CHEMICAL KINETIC MODELLING OF HYDROCARBON COMBUSTION

A DISSERTATION

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CANDIDATE'S DECLARATION

I hereby declare that the work which is being presented in the dissertation entitled **"CHEMICAL KINETIC MODELLING OF HYDROCARBON COMBUSTION"** in partial fulfilment of the requirements for the award of the Degree of **Master of Engineering** in **Mechanical Engineering** with specialization in **Thermal Engineering** submitted in the Department of Mechanical and Industrial Engineering, University of Roorkee, Roorkee, is an authentic record of my own work carried out from July, 1999 to January, 2000 under the supervision of **Dr. R.P. Gakkhar**, Associate Professor, Department of Mechanical and Industrial Engineering, University of Roorkee, Roorkee, U.P., India.

The matter embodied in this dissertation has not been submitted by me for the award of any other degree or diploma.

Dated : 30 January, 2000

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This is to certify that the above statement made by the candidate is correct to the best of my knowledge and belief.

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ABSTRACT

The oxidation mechanisms for the hydrocarbons, namely, methane, ethane and propane along with the hydrogen on the basis of low activation energy requirement have been considered. The rate expressions are taken from literature and the kinetic rate expressions for oxidation of hydrocarbons have been developed. By employing the steady state approximation a set of algebraic equations are formulated. The concentrations of the chain carriers are calculated by solving the algebraic equations using Newton-Raphson method. The concentrations of chain carriers are further substituted in the rate expressions of the final products for finding out the explosion limits, i.e., pressure and temperature.

A Turbo C++ program has been developed for the determination of the explosion limits at stoichiometric mixture ratio of hydrocarbon oxidation and hydrogen oxidation. The results obtained from the modelling have good agreement with the existing experimental results.

CONTENTS

NOMENCLATURE

		UNITS
v_j'	Stoichiometric coefficient of the reactants.	
v_j''	Stoichiometric coefficient of the products.	
M	Arbitrary specification of all chemical species.	
N	Total number of species.	
RR_i	Rate of disappearance of a chemical species i.	
x_i	Mole fraction of species i.	
n'	Total number of moles.	
α	Multiplication factor.	
α_{crit}	Critical value of α.	
M, M'	Reactant molecules in the system.	
P, P', P''	Products formed in the system.	
$\frac{d[i]}{dt}$	Rate of production of any species i.	$moles/m^3.sec$
k	Specific reaction rate constant.	$[(conc)^{n-1}(time)]^{-1}$
C_i	Concentration of species i.	$moles/m^3$
E_a	Activation Energy.	J/mol
R	Universal gas constant.	J/mol-K
A	Pre-exponential collision factor.	m^3/molecule-sec
T	Temperature	K
P	Total Pressure.	N/m^2
[M]	Concentration of species M.	$moles/m^3$

Ordering?

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CHAPTER 1

INTRODUCTION

Chemical kinetic modelling has become an important tool in the analysis of combustion systems. Though many fuels are encountered in combustion environments, hydrocarbons comprise the vast majority. In this work much attention is focussed on the oxidation of hydrocarbon fuels, namely methane (CH_4), ethane (C_2H_6), propane (C_3H_8). As the oxidation of hydrogen is the elementary in the above oxidation reaction mechanisms, the kinetic model of the reaction mechanism of hydrogen is also examined.

The work is mainly concentrated on the explosion domain of the chemical reactions. The chemical reactions with unmeasurably high rates are termed as explosion reactions. One possible way to explain these explosions is by the concept of chain reactions. Some reactions when initiated by some energetic process (i.e., by the initial supply of energy in the form of heat or light) proceed at a fast rate by chain process. If more than one chain carrier is produced in the chain, then it is said to be "branched chain reaction". Unless the chain carriers are lost by the system more rapidly than they are generated by chain branching, the overall reaction accelerates and branched chain explosion occurs. The explosion limits can be specified in terms of the chemical-kinetic and diffusion parameters that determine the rates of chain branching and chain breaking, notably temperature, pressure, mixture composition and environmental conditions such as the dimensions of the reaction vessel and the nature of the inner vessel surface.

This work includes the model for the kinetic reaction mechanism for oxidation of hydrogen (H_2), methane, ethane and propane. A computer software in Turbo C++ has been developed for finding out the explosion limits i.e., temperature and pressure for a stoichiometric fuel-air ratio of each fuel considering the steady-state approximation.

LITERATURE REVIEW

Analytic solutions for the rate equations of the following H_2-O_2 reaction mechanism were initially obtained [1] assuming isothermal conditions and negligible depletion of reactants during the induction period for the following set of reactions:

$$OH + H_2 \xrightarrow{k_1} H_2O + H$$

$$H + O_2 \xrightarrow{k_2} OH + O$$

$$O + H_2 \xrightarrow{k_3} OH + H$$

$$H + O_2 + M \xrightarrow{k_4} HO_2 + M$$

$$HO_2 + H_2 \xrightarrow{k_5} H_2O_2 + H$$

Three types of solutions have been deduced : $k_4[M] < 2k_2$ (explosion region) which includes high temperature and low pressure region, $k_4[M] > 2k_2$ (non-explosion region) which includes low temperature and high pressure region and $k_4[M] = 2k_2$ is the boundary between the two regions.

A theoretical model including a detailed chemical kinetic mechanism for hydrocarbon oxidation was used to examine detonation properties for mixtures of fuel-air, fuel-oxygen. Fuels considered were methane, ethane, ethylene, acetylene and methanol. Numerical data for the reaction rates was given for both forward and reverse reactions of the kinetic mechanisms [2].

The concentrations of all stable and unstable species have been measured in the reaction zone of lean and stoichiometric methane-oxygen flames. The rate constants of some reactions in the oxidation reaction mechanism of methane were found [3].

A kinetic reaction model for the reaction of ethane in spark ignition engine exhaust gases was constructed [4], based on mechanisms and rate constants. The model consisted of 33 elementary chemical reactions involving 20 chemical species and was tested by comparing calculated and experimentally measured species concentrations resulting from a step increase in the ethane concentration of isothermal, steady-flow, hydrocarbon free exhaust gases.

The oxidation of propane was studied experimentally and analytically near 1000K between 1 and 6 bars. A numerical model incorporating detailed chemical kinetics and thermal effects was proposed [5] for the interpretation of the experiments. The reaction mechanism used for the simulation predicted most of the experimental results. Most important steps in the detailed mechanism were identified and assembled in a simplified kinetic scheme describing the reaction processes.

Sensitivity and theoretical studies carried out using the mechanism [6] revealed that hydrocarbon reactions which are involved in the formation of the HO_2 radical and H_2O_2 molecule are very important at the lower temperature.

Modelling of hydrocarbon oxidation in the temperature range of 530-740 K was thought to be important for the validation of detailed models to be used for performing calculations related to automotive engine knock [7]. Addition of OH to propene and H-atom abstraction from propene were considered as important steps in determining the subsequent distributions of intermediate products, such as acetaldehyde and formaldehyde.

The consumption of CH_2O was promoted by addition of O_2 and the increase in CH_2O concentration also brought in the oxidation reaction. A mechanism that can explain the profiles obtained under the experimental conditions [8] was examined by simulation. The CH_2O decay rate was very sensitive to the rate constants of the reactions:

$$CH_2O + O_2 \rightarrow CHO + HO_2$$

$$CH_2O + HO_2 \rightarrow CHO + H_2O_2$$

$$HO_2 + H \rightarrow H_2 + O_2$$

CHAPTER-3

FORMULATION

3.1. RATES OF REACTIONS :

All chemical reaction, of combustion, hydrolysis or of any type take place at a definite rate and depend on the conditions of the system. The most important experimental parameters are the concentration of reactants, temperature, pressure and presence of a catalyst or inhibitor. The rate of the reaction may be expressed in terms of the rate of decrease of reactants or the rate of increase of products.

$$\text{Rate} = \frac{\text{Change in moles of species}}{\text{time increment} \times \text{Volume}}$$

Considering a one step stoichiometric chemical reaction as :

$$\sum_{j=1}^{N} v'_j M_j = \sum_{j=1}^{N} v''_j M_j \qquad \ldots(3.1)$$

Law of mass action: This law states that the rate of disappearance of a chemical species i is proportional to the product of concentrations of the reacting chemical species, each concentration raised to a power equal to the corresponding stoichiometric coefficient [9],i.e.,

$$RR_i = k \prod_{j=1}^{N} \left(C_j\right)^{v'_j} \qquad \ldots(3.2)$$

where, k is the proportionality constant. If no processes (such as, expansion or diffusion) other than chemical reactions cause the concentration C_i to change, then the time rate of increase of the concentration of species i:

$$\frac{dc_i}{dt} = \left[\left(v''_i - v''_i\right)k\right] \prod_{j=1}^{N} \left(C_j\right)^{v'_j} \qquad \ldots(3.3)$$

?

Specific Reaction Rate Constant: For modelling chemical kinetics, it is necessary to adopt a uniform way of expressing the variation of specific reaction rate with temperature. Conventionally these are expressed in modified Arrhenius form [9]:

$$k = AT^n \exp\left(-E_a/RT\right) \qquad \ldots(3.4)$$

where, n is a constant. The term $\exp\left(-E_a/RT\right)$ is called Boltzman factor. The suitable values of A, n, E_a for the elementary reactions are available [10].

Concentration of a species: If n is the total number of moles in the volume, the ideal gas law is $PV = nRT$. At constant temperature the partial pressure of species i is p_i and number of moles of i is n_i, then.,

$$p_i V = n_i RT$$

$$p_i = \left(\frac{n_i}{V}\right) RT \Rightarrow C_i RT$$

Furthermore $p_i = x_i P$. Therefore, concentration of species i is,

$$C_i = \frac{x_i P}{RT} \qquad \ldots(3.5)$$

3.2. CHAIN BRANCHING REACTIONS AND CRITERIA FOR EXPLOSION

The concept of chain reactions involves free radicals and an analysis of chain reactions was carried by Semenov [11]. In hydrocarbon oxidation Semenov proposes the idea of the degenerate branching chain. In a branching chain each carrier reacts and produces more than one new carrier, this process continues and increasing the number of chain carriers leading to an accelerating in the reaction rate.

If the combustion reaction involves intermediate chain carriers, and the rate of chain carriers generation exceeds the rate of their termination, the reaction becomes progressively fast and subsequently leads to chain branching reactions. The reaction in which more than one chain carrier is produced is termed as branching reaction. Branching chain explosions can be studied by following the concentration of active species with time. As the diffusion loss of these species to the environment is absent, they accumulate in the system enhancing the reaction rate and therefore their own production rate. This process continues in a self-accelerating manner to culminate in an explosion.

The generalized kinetic model explains the conditions under which chain branching can lead to an explosion is as follows [9]:

$M \xrightarrow{k_1} R$ (Initiating Step) ...(3.6)

$R + M \xrightarrow{k_2} \alpha R + M'$ (Overall Chain Branching Step) ...(3.7)

$R + M \xrightarrow{k_3} P + R$ (Propagating Step Forming Product) ...(3.8)

$R + M \xrightarrow{k_4} P'$ (Gas-Phase Termination Step) ...(3.9)

$R \xrightarrow{k_5} P''$ (Surface Destruction Termination Step) ...(3.10)

where, α is the multiplication factor, which is the necessary factor for checking whether the system leads to explosion or not. M and M' are reactant molecules in the system. R represents all radicals that are chain carriers and P, P' and P'' are products formed in the system. The value of α is determined by using steady state approximation.

Furthermore, the rate of formation of a major product P is,

$$\frac{d[P]}{dt} = k_3[R][M] \qquad \ldots(3.11)$$

The steady state condition for the chain carrier concentration $[R]$ is,

$$\frac{d[R]}{dt} = k_1[M] + k_2(\alpha - 1)[R][M] - k_4[M][R] - k_5[R] = 0 \qquad \ldots(3.12)$$

By rearranging,

$$[R] = \frac{k_1[M]}{k_4[M] + k_5 - k_2(\alpha - 1)[M]} \qquad \ldots(3.13)$$

Substituting Eq.(3.13) into Eq.(3.11) one obtains,

$$\frac{d[P]}{dt} = \frac{k_1 k_3 [M]^2}{k_4[M] + k_5 - k_2(\alpha - 1)[M]} \qquad \ldots(3.14)$$

The rate of formation of the product P becomes infinite, or the system explodes, when the denominator of Eq.(3.14) equals to zero. Solving for α when the denominator is zero gives the critical value for explosion, namely,

$$\alpha_{crit} = 1 + \frac{k_4[M] + k_5}{k_2[M]} \qquad \ldots(3.15)$$

Explosion limits i.e., temperature and pressure boundaries for a specific mixture ratio of fuel and oxidizer are determined where $\alpha_{reaction} > \alpha_{critical}$.

3.3. MECHANISM OF HYDROCARBON COMBUSTION :

In the oxidation of hydrocarbons the rate of reaction in the early stages increases slowly and exponentially with time. Semenov [11] explains the rate of reaction of hydrocarbon oxidation by considering, a moderately stable intermediate must be formed with an average life greater than that of the primary chains, and this intermediate reacted slowly to produce a supply of new radicals. The mechanism of hydrocarbon oxidation involves steps to explain initiation, propagation, branching and termination.

The mechanism of hydrocarbon combustion is divided into two main parts, namely, the low temperature oxidation process and the high temperature oxidation process. In high temperature oxidation if a sufficient quantity of air or oxygen is present the end-products will always be water vapour and carbon dioxide irrespective of the structure of hydrocarbon, while in low temperature oxidation process, various intermediate compounds are produced with an appreciable half life. The chemical structure of the intermediate compounds depends upon the temperature, pressure, initial structure of fuel and time elapsed after the reaction started.

The mechanism of hydrocarbon oxidation is explained below by taking a general hydrocarbon (say, a paraffin) represented by RH, where $R=C_nH_{2n+1}$ [9]:

$$RH+O_2 \rightarrow \dot{R}+HO_2 \qquad \text{(Initiation Step)}$$

$$\left.\begin{aligned} &\dot{R}+O_2 \rightarrow \text{olefin}+HO_2\\ &\dot{R}+O_2 \rightarrow R\dot{O}_2\\ &R\dot{O}_2+RH \rightarrow ROOH+\dot{R} \end{aligned}\right\} \text{(Chain Propagating Step)}$$

$$\left.\begin{aligned} &R\dot{O}_2+RH \rightarrow R'CHO+R''\dot{O}\\ &H\dot{O}_2+RH \rightarrow H_2O_2+\dot{R} \end{aligned}\right\} \text{(Chain Propagating Step)}$$

$$\left.\begin{aligned} &ROOH \rightarrow R\dot{O}+\dot{O}H\\ &R'CHO+O_2 \rightarrow R'\dot{C}O+H\dot{O}_2 \end{aligned}\right\} \text{(Degenerate Branching Step)}$$

$\overset{\bullet}{R O_2} \rightarrow \text{destruction}$ (Chain Termination Step)

The above mechanism is sufficient for all hydrocarbons with a few carbon atoms (<5). The major intermediate products are olefins, peroxides, aldehydes, ketones, alcohols. Based on the various experimental facts, the mechanism of slow oxidation is proposed by Knox and Kinnear [12].

Initiation: The initial attack by oxygen on hydrocarbon generally involves hydrogen abstraction to yield an alkyl radical and a hydroperoxy radical. These processes would be selective depending on the activation energies of a abstraction.

Propagation: At temperatures around 670 K, oxygen can react with an alkyl radical to form an alkene. High yields of propylene were found in the oxidation of propane and similarly large amounts of ethylene in ethane oxidation. In the early stages of oxidation the alkyl radicals can react by an HO_2 mechanism to form an alkene and the remaining alkyl radicals react with oxygen to form alkylperoxy radicals. These radicals are stable below 570 K but above 670 K they rapidly break down give HO_2 and the alkene.

Degenerate Branching: The two most likely agents for degenerate branching are aldehydes and peroxides. In the higher temperature range, 620-770 K for methane, ethylene, formaldehyde is proposed as the branching agent.

Termination: Two types of termination process, namely, homogeneous and heterogeneous. Radicals may react together in the gas-phase yielding species inactive as chain propagating species. Alternatively, the radicals may diffuse to the walls ehere they are destroyed. Homogeneous termination occurs by the disproportion of radicals, such as RO_2 and HO_2, which have relatively long lifetimes.

CHAPTER-4

KINETIC REACTION MECHANISM FOR HYDROCARBONS

The construction of a realistic mechanism involves principally the identification of the reactions, which actually occur and are rapid enough to have an impact on the overall progress of the combustion event. The combustion of a hydrocarbon fuel consists of the sequential fragmentation of the initial fuel molecule into smaller intermediate species, which are ultimately converted to final products, usually dominated by H_2O and CO_2. In many cases these intermediate species can be fuels themselves.

The reaction mechanism consists of many elementary reactions with all the chemical species, which affect a combustion event and overall rate of reaction. The elementary reactions with high specific reaction rates and less activation energy required for the combustion of hydrocarbon fuels are considered in the modelling. As the hydrogen oxidation also involves in the oxidation mechanism of hydrocarbon, the oxidation mechanism of hydrogen is also formulated.

4.1. ANALYSIS:

The reaction mechanism of each fuel along with the data for rate constant k, is taken from the literature [10]. The expression for rate of production of each intermediate species is formed. Thus, obtaining as many non-linear first order differential system of rate equations as intermediate species. For simplicity, we may safely assume that the steady state occurs after a certain time, i.e., the concentrations of chain carriers remain essentially constant. Thus, steady-state approximation [13] has been adopted for the description of reaction intermediaries. In this approach, $\frac{d[i]}{dt} = 0$ is employed for the intermediaries, where, $[i]$ is the concentration of species i. Thus, obtaining a set of algebraic equation.

The set of algebraic equations formed for all the species in the oxidation of a fuel are solved for the concentrations of the intermediate species by applying Newton-Raphson modified method of solving non-linear set of algebraic equations. Substituting the concentration of the intermediate species in the rate of production of the final product, the explosion limits are determined. If the expression gives the value ($\frac{d[P]}{dt} \leq 0$) then the system is considered to be explosive. The explosion limits, temperature and pressure are determined at stoichiometric fuel-air mixture ratio for the hydrocarbons, namely, methane, ethane and propane along with hydrogen, which is a sub-mechanism for the hydrocarbon oxidation.

4.2. OXIDATION OF HYDROGEN:

The hydrogen-oxygen system was the first combustion mechanism to be developed for a practical fuel. The reaction mechanism for hydrogen oxidation [14] explains clearly the three explosion limits. Fig. 4.1 shows the explosion limits of a stoichiometric hydrogen-oxygen mixture. In the chain branching reaction the chain branching rate exceeds the rate of chain breaking. In the region of no explosion the relation of these rates are reversed, and at the limit the two are equal [15].

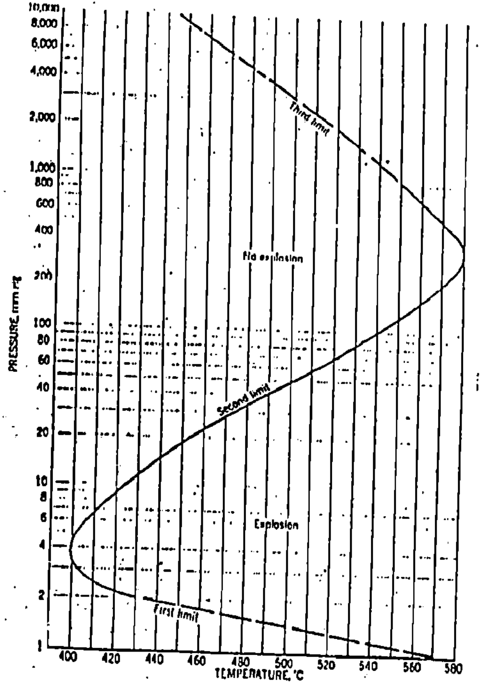

Fig. 4.1. Explosion limits of a stoichiometric hydrogen-oxygen mixture in a spherical KCl-coated vessel of 7.4 cm diameter. First and third limits are partly extrapolated [14].

4.2.1. First Explosion Limit: An increase of pressure anywhere along the first limit leads from no explosion to explosion. As the temperature is increased the first limit shifts to lower pressures. During the first explosion limit the chain branching occurs in successful collisions of H with O_2. The frequency of such collisions and hence the chain branching rate is increased by increasing the O_2 concentration, which is done by increasing the pressure. The reactions involved in the first explosion are:

$$H_2 + M \xrightarrow{k_1} 2H + M \qquad \ldots(4.1)$$

$$H + O_2 \xrightarrow{k_2} OH + O \qquad \ldots(4.2)$$

$$O + H_2 \xrightarrow{k_3} OH + H \qquad \ldots(4.3)$$

$$OH + H_2 \xrightarrow{k_4} H_2O + H \qquad \ldots(4.4)$$

$$H + OH + M \xrightarrow{k_5} H_2O + M \qquad \ldots(4.5)$$

$$2H + M \xrightarrow{k_6} H_2 + M \qquad \ldots(4.6)$$

The rates of production of intermediate species H, O and OH along with the rate of production of final product H_2O are formed as follows,

$$\frac{d[H]}{dt} = 2k_1[H_2]\overset{\boxed{[M]}}{\wedge} - k_2[H][O_2] + k_3[O][H_2] + k_4[OH][H_2] - 2k_6[H]^2 - k_5[H][OH]. \quad (4.7)$$

$$\frac{d[O]}{dt} = k_2[H][O_2] - k_3[O][H_2] \qquad \ldots(4.8)$$

$$\frac{d[OH]}{dt} = k_2[H][O_2] + k_3[O][H_2] - k_4[OH][H_2] - k_5[H][OH] \qquad \ldots(4.9)$$

$$\frac{d[H_2O]}{dt} = k_4[OH][H_2] + k_5[H][OH] \qquad \ldots(4.10)$$

The data for the rate expressions is given in the table. 4.1. The steady state approximation is employed for the chain carriers,

$$\frac{d[H]}{dt} = 0, \ \frac{d[O]}{dt} = 0 \text{ and } \frac{d[OH]}{dt} = 0.$$

Thus, obtaining the set of algebraic equations formed by deducing the above rate expressions are:

f1 = A1- A2*x[1] + A3*x[2] + A4*x[3] – A5*x[1]*x[3] –2*A6*$x[1]^2$ = 0 ...(4.7a)

f2 = A2*x[1] – A3*x[2] = 0 ...(4.8a)

f3 = A2*x[1] + A3*x[2] – A4*x[3] –A5*x[1]*x[3] = 0 ...(4.9a) where, $A1 = 2*k_1*[H_2]$; $A2 = k_2*[O_2]$; $A3 = k_3*[H_2]$; $A4 = k_4*[H_2]$; $A5 = k_5$; $A6 = k_6$;

Table. 4.1. Rate expressions for first explosion limit of H_2-O_2 oxidation mechanism.

$k = AT^n \exp\left(-E_a/_{RT}\right)$ m³/mol.sec [10].

S.No.	REACTIONS OF THE MECHANISM	A $*10^{-6}$ m³/molecule.sec	n	E_a *4.187 kJ/mol
1.	$H_2 + M \xrightarrow{k_1} 2H + M$	14.34	0.0	96.00
2.	$H + O_2 \xrightarrow{k_2} OH + O$	16.71	-0.816	16.51
3.	$O + H_2 \xrightarrow{k_3} OH + H$	10.26	1.0	8.90
4.	$OH + H_2 \xrightarrow{k_4} H_2O + H$	13.34	0.0	5.15
5.	$H + OH + M \xrightarrow{k_5} H_2O + M$	23.15	-2.0	0.00
6.	$2H + M \xrightarrow{k_6} H_2 + M$	15.48	0.0	0.00

Thus, solving the system of algebraic equations considering the initial concentrations of H_2 and O_2 and the rate constants by using the Newton-Raphson modified method, the concentrations of intermediate species are determined. The partial derivatives for each chain carrier x[i] is listed in table 4.2.

Table. 4.2. Expressions of $\frac{\partial f_i}{\partial x[j]}$ for the first explosion limit of H_2-O_2 oxidation mechanism.

	x[1]	x[2]	x[3]
f1	-(A2 + A5*x[3] + 4*A6*x[1])	A3	A4 – (A5*x[1])
f2	A2	-A3	0.0
f3	A2 – (A5*x[3])	A3	-(A4 + A5*x[1])

Note : x[1] = [H]; x[2] = [O]; x[3] = [OH]

Further, the concentrations of intermediate species are substituted in the rate of production of water vapour and determine the first explosion limits for H_2-O_2 oxidation mechanism.

4.2.2. Second Explosion Limit: As the pressure is increased above the first explosion limit the reaction remains explosive until a second critical pressure is reached above which a steady state reaction is observed. Just above this second explosion limit the reaction rate is very small and increases with pressure until a third explosion limit is reached. The second limit owes its existence to a chain-breaking rate that increases with pressure at a higher order than the chain-branching rate. The second limit is caused by the reaction,

$$H + O_2 + M \longrightarrow HO_2 + M$$

which is a chain-breaking because it destroys free H atoms. The reaction occurs in ternary collisions of H with O_2 and a third molecule M which serves as energy acceptor, whereas the chain-branching reaction,

$$H + O_2 \xrightarrow{k_3} OH + O$$

occurs in binary collision of H with O_2. The frequency with which an H atom enters into ternary collisions is proportional to square of the pressure, whereas, for binary collisions the relationship is linear and the chain-breaking rate correspondingly increases with pressure at a higher order than the chain-branching rate.

An increase in the pressure anywhere along the second explosion limit, leads from explosion to no explosion region. Furthermore, as the temperature is increased the second limit shifts to higher pressures. The limit pressure increases with increasing temperature because the chain-branching rate increases with increasing temperature according to the Arrhenius function of the chain-branching reaction.

The branched chain explosion limit condition derived from the set of reactions [16]:

$$OH + H_2 \xrightarrow{k_1} H_2O + H \qquad \text{...(4.11)}$$

$$H + O_2 \xrightarrow{k_2} OH + O \qquad \text{...(4.12)}$$

$$O + H_2 \xrightarrow{k_3} OH + H \qquad \text{...(4.13)}$$

$$H + O_2 + M \xrightarrow{k_4} HO_2 + M \qquad \text{...(4.14)}$$

Using the steady state approximation for the rate expressions of the above oxidation reactions yields to explosion condition as follows,

$$\frac{2*k_2}{k_4[M]} = 1 \qquad \text{...(4.15)}$$

Using the rate constants and expressing the concentration [M] in terms of temperature and pressure, by means of the gas law,

$$[M] = \frac{f_x P}{R T}$$

Eq. (4.15) becomes,

$$\frac{(3.11)*T*\exp\left(-8550/T\right)}{f_x * P} = 1 \qquad \text{...(4.16)}$$

where, f_x is an effective mole fraction of third bodies for the formation of HO_2 in reaction (4.14) and is given by the following empirical equation [16],

$$f_x = f_{H_2} + 0.35 f_{O_2} + 0.43 f_{N_2} + 0.20 f_{Ar} + 1.47 f_{CO_2} \qquad \text{...(4.17)}$$

The numerical factors in Eq. (4.17) express ratios of the rate of reaction (4.14) with various third bodies, to the rate with H_2 as the third body. The subsequent logarithmic form for the above Eq. (4.16) is,

$$\frac{3710}{T} - \log_{10}\left(\frac{T}{P}\right) = \log_{10}\left(\frac{3.11}{f_x}\right) \qquad \text{...(4.18)}$$

If a given hydrogen mixture, having a characteristic values of f_x dependent upon its composition, is raised to temperature and pressure that satisfy Eq. (4.16), then the mixture explodes.

The reaction mechanism of hydrogen oxidation for second explosion limit considered in this modelling is,

$$H_2 + O_2 \xrightarrow{k1} 2OH \qquad \text{...(4.19)}$$

$$OH + H_2 \xrightarrow{k_2} H_2O + H \qquad \text{...(4.11)}$$

$$H + O_2 \xrightarrow{k_3} OH + O \qquad \text{...(4.12)}$$

$$O + H_2 \xrightarrow{k_4} OH + H \qquad \text{...(4.13)}$$

$$H + O_2 + M \xrightarrow{k_5} HO_2 + M \qquad \text{...(4.14)}$$

The rates of production of intermediate species [17] H, O and OH along with the rate of production of final product H_2O are obtained as follows,

$$\frac{d[H]}{dt} = k_2[OH][H_2] - k_3[H][O_2] + k_4[O][H_2] - k_5[H][O_2][M] \qquad \text{...(4.20)}$$

$$\frac{d[O]}{dt} = k_3[H][O_2] - k_4[O][H_2] \qquad \text{...(4.21)}$$

$$\frac{d[OH]}{dt} = k_1[H_2][O_2] - k_2[OH][H_2] + k_3[H][O_2] + k_4[O][H_2] \qquad \text{...(4.22)}$$

$$\frac{d[H_2O]}{dt} = k_2[OH][H_2] \qquad \ldots(4.23)$$

The data for the rate expressions is given below in the table. 4.3. The steady state approximation is employed for the chain carriers as,

$$\frac{d[H]}{dt} = 0, \ \frac{d[O]}{dt} = 0 \text{ and } \frac{d[OH]}{dt} = 0.$$

Table. 4.3. Rate expressions for second explosion limit of H_2-O_2 oxidation mechanism.

$k = AT^n \exp\left(-E_a/RT\right)$ m^3/mol.sec [10].

S.No.	REACTIONS OF THE MECHANISM	A $*10^{-6}$ m^3/molecule.sec	n	E_a *4.187 KJ/mol
1.	$H_2 + O_2 \xrightarrow{k1} 2OH$	12.40	0.0	38.95
2.	$OH + H_2 \xrightarrow{k_2} H_2O + H$	13.34	0.0	5.15
3.	$H + O_2 \xrightarrow{k_3} OH + O$	16.71	-0.816	16.51
4.	$O + H_2 \xrightarrow{k_4} OH + H$	10.26	1.0	8.90
5.	$H + O_2 + M \xrightarrow{k_5} HO_2 + M$	15.18	0.0	-1.00

Thus, obtaining the set of algebraic equations formed by deducing the above rate expressions are:

f1 = A2*x[3] – A3*x[1] + A4*x[2] – A5*x[1] = 0. ...(4.20a)

f2 = A3*x[1] – A4*x[2] = 0. ...(4.21a)

f3 = A1 – A2*x[3] + A3*x[1] + A4*x[2] = 0. ...(4.22a)

where A1 = $k_1[H_2][O_2]$; A2 = $k_2[H_2]$; A3 = $k_3[O_2]$; A4 = $k_4[H_2]$; A5 = $k_5[O_2][M]$;

Thus, solving the system of algebraic equations considering the initial concentrations of H_2 and O_2 and the rate constants by using the Newton-Raphson modified method, the concentrations of intermediate species are determined. The partial derivatives for each chain carrier x[i] are listed in table 4.4.

Table. 4.4. Expressions of $\frac{\partial f_i}{\partial x[j]}$ for the second explosion limit of H_2-O_2 oxidation mechanism.

	x[1]	x[2]	x[3]
f1	-(A3 + A5)	A4	A2
f2	A3	-A4	0.0
f3	A3	A4	-A2

Note: x[1] = [H]; x[2] = [O]; x[3] = [OH];

Further, the concentrations are substituted in the rate of production of water vapour and determine the first explosion limits for H_2-O_2 oxidation mechanism.

4.2.3. Third Explosion Limit: More frequent collisions occur at much higher pressures, i.e., above the third limit. At these conditions, HO_2 radical is regularly interrupted in its diffusion path by reacting with colliding hydrogen molecule to yield an H atom. The later promptly reacts with O_2, either regenerating HO_2 or generating more H and correspondingly more HO_2 via the chain-branching reaction,

$$H + O_2 \longrightarrow OH + O$$

Along the third limit the rate of chain breaking corresponds to the rate of diffusion and destruction of HO_2 to the vessel wall. This rate increases and the branching rate decreases with decreasing pressure. An increase of pressure anywhere along the third limit, it leads from no explosion to explosion region. Furthermore, as the temperature is increased the third limit shifts to lower pressures.

The reaction mechanism of the H_2-O_2 oxidation for third limit is as follows:

$$H_2 + O_2 \xrightarrow{k1} 2OH \qquad \ldots(4.19)$$

$$OH + H_2 \xrightarrow{k_2} H_2O + H \qquad \ldots(4.11)$$

$$H + O_2 \xrightarrow{k_3} OH + O \qquad \ldots(4.12)$$

$$O + H_2 \xrightarrow{k_4} OH + H \qquad \ldots(4.13)$$

$$H + O_2 + M \xrightarrow{k_5} HO_2 + M \qquad \ldots(4.14)$$

$$HO_2 + O \xrightarrow{k_6} O_2 + OH \qquad \ldots(4.24)$$

$$HO_2 + H \xrightarrow{k_7} H_2 + O_2 \qquad \ldots(4.25)$$

$$HO_2 + OH \xrightarrow{k_8} H_2O + O_2 \qquad \ldots(4.26)$$

$$HO_2 + HO_2 \xrightarrow{k_9} H_2O_2 + O_2 \qquad \ldots(4.27)$$

$$H_2O_2 + OH \xrightarrow{k_{10}} H_2O + HO_2 \qquad \ldots(4.28)$$

$$H_2O_2 + H \xrightarrow{k_{11}} HO_2 + H_2 \qquad \ldots(4.29)$$

The rates of production of intermediate species H, O, OH, HO_2 and H_2O_2 along with the rate of production of final product H_2O are obtained as follows,

$$\frac{d[H]}{dt} = k_2[H_2][OH] - k_3[O_2][H] + k_4[O][H_2] - k_5[H][O_2][M] - k_{11}[H_2O_2][H] \ldots(4.30)$$

$$\frac{d[O]}{dt} = k_3[H][O_2] - k_4[O][H_2] - k_6[HO_2][O] \qquad \ldots(4.31)$$

$$\begin{aligned}\frac{d[OH]}{dt} = {} & k_1[H_2][O_2] - k_2[OH][H_2] + k_3[H][O_2] + k_4[O][H_2] + k_6[HO_2][O] \\ & - k_8[HO_2][OH] - k_{10}[H_2O_2][OH]\end{aligned} \qquad \ldots(4.32)$$

$$\frac{d[HO_2]}{dt} = k_5[H_2][O_2][M] - k_6[HO_2][O] - k_7[HO_2][H] -- k_8[HO_2][OH] - k_9[HO_2]^2 + k_{10}[H_2O_2][OH] + k_{11}[H_2O_2][OH] \quad \ldots(4.33)$$

$$\frac{d[H_2O_2]}{dt} = k_9[HO_2]^2 - k_{10}[H_2O_2][OH] - k_{11}[H_2O_2][H] \quad \ldots(4.34)$$

$$\frac{d[H_2O]}{dt} = k_2[H_2][OH] + k_8[HO_2][OH] + k_{10}[H_2O_2][OH] \quad \ldots(4.35)$$

The rate expressions for the reactions are given in the table. 4.5. The steady state approximation is employed for the chain carriers assuming that they remain constant,

$$\frac{d[H]}{dt} = 0, \frac{d[O]}{dt} = 0, \frac{d[OH]}{dt} = 0, \frac{d[HO_2]}{dt} = 0 \text{ and } \frac{d[H_2O_2]}{dt} = 0.$$

The set of algebraic equations formed from the above rate expressions are :

f1= -(A5+A3)*x[1]+A4*x[2]+A2*x[3]- A7*x[1]*x[4] --A11*x[1]*x[5]=0 ...(4.30a)

f2 = A3*x[1] – A4*x[2] – A6*x[2]*x[4] = 0. ...(4.31a)

f3 = A1 + A3*x[1] +A4*x[2] – A1*x[3] + A6*x[2]*x[4] –A8*x[3]*x[4]
 –A10*x[3]*x[5] = 0. ...(4.32a)

f4 = A5*x[1] –A6*x[2]*x[4] –A7*x[1]*x[4] -A8*x[3]*x[4] –A9*x[4]^2
 +A10*x[3]*x[5] + A11*x[1]*x[5] = 0. ...(4.33a)

f5 = A9*x[4]^2 +A10*x[3]*x[5] + A11*x[1]*x[5] = 0. ...(4.34a)

Where A1 = $k_1[H_2][O_2]$; A2 = $k_2[H_2]$; A3 = $k_3[O_2]$; A4 = $k_4[H_2]$; A5 = $k_5[O_2][M]$;

A6 = k_6; A7 = k_7; A8 = k_8; A9 = k_9; A10 = k_{10}; A11 = k_{11};

Thus, solving the system of algebraic equations by using Newton-Raphson modified method, the concentrations of intermediate species are determined.

Table. 4.5. Rate expressions for third explosion limit of H_2-O_2 oxidation mechanism.

$$k = AT^n \exp\left(-E_a/_{RT}\right) \; m^3/mol.sec \; [10].$$

S.No.	REACTIONS OF THE MECHANISM	A $*10^{-6}$ m^3/molecule.sec	N	E_a *4.187 kJ/mol
1.	$H_2 + O_2 \xrightarrow{k1} 2OH$	12.40	0.0	38.95
2.	$OH + H_2 \xrightarrow{k_2} H_2O + H$	13.34	0.0	5.15
3.	$H + O_2 \xrightarrow{k_3} OH + O$	16.71	-0.816	16.51
4.	$O + H_2 \xrightarrow{k_4} OH + H$	10.26	1.0	8.90
5.	$H + O_2 + M \xrightarrow{k_5} HO_2 + M$	15.18	0.0	-1.00
6.	$HO_2 + O \xrightarrow{k_6} O_2 + OH$	13.70	0.0	1.00
7.	$HO_2 + H \xrightarrow{k_7} H_2 + O_2$	13.40	0.0	0.70
8.	$HO_2 + OH \xrightarrow{k_8} H_2O + O_2$	13.70	0.0	1.00
9.	$HO_2 + HO_2 \xrightarrow{k_9} H_2O_2 + O_2$	13.00	0.0	1.00
10.	$H_2O_2 + OH \xrightarrow{k_{10}} H_2O + HO_2$	13.00	0.0	1.80
11.	$H_2O_2 + H \xrightarrow{k_{11}} HO_2 + H_2$	12.23	0.0	3.75

The partial derivatives for each chain carrier x[i] are listed in table 4.6.

Table. 4.6. Expressions of $\frac{\partial f_i}{\partial x[j]}$ for the third explosion limit of H_2-O_2 oxidation mechanism.

	x[1]	x[2]	x[3]	x[4]	x[5]
f1	-(A5 + A3 + A7*x[4] + A11*x[5])	A4	A2	-(A7*x[1])	-(A11*x[1])
f2	A3	-A3	0.0	-(A6*x[2])	0.0

f3	A3	A4 + A6*x[4]	-(A2 + A8*x[4] + A10*x[5])	A6*x[2] – A8*x[3]	-(A10*x[3])
f4	A5 – A7*x[4] + A11*x[5]	- (A6*x[4])	-A8*x[4] + A10*x[5]	-(4*A9 + A7*x[1] + A8*x[3] + A6*x[2])	A10*x[3] + A11*x[1]
f5	A11*x[5]	0.0	A10*x[4]	2*A9*x[4]	A10*x[3] + A11*x[1]

Note: x[1] = [H]; x[2] = [O]; x[3] = [OH]; x[4] = [HO_2]; x[5] = [H_2O_2];

The final product of the oxidation is water vapour if the mixture is stoichiometric and at high temperatures. Further the concentration of intermediate species are substituted in the rate expressions of final product and the third explosion limits of hydrogen oxidation are determined.

4.3. OXIDATION OF METHANE :

Methane exhibits certain different oxidation characteristics when compared to other hydrocarbons. The bond energy of the first broken C-H bond in methane is much more than the others. Thus, it is difficult to ignite methane-air mixtures than the other fuels. At low temperatures, even oxygen attack is slow [18]. Fig. 4.2. shows the explosion limits of methane along other fuels in different coated vessels.

Methane oxidation occurs through two roughly parallel paths, the first consisting of direct oxidation of methyl radicals to methoxy radicals and/or formaldehydes and the second of methyl recombination followed by oxidation of the resulting C_2 species. In particular, the C_2 species ethane, ethylene and acetylene can be formed. As the levels of C_2 species during the methane combustion are considerably smaller than CH_4 concentrations, the higher order species are not considered in the methane oxidation mechanism.

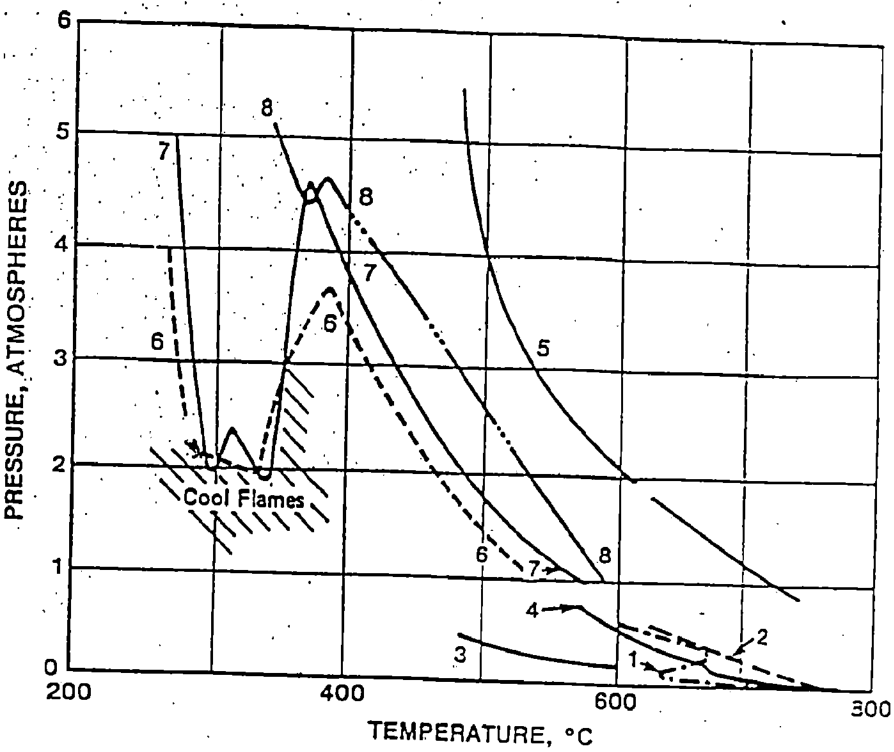

Fig. 4.2. Explosion regions of hydrocarbon-oxygen mixtures. 1. CH_4+$2O_2$ 4. C_2H_6 +$2O_2$ 5. 15% Methane in air [14].

Even though some elementary reactions are not incorporated in the mechanism, it is not implied that the reaction does not occur but it is insignificant under the specified conditions. Otherwise, the rate of those reactions is low or the activation energy of the reaction is more.

The reaction mechanism of the methane oxidation considering in the modelling is as follows:

$$CH_4 + O_2 \xrightarrow{k_1} CH_3 + HO_2 \quad ...(4.36)$$

$$CH_3 + O_2 \xrightarrow{k_2} CH_3O + O \quad ...(4.37)$$

$$CH_3O + O_2 \xrightarrow{k_3} CH_2O + HO_2 \quad ...(4.38)$$

$$CH_4 + O \xrightarrow{k_4} CH_3 + OH \quad ...(4.39)$$

$$CH_3 + HO_2 \xrightarrow{k_5} CH_3O + OH \quad ...(4.40)$$

$$CH_3 + OH \xrightarrow{k_6} CH_2O + H_2 \quad ...(4.41)$$

$$CH_2O + OH \xrightarrow{k_7} HCO + H_2O \quad ...(4.42)$$

$$CH_2O + O \xrightarrow{k_8} HCO + OH \quad ...(4.43)$$

$$HO_2 + O \xrightarrow{k_9} O_2 + OH \quad ...(4.44)$$

$$HO_2 + H \xrightarrow{k_{10}} OH + OH \quad ...(4.45)$$

$$HO_2 + OH \xrightarrow{k_{11}} H_2O + O_2 \quad ...(4.46)$$

$$HCO + O_2 \xrightarrow{k_{12}} CO + HO_2 \quad ...(4.47)$$

$$CO + OH \xrightarrow{k_{13}} CO_2 + H \quad ...(4.48)$$

$$CH_4 + OH \xrightarrow{k_{14}} CH_3 + H_2O \quad ...(4.49)$$

$$CH_4 + H \xrightarrow{k_{15}} CH_3 + H_2 \quad ...(4.50)$$

$$O_2 + M \xrightarrow{k_{16}} O + O + M \quad ...(4.51)$$

At high amounts of oxygen or at stoichiometric ratios the final products are water vapour (H_2O) carbon dioxide (CO_2). The rate expressions for the reactions in the mechanism are given in the table. 4.7.

Table. 4.7. Rate expressions of methane oxidation mechanism.

$$k = AT^n \exp\left(-E_a/RT\right) \ m^3/mol.sec \ [10].$$

S.No.	REACTIONS OF THE MECHANISM	A $*10^{-6}$ m^3/molecule.sec	n	E_a *4.187 KJ/mol
1.	$CH_4 + O_2 \xrightarrow{k_1} CH_3 + HO_2$	13.90	0.0	56.00
2.	$CH_3 + O_2 \xrightarrow{k_2} CH_3O + O$	13.68	0.0	29.00
3.	$CH_3O + O_2 \xrightarrow{k_3} CH_2O + HO_2$	12.00	0.0	6.00
4.	$CH_4 + O \xrightarrow{k_4} CH_3 + OH$	7.07	2.08	7.63
5.	$CH_3 + HO_2 \xrightarrow{k_5} CH_3O + OH$	13.30	0.0	0.00
6.	$CH_3 + OH \xrightarrow{k_6} CH_2O + H_2$	12.60	0.0	0.00
7.	$CH_2O + OH \xrightarrow{k_7} HCO + H_2O$	12.88	0.0	0.17
8.	$CH_2O + O \xrightarrow{k_8} HCO + OH$	13.70	0.0	4.60
9.	$HO_2 + O \xrightarrow{k_9} O_2 + OH$	13.70	0.0	1.00
10.	$HO_2 + H \xrightarrow{k_{10}} OH + OH$	14.40	0.0	1.90
11.	$HO_2 + OH \xrightarrow{k_{11}} H_2O + O_2$	13.70	0.0	1.00
12.	$HCO + O_2 \xrightarrow{k_{12}} CO + HO_2$	12.52	0.0	7.00
13.	$CO + OH \xrightarrow{k_{13}} CO_2 + H$	7.18	1.3	-0.77
14.	$CH_4 + OH \xrightarrow{k_{14}} CH_3 + H_2O$	3.54	3.08	2.00
15.	$CH_4 + H \xrightarrow{k_{15}} CH_3 + H_2$	4.35	3.0	8.75
16.	$O_2 + M \xrightarrow{k_{16}} O + O + M$	15.71	0.0	115.00

The rates of production for the intermediate species H, O, OH, HO_2, CH_3O, CH_2O, HCO, CH_3, CO and the final products are as follows:

$$\frac{d[H]}{dt}=-k_{10}[HO_2][H]+k_{13}[CO][OH]-k_{15}[CH_4][H] \qquad \ldots(4.52)$$

$$\frac{d[O]}{dt}=k_2[O_2][CH_3]-k_4[CH_4][O]-k_8[CH_2O][O]-k_9[HO_2][O]+2k_{16}[O_2] \qquad \ldots(4.53)$$

$$\begin{aligned}\frac{d[OH]}{dt}=&\,k_4[CH_4][O]+k_5[CH_3][HO_2]-k_6[CH_3][OH]-k_7[CH_2O][OH]\\&+k_8[CH_2O][O]+k_9[HO_2][O]+2k_{10}[H][HO_2]-k_{11}[OH][HO_2]\\&-k_{13}[CO][OH]-k_{14}[CH_4][OH]\end{aligned} \qquad \ldots(4.54)$$

$$\begin{aligned}\frac{d[HO_2]}{dt}=&\,k_1[CH_4][O_2]+k_3[O_2][CH_3O]-k_5[HO_2][CH_3]-k_9[HO_2][O]\\&-k_{10}[HO_2][H]-k_{11}[HO_2][OH]+k_{12}[O_2][HCO]\end{aligned} \qquad \ldots(4.55)$$

$$\frac{d[CH_3O]}{dt}=k_2[O_2][CH_3]+k_5[CH_3][HO_2]-k_3[O_2][CH_3O] \qquad \ldots(4.56)$$

$$\frac{d[CH_2O]}{dt}=k_6[CH_3][OH]+k_3[O_2][CH_3O]-k_7[CH_2O][OH]-k_8[CH_2O][O] \qquad \ldots(4.57)$$

$$\frac{d[HCO]}{dt}=k_7[CH_2O][OH]+k_8[O][CH_2O]-k_{12}[O_2][HCO] \qquad \ldots(4.58)$$

$$\begin{aligned}\frac{d[CH_3]}{dt}=&\,k_1[CH_4][O_2]-k_2[O_2][CH_3]-k_5[HO_2][CH_3]+k_4[CH_4][O]\\&-k_6[OH][CH_3]+k_{14}[CH_4][OH]+k_{15}[CH_4][H]\end{aligned} \qquad \ldots(4.59)$$

$$\frac{d[CO]}{dt}=k_{12}[O_2][HCO]-k_{13}[OH][CO] \qquad \ldots(4.60)$$

$$\frac{d[H_2O]}{dt}=k_7[CH_2O][OH]+k_{11}[HO_2][OH]+k_{14}[CH_4][OH] \qquad \ldots(4.61)$$

$$\frac{d[CO_2]}{dt}=k_{13}[OH][CO] \qquad \ldots(4.62)$$

The steady state approximation is employed for the rate expressions of the intermediate species assuming the concentration to remain constant after certain time. The exprssions deduced are as follows,

$$\frac{d[H]}{dt}=0,\ \frac{d[O]}{dt}=0,\ \frac{d[OH]}{dt}=0,\ \frac{d[HO_2]}{dt}=0,\ \frac{d[CH_3O]}{dt}=0,\ \frac{d[CH_2O]}{dt}=0,$$

$$\frac{d[HCO]}{dt}=0,\ \frac{d[CH_3]}{dt}=0 \text{ and } \frac{d[CO]}{dt}=0.$$

The set of algebraic expressions for the above rate expressions is as follows:

f1 = -A10*x[4]*x[1] + A13*x[9]*x[3] – A15*x[1] = 0. ...(4.52a)

f2 = A2*x[8] – A4*x[2] – A8*x[6]*x[2] – A9*x[4]*x[2] + 2*A16 = 0. ...(4.53a)

f3=A4*x[2]+A5*x[4]*x[8]–A6*x[8]*x[3]-A7*x[3]*x[6]+A8*x[6]*x[2]
+A9*x[4]*x[2] +2*A10*x[4]*x[1]–A11*x[3]*x[4]-A13*x[9]*x[3] A14*x[3] = 0
...(4.54a)

f4=A1+A3*x[5]-A5*x[4]*x[8]-A9*x[4]*x[2]-A10*x[4]*x[1]-
A11*x[1]*x[3]+A12*x[7] = 0. ...(4.55a)

f5= A2*x[8]+A5*x[4]*x[8]-A3*x[5] = 0. ...(4.56a)

f6=A6*x[8]*x[3]+A3*x[5]-A7*x[6]*x[3]-A8*x[6]*x[2] = 0. ...(4.57a)

f7=A7*x[6]*x[3]+A8*x[6]*x[2]-A12*x[7] = 0. ...(4.58a)

f8=A1-A2*x[8]-A5*x[4]*x[8]-A4*x[2]-A6*x[8]*x[3]+A14*x[3]
+A15*x[1]=0 ...(4.59a)

f9=A12*x[7]-A13*x[9]*x[3] = 0. ...(4.60a)

where, A1= $k_1[CH_4][O_2]$; A2 = $k_2[O_2]$; A3 = $k_3[O_2]$; A4=$[CH_4]$; A5 = k_5; A6 =k_6; A7 =k_7; A8=k_8; A9 = k_9; A10=k_{10}; A11=k_{11}; A12=$k_{12}[O_2]$; A13=k_{13}; A14 =$k_{14}[CH_4]$; A15 =$k_{15}[CH_4]$; A16=$k_{16}[O_2]$;

Solving the system of algebraic equations by using Newton-Raphson modified method, the concentration of intermediate species are determined. The partial derivatives for each chain carrier x[i] are listed in table 4.8. The concentrations of intermediate species are further substituted in the rate of production of products. The explosion conditions are calculated for stoichiometric methane-oxygen mixture.

4.4. OXIDATION OF ETHANE :

Ethane oxidation is a part of Methane oxidation and is a primary fuel itself. The explosion regions in the ethane-air mixture is shown in the Fig. 4.3. The oxidation of ethane at low temperatures and in oxidizing environments gives the initiating reaction with O_2 as shown in the mechanism below:

$$C_2H_6 + O_2 \xrightarrow{k_1} \cdot C_2H_5 + HO_2 \qquad \ldots(4.63)$$

$$O_2 + M \xrightarrow{k_2} O + O + M \qquad \ldots(4.64)$$

$$C_2H_5 + O \xrightarrow{k_3} CH_3CHO + H \qquad \ldots(4.65)$$

$$HO_2 + H \xrightarrow{k_4} H_2O + O \qquad \ldots(4.66)$$

$$CH_3CHO + H \xrightarrow{k_5} CH_3CO + H_2 \qquad \ldots(4.67)$$

$$C_2H_6 + O \xrightarrow{k_6} C_2H_5 + OH \qquad \ldots(4.68)$$

$$CH_3CO \xrightarrow{k_7} CO + CH_3 \qquad \ldots(4.69)$$

$$C_2H_5 + O_2 \xrightarrow{k_8} C_2H_4 + HO_2 \qquad \ldots(4.70)$$

$$C_2H_4 + OH \xrightarrow{k_9} CH_3 + CH_2O \qquad \ldots(4.71)$$

$$CH_3 + O \xrightarrow{k_{10}} CH_2O + H \qquad \ldots(4.72)$$

Table. 4.8. Expressions of $\frac{\partial f_i}{\partial x[j]}$ for methane oxidation mechanism.

	x[1]	x[2]	x[3]	x[4]	x[5]	x[6]	x[7]	x[8]	x[9]
f1	-(A10*x[4] + A15)	0.0	A13*x[9]	-(A10*x[1])	0.0	0.0	0.0	0.0	A13*x[3]
f2	0.0	-(A4 + A8*x[6] + A9*x[4])	0.0	-(A9*x[2])	0.0	-A8*x[2]	0.0	A2	0.0
f3	2*A10*x[4]	A4 + A8*x[6] + A9*x[4]	-(A6*x[8] + A7*x[6]+A11*x[4] +A13*x[9]+A14)	A5*x[8]+A9*x[2] + 2*A10*x[1] - A11*x[3]	0.0	-A7*x[3] + A8*x[2]	0.0	A5*x[4] - A6*x[3]	-A13*x[3]
f8	A15	A4	-(A6*x[8]) + A14	-(A5*x[8])	0.0	0.0	0.0	-(A2 + A5*x[4] + A6*x[3])	0.0
f5	0.0	0.0	0.0	A5*x[8]	-A3	0.0	0.0	A2 + A5*x[4]	0.0
f6	0.0	-(A8*x[6])	A6*x[8] - A7*x[6]	0.0	A3	-A7*x[3] - A8*x[2]	0.0	A6*x[3]	0.0
f7	0.0	A8*x[6]	A7*x[6]	0.0	0.0	A7*x[3]+ A8*x[2]	-A12	0.0	0.0
f4	-(A10*x[4])	-(A9*x[4])	-(A11*x[4])	-(A5*x[8]+A9* x[2]+A11*x[3]+ A10*x[1])	A3	0.0	A12	-A5*x[4]	0.0
f9	0.0	0.0	-(A13*x[9])	0.0	0.0	0.0	A12	0.0	-A13*x[3]

Note : x[1] = [H]; x[2] = [O]; x[3] = [OH]; x[4] = [HO_2]; x[5] = [CH_3]; x[6] = [CH_3O]; x[7] = [CH_2O]; x[8] = [HCO]; x[9] = [CO];

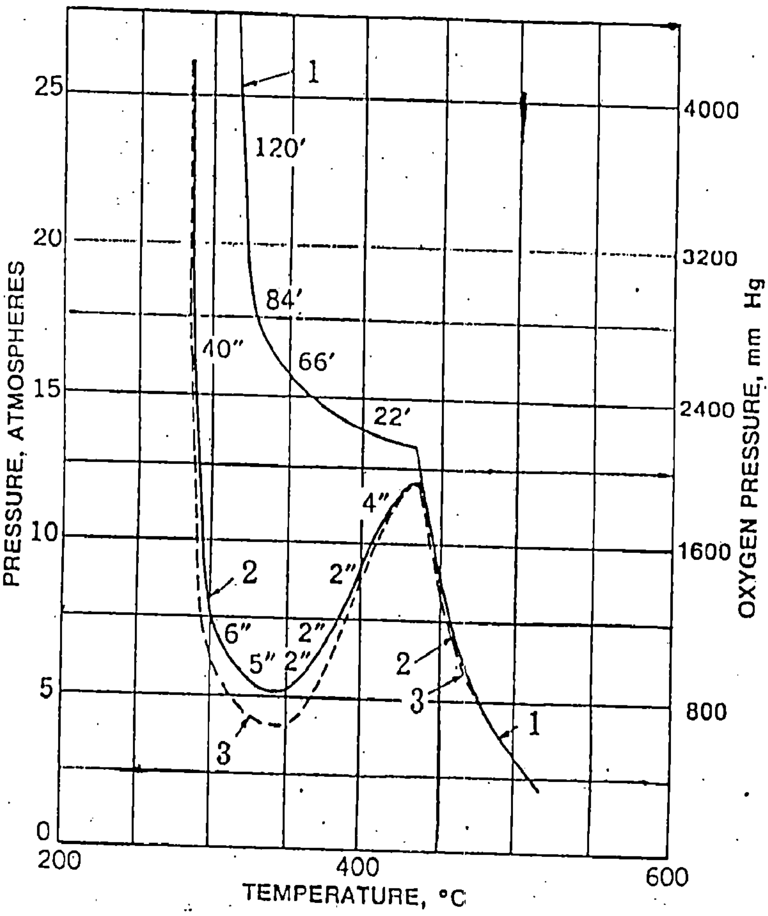

Fig. 4.3. Explosion regions and ignition lags in ethane-air mixtures; effect of adding acetaldehyde. 13% ethane in air. 1. No acetaldehyde, 2. 1% acetaldehyde, 3. 2%acetaldehyde [14].

$$CH_2O + OH \xrightarrow{k_{11}} HCO + H_2O \qquad \text{...(4.73)}$$

$$HCO + H \xrightarrow{k_{12}} CO + H_2 \qquad \text{...(4.74)}$$

$$HCO + O \xrightarrow{k_{13}} CO + OH \qquad \text{...(4.75)}$$

$$CO + OH \xrightarrow{k_{14}} CO_2 + H \qquad \text{...(4.76)}$$

The reaction of C_2H_6 with O_2 yields ethene (C_2H_4) which in turn is a primary fuel.

Oxidation of ethyl radical produces acetaldehyde (CH_3CHO) which is an important intermediate in the combustion of higher hydrocarbons. At sufficient amounts of oxygen the final products are water vapour (H_2O) carbon dioxide (CO_2). The rate expressions for the reactions in the mechanism are given in the table. 4.9.

Rates of production of the intermediate species H, O, OH, HO_2, C_2H_5, CH_3CHO, CH_3CO, CH_3, C_2H_4, CH_2O, HCO, CO and the final products are as follows:

$$\frac{d[H]}{dt}=k_3[O][C_2H_5]-k_4[H][HO_2]-k_5[H][CH_3CHO]+k_{10}[O][CH_3] -k_{12}[H][HCO] \quad \text{...(4.77)}$$

$$\frac{d[O]}{dt}=2k_2[O_2][M]-k_3[O][C_2H_5]+k_4[H][HO_2]-k_6[C_2H_6][O] -k_{10}[O][CH_3]-k_{13}[O][HCO] \quad \text{...(4.78)}$$

$$\frac{d[OH]}{dt}=k_6[C_2H_6][O]-k_9[OH][C_2H_4]-k_{11}[OH][CH_2O]+k_{13}[O][HCO] -k_{14}[OH][CO] \quad \text{...(4.79)}$$

$$\frac{d[HO_2]}{dt}=k_1[C_2H_6][O_2]-k_4[HO_2][H]+k_8[O_2][C_2H_5] \quad \text{...(4.80)}$$

$$\frac{d[C_2H_5]}{dt}=k_1[C_2H_6][O_2]-k_3[C_2H_5][O]+k_6[O][C_2H_6]-k_8[O_2][C_2H_5] \quad \text{...(4.81)}$$

$$\frac{d[CH_3CHO]}{dt}=k_3[C_2H_5][O]-k_5[CH_3CHO][H] \quad \text{...(4.82)}$$

$$\frac{d[CH_3CO]}{dt}=k_5[CH_3CHO][H]-k_7[CH_3CO] \quad \text{...(4.83)}$$

$$\frac{d[CH_3]}{dt}=k_7[CH_3CO]+k_9[OH][C_2H_4]-k_{10}[O][CH_3] \quad \text{...(4.84)}$$

$$\frac{d[C_2H_4]}{dt}=k_8[O_2][C_2H_5]-k_9[OH][C_2H_4] \quad \text{...(4.85)}$$

Table. 4.9. Rate expressions of ethane oxidation mechanism.

$k = AT^n \exp\left(-E_a / RT\right)$ m^3/mol.sec [10].

S.No.	REACTIONS OF THE MECHANISM	A $*10^{-6}$ m^3/molecule.sec	N	E_a *4.187 kJ/mol
1.	$C_2H_6 + O_2 \xrightarrow{k_1} C_2H_5 + HO_2$	13.00	0.0	51.00
2.	$O_2 + M \xrightarrow{k_2} O + O + M$	15.71	0.0	115.00
3.	$C_2H_5 + O \xrightarrow{k_3} CH_3CHO + H$	13.70	0.0	0.00
4.	$HO_2 + H \xrightarrow{k_4} H_2O + O$	13.70	0.0	1.00
5.	$CH_3CHO + H \xrightarrow{k_5} CH_3CO + H_2$	13.60	0.0	4.20
6.	$C_2H_6 + O \xrightarrow{k_6} C_2H_5 + OH$	13.40	0.0	6.36
7.	$CH_3CO \xrightarrow{k_7} CO + CH_3$	13.48	0.0	17.24
8.	$C_2H_5 + O_2 \xrightarrow{k_8} C_2H_4 + HO_2$	12.00	0.0	5.00
9.	$C_2H_4 + OH \xrightarrow{k_9} CH_3 + CH_2O$	12.30	0.0	0.96
10.	$CH_3 + O \xrightarrow{k_{10}} CH_2O + H$	14.11	0.0	2.00
11.	$CH_2O + OH \xrightarrow{k_{11}} HCO + H_2O$	12.88	0.0	0.17
12.	$HCO + H \xrightarrow{k_{12}} CO + H_2$	14.30	0.0	0.00
13.	$HCO + O \xrightarrow{k_{13}} CO + OH$	14.00	0.0	0.00
14.	$CO + OH \xrightarrow{k_{14}} CO_2 + H$	7.18	1.3	-0.77

$$\frac{d[CH_2O]}{dt} = k_9[OH][C_2H_4] + k_{10}[O][CH_3] - k_{11}[OH][CH_2O] \qquad \ldots(4.86)$$

$$\frac{d[HCO]}{dt} = k_{11}[OH][CH_2O] - k_{12}[H][HCO] - k_{13}[O][HCO] \qquad \ldots(4.87)$$

$$\frac{d[CO]}{dt} = k_7[CH_3CO] + k_{12}[H][HCO] + k_{13}[O][HCO] - k_{14}[OH][CO] \qquad \ldots(4.88)$$

$$\frac{d[H_2O]}{dt} = k_4[H][HO_2] + k_{11}[OH][CH_2O] \qquad \ldots(4.89)$$

$$\frac{d[CO_2]}{dt} = k_{14}[OH][CO] \qquad \ldots(4.90)$$

The steady state approximation has been employed for the above rate expressions assuming that the concentration of the chain carriers remain constant after a certain time. The expressions deduced are as follows:

$\frac{d[H]}{dt} = 0$, $\frac{d[O]}{dt} = 0$, $\frac{d[OH]}{dt} = 0$, $\frac{d[HO_2]}{dt} = 0$, $\frac{d[C_2H_5]}{dt} = 0$, $\frac{d[CH_3CHO]}{dt} = 0$, $\frac{d[CH_3CO]}{dt} = 0$, $\frac{d[CH_3]}{dt} = 0$, $\frac{d[C_2H_4]}{dt} = 0$, $\frac{d[CH_2O]}{dt} = 0$, $\frac{d[HCO]}{dt} = 0$ and $\frac{d[CO]}{dt} = 0$.

The set of algebraic equations obtained by applying the steady-state approximation for the intermediate species is follows:

f1 = A3*x[2]*x[5] - A4*x[1]*x[4] - A5*x[1]*x[6] + A10*x[2]*x[8]

- A12*x[1]*x[11] = 0. ...(4.77a)

f2 = 2*A2 - A3*x[2]*x[5] + A4*x[1]*x[4] - A6*x[2] - A10*x[2]*x[8]

- A13*x[2]*x[11] = 0. ...(4.78a)

f3 = A6*x[2] - A9*x[3]*x[9] - A11*x[3]*x[10] + A13*x[2]*x[11]

-A14*x[3]*x[12] = 0. ...(4.79a)

f4 = A1 – A4*x[4]*x[1] + A8*x[5] = 0. ...(4.80a)

f5 = A1 – A3*x[5]*x[2] +A6*x[2] – A8*x[5] = 0. ...(4.81a)

f6 = A3*x[5]*x[2] –A5*x[6]*x[1] = 0. ...(4.82a)

f7 = A5*x[6]*x[1] – A7*x[7] = 0. ...(4.83a)

f8 = A7*x[7] + A9* x[3]*x[9] –A10*x[2]*x[8] = 0. ...(4.84a)

f9 = A8*x[5]-A9*x[9]*x[3] = 0. ...(4.85a)

f10 = A9*x[9]*x[3] + A10*x[2]*x[8] –A11*x[10]*x[3] = 0. ...(4.86a)

f11 = A11*x[10]*x[3] – A12*x[1]*x[11] –A13*x[11]*x[2] = 0. ...(4.87a)

f12 = A7*x[7] + A12*x[11]*x[1] +A13*x[11]*x[2] -A14*x[12]*x[3] = 0. ...(4.88a)

where, A1 = $k_1[C_2H_6][O_2]$; A2 = $k_2[O_2][M]$; A3 = k_3; A4 = k_4; A5 = k_5; A6 = $k_6[C_2H_6]$; A7 = k_7; A8 = $k_8[O_2]$; A9 = k_9; A10 = k_{10}; A11 = k_{11}; A12 = k_{12};A13= k_{13}; A14 = k_{14};

Solving the system of algebraic equations thus formed considering the initial concentrations and rate constants by using Newton-Raphson modified method, the concentrations of intermediate species are determined. The partial derivatives for each chain carrier x[i] are listed in table 4.10.

The concentrations of intermediate species are further substituted in the rate of production of products. The explosion conditions are calculated for stoichiometric ethane-oxygen mixture.

4.5. OXIDATION OF PROPANE :

The detailed reaction mechanism of propane is a sequential and a hierarchical process, beginning with the simplest species and building up to include larger and more complex molecules. Propane is the first species to be encountered, in which distinctions between isomeric forms of a given species must be considered [19].

Table. 4.10. Expressions of $\frac{\partial f_i}{\partial x[j]}$ for ethane oxidation mechanism.

	x[1]	x[2]	x[3]	x[4]	x[5]	x[6]
f1	-(A4*x[4] + A5*x[6] + A12*x[11])	A3*x[5] + A10*x[8]	0.0	-(A4*x[1])	A3*x[2]	-(A5*x[1])
f2	A4*x[4]	-(A3*x[5] + A6 + A10*x[8]+ A13*x[11])	0.0	A4*x[1]	-(A3*x[2])	0.0
f3	0.0	A6 + A13*x[11]	-(A9*x[9] + A11*x[10]+A14*x[12])	0.0	0.0	0.0
f4	-(A4*x[4])	0.0	0.0	-A4*x[1]	A8	0.0
f5	0.0	-(A3*x[5]) + A6	0.0	0.0	-(A3*x[2] + A8)	0.0
f6	-(A5*x[6])	A3*x[5]	0.0	0.0	A3*x[2]	-(A5*x[1])
f7	A5*x[6]	0.0	0.0	0.0	0.0	A5*x[1]
f8	0.0	-(A10*x[2])	A9*x[9]	0.0	0.0	0.0
f9	0.0	0.0	-(A9*x[9])	0.0	A8	0.0
f10	0.0	-(A10*x[8])	A9*x[9] – A11*x[10]	0.0	0.0	0.0
f11	-(A12*x[11])	-(A13*x[11])	A11*x[10]	0.0	0.0	0.0
f12	A12*x[11]	A13*x[11]	-(A14*x[12])	0.0	0.0	0.0

continue...

Table. 4.10.(continued)

	x[7]	x[8]	x[9]	x[10]	x[11]	x[12]
f1	0.0	A10*x[2]	0.0	0.0	-(A12*x[1])	0.0
f2	0.0	-(A10*x[2])	0.0	0.0	-(A13*x[2])	0.0
f3	0.0	0.0	-(A9*x[3])	-(A11*x[3])	A13*x[2]	-(A14*x[3])
f4	0.0	0.0	0.0	0.0	0.0	0.0
f5	0.0	0.0	0.0	0.0	0.0	0.0
f6	0.0	0.0	0.0	0.0	0.0	0.0
f7	-A7	0.0	0.0	0.0	0.0	0.0
f8	A7	-(A10*x[2])	A9*x[3]	0.0	0.0	0.0
f9	0.0	0.0	-(A9*x[3])	0.0	0.0	0.0
f10	0.0	A10*x[2]	A9*x[3]	-(A11*x[3])	0.0	0.0
f11	0.0	0.0	0.0	A11*x[3]	-(A12*x[1] + A13*x[2])	0.0
f12	A7	0.0	0.0	0.0	0.0	-(A14*x[3])

Note: x[1] = [H]; x[2] = [O]; x[3] = [OH]; x[4] = [HO_2]; x[5] = [C_2H_5]; x[6] = [CH_3CHO]; x[7] = [CH_3CO]; x[8] = [CH_3]; x[9] = [C_2H_4]; x[10] = [CH_2O]; x[11] = [HCO]; x[12] = [CO];

The initial attack by oxygen on saturated hydrocarbons generally involves hydrogen abstraction to yield an alkyl radical and a hydroperoxy radical. Fig.4.4. shows the explosion limits of propane-air mixture.

The reaction mechanism of propane oxidation considered in this modelling is as follows:

$$C_3H_8 + O_2 \xrightarrow{k_1} nC_3H_7 + HO_2 \qquad ...(4.91)$$

$$O_2 + M \xrightarrow{k_2} 2O + M \qquad ...(4.92)$$

$$HO_2 + O \xrightarrow{k_3} O_2 + OH \qquad ...(4.93)$$

$$C_3H_8 + OH \xrightarrow{k_4} nC_3H_7 + H_2O \qquad ...(4.94)$$

$$nC_3H_7 + O_2 \xrightarrow{k_5} C_3H_6 + HO_2 \qquad ...(4.95)$$

$$C_3H_6 + O \xrightarrow{k_6} CH_2O + C_2H_4 \qquad ...(4.96)$$

$$C_3H_6 + OH \xrightarrow{k_7} C_2H_5 + CH_2O \qquad ...(4.97)$$

$$C_2H_5 + O_2 \xrightarrow{k_8} C_2H_4 + HO_2 \qquad ...(4.98)$$

$$C_2H_5 + O \xrightarrow{k_9} CH_3CHO + H \qquad ...(4.99)$$

$$HO_2 + H \xrightarrow{k_{10}} H_2O + O \qquad ...(4.100)$$

$$CH_3CHO + H \xrightarrow{k_{11}} CH_3CO + H_2 \qquad ...(4.101)$$

$$CH_3CO \xrightarrow{k_{12}} CH_3 + CO \qquad ...(4.102)$$

$$C_2H_4 + OH \xrightarrow{k_{13}} CH_3 + CH_2O \qquad ...(4.103)$$

$$CH_2O + OH \xrightarrow{k_{14}} HCO + H_2O \qquad ...(4.104)$$

$$CH_3 + O \xrightarrow{k_{15}} CH_2O + H \qquad ...(4.105)$$

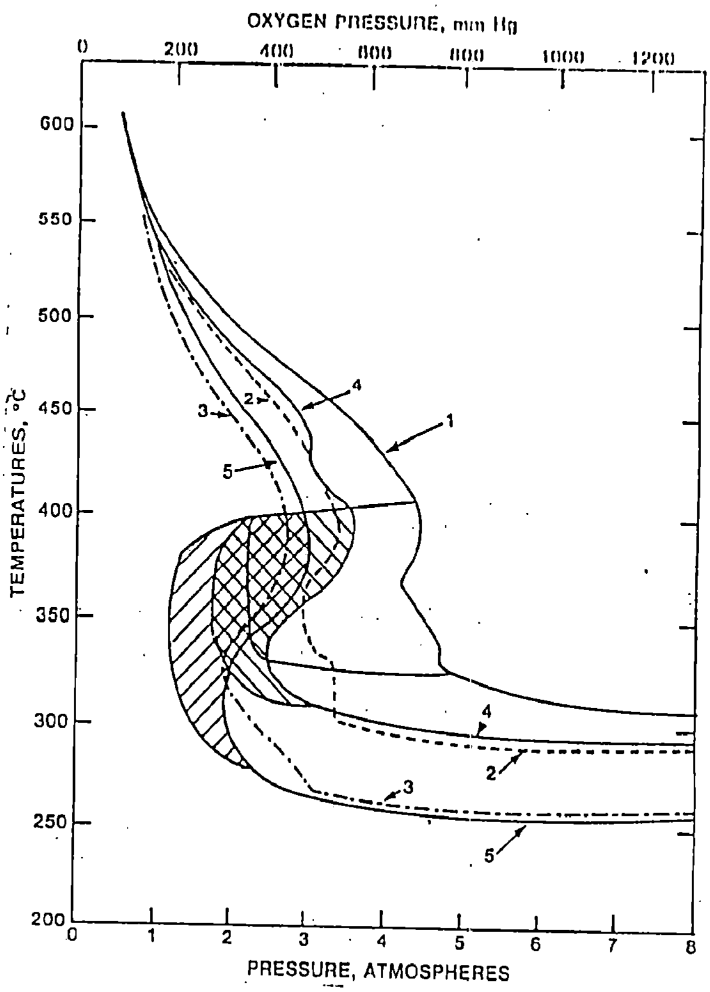

Fig. 4.4. Effect of adding aldehydes on the "cool flame" and explosion region of a 7.5% propane-air mixture. Curve 1. No aldehyde, 2. 1% Propionaldehyde, 3. 2% Propionaldehyde, 4. 1% Acetaldehyde, 5. 2% Acetaldehyde [14].

$$HCO + H \xrightarrow{k_{16}} CO + H_2 \qquad ...(4.106)$$

$$HCO + O \xrightarrow{k_{17}} CO + OH \qquad ...(4.107)$$

$$CO + OH \xrightarrow{k_{18}} CO_2 + H \qquad ...(4.108)$$

The reaction mechanism is selective depending on the activation energies of abstraction. In the oxidation of propane the abstraction of secondary hydrogen is easier than primary hydrogen abstraction although the probability of primary hydrogen abstraction is greater. It is apparent therefore that a mixture of alkyl radicals will be produced in varying amounts depending on the number of hydrogen atoms in the molecule. Generally, as the size of the alkyl or other radical hydrocarbon species increases, the thermal stability of the radical decreases and its decomposition rate grows. The rate expressions for the reactions in the propane oxidation mechanism are given in the table. 4.11.

Rates of production of the intermediate species H, O, OH, HO_2, nC_3H_7, C_3H_6, C_2H_5, C_2H_4, CH_3CHO, CH_3CO, CH_2O, CH_3, HCO, CO and the final products are as follows:

$$\begin{aligned}\frac{d[H]}{dt} &= k_9[O][C_2H_5]-k_{10}[H][HO_2]-k_{11}[H][CH_3CHO]+k_{15}[O][CH_3]\\ &\quad -k_{16}[H][HCO]+k_{18}[OH][CO]\end{aligned} \qquad \ldots(4.109)$$

$$\begin{aligned}\frac{d[O]}{dt} &= 2k_2[O_2][M]-k_3[O][HO_2]-k_6[O][C_3H_6]-k_9[O][C_2H_5]\\ &\quad +k_{10}[H][HO_2]-k_{15}[O][CH_3]-k_{17}[O][HCO]\end{aligned} \qquad \ldots(4.110)$$

$$\begin{aligned}\frac{d[OH]}{dt} &= k_3[O][HO_2]-k_4[C_3H_8][OH]-k_7[OH][C_3H_6]-k_{13}[OH][C_2H_4]\\ &\quad -k_{14}[OH][CH_2O]+k_{17}[O][HCO]-k_{18}[OH][CO]\end{aligned} \qquad \ldots(4.111)$$

$$\begin{aligned}\frac{d[HO_2]}{dt} &= k_1[O_2][C_3H_8]-k_3[O][HO_2]+k_5[O_2][nC_3H_7]+k_8[O_2][C_2H_5]\\ &\quad -k_{10}[H][HO_2]\end{aligned} \qquad \ldots(4.112)$$

$$\frac{d[nC_3H_7]}{dt} = k_1[O_2][C_3H_8]+k_4[OH][C_3H_8]-k_5[O_2][nC_3H_7] \qquad \ldots(4.113)$$

$$\frac{d[C_3H_6]}{dt} = k_5[O_2][nC_3H_7]-k_6[O][C_3H_6]-k_7[OH][C_3H_6] \qquad \ldots(4.114)$$

Table. 4.11. Rate expressions of propane oxidation mechanism.

$k = AT^n \exp\left(-E_a/_{RT}\right)$ m^3/mol.sec [10].

S.No.	REACTIONS OF THE MECHANISM	A $*10^{-6}$ m^3/molecule.sec	n	E_a *4.187 kJ/mol
1.	$C_3H_8 + O_2 \xrightarrow{k_1} nC_3H_7 + HO_2$	13.00	0.0	47.50
2.	$O_2 + M \xrightarrow{k_2} 2O + M$	15.71	0.0	115.00
3.	$HO_2 + O \xrightarrow{k_3} O_2 + OH$	13.70	0.0	1.00
4.	$C_3H_8 + OH \xrightarrow{k_4} nC_3H_7 + H_2O$	8.76	1.4	0.85
5.	$nC_3H_7 + O_2 \xrightarrow{k_5} C_3H_6 + HO_2$	12.00	0.0	5.00
6.	$C_3H_6 + O \xrightarrow{k_6} CH_2O + C_2H_4$	13.77	0.0	5.00
7.	$C_3H_6 + OH \xrightarrow{k_7} C_2H_5 + CH_2O$	12.90	0.0	0.00
8.	$C_2H_5 + O_2 \xrightarrow{k_8} C_2H_4 + HO_2$	12.00	0.0	5.00
9.	$C_2H_5 + O \xrightarrow{k_9} CH_3CHO + H$	13.70	0.0	0.00
10.	$HO_2 + H \xrightarrow{k_{10}} H_2O + O$	13.70	0.0	1.00
11.	$CH_3CHO + H \xrightarrow{k_{11}} CH_3CO + H_2$	13.60	0.0	4.20
12.	$CH_3CO \xrightarrow{k_{12}} CH_3 + CO$	13.48	0.0	17.24
13.	$C_2H_4 + OH \xrightarrow{k_{13}} CH_3 + CH_2O$	12.30	0.0	0.96
14.	$CH_2O + OH \xrightarrow{k_{14}} HCO + H_2O$	12.88	0.0	0.17
15.	$CH_3 + O \xrightarrow{k_{15}} CH_2O + H$	14.11	0.0	2.00
16.	$HCO + H \xrightarrow{k_{16}} CO + H_2$	14.30	0.0	0.00
17.	$HCO + O \xrightarrow{k_{17}} CO + OH$	14.00	0.0	0.00
18.	$CO + OH \xrightarrow{k_{18}} CO_2 + H$	7.18	1.3	-0.77

$$\frac{d[C_2H_5]}{dt} = k_7[OH][C_3H_6] - k_8[O_2][C_2H_5] - k_9[O][C_2H_5] \qquad \ldots(4.115)$$

$$\frac{d[C_2H_4]}{dt} = k_6[O][C_3H_6] + k_8[O_2][C_2H_5] - k_{13}[OH][C_2H_4] \qquad \ldots(4.116)$$

$$\frac{d[CH_3CHO]}{dt} = k_9[O][C_2H_5] - k_{11}[H][CH_3CHO] \qquad \ldots(4.117)$$

$$\frac{d[CH_3CO]}{dt} = k_{11}[H][CH_3CHO] - k_{12}[CH_3CO] \qquad \ldots(4.118)$$

$$\frac{d[CH_2O]}{dt} = k_6[O][C_3H_6] + k_7[OH][C_3H_6] + k_{13}[OH][C_2H_4] - k_{14}[OH][CH_2O] + k_{15}[O][CH_3] \qquad \ldots(4.119)$$

$$\frac{d[CH_3]}{dt} = k_{12}[CH_3CO] + k_{13}[OH][C_2H_4] - k_{15}[O][CH_3] \qquad \ldots(4.120)$$

$$\frac{d[HCO]}{dt} = k_{14}[OH][CH_2O] - k_{16}[H][HCO] - k_{17}[O][HCO] \qquad \ldots(4.121)$$

$$\frac{d[CO]}{dt} = k_{12}[CH_3CO] + k_{16}[H][HCO] + k_{17}[O][HCO] - k_{18}[OH][CO] \qquad \ldots(4.122)$$

$$\frac{d[H_2O]}{dt} = k_4[OH][C_3H_8] + k_{10}[H][HO_2] + k_{14}[OH][CH_2O] \qquad \ldots(4.123)$$

$$\frac{d[CO_2]}{dt} = k_{18}[OH][CO] \qquad \ldots(4.124)$$

The steady-state approximation is employed for the intermediate species considering the concentration of chain carriers remain constant after a certain time. Thus, a system of algebraic equations are obtained as follows:

F1=A9*x[2]*x[7]-A10*x[1]*x[4]-A11*x[1]*x[9]+A15*x[2]*x[12]-A16*x[1]*x[13]
+ A18*x[3]*x[14] = 0. ...(4.109a)

F2 = 2*A2-A3*x[2]*x[4]-A6*x[2]*x[6]-A9*x[2]*x[7]+A10*x[1]*x[4]
-A15*x[2]*x[12]-A17*x[2]*x[13] = 0. ...(4.110a)

$f3=A3*x[2]*x[4]-A4*x[3]-A7*x[3]*x[6]-A13*x[3]*x[8]-A14*x[3]*x[11]+$

$A17*x[2]*x[13]-A18*x[3]*x[14] = 0.$ ...(4.111a)

$f4 = A1-A3*x[4]*x[2]+A5*x[5]+A8*x[7]-A10*x[4]*x[1] = 0.$ ...(4.112a)

$f5 = A1+A4*x[3]- A5*x[5] = 0.$ ...(4.113a)

$f6 = A5*x[5] - A6*x[6]*x[2] -A7*x[6]*x[3] = 0.$ ...(4.114a)

$f7 = A7*x[6]*x[3] - A8*x[7] -A9*x[7]*x[2] = 0.$ ...(4.115a)

$f8 = A6*x[6]*x[2]+A8*x[7]-A13*x[8]*x[3] = 0.$ ...(4.116a)

$f9 = A9*x[7]*x[2] - A11*x[9]*x[1] = 0.$ ...(4.117a)

$f10 = A11*x[9]*x[1]-A12*x[10] = 0.$ ...(4.118a)

$f11 = A6*x[6]*x[2] + A7*x[6]*x[3] +A13*x[8]*x[3] - A14*x[11]* x[3]$

$+ A15*x[12]*x[2] = 0.$ ...(4.119a)

$f12 = A12*x[10]+ A13*x[8]*x[3] - A15*x[12]*x[2] = 0.$ ...(4.120a)

$f13 = A14*x[11]*x[3] - A16*x[13]*x[1] -A17*x[13]*x[2] = 0.$ ...(4.121a)

$f14 = A12*x[10] + A10*x[13]*x[1] + A17*x[13]*x[2] -A18*x[14]*x[3]=0.$.(4.122a)

where $A1 = k_1[C_3H_8][O_2]$; $A2=k_2[O_2][M]$; $A3 = k_3$; $A4 = k_4[C_3H_8]$; $A5 = k_5[O_2]$; $A6 = k_6$; $A7 = k_7$; $A8 = k_8[O_2]$; $A9 = k_9$; $A10 = k_{10}$; $A11=k_{11}$; $A12=k_{12}$; $A13=k_{13}$; $A14 = k_{14}$; $A15=k_{15}$; $A16=k_{16}$; $A17=k_{17}$; $A18=k_{18}$;

Thus, the system of algebraic equations formed is solved considering the initial concentrations of propane and oxygen, the rate constants for the reactions in the mechanism using Newton-Raphson modified method. The partial derivatives for each chain carrier x[i] are listed in table 4.12. The concentrations of intermediate species are determined and further substituted in the rate of production of products. The explosion conditions are calculated for stoichiometric propane-oxygen mixture ratio.

Table. 4.12. Expressions of $\frac{\partial f_i}{\partial x[j]}$ for propane oxidation mechanism.

	x[1]	x[2]	x[3]	x[4]	x[5]	x[6]
f1	-(A10*x[4] + A11*x[9] + A16*x[13])	A9*x[7] + A15*x[12]	A18*x[14]	-(A10*x[1])	0.0	0.0
f2	A10*x[4]	-(A3*x[4] + A6*x[6] + A9*x[7] + A15*x[12] + A17*x[13])	0.0	-(A3*x[2]) + A10*x[1]	0.0	-(A6*x[2])
f3	0.0	A3*x[4] + A17*x[13]	-(A4 + A7*x[6] + A13*x[8] + A14*x[11] + A18*x[14])	A3*x[2]	0.0	-(A7*x[3])
f4	-(A10*x[4])	-(A3*x[4])	0.0	-(A3*x[2] + A10*x[1])	A5	0.0
f5	0.0	0.0	A4	0.0	-A5	0.0
f6	0.0	-(A6*x[6])	-(A7*x[6])	0.0	A5	-(A6*x[2] + A7*x[3])
f7	0.0	-(A9*x[7])	A7*x[6]	0.0	0.0	A7*x[3]
f8	0.0	A6*x[6]	-(A13*x[8])	0.0	0.0	A6*x[2]
f9	-(A11*x[9])	A9*x[7]	0.0	0.0	0.0	0.0
f10	A11*x[9]	0.0	0.0	0.0	0.0	0.0
f11	0.0	A6*x[6] + A15*x[12]	A7*x[6] + A13*x[8] – A14*x[11]	0.0	0.0	A6*x[2] + A7*x[3]
f12	0.0	-(A15*x[12])	A13*x[8]	0.0	0.0	0.0
f13	-(A16*x[13])	-(A17*x[13])	A14*x[11]	0.0	0.0	0.0
f14	A16*x[13]	A17*x[13]	-(A18*x[14])	0.0	0.0	0.0

continue...

Table. 4.12. (continued)

	x[7]	x[8]	x[9]	x[10]	x[11]	x[12]	x[13]	x[14]
f1	A9*x[2]	0.0	-(A11*x[1])	0.0	0.0	A15*x[2]	-(A16*x[1])	A18*x[3]
f2	-(A9*x[2])	0.0	0.0	0.0	0.0	-(A15*x[2])	-(A17*x[2])	0.0
f3	0.0	-(A13*x[3])	0.0	0.0	-(A14*x[3])	0.0	A17*x[2]	-(A18*x[3])
f4	A8	0.0	0.0	0.0	0.0	0.0	0.0	0.0
f5	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
f6	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
f7	-(A8+A9*x[2])	0.0	0.0	0.0	0.0	0.0	0.0	0.0
f8	A8	-(A13*x[3])	0.0	0.0	0.0	0.0	0.0	0.0
f9	A9*x[2]	0.0	-(A11*x[1])	0.0	0.0	0.0	0.0	0.0
f10	0.0	0.0	A11*x[1]	-A12	0.0	0.0	0.0	0.0
f11	0.0	A13*x[3]	0.0	0.0	-(A14*x[3])	A15*x[2]	0.0	0.0
f12	0.0	A13*x[3]	0.0	A12	0.0	-(A15*x[2])	0.0	0.0
f13	0.0	0.0	0.0	0.0	A14*x[3]	0.0	-(A16*x[1] + A17*x[2])	0.0
f14	0.0	0.0	0.0	A12	0.0	0.0	A16*x[1] + A17*x[2]	-(A18*x[3])

Note : x[1] = [H]; x[2] = [O]; x[3] = [OH]; x[4] = [HO_2]; x[5] = [nC_3H_7]; x[6] = [C_3H_6]; x[7] = [C_2H_5]; x[8] = [C_2H_4]; x[9] = [CH_3CHO]; x[10] = [CH_3CO]; x[11] = [CH_2O]; x[12] = [CH_3]; x[13] = [HCO]; x[14] = [CO];

RESULTS AND DISCUSSION

Software in turbo C++ simulating the explosion limits of H_2-O_2, methane, ethane and propane considering the simplified reaction mechanisms has been developed.

- **H_2-O_2 EXPLOSION LIMITS:** No reactions occur below 560 K and above 930K the explosion occurs spontaneously at all pressures. Fig. 5.1 shows the three explosion limits of H_2-O_2 oxidation system as obtained by computer simulation which has a good agreement with the experimental investigation of Lewis and Von Elbe [14] as shown in Fig. 4.1. Hydrogen oxidation is divided into three explosion limits.

1. ***First Explosion Limit:*** For higher temperatures about 930 K, chain breaking occurs at low pressures of the range 100-150 N/m^2. For lower temperatures about 560 K chain breaking occurs in the pressure range of 250-300 N/m^2. The curve has a negative slope i.e., as the temperature increases the explosion limit pressure decreases. An increase of pressure anywhere along the limit at any temperature leads from no explosion to explosion region. This chain breaking is due to the diffusion of a large number of H atoms to the vessel wall.
2. ***Second Explosion Limit:*** For lower temperatures about 560 K the explosion limit pressure ranges about 250-300 N/m^2. As the temperature increases the explosion limit pressure also increases, i.e., at about 960 K the explosion limit pressure is 45000-50000 N/m^2. Hence, as the pressure increases anywhere along

the limit leads from explosion to no explosion. This is due to the increase in the chain breaking rate compared to the chain branching rate at higher pressures. ***Third Explosion Limit:*** This limit has a negative slope i.e., at higher temperatures the explosion limit pressures are low. At about 930 K the limit pressure is about 60000 N/m^2. Hence as the pressure increases anywhere along the limit leads from no explosion to explosion limit. This is due to the activating of the meta stable compound, i.e., HO_2 to form H_2O_2 by colliding with H_2 molecule at higher pressure.

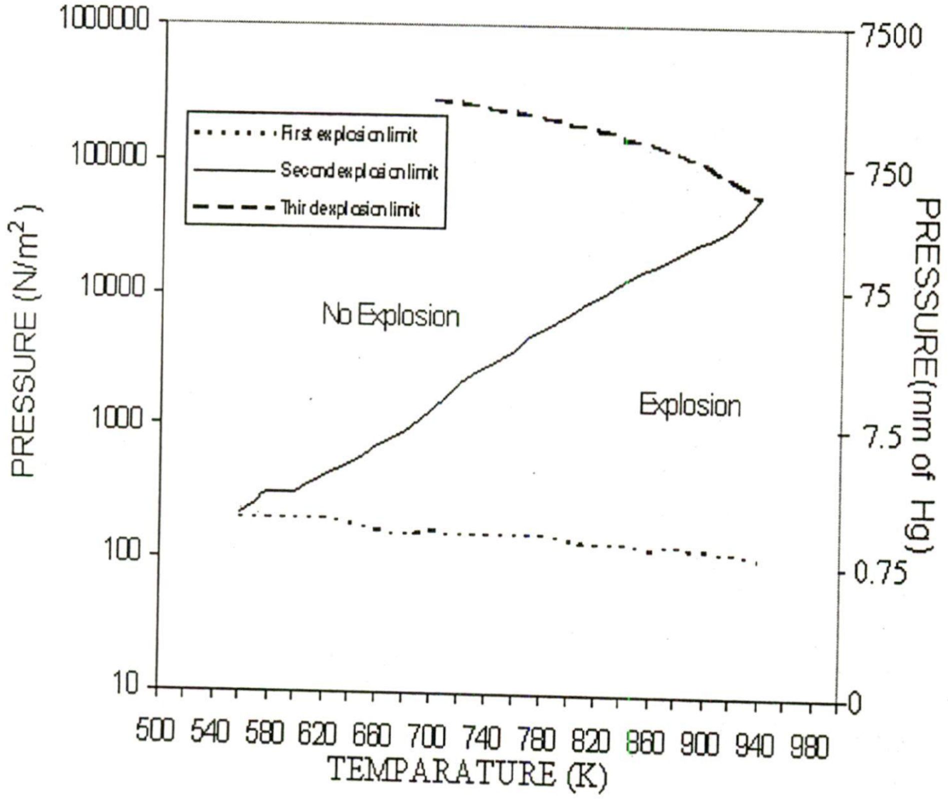

Fig. 5.1. Explosion Limits of hydrogen oxidation for stoichiometric mixture ratio from the simulation.

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- **METHANE EXPLOSION LIMITS:** The explosion limits of methane as obtained by the computer simulation has been shown in fig. 5.2. This figure gives the pressure temperature range for explosion to occur. The curve exhibits the negative slope showing the high explosion limit pressure for lower temperatures. At lower temperature about 560 K the explosion limit pressure is about 9.5 bar. At 960 K the limit pressure is about 3.5 bar. For methane only one explosion limit has been shown to occur. The meta stable compounds are responsible for the different limits as observed in the hydrogen oxidation. Such meta stable compounds in the methane oxidation is formaldehyde which has very minor role. The results obtained from the simulation has a close approximation with the curve obtained from the experimental investigation of Townend and Chamberlain shown in fig. 4.2, taken from Lewis and Von Elbe [14].

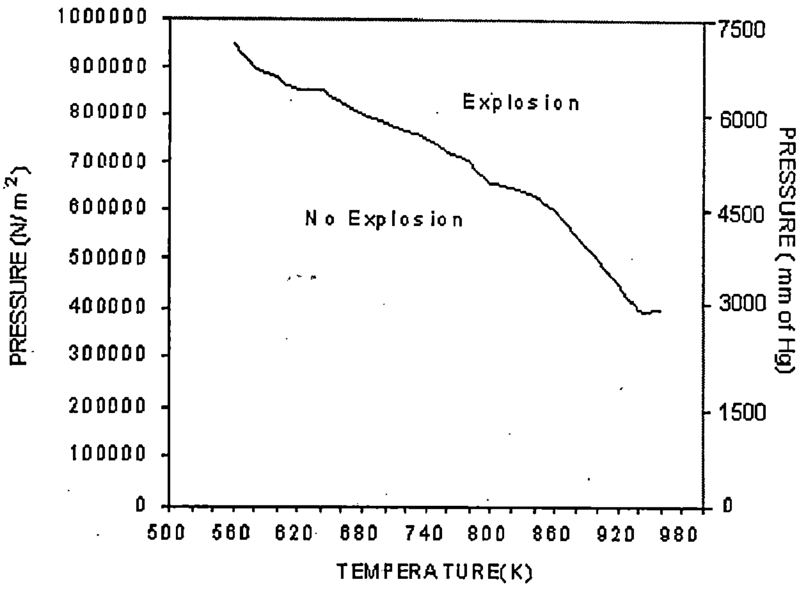

Fig.5.2. Explosion limits of methane oxidation for stoichiometric mixture ratio from the simulation.

- **ETHANE EXPLOSION LIMITS:** The explosion limits of ethane as obtained by the computer simulation has been shown in fig. 5.3. This figure gives the pressure temperature range for explosions to occur. The results obtained from the simulation has a close approximation with the curve obtained from the experimental investigation of Townend and Chamberlain shown in fig. 4.3, taken from Lewis and Von Elbe [14]. At lower temperature the explosion limit pressure is high but at higher temperature the limit pressure is low. In between, the change in slope of the curve is due to the meta stable compounds formed during the oxidation of ethane.

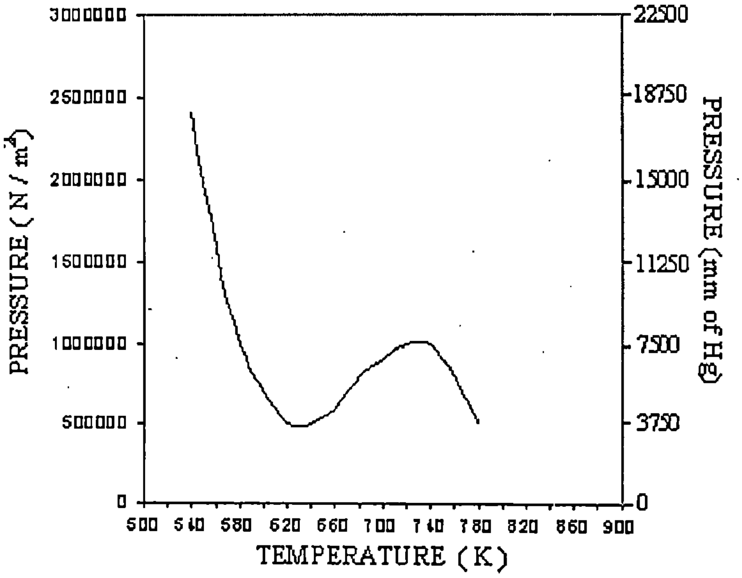

Fig. 5.3. Explosion limits of ethane oxidation for stoichiometric mixture ratio from the simulation.

- **PROPANE EXPLOSION LIMITS:** The explosion limit of propane as obtained by the computer simulation has been shown in the fig.5.4. This figure shows the pressure temperature range for explosions to occur. At lower temperatures about 540 K the explosion limit pressure is about 9 bar and the limit pressure decreases as the temperature increases. In between the trough in the curve is due to cool flames. The curve obtained from the simulation agrees well with the curve from experimental investigation of Townend and Chamberlain shown in fig. 4.4, taken from Lewis and Von Elbe [14].

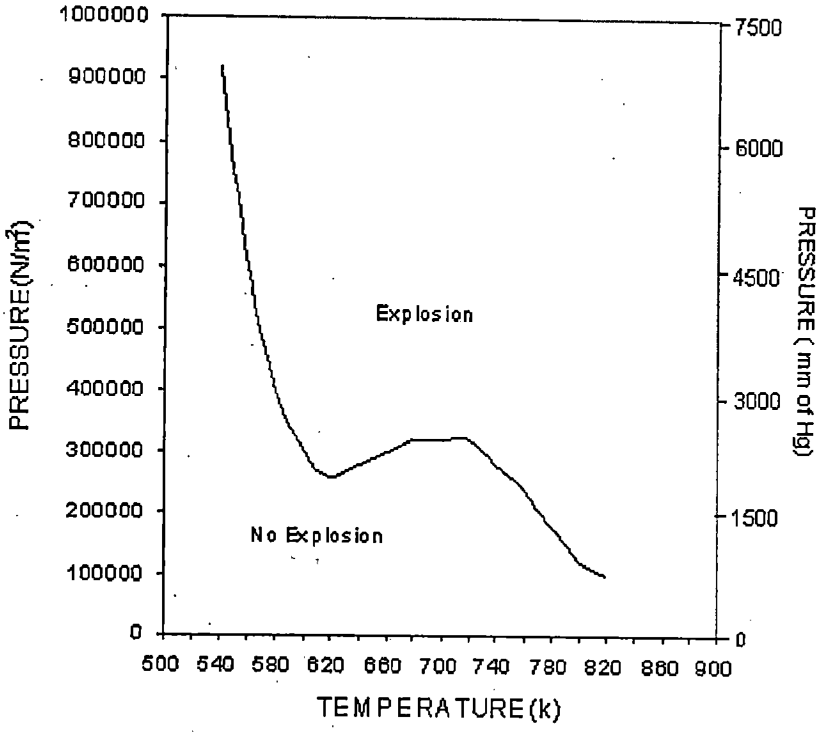

Fig. 5.4. Explosion limits of propane oxidation for stoichiometric mixture ratio from the simulation.

- **COMPARISON OF METHANE, ETHANE AND PROPANE EXPLOSION LIMITS:** The explosion limits, i.e., pressure and temperature ranges for methane, ethane and propane are shown in fig. 5.5. The explosion limits of propane predicts the early limits compared to the lower hydrocarbons. As the length of the hydrocarbon (more carbon atoms) increases the bond energy between of C-H decreases. Hence, the breaking of bond is easier when compared to the hydrocarbon with the low number of carbon atoms. Thus, the explosion limits for higher hydrocarbons shift towards the lower temperatures. The change in slopes also increases due to the increase in the number of meta stable species produced in the oxidation mechanism and due to the origin of cool flames starting from propane to higher hydrocarbons.

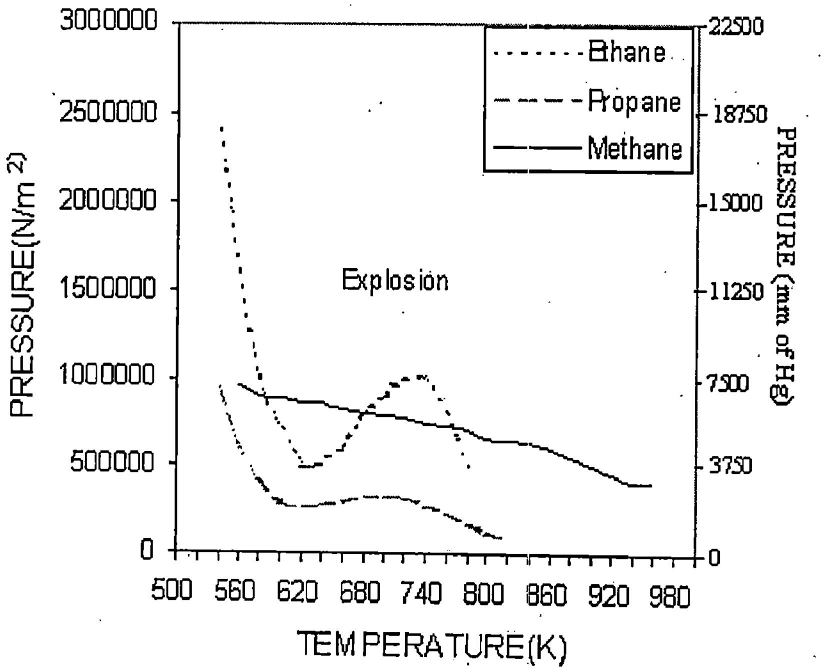

Fig.5.5. Explosion limits of hydrocarbons oxidation for stoichiometric mixture ratio from the simulation.

CONCLUSIONS

The results obtained from the simulation agree well with the experimental results. The work can be further extended to simulate the combustion of higher hydrocarbons from propane onwards. For combustion of higher hydrocarbons suitable reaction mechanisms will have to be taken into account to explain the characteristic features of hydrocarbon combustion viz.: origin and propagation of cool flames, negative temperature coefficient and long induction periods.

This simulation can be useful for modelling and simulating various kinetically controlled phenomena namely ignition, extinction and flame propagation processes.

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PROGRAM FOR EXPLOSION LIMITS OF H2-O2 OXIDATION MECHANISM

```
#include<stdlib.h>
#include<fstream.h>
#include<math.h>
#include<iomanip.h>
#include<conio.h>
#define N 6
#include"lud.cpp"
#define R 8314
#define error 0.01

void ludcmp(float Z[N][N],int n,int indx[N],float *d);
void lubksb(float Z[N][N],int n,int indx[N],float B[N]);
float *d;
int  n,indx[N];
float Z[N][N],B[N];

class hydrogen
 { private:
    double A1,A2,A3,A4,A5,A6,A7,A8,A9,A10,A11,dh2o;
    float Ch2,Co2,Ch2o,a[12],n[12],Ea[12],T,x[6],y[6];
    double K[11],P,M;
    float dx[6],phi;
    double f[6][6],R1[6];
    float xh2,xo2,xh2o;
    int i,j,limit,count;
    char fuel[10];

  public:
    void get( )
         {
          cout << "ENTER THE FUEL(H2 or h2 or H2_O2 or h2_o2):";
           cin >> fuel;
          cout << "ENTER THE EXPLOSION LIMIT(Number 1,2 or 3):";
           cin >> limit;
          cout << "ENTER THE EQUIVALENCE RATIO:";
           cin >> phi;
          }
    void display( )
         {
          cout.precision(3);
          cout<<setw(15)<<P<<setw(15)<<T<<endl;
```

```
     }
void calc1( )
     {
     float Xh2=0.667, Xo2=0.333,phi;
     xh2=phi*Xh2;
     xo2=Xo2;
     ifstream infile;
     infile.open("KH21.dat");
     ofstream outfile;
     outfile.open("H1.dat");
     for(i=1;i<7;i++)
       infile >> a[i] >> n[i] >> Ea[i];
     cout<<setw(15)<<"PRESSURE"<<setw(15)<<"TEMPERATURE"<<endl;
     for(T=500;T<=1000;T=T+20.0)
      {for(i=1;i<7;i++)
         K[i]=rate_const(a[i],n[i],Ea[i],T);
      for(P=100;P<=600;P=P+50.0)
       {
         Ch2=concen(P,T,xh2);
         Co2=concen(P,T,xo2);
         A1=2*K[1]*Ch2*P;            A2=K[2]*Co2;
         A3=K[3]*Ch2;                A4=K[4]*Ch2;
         A5=K[5]*P;                  A6=K[6]*P;
         x[1]=0.505;        x[2]=0.1005;  x[3]=.2015;  // assumed values
         int num=0;
       do{
           f[1][1]= -(A2+A5*x[3]+4*A6*x[1]);          f[1][2]= A3;
           f[1][3]= A4-(A5*x[1]);                     f[2][1]= A2;
           f[2][2]= -A3;                              f[2][3]= 0.0;
           f[3][1]= A2-(A5*x[3]);                      f[3][2]= A3;
           f[3][3]= -(A4+(A5*x[1]));
           R1[1]= -(A1-(A2+A5*x[3]+2*A6*x[1])*x[1]+A3*x[2]+A4*x[3]);
           R1[2]= -(A2*x[1]-A3*x[2]);
           R1[3]= -(A2*x[1]-A3*x[2]-(A4+A5*x[1])*x[3]);
           for(i=1;i<4;i++)
           for(j=1;j<4;j++)
             Z[i][j]=(float)f[i][j];
           for(i=1;i<4;i++)
             B[i]=(float)R1[i];
           ludcmp(Z,N,indx,&*d);
           lubksb(Z,N,indx,B);
           for(i=1;i<4;i++)
             { dx[i]=B[i];
               y[i]=dx[i]+x[i];
               x[i]=y[i];
```

```
                 }
              count=0;
              for(i=1;i<4;i++)
               { if(fabs(R1[i])<=error)
                      count++;
                }
              if(count>=2)
                break;
              num++;
         }while(1);
              dh2o= (A3+A4*x[1])*x[3];
              if(dh2o<=0.0)
               { display();
                 outfile.precision(3);
                 outfile << T << P <<endl;
                }
        }}infile.close();
         outfile.close();
      }
void calc2( )
      {
       float Xh2=0.667, Xo2=0.333,phi;
       xh2=phi*Xh2;
       xo2=Xo2;
       ifstream infile;
       infile.open("KH22.dat");
       ofstream outfile;
       outfile.open("H2.dat");
       for(i=1;i<6;i++)
         infile >> a[i] >> n[i] >> Ea[i];
       cout<<setw(15)<<"PRESSURE"<<setw(15)<<"TEMPERATURE"<<endl;
       for(T=500;T<=1000;T=T+20)
        { for(i=1;i<6;i++)
              K[i]=rate_const(a[i],n[i],Ea[i],T);
         for(P=100;P<=40000;P=P+200.0)
          {
           Ch2=concen(P,T,xh2);
           Co2=concen(P,T,xo2);
           x[1]=0.5005;      x[2]=0.2005;  x[3]=0.40015;
           A1= K[1]*Ch2*Co2;                A2= K[2]*Ch2;
           A3= K[3]*Co2;                    A4= K[4]*Ch2;
           A5= K[5]*Co2;
         do{
           f[1][1]= -(A3+A5);                f[1][2]= A4;
           f[1][3]= A2;                      f[2][1]= A3;
```

```
f[2][2]= -A4;                        f[2][3]= 0.0;
f[3][1]= A3;                         f[3][2]= A4;
f[3][3]= -A2;
R1[1]= -(A2*x[3]-A3*x[1]+A4*x[2]-A5*x[1]);
R1[2]= -(A3*x[1]-A4*x[2]);
R1[3]= -(A1-A2*x[3]+A3*x[1]+A4*x[2]);
for(i=1;i<4;i++)
for(j=1;j<4;j++)
    Z[i][j]=f[i][j];
for(i=1;i<4;i++)
    B[i]=R1[i];
ludcmp(Z,N,indx,&*d);
lubksb(Z,N,indx,B);
for(i=1;i<4;i++)
    { dx[i]=B[i];
     y[i]=dx[i]+x[i];
     x[i]=y[i];
    }
count=0;
for(i=1;i<4;i++)
    { if(fabs(R1[i])<=error)
      count++;
    }
if(count>=2)
    break;
}while(1);
dh2o= A2*Ch2*x[3];
float fx;
double P1;
fx = xh2+0.35*xo2;
P1 = (3.11*T*exp((-8550)/T))/fx;
P1 = P1*1.01325e05;
const double diff=100.0;
if(dh2o>=0.0)
 { if((fabs(P1-P))<diff)
      { display();
       outfile.precision(3);
       outfile << T << P << endl;
      }
   }
}}infile.close( );
 outfile.close( );
}
void calc3( )
{
```

```
float Xh2=0.667, Xo2=0.333,phi;
xh2=phi*Xh2;
xo2=Xo2;
ifstream infile;
infile.open("KH23.dat");
ofstream outfile;
outfile.open("H3.dat");
for(i=1;i<12;i++)
  infile >> a[i] >> n[i] >> Ea[i];
cout<<setw(15)<<"PRESSURE"<<setw(15)<<"TEMPERATURE"<<endl;
q=&x[1];
for(T=500;T<=1000;T=T+20)
 { for(i=1;i<12;i++)
      K[i]=rate_const(a[i],n[i],Ea[i],T);
  for(P=20000;P<=300000;P=P+20000.0)
   { Ch2=concen(P,T,xh2);
     Co2=concen(P,T,xo2);
     A1=K[1]*Ch2*Co2;  A2=K[2]*Ch2;
     A3=K[3]*Co2;      A4=K[4]*Ch2;
     A5=K[5]*Co2*P;    A6=K[6];
     A7=K[7];          A8=K[8];
     A9=K[9];          A10=K[10];
     A11=K[11];
     x[1]=0.0005;  x[2]=0.0005;  x[3]=0.0003;
     x[4]=0.0001;  x[5]=0.0001;
     int num=0;
  do{
     f[1][1]= -(A5+A3+(A7*x[4])+(A11*x[5]));           f[1][2]= A4;
     f[1][3]= A2;         f[1][4]= -(A7*x[1]);
     f[1][5]= -(A11*x[1]);            f[2][1]= A3;        f[2][2]= -A4;
     f[2][3]= 0.0;        f[2][4]= -(A6*x[2]);            f[2][5]= 0.0;
     f[3][1]= A3;         f[3][2]= A4+(A6*x[4]);
     f[3][3]= -(A2+(A8*x[4])+(A10*x[5]));
     f[3][4]= (A6*x[2])-(A8*x[3]);   f[3][5]= -(A10*x[3]);
     f[4][1]= A5-(A7*x[4])+(A11*x[5]);
     f[4][2]= -(A6*x[4]);             f[4][3]= -(A8*x[4])+(A10*x[5]);
     f[4][4]= -((4*A9)+(A7*x[1])+(A8*x[3])+(A6*x[2]));
     f[4][5]= (A10*x[3])+(A11*x[1]);                f[5][1]= A11*x[5];
     f[5][2]= 0.0;        f[5][3]= A10*x[5];          f[5][4]= 2*A9*x[4];
     f[5][5]= (A10*x[3])+(A11*x[1]);
     R1[1]= -(-(A5+A3)*x[1]+A4*x[2]+A2*x[3]-A7*x[1]*x[4]-
            A11*x[1]*x[5]);
     R1[2]= -(A3*x[1]-A4*x[2]-A6*x[2]*x[4]);
     R1[3]= -(A1+A3*x[1]+A4*x[2]-A2*x[3]+A6*x[2]*x[4]
            -A8*x[3]*x[4]-A10*x[3]*x[5]);
```

```
                R1[4]= -(A5*x[1]-(A6*x[2]+A7*x[1]+A8*x[3]+A9*x[4])*x[4]
                        +(A10*x[3]+A11*x[1])*x[5]);
                R1[5]= -(A9*x[4]*x[4]+(A10*x[3]+A11*x[1])*x[5]);
                for(i=1;i<N;i++)
                for(j=1;j<N;j++)
                    Z[i][j]=f[i][j];
                for(i=1;i<N;i++)
                     B[i]=R1[i];
                ludcmp(Z,N,indx,&*d);
                 lubksb(Z,N,indx,B);
                for(i=1;i<N;i++)
                    { dx[i]=B[i];
                      y[i]=dx[i]+x[i];
                      x[i]=y[i];
                     }
                count=0;
                for(i=1;i<N;i++)
                  { if(fabs(R1[i])<=error)
                      count++;
                   }
                 if(count>=3)
                     break;
                 num++;
             }while(1);
                dh2o= A1+2*A3*Co2*x[1];
                if(dh2o<=0.0)
                 { display( );
                   outfile.precision(3);
                   outfile << T << P <<endl;
                  }
          }}infile.close( );
            outfile.close( );
  }
void check( )
  { if(limit==1)
        calc1( );
      else
       { if(limit==2)
             calc2( );
        else if(limit=3)
             calc3( );
        }
  }
float concen(double p,float t,float xi)
  { float Ci;
```

```
      Ci=(xi*p)/(R*t);
      return(Ci);
     }
   double rate_const(float a1,float m,float E,float t)
     { double ki;
      const float Rm=1.98567;
      ki= pow(10,a1)*pow(t,m)*exp(-E/(Rm*t));
      ki=ki*1.0e-06;   //ki Cm3/mol/sec  ->m3/mol/sec
      return(ki);
     }
 };
void main( )
{ hydrogen h;
 clrscr( );
 h.get( );
 h.check( );
 getch( );
}
```

PROGRAM FOR EXPLOSION LIMITS OF METHANE, ETHANE AND PROPANE OXIDATION

```
#include<string.h>
#include<fstream.h>
#include<stdlib.h>
#include<math.h>
#include<iomanip.h>
#include<conio.h>
#define N 15
#include"lud.cpp"
#define R 8314
#define error 0.001

void ludcmp(float Z[N][N],int n,int indx[N],float *d);
void lubksb(float Z[N][N],int n,int indx[N],float B[N]);
float *d;
int  n,indx[N];
float Z[N][N],B[N];

class hcarbon
 { private:
    double
A1,A2,A3,A4,A5,A6,A7,A8,A9,A10,A11,A12,A13,A14,A15,A16,A17,A18;
    float Cch4,Co2,Ch2o,Cc2h6,Cc3h8,a[20],n[20],Ea[20],T,KP;
    double K[20],P,dh2o,dco2;
    float dx[20];
    double f[20][20],R1[20];
    float x[20],y[20];
    int i,j,count;
    float xo2,xh2o;
    float Xo2,phi,xch4,xc2h6,xc3h8;
    char fuel[10];

  public:
    void get( )
       { cout << "ENTER THE FUEL(CH4 or C2H6 or C3H8):";
         cin >> fuel;
        cout << "ENTER THE EQUIVALENCE RATIO:";
         cin >> phi;
        }
    void display( )
        {
         cout.precision(3);
```

```
   cout<<setw(15)<<P<<setw(15)<<T<<endl;
   }
void methane( )
   { const float Xch4=0.333, Xo2=0.667;
    xch4=phi*Xch4;
    xo2=Xo2;
    ifstream infile;
    infile.open("KCH4.dat");
    ofstream outfile;
    outfile.open("M.dat");
    for(i=1;i<17;i++)
      infile >> a[i] >> n[i] >> Ea[i];
    for(T=500;T<=1000;T=T+20)
     { for(i=1;i<17;i++)
           K[i]=rate_const(a[i],n[i],Ea[i],T);
       for(P=1e05;P<=1e06;P=P+5e04)
        {
        Cch4= concen(P,T,xch4);
        Co2= concen(P,T,xo2);
        A1= K[1]*Cch4*Co2;          A2= K[2]*Co2;       A3= K[3]*Co2;
        A4= K[4]*Cch4;              A5= K[5];           A6= K[6];
        A7= K[7];                   A8= K[8];           A9= K[9];
        A10= K[10];                 A11= K[11];         A12= K[12]*Co2;
        A13= K[13];                 A14= K[14]*Cch4;
        A15= K[15]*Cch4;            A16= K[16]*Co2*P;
        x[1]=0.002;                 x[2]=0.01;          x[3]=0.001;
        x[4]=0.02;                  x[5]=0.0001;        x[6]=0.0001;
        x[7]=0.0001;                x[8]=0.001;         x[9]=0.001;
        int num=0;
    do{
       f[1][1]= -(A10*x[4]+A15);    f[1][2]= 0.0;  f[1][3]= A13*x[9];
       f[1][4]= -A10*x[1];          f[1][5]= 0.0;  f[1][6]= 0.0;
       f[1][7]= 0.0;                f[1][8]= 0.0;  f[1][9]= A13*x[3];
       f[2][1]= 0.0;                f[2][2]= -(A4+A8*x[6]+A9*x[4]);
       f[2][3]= 0.0;                f[2][4]= -A9*x[2];     f[2][5]= 0.0;
       f[2][6]= -(A8*x[2]);         f[2][7]= 0.0;          f[2][8]= A2;
       f[2][9]= 0.0;                f[3][1]= 2*A10*x[4];
       f[3][2]= (A4+A8*x[6]+A9*x[4]);
       f[3][3]= -(A6*x[8]+A7*x[6]+A11*x[4]+A13*x[9]+A14);
       f[3][4]= A5*x[8]+A9*x[2]+2*A10*x[1]-A11*x[3];
       f[3][5]= 0.0;                f[3][6]= -A7*x[3]+A8*x[2];
       f[3][7]= 0.0;                f[3][8]= A5*x[4]-A6*x[3];
       f[3][9]= -A13*x[3];          f[4][1]= -A10*x[4];    f[4][2]= -A9*x[4];
       f[4][3]= -A11*x[4];
       f[4][4]= -5*x[8]+A9*x[2]+A11*x[3]+A10*x[1]);
```

```
f[4][5]= A3;                      f[4][6]= 0.0;          f[4][7]= A12;
f[4][8]= -A5*x[4];                f[4][9]= 0.0;          f[5][1]= 0.0;
f[5][2]= 0.0;                     f[5][3]= 0.0;          f[5][4]= A5*x[8];
f[5][5]= -A3;                     f[5][6]= 0.0;          f[5][7]= 0.0;
f[5][8]= A2+A5*x[4];f[5][9]= 0.0;                        f[6][1]= 0.0;
f[6][2]= -A8*x[6];f[6][3]= A6*x[8]-A7*x[6];
f[6][4]= 0.0;        f[6][5]= A3;           f[6][6]= -(A7*x[3]+A8*x[2]);
f[6][7]= 0.0;        f[6][8]= A6*x[3];f[6][9]= 0.0;      f[7][1]= 0.0;
f[7][2]= A8*x[6];f[7][3]= A7*x[6];          f[7][4]= 0.0;  f[7][5]= 0.0;
f[7][6]= A7*x[3]+A8*x[2];                  f[7][7]= -A12; f[7][8]= 0.0;
f[7][9]= 0.0;        f[8][1]= A15; f[8][2]= A4;  f[8][3]= -A6*x[8]+A14;
f[8][4]= -A5*x[8];          f[8][5]= 0.0;          f[8][6]= 0.0;  f[8][7]= 0.0;
f[8][8]= -(A2+A5*x[4]+A6*x[3]);                    f[8][9]= 0.0;  f[9][1]= 0.0;
f[9][2]= 0.0;               f[9][3]= -A13*x[9];    f[9][4]= 0.0;  f[9][5]= 0.0;
f[9][6]= 0.0;        f[9][7]= A12;          f[9][8]= 0.0;  f[9][9]= -A13*x[3];
R1[1]= -(-(A10*x[4]*x[1])+(A13*x[9]*x[3])-(A15*x[1]));
R1[2]= -((A2*x[8])-(A4*x[2])-(A8*x[2]*x[6])-(A9*x[4]*x[2])+(2*A16));
R1[3]= -((A4*x[2])+(A5*x[8]+2*A10*x[1])*x[4]-((A6*x[8]+A7*x[6]
       +A11*x[4]+A13*x[9]+A14)*x[3])+(A8*x[6]-A9*x[4])*x[2]);
R1[4]= -(A1+A3*x[5]+A12*x[7]-(A5*x[8]+A9*x[2]+ A10*x[1]
          +A11*x[3])*x[4]);
R1[5]= -((A2+A5*x[4])*x[8]-A3*x[5]);
R1[6]= -(A6*x[8]*x[3]+A3*x[5]-(A7*x[3]+A8*x[2])*x[6]);
R1[7]= -(A7*x[3]*x[6]+A8*x[6]*x[2]-A12*x[7]);
R1[8]= -(A1-(A2+A5*x[4]+A6*x[3])*x[8]+A4*x[2]+A14*x[3]+A15*x[1]);
R1[9]= -(A12*x[7]-A13*x[9]*x[3]);
for(i=1;i<N;i++)
for(j=1;j<N;j++)
    Z[i][j]=f[i][j];
for(i=1;i<N;i++)
    B[i]=R1[i];
ludcmp(Z,N,indx,&*d);
lubksb(Z,N,indx,B);
for(i=1;i<N;i++)
    { dx[i]=B[i];
     y[i]=dx[i]+x[i];
     x[i]=y[i];
    }
count=0;
for(i=1;i<N;i++)
    { if(fabs(dx[i])<=error)
       count++;
    }
if(count>=4)
     break;
```

```
        num++;
       }while(1);
        dh2o= (A7*x[7]+A11*x[4]+A14)*x[3];
        dco2= A7*x[3]*x[9];
        if(dh2o>=0.0)
            {display( );
            outfile.precision(3);
            outfile << T << P <<endl;
            }
       }}infile.close( );
        outfile.close( );
  }
void check( )
  { if(!strcmp(fuel,"CH4")||!strcmp(fuel,"ch4"))
      methane( );
     else
       { if(!strcmp(fuel,"C2H6")||!strcmp(fuel,"c2h6"))
            ethane( );
        else if(!strcmp(fuel,"C3H8")||!strcmp(fuel,"c3h8"))
              propane( );
        }
  }
float concen(double p,float t,float xi)
 { float Ci;
  Ci=(xi*p)/(R*t);
  return(Ci);
 }
double rate_const(float a1,float m,float E,float t)
 { double ki;
  const float Rm=1.98567;
  ki= pow(10,a1)*pow(t,m)*exp(-E/(Rm*t));
  ki=ki*1.0e-06;   //ki Cm3/mol/sec  ->m3/mol/sec
  return(ki);
 }
void ethane( )
  {
  const float Xc2h6=(1/4.5),Xo2=(3.5/4.5);
  xc2h6=phi*Xc2h6;
  xo2=Xo2;
  ifstream infile;
  infile.open("KC2H6.dat");
  ofstream outfile;
  outfile.open("E.dat");
  for(i=1;i<15;i++)
      infile >> a[i] >> n[i] >> Ea[i];
```

```
for(T=500;T<=1000;T=T+20)
    { for(i=1;i<15;i++)
     K[i]=rate_const(a[i],n[i],Ea[i],T);
     for(P=25e5;P>=1e5;P=P-1e5)
      {
      Cc2h6= concen(P,T,xc2h6);
      Co2= concen(P,T,xo2);
      A1= K[1]*Cc2h6*Co2;     A2= K[2]*Co2*P;               A3= K[3];
      A4= K[4];               A5= K[5];                     A6= K[6]*Cc2h6;
      A7= K[7];               A8= K[8]*Co2;                 A9= K[9];
      A10= K[10];             A11= K[11];                   A12= K[12];
      A13= K[13];             A14=K[14];
      x[1]=1.0;   x[2]=1.0;   x[3]=1.0;    x[4]=1.0;
      x[5]=1.0;   x[6]=1.0;   x[7]=1.0;    x[8]=1.0;
      x[9]=1.0;   x[10]=1.0;  x[11]=1.0;   x[12]=1.0;
      int num=0;
    do{
     f[1][1]= -(A4*x[4]+A5*x[6]+A12*x[11]); f[1][2]= (A3*x[5]+A10*x[8]);
     f[1][3]= 0.0;           f[1][4]= -A4*x[1];     f[1][5]= A3*x[2];
     f[1][6]= -A5*x[1];  f[1][7]= 0.0;              f[1][8]= A10*x[2];    f[1][9]= 0.0;
     f[1][10]= 0.0;          f[1][11]= -A12*x[1];  f[1][12]= 0.0;
     f[2][1]= A4*x[4];     f[2][2]= -(A3*x[5]+A6+A10*x[8]+A13*x[11]);
     f[2][3]= 0.0;           f[2][4]= A4*x[1];      f[2][5]= -A3*x[2];    f[2][6]= 0.0;
     f[2][7]= 0.0;           f[2][8]= -A10*x[2];   f[2][9]= 0.0;
     f[2][10]= 0.0;          f[2][11]= -A13*x[2];  f[2][12]= 0.0;        f[3][1]= 0.0;
     f[3][2]= A6+A13*x[11];             f[3][3]= -(A9*x[9]+A11*x[10]+A14*x[12]);
     f[3][4]= 0.0;           f[3][5]= 0.0;          f[3][6]= 0.0;         f[3][7]= 0.0;
     f[3][8]= 0.0;           f[3][9]= -A9*x[3];     f[3][10]=-A11*x[3];
     f[3][11]= A13*x[2]; f[3][12]= -A14*x[3];  f[4][1]= -A4*x[4];     f[4][2]= 0.0;
     f[4][3]= 0.0;           f[4][4]= -A4*x[1];     f[4][5]= A8;          f[4][6]= 0.0;
     f[4][7]= 0.0;           f[4][8]= 0.0;          f[4][9]= 0.0;
     f[4][10]= 0.0;          f[4][11]= 0.0;         f[4][12]= 0.0;        f[5][1]= 0.0;
     f[5][2]= -A3*x[5]+A6;                          f[5][3]= 0.0;         f[5][4]= 0.0;
     f[5][5]= -(A3*x[2]+A8);                        f[5][6]= 0.0;         f[5][7]= 0.0;
     f[5][8]= 0.0;           f[5][9]= 0.0;          f[5][10]= 0.0;
     f[5][11]= 0.0;          f[5][12]= 0.0;         f[6][1]= -A5*x[6];
     f[6][2]= A3*x[5];     f[6][3]= 0.0;          f[6][4]= 0.0;
     f[6][5]= A3*x[2];     f[6][6]= -A5*x[1];     f[6][7]= 0.0;      f[6][8]= 0.0;
     f[6][9]= 0.0;           f[6][10]= 0.0;         f[6][11]= 0.0;     f[6][12]= 0.0;
     f[7][1]= A5*x[6];     f[7][2]= 0.0;          f[7][3]= 0.0;      f[7][4]= 0.0;
     f[7][5]= 0.0;           f[7][6]= A5*x[1];      f[7][7]= -A7;      f[7][8]= 0.0;
     f[7][9]= 0.0;           f[7][10]= 0.0;         f[7][11]= 0.0;     f[7][12]= 0.0;
     f[8][1]= 0.0;           f[8][2]= -A10*x[2];   f[8][3]= A9*x[9];
```

```
f[8][4]= 0.0;         f[8][5]= 0.0;          f[8][6]= 0.0;      f[8][7]= A7;
f[8][8]= -A10*x[2]; f[8][9]= A9*x[3];        f[8][10]= 0.0;    f[8][11]= 0.0;
f[8][12]= 0.0;        f[9][1]= 0.0;          f[9][2]= 0.0;      f[9][3]= -A9*x[9];
f[9][4]= 0.0;         f[9][5]= A8;           f[9][6]= 0.0;      f[9][7]= 0.0;
f[9][8]= 0.0;         f[9][9]= -A9*x[3];     f[9][10]= 0.0;     f[9][11]= 0.0;
f[9][12]= 0.0;        f[10][1]= 0.0;         f[10][2]= -A10*x[8];
f[10][3]= A9*x[9]-A11*x[10];                 f[10][4]= 0.0;     f[10][5]= 0.0;
f[10][6]= 0.0;        f[10][7]= 0.0;         f[10][8]= A10*x[2];
f[10][9]= A9*x[3];  f[10][10]= -A11*x[3]; f[10][11]= 0.0;  f[10][12]= 0.0;
f[11][1]= -A12*x[11];                         f[11][2]= -A13*x[11];
f[11][3]= A11*x[10];          f[11][4]= 0.0; f[11][5]= 0.0;  f[11][6]= 0.0;
f[11][7]= 0.0;        f[11][8]= 0.0;          f[11][9]= 0.0;
f[11][10]= A11*x[3]; f[11][11]= -(A12*x[1]+A13+x[2]);   f[11][12]= 0.0;
f[12][1]= A12*x[11]; f[12][2]= A13*x[11];  f[12][3]= -A14*x[12];
f[12][4]= 0.0;        f[12][5]= 0.0;         f[12][6]= 0.0;     f[12][7]= A7;
f[12][8]= 0.0;        f[12][9]= 0.0;         f[12][10]= 0.0;
f[12][11]= A12*x[1]+A13*x[2];                f[12][12]= -A14*x[3];
R1[1]= -((A3*x[5]+A10*x[8])*x[2]-(A4*x[4]+A5*x[6]+A12*x[11])*x[1]);
R1[2]= -(2*A2-(A3*x[5]+A6+A10*x[8]+A13*x[11])*x[2]+A4*x[1]*x[4]);
R1[3]= -((A6+A13*x[11])*x[2]-(A9*x[9]+A11*x[10]+A14*x[12])*x[3]);
R1[4]= -(A1-A4*x[1]*x[4]+A8*x[5]);
R1[5]= -(A1+A6*x[2]-(A3*x[2]+A8)*x[5]);
R1[6]= -(A3*x[2]*x[5]-A5*x[6]*x[1]);
R1[7]= -(A5*x[6]*x[1]-A7*x[7]);
R1[8]= -(A7*x[7]+A9*x[3]*x[9]-A10*x[2]*x[8]);
R1[9]= -(A8*x[5]-A9*x[9]*x[3]);
R1[10]= -(A10*x[2]*x[8]-(A11*x[10]-A9*x[9])*x[3]);
R1[11]= -(A11*x[10]*x[3]-(A12*x[1]+A13*x[2])*x[11]);
R1[12]= -(A7*x[7]+(A12*x[1]+A13*x[2])*x[11]-A14*x[12]*x[3]);
for(i=1;i<13;i++)
for(j=1;j<13;j++)
  Z[i][j]=(float)f[i][j];
for(i=1;i<13;i++)
  B[i]=(float)R1[i];
ludcmp(Z,N,indx,&*d);
lubksb(Z,N,indx,B);
for(i=1;i<13;i++)
  {  dx[i]=B[i];
     y[i]=dx[i]+x[i];
     x[i]=y[i];
  }
count=0;
for(i=1;i<13;i++)
 { if(fabs(dx[i])<=error)
      count++;
```

```
           }
         if(count>=10)
           break;
         num++;
        }while(1);
        dh2o= A4*x[1]*x[4]+A11*x[3]*x[10];
        dco2= A14*x[12]*x[3];
        if(dh2o>=0.0);
          { display( );
           outfile.precision(3);
           outfile << T << P <<endl;
           }
        }}infile.close( );
         outfile.close( );
 }
void propane( )
 {
        const float Xc3h8=(1/6.0),Xo2=(5/6.0);
        ifstream infile;
        infile.open("KC3H8.dat");
        ofstream outfile;
        outfile.open("P.dat");
        for(i=1;i<19;i++)
        infile >> a[i] >> n[i] >> Ea[i];
        for(T=500;T<=1000;T=T+20)
          { for(i=1;i<19;i++)
           K[i]=rate_const(a[i],n[i],Ea[i],T);
           for(P=1e6;P>=1e5;P=P-2e4)
            {
               Cc3h8= concen(P,T,xc3h8);
               Co2= concen(P,T,xo2);
               A1= K[1]*Cc3h8*Co2;         A2= K[2]*Co2*P;              A3= K[3];
               A4= K[4]*Cc3h8;             A5= K[5]*Co2;                A6= K[6];
               A7= K[7];                   A8= K[8]*Co2;                A9= K[9];
               A10= K[10];                 A11= K[11];                  A12= K[12];
               A13= K[13];                 A14=K[14];                   A15= K[15];
               A16= K[16];                 A17= K[17];                  A18= K[18];
               x[1]=0.5;      x[2]=1.0;    x[3]=.5;      x[4]=1.0;
               x[5]=0.1;      x[6]=0.1;    x[7]=0.1;     x[8]=0.1;
               x[9]=0.1;      x[10]=0.1;   x[11]=0.1;    x[12]=0.1;
               x[13]=0.1;     x[14]=0.1;
            do{
               f[1][1]= -(A10*x[4]+A11*x[9]+A16*x[13]);
               f[1][2]= (A9*x[7]+A15*x[12]);
```

```
f[1][3]= A18*x[14];   f[1][4]= -A10*x[1];   f[1][5]= 0.0;
f[1][6]= 0.0;                 f[1][7]= A9*x[2];       f[1][8]= 0.0;
f[1][9]= -A11*x[1];   f[1][10]= 0.0;                f[1][11]= 0.0;
f[1][12]= A15*x[2];   f[1][13]= -A16*x[1];
f[1][14]= A18*x[3];   f[2][1]= A10*x[4];
f[2][2]= -(A3*x[4]+A6*x[6]+A9*x[7]+A15*x[12]+A17*x[13]);
f[2][3]= 0.0;         f[2][4]= -A3*x[2]+A10*x[1];
f[2][5]= 0.0;         f[2][6]= -A6*x[2];    f[2][7]= -A9*x[2];
f[2][8]= 0.0;         f[2][9]= 0.0;         f[2][10]= 0.0;
f[2][11]= 0.0;        f[2][12]= -A15*x[2];
f[2][13]= -A17*x[2];  f[2][14]= 0.0;        f[3][1]= 0.0;
f[3][2]= A3*x[4]+A17*x[13];
f[3][3]= -(A4+A7*x[6]+A13*x[8]+A14*x[11]+A18*x[14]);
f[3][4]= A3*x[2];     f[3][5]= 0.0;         f[3][6]= -A7*x[3];
f[3][7]= 0.0;         f[3][8]= -A13*x[3];   f[3][9]= 0.0;
f[3][10]= 0.0;
f[3][11]= -A14*x[3];  f[3][12]= 0.0;        f[3][13]= A17*x[2];
f[3][14]= -A18*x[3];  f[4][1]= -A10*x[4];   f[4][2]= -A3*x[4];
f[4][3]= 0.0;         f[4][4]= -(A3*x[2]+A10*x[1]);
f[4][5]= A5;          f[4][6]= 0.0;         f[4][7]= A8;
f[4][8]= 0.0;         f[4][9]= 0.0;         f[4][10]= 0.0;
f[4][11]= 0.0;        f[4][12]= 0.0;        f[4][13]= 0.0;
f[4][14]= 0.0;
f[5][1]= 0.0;         f[5][2]= 0.0;         f[5][3]= A4;
f[5][4]= 0.0;         f[5][5]= -A5;         f[5][6]= 0.0;
f[5][7]= 0.0;         f[5][8]= 0.0;         f[5][9]= 0.0;
f[5][10]= 0.0;        f[5][11]= 0.0;        f[5][12]= 0.0;
f[5][13]= 0.0;        f[5][14]= 0.0;        f[6][1]= 0.0;
        f[6][2]= -A6*x[6];    f[6][3]= -A7*x[6];    f[6][4]= 0.0;
f[6][5]= A5;          f[6][6]= -(A6*x[2]+A7*x[3]);
f[6][7]= 0.0;         f[6][8]= 0.0;         f[6][9]= 0.0;
f[6][10]= 0.0;        f[6][11]= 0.0;        f[6][12]= 0.0;
f[6][13]= 0.0;        f[6][14]= 0.0;        f[7][1]= 0.0;
f[7][2]= -A9*x[2];    f[7][3]= A7*x[6];     f[7][4]= 0.0;
f[7][5]= 0.0;         f[7][6]= A7*x[3];     f[7][7]= -(A8+A9*x[2]);
f[7][8]= 0.0;         f[7][9]= 0.0;         f[7][10]= 0.0;
f[7][11]= 0.0;        f[7][12]= 0.0;
f[7][13]= 0.0;        f[7][14]= 0.0;        f[8][1]= 0.0;
f[8][2]= A6*x[6];     f[8][3]= -A13*x[8];   f[8][4]= 0.0;
f[8][5]= 0.0;         f[8][6]= A6*x[2];     f[8][7]= A8;
f[8][8]= -A13*x[3];   f[8][9]= 0.0;         f[8][10]= 0.0;
f[8][11]= 0.0;        f[8][12]= 0.0;        f[8][13]= 0.0;
f[8][14]= 0.0;        f[9][1]= -A11*x[9];   f[9][2]= A9*x[7];
f[9][3]= 0.0;         f[9][4]= 0.0;         f[9][5]= 0.0;
f[9][6]= 0.0;         f[9][7]= A9*x[2];     f[9][8]= 0.0;
```

```
f[9][9]= -A11*x[1];   f[9][10]= 0.0;          f[9][11]= 0.0;
f[9][12]= 0.0;        f[9][13]= 0.0;          f[9][14]= 0.0;
f[10][1]= A11*x[9];   f[10][2]= 0.0;          f[10][3]= 0.0;
f[10][4]= 0.0;        f[10][5]= 0.0;          f[10][6]= 0.0;
f[10][7]= 0.0;        f[10][8]= 0.0;
f[10][9]= A11*x[1];   f[10][10]= -A12;        f[10][11]= 0.0;
f[10][12]= 0.0;       f[10][13]= 0.0;         f[10][14]= 0.0;
f[11][1]= 0.0;        f[11][2]= A6*x[6]+A15*x[12];
f[11][3]= A13*x[8]+A7*x[6]-A14*x[11];  f[11][4]= 0.0;
f[11][5]= 0.0;        f[11][6]= A6*x[2]+A7*x[3];
f[11][7]= 0.0;        f[11][8]= A13*x[3];  f[11][9]= 0.0;
f[11][10]= 0.0;       f[11][11]= -A14*x[3];f[11][12]= A15*x[2];
f[11][13]= 0.0;       f[11][14]= 0.0;         f[12][1]= 0.0;
f[12][2]= -A15*x[12];f[12][3]= A13*x[8];  f[12][4]= 0.0;
f[12][5]= 0.0;        f[12][6]= 0.0;          f[12][7]= 0.0;
f[12][8]= A13*x[3];  f[12][9]= 0.0;          f[12][10]= A12;
f[12][11]= 0.0; f[12][12]= -A15*x[2];         f[12][13]= 0.0;
f[12][14]= 0.0;       f[13][1]= -A16*x[13];f[13][2]= -A17*x[13];
f[13][3]= A14*x[11];  f[13][4]= 0.0;          f[13][5]= 0.0;
f[13][6]= 0.0;        f[13][7]= 0.0;          f[13][8]= 0.0;
f[13][9]= 0.0;        f[13][10]= 0.0; f[13][11]= A14*x[3];
f[13][12]= 0.0;       f[13][13]= -(A16*x[1]+A17*x[2]);
f[13][14]= 0.0;       f[14][1]= A16*x[13];  f[14][2]= A17*x[13];
f[14][3]= -A18*x[14];f[14][4]= 0.0;          f[14][5]= 0.0;
f[14][6]= 0.0;        f[14][7]= 0.0;          f[14][8]= 0.0;
f[14][9]= 0.0;        f[14][10]= A12;         f[14][11]= 0.0;
f[14][12]= 0.0;       f[14][13]= A16*x[1]+A17*x[2];
f[14][14]= -A18*x[3];
R1[1]= -((A9*x[7]+A15*x[12])*x[2]-(A10*x[4]+A11*x[9]+
        A16*x[13])*x[1]+A18*x[3]*x[14]);
R1[2]= -(2*A2-A3*x[4]+A6*x[6]+A9*x[7]+A15*x[12]+
        A17*x[13])*x[2] +A10*x[1]*x[4]);
R1[3]= -((A3*x[4]+A17*x[13])*x[2]-(A4+A7*x[6]+A13*x[8]
        +A14*x[11] + A18*x[14])*x[3]);
R1[4]= -(A1+A5*x[5]+A8*x[7]-(A3*x[2]+A10*x[1])*x[4]);
R1[5]= -(A1+A4*x[3]-A5*x[5]);
R1[6]= -(A5*x[5]-(A6*x[2]+A7*x[3])*x[6]);
R1[7]= -(A7*x[3]*x[6]-(A8+A9*x[2])*x[7]);
R1[8]= -(A6*x[6]*x[2]+A8*x[7]-A13*x[8]*x[3]);
R1[9]= -(A9*x[7]*x[2]-A11*x[9]*x[1]);
R1[10]= -(A11*x[1]*x[9]-A12*x[10]);
R1[11]= -((A6*x[6]+A15*x[12])*x[2]+(A7*x[6]+A13*x[8]-
        A14*x[11])*x[3]);
R1[12]= -(A12*x[10]+A13*x[8]*x[3]-A15*x[12]*x[2]);
R1[13]= -(A14*x[11]*x[3]-(A16*x[1]+A17*x[2])*x[13]);
```

```
                R1[14]= -(A12*x[10]+(A16*x[1]+A17*x[2])*x[13]-A18*x[14]*x[3]);
                for(i=1;i<N;i++)
                for(j=1;j<N;j++)
                  Z[i][j]=f[i][j];
                for(i=1;i<N;i++)
                  B[i]=R1[i];
                ludcmp(Z,N,indx,&*d);
                lubksb(Z,N,indx,B);
                for(i=1;i<N;i++)
                  { dx[i]=B[i];
                    y[i]=dx[i]+x[i];
                    x[i]=y[i];
                  }
                count=0;
                for(i=1;i<N;i++)
                  { if(abs(R1[i])<=error)
                      count++;
                  }
            }while(1);
                dh2o= A4*x[3]+A10*x[4]*x[1]+A14*x[11]*x[3];
                dco2= A18*x[14]*x[3];
                if(dh2o>=0.0);
                  { display( );
                    outfile.precision(3);
                    outfile << T << P <<endl;
                  }
          }}infile.close( );
            outfile.close( );
        }
 };

void main( )
{ hcarbon w;
  clrscr( );
  w.get( );
  w.check( );
  getch( );
}
```

LUD.CPP

```
/*this program is to find the LU decomposition of matrix A and replaces the LU
components in the matrix A hence A gets destroyed*/


#define TINY 0.001

void ludcmp(float Z[N][N],int n,int indx[N],float *d)
{
 int i,imax,j,k;
 float big, dum, sum,temp;
 float vv[20];

 *d=1.0;

 for(i=1;i<n;i++){
   big=0.0;
   for(j=1;j<n;j++){
         if ((temp=fabs(Z[i][j]))>big) big=temp;}
         if (big==0.0) cout<<"Singular matrix in routine ludcmp\n";
         vv[i]=1.0/big;
 }

 for (j=1;j<n;j++){
  for (i=1;i<j;i++){
   sum=Z[i][j];
   for (k=1;k<i;k++) {sum -=Z[i][k]*Z[k][j];}
   Z[i][j]=sum;
  }
 big=0.0;
  for (i=j;i<n;i++){
   sum=Z[i][j];
   for (k=1;k<j;k++)
       sum -=Z[i][k]*Z[k][j];
   Z[i][j]=sum;
   if ((dum=vv[i]*fabs(sum)) >=big){
       big=dum;
       imax=i;
       }
 }
if(j!=imax){
 for(k=1;k<n;k++){
       dum=Z[imax][k];
       Z[imax][k]=Z[j][k];
```

```
         Z[j][k]=dum;
     }
     *d=-(*d);
     vv[imax]=vv[j];
   }
   indx[j]=imax;
  if (Z[j][j]==0.0)Z[j][j]=TINY;
  if(j!=n){
    dum=1.0/(Z[j][j]);
    for(i=j+1;i<n;i++) Z[i][j]*=dum;
  }
 }
 }
void  lubksb(float Z[N][N],int n,int indx[N],float B[N])
{
  int i,ii=0,ip,j;
  float sum;
  for(i=1;i<n;i++){
  ip=indx[i];
  sum=B[ip];
  B[ip]=B[i];
  if(ii)
  for(j=ii;j<=i-1;j++)
  sum -=Z[i][j]*B[j];
 else if(sum) ii=i;
  B[i]=sum;
  }
  for(i=n-1;i>=1;i--){
  sum=B[i];
  for(j=i+1;j<n;j++)
   sum -=Z[i][j]*B[j];
  B[i]=sum/Z[i][i];
 }
 }
```