E11	0.0	3986	[Park et al. 1999 HP-limit]
!				
A2C2H-1+C6H4C2H=BAPYR+H	8.51E11	0.0	3986	[Park et al. 1999 HP-limit]
! Benzo[a]pyrene-Oxidation				
!				
BAPYR+OH=PYC2H-2+CH2CO+H	6.50E12	0.0	10600	[wang and Frenklach 1997]
BAPYR+O=PYC2H-2+CH2CO	1.10E13	0.0	4530	[wang and Frenklach 1997]
BAPYR*S+O2=PYC2H-2+HCO+CO	2.10E12	0.0	7470	[wang and Frenklach 1997]
PYC2H-2+OH=PYRENE*2+CH2CO	2.18E-4	4.5	-1000	[wang and Frenklach 1997]
PYC2H-2+O=PYRENE*2+HCCO	2.04E07	2.0	1900	[wang and Frenklach 1997]
! Benzo[e]pyrene				
!				
PYC2H-4+H=PYC2H-4*S+H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
PYC2H-4+OH=PYC2H-4*S+H2O	2.10E13	0.0	4600	[Harris et al. 1988]
PYC2H-4*S+C2H2=BEPYREN*S	1.87E07	1.787	3262	[O. Mazyar, HP-limit]
BEPYREN*S + H = BEPYREN	5.00E13	0.0	0	[estimate, p.w.]
! Perylene and benzo[ghi]perylene				
!				
BEPYREN+H=BEPYREN*S+H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
BEPYREN+OH=BEPYREN*S+H2O	2.10E13	0.0	4600	[Harris et al. 1988]
BEPYREN*S+C2H2=BGHIPER+H	1.87E07	1.787	3262	[O. Mazyar, HP-limit]
C10H7*1+C10H7*1=PERYLEN+2H	1.39E13	0.0	111	[Park and Lin 1997]
C10H7*1+C10H8=PERYLEN+H2+H	8.51E11	0.0	3986	[Park et al. 1999 HP-limit]
!				
PERYLEN+H=PERYLEN*S+H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
PERYLEN+OH=PERYLEN*S+H2O	2.10E13	0.0	4600	[Harris et al. 1988]
PERYLEN*S+C2H2=BGHIPER+H	1.87E07	1.787	3262	[O. Mazyar, HP-limit]
! Cyclopenta[cd,fg]benzo[ghi]perylene				
!				
BGHIPER+H=BGHIPE*S1+H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
BGHIPER+OH=BGHIPE*S1+H2O	2.10E13	0.0	4600	[Harris et al. 1988]
BGHIPE*S1+C2H2=CPBPER+H	1.43E13	0.353	15790	[QRRK-HR, A4, 1 atm]
! ANTHANTHRACENE				
!				
BAPYR + H = BAPYR*S + H2	3.23E07	2.095	15842	[Mebe] et al. 1997]
BAPYR + OH = BAPYR*S + H2O	2.10E13	0.0	4600	[Harris et al. 1988]
BAPYR*S + C2H2 = ANTHAN + H	1.87E07	1.787	3262	[O. Mazyar, HP-limit]
! Anthanthracene-Oxidation				
!				

ANTHAN+H=ANTHAN*S+H2 3.23E07 2.095 15842 ! [Mebe] et al. 1997
 ANTHAN+OH=ANTHAN*S+H2O 2.10E13 0.0 4600 ! [Harris et al. 1988]
 ANTHAN+OH=BAPYR*S+CH2CO 1.30E13 0.0 10600 ! [Wang and Frenklach
 ! 1997]
 ANTHAN+O=BAPYR*S+HCCO 2.20E13 0.0 4530 ! [Wang and Frenklach
 ! 1997]
 ANTHAN*S+O2=BAPYR*S+2CO 2.10E12 0.0 7470 ! [Wang and Frenklach
 ! 1997]
 ! CORONENE
 BGHIPE*S1+C2H2=CORONEN+H 1.87E07 1.787 3262 ! [O. Mazyar, HP-limit]
 CH2*+HCO=CO+CH3 1.81E13 0.0 0.0 ! [Zhang and McKinnon 1995]
 CH2+HCO=CH3+CO 1.81E13 0.0 0.0 ! [Zhang and McKinnon 1995]
 !above-gri CH2*+CO2=CH2O+CO 3.00E12 0.0 0.0 ! [Miller and Melius 1992]
 CH2+CO2=CH2O+CO 1.10E11 0.0 1000.0 ! [Miller and Melius 1992]
 2CH2=C2H4 1.11E20 -3.43 2070.0 ! [Westmoreland 1986]
 !gri CH2+CH3=C2H4+H 4.20E13 0.0 0.0 ! [Westmoreland 1986]
 C2H4+C2H2=2C2H3 2.41E13 0.0 68360.0 ! [Tsang et al. 1986]
 C2H4+O2=C2H3+HO2 4.22E13 0.0 57594.0 ! [Zhang and McKinnon 1995]
 2C2H4=C2H5+C2H3 4.82E14 0.0 71539.0 ! [Tsang et al. 1986]
 ! Reactions of n-C4H5
 CH2CHCHCH = CH2CHCCH2 1.5E+67 -16.89 59100. !97WAN/FRE
 CH2CHCHCH+H = CH2CHCCH2+H 3.1E+26 -3.35 17423. !97WAN/FRE
 CH2CHCHCH+H = CH2CHCCH+H2 1.5E+13 0.00 0. !97WAN/FRE
 CH2CHCHCH+OH = CH2CHCCH+H2O 2.0E+12 0.00 0. !97WAN/FRE
 CH2CHCHCH+HCO = CH2CHCCH2+CO 5.00E+12 0.0 0. !97WAN/FRE
 CH2CHCHCH+HO2 = C2H3+CH2CO+OH 6.60E+12 0.0 0. !97WAN/FRE
 CH2CHCHCH+H2O2 = CH2CHCCH2+HO2 1.21E+10 0.0 -596. !97WAN/FRE
 CH2CHCHCH+HO2 = CH2CHCCH2+O2 6.00E+11 0.0 0. !Estimated
 CH2CHCHCH+O2 = CH2CHCCH+O 3.00E+11 0.29 11. ! = C2H3+O2=>CH2CHO+O-large K, check marinov
 CH2CHCHCH+O2 = HCO+CH2CHCHO 9.20E+16 -1.39 1010. ! = C2H3+O2=>HCO+CH2O
 CH2CHCHCH+C2H2 = C6H6+H 1.60E+16 -1.33 5400. !97WAN/FRE
 CH2CHCHCH+C2H3 = C6H6+H2 1.84E-13 7.07 -3611. !89WES/DEA
 ! Reactions of i-C4H5
 CH2CHCCH2+H = CH2CHCCH+H2 3.0E+13 0.00 0. !97WAN/FRE
 CH2CHCCH2+H = C3H3+CH3 2.00E+13 0.0 2000.0 !Estimated
 CH2CHCCH2+OH = CH2CHCCH+H2O 4.0E+12 0.00 0. !97WAN/FRE
 CH2CHCCH2+HCO = CH2CHCCH2+CO 5.00E+12 0.0 0. !97WAN/FRE
 CH2CHCCH2+HO2 = CH2CHCCH2+O2 6.00E+11 0.00 0. !Estimated
 CH2CHCCH2+HO2 = C2H3+CH2CO+OH 6.60E+12 0.0 0. !97WAN/FRE
 CH2CHCCH2+H2O2 = CH2CHCCH2+HO2 1.21E+10 0.000 -596. !97WAN/FRE
 CH2CHCCH2+O2 = CH2CO+CH2CHO 2.16E+10 0.00 2500. ! = C4H5-2+O2
 CH2CHCCH2+CH2CHCCH = C6H5C2H3+H 5.00E+14 0.0 25000. !Estimated
 ! Reactions of C4H5-2
 CH3CCCH2 = CH2CHCCH2 1.5E+67 -16.89 59100. ! = n-C4H5=>i-C4H5
 CH3CCCH2+HO2 = OH+C2H2+CH3CO 8.00E+11 0.0 0. !Estimated
 CH3CCCH2+O2 = CH3CO+CH2CO 2.16E+10 0.00 2500. !92SLA/BEN
 CH3CCCH2+C2H2 = C6H6+H 5.00E+14 0.00 25000.0 !Estimated
 CH3CCCH2+C2H4 = C-C5H6+CH3 5.00E+14 0.000 25000.0 !Estimated
 CH3CCCH2+CH2CHCCH = C6H5C2H3+H 5.00E+14 0.0 25000. !Estimated
 ! Reactions of 1,3-C4H6
 CH2CHCHCH2 = CH2CHCCH2+H 5.70E+36 -6.27 112353. !97WAN/FRE
 CH2CHCHCH2 = CH2CHCHCH+H 5.30E+44 -8.62 123608. !97WAN/FRE
 CH2CHCHCH2 = CH2CHCCH+H2 2.50E+15 0.0 94700.0 !96HID/HIG
 CH2CHCHCH2+H = CH2CHCHCH+H2 1.33E+06 2.53 12240.0 ! = C2H4+H
 CH2CHCHCH2+H = CH2CHCCH2+H2 6.65E+05 2.53 9240.0 !Estimated
 CH2CHCHCH2+H = pc3H4+CH3 2.00E+12 0.0 7000.0 !Estimated
 CH2CHCHCH2+H = ac3H4+CH3 2.00E+12 0.0 7000.0 !Estimated
 CH2CHCHCH2+O = CH2CHCHCH+OH 0.75E+07 1.900 3740 ! = C2H4+O
 CH2CHCHCH2+O = CH2CHCCH2+OH 0.75E+07 1.900 3740 ! = C2H4+O
 CH2CHCHCH2+O = CH3CHCHCO+H 1.5E+08 1.45 -860.0 !93ADU/FON#
 CH2CHCHCH2+O = CH2CHCHCHO+H 4.5E+08 1.45 -860.0 !93ADU/FON#
 CH2CHCHCH2+OH = CH2CHCHCH+H2O 6.20E+06 2.0 3430.0 !88LIU/MUL
 CH2CHCHCH2+OH = CH2CHCCH2+H2O 3.10E+06 2.0 430.0 !Estimated
 CH2CHCHCH2+CH3 = CH2CHCHCH+CH4 2.00E+14 0.0 22800.0 !96HID/HIG
 CH2CHCHCH2+CH3 = CH2CHCCH2+CH4 1.00E+14 0.0 19800.0 !96HID/HIG
 CH2CHCHCH2+C2H3 = CH2CHCHCH+C2H4 5.00E+13 0.0 22800.0 !96HID/HIG
 CH2CHCHCH2+C2H3 = CH2CHCCH2+C2H4 2.50E+13 0.0 19800.0 !96HID/HIG
 CH2CHCHCH2+C3H3 = CH2CHCHCH+ac3H4 1.00E+13 0.0 22500.0 !96HID/HIG
 CH2CHCHCH2+C3H3 = CH2CHCCH2+ac3H4 0.50E+13 0.0 19500.0 !96HID/HIG
 CH2CHCHCH2+ac3H5 = CH2CHCHCH+C3H6 1.00E+13 0.0 22500.0 !Estimated
 CH2CHCHCH2+ac3H5 = CH2CHCCH2+C3H6 0.50E+13 0.0 19500.0 !Estimated
 CH2CHCHCH2+C2H3 = C6H6+H2+H 5.62E+11 0.0 3240. !95LEU/LIN
 ! Reactions of 1,2-C4H6
 C4H612 = CH2CHCHCH2+H 4.20E+15 0.0 92600.0 !95LEU/LIN
 C4H612+H = CH2CHCHCH2+H 2.00E+13 0.0 4000.0 !Estimated
 C4H612+H = CH2CHCCH2+H2 1.70E+05 2.5 2490.0 ! = C3H6+H
 C4H612+H = ac3H4+CH3 2.00E+13 0.0 2000.0 !97WAN/FRE
 C4H612+H = pc3H4+CH3 2.00E+13 0.0 2000.0 !97WAN/FRE
 C4H612+CH3 = CH2CHCHCH2+CH4 7.00E+13 0.0 18500.0 !88KER/SIN
 C4H612+O = CH2CO+C2H4 1.20E+08 1.65 327.0 ! = C3H6+O
 C4H612+O = CH2CHCCH2+OH 1.80E+11 0.70 5880.0 ! = C3H6+O
 C4H612+OH = CH2CHCCH2+H2O 3.10E+06 2.00 -298.0 ! = C3H6+OH
 C4H612 = CH2CHCHCH2 3.00E+13 0.0 65000.0 !96HID/HIG
 ! Reactions of C4H6-2

```

!
C4H6-2 = CH2CHCHCH2      3.00E+13  0.000 65000.00 !96HID/HIG
C4H6-2 = C4H6I2          3.00E+13  0.000 67000.00 !96HID/HIG
C4H6-2+H = C4H6I2+H      2.00E+13  0.0 4000.0 !Estimated
C4H6-2+H = CH3CCCH2+H2    3.40E+05  2.5 2490.0 != C3H6+H
C4H6-2+H = CH3+pc3H4      2.60E+5  2.500 1000.00 !96HID/HIG
C4H6-2 = H+CH3CCCH2       5.00E+15  0.000 87300.00 !96HID/HIG
C4H6-2+CH3 = CH3CCCH2+CH4 1.40E+14  0.0 18500.0 !Estimated
!
Reactions of C4H4O
Reactions of CH3CHCHCHO
!
CH3CHCHCHO = C3H6+CO      3.90E+14  0.0 69000.0 != HCCCHO=>C2H2+CO
CH3CHCHCHO+H = CH2CHCHCHO+H2 1.70E+5  2.5 2490.00 != C3H6+H=>aC3H5+H2
CH3CHCHCHO+H = CH3CHCHCHO+H2 1.00E+5  2.5 2490.00 !Estimated
CH3CHCHCHO+H = CH3+CH2CHCHO 4.00E+21 -2.390 11180.00!= C3H6+H=>C2H4+CH3
CH3CHCHCHO+H = C3H6+HCO 4.00E+21 -2.390 11180.00!= C3H6+H=>C2H4+CH3
CH3CHCHCHO+CH3 = CH2CHCHCHO+CH4 2.10E+00 3.50 5675.0 != C3H6+CH3=>aC3H5+CH4
CH3CHCHCHO+CH3 = CH3CHCHCO+CH4 1.10E+00 3.50 5675.0 !Estimated
CH3CHCHCHO+CH2H3 = CH2CHCHCHO+CH4 2.210E+00 3.50 4682.00!=C3H6+CH2H3=>aC3H5+CH4
CH3CHCHCHO+CH2H3 = CH3CHCHCO+CH4 1.110E+00 3.50 4682.00!Estimated
!
Reactions of CH3CHCHCO
!
CH3CHCHCO = pc3H5+CO      1.00E14  0.0 30000.00 !Estimated
CH3CHCHCO+H = CH3CHCHCHO 1.00E+14  0.0 00.0 !Estimated
!
Reactions of CH2CHCHCHO
!
CH2CHCHCHO = ac3H5+CO     1.00E14  0.0 25000.00 !Estimated
CH2CHCHCHO+H = CH3CHCHCHO 1.00E+14  0.0 00.0 !Estimated
!
Reactions of C2H3CHO
!
!07/11/02, marinov CH2CHCHO+H = C2H4+HCO 1.08E+11 0.454 5820.00 != C2H4+H
CH2CHCHO+O = C2H3+OH+CO 3.00E+13 0.00 3540.00 != CH2O+O
CH2CHCHO+O = CH2O+CH2CO 1.90E+07 1.80 220.00 != C2H4+O
CH2CHCHO+OH = C2H3+H2O+CO 3.43E+09 1.18 -447.00 != CH2O+OH
CH2CHCHO+CH3 = CH2CHCO+CH4 2.00E+13 0.000 11000.00 !Estimated
CH2CHCHO+CH2H3 = CH2CHCHCH2+HCO 2.80E+21 -2.440 14720.00 != C2H4+CH2H3
!
Reactions of CH2CHCO
CH2CHCO+H = CH2CHCHO      1.00E+14  0.000 00.00 !Estimated
CH2+C2H2=C3H3+H          1.20E+13  0.0 6600.0 ! Miller 1992
CH2*+C2H2=C3H3+H         1.50E+14  0.0 0.0 ! CanOsa-Mas85
CH2*+C2H4=aC3H5+H        1.30E+14  0.0 0.0 ! CanOsa-Mas85
C2H3+CH3=C3H6            4.46E+56 -13.0 13865.0 ! (i)
C2H3+C2H2=CH2CHCCH+H    2.00E+12  0.0 5000.0 ! Miller 1992
C2H3+C2H4=CH2CHCHCH2+H  5.00E+11  0.0 7304.0 ! Tsang 1986
C2H3+C2H3=CH2CHCCH2+H   7.00E+13  0.0 0.0 ! FaHr 1991
C2H4+C2H2=C4H2+H        9.64E+13  0.0 0.0 ! FarHat 1993
C2H4+C2H4=CH2CHCCH+H    1.20E+13  0.0 0.0 ! Tsang 1986
HCCO+C2H2=C3H3+CO       1.00E+11  0.0 3000.0 ! Miller 1992
C3H8(+M)=C2H5+CH3(+M)   7.90E+22 -1.8 88629.0 ! Tsang 1988
low / 7.237E+27 -2.88 67448.0 / ! Al-Alami 1983
trOe /1.0 1.0E-15 1500.0 1.0E+15/
H2O/5.0/ CO2/3.0/ CO/2.0/ H2/2.0/
C3H8+O2=iC3H7+HO2       4.00E+13  0.0 48610.0 ! Tsang 1988
C3H8+O2=nC3H7+HO2       4.00E+13  0.0 51360.0 ! Tsang 1988
C3H8+HO2=nC3H7+H2O2     4.76E+04  2.55 16492.0 ! Tsang 1988
C3H8+HO2=iC3H7+H2O2     9.64E+03  2.6 13909.0 ! Tsang 1988
C3H8+OH=nC3H7+H2O       3.16E+07  1.8 934.0 ! COHEN 1991
C3H8+OH=iC3H7+H2O       7.08E+06  1.9 -159.0 ! COHEN 1991
C3H8+O=nC3H7+OH         3.73E+06  2.4 5504.0 ! COHEN 1986
C3H8+O=iC3H7+OH         5.48E+05  2.5 3139.0 ! COHEN 1986
C3H8+H=iC3H7+H2        1.30E+06  2.4 4471.0 ! Tsang 1988
C3H8+H=nC3H7+H2        1.33E+06  2.54 6756.0 ! Tsang 1988
C3H8+CH3=nC3H7+CH4      9.04E-01  3.65 7153.0 ! Tsang 1988
C3H8+CH3=iC3H7+CH4      1.51E+00  3.46 5480.0 ! Tsang 1988
C3H8+C2H3=iC3H7+C2H4    1.00E+03  3.1 8830.0 ! Tsang 1988
C3H8+C2H3=nC3H7+C2H4    6.00E+02  3.3 10500.0 ! Tsang 1988
!mit C3H8+C2H5=iC3H7+C2H6 1.51E+00 3.46 7470.0 ! Tsang 1988
!mit C3H8+C2H5=nC3H7+C2H6 9.03E-01 3.65 9140.0 ! Tsang 1988
!mit C3H8+aC3H5=C3H6+nC3H7 2.35E+02 3.3 19842.0 ! Tsang 1988
C3H8+aC3H5=C3H6+iC3H7   7.83E+01  3.3 18169.0 ! Tsang 1988
nC3H7(+M)=C2H4+CH3(+M)  1.23E+13 -0.1 30202.0 ! BenCsurra 1992
low / 5.485E+49 -10.0 35766.0 / ! BenCsurra 1992
trOe / 2.17 1.0E-15 251.0 1185.0 /
H2O /5.0/ H2/2.0/ CO2/3.0/ CO/2.0/
nC3H7+O2=C3H6+HO2       3.58E+09  0.0 -3532.0 ! Dagaut 1992
iC3H7+O2=C3H6+HO2       6.10E+20 -2.86 7910.0 ! (p)
C3H6+H(+M)=iC3H7(+M)    5.70E+09  1.16 874.0 ! Seakins 1993
low / 1.64E+54 -11.1 9364.0 / ! Marinov 1996
trOe / 1.0 1.0E-15 260.0 3000.0 /
H2O /5.0/ H2/2.0/ CO2/3.0/ CO/2.0/
iC3H7+H=C2H5+CH3        5.00E+13  0.0 0.0 ! Tsang 1988
nC3H7+H=C2H5+CH3        1.00E+14  0.0 0.0 ! Tsang 1988
pc3H5+H=C3H6            1.e14  0. 0. !98MAR/pit,vb
sc3H5+H=C3H6            5.e13  0. 0. !98MAR/pit,vb
C3H6=C2H2+CH4           2.50E+12  0.0 70000.0 ! Hidaka 1992
C3H6=ac3H4+H2           3.00E+13  0.0 80000.0 ! Hidaka 1992
C3H6+HO2=ac3H5+H2O2     9.64E+03  2.6 13910.0 ! Tsang 1991

```


C3H6+OH+O2=CH3CHO+CH2O+OH 3.00E+10 0.0 -8280.0 ! Dagaut 1992
 C3H6+OH=ac3H5+H2O 3.12E+06 2.0 -298.0 ! Tsang 1991
 C3H6+OH=sc3H5+H2O 1.11E+06 2.0 1451.0 ! Tsang 1991
 C3H6+OH=pc3H5+H2O 2.11E+06 2.0 2778.0 ! Tsang 1991
 C3H6+O=CH3CHCO+H+H 5.01E+07 1.76 76.0 ! Tsang 1991
 C3H6+O=C2H5+HCO 1.58E+07 1.76 -1216.0 ! Tsang 1991
 C3H6+O=ac3H5+OH 5.24E+11 0.7 5884.0 ! Tsang 1991
 C3H6+O=pc3H5+OH 1.20E+11 0.7 8959.0 ! Tsang 1991
 C3H6+O=sc3H5+OH 6.03E+10 0.7 7632.0 ! Tsang 1991
 C3H6+H=C2H4+CH3 7.23E+12 0.0 1302.0 ! Tsang 1991
 C3H6+H=ac3H5+H2 1.73E+05 2.5 2492.0 ! Tsang 1991
 C3H6+H=sc3H5+H2 4.09E+05 2.5 9794.0 ! Tsang 1991,tc3h5
 C3H6+H=pc3H5+H2 8.04E+05 2.5 12284.0 ! Tsang 1991,
 pc3H5+H2=C3H6+O2 2.00E+12 0.0 0.0 ! marinov, 27symp
 sc3H5+H2=C3H6+O2 1.00E+12 0.0 0.0 ! marinov, 27symp
 C3H6+O2=ac3H5+H2O 2.29E+12 0.0 39200.0 ! Dagaut 1992
 C3H6+CH3=ac3H5+CH4 2.22E+00 3.5 5675.0 ! Tsang 1991
 C3H6+CH3=sc3H5+CH4 8.43E-01 3.5 11656.0 ! Tsang 1991
 C3H6+CH3=pc3H5+CH4 1.35E+00 3.5 12848.0 ! Tsang 1991
 C3H6+HCO=ac3H5+CH2O 1.08E+07 1.9 17010.0 ! Tsang 1991
 CH3CHCO+OH=CH2CHCO+H2O 4.00E+06 2.0 0.0 ! (q)
 CH3CHCO+O=CH2CHCO+OH 7.60E+08 1.5 8500.0 ! (q)
 CH3CHCO+H=CH2CHCO+H2 2.00E+05 2.5 2500.0 ! (q)
 CH3CHCO+H=C2H5+CO 2.00E+13 0.0 2000.0 ! (r)
 CH3CHCO+O=CH3+HCO+CO 3.00E+07 2.0 0.0 ! (s)
 !07/11/02,laskin CH2CHCHO+OH=CH2CHCO+H2O 1.00E+13 0.0 0.0 ! (t)
 !07/11/02,laskin CH2CHCHO+O=CH2CHCO+OH 7.24E+12 0.0 1970.0 ! (t)
 !07/11/02,laskin CH2CHCHO+O=CH2CO+HCO+H 5.01E+07 1.76 76.0 ! (s)
 CH2CHCHO+H=CH2CHCO+H2 3.98E+13 0.0 4200.0 ! (t)
 CH2CHCHO+H=C2H4+HCO 2.00E+13 0.0 3500.0 ! (r)
 CH2CHCHO+O2=CH2CHCO+HO2 3.00E+13 0.0 36000.0 ! (u)
 ! mit CH2CHCO=C2H3+CO 1.00E+14 0.0 34000.0 ! (v)
 CH2CHCO+O=C2H3+CO2 1.00E+14 0.0 0.0 ! (w)
 ac3H5+O2=CH2CHCHO+OH 1.82E+13 -0.41 22859.0 ! Bozzelli 1993
 ac3H5+O2=ac3H4+HO2 4.99E+15 -1.4 22428.0 ! Bozzelli 1993
 ac3H5+O2=CH2CHO+CH2O 1.06E+10 0.34 12838.0 ! Bozzelli 1993
 ac3H5+O2=C2H2+CH2O+OH 2.78E+25 -4.8 15468.0 ! Bozzelli 1993
 ac3H5+HO2=CH2CHCHO+H+OH 1.00E+13 0.0 0.0 ! Tsang 1991
 ac3H5+OH=ac3H4+H2O 1.00E+13 0.0 0.0 ! Tsang 1991
 ac3H5+H=ac3H4+H2 5.00E+13 0.0 0.0 ! Tsang 1991 (x)
 ac3H5+H=C3H6 1.88E+26 -3.6 5468.0 ! (y)
 ac3H5+O=CH2CHCHO+H 1.81E+14 0.0 0.0 ! Slagle 1992
 ac3H5+CH3=ac3H4+CH4 3.02E+12 -0.32 -131.0 ! Tsang 1991
 ac3H5+C2H2=C-C5H6+H 2.95E+32 -5.83 25733.0 ! (y)
 ac3H5+C2H3=C-C5H6+H+H 1.59E+65 -14.0 61265.0 ! (y)
 pc3H5+O2=CH3CHO+HCO 1.09E+23 -3.29 3892.0 ! (z)
 pc3H5+O2=CH3CHCO+H+O 1.60E+15 -0.78 3135.0 ! (z)
 pc3H5+O=CH3CHCO+H 1.00E+14 0.0 0.0 ! (aa)
 pc3H5+H=pc3H4+H2 2.00E+13 0.0 0.0 ! (aa)
 pc3H5+OH=pc3H4+H2O 1.00E+13 0.0 0.0 ! (aa)
 pc3H5+H=ac3H5+H 1.00E+14 0.0 0.0 ! Marinov 1996
 sc3H5+H=ac3H5+H 1.00E+14 0.0 0.0 ! Marinov 1996
 sc3H5+O2=CH3CO+CH2O 1.09E+22 -3.29 3892.0 ! (z)
 sc3H5+O=CH2CO+CH3 1.00E+14 0.0 0.0 ! (aa)
 sc3H5+H=pc3H4+H2 4.00E+13 0.0 0.0 ! (aa)
 sc3H5+OH=pc3H4+H2O 2.00E+13 0.0 0.0 ! (aa)
 ac3H4+H=C3H3+H2 2.00E+07 2.0 5000.0 ! Marinov 1998
 ac3H4+O=C2H4+CO 1.34E+07 1.88 179.0 ! (bb)
 ac3H4+OH=C3H3+H2O 1.00E+07 2.0 1000.0 ! Marinov 1998
 ac3H4+CH3=C3H3+CH4 1.50E+00 3.5 5600.0 ! Marinov 1998
 ac3H4=pc3H4 1.48E+13 0.0 60401.0 ! Lifshitz 1975
 pc3H4+H=C3H3+H2 2.00E+07 2.0 5000.0 ! Marinov 1998
 pc3H4+O=C2H4+CO 1.50E+13 0.0 2102.0 ! warnatz84 (cc)
 pc3H4+OH=C3H3+H2O 1.00E+07 2.0 1000.0 ! Marinov 1998
 pc3H4+CH3=C3H3+CH4 1.50E+00 3.5 5600.0 ! Marinov 1998
 pc3H4+H=CH3+C2H2 5.12E+10 1.0 2060.0 ! Marinov 1998
 pc3H4+H(+M)=sc3H5(+M) 6.50E+12 0.0 2000.0 ! Wagner 1972
 low / 8.45E+39 -7.27 6577.0 / ! (dd)
 ac3H4+H(+M)=ac3H5(+M) 1.20E+11 0.69 3007.0 ! Tsang 1992
 low / 5.56E+33 -5.0 4448.0 / ! (ee)
 ac3H4+H(+M)=sc3H5(+M) 8.49E+12 0.0 2000.0 ! Wagner 1972
 low / 1.11E+34 -5.0 4448.0 / ! (ee)
 C3H3+O2=CH2CO+HCO 3.00E+10 0.0 2868.0 ! Miller 1992
 !mit ? C3H3+O=CH2O+C2H 2.00E+13 0.0 0.0 ! Miller 1992
 C3H3+H=C3H2+H2 5.00E+13 0.0 3000.0 ! Miller 1992
 C3H3+OH=C3H2+H2O 2.00E+13 0.0 0.0 ! Miller 1992
 C3H3+C2H3=C-C5H5+H 9.63E+40 -7.8 28820.0 ! Marinov 1996
 C3H3+CH3=CH3CHCC2 5.00E+12 0.0 0.0 ! Wu 1987
 C3H3+CH3=CH3CH2CC2 5.00E+12 0.0 0.0 ! Wu 1987
 C3H3+CH=HCCCHCC2H 7.00E+13 0.0 0.0 ! Miller 1992
 C3H3+CH=H2CCCC2H 7.00E+13 0.0 0.0 ! Miller 1992
 C3H3+H(+M)=ac3H4(+M) 1.66E+15 -0.37 0.0 ! (ff)
 low / 3.36E+45 -8.52 6293.0 / ! Kiefer 1995 (gg)
 H2O/5.0/ H2/2.0/ CO2/3.0/ CO/2.0/ O2/2.0/ C2H2/2.0/
 C3H3+H(+M)=pc3H4(+M) 1.66E+15 -0.37 0.0 ! (ff)
 low / 8.78E+45 -8.9 7974.0 / ! Kiefer 1995 (gg)
 H2O/5.0/ H2/2.0/ CO2/3.0/ CO/2.0/ O2/2.0/ C2H2/2.0/
 C3H3+C3H3=C6H6 5.562e20 -2.535 1692.0 ! Marinov 1998
 C3H3+ac3H5=fulvene+H+H 5.562e20 -2.535 1692.0 ! Marinov 1998
 C3H3+C3H3=C6H5+H 2.00E12 0.0 0.0 ! Marinov 1998
 C3H2+O2=HCCO+CO+H 5.00E+13 0.0 0.0 ! Miller 1992
 C3H2+OH=C2H2+HCO 5.00E+13 0.0 0.0 ! Miller 1992

```

CHCHCHO+O2=HCO+CHOCHO 3.00E+12 0.0 0.0 ! (HH)
CHCHCHO=C2H2+HCO 1.00E+14 0.0 33000.0 ! (ii)
CHCHCHO+H=CH2CHCO+H 1.00E+14 0.0 0.0 ! Marinov 1996
CHCHCHO+OH=HCCCHO+H2O 1.00E+13 0.0 0.0 ! (aa)
CHCHCHO+H=HCCCHO+H2 2.00E+13 0.0 0.0 ! (aa)
HCCCHO+H=C2H2+HCO 1.00E+14 0.0 3000.0 ! (jj)
HCCCHO+OH=HCCCO+H2O 1.00E+13 0.0 0.0 ! (t)
HCCCHO+H=HCCCO+H2 4.00E+13 0.0 4200.0 ! (t)
HCCCO+O2=HCO+CO+CO 1.40E+09 1.0 0.0 ! (kk)
HCCCO+H=C2H2+CO 1.00E+14 0.0 0.0 ! (kk)
C4H10=C2H5+C2H5 2.00E+16 0.0 81300.0 ! Pitz 1991
C4H10=nC3H7+CH3 1.74E+17 0.0 85700.0 ! Pitz 1991
C4H10=pC4H9+H 1.00E+14 0.0 100000.0 ! Pitz 1991
C4H10=sC4H9+H 1.00E+14 0.0 100000.0 ! Pitz 1991
C4H10+O2=pC4H9+HO2 2.50E+13 0.0 49000.0 ! Pitz 1991
C4H10+O2=sC4H9+HO2 4.00E+13 0.0 47600.0 ! Pitz 1991
C4H10+ac3H5=pC4H9+C3H6 7.94E+11 0.0 20500.0 ! Pitz 1991
C4H10+ac3H5=sC4H9+C3H6 3.16E+11 0.0 16400.0 ! Pitz 1991
C4H10+CH3=pC4H9+CH4 5.00E+11 0.0 13600.0 ! Marinov 1998
C4H10+CH3=sC4H9+CH4 4.30E+11 0.0 10500.0 ! Marinov 1998
C4H10+H=pC4H9+H2 2.84E+05 2.54 6050.0 ! Marinov 1998
C4H10+H=sC4H9+H2 5.68E+05 2.40 3765.0 ! Marinov 1998
C4H10+OH=pC4H9+H2O 4.13E+07 1.73 753.0 ! Pitz 1991
C4H10+OH=sC4H9+H2O 7.23E+07 1.64 -247.0 ! Pitz 1991
C4H10+O=pC4H9+OH 1.13E+14 0.0 7850.0 ! Pitz 1991
C4H10+O=sC4H9+OH 5.62E+13 0.0 5200.0 ! Pitz 1991
C4H10+HO2=pC4H9+H2O2 1.70E+13 0.0 20460.0 ! Pitz 1991
C4H10+HO2=sC4H9+H2O2 1.12E+13 0.0 17700.0 ! Pitz 1991
sC4H9(+M)=C3H6+CH3(+M) 2.14E+12 0.65 30856.0 ! Knyazev 1996
low / 6.323e58 -12.85 35567./
H2O/5./ H2/2./ CO2/3./ CO/2./
sC4H9=C4H8-1+H 2.00E+13 0.0 40400.0 ! Pitz 1991
sC4H9=C4H8-2+H 5.01E+12 0.0 37900.0 ! Pitz 1991
pC4H9(+M)=C2H5+C2H4(+M) 1.06E13 0.0 27828.0 ! Knyazev 1996
low / 1.897e55 -11.91 32263./
H2O/5./ H2/2.0/ CO2/3.0/ CO/2.0/
pC4H9=C4H8-1+H 1.26E+13 0.0 38600.0 ! Pitz 1991
C4H8-1=ac3H5+CH3 1.91E+22 -1.817 77800.0 ! wt,08/02
C4H8-1=H+C4H71-3 1.26E+15 0.0 82400.0 ! 85DEA
C4H8-1+CH3=C4H71-3+CH4 1.00E+11 0.0 7300.0 ! Pitz 1991(51TRO/STE,sreric factor-low)
C4H8-1+H=C4H71-3+H2 5.00E+13 0.0 3900.0 ! Pitz 1991
C4H8-1+O=nC3H7+HCO 1.80E+05 2.5 -1029.0 ! Pitz 1991
C4H8-1+O=CH2CHCHO+CH3+H 9.67E+04 2.5 -1029.0 ! Pitz 1991
C4H8-1+OH=C4H71-3+H2O 2.25E+13 0.0 2217.0 ! Pitz 1991(88TUL)
C4H8-1+ac3H5=C4H71-3+C3H6 7.9E+10 0.0 12400.0 ! Pitz 1991
C4H8-1+O2=C4H71-3+HO2 1.60E+12 0.0 33200.0 ! Pitz 1991
C4H8-2=H+C4H72 4.11E+18 -1.0 97350.0 ! Pitz 1991
C4H8-2+CH3=C4H72+CH4 1.00E+11 0.0 8200.0 ! Pitz 1991
C4H8-2+H=C4H72+H2 5.00E+13 0.0 3800.0 ! Pitz 1991
C4H8-2+O=iC3H7+HCO 2.79E+06 2.12 -1775.0 ! Pitz 1991
C4H8-2+OH=C4H72+H2O 3.90E+13 0.0 2217.0 ! Pitz 1991
C4H8-2+O=CH3CO+C2H5 1.53E+07 1.87 -1476.0 ! Adusei 1994
C4H8-2+O=CH3+CH3CHCO+H 8.22E+06 1.87 -1476.0 ! Adusei 1994
C4H8-2+O2=C4H72+HO2 8.00E+13 0.0 37400.0 ! Pitz 1991
C4H71-3=CH2CHCHCH2+H 3.38E+7 1.678 44310.0 ! wt, may,2002
C4H72=CH2CHCHCH2+H 3.38E+7 1.678 44310.0
C4H71-3+OH=CH2CHCHCH2+H2O 1.00E+13 0.0 0.0 ! Pitz 1991
C4H71-3+CH3=CH2CHCHCH2+CH4 8.00E+12 0.0 0.0 ! Pitz 1991
C4H71-3+ac3H5=C3H6+CH2CHCHCH2 6.31E+12 0.0 0.0 ! Pitz 1991
C4H71-3+O2=CH2CHCHCH2+HO2 1.00E+09 0.0 0.0 ! Pitz 1991
C4H71-3+H=CH2CHCHCH2+H2 3.16E+13 0.0 0.0 ! Pitz 1991
C4H72+OH=CH2CHCHCH2+H2O 1.00E+13 0.0 0.0 ! Pitz 1991
C4H72+CH3=CH2CHCHCH2+CH4 8.00E+12 0.0 0.0 ! Pitz 1991
C4H72+ac3H5=C3H6+CH2CHCHCH2 6.31E+12 0.0 0.0 ! Pitz 1991
C4H72+O2=CH2CHCHCH2+HO2 1.00E+09 0.0 0.0 ! Pitz 1991
C4H72+H=CH2CHCHCH2+H2 3.16E+13 0.0 0.0 ! Pitz 1991
CH3CH2CCCH+OH=CH3CHCCCH+H2O 1.00E+07 2.0 2000.0 ! (q)
CH3CH2CCCH+H=C2H5+C2H2 1.00E+14 0.0 3000.0 ! (jj)
CH3CHCCCH2+OH=CH2CHCCCH2+H2O 2.00E+07 2.0 1000.0 ! (q)
CH3CHCCCH2+OH=CH3CCCH2+H2O 1.00E+07 2.0 2000.0 ! (ll)
CH3CHCCCH2+OH=CH3CHCCCH+H2O 2.00E+07 2.0 2500.0 ! (ll)
CH3CHCCCH2+H=CH2CHCCCH2+H2 5.00E+07 2.0 5000.0 ! (q)
CH3CHCCCH2+H=CH3CCCH2+H2 1.50E+07 2.0 6000.0 ! (ll)
CH3CHCCCH2+H=CH3CHCCCH+H2 3.00E+07 2.0 6500.0 ! (ll)
CH3CHCCCH2+H=CH3+ac3H4 2.00E+13 0.0 2000.0 ! (r)
CH3CHCCCH+H=CH3+C3H3 1.00E+14 0.0 0.0 ! Marinov 1996
CH3CHCCCH+O2=CH3CHCO+HCO 4.16E+10 0.0 2510.0 ! Slagle 1992
CH3CHCCCH+OH=CH2CHCCCH+H2O 3.00E+13 0.0 0.0 ! (MM)
CH2CHCCCH2+H=CH3CCCH2+H 3.00E+13 0.0 0.0 ! (nn)
CH2CHCCCH2+C2H2=C6H6+H 3.00E+11 0.0 14900.0 ! Marinov 1996
CH3CCCH2+H=CH3+C3H3 1.00E+14 0.0 0.0 ! Marinov 1996
CH3CCCH2+H=H2CCCH2+H2 1.00E+14 0.0 8000.0 ! (MM)
CH3CCCH2+OH=H2CCCH2+H2O 1.00E+13 0.0 0.0 ! (MM)
CH3CHCCCH(+M)=CH2CHCCCH(+M) 1.00E+13 0.0 49000.0 ! (pp)
low / 2.00E+14 0.0 41000.0 /
CH3CCCH2(+M)=H2CCCH2(+M) 1.00E+13 0.0 56000.0 ! Marinov 1996
low / 2.00E14 0.0 48000.0 /
CH2CHCCCH2(+M)=CH2CHCCCH(+M) 1.00E+14 0.0 50000.0 ! Miller 1992
low / 2.00E+15 0.0 42000.0 /
CH2CHCHCH(+M)=CH2CHCCCH(+M) 1.00E+14 0.0 37000.0 ! Miller 1992
low / 1.00E+14 0.0 30000.0 /
CH3CCCH2+C3H3=C6H5CH2+H 1.00E+11 0.0 0.0 ! vb,98MAR/PIT/27Symp

```

CH3CHCCH+CH3H3=C6H5CH2+H 1.00E+11 0.0 0.0 ! vb,98MAR/PIT/27Symp
 CH3CCCCH2+CH3CCCCH2=CH3C6H4CH2+H 1.00E+9 0.0 0.0 ! vb,98MAR/PIT/27Symp
 CH3CHCCH+CH3CHCCH=CH3C6H4CH2+H 1.00E+9 0.0 0.0 ! vb,98MAR/PIT,27Symp
 H2CCCCCH2+OH=H2CCCCCH+H2O 2.00E+07 2.0 2000.0 ! (ss)
 H2CCCCCH2+H=H2CCCCCH+H2 3.00E+07 2.0 6000.0 ! (ss)
 CH2CHCCH+OH=H2CCCCCH+H2O 7.50E+06 2.0 5000.0 ! Miller 1992
 CH2CHCCH+H=H2CCCCCH+H2 2.00E+07 2.0 15000.0 ! Miller 1992
 CH2CHCCH+OH=H2CCCCCH+H2O 1.00E+07 2.0 2000.0 ! Miller 1992
 CH2CHCCH+H=H2CCCCCH+H2 3.00E+07 2.0 5000.0 ! Miller 1992
 H2CCCCCH+H=H2CCCCCH+H 1.00E+14 0.0 0.0 ! Miller 1992
 H2CCCCCH+C2H2=C6H5 9.60E+70 -17.77 31300. ! wang 1994
 H2CCCCCH+O2=H2CCCCCH+HCO 3.00E+12 0.0 0.0 ! (tt)
 H2CCCCCH+O2=CH2CO+H2CO 1.00E+12 0.0 0.0 ! Miller 1992
 H2CCCCCH+OH=C4H2+H2O 3.00E+13 0.0 0.0 ! Miller 1992
 H2CCCCCH+O=CH2CO+C2H 2.00E+13 0.0 0.0 ! Miller 1992
 H2CCCCCH+O=H2C4O+H 2.00E+13 0.0 0.0 ! Miller 1992
 H2CCCCCH+H=C4H2+H2 5.00E+13 0.0 0.0 ! Miller 1992
 H2CCCCCH+CH2=aC3H4+C2H 2.00E+13 0.0 0.0 ! Miller 1992
 H2CCCCCH+C2H2=C6H5 3.00E+11 0.0 14900.0 ! (uu)
 H2CCCCCH(+M)=C4H2+H(+M) 1.00E+14 0.0 47000.0 ! Marinov 1998
 low / 2.0E+15 0.0 40000.0 / ! Marinov 1998
 H2CCCCCH(+M)=C4H2+H(+M) 1.00E+14 0.0 36000.0 ! Miller 1992
 low / 1.00E+14 0.0 30000.0 / ! Miller 1992
 C4H2+OH=H2C4O+H 6.66E+12 0.0 -410.0 ! Miller 1992
 C4H2+O=C3H2+CO 1.20E+12 0.0 0.0 ! Miller 1992
 H2C4O+H=C2H2+H2CO 5.00E+13 0.0 3000.0 ! Miller 1992
 H2C4O+OH=CH2CO+H2CO 1.00E+07 2.0 2000.0 ! Miller 1992
 1-C5H8+OH=1-C5H7+H2O 7.00E+06 2.0 0.0 ! (q)
 1-C5H8+H=1-C5H7+H2 7.00E+06 2.0 5000.0 ! (q)
 1-C5H8+H=aC3H5+C2H4 3.35E+08 1.5 2000.0 ! (r)
 C-C5H7=C-C5H6+H 3.16E+15 0.0 36000.0 ! Arends 1993
 C-C5H7=1-C5H7 3.16E+15 0.0 39500.0 ! Arends 1993
 1-C5H7+O=CH2CHCHO+C2H3 2.00E+14 0.0 0.0 ! Marinov 1996
 1-C5H7+H=1-C5H8 1.00E+14 0.0 0.0 ! Marinov 1996
 C-C5H6+O2=C-C5H5+HO2 5.00E+13 0.0 35400.0 ! (vv)
 C-C5H6+HO2=C-C5H5+H2O2 1.99E+12 0.0 11660.0 ! Emdee 1992
 C-C5H6+OH=C-C5H5+H2O 3.43E+09 1.18 -447.0 ! Emdee 1992
 C-C5H6+O=C-C5H5+OH 1.81E+13 0.0 3080.0 ! Emdee 1992
 C-C5H6+H=C-C5H5+H2 2.19E+08 1.77 3000.0 ! Emdee 1992
 C-C5H6+CH3=C-C5H5+CH4 3.11E+11 0.0 5500.0 ! (ww)
 C-C5H6+C2H3=C-C5H5+C2H4 6.00E+12 0.0 0.0 ! Emdee 1992
 C-C5H6+C6H5O=C-C5H5+C6H5OH 3.16E+11 0.0 8000.0 ! Emdee 1992
 C-C5H5+H=C-C5H6 2.00E+14 0.0 0.0 ! Marinov 1996
 C-C5H5+O=C-C5H4O+H 1.00E+14 0.0 0.0 ! Marinov 1996
 C-C5H5+HO2=C-C5H5O+OH 3.00E+13 0.0 0.0 ! Emdee 1992
 C-C5H5+OH=C-C5H4OH+H 3.00E+13 0.0 0.0 ! Emdee 1992
 !mit-decreased C-C5H5+C-C5H5=C10H8+H+H 2.00E+13 0.0 8000.0 ! Marinov 1998
 !mit C-C5H5O=CH2CHCCH+CO 2.51E+11 0.0 43900.0 ! Emdee 1992
 !mit C-C5H4OH=C-C5H4O+H 2.10E+13 0.0 48000.0 ! Emdee 1992
 !mit C-C5H4O=CO+C2H2+C2H2 1.00E+15 0.0 78000.0 ! Emdee 1992
 C6H6+O2=C6H5+HO2 6.30E+13 0.0 60000.0 ! Emdee 1992
 C6H6+OH=C6H5+H2O 1.63E+08 1.42 1454.0 ! Baulch 1992
 C6H6+OH=C6H5OH+H 6.70E+12 0.0 10592.0 ! He 1988 (xx)
 C6H6+O=C6H5O+H 2.40E+13 0.0 4670.0 ! Leidreiter 1989
 C6H6+H=C6H5+H2 3.03E+02 3.3 5690.0 ! (yy)
 C6H5+H=C6H6 8.00E+13 0.0 0.0 ! Baulch 1992
 C6H5+C2H4=C6H5C2H3+H 7.23E+01 3.5 8345.0 ! Yu 1994
 C6H5+OH=C6H5O+H 5.00E+13 0.0 0.0 ! Miller 1992
 C6H5+O=C-C5H5+CO 1.00E+14 0.0 0.0 ! Frank 1994
 C6H5+O2=C6H5O+O 2.60E+13 0.0 6120.0 ! Frank 1994
 C6H5O=CO+C-C5H5 7.40E+11 0.0 43850.0 ! Frank 1994
 C6H5O+H=C6H5OH 1.00E+14 0.0 0.0 ! Arends 1993
 C6H5O+H=C-2*4C6H6O 1.00E+14 0.0 0.0 ! Arends 1993
 C6H5OH+CH3=C6H5O+CH4 1.81E+11 0.0 7716.0 ! Mulcahy 1965
 C6H5OH+H=C6H5O+H2 1.58E+13 0.0 6100.0 ! Arends 1993
 C6H5OH+O=C6H5O+OH 2.81E+13 0.0 7352.0 ! Emdee 1992
 C6H5OH+C2H3=C2H4+C6H5O 6.00E+12 0.0 0.0 ! Emdee 1992
 C6H5OH+C6H5=C6H6+C6H5O 4.91E+12 0.0 4400.0 ! Emdee 1992
 C-2*4C6H6O+H=C-C5H7+CO 2.51E+13 0.0 4700.0 ! Arends 1993
 C6H5CH3=C6H5+CH3 1.40E+16 0.0 99800.0 ! Emdee 1992
 C6H5CH3+O2=C6H5CH2+HO2 2.00E+12 0.0 39080.0 ! Ingram 1994
 C6H5CH3+OH=C6H5CH2+H2O 1.26E+13 0.0 2583.0 ! Emdee 1992
 C6H5CH3+O=C6H5CH2+OH 5.00E+08 1.5 8000.0 ! Emdee 1992
 C6H5CH3+H=C6H5CH2+H2 3.98E+02 3.44 3120.0 ! Emdee 1992
 C6H5CH3+H=C6H6+CH3 1.20E+13 0.0 5148.0 ! Emdee 1992
 C6H5CH3+O=OC6H4CH3+H 1.63E+13 0.0 3418.0 ! Emdee 1992
 C6H5CH3+CH3=CH4+C6H5CH2 3.16E+11 0.0 9500.0 ! Emdee 1992
 C6H5CH3+C6H5=C6H6+C6H5CH2 2.10E+12 0.0 4400.0 ! Emdee 1992
 C6H5CH2+H=C6H5CH3 1.80E+14 0.0 0.0 ! Emdee 1992
 C6H5CH2+C6H5OH=C6H5O+C6H5CH3 1.05E+11 0.0 9500.0 ! Emdee 1992
 C6H5CH2+HOC6H4CH3=OC6H4CH3+C6H5CH3 1.05E+11 0.0 9500.0 ! Emdee 1992
 C6H5CH2+O=C6H5CHO+H 2.50E+14 0.0 0.0 ! Emdee 1992
 C6H5CH2+O=C6H5+CH2O 8.00E+13 0.0 0.0 ! Emdee 1992
 C6H5CH2+HO2=C6H5CHO+H+OH 2.50E+14 0.0 0.0 ! Emdee 1992
 C6H5CH2+HO2=C6H5+CH2O+OH 8.00E+13 0.0 0.0 ! Emdee 1992
 C6H5CH2+CH3=C6H5C2H5 1.19E+13 0.0 221.0 ! Brand 1990
 C6H5CH2+C3H3=C10H10 1.00E+10 0.0 0.0 ! (zz)
 C6H5CH2+C6H5CHO=C6H5CH3+C6H5CO 2.77E+03 2.81 5773.0 ! Emdee 1992
 C6H5CH2+OH=C6H5CH2OH 6.00E+13 0.0 0.0 ! Emdee 1992
 C6H5CH2OH+OH=C6H5CHO+H2O+H 8.43E+12 0.0 2583.0 ! Emdee 1992
 C6H5CH2OH+H=C6H5CHO+H2+H 8.00E+13 0.0 8235.0 ! Emdee 1992
 C6H5CH2OH+H=C6H6+CH2OH 1.20E+13 0.0 5148.0 ! Emdee 1992

C6H5CH2OH+C6H5CH2=C6H5CHO+C6H5CH3+H 2.11E+11 0.0 9500. ! Emdee92
 C6H5CH2OH+C6H5=C6H5CHO+C6H6+H 1.40E+12 0.0 4400.0 ! Emdee 1992
 C6H5CHO+O2=C6H5CO+HO2 1.02E+13 0.0 38950.0 ! Emdee 1992
 C6H5CHO+OH=C6H5CO+H2O 1.71E+09 1.18 -447.0 ! Emdee 1992
 C6H5CHO+H=C6H5CO+H2 5.00E+13 0.0 4928.0 ! Emdee 1992
 C6H5CHO+H=C6H5+CH2O 2.00E+13 0.0 2000.0 ! (r)
 C6H5CHO+H=C6H6+HCO 1.20E+13 0.0 5148.0 ! Emdee 1992
 C6H5CHO+O=C6H5CO+OH 9.04E+12 0.0 3080.0 ! Emdee 1992
 C6H5CHO+CH3=CH4+C6H5CO 2.77E+03 2.81 5773.0 ! Emdee 1992
 C6H5CHO+C6H5=C6H6+C6H5CO 7.01E+11 0.0 4400.0 ! Emdee 1992
 C6H5CO=C6H5+CO 3.98E+14 0.0 29400.0 ! Emdee 1992
 OC6H4CH3+H=HOC6H4CH3 2.50E+14 0.0 0.0 ! Emdee 1992
 OC6H4CH3=C6H6+H+CO 2.51E+11 0.0 43900.0 ! Emdee 1992
 HOC6H4CH3+OH=OC6H4CH3+H2O 6.00E+12 0.0 0.0 ! Emdee 1992
 HOC6H4CH3+H=OC6H4CH3+H2 1.15E+14 0.0 12400.0 ! Emdee 1992
 HOC6H4CH3+H=C6H5CH3+OH 2.21E+13 0.0 7910.0 ! Emdee 1992
 HOC6H4CH3+H=C6H5OH+CH3 1.20E+13 0.0 5148.0 ! Emdee 1992
 C6H5C2H5+OH=C6H5C2H3+H2O+H 8.43E+12 0.0 2583.0 ! Emdee 1992
 C6H5C2H5+H=C6H5C2H3+H2+H 8.00E+13 0.0 8235.0 ! Emdee 1992
 C6H5C2H3+OH=C6H4C2H3+H2O 1.63E+08 1.42 1454.0 ! Marinov 1996
 C6H5C2H3+H=C6H4C2H3+H2 3.03E+02 3.3 5690.0 ! Marinov 1996
 C6H5C2H3+OH=C6H5CC2H2+H2O 1.00E+07 2.0 2000.0 ! Marinov 1996
 C6H5C2H3+H=C6H5CC2H2+H2 2.00E+07 2.0 6000.0 ! Marinov 1996
 C6H5CHCH+H=C6H5CC2H2+H 1.00E+14 0.0 0.0 ! Marinov 1996
 C6H5CC2H2+OH=C6H5C2H+H2O 2.00E+13 0.0 0.0 ! Marinov 1996
 C6H5CC2H2+H=C6H5C2H+H2 5.00E+13 0.0 0.0 ! Marinov 1996
 C6H5C2H+O=C6H5CCO+H 4.80E+09 1.0 0.0 ! (bbb)
 C6H5CCO+O2=C6H5CO+CO2 1.00E+12 0.0 0.0 ! (ccc)
 C6H5C2H+OH=C6H4C2H+H2O 1.63E+08 1.42 1454.0 ! Marinov 1996
 C6H5C2H+H=C6H4C2H+H2 3.03E+02 3.3 5690.0 ! Marinov 1996
 C6H5C2H+CH3=C6H4C2H+CH4 1.67E+12 0.0 15057.0 ! Marinov 1996
 C6H4C2H3+CH3=INDENE+H+H 2.00E+13 0.0 0.0 ! (eee)
 CH3C6H4CH3+OH=CH3C6H4CH2+H2O 2.95E+13 0.0 2623.0 ! Marinov 1996
 CH3C6H4CH3+O=CH3C6H4CH2+OH 5.00E+08 1.5 8000.0 ! Marinov 1996
 CH3C6H4CH3+H=CH3C6H4CH2+H2 3.98E+02 3.44 3120.0 ! Marinov 1996
 CH3C6H4CH2+C2H2=C10H10+H 3.20E+11 0.0 7000.0 ! Marinov 1996
 CH3C6H4CH2+C2H2=CH3indene+H 3.20E+11 0.0 7000.0 ! Marinov 1996
 CH3C6H4CH2+H=CH3C6H4CH3 7.46E+13 0.0 78.0 ! Brand 1990
 CH3C6H4CH2+CH3=CH3C6H4C2H5 6.00E+12 0.0 221.0 ! Marinov 1996
 CH3C6H4C2H5+OH=CH3C6H4C2H3+H2O+H 8.43E+12 0.0 2583.0 ! Marinov 1996
 CH3C6H4C2H5+H=CH3C6H4C2H3+H2+H 8.00E+13 0.0 8235.0 ! Marinov 1996
 CH3C6H4C2H3+OH=INDENE+H+H2O 1.26E+13 0.0 2583.0 ! Marinov 1996, ?
 CH3C6H4C2H3+H=INDENE+H+H2 3.98E+02 3.44 3120.0 ! Marinov 1996, ?
 CH3indene+OH=CH3indeny1+H2O 3.43E+09 1.18 -447.0 ! Marinov 1996
 CH3indene+O=CH3indeny1+OH 1.81E+13 0.0 3080.0 ! Marinov 1996
 CH3indene+H=CH3indeny1+H2 2.19E+08 1.77 3000.0 ! Marinov 1996
 CH3indene+H=INDENE+CH3 1.20E+13 0.0 5200.0 ! Marinov 1996
 CH3indeny1+H=CH3indene 2.00E+14 0.0 0.0 ! Marinov 1996
 CH3indeny1+C-C5H5=CH3phnthrn+H+H 1.00E+13 0.0 8000.0 ! Marinov 1998
 INDENE*+CH3=CH3indene 1.e13 0.0 0.0 ! lvb, Olin/MAU
 C10H10+OH=C10H9+H2O 5.00E+06 2.0 0.0 ! Marinov 1996
 C10H10+O=C10H9+OH 7.00E+11 0.7 6000.0 ! Marinov 1996
 C10H10+H=C10H9+H2 2.00E+05 2.5 2500.0 ! Marinov 1996
 C10H9+H=C10H10 1.00E+14 0.0 0.0 ! Marinov 1996
 C10H8+H=C10H9 5.00E+14 0.0 5000.0 ! Sauer 1970
 C10H8+O=C10H7O-1+H 1.40E+13 0.0 1792.0 ! Frerichs 1990/mit
 C10H8+O=C10H7O-2+H 1.40E+13 0.0 1792.0 ! Frerichs 1990/mit
 A2CH3-1+OH=A2CH2-1+H2O 1.27E+13 0.0 2583.0 ! Marinov 1996
 A2CH3-2+OH=A2CH2-2+H2O 1.27E+13 0.0 2583.0 ! Marinov 1996
 A2CH3-1+O=A2CH2-1+OH 5.00E+08 1.5 8000.0 ! Marinov 1996
 A2CH3-2+O=A2CH2-2+OH 5.00E+08 1.5 8000.0 ! Marinov 1996
 A2CH3-1+H=A2CH2-1+H2 3.98E+02 3.44 3120.0 ! Marinov 1996
 A2CH3-2+H=A2CH2-2+H2 3.98E+02 3.44 3120.0 ! Marinov 1996
 A2CH2-1+O=C10H7*1+CH2O 1.00E+14 0.0 0.0 ! Marinov 1996-mit?
 A2CH2-2+O=C10H7*2+CH2O 1.00E+14 0.0 0.0 ! Marinov 1996-mit?
 A2CH2-1+C2H2=bz(a)ndene+H 3.20E+11 0.0 7000.0 ! Marinov 1996/vb-overall bz(x)indene
 A2CH2-2+C2H2=bz(a)ndene+H 3.20E+11 0.0 7000.0 ! Marinov 1996/vb-overall bz(x)indene
 A2CH2-1+CH3=C10H7C2H5 1.19E+13 0.0 221.0 ! Marinov 1996/overall c10h7c2h5
 A2CH2-2+CH3=C10H7C2H5 1.19E+13 0.0 221.0 ! Marinov 1996
 A2C2H3-2+OH=A2VINP+H2O 1.00E+07 2.0 2000.0 ! Marinov 1996-mit
 A2C2H3-2+H=A2VINP+H2 2.00E+07 2.0 6000.0 ! Marinov 1996-mit
 A2VINP+OH=A2C2H-1+H2O 2.00E+13 0.0 0.0 ! Marinov 1996-mit
 A2VINP+OH=A2C2H-2+H2O 2.00E+13 0.0 0.0 ! Marinov 1996-mit
 FLUORENE+OH=fluoryl+H2O 3.43E+09 1.18 -447.0 ! Marinov 1996
 FLUORENE+O=fluoryl+OH 1.81E+13 0.0 3080.0 ! Marinov 1996
 FLUORENE+H=fluoryl+H2 2.19E+08 1.77 3000.0 ! Marinov 1996
 fluoryl+H=FLUORENE 2.00E+14 0.0 0.0 ! Marinov 1996
 bz(a)ndnyl+H=bz(a)ndene 2.00E+14 0.0 0.0 ! Marinov 1996
 bz(a)ndene+OH=bz(a)ndnyl+H2O 3.43E+09 1.18 -447.0 ! Marinov 1996
 bz(a)ndene+O=bz(a)ndnyl+OH 1.81E+13 0.0 3080.0 ! Marinov 1996
 bz(a)ndene+H=bz(a)ndnyl+H2 2.19E+08 1.77 3000.0 ! Marinov 1996
 A3*1+O2= phnthroxy-1+O 1.00E+13 0.0 0.0 ! (fff)
 A3*9+O2= phnthroxy-9+O 1.00E+13 0.0 0.0 ! (fff)
 phnthrol-1+OH=phnthroxy-1+H2O 2.95E+06 2.0 -1310.0 ! Marinov 1996
 phnthrol-1+H=phnthroxy-1+H2 1.59E+13 0.0 6100.0 ! Marinov 1996
 phnthroxy-1+H=phnthrol-1 1.00E+14 0.0 0.0 ! Marinov 1996
 phnthrol-9+OH=phnthroxy-9+H2O 2.95E+06 2.0 -1310.0 ! Marinov 1996
 phnthrol-9+H=phnthroxy-9+H2 1.59E+13 0.0 6100.0 ! Marinov 1996
 phnthroxy-9+H=phnthrol-9 1.00E+14 0.0 0.0 ! Marinov 1996
 phnthroxy-1=bz(a)ndnyl+CO 7.40E+11 0.0 43850.0 ! Marinov 1996
 phnthroxy-9=fluoryl+CO 7.40E+11 0.0 43850.0 ! Marinov 1996
 CH3phnthrn+H=A3+CH3 1.20E+13 0.0 5148.0 ! Marinov1996

```

C3H3+CH2=CH2CHCCH+H      4.00E+13  0.0  0.0 !Miller 1992
C-C5H5+CH3=ch3cy24pd      1.76E+50 -11.0 18600. !Ritter 1990
ch3cy24pd+H=C-C5H6+CH3    1.00E+13  0.0 1300.0 !Ritter 1990
C6H6+H=ch3cy24pd1         2.39E+27 -3.92 29200. !Ritter 1990
cyc6h7=ch3cy24pd1         5.00E+12  0.0 38100. !Ritter 1990
ch3cy24pd1+H=ch3cy24pd    1.00E+14  0.0 0.0 !Marinov 1998
ch3cy24pd1+H=C-C5H5+CH3   1.00E+14  0.0 0.0 !Marinov 1998
cyc6h7=ch3dcy24pd         5.50E+10  0.0 23500. !Ritter 1990
C6H6+H=cyc6h7             4.87E+56 -12.73 26800. !Ritter 1990
ch3dcy24pd+H2=ch3cy24pd+H 4.00E+12  0.0 15000. !Ritter 1990
fulvene=C6H6               9.84E+37 -7.4 76979. !ShandroSs1996
fulvene+H=C6H6+H          3.00E+12  0.5 2000.0 !Marinov 1998
fulvene+H=fulvenyl+H2     3.03E+2  3.3 5690. !Marinov 1998
fulvene+OH=fulvenyl+H2O   1.63E+8  1.42 1454. !Marinov 1998
fulvenyl+H=C6H5+H         1.00E+14  0.0 0.0 !Marinov 1998
fulvenyl+O2=C-C5H4O+HCO   1.00E+12  0.0 0.0 !Marinov 1998
!
*****
FLTHN*7+CH3=FLTHNCH2+H      5.00E+13  .0 .0 !vb, ch3-subst only
FLTHNCH2+H=FLTHNCH3        1.00E+14  .0 .0 !mit,
FLTHNCH3+H=FLTHN+CH3       1.20E+13  .0 5148.0 !mit,
!methylbenzo[ghi]fluoranthene
BGHIF+CH3=BGHIFCH2+H       5.00E+13  .0 .0 !mit,
BGHIFCH2+H=BGHIFCH3       1.00E+14  .0 .0 !mit,
BGHIFCH3+H=BGHIF+CH3      1.20E+13  .0 5148.0 !mit,
BGHIF+CH2=BGHIFC2H+H      3.98E+13  .0 10100.0 !mit,
COR+CH3=CORCH2+H          5.00E+13  .0 .0 !mit,
CORCH2+H=CORCH3           1.00E+14  .0 .0 !mit,
CORCH3+H=COR+CH3          1.20E+13  .0 5148.0 !mit,
FLTHN*7+C2H2=FLTHNC2H+H   3.98E+13  .0 10100.0 !mit,vb c2hsustitued only
flthn*7
!
! *** additions from c7-pah-c-b.m, 07/11/02 ***
C6H6+CH2*=C6H5CH3          4.0E+13  0.0 8680.0
C6H6+CH2=C6H5CH3          1.7E+13  0.0 8680.0
INDENE*+CH2*=C10H9         1.e14  0. 0.
C-C5H5+C-C5H5=C10H9+H      2.e13  0. 8000.
!*** growing up to c32 *****
CORONEN+H=cor- +H2        3.23E07  2.095 15842. !pyrene- [Mebel et al. 1997]
CORONEN+C2H=corC2H+H      5.00E+13  0.00 0. !abf, Estimated
!cor- +C2H2=corC2H2
cor- +C2H2=corC2H+H       1.6E14  -0.19 20000.0 ! [99,bohm]
!corC2H2+H=corC2H
!corC2H+H=corC2H2
corC2H+H=corC2H*+H2       3.23E07  2.095 15842. !pyrene, mmt
corC2H*+C2H2=cor1-        5.1e48  -10.53 28000. ! [99,bohm]
cor1-+H=cor1              5.00E13  0.0 0. !pyrene, mmt
corC2H*+C2H2=corC2H)2+H   1.8E+19  -1.67 18800. !abf,a2 760 t
corC2H)2+H=cor1-         6.9E+63  -14.57 29900. !abf,a2, 760 t
!cor-+C4H4=cor1+H        3.3E+33  -5.70 25500. !abf,a2, 760 t
! ch2chccch; h2cccch2
corC2H*+H=corC2H          5.00E13  0.0 0. !pyrene, mmt
corC2H+C2H=corC2H)2+H     5.00E+13  0.0 0. !abf,a2, Estimated
cor-+CH2CHCCH=cor1+H      3.3E+33  -5.70 25500. !abf,a2, 760 t
cor-+C4H2=cor1-          5.1e48  -10.53 28000. ! [99,bohm]
CORONEN+HCCCHCCH=cor1+H   1.e12  0. 0. ! [99,bohm]
cor1+H=cor1-+H2          3.23E07  2.095 15842. !pyrene, mmt
cor1+C2H=cor1C2H+H        5.00E+13  0.00 0. !abf Estimated
cor1-+C2H2=cor1C2H+H      1.6E14  -0.19 20000.0 ! [99,bohm]
cor1-+C2H2=cor2+H         4.6E6  1.97 7300.0 ! [99,bohm]
cor1C2H+H=cor2+H          9.0E+38  -7.39 20700. !abf, pyrene, 760 t
cor2-+H=cor2              5.00E13  0.0 0. !pyrene, mmt
cor1-+C4H2=cor2+C2H       4.6E6  1.97 7300. ! [99,bohm]
cor1-+C2H3=cor2+H2        1.e13  0.0 0.0 ! [99,bohm]
cor2+H= cor2-+H2         3.23E07  2.095 15842. !pyrene, mmt
!cor2+C2H=oval+H
cor2+C2H=cor2C2H+H        5.00E+13  0.00 0. !abf Estimated
cor2-+C2H2=cor2C2H+H      1.6E14  -0.19 20000.0 ! [99,bohm]
cor2-+C2H2=oval+H         4.6E6  1.97 7300.0 ! [99,bohm]
cor2C2H+H=oval+H          9.0E+38  -7.39 20700. !abf, pyrene, 760 t
cor2-+C4H2=oval+C2H       4.6E6  1.97 7300. ! [99,bohm]
cor2-+C2H3=oval+H2        1.e13  0.0 0.0 ! [99,bohm]
PYRENE+CH3=PYRENECH3+H    2.e12  0.0 17000. !duplicate ?
PYRENECH3+H=PYRENECH3*+H2 3.23E07  2.095 15842. !pyrene, mmt
PYRENECH3*+C3H3=BEPYREN+H+H 6.03e11  0. 0.
!BEPYREN+H=BEPYREN*+H2    3.23E07  2.095 15842. !pyrene, mmt, duplicate
BEPYREN*+C4H2=BGHIPER+C2H 4.6E6  1.97 7300.
! bohm et al growing through ch3/ch3h3 starting from coronene (1999)
CORONEN+CH3=corCH3+H      2.e12  0.0 17000. !bohm et al, 1999
corCH3+H=corCH3*+H2       3.23E07  2.095 15842. !pyrene, mmt
corCH3*+C3H3=cor1+H+H     6.03e11  0. 0. !bohm et al, 1999
! from b[a]pyrene +c6h5
BAPYR+C6H5=BAPYRC6H5+H    1.1e23  -2.92 15890. !bohm et al, 1999
BAPYRC6H5=BAPYRC6)2+H2    5.1e12  0. 64000. !bohm et al, 1999
BAPYRC6)2+H=BAPYRC6)2*+H2 3.23E07  2.095 15842. !pyrene, mmt
BAPYRC6)2*+C2H2=BAPYRC6)3+H 4.6E6  1.97 7300.0 ! [99,bohm]
BAPYRC6)3+H=BAPYRC6)3*+H2 3.23E07  2.095 15842. !pyrene, mmt
BAPYRC6)3*+C2H2=BAPYRC6)4+H 4.6E6  1.97 7300.0 ! [99,bohm]
BAPYRC6)4+H=BAPYRC6)4*+H2 3.23E07  2.095 15842. !pyrene, mmt
BAPYRC6)4*+C2H2=oval+H    4.6E6  1.97 7300.0 ! [99,bohm]
! from chrysene*4+c6h5
CHRYSEN+C6H5=CHRYSENC6H5+H 1.1e23  -2.92 15890. !bohm et al, 1999
CHRYSENC6H5=CHRYSENC6)2+H2 5.1e12  0. 64000. !bohm et al, 1999

```

```

CHRYSENC6)2+H=CHRYSENC6)2*+H2      3.23E07    2.095    15842.    !pyrene,mmt
CHRYSENC6)2*+C2H2=BAPYRC6)2+H      4.6E6        1.97    7300.0    ![99,bohm]
! FROM a3*4
A3+C6H5=A3C6H5+H                      1.1e23    -2.92    15890.    !bohm etal, 1999
A3C6H5=BEPYREN+H2                     5.1e12     0.      64000.    !bohm etal, 1999
! *****
C5H91-3=CH2CHCHCH2+CH3                9.74e+11    0.4493    35210.00    !wt
C5H10-1=C2H5+ac3H5                     6.65e+20    -1.344    74400.    !wt, 08/2002
C5H10-1=C3H6+C2H4                       2.47E6      1.7338    53300.    !wt,08/2002
C5H10-1+H=C5H91-3+H2                   2.800e+13    0.000    4000.00
C5H10-1+O=C5H91-3+OH                   2.540e+05    2.560    -1130.02
C5H10-1+O=PC4H9+HCO                    1.000e+11    0.000    0.00
C5H10-1+O=NC3H7+CH3CO                  1.000e+11    0.000    0.00
C5H10-1+OH=C5H91-3+H2O                  6.800e+13    0.000    3059.99
C5H10-1+OH=PC4H9+CH2O                   1.000e+11    0.000    0.00
C5H10-1+OH=NC3H7+CH3CHO                 1.000e+11    0.000    0.00
C5H10-1+CH3=C5H91-3+CH4                 1.000e+11    0.000    7299.95
! *****
CH3CO+H=>CH2CO+H2                      2.000e+13    0.000    0.00
CH2CO+H2=>CH3CO+H                      7.270e+09    0.000    83039.91
CH3CO+O=>CH2CO+OH                      2.000e+13    0.000    0.00
CH2CO+OH=>CH3CO+O                      7.270e+09    0.000    83039.91
!CH3CO+CH3=>CH2CO+CH4                  5.000e+13    0.000    0.00
!CH2CO+CH4=>CH3CO+CH3                  7.270e+09    0.000    83039.91
C2H6+CH=>C2H5+CH2                      1.100e+14    0.000    -260.04
C2H5+CH2=>C2H6+CH                      3.829e+10    0.560    440.01
CH2OH+CH2O=>CH3OH+HCO                  1.292e-01    4.560    6596.08
CH3OH+HCO=>CH2OH+CH2O                  9.630e+03    2.900    13109.94
CH2CHCHO+HO2=>CH2CHCO+H2O2             3.010e+12    0.000    11929.97
CH2CHCO+H2O2=>CH2CHCHO+HO2             2.783e+13    -0.300    17880.02
C3H5O=>CH2CHCHO+H                      1.000e+14    0.000    29099.90
CH2CHCHO+H=>C3H5O                      7.714e+11    0.480    17750.00
C3H5O=>C2H3+CH2O                       2.028e+12    0.090    23559.99
C2H3+CH2O=>C3H5O                       1.500e+11    0.000    10599.90
C3H5O+O2=>CH2CHCHO+HO2                 1.000e+12    0.000    6000.00
CH2CHCHO+HO2=>C3H5O+O2                 1.288e+11    0.000    32000.00
ac3H5+HO2=>C3H5O+OH                    7.000e+12    0.000    -1000.00
C3H5O+OH=>ac3H5+HO2                    2.041e+13    -0.160    12260.04
ac3H4+HO2=>C2H4+CO+OH                  1.000e+12    0.000    14000.00
C2H4+CO+OH=>ac3H4+HO2                  1.000e+00    0.000    0.00
ac3H4+HO2=>C3H3+H2O2                   3.000e+13    0.000    14000.00
C3H3+H2O2=>ac3H4+HO2                   1.551e+16    -1.380    44000.00
ac3H5+C2H5=>C2H4+C3H6                  4.000e+11    0.000    0.00
C2H4+C3H6=>ac3H5+C2H5                   6.937e+16    -1.330    52799.95
ac3H4+ac3H5=>C3H3+C3H6                 2.000e+11    0.000    7700.05
C3H3+C3H6=>ac3H4+ac3H5                 2.644e+19    -2.710    42140.06
PC3H4+HO2=>C2H4+CO+OH                  3.000e+12    0.000    19000.00
C2H4+CO+OH=>PC3H4+HO2                  1.000e+00    0.000    0.00
PC3H4+O=>C3H3+OH                       7.650e+08    1.500    8599.90
C3H3+OH=>PC3H4+O                       2.177e+08    1.310    22469.89
PC3H4+O=>C2H3+HCO                      3.200e+12    0.000    2010.04
C2H3+HCO=>PC3H4+O                      2.548e+12    -0.390    32349.90
PC3H4+C2H3=>C3H3+C2H4                  1.000e+12    0.000    7700.05
C3H3+C2H4=>PC3H4+C2H3                   9.541e+11    -0.390    52450.05
PC3H4+ac3H5=>C3H3+C3H6                 1.000e+12    0.000    7700.05
C3H3+C3H6=>PC3H4+ac3H5                 4.931e+16    -1.730    37950.05
HCCO+O2=>CO2+HCO                       2.400e+11    0.000    -853.97
CO2+HCO=>HCCO+O2                       1.474e+14    0.000    133599.90
CH3CHCO+OH=C2H5+CO2                   1.730e+12    0.000    -1010.04
CH3CHCO+O=CH3CHO+CO                    3.200e+12    0.000    -436.90
CH2*+CH2CO=>C2H4+CO                   1.600e+14    0.000    0.00
C2H4+CO=>CH2*+CH2CO                    4.596e+15    -0.060    105599.90
! *** block of c6 reactions ***
C6H13-1=>C2H4+PC4H9                     5.446e+17    -1.290    29580.07
C2H4+PC4H9=>C6H13-1                    3.300e+11    0.000    7200.05
C6H13-1=>C6H12-1+H                     2.091e+16    -0.890    37950.05
C6H12-1+H=>C6H13-1                     1.000e+13    0.000    2900.10
C6H12-1+OH=C6H111-3+H2O                3.000e+13    0.000    1229.92
C6H12-1+H=C6H111-3+H2                  3.700e+13    0.000    3900.10
C6H12-1+CH3=C6H111-3+CH4               1.000e+12    0.000    7299.95
C6H12-1+O=C6H111-3+OH                  2.120e+11    0.130    9125.00
C6H12-1+OH=C2H4+NC3H7+CH2O             17168841800    0.18487    -2672.4997
!wt/c5h11-1
C6H12-1+OH=C3H6+C2H5+CH2O              6.91067E+16    -1.8177    -1252.84975
!wt/c5h11-1
C6H12-1+OH=C4H8-1+CH3+CH2O             841.056    2.09724    -7059.418705
!wt/c5h11-1
C6H12-1+O=C2H4+NC3H7+HCO              17168841800    0.18487    277.5503
!wt/c5h11-1
C6H12-1+O=C3H6+C2H5+HCO                6.91067E+16    -1.8177    1697.20025
!wt/c5h11-1
C6H12-1+O=C4H8-1+CH3+HCO              841.056    2.09724    -4109.368705
!wt/c5h11-1
C6H111-3=CH2CHCHCH2+C2H5              1.857e+10    0.95655    32880.00
!wt, may 2002
C6H12-1=NC3H7+ac3H5                    1.877e22    -1.799    74750.00    !wt,08/2000
C6H12-1=C3H6+C3H6                      1.8e6      1.8133    53260.00    !wt,08/2000
! *** main n-heptane decomposition reactions, WT, april, 2001, data for 760 torr ***
nc7H16=C6H13-1+CH3                     4.15e+132    -33.37    158270.0    !wt,04/01
!nc7H16=C5H11-1+C2H5                   7.53e+130    -32.851    154720.0    !wt,04/01
nc7H16=C2H4+NC3H7+C2H5                 1.2928E+130    -32.66613
156047.5003    !c5h11, wt

```

```

nc7H16=C3H6+C2H5+C2H5          5.2037E+136      -34.6687
157467.1503      !c5h11, wt
nc7H16=C4H8-1+CH3+C2H5          6.3332E+122      -30.75376
151660.5813      !c5h11, wt
nc7H16=PC4H9+nc3H7          3.18e+129      -32.451 153300.0      !wt, 04/01
! *** H atom abstractions/isomerization/decomposition - westbrook(01)+wt data ***
! including c5h11 decomposition
nc7H16+H=C2H4+C2H4+nc3H7+H2          141.1296631      3.76521 9899.0723
DUPLICATE
nc7H16+OH=C2H4+C2H4+nc3H7+H2O          7936304.178      1.98521 5209.0723
DUPLICATE
nc7H16+O=C2H4+C2H4+nc3H7+OH          1583.500865      3.43521 8385.0723
DUPLICATE
nc7H16+CH3=C2H4+C2H4+nc3H7+CH4          0.000691223      4.66521 10773.0723
DUPLICATE
nc7H16+HO2=C2H4+C2H4+nc3H7+H2O2          12578194465      1.01521 24059.0723
DUPLICATE
nc7H16+CH3O=C2H4+C2H4+nc3H7+CH3OH          723799543.5      1.01521 10619.0723
DUPLICATE
nc7H16+O2=C2H4+C2H4+nc3H7+HO2          95415362558      1.01521 54379.0723
DUPLICATE
nc7H16+C2H5=C2H4+C2H4+nc3H7+C2H6          228885512.7      1.01521 17019.0723
DUPLICATE
nc7H16+C2H3=C2H4+C2H4+nc3H7+C2H4          2288855127      1.01521 21619.0723
DUPLICATE
nc7H16+H=C2H4+C3H6+C2H5+H2          568064050.3      1.76264 11318.72225
DUPLICATE
nc7H16+OH=C2H4+C3H6+C2H5+H2O          3.19446E+13      -0.01736 6628.72225
DUPLICATE
nc7H16+O=C2H4+C3H6+C2H5+OH          6373783476      1.43264 9804.72225
DUPLICATE
nc7H16+CH3=C2H4+C3H6+C2H5+CH4          2782.257399      2.66264 12192.72225
DUPLICATE
nc7H16+HO2=C2H4+C3H6+C2H5+H2O2          5.06288E+16      -0.98736 25478.72225
DUPLICATE
nc7H16+CH3O=C2H4+C3H6+C2H5+CH3OH          2.91338E+15      -0.98736 12038.72225
DUPLICATE
nc7H16+O2=C2H4+C3H6+C2H5+HO2          3.84058E+17      -0.98736 55798.72225
DUPLICATE
nc7H16+C2H5=C2H4+C3H6+C2H5+C2H6          9.21292E+14      -0.98736 18438.72225
DUPLICATE
nc7H16+C2H3=C2H4+C3H6+C2H5+C2H4          9.21292E+15      -0.98736 23038.72225
DUPLICATE
nc7H16+H=C2H4+C4H8-1+CH3+H2          6.91357E-06      5.67758 5512.153295
DUPLICATE
nc7H16+OH=C2H4+C4H8-1+CH3+H2O          0.388778482      3.89758 822.153295
DUPLICATE
nc7H16+O=C2H4+C4H8-1+CH3+OH          7.75715E-05      5.34758 3998.153295
DUPLICATE
nc7H16+CH3=C2H4+C4H8-1+CH3+CH4          3.38612E-11      6.57758 6386.153295
DUPLICATE
nc7H16+HO2=C2H4+C4H8-1+CH3+H2O2          616.172369      2.92758 19672.1533
DUPLICATE
nc7H16+CH3O=C2H4+C4H8-1+CH3+CH3OH          35.45701894      2.92758 6232.153295
DUPLICATE
nc7H16+O2=C2H4+C4H8-1+CH3+HO2          4674.145414      2.92758 49992.1533
DUPLICATE
nc7H16+C2H5=C2H4+C4H8-1+CH3+C2H6          11.21249389      2.92758 12632.1533
DUPLICATE
nc7H16+C2H3=C2H4+C4H8-1+CH3+C2H4          112.1249389      2.92758 17232.1533
DUPLICATE
nc7H16+H=C3H6+PC4H9+H2          3.06294E+17      -0.97526 11696.754
DUPLICATE
nc7H16+OH=C3H6+PC4H9+H2O          1.72242E+22      -2.75526 7006.754
DUPLICATE
nc7H16+O=C3H6+PC4H9+OH          3.43668E+18      -1.30526 10182.754
DUPLICATE
nc7H16+CH3=C3H6+PC4H9+CH4          1.50016E+12      -0.07526 12570.754
DUPLICATE
nc7H16+HO2=C3H6+PC4H9+H2O2          2.72985E+25      -3.72526 25856.754
DUPLICATE
nc7H16+CH3O=C3H6+PC4H9+CH3OH          1.57086E+24      -3.72526 12416.754
DUPLICATE
nc7H16+O2=C3H6+PC4H9+HO2          2.0708E+26      -3.72526 56176.754
DUPLICATE
nc7H16+C2H5=C3H6+PC4H9+C2H6          4.96751E+23      -3.72526 18816.754
DUPLICATE
nc7H16+C2H3=C3H6+PC4H9+C2H4          4.96751E+24      -3.72526 23416.754
DUPLICATE
nc7H16+H=C4H8-1+nc3H7+H2          1.83664E+18      -0.7665 12537.456
DUPLICATE
nc7H16+OH=C4H8-1+nc3H7+H2O          1.03282E+23      -2.5465 7847.456
DUPLICATE
nc7H16+O=C4H8-1+nc3H7+OH          2.06075E+19      -1.0965 11023.456
DUPLICATE
nc7H16+CH3=C4H8-1+nc3H7+CH4          8.9955E+12      0.1335 13411.456
DUPLICATE
nc7H16+HO2=C4H8-1+nc3H7+H2O2          1.63691E+26      -3.5165 26697.456
DUPLICATE
nc7H16+CH3O=C4H8-1+nc3H7+CH3OH          9.41944E+24      -3.5165 13257.456
DUPLICATE
nc7H16+O2=C4H8-1+nc3H7+HO2          1.24172E+27      -3.5165 57017.456

```

DUPLICATE			
nc7H16+C2H5=C4H8-1+nc3H7+C2H6	2.97869E+24	-3.5165	19657.456
DUPLICATE			
nc7H16+C2H3=C4H8-1+nc3H7+C2H4	2.97869E+25	-3.5165	24257.456
DUPLICATE			
nc7H16+H=C6H12-1+CH3+H2	3.92501E+12	0.54123	11377.008
DUPLICATE			
nc7H16+OH=C6H12-1+CH3+H2O	2.2072E+17	-1.23877	6687.008
DUPLICATE			
nc7H16+O=C6H12-1+CH3+OH	4.40394E+13	0.21123	9863.008
DUPLICATE			
nc7H16+CH3=C6H12-1+CH3+CH4	19223889.63	1.44123	12251.008
DUPLICATE			
nc7H16+HO2=C6H12-1+CH3+H2O2	3.49817E+20	-2.20877	25537.008
DUPLICATE			
nc7H16+CH3O=C6H12-1+CH3+CH3OH	2.01299E+19	-2.20877	12097.008
DUPLICATE			
nc7H16+O2=C6H12-1+CH3+HO2	2.65364E+21	-2.20877	55857.008
DUPLICATE			
nc7H16+C2H5=C6H12-1+CH3+C2H6	6.36563E+18	-2.20877	18497.008
DUPLICATE			
nc7H16+C2H3=C6H12-1+CH3+C2H4	6.36563E+19	-2.20877	23097.008
DUPLICATE			
nc7H16+H=C5H10-1+C2H5+H2	2252.129279	3.318133	7639.095
DUPLICATE			
nc7H16+OH=C5H10-1+C2H5+H2O	126646536.3	1.538133	2949.095
DUPLICATE			
nc7H16+O=C5H10-1+C2H5+OH	25269.30612	2.988133	6125.095
DUPLICATE			
nc7H16+CH3=C5H10-1+C2H5+CH4	0.011030452	4.218133	8513.095
DUPLICATE			
nc7H16+HO2=C5H10-1+C2H5+H2O2	2.00721E+11	0.568133	21799.095
DUPLICATE			
nc7H16+CH3O=C5H10-1+C2H5+CH3OH	11550301388	0.568133	8359.095
DUPLICATE			
nc7H16+O2=C5H10-1+C2H5+HO2	1.52263E+12	0.568133	52119.095
DUPLICATE			
nc7H16+C2H5=C5H10-1+C2H5+C2H6	3652526005	0.568133	14759.095
DUPLICATE			
nc7H16+C2H3=C5H10-1+C2H5+C2H4	36525260047	0.568133	19359.095
DUPLICATE			
! including c5h11			
nc7H16+H=C2H4+C2H4+nc3H7+H2	6.520313511	3.506966	2167.1393
DUPLICATE			
nc7H16+OH=C2H4+C2H4+nc3H7+H2O	236.7382746	2.716966	-2338.8607
DUPLICATE			
nc7H16+O=C2H4+C2H4+nc3H7+OH	2.980358299	3.546966	542.1393
DUPLICATE			
nc7H16+CH3=C2H4+C2H4+nc3H7+CH4	0.420986799	3.236966	5270.1393
DUPLICATE			
nc7H16+HO2=C2H4+C2H4+nc3H7+H2O2	28462200.79	1.106966	15386.1393
DUPLICATE			
nc7H16+CH3O=C2H4+C2H4+nc3H7+CH3OH	554968.685	1.106966	4696.1393
DUPLICATE			
nc7H16+O2=C2H4+C2H4+nc3H7+HO2	71493815.97	1.106966	45906.1393
DUPLICATE			
nc7H16+C2H5=C2H4+C2H4+nc3H7+C2H6	253669.6315	1.106966	8096.1393
DUPLICATE			
nc7H16+C2H3=C2H4+C2H4+nc3H7+C2H4	2014969.506	1.106966	14496.1393
DUPLICATE			
nc7H16+H=C2H4+C3H6+C2H5+H2	26245054.52	1.504396	3586.78925
DUPLICATE			
nc7H16+OH=C2H4+C3H6+C2H5+H2O	952900334.1	0.714396	-919.21075
DUPLICATE			
nc7H16+O=C2H4+C3H6+C2H5+OH	11996304.45	1.544396	1961.78925
DUPLICATE			
nc7H16+CH3=C2H4+C3H6+C2H5+CH4	1694523.044	1.234396	6689.78925
DUPLICATE			
nc7H16+HO2=C2H4+C3H6+C2H5+H2O2	1.14564E+14	-0.895604	16805.78925
DUPLICATE			
nc7H16+CH3O=C2H4+C3H6+C2H5+CH3OH	2.23382E+12	-0.895604	6115.78925
DUPLICATE			
nc7H16+O2=C2H4+C3H6+C2H5+HO2	2.87771E+14	-0.895604	47325.78925
DUPLICATE			
nc7H16+C2H5=C2H4+C3H6+C2H5+C2H6	1.02105E+12	-0.895604	9515.78925
DUPLICATE			
nc7H16+C2H3=C2H4+C3H6+C2H5+C2H4	8.1105E+12	-0.895604	15915.78925
DUPLICATE			
nc7H16+H=C2H4+C4H8-1+CH3+H2	3.19413E-07	5.419336	-2219.779705
DUPLICATE			
nc7H16+OH=C2H4+C4H8-1+CH3+H2O	1.15972E-05	4.629336	-6725.779705
DUPLICATE			
nc7H16+O=C2H4+C4H8-1+CH3+OH	1.46E-07	5.459336	-3844.779705
DUPLICATE			
nc7H16+CH3=C2H4+C4H8-1+CH3+CH4	2.0623E-08	5.149336	883.220295
DUPLICATE			
nc7H16+HO2=C2H4+C4H8-1+CH3+H2O2	1.394287688	3.019336	10999.2203
DUPLICATE			
nc7H16+CH3O=C2H4+C4H8-1+CH3+CH3OH	0.027186443	3.019336	309.220295
DUPLICATE			
nc7H16+O2=C2H4+C4H8-1+CH3+HO2	3.502292326	3.019336	41519.2203
DUPLICATE			

nc7H16+C2H5=C2H4+C4H8-1+CH3+C2H6 DUPLICATE	0.012426602	3.019336	3709.220295
nc7H16+C2H3=C2H4+C4H8-1+CH3+C2H4 DUPLICATE	0.098708009	3.019336	10109.2203
nc7H16+H=C3H6+pC4H9+H2 DUPLICATE	6081027.419	2.361345	5064.7435
nc7H16+OH=C3H6+pC4H9+H2O DUPLICATE	220788760.6	1.571345	558.7435
nc7H16+O=C3H6+pC4H9+OH DUPLICATE	2779565.814	2.401345	3439.7435
nc7H16+CH3=C3H6+pC4H9+CH4 DUPLICATE	392624.107	2.091345	8167.7435
nc7H16+HO2=C3H6+pC4H9+H2O2 DUPLICATE	2.65446E+13	-0.038655	18283.7435
nc7H16+CH3O=C3H6+pC4H9+CH3OH DUPLICATE	5.17579E+11	-0.038655	7593.7435
nc7H16+O2=C3H6+pC4H9+HO2 DUPLICATE	6.66771E+13	-0.038655	48803.7435
nc7H16+C2H5=C3H6+pC4H9+C2H6 DUPLICATE	2.36579E+11	-0.038655	10993.7435
nc7H16+C2H3=C3H6+pC4H9+C2H4 DUPLICATE	1.87922E+12	-0.038655	17393.7435
nc7H16+H=C4H8-1+nc3H7+H2 DUPLICATE	424371302.6	1.567678	4510.01331
nc7H16+OH=C4H8-1+nc3H7+H2O DUPLICATE	15407990704	0.777678	4.01331
nc7H16+O=C4H8-1+nc3H7+OH DUPLICATE	193975110.4	1.607678	2885.01331
nc7H16+CH3=C4H8-1+nc3H7+CH4 DUPLICATE	27399712.62	1.297678	7613.01331
nc7H16+HO2=C4H8-1+nc3H7+H2O2 DUPLICATE	1.85245E+15	-0.832322	17729.01331
nc7H16+CH3O=C4H8-1+nc3H7+CH3OH DUPLICATE	3.61199E+13	-0.832322	7039.01331
nc7H16+O2=C4H8-1+nc3H7+HO2 DUPLICATE	4.65314E+15	-0.832322	48249.01331
nc7H16+C2H5=C4H8-1+nc3H7+C2H6 DUPLICATE	1.651E+13	-0.832322	10439.01331
nc7H16+C2H3=C4H8-1+nc3H7+C2H4 DUPLICATE	1.31143E+14	-0.832322	16839.01331
nc7H16+H=C6H12-1+CH3+H2 DUPLICATE	2885.678996	3.013404	3316.645
nc7H16+OH=C6H12-1+CH3+H2O DUPLICATE	104772.6716	2.223404	-1189.355
nc7H16+O=C6H12-1+CH3+OH DUPLICATE	1319.009788	3.053404	1691.645
nc7H16+CH3=C6H12-1+CH3+CH4 DUPLICATE	186.3150847	2.743404	6419.645
nc7H16+HO2=C6H12-1+CH3+H2O2 DUPLICATE	12596445684	0.613404	16535.645
nc7H16+CH3O=C6H12-1+CH3+CH3OH DUPLICATE	245611115.9	0.613404	5845.645
nc7H16+O2=C6H12-1+CH3+HO2 DUPLICATE	31640841000	0.613404	47055.645
nc7H16+C2H5=C6H12-1+CH3+C2H6 DUPLICATE	112265940.3	0.613404	9245.645
nc7H16+C2H3=C6H12-1+CH3+C2H4 DUPLICATE	891760062	0.613404	15645.645
nc7H16+H=C5H10-1+C2H5+H2 DUPLICATE	18980733.95	1.6061	3958.8104
nc7H16+OH=C5H10-1+C2H5+H2O DUPLICATE	689148796.1	0.8161	-547.1896
nc7H16+O=C5H10-1+C2H5+OH DUPLICATE	8675869.319	1.6461	2333.8104
nc7H16+CH3=C5H10-1+C2H5+CH4 DUPLICATE	1225499.114	1.3361	7061.8104
nc7H16+HO2=C5H10-1+C2H5+H2O2 DUPLICATE	8.28539E+13	-0.7939	17177.8104
nc7H16+CH3O=C5H10-1+C2H5+CH3OH DUPLICATE	1.61552E+12	-0.7939	6487.8104
nc7H16+O2=C5H10-1+C2H5+HO2 DUPLICATE	2.0812E+14	-0.7939	47697.8104
nc7H16+C2H5=C5H10-1+C2H5+C2H6 DUPLICATE	7.38436E+11	-0.7939	9887.8104
nc7H16+C2H3=C5H10-1+C2H5+C2H4 DUPLICATE	5.86561E+12	-0.7939	16287.8104
! including c5h11			
nc7H16+H=C2H4+C2H4+nc3H7+H2 DUPLICATE	21333.01488	2.607859	4931.8882
nc7H16+OH=C2H4+C2H4+nc3H7+H2O DUPLICATE	774554.9547	1.817859	425.8882
nc7H16+O=C2H4+C2H4+nc3H7+OH DUPLICATE	9751.069152	2.647859	3306.8882
nc7H16+CH3=C2H4+C2H4+nc3H7+CH4 DUPLICATE	1377.375128	2.337859	8034.8882
nc7H16+HO2=C2H4+C2H4+nc3H7+H2O2 DUPLICATE	93121987464	0.207859	18150.8882
nc7H16+CH3O=C2H4+C2H4+nc3H7+CH3OH DUPLICATE	1815734044	0.207859	7460.8882
nc7H16+O2=C2H4+C2H4+nc3H7+HO2 DUPLICATE	2.33912E+11	0.207859	48670.8882
nc7H16+C2H5=C2H4+C2H4+nc3H7+C2H6	829950586.9	0.207859	10860.8882

DUPLICATE			
nc7H16+C2H3=C2H4+C2H4+nc3H7+C2H4	6592531846	0.207859	17260.8882
DUPLICATE			
nc7H16+H=C2H4+C3H6+C2H5+H2	85867978226	0.605289	6351.53815
DUPLICATE			
nc7H16+OH=C2H4+C3H6+C2H5+H2O	3.11768E+12	-0.184711	1845.53815
DUPLICATE			
nc7H16+O=C2H4+C3H6+C2H5+OH	39249238713	0.645289	4726.53815
DUPLICATE			
nc7H16+CH3=C2H4+C3H6+C2H5+CH4	5544102328	0.335289	9454.53815
DUPLICATE			
nc7H16+HO2=C2H4+C3H6+C2H5+H2O2	3.74827E+17	-1.794711	19570.53815
DUPLICATE			
nc7H16+CH3O=C2H4+C3H6+C2H5+CH3OH	7.30855E+15	-1.794711	8880.53815
DUPLICATE			
nc7H16+O2=C2H4+C3H6+C2H5+HO2	9.41524E+17	-1.794711	50090.53815
DUPLICATE			
nc7H16+C2H5=C2H4+C3H6+C2H5+C2H6	3.34065E+15	-1.794711	12280.53815
DUPLICATE			
nc7H16+C2H3=C2H4+C3H6+C2H5+C2H4	2.65357E+16	-1.794711	18680.53815
DUPLICATE			
nc7H16+H=C2H4+C4H8-1+CH3+H2	0.001045048	4.520229	544.969195
DUPLICATE			
nc7H16+OH=C2H4+C4H8-1+CH3+H2O	0.037943392	3.730229	-3961.030805
DUPLICATE			
nc7H16+O=C2H4+C4H8-1+CH3+OH	0.000477679	4.560229	-1080.030805
DUPLICATE			
nc7H16+CH3=C2H4+C4H8-1+CH3+CH4	6.7474E-05	4.250229	3647.969195
DUPLICATE			
nc7H16+HO2=C2H4+C4H8-1+CH3+H2O2	4561.799054	2.120229	13763.9692
DUPLICATE			
nc7H16+CH3O=C2H4+C4H8-1+CH3+CH3OH	88.94799251	2.120229	3073.969195
DUPLICATE			
nc7H16+O2=C2H4+C4H8-1+CH3+HO2	11458.72115	2.120229	44283.9692
DUPLICATE			
nc7H16+C2H5=C2H4+C4H8-1+CH3+C2H6	40.65707687	2.120229	6473.969195
DUPLICATE			
nc7H16+C2H3=C2H4+C4H8-1+CH3+C2H4	322.950641	2.120229	12873.9692
DUPLICATE			
nc7H16+H=C3H6+pc4H9+H2	52122.57686	2.604418	1375.784
DUPLICATE			
nc7H16+OH=C3H6+pc4H9+H2O	1892456.382	1.814418	-3130.216
DUPLICATE			
nc7H16+O=C3H6+pc4H9+OH	23824.6143	2.644418	-249.216
DUPLICATE			
nc7H16+CH3=C3H6+pc4H9+CH4	3365.316218	2.334418	4478.784
DUPLICATE			
nc7H16+HO2=C3H6+pc4H9+H2O2	2.27523E+11	0.204418	14594.784
DUPLICATE			
nc7H16+CH3O=C3H6+pc4H9+CH3OH	4436350782	0.204418	3904.784
DUPLICATE			
nc7H16+O2=C3H6+pc4H9+HO2	5.71513E+11	0.204418	45114.784
DUPLICATE			
nc7H16+C2H5=C3H6+pc4H9+C2H6	2027803547	0.204418	7304.784
DUPLICATE			
nc7H16+C2H3=C3H6+pc4H9+C2H4	16107416121	0.204418	13704.784
DUPLICATE			
nc7H16+H=C4H8-1+nc3H7+H2	1271510552	1.653316	6374.324
DUPLICATE			
nc7H16+OH=C4H8-1+nc3H7+H2O	46165757796	0.863316	1868.324
DUPLICATE			
nc7H16+O=C4H8-1+nc3H7+OH	581192456.4	1.693316	4749.324
DUPLICATE			
nc7H16+CH3=C4H8-1+nc3H7+CH4	82095616.54	1.383316	9477.324
DUPLICATE			
nc7H16+HO2=C4H8-1+nc3H7+H2O2	5.55034E+15	-0.746684	19593.324
DUPLICATE			
nc7H16+CH3O=C4H8-1+nc3H7+CH3OH	1.08223E+14	-0.746684	8903.324
DUPLICATE			
nc7H16+O2=C4H8-1+nc3H7+HO2	1.39418E+16	-0.746684	50113.324
DUPLICATE			
nc7H16+C2H5=C4H8-1+nc3H7+C2H6	4.94675E+13	-0.746684	12303.324
DUPLICATE			
nc7H16+C2H3=C4H8-1+nc3H7+C2H4	3.92934E+14	-0.746684	18703.324
DUPLICATE			
nc7H16+H=C6H12-1+CH3+H2	20493.47387	3.000164	5215.0323
DUPLICATE			
nc7H16+OH=C6H12-1+CH3+H2O	744073.0628	2.210164	709.0323
DUPLICATE			
nc7H16+O=C6H12-1+CH3+OH	9367.324869	3.040164	3590.0323
DUPLICATE			
nc7H16+CH3=C6H12-1+CH3+CH4	1323.169807	2.730164	8318.0323
DUPLICATE			
nc7H16+HO2=C6H12-1+CH3+H2O2	89457258011	0.600164	18434.0323
DUPLICATE			
nc7H16+CH3O=C6H12-1+CH3+CH3OH	1744277514	0.600164	7744.0323
DUPLICATE			
nc7H16+O2=C6H12-1+CH3+HO2	2.24706E+11	0.600164	48954.0323
DUPLICATE			
nc7H16+C2H5=C6H12-1+CH3+C2H6	797288651.3	0.600164	11144.0323
DUPLICATE			
nc7H16+C2H3=C6H12-1+CH3+C2H4	6333088869	0.600164	17544.0323

DUPLICATE			
nc7H16+H=C5H10-1+C2H5+H2	4.00671E+12	0.208343	8083.878
DUPLICATE			
nc7H16+OH=C5H10-1+C2H5+H2O	1.45475E+14	-0.581657	3577.878
DUPLICATE			
nc7H16+O=C5H10-1+C2H5+OH	1.83142E+12	0.248343	6458.878
DUPLICATE			
nc7H16+CH3=C5H10-1+C2H5+CH4	2.58695E+11	-0.061657	11186.878
DUPLICATE			
nc7H16+HO2=C5H10-1+C2H5+H2O2	1.74899E+19	-2.191657	21302.878
DUPLICATE			
nc7H16+CH3O=C5H10-1+C2H5+CH3OH	3.41026E+17	-2.191657	10612.878
DUPLICATE			
nc7H16+O2=C5H10-1+C2H5+HO2	4.39327E+19	-2.191657	51822.878
DUPLICATE			
nc7H16+C2H5=C5H10-1+C2H5+C2H6	1.55879E+17	-2.191657	14012.878
DUPLICATE			
nc7H16+C2H3=C5H10-1+C2H5+C2H4	1.23819E+18	-2.191657	20412.878
DUPLICATE			
! c5h11			
nc7H16+H=C2H4+C2H4+nc3H7+H2	21333.01488	2.607859	4931.8882
DUPLICATE			
nc7H16+OH=C2H4+C2H4+nc3H7+H2O	774554.9547	1.817859	425.8882
DUPLICATE			
nc7H16+O=C2H4+C2H4+nc3H7+OH	9751.069152	2.647859	3306.8882
DUPLICATE			
nc7H16+CH3=C2H4+C2H4+nc3H7+CH4	1377.375128	2.337859	8034.8882
DUPLICATE			
nc7H16+HO2=C2H4+C2H4+nc3H7+H2O2	93121987464	0.207859	18150.8882
DUPLICATE			
nc7H16+CH3O=C2H4+C2H4+nc3H7+CH3OH	1815734044	0.207859	7460.8882
DUPLICATE			
nc7H16+O2=C2H4+C2H4+nc3H7+HO2	2.33912E+11	0.207859	48670.8882
DUPLICATE			
nc7H16+C2H5=C2H4+C2H4+nc3H7+C2H6	829950586.9	0.207859	10860.8882
DUPLICATE			
nc7H16+C2H3=C2H4+C2H4+nc3H7+C2H4	6592531846	0.207859	17260.8882
DUPLICATE			
nc7H16+H=C2H4+C3H6+C2H5+H2	85867978226	0.605289	6351.53815
DUPLICATE			
nc7H16+OH=C2H4+C3H6+C2H5+H2O	3.11768E+12	-0.184711	1845.53815
DUPLICATE			
nc7H16+O=C2H4+C3H6+C2H5+OH	39249238713	0.645289	4726.53815
DUPLICATE			
nc7H16+CH3=C2H4+C3H6+C2H5+CH4	5544102328	0.335289	9454.53815
DUPLICATE			
nc7H16+HO2=C2H4+C3H6+C2H5+H2O2	3.74827E+17	-1.794711	19570.53815
DUPLICATE			
nc7H16+CH3O=C2H4+C3H6+C2H5+CH3OH	7.30855E+15	-1.794711	8880.53815
DUPLICATE			
nc7H16+O2=C2H4+C3H6+C2H5+HO2	9.41524E+17	-1.794711	50090.53815
DUPLICATE			
nc7H16+C2H5=C2H4+C3H6+C2H5+C2H6	3.34065E+15	-1.794711	12280.53815
DUPLICATE			
nc7H16+C2H3=C2H4+C3H6+C2H5+C2H4	2.65357E+16	-1.794711	18680.53815
DUPLICATE			
nc7H16+H=C2H4+C4H8-1+CH3+H2	0.001045048	4.520229	544.969195
DUPLICATE			
nc7H16+OH=C2H4+C4H8-1+CH3+H2O	0.037943392	3.730229	-3961.030805
DUPLICATE			
nc7H16+O=C2H4+C4H8-1+CH3+OH	0.000477679	4.560229	-1080.030805
DUPLICATE			
nc7H16+CH3=C2H4+C4H8-1+CH3+CH4	6.7474E-05	4.250229	3647.969195
DUPLICATE			
nc7H16+HO2=C2H4+C4H8-1+CH3+H2O2	4561.799054	2.120229	13763.9692
DUPLICATE			
nc7H16+CH3O=C2H4+C4H8-1+CH3+CH3OH	88.94799251	2.120229	3073.969195
DUPLICATE			
nc7H16+O2=C2H4+C4H8-1+CH3+HO2	11458.72115	2.120229	44283.9692
DUPLICATE			
nc7H16+C2H5=C2H4+C4H8-1+CH3+C2H6	40.65707687	2.120229	6473.969195
DUPLICATE			
nc7H16+C2H3=C2H4+C4H8-1+CH3+C2H4	322.950641	2.120229	12873.9692
DUPLICATE			
nc7H16+H=C3H6+pc4H9+H2	48266974778	0.46756	6714.58
DUPLICATE			
nc7H16+OH=C3H6+pc4H9+H2O	1.75247E+12	-0.32244	2208.58
DUPLICATE			
nc7H16+O=C3H6+pc4H9+OH	22062264120	0.50756	5089.58
DUPLICATE			
nc7H16+CH3=C3H6+pc4H9+CH4	3116377639	0.19756	9817.58
DUPLICATE			
nc7H16+HO2=C3H6+pc4H9+H2O2	2.10693E+17	-1.93244	19933.58
DUPLICATE			
nc7H16+CH3O=C3H6+pc4H9+CH3OH	4.10819E+15	-1.93244	9243.58
DUPLICATE			
nc7H16+O2=C3H6+pc4H9+HO2	5.29237E+17	-1.93244	50453.58
DUPLICATE			
nc7H16+C2H5=C3H6+pc4H9+C2H6	1.8778E+15	-1.93244	12643.58
DUPLICATE			
nc7H16+C2H3=C3H6+pc4H9+C2H4	1.49159E+16	-1.93244	19043.58
DUPLICATE			

nc7H16+H=C4H8-1+nc3H7+H2	19089740474	0.7238	7337.681	
DUPLICATE				
nc7H16+OH=C4H8-1+nc3H7+H2O	6.93107E+11	-0.0662	2831.681	
DUPLICATE				
nc7H16+O=C4H8-1+nc3H7+OH	8725694913	0.7638	5712.681	
DUPLICATE				
nc7H16+CH3=C4H8-1+nc3H7+CH4	1232537167	0.4538	10440.681	
DUPLICATE				
nc7H16+HO2=C4H8-1+nc3H7+H2O2	8.33297E+16	-1.6762	20556.681	
DUPLICATE				
nc7H16+CH3O=C4H8-1+nc3H7+CH3OH	1.6248E+15	-1.6762	9866.681	
DUPLICATE				
nc7H16+O2=C4H8-1+nc3H7+HO2	2.09315E+17	-1.6762	51076.681	
DUPLICATE				
nc7H16+C2H5=C4H8-1+nc3H7+C2H6	7.42677E+14	-1.6762	13266.681	
DUPLICATE				
nc7H16+C2H3=C4H8-1+nc3H7+C2H4	5.89929E+15	-1.6762	19666.681	
DUPLICATE				
nc7H16+H=C6H12-1+CH3+H2	188563.6634	2.121224	5837.154	
DUPLICATE				
nc7H16+OH=C6H12-1+CH3+H2O	6846332.81	1.331224	1331.154	
DUPLICATE				
nc7H16+O=C6H12-1+CH3+OH	86190.22352	2.161224	4212.154	
DUPLICATE				
nc7H16+CH3=C6H12-1+CH3+CH4	12174.69267	1.851224	8940.154	
DUPLICATE				
nc7H16+HO2=C6H12-1+CH3+H2O2	8.2311E+11	-0.278776	19056.154	
DUPLICATE				
nc7H16+CH3O=C6H12-1+CH3+CH3OH	16049370653	-0.278776	8366.154	
DUPLICATE				
nc7H16+O2=C6H12-1+CH3+HO2	2.06756E+12	-0.278776	49576.154	
DUPLICATE				
nc7H16+C2H5=C6H12-1+CH3+C2H6	7335977776	-0.278776	11766.154	
DUPLICATE				
nc7H16+C2H3=C6H12-1+CH3+C2H4	58271742768	-0.278776	18166.154	
DUPLICATE				
nc7H16+H=C5H10-1+C2H5+H2	4166763.303	2.33486	4609.057	
DUPLICATE				
nc7H16+OH=C5H10-1+C2H5+H2O	151286031.5	1.54486	103.057	
DUPLICATE				
nc7H16+O=C5H10-1+C2H5+OH	1904578.295	2.37486	2984.057	
DUPLICATE				
nc7H16+CH3=C5H10-1+C2H5+CH4	269028.8348	2.06486	7712.057	
DUPLICATE				
nc7H16+HO2=C5H10-1+C2H5+H2O2	1.81886E+13	-0.06514	17828.057	
DUPLICATE				
nc7H16+CH3O=C5H10-1+C2H5+CH3OH	3.54649E+11	-0.06514	7138.057	
DUPLICATE				
nc7H16+O2=C5H10-1+C2H5+HO2	4.56877E+13	-0.06514	48348.057	
DUPLICATE				
nc7H16+C2H5=C5H10-1+C2H5+C2H6	1.62106E+11	-0.06514	10538.057	
DUPLICATE				
nc7H16+C2H3=C5H10-1+C2H5+C2H4	1.28765E+12	-0.06514	16938.057	
DUPLICATE				
C4H2+H=C4H+H2	5.000E+13	0.0	20000.	!83.682 ! (4) 99BAK/DEL
C6H6+C2H=C6H5+C2H2	2.000E+13	0.0	0.0	! (5)99BAK/DEL?
! ***** Nitrate Mechanism *****				Ref
CH3NO2(+M)=CH3+NO2(+M)		1.78E16	0.00	58878 ! 01
LOW /1.26E17	0.00	42254	/	
CH3ONO=CH3O+NO	6.31E18	0.00	41466.	!20733 ! 05
CH3ONO+M=CH3O+NO+M	2.29E16	0.00	30596.	!15298 ! 06
CH3ONO(+M)=CH2O+HNO(+M)		3.98E13	0.00	38748. !19374 ! 08
LOW /4.63E012	0.00	0/		
CH3NO2+CH3=CH4+CH2NO2	2.40E11	0.00	9058.	!4529 ! 02
CH3+NO2=CH3O+NO	1.30E13	0.00	0	! 01
NO2+NO2(+M)=N2O4(+M)		2.63E14	-1.10	0
LOW /1.28E24	-3.80	0/		
NO2+NO2=>NO+NO3	9.64E09	0.73	21060.	!10530 ! 12
NO3+NO=>N2O2	8.00E012	0.00	0	! 13
CH3+NO+M=CH3NO+M	8.20E31	-5.24	1902.	! 02
NO2+NO=N2O3	1.60E09	1.40	0	! 14
CH3O+NO2(+M)=CH3ONO2(+M)		1.21E13	0.00	0 ! 15
LOW /3.27E19	0.00	0/		
CH3ONO2=CH3O+NO2	1.00E13	0.00	37604.	!16802 ! 16
CH3O+NO2=CH2O+HNO2	4.00E011	0.00	0	! 02
CH3OH+NO2=CH2OH+HNO2	2.00E12	0.00	22744.	!11372 ! 17
2HNO2=H2O+NO+NO2	5.71E05	0.00	0	! 18
CH2O+NO2=HCO+HNO2	2.95E11	0.00	12940.	! 6470 ! 21
NO2+NO2=NO+NO+O2	1.63E12	0.00	26294.	! 13147 ! 12
CH3CHO+NO2=HNO2+CH3CO	3.12E11	0.00	27264.	! 13632 ! 22
HCO+NO=CO+HNO	2.00E11	0.50	2014.	! 1007 ! 10
HCO+HNO=NO+CH2O	6.03E11	0.00	2000.	! 1000 ! 12
CH3O+HNO=CH3OH+NO	3.16E13	0.00	0	! 23
CH3+HNO=CH4+NO	2.00E12	0.00	0	! 24
CH3NO2+H=CH3+HNO2	3.18E12	0.00	15844	! 7922 ! 26
CH3+HNO2=CH4+NO2	2.14E11	0.00	20104.	! 10052 ! 26
CH3NO2+H=CH2NO2+H2	2.50E09	1.27	2658.	! 1329 ! 02
CH2NO2=CH2O+NO	1.00E13	0.00	36240.	! 18120 ! 02
CH3NO=HCN+H2O	7.90E09	0.00	39560.	! 19780 ! 02
HNO2+M=NO+OH+M	1.80E30	-3.86	52640.	! 26320 ! 02
HCO+NO2=HNO2+CO	1.00E14	0.00	0	! 02
CO+NO2=NO+CO2	1.90E12	0.00	29500.	! 14750 ! 02

```

C2H5+NO2=CH3+CH2O+NO      1.30E13      0.00      0      !      02
! ***** Reactions from Grimech-3 *****
N+NO<=>N2+O      2.700E+13      .000      355.00
N+O2<=>NO+O      9.000E+09      1.000      6500.00
N+OH<=>NO+H      3.360E+13      .000      385.00
N2O+O<=>N2+O2      1.400E+12      .000      10810.00
N2O+O<=>2NO      2.900E+13      .000      23150.00
N2O+H<=>N2+OH      3.870E+14      .000      18880.00
N2O+OH<=>N2+HO2      2.000E+12      .000      21060.00
N2O(+M)<=>N2+O(+M)      7.910E+10      .000      56020.00
LOW / 6.370E+14      .000      56640.00/
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .625/
HO2+NO<=>NO2+OH      2.110E+12      .000      -480.00
NO+O+M<=>NO2+M      1.060E+20      -1.410      .00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
NO2+O<=>NO+O2      3.900E+12      .000      -240.00
NO2+H<=>NO+OH      1.320E+14      .000      360.00
NH+O<=>N+H      4.000E+13      .000      .00
NH+H<=>N+H2      3.200E+13      .000      330.00
NH+OH<=>HNO+H      2.000E+13      .000      .00
NH+OH<=>N+H2O      2.000E+09      1.200      .00
NH+O2<=>HNO+O      4.610E+05      2.000      6500.00
NH+O2<=>NO+OH      1.280E+06      1.500      100.00
NH+N<=>N2+H      1.500E+13      .000      .00
NH+H2O<=>HNO+H2      2.000E+13      .000      13850.00
NH+NO<=>N2+OH      2.160E+13      -.230      .00
NH+NO<=>N2O+H      3.650E+14      -.450      .00
NH2+O<=>OH+NH      3.000E+12      .000      .00
NH2+O<=>H+HNO      3.900E+13      .000      .00
NH2+H<=>NH+H2      4.000E+13      .000      3650.00
NH2+OH<=>NH+H2O      9.000E+07      1.500      -460.00
NNH<=>N2+H      3.300E+08      .000      .00
NNH+M<=>N2+H+M      1.300E+14      -.110      4980.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
NNH+O2<=>HO2+N2      5.000E+12      .000      .00
NNH+O<=>OH+N2      2.500E+13      .000      .00
NNH+O<=>NH+NO      7.000E+13      .000      .00
NNH+H<=>H2+N2      5.000E+13      .000      .00
NNH+OH<=>H2O+N2      2.000E+13      .000      .00
NNH+CH3<=>CH4+N2      2.500E+13      .000      .00
H+NO+M<=>HNO+M      4.480E+19      -1.320      740.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
HNO+O<=>NO+OH      2.500E+13      .000      .00
HNO+H<=>H2+NO      9.000E+11      .720      660.00
HNO+OH<=>NO+H2O      1.300E+07      1.900      -950.00
HNO+O2<=>HO2+NO      1.000E+13      .000      13000.00
CN+O<=>CO+N      7.700E+13      .000      .00
CN+OH<=>NCO+H      4.000E+13      .000      .00
CN+H2O<=>HCN+OH      8.000E+12      .000      7460.00
CN+O2<=>NCO+O      6.140E+12      .000      -440.00
CN+H2<=>HCN+H      2.950E+05      2.450      2240.00
NCO+O<=>NO+CO      2.350E+13      .000      .00
NCO+H<=>NH+CO      5.400E+13      .000      .00
NCO+OH<=>NO+H+CO      0.250E+13      .000      .00
NCO+N<=>N2+CO      2.000E+13      .000      .00
NCO+O2<=>NO+CO2      2.000E+12      .000      20000.00
NCO+M<=>N+CO+M      3.100E+14      .000      54050.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
NCO+NO<=>N2O+CO      1.900E+17      -1.520      740.00
NCO+NO<=>N2+CO2      3.800E+18      -2.000      800.00
HCN+M<=>H+CN+M      1.040E+29      -3.300      126600.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
HCN+O<=>NCO+H      2.030E+04      2.640      4980.00
HCN+O<=>NH+CO      5.070E+03      2.640      4980.00
HCN+O<=>CN+OH      3.910E+09      1.580      26600.00
HCN+OH<=>HOCN+H      1.100E+06      2.030      13370.00
HCN+OH<=>HNCO+H      4.400E+03      2.260      6400.00
HCN+OH<=>NH2+CO      1.600E+02      2.560      9000.00
H+HCN(+M)<=>H2CN(+M)      3.300E+13      .000      .00
LOW / 1.400E+26      -3.400      1900.00/
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ .70/
H2CN+N<=>N2+CH2      6.000E+13      .000      400.00
C+N2<=>CN+N      6.300E+13      .000      46020.00
CH+N2<=>HCN+N      3.120E+09      0.880      20130.00
CH+N2(+M)<=>HCNN(+M)      3.100E+12      .150      .00
LOW / 1.300E+25      -3.160      740.00/
TROE/ .6670      235.00      2117.00      4536.00 /
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/ 1.0/
CH2+N2<=>HCN+NH      1.000E+13      .000      74000.00
CH2*+N2<=>NH+HCN      1.000E+11      .000      65000.00
C+NO<=>CN+O      1.900E+13      .000      .00
C+NO<=>CO+N      2.900E+13      .000      .00
CH+NO<=>HCN+O      4.100E+13      .000      .00
CH+NO<=>H+NCO      1.620E+13      .000      .00
CH+NO<=>N+HCO      2.460E+13      .000      .00
CH2+NO<=>H+HNCO      3.100E+17      -1.380      1270.00
CH2+NO<=>OH+HCN      2.900E+14      -.690      760.00
CH2+NO<=>H+HCNO      3.800E+13      -.360      580.00
CH2*+NO<=>H+HNCO      3.100E+17      -1.380      1270.00
CH2*+NO<=>OH+HCN      2.900E+14      -.690      760.00
CH2*+NO<=>H+HCNO      3.800E+13      -.360      580.00
CH3+NO<=>HCN+H2O      9.600E+13      .000      28800.00

```

CH3+NO<=>H2CN+OH	1.000E+12	.000	21750.00
HCNN+O<=>CO+H+N2	2.200E+13	.000	.00
HCNN+O<=>HCN+NO	2.000E+12	.000	.00
HCNN+O2<=>O+HCO+N2	1.200E+13	.000	.00
HCNN+OH<=>H+HCO+N2	1.200E+13	.000	.00
HCNN+H<=>CH2+N2	1.000E+14	.000	.00
HNCO+O<=>NH+CO2	9.800E+07	1.410	8500.00
HNCO+O<=>HNO+CO	1.500E+08	1.570	44000.00
HNCO+O<=>NCO+OH	2.200E+06	2.110	11400.00
HNCO+H<=>NH2+CO	2.250E+07	1.700	3800.00
HNCO+H<=>H2+NCO	1.050E+05	2.500	13300.00
HNCO+OH<=>NCO+H2O	3.300E+07	1.500	3600.00
HNCO+OH<=>NH2+CO2	3.300E+06	1.500	3600.00
HNCO+M<=>NH+CO+M	1.180E+16	.000	84720.00
H2/2.00/ H2O/6.00/ CH4/2.00/ CO/1.50/ CO2/2.00/ C2H6/3.00/ AR/		.70/	
HCNO+H<=>H+HNCO	2.100E+15	-.690	2850.00
HCNO+H<=>OH+HCN	2.700E+11	.180	2120.00
HCNO+H<=>NH2+CO	1.700E+14	-.750	2890.00
HOCN+H<=>H+HNCO	2.000E+07	2.000	2000.00
HCCO+NO<=>HCNO+CO	0.900E+13	.000	.00
CH3+N<=>H2CN+H	6.100E+14	-.310	290.00
CH3+N<=>HCN+H2	3.700E+12	.150	-90.00
NH3+H<=>NH2+H2	5.400E+05	2.400	9915.00
NH3+OH<=>NH2+H2O	5.000E+07	1.600	955.00
NH3+O<=>NH2+OH	9.400E+06	1.940	6460.00
NH+CO2<=>HNO+CO	1.000E+13	.000	14350.00
CN+NO2<=>NCO+NO	6.160E+15	-0.752	345.00
NCO+NO2<=>N2O+CO2	3.250E+12	.000	-705.00
N+CO2<=>NO+CO	3.000E+12	.000	11300.00

! *****

CH3NO2+OH=H2O+CH2NO2	1.49e13	0.	5743.
CH3NO2+O=CH2NO2+OH	1.5e13	0.	5354.
CH3NO2+O=CH3NO+O2	1.5e13	0.	5354.

!Reactions from updated A4 Heptane mechanism-copied by Moshan Kahandawala UDRI

!From C7NIST_chem_A4_03_07_04_Pyridine

! following EtNO2 reactions from TAL, as modified by MBC

nc3H7 + NO2 = C2H5 + CH2O + NO	1.00E+13	0	0	!Analogy to C2H5 + NO2
pc4H9 + NO2 = nc3H7 + CH2O + NO	1.00E+13	0	0	!Analogy to C2H5 + NO2
C6H5CH2 + NO2 = C6H5CHO + NO	+ H 1.00E+13	0	0	!Analogy to CH3 + NO2; Note: C6H5CH2O assumed to decompose

! R + NO Reactions

C3H3 + NO = HCN + CH2O	9.60E+13	0	28800	!Analogy to CH3 reaction
------------------------	----------	---	-------	--------------------------

C3H3 + NO = H2CN + HCCO	1.00E+12	0	21750	!Analogy to CH3 reaction
-------------------------	----------	---	-------	--------------------------

! ETNO2 Reactions will need new Thermo & Transport for EtNO2 and related species

CH3NO2 = CH3 + NO2	1.78E+16	0	58880	!NIST HP limit
--------------------	----------	---	-------	----------------

! *****

! Pyridine reaction mechanism

! Obtained from John Mackie,

! work by Ikeda, Nicholls and Mackie and reported at the 28th symposium

! Proc Comb Inst. 28, p.1709 (2000)

PYRIDINE<=>A-C5H4N+H	7.94E+15	0	98000	
PYRIDINE+H<=>A-C5H4N+H2	1E+14	0	5000	
PYRIDINE+O2<=>A-C5H4N+HO2	6.31E+13	0	51000	
PYRIDINE+O<=>A-C5H4N+OH	4E+12	0	5000	
PYRIDINE+O=>C5H5NO	4E+12	0	5000	
C5H5NO=>PYRIDINE+O	1E+14	0	30000	
C5H5NO=>C2H2+CH2CO+HCN	6E+12	0	5000	
PYRIDINE+OH<=>A-C5H4N+H2O	1.6E+8	1.42	1450	
PYRIDINE+OH=>C5H4NOH+H	1.3E+13	0	10600	
C5H4NOH+H=>PYRIDINE+OH	2.21E+13	0	19400	
PYRIDINE+N2O=>C5H5NO+N2	7.94E+9	0	20000	
A-C5H4N+O2<=>C5H4NO+O	2E+13	0	15000	
A-C5H4N+O2=>OCNC4H4O	5E+12	0	13000	
OCNC4H4O=>CO+HCN+C3H3O	1E+15	0	32000	
A-C5H4N+HO2<=>C5H4NO+OH	3E+12	0	0	
C5H4NO<=>PYRILYL+CO	2E+14	0	45000	
C5H4NO=>NC4H4CO	2E+15	0	70000	
NC4H4CO=>C5H4NO	5E+11	0	1000	
NC4H4CO=>HCN+C3H3CO	6.3E+13	0	12500	
HCN+C3H3CO=>NC4H4CO	7.9E+11	0	5000	
C3H3CO=>C2H2+HCCO	1E+12	0	37000	
HCCO+C2H2=>C3H3CO	2.51E+11	0	5000	
NC4H4CO=>NCC3H4CO	1E+13	0	5000	
NCC3H4CO=>NC4H4CO	1E+12	0	48000	
NCC3H4CO=>CH2CO+HCCHCN	1.6E+13	0	39000	
CH2CO+HCCHCN=>NCC3H4CO	7.9E+10	0	5000	
C5H4NO=>C4H4NCO	5E+15	0	35000	
C4H4NCO=>C5H4NO	5E+11	0	5000	
C4H4NCO=>C2H2+C2H2NCO	1E+15	0	41800	
C2H2+C2H2NCO=>C4H4NCO	1E+12	0	5000	
C2H2NCO=>NCO+C2H2	1E+12	0	19200	
NCO+C2H2=>C2H2NCO	2.5E+11	0	5000	
C4H4NCO+O2=>HCO+NACROLEIN	5.42E+12	0	0	
NACROLEIN=>HCO+C2H2NCO	5E+16	0	99300	
PYRROLE+M<=>PYRLNE+M	1.2E+36	-5.5	57240	
PYRROLE<=>HCN+PC3H4	1.1E+14	0	77200	

PYRLNE<=>PYRLYL+H	6.3E+14	0		83389
PYRLNE+H<=>PYRLYL+H2	6E+14	0		11998
PYRLYL+PYRIDINE<=>PYRROLE+A-C5H4N	5E+11	0	10000	
PYRROLE+O2<=>PYRLYL+HO2	5E+13	0		45500
PYRLYL+O2<=>HNACROLEIN	5E+12	0		25000
HNACROLEIN<=>C3H3O+HNCO	1E+15	0		32000
C3H3O<=>C2H2+HCO	5E+14	0		24000
C5H4NOH<=>C5H4NO+H	2.7E+16	0	89000	
C5H4NO+H<=>C5H4NOH	2.5E+14	0	0	
C5H4NOH+OH<=>C5H4NO+H2O	2E+13	0		15000
C5H4NO+H2O<=>C5H4NOH+OH	1E+13	0		44000
C5H4NOH+O<=>C5H4NO+OH	1E+13	0		3200
C5H4NO+OH<=>C5H4NOH+O	1E+13	0		15300
CO+N2O<=>CO2+N2	8E+12	0		36000
A-C5H4N<=>C4H4CN	1E+14	0		40000
C4H4CN<=>C2H2+HCCHCN	1.01E+13	0	30000	
C4H4CN<=>CVA+H	1E+12	0		40000
C4H4CN<=>HCN+HCCHCCH	5E+13	0		45000
C4H4CN<=>A-C4H4CN	1E+13	0		18000
HCCCN+C2H3<=>A-C4H4CN	7E+11	0		8000
H+CVA<=>A-C4H4CN	1E+12	0		5000
CVA+H<=>HCN+HCCHCCH	5E+12	0	6000	
H+HCCHCN<=>H2CCHCN	2E+13	0		0
H+H2CCHCN<=>HCN+C2H3	1E+13	0		4000
HCCHCCH<=>C4H2+H	3E+11	0		54000
2C3H3<=>CH2CHCCH+C2H2		5.01E+12	0	0
2A-C5H4N<=>BIPY	1E+13	0		0
CH3CN<=>CH3+CN	1E+16	0		117000
HCCHCN<=>HCCCN+H	1E+12	0		42000
H+H2CCHCN<=>HCCHCN+H2	5.01E+13	0	8000	
H2CCHCN+M<=>HCCCN+H2+M	3E+17	0		76000
H2CCHCN+M<=>C2H2+HCN+M	1E+17	0		73380
CH2CHCCH<=>C4H2+H2		2E+14	0	87000
HCCHCN<=>C2H2+CN	5.01E+13	0	58000	
C2N2+M<=>2CN+M	1.39E+68	-13.22	171100	!kinetics average
H+C2N2<=>HCN+CN	3.09E+14	0		7870
END				

REFERENCES

- [1] Canfield, C.A. Effects of Diesel-Water Emulsion Combustion on Diesel Engine NO_x Emissions. University of Florida, 1999.
- [2] Owen, K.; Coley, T. *Automotive Fuels Reference Book*, 2nd ed.; Society of Automotive Engineers, Inc.: Warrendale, PA, 1995.
- [3] Siemiatycki, J.; Dewar, R.; Nadon, L.; Gerin, M.; Richardson, L.; Wacholder, S. Cancer and petroleum-derived liquids: Results from a case-referent study in Montreal. *Scand J. Work Environ. Health* 13; 493-504, 1987.
- [4] Rosner, G. *International Program on Chemical Safety Diesel Fuel and Exhaust Emissions*, Environmental Health Criteria 171, Geneva, 1996.
- [5] *Health Assessment Document for Diesel Engine Exhaust*; EPA/600/8-90/057F; U.S. Environmental Protection Agency: Washington, DC, 2002.
- [6] *World Energy Outlook*; International Energy Agency: Paris, 2004.
- [7] Stone, R. *Introduction to Internal Combustion Engines*. Society of Automotive Engineers: Warrendale, PA, 1999.
- [8] Edwards, S.P.; Fränkle, G.R.; Binder, K.; Wirbeleit, F. *Strategic Analysis of Technologies for Future Truck Engines*; SAE Paper 2000-01-3458; Society of Automotive Engineers: Warrendale, PA, 2000.
- [9] Walsh, M. P. Global Trends in Diesel Emissions Regulation - A 2001 Update; SAE Paper 01-01-0183; Society of Automotive Engineers: Warrendale, PA, 2001.
- [10] Heywood, J.B. *Internal Combustion Engine Fundamentals Book*; McGraw-Hill, McGraw-Hill Series in Mechanical Engineering, International Ed., 1988.
- [11] Cen, Y.P.; Sage, R.E. The regulation of rubisco activity in response to variation in temperature and atmospheric CO₂ partial pressure. 139; 979-990, 2005.
- [12] Gupta, A.K.; Lilley, d.G. The environmental challenge of gas turbines. *J. Inst. Energy* 65; 106-117, 1992.

REFERENCES CONTINUED

- [13] Chan, T.T.; Borman, G.L. *An Experimental Study of Swirl and EGR Effects on Diesel Combustion by Use of the Dumping Method*; SAE Paper 820359, Society of Automotive Engineers: Warrendale, PA, 1982.
- [14] Dec, J.E. A Conceptual Model of DI Diesel Combustion Based on Laser-Sheet Imaging. Presented at the International Congress & Exposition, Session: Comb & Flow Diagnostics, Detroit, MI. SAE Paper 970873, Society of Automotive Engineers: Warrendale, PA, 1997.
- [15] Siebers, D.L.; Higgins, B.S. *Effects of Injector Conditions on the Flame Lift-Off Length of DI Diesel Sprays*; Sandia Report SAND2000-8249, Sandia National Laboratory, NM, 2000.
- [16] Siebers, D.L.; Higgins, B.S. *Flame Lift-Off on Direct-Injection Diesel Sprays Under Quiescent Conditions*; SAE Paper 2001-01-0530, Society of Automotive Engineers: Warrendale, PA, 2001.
- [17] Higgins, B.S.; Siebers, D.L. *Measurement of the Flame Lift-Off Location on DI Diesel Sprays Using OH Chemiluminescence*; SAE Paper 2001-01-0918, Society of Automotive Engineers: Warrendale, PA, 2001.
- [18] Flynn, P.F.; Durett, R.P.; Hunter, G.L; Zur-Loye, A.O.; Akinyemi, O.C.; Dec, J.E., Westbrook, C.K. *Diesel Combustion: An Integrated View Combining Laser Diagnostics, Chemical Kinetics, and Empirical Validation*; SAE Paper 99-01-0509, Society of Automotive Engineers: Warrendale, PA, 1999.
- [19] Glassman, I. Soot Formation in Combustion Processes. Presented at the 22nd Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1988; pp. 295-311.
- [20] Glassman, I. *Environmental Combustion Considerations, Combustion*, 3rd ed., Academic Press, Inc: New York, 2000; Chapter 8:
- [21] Warnatz, J.; Maas, U.; Dibble, R.W. *Combustion - Physical and Chemical Fundamentals, Pollutant Formation*, Springer-Verlag: Berlin, 1996.
- [22] D'Anna A.; Violi, A. Kinetic Evaluation of High Molecular Weight Aromatic Formation in Rich Premixed Ethylene Flames, Presented at the Fourth International Conference on Chemical Kinetics, Gaithersburg, MD, July 1997.
- [23] Violi, A.; D'Anna, A.; D'Alessio, A. Modeling of particulate formation in combustion and pyrolysis. *Chem. Eng. Sci.* 1999, 54, 3433-3442.
- [24] Frenklach, M.; Warnatz, J. Detailed modeling of PAH profiles in a sooting low-pressure acetylene flame. *Combust. Sci. Technol.* 1987, 51, 265-283.

REFERENCES CONTINUED

- [25] Colket, M.B.; Seery, D.J. Reaction Mechanisms for Toluene Pyrolysis, Presented at the Twenty-Fifth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1994; pp. 883-891.
- [26] Marinov, N.M.; Pitz, W.J.; Westbrook, C.K.; Castaldi, M.J.; Senkan, S.M. Modeling of aromatic and polycyclic aromatic hydrocarbon formation in premixed methane and ethane flames. *Combust. Sci. Technol.* 1996. 116, 211.
- [27] Castaldi, M.J.; Marinov, N.M.; Melius, C.F.; Huang, J.; Senkan, S.M.; Pitz, W.J.; Westbrook, C.K. *Experimental and Modeling Investigation of Aromatic and Polycyclic Aromatic Hydrocarbon Formation in a Premixed Ethylene Flame*, Proceedings of the 26th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1996, p. 693.
- [28] Turns, S.R. *An Introduction to Combustion: Concepts and Applications*; McGraw-Hill, Inc: New York, 1995.
- [29] Dec, J.E.; Kelly-Zion, P.L. *The Effects of Injection Timing and Diluent Addition on Late-Combustion Soot Burnout in a Diesel Engine Based on Simultaneous 2-D Imaging of OH and Soot*; SAE Paper 2000-01-0238, Society of Automotive Engineers:Warrendale, PA, 2000.
- [30] Pipho, M.J.; Kittelson, D.B.; Luo, L.; Zarling, D.D. *Injection Timing and Bowl Configuration Effects on In-Cylinder Particle Mass*; SAE Paper 921646, Society of Automotive Engineers:Warrendale, PA, 1992.
- [31] Donahue, R.J.; Borman, G.L.; Bower, G.R. *Cylinder-Averaged Histories of Nitrogen Oxide in a D.I. Diesel with Simulated Turbocharging*; SAE Paper 942046, Society of Automotive Engineers:Warrendale, PA, 1994.
- [32] Fenimore, C.P. Formation of Nitric Oxide in Premixed Hydrocarbon Flames. Presented at the 13th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1971; pp. 373-380.
- [33] Sarofim, A.F.; Pohl, J.H. *Kinetics of Nitric Oxide Formation in Premixed Laminar Flames*, Proceedings of the Fourteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1973; pp 739-754.
- [34] Toof, J.L. A model for the prediction of thermal, prompt and fuel NO_x emissions from combustion turbines. *J. Eng. Gas Turbines and Power*, 1986, 108, 340-347.
- [35] Akinyemi, O.C.; Cheng, W.K. A Flame Sheet Model for NO Production in Diesel Combustion Simulation; SAE Paper 982586, Society of Automotive Engineers:Warrendale, PA, 1998.

REFERENCES CONTINUED

- [36] Arun, S.; Solomon, P. *Photographic Study of Fuel Spray Ignition in a Rapid Compression Machine*; SAE Paper 86065, Society of Automotive Engineers:Warrendale, PA, 1986.
- [37] Larsson, A. Optical Studies in a DI Diesel Engine; SAE Paper 1999-01-3650, Society of Automotive Engineers:Warrendale, PA, 1999.
- [38] Larsson, A., Visualization of Fuel Injection and Combustion in a DI Diesel Engine", Licentiate Thesis, KTH, 1999.
- [39] Edwards, W.C.;Trask, T.C.; Kazmi, J.; Krstic, G. *Emission Reduction Options for Heavy Duty Diesel Fleet Vehicles*, Final Report, Levelton Consultants Ltd., Richmond, BC, 2005.
- [40] Müller, E., Zillmer, M., "Modeling of Nitric Oxide and Soot Formation in Diesel Engine Combustion", SAE paper 1998-01-2457, 1998.
- [41] Schwarz, V.; König, G.; Dittrich, P.; Binder, K. Analysis of Mixture Formation, Combustion and Pollutant Formation in HD Diesel Engines using Modern Optical Diagnostics and Numerical Simulation. 1999, vol. 108, pp. 2106-2121.
- [42] Dec, J.E.; Canaan, R.E., *PLIF Imaging of NO Formation in a DI Diesel Engine*; SAE Paper 1998-01-0147, Society of Automotive Engineers:Warrendale, PA, 1998.
- [43] Mellor, A.M.; Mello, J.P.; Duffy, K.P.; Easley, W.L.; Faulkner, J.C. *Skeletal Mechanism for NO_x Chemistry in Diesel Engines*; SAE Paper 1998-01-1450, Society of Automotive Engineers:Warrendale, PA, 1998.
- [44] Westbrook, C.K. *Chemical Kinetics of Hydrocarbon Ignition in Practical Combustion Systems*, Conference Paper ADA452727, Physical Chemistry Publication 4E07, Lawrence Livermore National Laboratory, MA, 2000.
- [45] Samec, N.; Kegl, B.; Dibble, R.W. Numerical and experimental study of water/oil emulsified fuel combustion in a diesel engine. *Fuel* 2002, 81, 2035-2044.
- [46] Egnell, R. A Theoretical Study of the Potential of NO_x Reduction by Fuel Rate Shaping in a DI Diesel Engine; SAE Paper 2000-01-2935, Society of Automotive Engineers:Warrendale, PA, 2000.
- [47] Kimura, S.; Aoki O.; Kitihara, Y.; Aiyoshizawa E. Ultra-Clean Combustion Technology Combining a Low-Temperature and Premixed Combustion Concept for Meeting Future Emission Standards; SAE Paper 2001-01-0200, Society of Automotive Engineers:Warrendale, PA, 2000.

REFERENCES CONTINUED

- [48] Pipho, M.J.; Kittelson, D.B.; Zarling, D.D. NO₂ Formation in a Diesel Engine; SAE Paper 1991-01-0231, Society of Automotive Engineers: Warrendale, PA, 1991.
- [49] Bedford, F.; Rutland, C.; Dittrich, P.; Raab, A.; Wirbeleit, F. Effects of Direct Water Injection on DI Diesel Engine Combustion; SAE Paper 2000-01-2938, Society of Automotive Engineers: Warrendale, PA, 2000.
- [50] Ishida, M.; Ueki, H.; Sakaguchi, D. Prediction of NO_x Reduction Rate Due To Port Water Injection in a DI Diesel Engine; SAE Paper 972961, Society of Automotive Engineers: Warrendale, PA, 1997.
- [51] Wirbeleit, F.; Enderle, Ch.; Lehner, W.; Raab, A.; Binder, K. Stratified Diesel Fuel-Water-Diesel Fuel Injection Combined with EGR—The Most Efficient In-Cylinder NO_x and PM Reduction Technology; SAE Paper 972962, Society of Automotive Engineers: Warrendale, PA, 1997.
- [52] Gollahalli, S.R.; Rasmussen, M.L.; Moussavi, S.J. *Combustion of Drops and Sprays of Diesel Oil and its Emulsions with Water*, Proceedings of the 18th Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, PA, 1981; pp. 349–60.
- [53] Kimura, S.; Aoki, O.; Ogawa, H.; Muranaka, O.; Enomoto, Y. New Combustion Concept for Ultra-Clean and High-Efficiency Small DI Diesel Engines; SAE Paper 1999-01-3681, Society of Automotive Engineers: Warrendale, PA, 1999.
- [54] Vollenweider, J. Emissions Control of Marine Diesel Engines The Slow-Speed Engineering Industry View. Presented at the IMar E Seminar on Emissions from Large Diesel Engines, London, England, 1993.
- [55] Lundqvist, U.; Smedler, G.; Stalhammar, P. *A Comparison Between Different EGR Systems for HD Diesel Engines and Their Effect on Performance, Fuel Consumption and Emissions*; SAE Paper 2000-01-0226, Society of Automotive Engineers: Warrendale, PA, 2000.
- [56] Neumann, K.H.; Schürmann, D.; Kohoutek, P.; Beyersdorf, J.; Hartung, A.; Nagel, C.; Schulze, J. *Unregulated Exhaust Gas Components of Modern Diesel Passenger Cars*; SAE Paper 1999-01-0514, Society of Automotive Engineers: Warrendale, PA, 1999.
- [57] Tsukahara, M.; Yoshimoto, Y. *W/O Emulsion Realizes Low Smoke and Efficient Operation of DI Engines Without High Pressure Injection*; SAE Paper 890449, Society of Automotive Engineers: Warrendale, PA, 1989.

REFERENCES CONTINUED

- [58] Lif, A.; Holmberg, K. Water-in-diesel emulsions and related systems. *Adv. Colloid Interface Sci.* 2006, 123–126; 231–239.
- [59] Storment, J.O.; Coon, C.W. Single-cylinder Diesel Engine Tests With Unstabilized Water-in-fuel Emulsions'; Report No. CG-D-13-78, Department of Transportation, U.S. Coast Guard, Washington, DC, 1978.
- [60] Samec, N.; Dibble, R.W.; Chen, J.Y.; Pagon, A. Reduction of NO_x and Soot Emission by Water Injection During Combustion in a Diesel Engine, Presented at FISITA 2000, Seoul, Korea, 2000.
- [61] Samec, N.; Dibble, R.W. *The Strategies for Reducing Emission from Heavy Duty Diesel Vehicles*; Urban Transport 2000, Cambridge, UK, 2000.
- [62] Miyamo, H.; Yasueda, S.; Tayama, K.; Tabeishi, M.; Tosa, Y.; Nago, E. Development of Stratified Fuel–water Injection System for Low-NO_x Diesel Combustion, SAE Paper D24, 2000-01-2004, Society of Automotive Engineers: Warrendale, PA, 2004.
- [63] Radloff, E.; Gautier, C. *Diesel Engine NO_x Reduction Using Charge Air Water Injection*, ICEF2005-1235, Proceedings of the ICED of ASME: 2005 Fall Technical Conference, Transportation Development Centre, Ottawa, Canada, 2005.
- [64] Velji, A.; Eichel, E.; Remmels, W.; Haug, F. Diesel engines with water addition meet future NO_x and soot limits. *MTZ Motortech Z.* 1996, 57, 400-407.
- [65] Law, C.K. A model for the combustion of oil/water emulsion droplets. *Combust. Sci. Technol.* 1977, 17, 29–38.
- [66] Park, J.W.; Huh, Y.; Park, K.H. *Experimental study on the combustion characteristics of emulsified diesel in rapid compression and expansion machine Process*. Inst. Engneers D 2000, ImechE, 214.
- [67] Isihada, M.; Chen, Z.L. An Analysis of the Added Water Effect on NO_x Formation in DI Diesel Engines; SAE Paper 941691, Society of Automotive Engineers: Warrendale, PA, 1994.
- [68] Hall, R.E. *Effect of water/residual oil emulsions on air pollutant emissions and efficiency of commercial boilers*. Environmental Protection Agency, Research Triangle Park, NC; ASME J. Eng. Power; 1976, 98, 425-434.
- [69] Nageli, D.W.; Moses, C.A. A Correlation for Soot Formation in Turbine Combustion that Includes Emulsified Fuels', in *Proceedings of the Symposium on Water-in-Fuel Emulsions in Combustion*, Walter, R., White, J., Eds.; Report No. CG-D-12-78, U.S. Department of Transportation, Washington, DC, 1978.

REFERENCES CONTINUED

- [70] Cernej, A.; Dobovis, ek .Z.; Bhattacharya, S.; Kegl B. Experimental Study on the Effect of the Multipoint Timed Port Water Injection in a Vehicular Diesel Engine. Proceedings of KONES 93, International Science Conference on IC Engines, Gdansk, Poland, 1993; pp. 81-9.
- [71] Mello, J.P.; Mello, A.M. *NOx Emission from Direct Injection Diesel Engines with Water/steam Dilution*; SAE Inc. 01-0836, Society of Automotive Engineers:Warrendale, PA, 1999, pp. 15-30.
- [72] Yoshimoto, Y.; Tsukahara, M.; Kuramoto, T. *Improvement of BSFC by Reducing Diesel Engine Cooling Losses with Emulsified Fuel*; SAE Paper 962022, Society of Automotive Engineers:Warrendale, PA, 1996.
- [73] Kozinski, J.A. PACs formation and interaction in semipractical flames of liquid fuels. *Combust. Flame* 1994, 96, 249-260.
- [74] Schlitt, H-G.; Exner, P. Emission of diesel motors when run on alternative fuels. *Glueckauf-Forschungshefte* 1991, 52, 278-282.
- [75] Lawson, A.; Vergeer, E.C.; Mitchell, E.W.; Dainty, E.D. Heavy-duty diesel emission control. *Review of Technology*, 1986, 36, 238.
- [76] Gunnerman, R.W.; Russell, R. *Emission and Efficiency Benefits of Emulsified Fuels to Internal Combustion Engines*; SAE Paper 972009, Society of Automotive Engineers:Warrendale, PA, 1997.
- [77] Vchniesky, R.; Murat, M.; Parois, A.; Dujou, M., Employment of Fuel-water Emulsion in Compression Ignition Engines, Presented at the CIMAC Conference, Barcelona, Spain, 1975.
- [78] Spadaccini, L.J.; Pelmas, R. in *Symposium on Vaporization and Combustion of Fuel Droplets*, American Chemical Society San Francisco Meeting, 1976.
- [79] Yoshimoto, Y.; Tsukahara, M.; Murayama, T. Studies on the microexplosion of emulsified fuels. *Trans. JSME B* 1989, 89-0059
- [80] Lasheras, J.C.; Fernandez-Pello, A.C.; Dryer, F.L. Experimental observations on the disruptive combustion of free droplets of multicomponent fuels. *Combust. Sci. Technol.* 1980, 22, 195-209.
- [81] Jacques, M.T., Transient heating of an emulsified water-in-oil droplet. *Combust. Flame* 1977, 29.

REFERENCES CONTINUED

- [82] Kee, R.J.; Rupley, F.M.; Miller, J.A.; Coltrin, M.E.; Grcar, J.F.; Meeks, E.; Moffat, H.K.; Lutz, A.E.; Dixon-Lewis, G.; Smooke, M.D.; Warnatz, J.; Evans, G.H.; Larson, R.S.; Mitchell, R.E.; Petzold, L.R.; Reynolds, W.C.; Caracotsios, M.; Stewart, W.E.; Glarborg, P.; Wang, C.; McLellan, C.L.; Adigun, O.; Houf, W.G.; Chou, C.P.; Miller, S.F.; Ho, P.; Young, P.D.; Young, D.J.; Hodgson, D.W.; Petrova, M.V.; Puduppakkam, K.V. CHEMKIN, Release 4.1, Reaction Design, San Diego, CA, 2006.
- [83] Curran, H.J.; Pitz, W.J.; Westbrook, C. K. Extinction and Autoignition of n-Heptane in Counterflow Configuration. Proceedings of the Combustion Institute, 2002, 28, pp. 2029-2037; UCRL-WEB-204236, 2004.
- [84] Easley, W.L.; Mellor, A.M. NO Decomposition in Diesel Engines; SAE Paper 01-3546, Society of Automotive Engineers:Warrendale, PA, 1999.
- [85] Curran, H.J.; Fisher, E.M.; Glaude, P.-A.; Marinov, N.M.; Pitz, W.J.; Westbrook, C.K.; Westbrook, D.W.; Layton, P.F.; Flynn, R.P.; Durrett, A.O.; zur Loye; Akinyemi, O.C.; Dryer, F.L. *Detailed Chemical Kinetic Modeling of Diesel Combustion with Oxygenated Fuels*; SAE Paper 2001-01-0653, Society of Automotive Engineers:Warrendale, PA, 2001.
- [86] Bartok, W.; Sarofim, A.F. Sarofim., Eds. *Fossil Fuel Combustion: A Source Book*. John Wiley & Sons, Inc:New York, 1991.
- [87] Haynes, B.S.; Wagner, H.G.G. Soot formation." *Prog. Energy Combust. Sci.* 1981, 7, 229-273.
- [88] Markides, C.N.; Mastorakos, E. Turbulent Autoignition of Hydrogen and Acetylene in a Duct. Hopkinson Laboratory, Department of Engineering, University of Cambridge Cambridge, UK. Wright, EM2C & CNRS 12th International Conference on Fluid Flow Technologies, Budapest, 2003.
- [89] Glassman, I., *Combustion*, 3rd ed., Academic:San Diego CA, 1996, 20-29.
- [90] Mary, F.B.; Charles, D.J.; William, A.M. Rate Constants for the Reaction OH + CO as Functions of Temperature and Water Concentration. Chemistry Division, Argonne National Laboratory, Argonne, IL, 2000.
- [91] Adams, B.R.; Cremer, M.A.; Wang, D.H. Modeling Non-equilibrium CO Oxidation in Combustion Systems. Presented at the International Mechanical Engineering Congress & Exposition, Orlando, FL, 2000.

REFERENCES CONTINUED

- [92] XI, J., Zhong, B.J., 'Review of Soot in Diesel Combustion Systems' School of Aerospace Engineering, Tsinghua University, Beijing 100084, China. Chemical Engineering Technology, 29, NO.6, 2006.
- [93] Miller, J.A.; Kee, R.J.; Westbrook, C.K. *Chemical kinetics and combustion modeling*. Annu. Rev. Phys. Chem. 1990, 41, 345-387.
- [94] Onwudili, J.A., Williams, P.T., "Reaction mechanisms for the decomposition of phenanthrene and naphthalene under hydrothermal conditions", Energy and Resources Research Institute, The University of Leeds, Leeds LS2 9JT, UK, The journal of supercritical fluids, 2006.
- [95] CFD-ACE+™, 'CFD Research Corporation' Cummings Research Park 215 Wynn Drive. Huntsville, AL 35805, CFD-ACE+ User Manual: Vol 2, 2004
- [96] Siebers, D.L. *Liquid-Phase Fuel Penetration in Diesel Sprays*; SAE Paper No. 980809, Society of Automotive Engineers: Warrendale, PA, 1998.
- [97] Yamamoto, H.; Niimura, K. *Characteristics of Fuel Sprays from Specially Shaped and Impinging Flow Nozzles*; SAE Paper No. 9500, Society of Automotive Engineers: Warrendale, PA, 1982.
- [98] Ahmed, A., and Briec, E. 'Overview of CFD in Automotive Engine Combustion', Renault, Department of Engine engineering 92500- Advanced Tools for Analysis of Gasoline Malmaison -France, 2000.
- [99] Jackson, G.S.; Avedisian, C.T. 'Modeling of spherical symmetric droplet flames including complex chemistry: effect of water addition on n-heptane droplet', Combustion Science and Technology, Volume 115, Issue 1 - 3 June 1996 , pages 125 - 149.
- [100] Higgins, B.; Siebers, D.; Aradi, A. Diesel-Spray Ignition and Premixed-Burn Behavior; SAE Paper No. 00-01-0940, Society of Automotive Engineers: Warrendale, PA, 2000.
- [101] Chickosa, J.S.; William E.; Acree, Jr. 'Enthalpies of Vaporization of Organic and Organometallic Compounds', Department of Chemistry, University of Missouri-St. Louis, St. Louis, MO; Department of Chemistry, University of North Texas, Denton, TX, Received 17 June 2002; accepted 17 October 2002; published 21 April 2003.
- [102] Wang, Li-Po; Wei-Biao, Fu. Analysis of the combustion characters and the mechanism of oil-consumption economy for diesel engines using water-in-oil. *Fuel Process. Technol.* 2001, 72, 47-61.

R702034067

REFERENCES CONTINUED

- [103] Amsden, A.A., Kiva-3; "A Kiva Program with Block-Structured Mesh for Complex Geometries", Technical Report, LA-12503-MS, UC-361. Mar 01, 1993.
- [105] Suresh, K.; Aggarwal, M. Modeling of a dilute vaporizing multicomponent fuel spray. *Int. J. Heat Mass Transfer* 1987, 30, 1949-1961.
- [106] Nazha, M.A.A.; Rajakaruna, H.; Crookes, R.J. *Soot and gaseous species formation in a water-in-liquid fuel emulsion spray a mathematical approach*. Energy Convers. Manage. 1981, 39, 16-18. 1998.
- [107] Murayama, T.; Morishima, Y. Experimental Reduction of NO_x, Smoke and BSFC in a Diesel Engine. Using Uniquely Produced Water (0-80%) to Fuel Emulsion; SAE Paper No. 780224, Society of Automotive Engineers: Warrendale, PA, 1978.
- [108] Abu-Zaid, M. *Performance of single cylinder, direct injection diesel engine using water fuel emulsions*. Energy Convers. Manage. 2004, 45, 697-705.
- [109] Katsoulakos, P.S. Effectiveness of the Combustion of Emulsified Fuels in Diesel Engines. Paper No. C84/83, *International Conference on Combustion Engineering* Vol. II, Institution of Mechanical Engineers: London, UK.
- [110] Bowman, C.T. *Kinetics of Pollutant Formation and Destruction in Combustion*. Progress in Engineering and Combustion Science, Pergamon Press Ltd., 1979.
- [111] Miller, J.A.; Melius, C.F. Kinetic and thermodynamic issues in the formation of aromatic compounds in flames of aliphatic fuels. *Combust. Flame* 1992, 91, 21-39.
- [112] Mueller, C.J.; Pitz, W.J.; Pickett, L.M.; Martin, G.C.; Siebers, D.L., Westbrook, C.K. Effects of Oxygenates on Soot Processes in DI Diesel Engines' Experiments and Numerical Simulations; SAE Paper No. 2003-01-1791, Society of Automotive Engineers: Warrendale, PA, 2003
- [113] Lee, M.L.; Novotny, M.V.; Bartle, K.D. *Analytical Chemistry of Polycyclic Aromatic Compounds*; Academic Press Inc. Ltd.: London, 1981.
- [114] Krajnc, M.; Levec, J. Catalytic oxidation of toxic organics in supercritical water. *Appl. Catal., B*. 1994, 3, L101-L107.
- [115] Larson, R.A.; Ju, H.L.; Snoeyink, V.L.; Recktenwalt, M.A.; Dowd, P.A. Some intermediates in the wet air oxidation of phenanthrene adsorbed on powdered activated carbon. *Water Res.* 1988, 22, 337-342.