

Analysis of a Detailed Kinetic Model of Natural Gas Combustion in IC Engine

Mansha M.*, Saleemi A.R., Javed S.H., Nadeem Feroz

University of Engineering & Technology Lahore, Department of Chemical Engineering, Pakistan

*Corresponding Author: e-mail: muhammad_mansha@uet.edu.pk

Detailed kinetic models are important to describe the oxidation of hydrocarbon fuels. In the present study, a detailed kinetic models has been developed to simulate the combustion of natural gas in IC engine. The proposed models consists of 208 elementary reactions and 72 species. The rate of the production and sensitivity analysis of the proposed reaction models were carried out to visualize the effect of reactions on the formation of various pollutants. In the rate of production analysis, an absolute rate of production coefficients and the normalized rate of production coefficients were calculated for the reactions involved in the formation of pollutant species (CO, NO, NO₂, & NH₃). In sensitivity analysis, normalized logarithmic sensitivity coefficients were determined the reactions of rates affects the output concentrations of the pollutant species. These two analysis were carried out for two temperatures ranges i.e. 1500 °C and 4000 °C under stoichiometric conditions (when $\phi=1.0$).

Keywords: Sensitivity Analysis, models, Rate of Production Analysis.

INTRODUCTION

Combustion is a very complex phenomenon, characterized by interaction and competition of various physical and chemical processes. The correct description of chemical changes requires the application of reaction models consisting of several hundred or thousand reactions. Detailed combustion models are based on the measurements of the elementary gas phase reaction coefficients. The measurements have provided the temperature and pressure dependencies of the overoverall rate coefficient. The models of Warnatz¹⁻² have been used by many people, but were mainly created as illustrations in combustion modeling papers. Another widely used model is of Miller-Bowman NO model³ which, like the Warnatz model, is now out of-date in many respects. The GRI model is used for the study of the oxidation of methane. This model is based on elementary reactions, where the combinations of the experimental and theoretically determined values are assigned to the rate parameters⁴. Other combustion models are available over the Internet⁵. These models can be used to simulate the combustion methane in internal combustion engines⁶.

The kinetic models development and validation have been investigated by Mansha et al⁷. In the present study, a kinetic model has been developed to simulate the combustion of natural gas (used as CNG in automobile engines) and investigated using Rate of Production Analysis (ROP) and Local Sensitivity Analysis.

The sensitivity analysis methods for chemical kinetics have been reviewed by several researchers. For example; Rabitz et al focused mainly on the interpretation of sensitivity coefficients in reaction-diffusion systems⁸; Turanyi applied the sensitivity analysis methods as tools for investigating the reaction kinetics problems. These studies have an almost complete list of publications on the application of sensitivity analysis in reaction kinetics up to 1989⁹.

The studies on the numerical comparison of the methods for the calculation of local sensitivities have been published by Radhakrishnan¹⁰⁻¹¹. Tomlin *et al.* have considered sensitivity analysis as one of the mathematical

tools applied in combustion chemistry¹². Several publications on sensitivity analysis are available^{8,12-20}. The rate-of-production analysis helps to determine the contribution of each elementary reaction in the kinetic model to the net production or destruction rates of a species.

In the present work, a reaction kinetic model has been developed to simulate the natural gas combustion in IC engine predicting the formation pollutants species. The proposed model was analyzed by Sensitivity Analysis and Rate of Production analysis to identify the reactions involved in the formation of selected pollutants species such as CO, NO, NO₂ and NH₃.

MATERIAL AND METHODS

A detailed reaction model was developed by coupling (i) EXGAS hydrocarbon oxidation mechanism and (ii) Leeds NO_x model⁵. The strategy adopted in the coupling of two reaction models is shown in Figure 1. The coupling generated a model consisting of 935 reactions steps and 185 species. The EXGAS²¹ model consisted of; (a) C₀-C₁-C₂ reaction base, (b) primary reaction model in which the species in the initial gas mixture are taken as the reactants and (c) secondary model which contains the reactions whose reactants are the molecular products of the primary model. The comprehensive model was reduced by using the chemical lumping techniques. In this model reduction technique, the reactions having similar reactants and product species are omitted.

The types of reactions number of species/radicals are given in Table 1 and Table 2 respectively. This reduction of a resulted model composed of 208 reactions and 72 species as given in Table 3. Thermodynamic data (JANAF format) necessary in CHEMKIN is produced by THERGAS (built-in-module in EXGAS) automatically.

Chemkin 4.1.1 package was used for simulating the natural gas combustion using the proposed reaction model and to carry out the sensitivity analysis and the rate of production analysis. The rate of production analysis of the each kinetic model identified the reactions involved in the

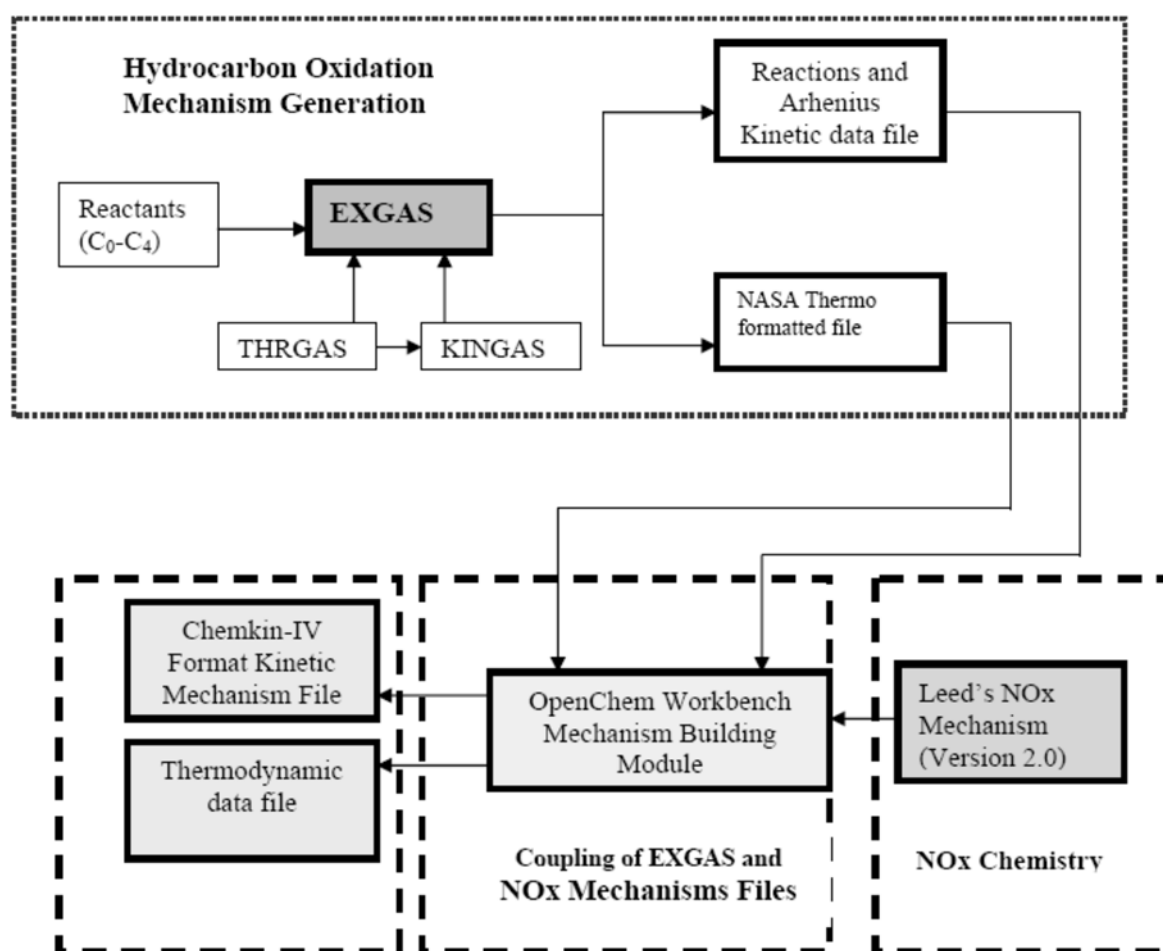


Figure 1. Reaction Mechanisms Coupling Schemes

Table 1. Menu Followed for Generation of Primary Models by EXGAS

Primary Reactions	Options chosen for mechanism generation	
	Yes/No	No. of Reactions
Unimolecular initiations	Yes	3
Bimolecular initiations	Yes	3
Additions with oxygen	No	0
Isomerizations	No	0
Beta-scissions	Yes	2
Decompositions to o-rings	No	2
Oxidations	Yes	2
Branching	No	0
Metatheses	Yes	26
Combinations	Yes	3
Dismutations	No	0
Number of Reactions in Lumped Primary Mechanism generated using EXGAS- I	44	
Number of Reactions in Leeds Mechanism (Version 2.0)- II	164	
Total Number of Reactions in Proposed Detailed Kinetic Mechanism (I+II)	208	

Table 2. No of Species in Proposed Detailed Kinetic Model

Sr. No	Type of Molecules and Radicals	No of Molecules and Radicals
1	Primary molecules	23
2	Free radicals	22
3	Lumped molecules	34
<i>Total Number of Species</i>		72

formation and consumption of major pollutants. In this analysis, the absolute rate of production (ROP) coefficient and the normalized rate of production coefficients were determined with selected simulation conditions of combustion (as given in Table 4 and Table 5).

Similarly, the normalized (logarithmic) sensitivity coefficients were calculated as defined by the equation (5) using the Local Sensitivity solver in the Chemkin package. The results were plotted by the sensitivity bar charts for CO, CO₂, NO, NO₂ and NH₃. The input keywords for the input parameters, solver and outputs for the rate of production and sensitivity analysis are given in Table 3.

RESULTS AND DISCUSSION

This automatically simplified model consists of 208 elementary reactions and 72 species. Mostly the reactions are of primary type including unimolecular initiations, bimolecular initiations, beta-scissions, oxidations, branching, metatheses and combinations.

The simulation study of natural gas combustion with a proposed kinetic model shows that the maximum peak temperature and pressure was achieved when equivalence ratio (Fuel/air) was ≈ 1.3 , compression ratio of ≈ 10.51 , engine speed of ≈ 3000 rpm and initial inlet temperature of ≈ 1000 °C. The cycle variation in the cylinder pressure and temperature is shown in Figure 2.

The rate of production analysis of the proposed model (Table 3) was carried out using the input variables as given in Table 4 to Table 6 to identify the reactions of the model contributing to the formation of gaseous pollutants (NO, NO₂, MH₃ and CO). The normalized rate of production coefficients of each reaction contributes to the formation of the pollutants. The total rate of production

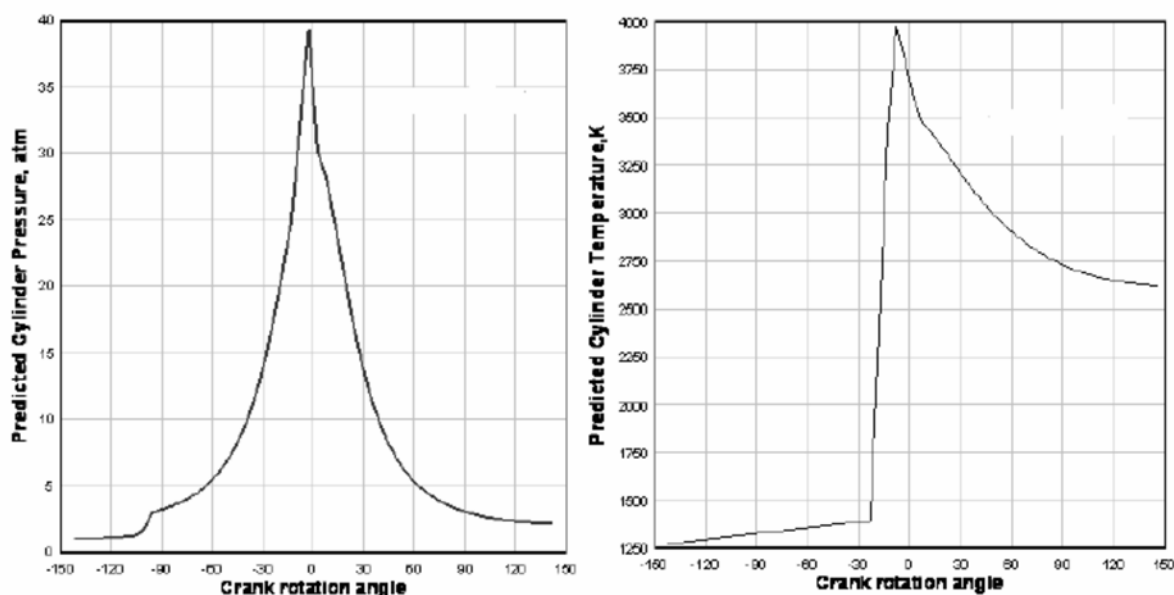
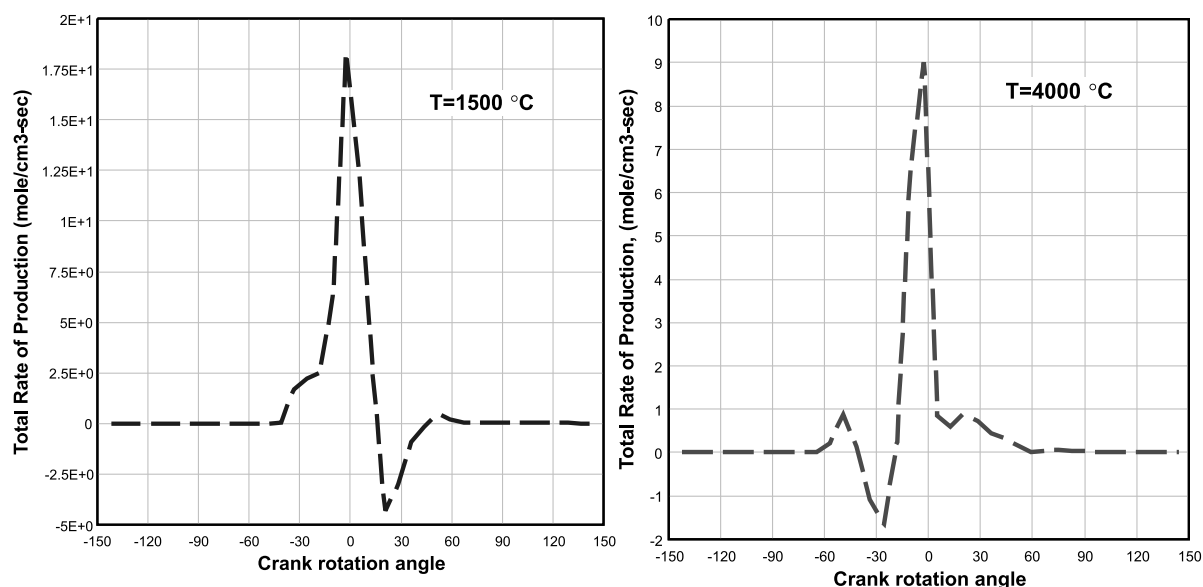
**Figure 2.** Predicted In-Cylinder Pressure (atm) and Temperature (K)**Figure 3.** Variation of rate of production of CO at extreme temperatures of T=1500 °C and T=4000 °C in IC engine for equivalence ratio ≈ 1.0

Table 3. Detailed Kinetic Reaction Model for Natural Gas Combustion in IC Engine

R-1	C3H8=>R4CH3+R11C2H5	9.40E+16	0	86903.5
R-2	C4H10=>R11C2H5+R11C2H5	2.20E+16	0	86135.6
R-3	C4H10=>R4CH3+R19C3H7	9.70E+16	0	88015.9
R-4	C3H8+O2=>R3OOH+R19C3H7	4.20E+13	0	54334.2
R-5	C4H10+O2=>R3OOH+R20C4H9	4.20E+13	0	54334.3
R-6	R19C3H7=>R4CH3+C2H4Z	2.00E+13	0	31000
R-7	R19C3H7=>R1H+C3H6Y	3.00E+13	0	38000
R-8	R20C4H9=>R11C2H5+C2H4Z	2.00E+13	0	28700
R-9	R20C4H9=>R1H+C4H8Y	3.00E+13	0	38000
R-10	R22C4H9=>R4CH3+C3H6Y	2.00E+13	0	31000
R-11	R19C3H7+O2=>C3H6Y+R3OOH	2.80E+12	0	5000
R-12	R20C4H9+O2=>C4H8Y+R3OOH	1.30E+12	0	5000
R-13	B1O+C3H8=>R2OH+R19C3H7	1.00E+14	0	7850
R-14	B1O+C4H10=>R2OH+R20C4H9	1.00E+14	0	7850
R-15	C3H8+R1H=>H2+R21C3H7	9.00E+06	2	5000
R-16	C4H10+R1H=>H2+R20C4H9	5.70E+07	2	7700
R-17	C3H8+R2OH=>H2O+R21C3H7	2.60E+06	2	-765
R-18	C4H10+R2OH=>H2O+R20C4H9	5.40E+06	2	450
R-19	C3H8+R3OOH=>H2O2+R21C3H7	4.00E+11	0	15500
R-20	C4H10+R3OOH=>H2O2+R20C4H9	1.20E+12	0	17000
R-21	C3H8+R4CH3=>CH4+R21C3H7	2.00E+11	0	9600
R-22	C4H10+R4CH3=>CH4+R20C4H9	6.00E-01	4	8200
R-23	C3H8+R5CHO=>HCHO+R21C3H7	1.00E+07	1.9	17000
R-24	C4H10+R5CHO=>HCHO+R20C4H9	2.00E+05	2.5	18500
R-25	C3H8+R6CH2OH=>CH3OH+R21C3H7	6.00E+01	3	12000
R-26	C4H10+R6CH2OH=>CH3OH+R20C4H9	2.00E+02	3	14000
R-27	C3H8+R7CH3O=>CH3OH+R21C3H7	1.50E+11	0	4500
R-28	C4H10+R7CH3O=>CH3OH+R20C4H9	3.20E+11	0	7300
R-29	C3H8+R8CH3OO=>CH3OOH+R21C3H7	3.00E+12	0	17500
R-30	C4H10+R8CH3OO=>CH3OOH+R20C4H9	1.20E+13	0	20000
R-31	C3H8+R11C2H5=>C2H6+R21C3H7	2.00E+11	0	11000
R-32	C4H10+R11C2H5=>C2H6+R20C4H9	6.00E+11	0	13500
R-33	C3H8+R21C3H7=>C3H8+R19C3H7	8.40E-03	4.2	8700
R-34	C4H10+R21C3H7=>C3H8+R22C4H9	5.60E-03	4.2	8000
R-35	R1H+R21C3H7=>C3H8	8.30E+12	0	0
R-36	R2OH+R21C3H7=>C3H7OH	5.90E+12	0	0
R-37	R3OOH+R21C3H7=>C3H7OOH	4.80E+12	0	0
R-38	R4CH3+R21C3H7=>C4H10	1.50E+13	0	0
R-39	R5CHO+R21C3H7=>C3H7CHO	5.20E+12	0	0
R-40	R6CH2OH+R21C3H7=>C4H9OH	5.10E+12	0	0
R-41	R7CH3O+R21C3H7=>C4H10O	4.90E+12	0	0
R-42	R8CH3OO+R21C3H7=>C4H10OO	4.40E+12	0	0
R-43	R11C2H5+R21C3H7=>C5H12	5.20E+12	0	0
R-44	R21C3H7+R21C3H7=>C6H14	2.30E+12	0	0
R-45	H2+CN=HCN+H	1.93E+04	2.9	6.8
R-46	CH4+N=NH+CH3	1.00E+13	0	100.4
R-47	CH4+CN=HCN+CH3	9.03E+04	2.6	-1.2
R-48	O2+N=NO+O	9.03E+09	1	27.2
R-49	O2+NH=HNO+O	3.91E+13	0	74.8
R-50	O2+NH=NO+OH	7.59E+10	0	6.4
R-51	O2+NH2=HNO+OH	1.51E+12	-0.4	151
R-52	O2+NH2=H2NO+O	1.10E+18	-1.3	140.6
R-53	O2+CN=NCO+O	7.23E+12	0	-1.7
R-54	O2+NCO=NO+CO2	1.72E+07	0	-3.1
R-55	CO+N2O=CO2+N2	9.77E+10	0	73
R-56	CO2+N=NO+CO	1.90E+11	0	14.2
R-57	N2+CH=HCN+N	1.57E+12	0	75.1
R-58	N2+CH2=HCN+NH	1.00E+13	0	309.6
R-59	NO+N2O=N2+NO2	1.00E+14	0	207.8
R-60	NO+N2H2=N2O+NH2	3.00E+12	0	0
R-61	NO+C=CN+O	1.93E+13	0	0
R-62	NO+C=CO+N	2.89E+13	0	0
R-63	NO+H=>N+OH	2.17E+14	0	207.1
R-64	N+OH=>NO+H	2.83E+13	0	0
R-65	NO+CH=CO+NH	1.20E+13	0	0
R-66	NO+CH=CN+OH	1.20E+13	0	0
R-67	NO+CH=HCN+O	9.60E+13	0	0
R-68	NO+CH2=HOCN+H	1.39E+12	0	-4.6
R-69	NO+CH2(S)=HCN+OH	9.64E+13	0	0
R-70	NO+CH3=HCN+H2O	9.28E+11	0	69.9
R-71	NO+CH3=H2CN+OH	9.28E+11	0	69.9
R-72	NO+HO2=NO2+OH	2.09E+12	0	-2
R-73	NO+HO2=HNO+O2	2.00E+11	0	8.3
R-74	NO+HCCO=HOCN+CO	2.00E+13	0	0
R-75	NO+N=>N2+O	4.28E+13	0	6.6
R-76	N2+O=>NO+N	1.81E+14	0	318.4
R-77	NO+NH=N2+OH	3.20E+13	0	53.2
R-78	NO+NH=N2O+H	4.16E+14	-0.5	0
R-79	NO+NH2=NNH+OH	2.41E+15	-1.2	0
R-80	NO+NH2=N2+H2O	5.48E+15	-1.2	0
R-81	NO+NNH=N2+HNO	5.00E+13	0	0
R-82	NO+HNO=N2O+OH	2.95E+05	0	0
R-83	NO+NCO=N2O+CO	1.39E+18	-1.7	3.2
R-84	NO+M=N+O+M	3.62E+15	0	620.6
R-85	NO2+NO2=NO+NO+O2	2.00E+12	0	112.2
R-86	NO2+H=NO+OH	3.47E+14	0	6.2
R-87	NO2+O=NO+O2	1.00E+13	0	2.5
R-88	NO2+N=NO+NO	8.07E+11	0	0
R-89	NO2+N=N2O+O	1.00E+12	0	0
R-90	NO2+NH=HNO+NO	1.00E+11	0.5	16.6
R-91	NO2+NH=N2O+OH	9.71E+12	0	0
R-92	NO2+NH2=N2O+H2O	2.03E+17	-1.7	0
R-93	NO2+CN=NCO+NO	3.00E+13	0	0
R-94	NO2+M=NO+O+M	3.13E+16	0	274.4
R-95	N2O+C=CN+NO	5.12E+12	0	0
R-96	N2O+H=N2+OH	4.37E+14	0	79
R-97	N2O+O=N2+O2	1.00E+14	0	117.2
R-98	N2O+O=NO+NO	6.92E+13	0	111.4
R-99	N2O+OH=N2+HO2	6.31E+11	0	41.6
R-100	N2O+N=N2+NO	1.00E+13	0	83.1
R-101	N2O+NH=HNO+N2	2.00E+12	0	24.9
R-102	N2O+CN=NCO+N2	1.00E+13	0	0
R-103	N2O+M=N2+O+M	2.86E+15	0	251
R-104	NH3+H=NH2+H2	5.42E+05	2.4	41.5
R-105	NH3+O=>NH2+OH	9.64E+12	0	30.5
R-106	NH3+OH=NH2+H2O	3.16E+12	0	8.4
R-107	NH3+HO2=NH2+H2O2	2.51E+12	0	99.8
R-108	NH3+NH2=N2H3+H2	7.94E+11	0.5	90.2
R-109	NH3(M)=NH2+H(M)	8.30E+15	0	458.7
R-110	NH3+M=NH+H2+M	1.80E+15	0	390.8
R-111	N2H2+H=NNH+H2	1.00E+13	0	4.2
R-112	N2H2+O=NH2+NO	1.00E+13	0	0
R-113	N2H2+O=NNH+OH	1.00E+11	0.5	0

R-114	N2H2+OH=NNH+H2O	1.00E+13	0	8.3
R-115	N2H2+NH=NNH+NH2	1.00E+13	0	4.2
R-116	N2H2+NH2=NH+N2H3	1.00E+11	0.5	141.3
R-117	N2H2+NH2=NH3+NNH	1.00E+13	0	16.6
R-118	N2H2+M=NNH+H+M	2.50E+16	0	207.8
R-119	N2H2+M=NH+NH+M	7.91E+16	0	415.7
R-120	C2N2+O=NCO+CN	1.29E+14	0	59.3
R-121	C2N2+OH=HOCN+CN	1.87E+11	0	12
R-122	HCN+O=NCO+H	8.45E+05	2.1	25.6
R-123	HCN+O=NH+CO	3.19E+05	2.1	25.6
R-124	HCN+O=CN+OH	2.22E+05	2.1	25.6
R-125	HCN+OH=CN+H2O	9.03E+12	0	44.9
R-126	HCN+OH=HOCN+H	5.85E+04	2.4	52.3
R-127	HCN+OH=HNCO+H	1.98E-03	4	4.2
R-128	HCN+CN=C2N2+H	3.80E+07	1.6	0.4
R-129	HOCN+H=H2O+CN	1.00E+12	0	0
R-130	HOCN+H=H2+NCO	1.00E+12	0	0
R-131	HOCN+H=HNCO+H	1.00E+13	0	0
R-132	HNCO+H=NCO+H2	2.05E+14	-0.3	84.7
R-133	HNCO+H=NH2+CO	1.10E+14	0	53.2
R-134	HNCO+O=NH+CO2	2.00E+13	0	54.5
R-135	HNCO+O=HNO+CO	1.90E+12	0	43.1
R-136	HNCO+O=OH+NCO	2.00E+14	0	96.4
R-137	HNCO+OH=NCO+H2O	1.99E+12	0	23.2
R-138	HNCO+OH=NH2+CO2	6.62E+11	0	23.2
R-139	HNCO+HO2=NCO+H2O2	3.00E+13	0	121.3
R-140	HNCO+N=NH+NCO	3.98E+13	0	149.7
R-141	HNCO+NH=NH2+NCO	3.00E+13	0	99.2
R-142	HNCO+NH2=NH3+NCO	1.00E+12	0	29.1
R-143	HNCO+M=NH+CO+M	2.40E+16	0	354.5
R-144	HNCO+M=H+NCO+M	2.86E+17	0	468.9
R-145	H+NH=N+H2	1.02E+13	0	0
R-146	H+NH2=NH+H2	6.02E+12	0	0
R-147	H+NNH=N2+H2	3.98E+13	0	12.5
R-148	H+N2H3=NH2+NH2	1.58E+12	0	0
R-149	H+N2H3=NH+NH3	1.00E+11	0	0
R-150	H+N2H3=N2H2+H2	1.00E+12	0	8.3
R-151	H+HNO=H2+NO	1.26E+13	0	16.6
R-152	H+NCO=NH+CO	5.24E+13	0	0
R-153	CH+N=CN+H	1.26E+13	0	0
R-154	CH+NH=HCN+H	5.00E+13	0	0
R-155	CH+NH2=HCN+H+H	3.00E+13	0	0
R-156	CH2+N=HCN+H	5.00E+13	0	0
R-157	CH2+NH=HCN+H+H	3.00E+13	0	0
R-158	CH3+N=H2CN+H	2.59E+14	0	3.5
R-159	C2H3+N=HCN+CH2	2.00E+13	0	0
R-160	H2CCCH+N=HCN+C2H2	1.00E+13	0	0
R-161	O+NH=N+OH	3.72E+13	0	0
R-162	O+NH=NO+H	5.50E+13	0	0
R-163	O+NH2=NH+OH	6.90E+11	0.3	-0.8
R-164	O+NH2=HNO+H	8.93E+14	-0.5	1.4
R-165	O+NNH=N2+OH	1.00E+13	0	20.8
R-166	O+NNH=N2O+H	1.00E+13	0	12.5
R-167	O+NNH=NH+NO	1.65E+14	-0.2	-4.2
R-168	O+HNO=OH+NO	5.01E+11	0.5	8.3
R-169	O+CN=CO+N	1.02E+13	0	0
R-170	O+NCO=NO+CO	3.16E+13	0	0
R-171	OH+NH=HNO+H	1.00E+12	0.5	8.3
R-172	OH+NH=N+H2O	5.01E+11	0.5	8.3
R-173	OH+NH2=>O+NH3	1.99E+10	0.4	2.1
R-174	OH+NH2=NH+H2O	5.01E+11	0.5	8.3
R-175	OH+NNH=N2+H2O	3.16E+13	0	0
R-176	OH+HNO=NO+H2O	1.08E+13	0	0
R-177	OH+CN=NCO+H	6.02E+13	0	0
R-178	OH+NCO=NO+HCO	5.00E+12	0	62.8
R-179	OH+NCO=NO+CO+H	1.00E+13	0	0
R-180	HO2+NH2=HNO+H2O	1.57E+13	0	0
R-181	HCCO+N=HCN+CO	5.00E+13	0	0
R-182	N+N+M=N2+M	6.52E+15	0	0
R-183	N+NH=N2+H	6.31E+11	0.5	0
R-184	N+NH2=N2+H+H	6.93E+13	0	0
R-185	N+NNH=NH+N2	3.16E+13	0	8.3
R-186	N+CN=>C+N2	1.81E+14	0	0
R-187	C+N2=>N+CN	5.24E+13	0	187.9
R-188	N+H2CN=N2+CH2	2.00E+13	0	0
R-189	N+NCO=NO+CN	2.77E+18	-1	72.2
R-190	N+NCO=N2+CO	1.99E+13	0	0
R-191	NH+NH=N2+H+H	5.13E+13	0	0
R-192	NH+NH2=N2H2+H	1.51E+15	-0.5	0
R-193	NH+NNH=N2+NH2	2.00E+11	0.5	8.3
R-194	NH+M=N+H+M	7.57E+14	0	315.9
R-195	NH2+NH2=N2H2+H2	3.98E+13	0	49.9
R-196	NH2+NH2=NH3+NH	5.00E+13	0	41.8
R-197	NH2+M=NH+H+M	7.91E+23	-2	382.4
R-198	NH2+NNH=N2+NH3	1.00E+13	0	0
R-199	NH2+HNO=NH3+NO	5.01E+11	0.5	4.2
R-200	NNH=N2+H	3.00E+08	0	0
R-201	NNH+M=N2+H+M	2.50E+13	0.5	12.8
R-202	NNH+O2=N2+HO2	5.00E+12	0	0
R-203	N2H3+M=N2H2+H+M	2.50E+16	0	207.8
R-204	N2H3+M=NH2+NH+M	2.50E+16	0	174.6
R-205	HNO+M=H+NO+M	5.09E+16	0	203.7
R-206	H2CN+M=HCN+H+M	7.50E+14	0	92
R-207	NCO+M=N+CO+M	2.91E+15	0	195.4
R-208	H2O+CH=CH2O+H	5.72E+12	0	-3.2

(net value of the absolute rate of production or consumption) of each selected pollutants during the engine cycle and plotted versus crank rotation angle as shown in Figure 3 to Figure 6 for CO, NO, NO₂ and NH₃, respectively.

The total rate of production (mole/cm³-sec) was calculated at two ranges of temperature of 1500°C and 4000 °C. The effect of temperature variation on the contribution of each reaction in emissions is clear (from the values of Normalized ROP coefficients) from the formation and consumption profiles (Figure 3 to 6) for each pollutant. The variation in the pattern of each profile of both of the temperature ranges is correlated with the reactions and

their contribution to the total rate of production. It is clear from each profile that the formation of each pollutant occurs during the combustion process after the compression stroke.

Table 4. Common Input Variables for Rate of Production Analysis and Sensitivity Analysis (Local) of Kinetic Models

Sr. No	Operating Parameter	Value
1	Equivalence Ratio (F/A)	1.0
2	Initial Inlet Temperature	1500 °C & 4000 °C
3	Initial Inlet Pressure	1.0 atm
4	Engine Speed	3000 rpm
5	Starting Crank Angle	-142°

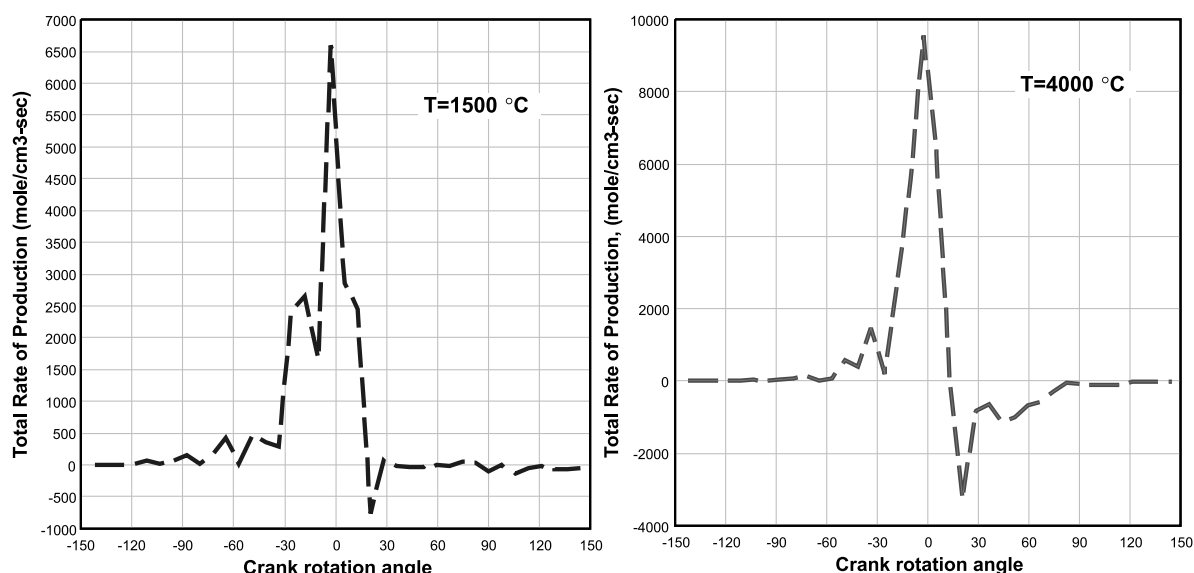


Figure 4. Variation of rate of production of NO at extreme temperatures of $T=1500\text{ }^{\circ}\text{C}$ and $T=4000\text{ }^{\circ}\text{C}$ in IC engine for equivalence ratio ≈ 1.0

Table 5. Typical Engine Geometrical Input Parameters and Gas Mixture Composition

Sr. No	Engine Geometrical Input Parameters		Initial Gas Mixture (CNG composition), Mole Fraction	
	Parameter (unit)	Value	Component	Mole Fraction
1	Cylinder volume (cm^3)	63	Methane (CH_4)	0.8903
2	Displaced Volume (cm^3)	56.52	Ethane (C_2H_6)	0.0105
3	Clearance Volume (cm^3)	6.48	Propane (C_3H_8)	0.027
4	Cylinder Diameters (cm)	14.67	Butane (C_4H_{10})	0.0017
5	Crank to Connecting rod ratio	1.632	Nitrogen (N_2)	0.072
6	Combustion Starting Crank Angle	-142°	Carbon Dioxide (CO_2)	0.026

Table 7 shows the reactions involved in the formation or consumption of each pollutant at $1500\text{ }^{\circ}\text{C}$ and $4000\text{ }^{\circ}\text{C}$ and their normalized rate of production coefficients and the absolute rate of production coefficients. In the last column of Table 6 the reference number of the reaction

designated in the model shows. According to the data, it is predicted that the reaction $\text{HNCO} + \text{M} \rightleftharpoons \text{NH} + \text{CO} + \text{M}$ (0.98) significantly contributes to the formation of CO at $1500\text{ }^{\circ}\text{C}$ and the reaction $\text{NCO} + \text{M} \rightleftharpoons \text{N} + \text{CO} + \text{M}$ (0.907) produces more CO at $4000\text{ }^{\circ}\text{C}$. Similarly nitric oxide (NO) is formed from reactions $\text{NO} + \text{M} \rightleftharpoons \text{N} + \text{O} + \text{M}$ (0.905) and $\text{N} + \text{OH} \rightleftharpoons \text{NO} + \text{H}$ (0.712) of the model at $1500\text{ }^{\circ}\text{C}$ and $4000\text{ }^{\circ}\text{C}$, respectively in the IC engine simulated under the given conditions. The only reaction $\text{NO}_2 + \text{H} \rightleftharpoons \text{NO} + \text{OH}$ take part in the formation of other important component of NO_x at $1500\text{ }^{\circ}\text{C}$ and $4000\text{ }^{\circ}\text{C}$.

When the local sensitivity analysis of this automatically simplified kinetic model (Table 3) was carried out, we were able to identify that the reactions of the rates have influence on the formation of gaseous pollutants including nitrogen, containing compounds (NO , NO_2 and NH_3)

Table 6. Key words Input for Rate of Production and Sensitivity Analysis of Kinetic Mechanisms

For Rate of Production Analysis	For Local Sensitivity Analysis
ICEN ! Internal Combustion Engine	ICEN ! Internal Combustion Engine
TRAN ! Transient Solver	TRAN ! Transient Solver
EQUI 1.0 ! Equivalence Ratio	EQUI 1.0 ! Equivalence Ratio
PRES 2.24551668 ! Pressure (atm)	PRES 2.24551668 ! Pressure (atm)
TEMP 1573.15 ! Temperature (K)	TEMP 1573.15 ! Temperature (K)
CMPR 10.51 ! Engine Compression Ratio	CMPR 10.51 ! Engine Compression Ratio
DEG0 -142.0 ! Starting Crank Angle (degrees)	DEG0 -142.0 ! Starting Crank Angle (degrees)
LOLR 1.632 ! Engine Connecting Rod to Crank Radius Ratio	LOLR 1.632 ! Engine Connecting Rod to Crank Radius Ratio
RPM 2000.0 ! Engine Speed (rpm)	RPM 2000.0 ! Engine Speed (rpm)
VOLD 63.0 ! Engine Cylinder	VOLD 63.0 ! Engine Cylinder
Displacement Volume (cm^3)	Displacement Volume (cm^3)
CPROD CO2 ! Complete-Combustion Products	CPROD CO2 ! Complete-Combustion Products
CPROD H2O ! Complete-Combustion Products	CPROD H2O ! Complete-Combustion Products
CPROD N2 ! Complete-Combustion Products	CPROD N2 ! Complete-Combustion Products
SDIR ! Staggered Direct Method	TIME 0.043 ! End Time (sec)
	DELT 0.01 ! Time Interval for Printing (sec)
	LSEN ! Local Sensitivity Method
	ASEN CO ! A-factor Sensitivity
	ASEN CO2 ! A-factor Sensitivity
	ASEN H2O ! A-factor Sensitivity
	ASEN NO ! A-factor Sensitivity
	ASEN NO2 ! A-factor
	END

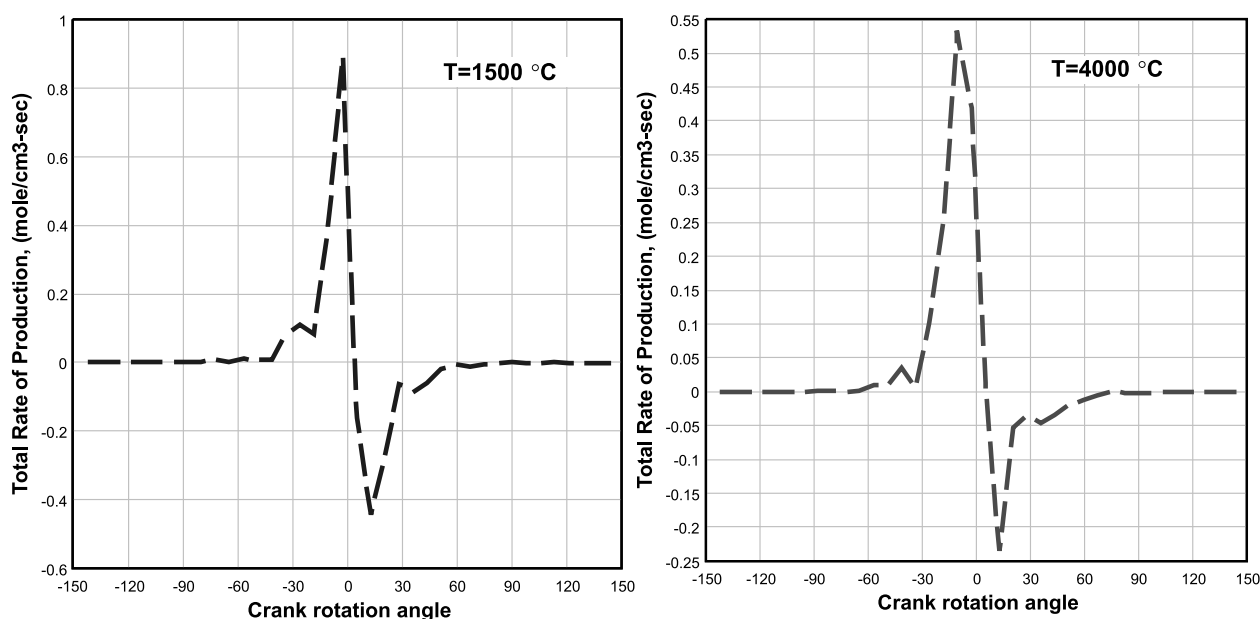


Figure 5. Variation of rate of production of NO_2 at extreme temperatures of $T=1500\text{ }^\circ\text{C}$ and $T=4000\text{ }^\circ\text{C}$ in IC engine for equivalence ratio ≈ 1.0

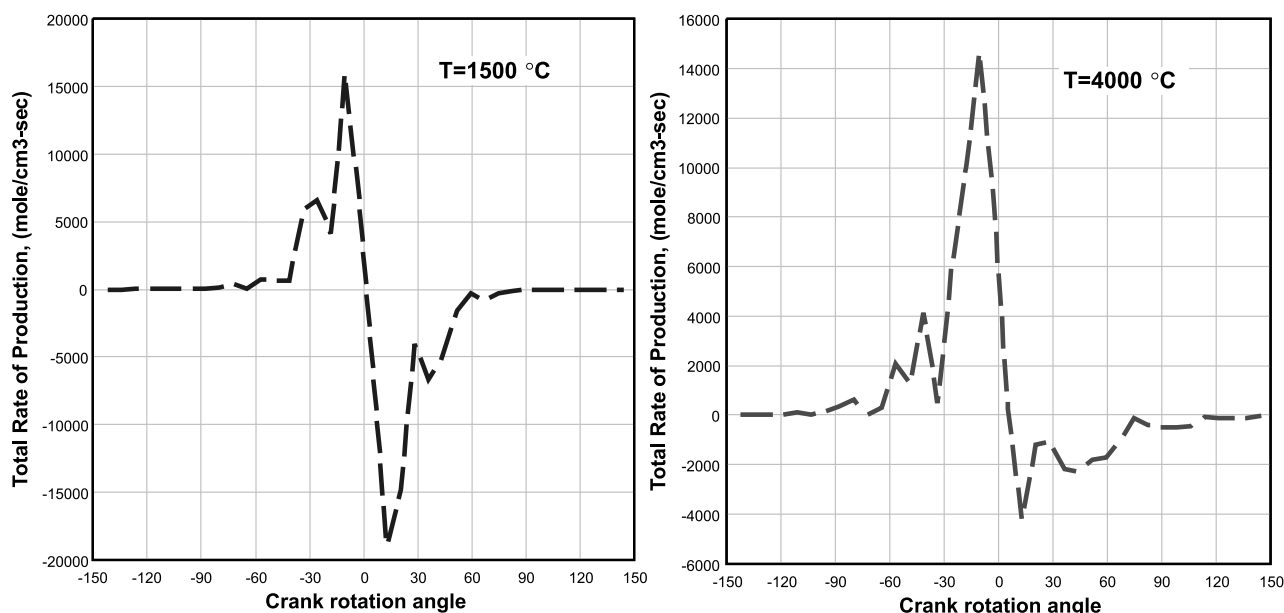


Figure 6. Variation of rate of production of NH_3 at extreme temperatures of $T=1500\text{ }^\circ\text{C}$ and $T=4000\text{ }^\circ\text{C}$ in IC engine for equivalence ratio ≈ 1.0

and carbon oxides (CO & CO_2). The sensitivity bar-plot for each of the said pollutants is shown in Figure 7 to 11 respectively for CO , CO_2 , NO , NO_2 and NH_3 . In these plots, normalized logarithmic sensitivity coefficients were calculated at the condition mentioned for the each of the reaction step.

In Figure 7, the sensitivity of CO concentrations towards some important reaction rates is shown. This plot illustrates that the dominant reactions are $\text{O}_2 + \text{N} \rightleftharpoons \text{NO} + \text{O}$ and $\text{O}_2 + \text{CN} \rightleftharpoons \text{NCO} + \text{O}$ for the formation of carbon monoxide in the combustion chamber of IC engine at $1500\text{ }^\circ\text{C}$ and $4000\text{ }^\circ\text{C}$. These reactions show positive sensitivity in the forwards direction. Similarly, the CO_2 sensitivity bar-plot predicts that sensitivity of CO_2 concentrations (Figure 8) are greatly affected by the reactions at the;

AT $T=1500\text{ }^\circ\text{C}$;



And at $T=4000\text{ }^\circ\text{C}$



From the NO and NO_2 sensitivity bar-plots (Figure 9 & Figure 10), it is predicted that NO & NO_2 concentrations are dominantly affected by the rates of the following reactions at $1500\text{ }^\circ\text{C}$ and $4000\text{ }^\circ\text{C}$;

– For Nitric Oxide (NO); the important reactions are; $\text{N} + \text{OH} \rightleftharpoons \text{NO} + \text{H}$ (R-62) and $\text{N}_2 + \text{O} \rightleftharpoons \text{NO} + \text{N}$ (R-74) which greatly affects the NO concentrations.

– For Nitric Oxide (NO_2); the NO_2 concentrations show sensitivity towards the following reaction; $\text{N} + \text{OH} \rightleftharpoons \text{NO} + \text{H}$ (R-62) $\text{CH}_4 + \text{CN} \rightleftharpoons \text{HCN} + \text{CH}_3$ (R-45) and $\text{NO}_2 + \text{H} \rightleftharpoons \text{NO} + \text{OH}$ (R-84) at $1500\text{ }^\circ\text{C}$ and $\text{N} + \text{OH} \rightleftharpoons \text{NO} + \text{H}$ (R-62), $\text{NO}_2 + \text{H} \rightleftharpoons \text{NO} + \text{OH}$ (R-84) and $\text{NO} + \text{NH} \rightleftharpoons \text{N}_2\text{O} + \text{H}$ (R-75) at $4000\text{ }^\circ\text{C}$ during the combustion of natural gas in IC engine.

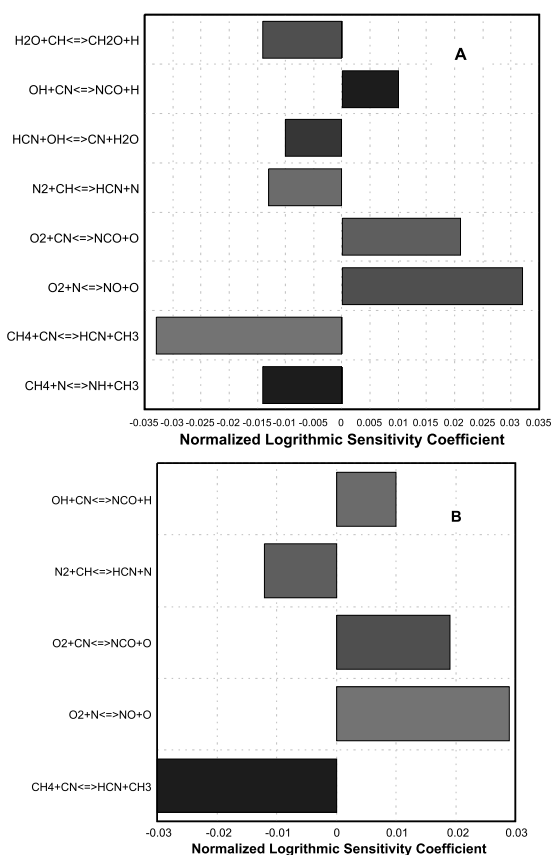


Figure 7. CO sensitivity bar plot for natural gas combustion with proposed kinetic model in IC engine at equivalence ratio =1.0 when (A) $T=1500\text{ }^{\circ}\text{C}$ and (B) $T=4000\text{ }^{\circ}\text{C}$

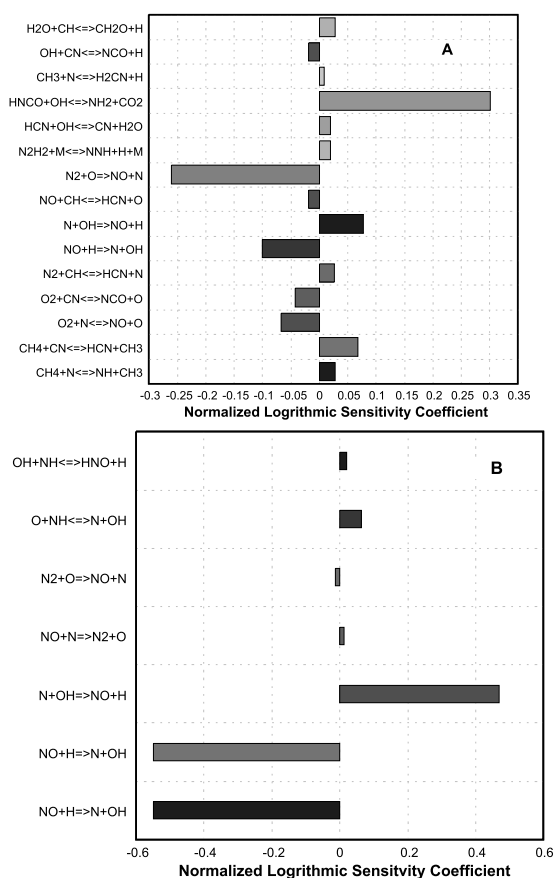


Figure 8. CO_2 sensitivity bar plot for natural gas combustion with proposed kinetic model in IC engine at equivalence ratio =1.0 when (A) $T=1500\text{ }^{\circ}\text{C}$ and (B) $T=4000\text{ }^{\circ}\text{C}$

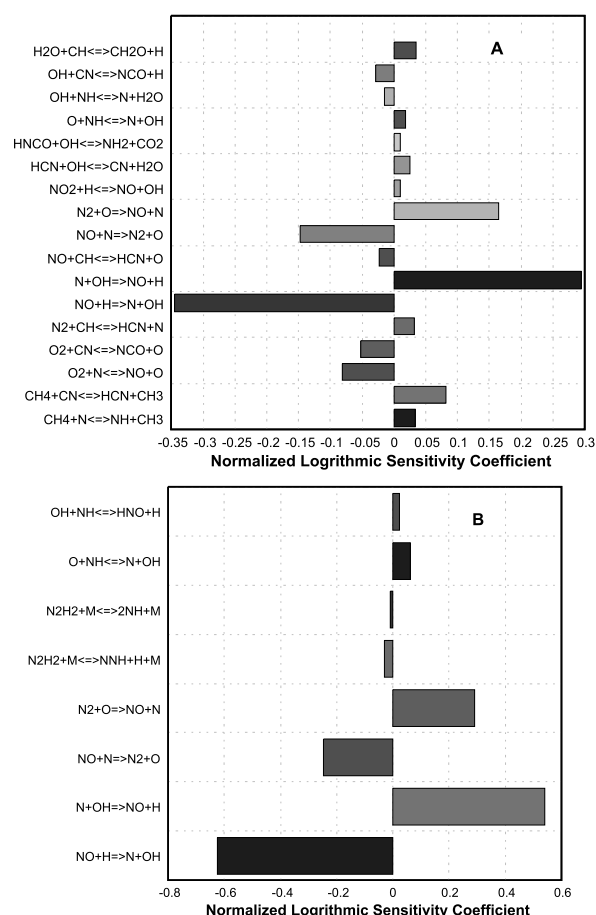


Figure 9. NO sensitivity bar Plot for natural gas combustion with proposed kinetic model in IC engine at equivalence ratio =1.0 when (A) $T=1500\text{ }^{\circ}\text{C}$ and (B) $T=4000\text{ }^{\circ}\text{C}$

Similarly, in Figure 11 sensitivity of NH_3 concentrations towards the most important reactions are shown at temperature of $1500\text{ }^{\circ}\text{C}$ and $4000\text{ }^{\circ}\text{C}$. This sensitivity bar-plot shows that $N_2 + O \rightleftharpoons NO + N$, $N + OH \rightleftharpoons NO + H$ and $O_2 + N \rightleftharpoons NO + O$

CONCLUSION

The rate of production analysis and sensitivity analysis of the proposed reaction model was carried out using Chemkin 4.1.1. The two analyses were carried out for stoichiometric conditions ($\phi=1.0$) at $1500\text{ }^{\circ}\text{C}$ and $4000\text{ }^{\circ}\text{C}$ to identify the reactions contributing the formation of pollutant species of NO, NO_2 , NH_3 , CO and CO_2 . The rate of production analysis revealed that different types of reactions are involved at both temperatures. The sensitivity analysis of the detailed kinetic model identified the reactions of reaction rates influenced the output concentrations of pollutants species. The rate of production analysis and sensitivity analysis indicate that the proposed reaction model is the representative reaction schemes of natural gas combustion in IC engines predict the pollutants species.

ACKNOWLEDGEMENT

Authors extend their gratitude to the Higher Education Commission of Pakistan for sponsoring this research work.

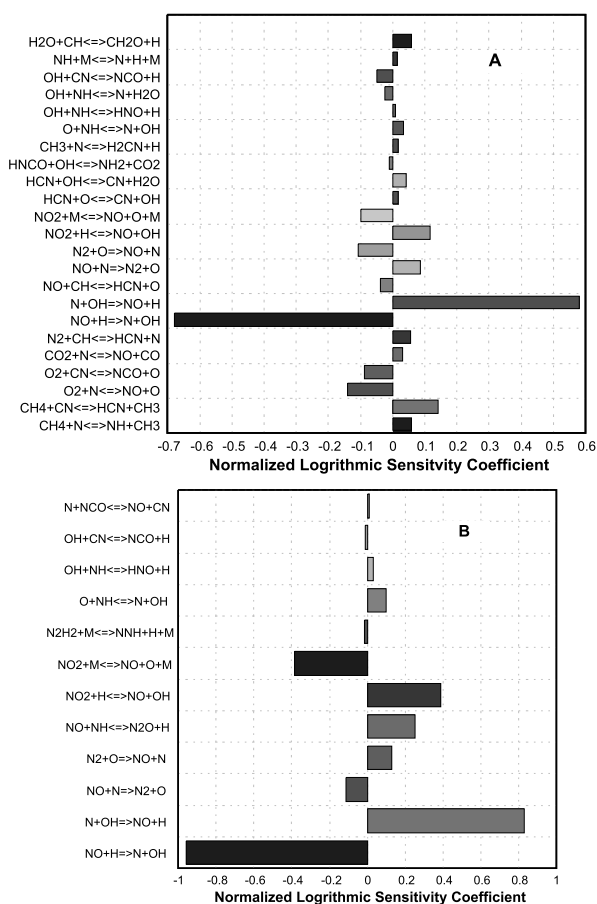


Figure 10. NO_2 sensitivity bar plot for natural gas combustion with proposed kinetic model in IC engine at equivalence ratio =1.0 when (A) $T=1500\text{ }^\circ\text{C}$ and (B) $T=4000\text{ }^\circ\text{C}$

LITERATURE CITED

1. Wartnatz, J. (1983). Hydrocarbon oxidation at high temperatures, *Phy Chem.* 87, 1008-1022.
2. Warnatz, J. (1993). In *Reduced Kinetics Mechanisms for Applied in Combustion Systems*; Peters, N., and Rogg, B., Eds.; Springer-Verlag: New York.
3. Miller, J. A. & Bowman, C.T. (1989). Mechanism and modeling of nitrogen chemistry in combustion, *Prog. Energy Combust Sci.* 15, 287-338.
4. Gregory P. Smith, David M. Golden, Michael Frenklach, Nigel W. Moriarty, Boris Eiteneer, Mikhail Goldenberg, C. Thomas Bowman, Ronald K. Hanson, Soonho Song, William C. Gardiner, Jr., Vitali V. Lissianski & Zhiwei Qin http://www.me.berkeley.edu/gri_mech/
5. Pilling, M.J., Turanyi, T., Hughes, K.J. & Clague, A.R. <http://www.chem.leeds.ac.uk/combustion/combustion.html>
6. Mansha, M., Saleemi, A.R & Badar Ghauri, M., (2010). Kinetic Models of Natural Gas Combustion in an Internal Combustion Engine, *Journal of Natural Gas Chemistry*, 19 (1):6-14.
7. Mansha, M., Saleemi, A.R, Ghauri Badar, M. & Ramzan Naveed, (2010). Development and Testing of a Detailed Kinetics Mechanism of Natural Gas Combustion in IC Engine, *Journal of Natural Gas Chemistry*, 19 (2):97-106.
8. Rabitz, H., Kramer, M. & Dacol, D., (1983). Sensitivity analysis in chemical kinetics. *Annals of Reviews of Physical Chemistry*, 34, 419-461.
9. Turanyi, T., (1990). Sensitivity analysis of complex kinetic systems: tools and applications. *Journal of Mathematical Chemistry*, 5, 203-248.

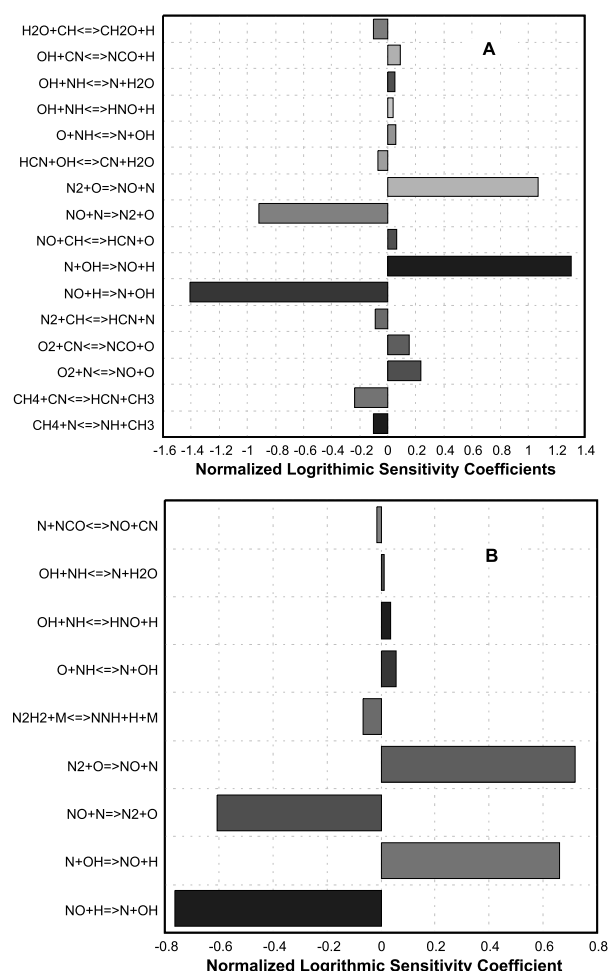


Figure 11. NH_3 sensitivity bar plot for natural gas combustion with proposed kinetic model in IC engine at equivalence ratio =1.0 when (A) $T=1500\text{ }^\circ\text{C}$ and (B) $T=4000\text{ }^\circ\text{C}$

10. Radhakrishnan, K., (1987). *Advances in Computer Methods for Partial Differential Equations – VI*, eds Vichnevetsky R., Stepleman R. S. IMACS, New Brunswick, NJ.
11. Radhakrishnan, K., (1990). Numerical approaches to combustion modelling. In *Progress in Astronautics and Aeronautics*, Vol 135 eds Oran E. S., and Boris J. P. AIAA, Washington.
12. Tomlin, A. S., Turyinyi, T. & Pilling, M. J., Mathematical tools for the construction, investigation and reduction of combustion mechanisms. In *Oxidation Kinetics And Autoignition Of Hydrocarbons*, ed. M. J. Pilling, Elsevier, Oxford.
13. Turanyi, T., (1990a). Sensitivity analysis of complex kinetic systems: tools and applications. *J. Math. Chem.* 5, 203-248.
14. Radhakrishnan, K., (1991). Combustion kinetics and sensitivity analysis computations. In: Oran, E.S., Boris, J.P. (Eds.), *Numerical Approaches to Combustion Modeling*. American Institute of Aeronautics and Astronautics, Washington, DC, pp. 83-128.
15. Smooke, M. D., Rabitz, H., Reuven, Y. & Dryer, F. L., (1988). Application of sensitivity analysis to premixed hydrogen-air flames. *Combustion Science Technology*, 59, 295-319.
16. Vajda, S. and Rabitz, H., (1992). Parametric sensitivity and self-similarity in thermal explosion theory. *Chemical Engineering Science*, 47, 1063-1078.
17. Hwang, Y-T., (1982). On the proper usage of sensitivities of chemical kinetics models to the uncertainties in rate coefficients. *Proceedings of the National Science Council B. ROC*, 6, 270-278.

18. Nowak, U. & Warnatz, J., (1987). Sensitivity analysis in aliphatic hydrocarbon combustion. *Progress in Astronautics and Aeronautics*, 113, 87-103.

19. Yetter, R.A., Dryer, F.L. & Rabitz, H., (1985). Some interpretive aspects of elementary sensitivity gradients in combustion kinetics modeling. *Combust. Flame* 59, 107-133.

20. Lutz, A.E., Kee, R.J., Miller, J.A., 1988. (SENKIN). A FORTRAN program for predicting homogenous gas phase chemical kinetics with sensitivity analysis. SAND87-8248. Sandia National Laboratories, Livermore, CA, USA.

21. Battin F.Leclerc, R. Bounaceur, G.M. Côme, R. Fournet, P.A. Glaude, G. Scacchi & V. Warth (2004). EXGAS User's Guide, Department of Chemical Physical Reaction, NANCY Cedex, France.