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Reaction Pathways in High Temperature Combustion of Iso-octane

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Abstract-

This article presents the reaction pathways in high temperature combustion of wide range of hydrocarbon fuel Iso-octane. The activation energies of iso-octane are higher than n-octane. Hence iso-octane is widely used for combustion simulations. For this study a chemical kinetic scheme of iso-octane with 994 elementary reactions and 201 species has been developed and validated with LLNL (Lawrence Livermore National Laboratory) detailed mechanism with 3606 reactions and 857 species. A detailed study on the oxidation and soot formation has been conducted analytically using the reduced chemical mechanism with 994 reactions and 201 species. Species like CH, C2H, C2H2, C3H3, C3H4, C3H6, and C4H6 play a major role in the formation of soot as their decomposition leads to the production of radicals involved in the formation of Polycyclic Aromatic Hydrocarbon (PAH) and the further growth of soot particles. Temperature, pressure, fuel, O2 and OH concentration are also considered in soot formation process. It is also depending upon the nature of air fuel mixture (lean, stoichiometric or rich). A program has been developed in MATLAB for the calculation and prediction of the concentration of 201 intermediate species and the ignition delay in the combustion of Iso-octane. The various initial conditions considered was in between the temperatures of 600K to 1250K with pressure ranging from 10atm to 40atm at various equivalence ratios of 0.3 and 0.6. Nitrogen is considered as the diluent. The diluent percentage is assumed as 79% to make a comparison with atmospheric condition. The criteria for determination of ignition delay times are based on the OH concentrations to reach to a value of $1x10^{-9}$ moles/cc. The ignition delay times are obtained by varying initial conditions of the mixture in the combustion of Iso-octane. The results on ignition delays have been found to be agreeable with those available in the literature. Cantera (an object oriented software for reacting flows) software is used in this study.

Keywords- *Ignition delay,Reaction mechanism,Iso-octane*

The goal of present study is to establish the understanding of auto ignition in premixed combustion system and the understanding of the behavior of important species which are responsible for soot formation at various initial conditions. Mainly CH, C2H, C2H2, C3H3, C3H4, C3H6 and C4H6 etc are the important species responsible for soot formation. In addition to them temperature, pressure, O2, OH concentration, fuel mixture (lean, stoichiometric, rich) and the fuel structure plays a vital role in soot formation. By increasing the temperature the soot can be burnt out. But the problem is the formation of NOx. By increasing pressure the fuel breaks down in to molecular level hydrocarbons and radicals and they can easily oxidized, by both OH and O2 in lean mixture and soot formation. Soot is oxidized by OH under fuel-rich and stoichiometric conditions. Soot formation is more at fuel rich zone areas due to the incomplete burning process. Soot is roughly defined as a solid substance that consists of 8 parts of carbon and 1 part of hydrogen. Soot can be formed by 6 process viz. pyrolysis, nucleation, coalescence, surface growth, agglomeration and oxidation. The present study explores oxidation process which converts hydrocarbons to CO, CO2 and H2O.

As computational capacity improves numerical simulations are becoming more attractive for combustion studies. Comprehensive detailed kinetic mechanisms have been compiled to fully describe the fundamental chemical processes involved in fuel oxidation .For example, Curran et al. [1,2] have developed comprehensive mechanisms to study the oxidation of n-heptane and iso-octane. The former mechanism comprised of 560 species and 2539 reactions, while the latter contains 857 species and 3606 reactions. These mechanisms were tested by comparing computed results with various experimental data from laboratory devices, and a reasonably good agreement was reported between the predicted and the measured results, implying that the reaction mechanisms represent correctly the imported reaction pathways and rates of oxidation for these fuels.

With reaction mechanisms that consist of several hundred species and several thousand reactions, it is still much too costly to use a detailed chemical kinetic mechanism directly in engine combustion studies using multidimensional CFD codes. It is necessary to develop chemical reaction mechanisms that retain the essential features of the fuel chemistry predicted by comprehensive reaction mechanisms, but with much improved computational efficiency in terms of memory usage and CPU time. The extent of comprehensiveness depends on the available computational resources and the type of information desired from the simulation.

The basic aim of mechanism reduction is to identify unimportant species and reaction pathways in order to reduce the complexity of chemistry of mechanisms and important features of full schemes. Various methods have been suggested to determine the importance of species and reaction pathways in a mechanism.

Sensitivity analysis [3-4] is one of the earliest methods, which is simple to apply, but requires extensive post processing to provide decoupled information about the reactions and species. A reaction elimination method [5] was suggested to identity optimal sets of reactions under given constraints. But the optimization approach is asymptotically slower than sensitivity analysis. The method of detailed reduction [6] uses direct comparisons of reaction rates with preselected critical values in order to speed up the identification of unimportant reactions. However this method is likely to neglect important slower reactions that involve crucial radicals. Another technique to reduce the complexity of a chemical reaction mechanism is chemical lumping [7] which simplifies a mechanism by replacing a set of lumped pseudo species. This method is effective for reducing the number of species and still maintains the important features of full schemes when the importance of a single isomeric species is low but the reaction path via all isomers is significant.

Automation of reduction procedures has drawn much interest as well. Soyhan et al.[8] developed an automatic reduction technique to reduce a natural gas mechanism from 53 species and 589 reactions to 23 species and 20 global reactions. Montgomery et al. [9] used the CARM (computer aided reduction method) to automate the mechanism reduction process to generate a variety of reduced ethylene and n-heptane mechanism. More recently, the direct relation graph method [10] has been suggested and used to help automation of reduction procedures.

I. ISO-OCTANE

Iso-octane (2,2,4-trimethylpentane), a primary reference fuel for octane rating in spark ignition engines, has drawn considerable interest as a model compound for branched alkane components found particularly in gasoline [11], but also those found in diesel [12] and jet fuels [13]. Due to its relevance to practical liquid fuels, iso-octane has been the subject of many experimental and kinetic modeling studies. Experimental investigations of iso-octane oxidation and ignition have been carried out in shock tubes, rapid compression machine (RCMs), flames, jet stirred reactors and flow reactors.

II. INVESTIGATIONS

In building up a chemical kinetic model, a number of assumptions have to be made. In fact the assumptions are made so that the conditions simulated correspond to the conditions that are in effect in the experimental side.

A. Reaction Mechanism for iso-octane Oxidation

The complete reaction mechanism (994 reactions and 201species) which involve in the combustion of iso-octane is proposed & validated [14] with LLNL (Lawrence Livermore National Laboratory) detailed mechanism. There are 3606 reactions and 857 species. Figure.1. shows the validation of present mechanism with LLNL detailed mechanism.

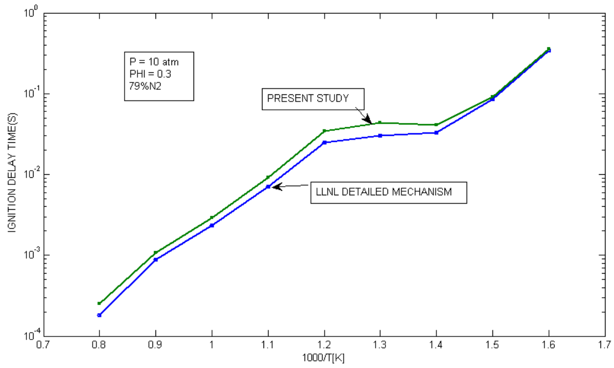

Fig 1: Validation of the reaction mechanism

B. Software

CANTERA object oriented software for reacting flows is used to simulate the results.

III.CRITERIA FOR FINDING IGNITION DELAY

Ignition delay time(t) is the time corresponding to the maximum rate of reactions between CO and O atoms. Induction period is the time at which the temperature had completed about half its total increase, often defined as the time required for a small(ie 1-5%) temperature or pressure rise. Bowman [15] found that ignition delay time to vary inversely with approximately the first power of the propane concentration, to be only slightly dependant upon oxygen concentration and to decrease with increasing pressure and temperature. It is the time to reach the concentration value of OH to $1x10^{-9}$ moles/cc .It is the time required to start the decomposition of H_2O_2.Figure.2 shows the criteria used for finding out the induction or ignition delay period.

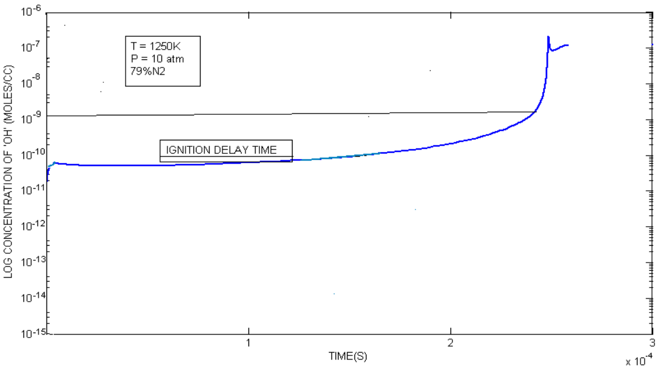

Fig 2: Ignition criteria.

IV.TEMPERATURE PROFILE

The temperature profile is shown in figure.3. The initial condition taken to plot this variation is temperature 1250K,pressure 10 atm and phi=0.3. From the graph it can be seen that the initial dip of temperature occurs. This is due to initiation reaction which are endo-thermic that initially dips and gradually rises until a region when the curve shoots up. These sets of reactions require a large amount of energy and the reactions are endothermic in nature. The heat that is required for the reaction to occur is extracted from the surrounding thus causing the temperature to dip. Once the reaction are complete, a fraction of fuel breaks down in to molecular weight hydrocarbons or the radicals, the temperature steadies on. Once the radicals are formed by the pyrolytic the propagation reaction starts. Initially the reaction proceeds slowly until the self ignition temperature is achieved. Once the temperature is attained, the ignition occurs. The fuel breaks down completely at this stage and the combustion progresses very fast. In the curve, it is the region at which the curve steeps down. The time between the initial time of input and this corresponding time gives the induction period, of course the chemical ignition delay. The curve steeps up and then maintains a particular value. After a while it can be observed that the temperature goes on reducing. This is due to the fact that at this stage there is no fuel to burn to energy. Hence temperature reduces.

The initial condition taken to plot this variation is temperature 1250K,pressure 10 atm and phi=0.3.we can see that at the point of ignition delay, there is a steep increase in temperature and pressure. Sufficient oxygen is not available to start spontaneous combustion at high equivalence ratio, which increases the ignition delay time.

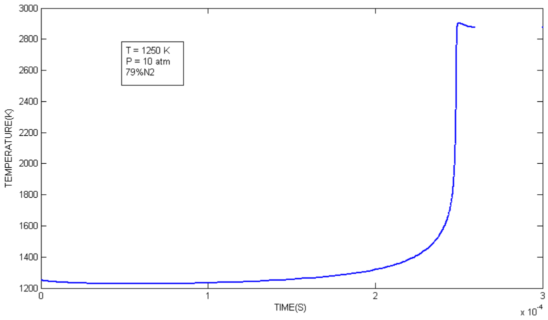

Fig.3. Temperature profile

V. VARIATION OF IGNITION DELAY WITH TEMPERATURE

The variation of ignition delay [16] with temperature is plotted on the figure.8&9 the ignition delay drops when temperature rises. This is so because as the pressure increases, density of fuel oxygen mixtures increases and hence the probability of fuel particle coming in contact with the reacting radicals also increases.

The variation of ignition delay [17] with temperature illustrated in figure.8&9 show that for higher temperature the ignition delay time is decreased. There is profound influence on ignition delay when the initial temperature is increased by 100K.

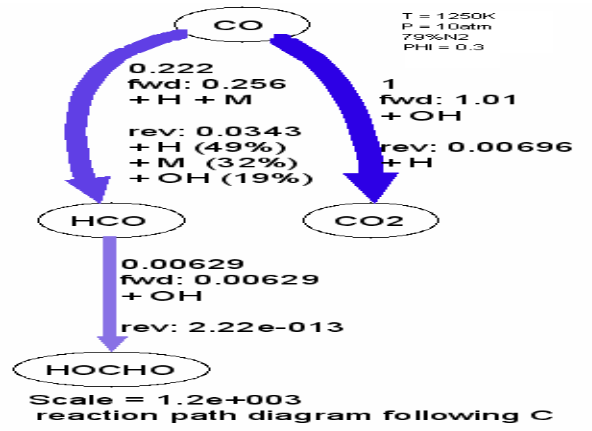

Fig.4.reaction path way of C

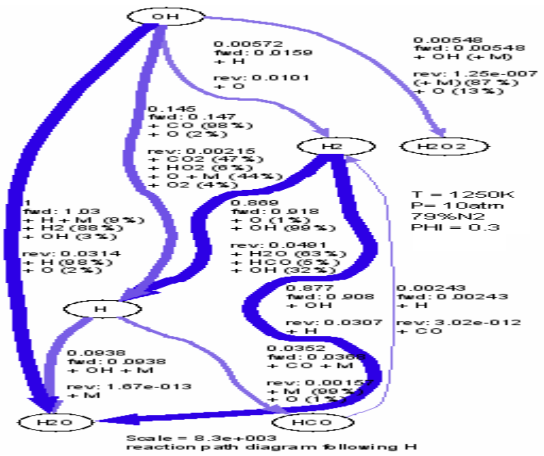

Fig.5. reaction path way of H.

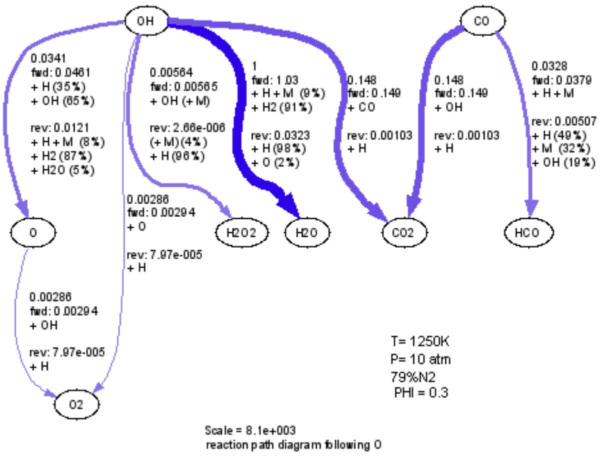

Fig.6.reaction path way of O

VI.SPECIES CONCENTRATION PROFILES

Concentration profiles of major species of C_8H_{18} are show in figure. 7. During the combustion of iso-octane at the point of ignition, the fuel curve steeps down. This proves that ignition has occurred and the fuel is being consumed very fast.

From the figure. 7. the consumption of O_2 is due the combustion of iso-octane, at the point of ignition. The concentration profile of H_2O_2 steeps down because it is also considered as the ignition citeria of iso-octane.

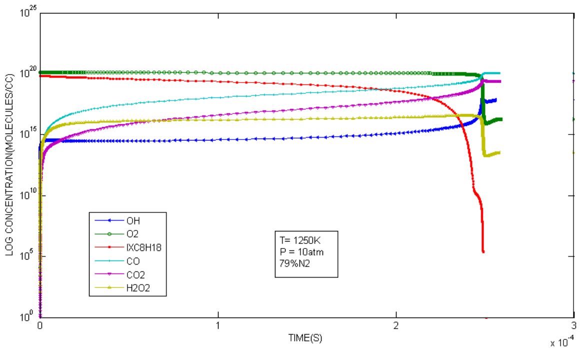

Fig.7 . Species concentration profile

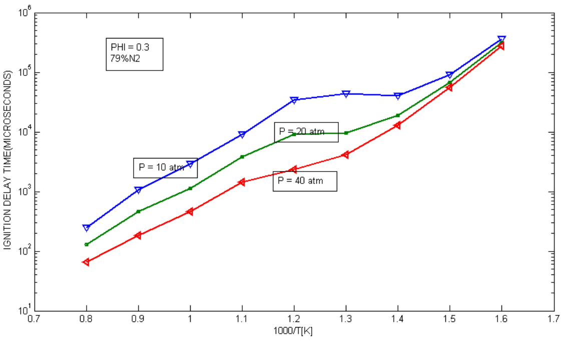

Fig.8 . Variation of ignition delay with temperature

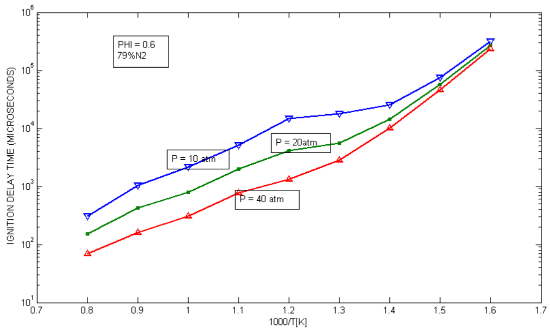

Fig.9. Variation of ignition delay with temperature

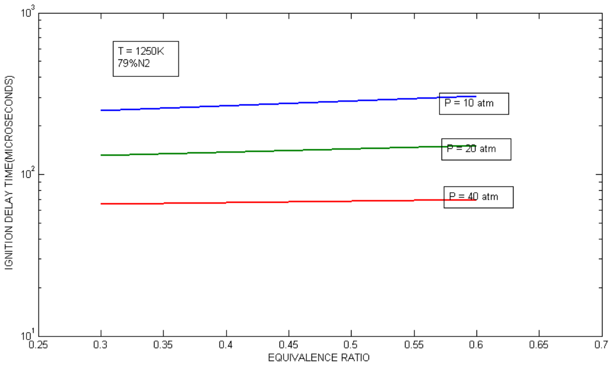

Fig.10.variation of ignition delay with equivalence ratio

VII. REACTION PATH WAYS

Figures.4,5&6 shows the reaction path ways of C,H&O Reaction path ways play an important role in determining the unimportant paths which is useful in reaction mechanism reduction.

VIII. SOOT FORMATION

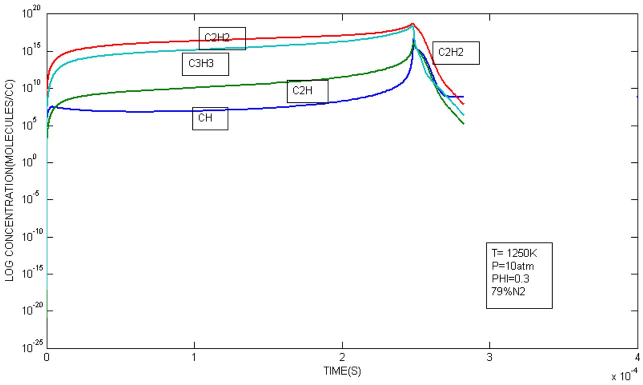

Fig.11.Species Concentration Profile

In the proposed reaction mechanism of 994 elementary reactions and 201 species for Iso-octane the important species which are responsible for formation of soot are plotted in the figure.11, it is observed that the the species C2H2 and C3H3 are very important in soot formation.

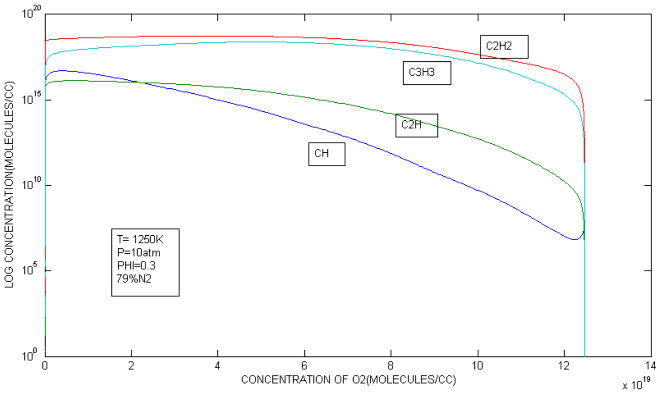

Fig.12. Variation with O2 (lean mixture)

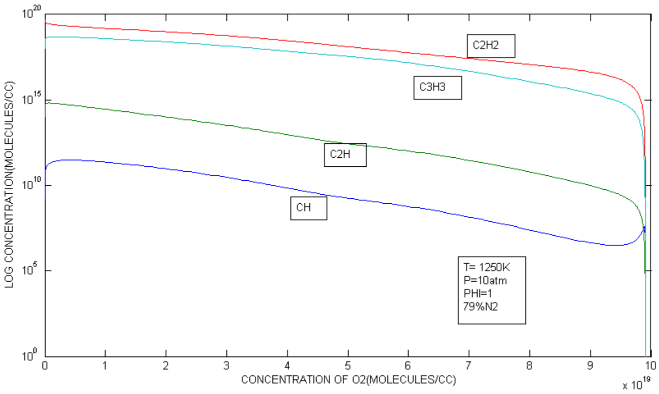

Fig.13. Variation with O2 (Stoichoimetric mixture)

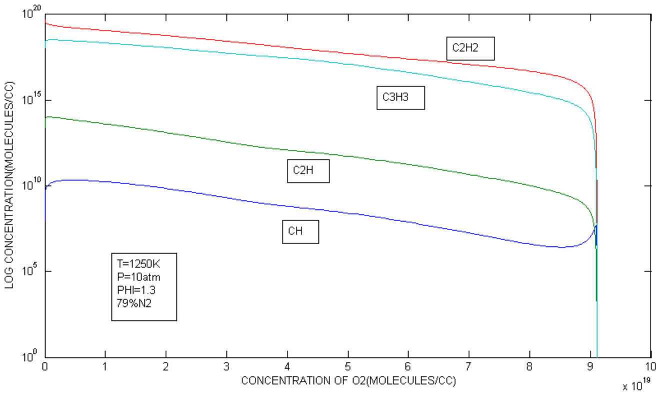

Fig.14. Variation with O2 (Rich mixture)

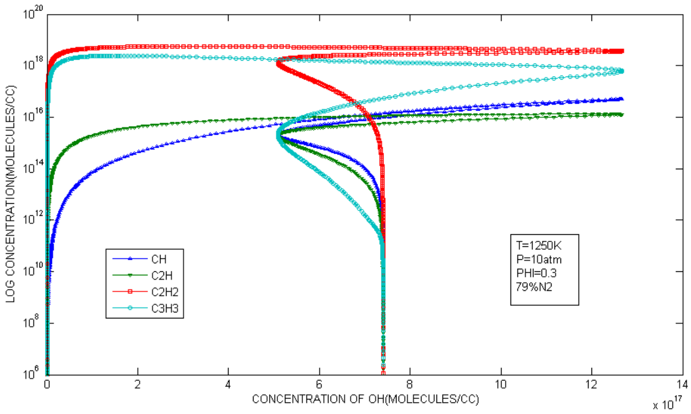

Fig.15. Variation with OH (lean mixture)

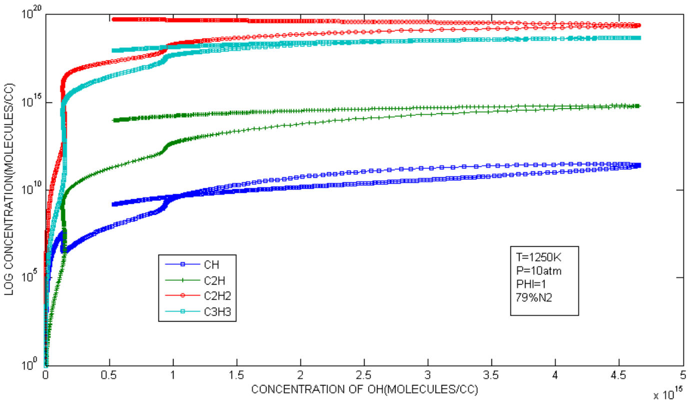

Fig.16. Variation with OH (Stoichoimetric mixture)

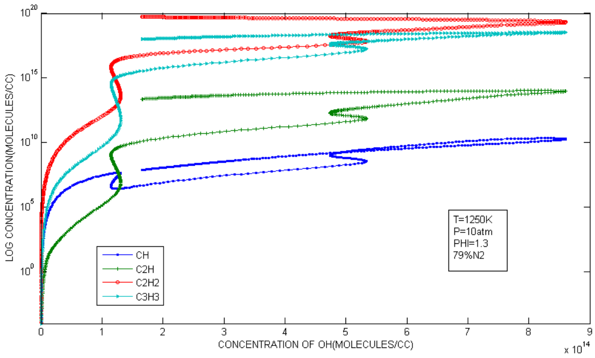

Fig.17. Variation with OH (Rich mixture)

From figures.12,13 and 14 it is observed that concentration level of O2 is maximum at lean mixture because O2 is consumed more for oxidation of soot. At stoichiometric and fuel rich conditions O2 has no role for soot oxidation as shown in figure 13.

At stoichiometric and fuel rich conditions OH radical are responsible for the oxidation of soot is plotted in Figure 16, 17. The concentration levels of OH radical are very high in stoichiomeric and fuel rich conditions as compared with lean mixture condition. Soot is formed by both OH and O2 at lean mixture condition.

Theoretically temperature becomes maximum at equivalence ratio of unity (stoichiometric fuel-air ratio) but using the proposed mechanism it is found that maximum temperature occurs at equivalence ratio of 1.2 as shown in Figure.18. Soot formation increases with equivalence ratio because when equivalence ratio increases fuel percentage in the mixture also increases, if sufficient oxygen is not available for oxidation process unburnt hydrocarbons are produced.

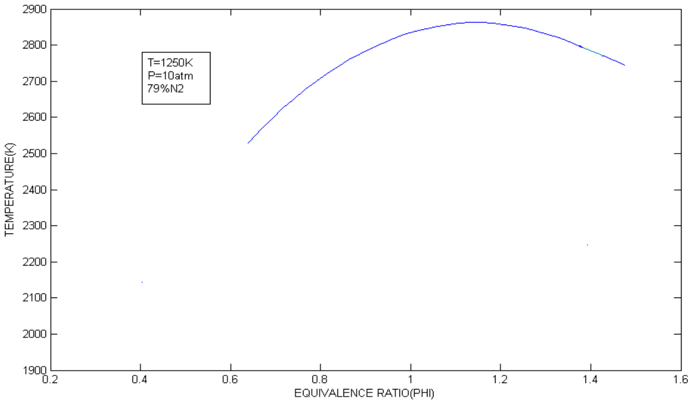

Fig.18.Variation of Temperature with Equivalence ratio

IX. RESULTS

Table 1 : 79%N2, P=10atm, Φ=0.3

Temperature(K)	Ignition Delay Time(μs)
1300	248.6
1100	1065.5
1000	2892.7
900	9093.2
800	3468.97
750	37718.6
700	40563.9
650	92108.4
600	360909.7

Table 2 : 79%N2, P=20atm, Φ=0.3

Temperature(K)	Ignition Delay Time(μs)
1300	130.9
1100	465.3
1000	1121.2
900	3804.9
800	9213.6
750	9585.5
700	18996.5
650	67803.9
600	313171.9

Table 3: 79%N2, P=40atm, Φ=0.3

Temperature(K)	Ignition Delay Time(μs)
1300	65.2
1100	186.3
1000	465.6
900	1452.2
800	1452.2
750	2377.7
700	4096.6
650	13004.9
600	278324.0

Table 4 : 79%N2, P=10atm, Φ=0.6

Temperature(K)	Ignition Delay Time(µs)
1300	305.4
1100	1048.3
1000	2188.8
900	5082.3
800	14904.0
750	18073.7
700	25334.7
650	74836.3
600	314074.4

Table 5 : 79%N2, P=20atm, Φ=0.6

Temperature(K)	Ignition Delay Time(µs)
1300	150.6
1100	426.1
1000	787.9
900	1998.0
800	4107.0
750	5619.9
700	14429.1
650	57178.1
600	270542.5

Table 6 : 79%N2, P=40atm, Φ=0.6

Temperature(K)	Ignition Delay Time(µs)
1300	70.2
1100	160.1
1000	309.7
900	768.7
800	1316.5
750	2869.2
700	10222.3
650	46080.8
600	232320.1

X. CONCLUSION

The analytical study on the reaction pathways in high temperature combustion of iso-octane has been conducted. A reaction mechanism containing 994 reactions among 201 species was proposed and the ignition delay times at various initial conditions of temperatures, pressures and equivalence ratio are determined. The condition used to determine the ignition delay is the time when OH concentration reaches $1x10^{-9}$ moles/cc .It is found that with increase in initial temperature and pressure during the combustion of Iso-octane, the ignition delay time and formation soot decreases. This is because at high pressure the fuel-air mixture density is increased which result in proper mixing in turn shortens ignition delay times and the formation of soot. With increase in equivalence ratio from lean to rich the ignition delay time and the formation of soot also increases. The reason behind this is when equivalence ratio is increased the fuel concentration in iso-octane is increased and oxygen concentration is reduced so that sufficient oxygen is not available for the combustion to take place quickly. Thus incomplete combustion occurs. In this study the species C2H2 and C3H3 is found to be the most important species for soot formation. A detailed study has been made in this range of temperatures, pressures and the equivalence ratio ranges from 0.3 to 0.6. From the results it is agreeable that for reducing CH emission low temperature, pressure very lean air fuel mixture is best suited. The results obtained are found to be agreeable with previous studies described herein.

REFERENCES

[1] H.J. Curran, P. Gauffuri, W.J. Pitz, C.K. Westbrook, Combust. Flame 114 (1998) 149–177.
[2] H.J. Curran, P. Gauffuri, W.J. Pitz, C.K. Westbrook, Combust. Flame 129 (2002) 253–280.
[3] T. Turanyi, J. Math. Chem. 5 (1990) 203–248.
[4] A.S. Tomlin, T. Turanyi, M.J. Pilling, Comprehensive Chemical Kinetics, Elsevier, Amsterdam, 1997, p. 293.
[5] B. Bhattacharjee, D.A. Schwer, P.I. Barton, W.H. Green, Combust. Flame 135 (2003) 191–208.
[6] H. Wang, M. Frenklach, Combust. Flame 87 (1991) 365–370.
[7] S.S. Ahmed, F. Mauß, G. Moréac, T. Zeuch, Phys. Chem. Chem. Phys. 9 (2007) 1107–1126.
[8] H.S. Soyhan, T. Løvås, F. Mauss, A stochastic simulation of an HCCI engine using an automatically reduced mechanism, ASME 2001-ICE-416, 2001.
[9] C.J. Montgomery, M.A. Cremer, J.Y. Chen, C.K.Westbrook, L.Q. Maurice, J. Propul. Power 18 (1) (2002) 192–198.
[10] T. Lu, C.K. Law, Combust. Flame 144 (2006) 24–36.
[11] W.J. Pitz, N.P. Cernansky, F.L. Dryer, F.N. Egolfopoulos, J.T. Farrell, D.G. Friend, H. Pitsch, SAE Paper 2007-01-0175, 2007.
[12] J.T. Farrell, N.P. Cernansky, F.L. Dryer, D.G. Friend, C.A. Hergart, C.K. Law, R. McDavid, C.J. Mueller, H.Pitsch, SAE Paper 2007-01-0201, 2007.
[13] M. Colket, J.T. Edwards, S. Williams, N.P. Cernan-sky, D.L. Miller, F.N. Egolfopoulos, P. Lindstedt, K.Seshadri, F.L. Dryer, C.K. Law, D.G. Friend, D.B. Lenhert, H. Pitsch, A. Sarofim, M. Smooke, W. Tsang, AIAA Paper AIAA-2007-0770, 2007.
[14] Hidaka et al-J Mol sci 2,141(1982)
[15] Seery D.J and Bowman, CT'' Ignition delays in several CH4-02-Ar mixtures'', combustion flame, 1970, 14-37.
[16] K A Bhaskaran and P.Roth,The shock tube as wave reactor for Kinetic studies progress in energy and combustion Science,28(2002) 151-192.
[17] E L Peterson,D F Davidson and R K Hanson, Kinetic modeling of shock induced induction in low dilution CH4/02 mixtures at high pressure and intermediate.