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Detailed Kinetic Mechanism of CNG Combustion in an IC Engine

Muhammad Mansha[1*], Javed Syed Hassan[1], Anwar Rashid Saleemi[1], Badar M. Ghauri[2]
[1]*Department of Chemical Engineering, University of Engineering and Technology, Lahore, Pakistan*
[2]*Institute of Space Technology, Islamabad, Pakistan*
E-mail: [*]*muhammad_mansha@uet.edu.pk*
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Abstract

In this study, the four kinetic reaction mechanisms were developed to simulate the formation of pollutant species in CNG fired IC engine. The reactions were generated using EXGAS and coupled with Leed's NOx reactions to develop four kinetic mechanisms. These reaction mechanisms described the combustion of natural gas at low (below 800 K) to high (above 1000 K) temperature in combustion chamber. The simulation studies predicted that the maximum cylinder pressure was achieved up to 18.0 atm & 40.0 atm under fuel leaner conditions ($\varphi \approx 0.6$) and fuel rich conditions ($\varphi = 1.13$ to 1.3) respectively. The simulation based data was compared with the experimental data (when engine was operated at 3000 rpm, $\varphi = 1.0$, $P_{inlet} = 0.67$ atm). For fuel rich conditions, high concentrations of CO were observed while NO_x levels were lowered while the fuel leaner mixture produced the lower CO emissions and moderate levels of NO_x emissions. The NO_x and CO profiles depicted that Mechanism-I, Mechanism-II and Mechanism III seemed to be inappropriate for predicting the emissions in due to CNG combustion IC engine. The molded data for Mechanism-IV exhibited closer agreement with experimental measurements. The rate of production analysis identified the important reactions in each mechanism which were contributing in the formation of emission concentrations of pollutant species. Although each proposed mechanism illustrated some discrepancies among the profiles, Mechanism-IV (consisting of 208 reactions and 78 species) showed good agreement with experimental data for pressure, temperature and pollutant species profiles.

Keywords: Simulation, EXGAS, Mechanism, Oxidation, Species Profile

1. Introduction

Combustion is a key process of converting chemical energy to heat which is ultimately converted to mechanical energy to derive in IC engine. Due this combustion, pressure and temperature suddenly rise within the engine chamber which provides the driving force to push the piston back to produce the motion in the automobile [1]. Zheng *et al*. [2] discussed the application of Compressed Natural Gas (CNG) in light-duty engines. The authors concluded that the direct injection of CNG has shown better results in the thermal efficiencies comparable to those attained by high compression ratio. It was also concluded that the CNG fired engines produced lower NO_x emissions while maintaining the smoke-free operation of Spark Ignition (SI) engines. To meet more stringent emission regulations, there are still many technical obstacles are required to be resolved in reducing the emissions both NO and CO simultaneously emitted from the internal combustion engine as discussed by Aslam *et al.* [3]. In the recent decade, CNG has been promoted as a promising clean fuel alternative to spark ignition engines because of its relatively high octane level. Lean burning of CNG in SI engines has the potential to improve thermal efficiency and reduce emissions compared with the burning of gasoline. Recently, an in-depth understanding of the physical and chemical processes is required to speed up the greener engine designs.

In literature, it is reported that many research groups recently have been working on natural gas-fuelled engines worldwide via experimental work or through simulation studies. For example; Shiga *et al.* [4] have investigated the characteristics of emissions from CNG direct injection combustion using experiment on a rapid com-

pression-machine. In study cited at [5], Computational Fluid Dynamics (CFD) codes have been utilized to study the fuel combustion. Kusaka *et al.* [6] have investigated the dual fuel engine for both diesel and natural gas engine. Ando *et al.* [7] has carried out the computational analysis of combustion with self-ignited natural gas engine. Zheng *et al.* [2] have studied combustion process and fluid flow in a compression ignition natural gas engine with separated chamber using the CFD code. These CFD based studies required the reaction mechanisms to study the turbulence, flame development, flame propagation etc in combustion of various fuels using Fluent, ANSYS etc. In the literature, several detailed mechanisms [8-13] and reduced mechanisms [14-20] for methane (CH_4) combustion exist. The reported studies discussed the reaction mechanisms of single component hydrocarbon fuels such as methane, butane, octane, hydrogen etc. [21-26].

Mansha *et al.* has implemented the oxidation mechanisms of methane in IC engine and predicted the combustion temperature and pressure in the combustion chamber of the IC engine [27]. In this study, authors successfully predicted the emission profiles of CO using the GRI 3.0 mechanism and concluded that the kinetic mechanisms can be implemented in IC engine to simulation combustion process. In another study, the authors developed the kinetic mechanisms of CNG and simulation based investigation of CNG combustion was carried out [28].

CNG is multi-component (mixture of CH_4, C_2H_6, C_3H_8, C_4H_{10}, N_2, CO_2) fuel and the combustion mechanism of this mixture is needed to develop for the understanding the formation of various products gases especially pollutants (CO, NO. NO_2, NH_3 etc.).

In present study, reaction mechanisms (models) of CNG combustion in IC engine have been developed to predict the emission profiles of pollutants including Carbon monoxide (CO) and Oxides of Nitrogen (as NO and NO_2). The model based results were validated through experimental measurements of the in-cylinder measurements of pressure, temperature and pollutant species on the dedicated experimental setup developed for this study.

2. Experimental (Material and Methods)

2.1. Development of Kinetic Reaction Mechanisms of Natural Gas Combustion

In this study, four kinetic reaction mechanisms were generated using EXGAS (an automatic mechanism generation tool). The EXGAS has three types of input (reactants, kinetic data and thermo-chemical data) to generate the reaction mechanisms of natural gas combustion. The reacting mixture species (as input to the EXGAS) have special one dimensional (1D) notation [29]. The software has built-in-notations for methane, ethane species as base species. These 1D notation were linked by the computer to an internal representation, which allows species reactants and products) to be stored in a unique format by using a canonicity algorithm. Further details of mechanism generation of EXGAS exist in *User's Guide* of the EXGAS [23]. The mechanisms generated were composed of a) C_0-C_1-C_2 reaction base b) primary reaction mechanism in which the species in the initial gas mixture are taken as the reactants and c) secondary mechanism which contain reactions of inputs are the molecular products of the primary mechanism. The types of considered in each of each of the four kinetic reaction mechanisms are given in **Table 1**. The types of primary molecules formed during the combustion of low hydrocarbons include *Monohydroperoxides* (*OOH*), *Dihydroperoxydes* $(OOH)_2$, *Allylic molecules YH*, *Ethers* (*O*), *Ketones* (*CO*), *aldehydes* (*CHO*) *etc* are given in **Table 2**. Each of the four EXGAS generated reaction mechanisms were coupled with Leeds NO_x Mechanism 2.0 (http://www.chem.leeds.ac.uk/Combustion/nox.htm).

Mechanism-I is a comprehensive reaction mechanism containing reactions feasible at range of temperature conditions (below 800 K and above 1000 K). This mechanism is composed of 935 elementary reactions and 185 species. **Mechanism-II** is a high temperature (above 1000 K) reaction mechanism and consists of 124 species and 792 elementary reactions. This mechanism composed of that type of reaction feasibly at high temperature during the combustion of natural gas. **Mechanism-III** is a low tmperature (below 800 K) reaction mechanism and consists of 152 species and 864 elementary reaction. **Mechanism-IV** is developed by the simplification of Mechanism-I by the chemical lumping technique. By this technique, the reaction steps with similar reactants and products have been eliminated. This reaction model is consisting of only 72 species and 208 elementary reactions. The proposed reaction mechanisms were used to simulate the combustion of natural gas under various temperature conditions and to predict the emissions.

2.2. Simulation of Natural Gas (as CNG) Combustion Using Kinetic Reaction Mechanisms in IC Engine

The combustion of CNG in IC engine was simulated using CHEMKIN 4.1.1 simulation package. It is a powerful set of software tools used to study reacting flows, such as those found in combustion, catalysis, chemical

Table 1. Primary reactions in different reaction mechanisms (generated by EXGAS) for natural gas oxidation.

Sr. No	Types of Reactions	Mechanism-I	Mechanism-II	Mechanism-III	Mechanism-IV
1	Unimolecular Initiations	√	√	√	√
2	Bimolecular Initiations	√	√	√	√
3	Additions	√	X	X	X
4	Additions with Oxygen	√	X	√	X
5	Isomerizations	√	√	√	X
6	Decomposition of OOQOOH into Branching Agents	√	X	√	X
7	Beta-scissions	√	√	√	√
8	Decompositions to O-rings	√	X	√	X
9	Oxidations	√	√	√	√
10	Branching	√	√	√	√
11	Metatheses	√	√	√	√
12	Combinations	√	√	√	√
13	Dismutations	√	X	√	X

Table 2. Different primary molecules classes in four reaction mechanisms (generated by EXGAS) of natural gas oxidation.

Sr.No	PRIMARY MOLECULES CLASSES	Mechanism-I	Mechanism-II	Mechanism-III	Mechanism-IV
1	Monohydroperoxides (ooh)	26	4	6	4
2	Dihydroperoxydes (ooh)2	X	X	X	X
3	O-rings	X	X	X	X
4	Allylic molecules YH	6	3	2	2
5	Alkohols (oh)	5	5	5	5
6	Ethers (o)	1	1	1	1
7	Ketones (co)	10	5	5	5
8	Aldehydes (cho)	11	5	5	5

vapour deposition, and plasma etching. It consists of rigorous gas-phase and gas-surface chemical kinetics in a variety of reactor models that can be used to represent the specific set of systems of interest [30].

The IC engine module (of CHEMKIN 4.1.1) is a model developed by supposing that the combustion chamber is a 0-D closed system which assumes the complete homogenous gas mixture as working fluid. The simulation is only valid within the time period when both intake and exhaust valves are closed. Conventionally, the engine cylinder events are expressed in crank rotation angle relative to the top dead center (TDC). The intake valve close (IVC) time of our test engine is –142 degrees (crank angle) before TDC (BTDC). The general inputs of the simulation (**Table 3**) are:

- Chemical reaction mechanisms with Arrhenius Coefficients,
- Thermodynamic data,
- Molar fractions of reactive species (Natural Gas: CH_4, C_2H_6,C_3H_8, and air—O_2, N_2) for various equivalence ratios and

Geometrical parameters of the IC Engine (cylinder displaced volume, clearance volume, crank to connecting rod ratio etc.).

The outputs extracted from the simulation studies were:

- Temperatures profiles,
- pressures profiles,
- Main species profiles

2.3. Experimental Setup

An experimental set up was designed and developed to measure the engine in-cylinder pressure, temperature and concentration of carbon monoxide (CO) and oxides of nitrogen (as NO and NO_2) when the engine is fully operated on CNG. The experimental results were compared with those obtained by the simulation studies using the proposed kinetic reaction mechanisms.

The engine used in the present study is a spark ignition IC engine that is widely used in three-wheeled automobile rickshaw in Pakistan (called a CNG rickshaw). The engine is having bi-fuel system operating on both petrol and CNG. The schematic diagram of this bi-fuel system

Table 3. Typical engine geometrical input parameters and initial gas (feed) 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
			Carbon Dioxide (CO_2)	0.026

is shown in **Figure 1** and lab view is shown in **Figure 2**.

The other details of this experimental setup and specifications of engine are given in **Tables 4** and **5**.

The in-cylinder pressure and temperature were measured using a special spark plug with a built-in pressure sensor and thermocouple. The spark plug used in this study is a diode laser based electric spark plug and has a fast transient pressure transducer (Kistler, Model 603B1). This sensor was combined with a charge amplifier (Kistler, Model 5010. A high precision angle displacement sensor with a one degree resolution was added to the crankshaft. The data acquisition for the pressure sensor was triggered by the crank angle sensor such that a pressure measurement was taken every crank angle degree. During the pressure measurements, substantial variation was observed in consecutive operating cycles (One engine cycle consist of 4-strokes and completed in 0.0077 sec and swap 720˚ crank rotation angle). The in-cylinder CO and NOx (as NO plus NO_2) were determined through fast sampling valve. On the exhaust side, an emission analyzer (Test 350 XL) was used to determine the composition of the gases. The data was acquired at 100 Hz through a 12 bit data acquisition system. Eight channels of data collected are the time histories of the trigger signal (used as time reference) and cylinder pressure. Data for all individual tests are normalized based on the initial time reference signal. The data collection is performed with a personal computer equipped with an AJD board (Data Translation, Model DT2837).

3. Results and Discussion

An IC engine performance was characterized by measuring the profiles of in-cylinder pressure and temperature variations during engine cycle. The formation of carbon monoxide (CO) and oxides of nitrogen (as NO, NO_2) was studied.

The measured data of cylinder temperature, pressure and pollutants emission profiles (for CO, NO, NO_2) were compared with the simulation (modeled) outcomes. During the measurements, significant variations in the selected parameters were observed within the combustion chamber. This comparison provided the baseline information for the selection of an appropriate kinetic model (mechanism) of oxidation of natural gas (as CNG) in IC engine.

3.1. The In-Cylinder Pressure and Temperature

The recorded pressure data was plotted versus crank angle (the time of complete cycle duration which four-stroke was converted to crank angle position with simulation model (Chemkin 4.1.1). This variation in measurements is plotted for the results obtained when engine operating conditions were under stoichiometric ($\varphi = 1.0$) conditions and at 3000 rpm. In **Figure 3**, each plot showed the similar pattern of variations of chamber pressure for each cycle while the major variations were observed for peak pressures during the combustion process occurring from –20˚ to 0˚ crank angle. The plot has not smooth variation in the each profile (both model based and experimental based data) which indicate the occurrence of unpredicted reactions and sudden release of energy as discussed in reference cited at [1]. The average measured cylinder pressure varied from 0.61 atm to 32.62 atm for six (06) consecutive engine cycles. Under fuel-lean conditions ($\varphi \approx 0.6$), the maximum cylinder pressure was reached up to 18.0 atm. Similarly, for fuel-rich conditions, a maximum pressure of about 40.0 atm was achieved for equivalence ratio of $\varphi = 1.13$ and 1.3. Unexpectedly, there was lower maximum cylinder pressure (≈38 atm) was observed at $\varphi \approx 1.4$.

This high cylinder pressure indicates the degree of completion of the combustion which depicts the maximum release of the energy from the fuel contents during combustion. Similarly, the low pressure indicates the in-complete combustion which means that net heat of reaction released is low [1]. The cylinder pressure is studied by a number of researchers [31-35] and obtained the pressure profiles as shown in **Figure 3**. For example, Ridha *et al.* [31] in the study of three chemical kinetic mechanisms of methane combustion obtained the similar pressure profiles under stoichiometric conditions. Li Cao *et al.* [30] simulated the engine flow using the turbulence model

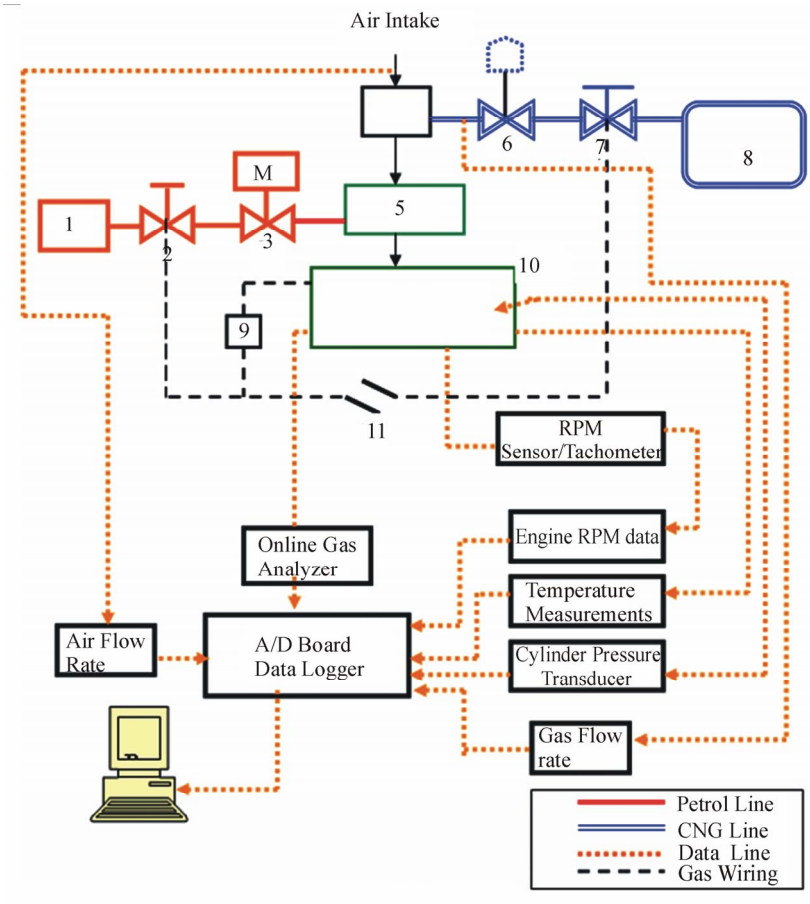

Figure 1. Schematic diagram of experimental setup.

Figure 2. Lab view of experimental setup.

and correlated the engine pressure variation with the heat released during the engine cycle. Ibrahim *et al.* [33] investigated the cylinder pressure for various engine speeds and obtained the pressure profiles experimentally for

Table 4. Experimental setup components.

No	Component	No	Component
1	Petrol Tank	7	CNG Solenoid Valve
2	Petrol Solenoid	8	GAS (CNG, Methane, Fuel B) Storage Tank
3	Petrol Flow Meter	9	Spark Timing Advancer
4	CNG Mixer	10	Spark Plug
5	Carburetor	11	Fuel Selector switch
6	CNG Pressure Regulator		

Table 5. Specification tested engine used in 4-stoke automobile rickshaws.

Parameter	Typical Value
Engine Capacity	200 CC
Compression Ratio	10.51
Bore, mm	33.5
Stroke, mm	35.5
Cylinder Volume (cm^3)	63
Displaced Volume (cm^3)	56.52
Clearance Volume (cm^3)	6.48
Cylinder Diameters (cm)	14.67
Crank to Connecting rod ratio	1.632
Carburetor	2-barreldown-draft
Specification of CNG carburetion system	
Regulator	LANDI RENZO TN1-B-SIC
Mixer	Remote extractor
Spark advancer	STAP 51

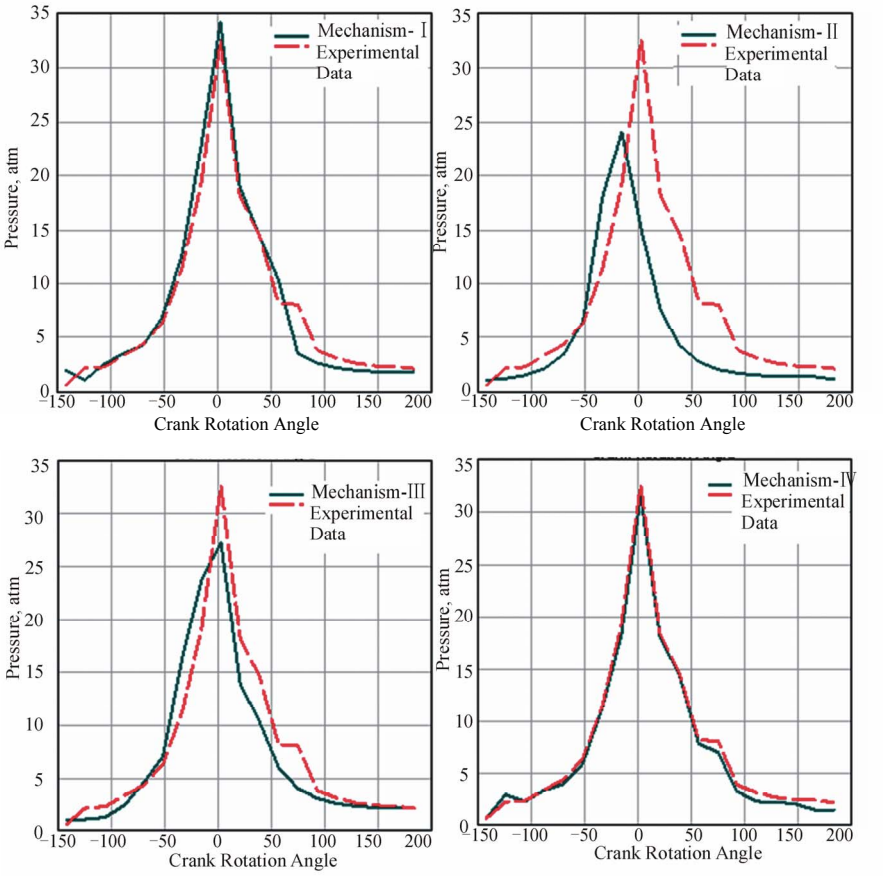

Figure 3. Pressure profiles for four proposed kinetic models (simulation with IC modules of Chemkin 4.1.1 and experimental cylinder pressure data.

CNG fuel in IC engine.

It clear from **Figure 3** that the curves for proposed kinetic Mechanism-I and Mechanism-IV shows similar behavior throughout the cycle but the profile of Mechanism-IV are much closer agreement with the experimental data plot. Although, the both the experimental and simulation profiles for Mechanism-IV do not follow the normal trend but the Mechanism-IV predicted the closer trend with the experimental trend. On the basis of pressure profiles (both simulation data and experimental data) for Mechanism-IV, it can be conclude that Mechanism-IV is an appropriate mechanism of CNG combustion in IC engine as shown experimental setup (**Figure 1**).

Figure 4 shows the variation of average cylinder temperature measured for six successive engine cycles (*each cycle consists of* 4-*strokes*). Mechanism-I over predict the chamber temperature (up to about 5000 K) during the combustion of reacting mixture (CNG-Air) while Mechanism-II and Mechanism-III indicate the early start of the combustion which do not coincide with the experimental data.

According to **Figure 4**, the experimental data showed the good agreement with simulation results were obtained using Mechanism-IV. The average peaks cylinder temperature reached up to 4000 K while the engine was operating at 3000 rpm, φ = 1.0, P_{inilet} = 0.67 atm for Mechanism-IV. The initial temperature rises (up to 1600 K) due to the compression stroke from –100˚ to –20˚ of crank angle position and after this there is substantial increase in the temperature which is due to start of combustion process (occurring between –20˚ and 2˚). When expansion stroke starts, then fall of temperature was observed and it continued with higher gradient for exhaust stroke.

The effect of fuel/air equivalence ratio on the cylinder temperature has been investigated in the engine operating at 3000 rpm, P_{inilet} = 0.67 atm. The plots in **Figure 5** shows that a smooth trend of variation in cylinder temperature was observed for fuel rich conditions for equivalence ratios of φ = 1.1, 1.3 and 1.4.

The maximum peak temperature (about 4100 K) was observed when the engine was achieved equivalence ratio of 1.3. The peak temperatures and pressure observed in the combustion cylinder are given in **Table 6** along with mean values and St. Dev. in the data for various equivalence ratios.

3.2. Investigation of Formation of Pollutant Species

The formation of two criteria gaseous pollutants (CO and NO_x) were studied in present research work. A fast response NO detector, based on the chemiluminescence

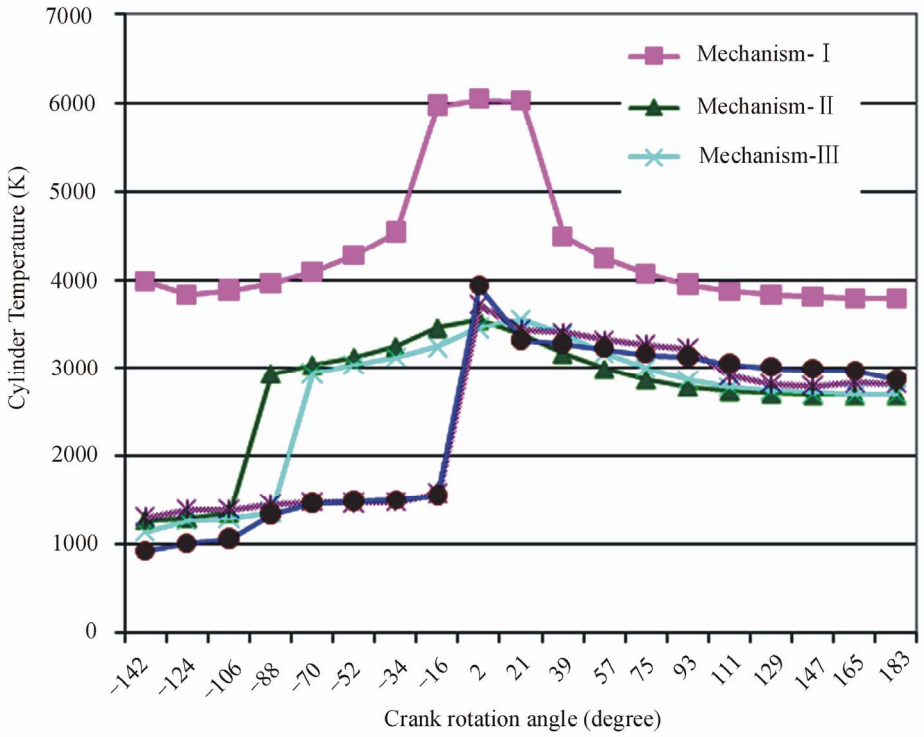

Figure 4. Cylinder temperature of predicted for four mechanisms and average of six (06) consecutive operating cycles of engine operating at 300 rpm, φ = 1.0, P_{inilet} = 0.67 atm.

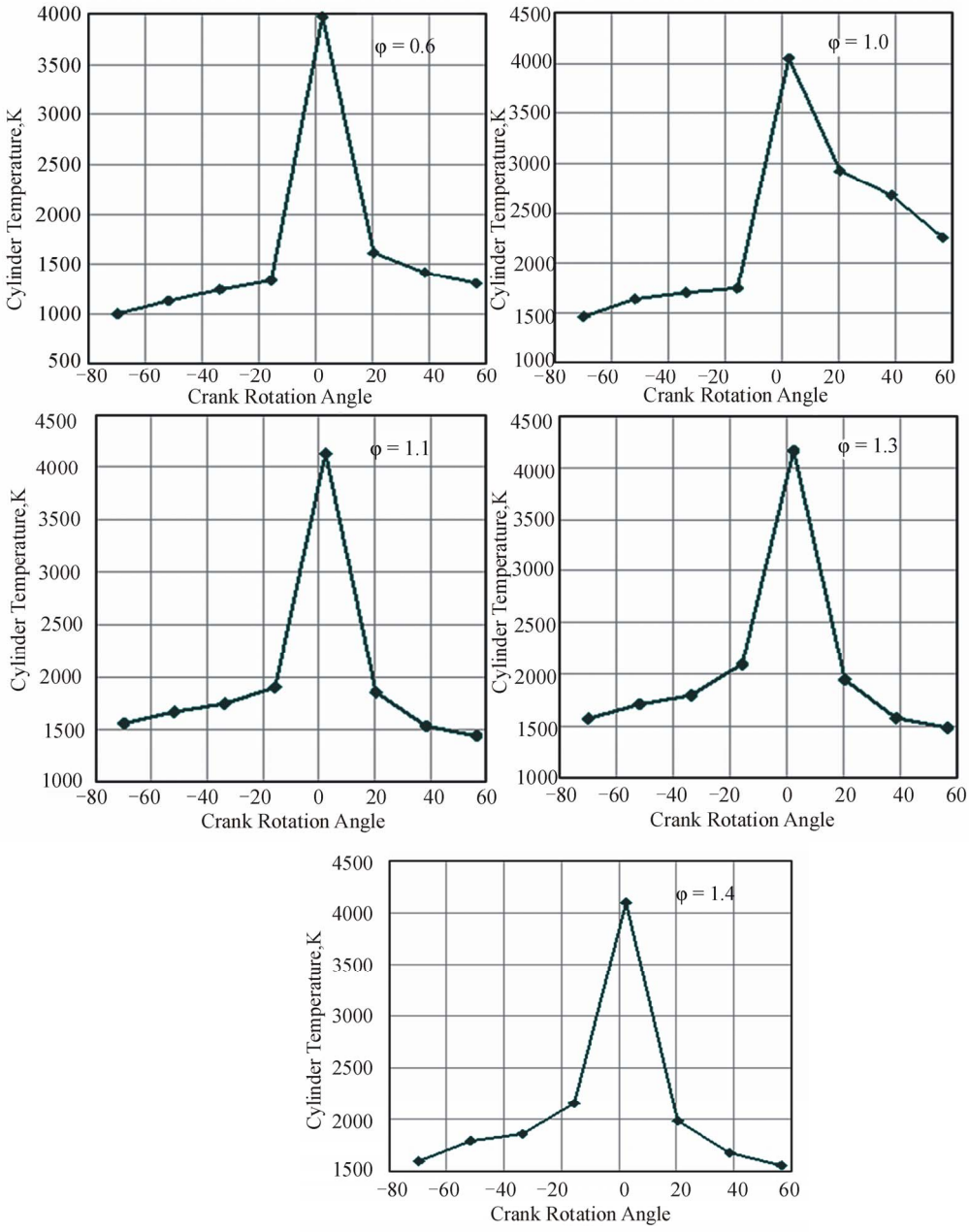

Figure 5. Measured cylinder temperatures at various equivalence ratios of CNG fired IC Engine operating at 3000 rpm, P_{inilet} = 0.67 atm.

Table 6. Peak cylinder temperature and pressure at various equivalence ratios.

Equivalence Ratio (φ)	Temperature, (K)			Pressure, (atm)		
	Peak	Mean	St. Dev	Peak	Mean	St. Dev
0.6	3976.07	3587.14	676.14	31.06	8.27	8.75
1.0	3994.09	3613.25	597.88	28.37	7.55	7.97
1.13	4053.30	3753.77	656.50	30.30	8.06	8.52
1.3	4102.4	3808.46	686.05	33.76	8.45	8.94
1.4	4100.56	3783.11	711.84	32.87	8.68	9.27

(CLD) method has been used to measure continuous, real-time levels of NO in the cylinder. The NO_x concentrations data (as calculated as mole fraction of sum of NO and NO_2 data) is plotted versus crank angle position as shown in **Figure 6**. The data was collected when engine was operated at 3000 rpm under stoichiometric conditions (when $\varphi = 1.0$).

The fluctuations in the NO_x levels in the combustion chamber were observed after combustion process during expansion and exhaust phases. The NO_x profile showed that maximum NO_x concentrations were produced when engine was fired by the CNG. The increase or decrease of the concentrations of NO_x after combustion indicates occurring of the reactions during the expansion of the burned gas mixture but reactions consuming NO_x molecules are seems to dominant the producer reactions. During the exhaust phase, the constant levels indicate the freezing of the NO_x chemistry at the low temperature [1]. It can be concluded that higher NO_x levels were observed at higher temperatures in the combustion chamber. The curves of **Figures 6** and **7** illustrated that lower emissions were observed under lean mixture conditions ($\varphi <$ 1.0). The shapes of these curves showed the complexities emission controls. When engine operation becomes stable (usually when fuel flow increased and combustible mixture become fuel-rich), high concentrations of CO were observed while NO_x levels were lowered. During the measurements, it was also observed that when engine was operated under load condition, leaner mixture produced lower CO emissions and moderate levels of NO_x emissions.

Figures 7 and **8** also indicate that highest concentration of NO_x were near the stoichiometric conditions and then become lower while CO level shows increasing trend. Maximum variation in the concentrations of these pollutants (NO and NO_2) is clearly shown in **Figures 7** and **8**.

There are two major sources of nitrogen to in fuel

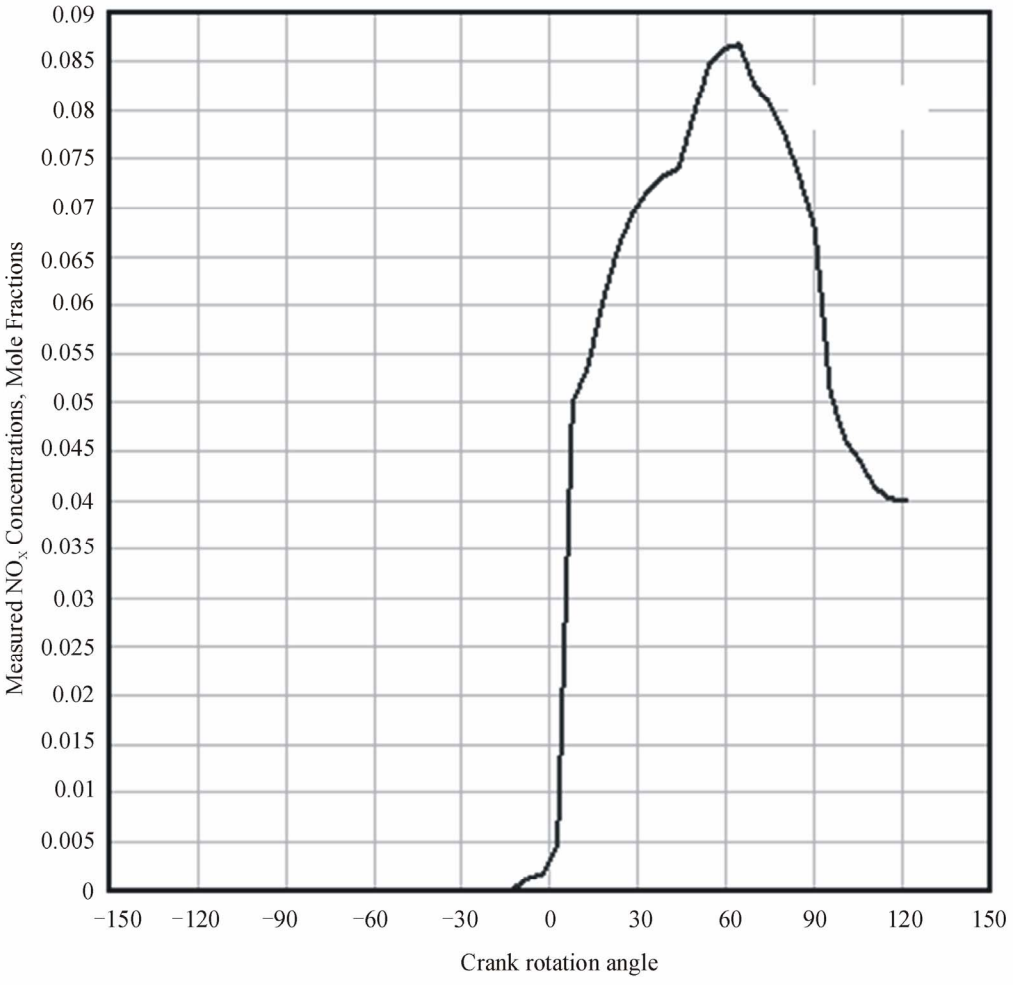

Figure 6. Measured NO_x concentrations (in-cylinder) for three fuel (3000 rev/min, $\varphi = 1.0$ and $P_{inlet} = 0.67$ atm).

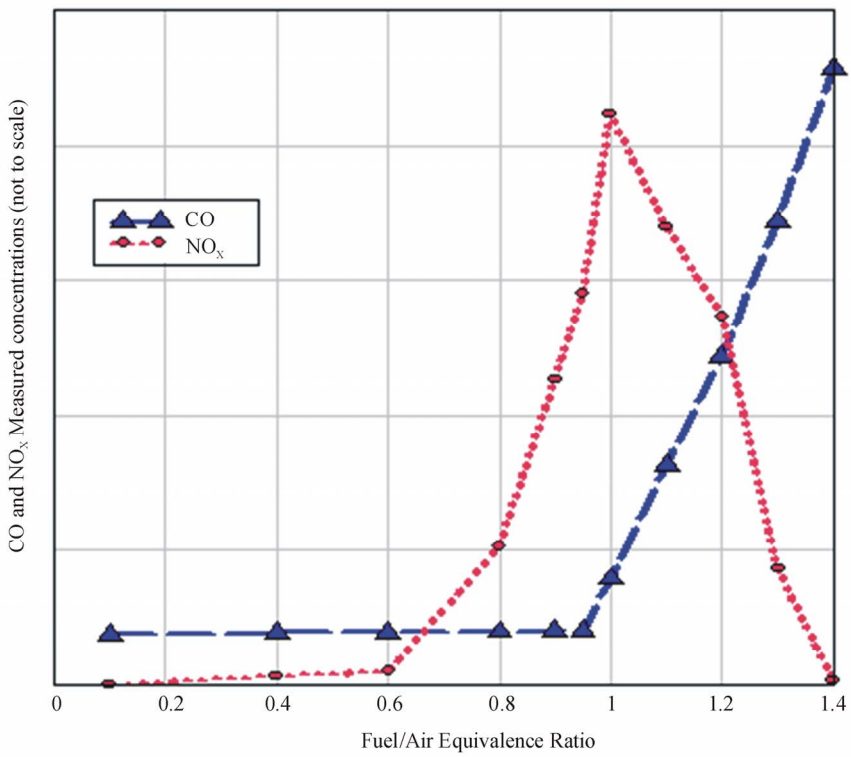

Figure 7. Variation of CO and NOx concentration in exhaust of CNG fired IC engine (200 CC) at various equivalence ratio (fuel/ratio).

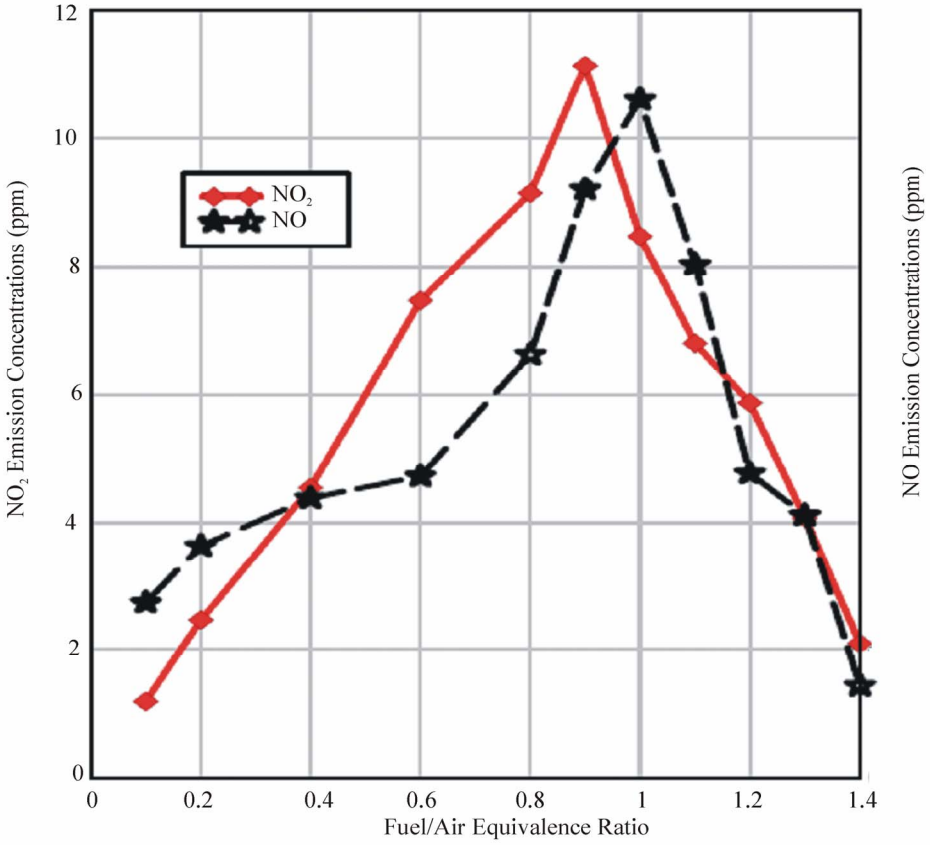

Figure 8. Variation in concentrations of NO and NO_2 in engine exhaust as function of equivalence ratio.

mixture (fuel nitrogen and air nitrogen) in pre-mixed combustion of CNG in IC engine. Studies [1] revealed that the fuel nitrogen is source of NO via different mechanisms.

Figure 9 shows the comparison of results of experimental data of in-cylinder NOx data of IC engine fired with CNG operating at 3000 rpm and equivalence ratio of ≈ 1.0 and simulation data of NO_x (as mole fraction) obtained for four kinetic mechanisms using IC engine module of Chemkin 4.1.1.

During combustion lower hydrocarbons, lower molecular weight nitrogen-containing compounds such as ammonia (NH_3), hydrogen cyanide (HCN) and cyanide (CN) are formed [1,29]. Simulation of CNG combustion in IC engine (Chemkin 4.1.1) predicts the existence and formation of these precursor compounds on NO formation.

Rate of Production (ROP) analysis of each of mechanism was carried out to know which type of reaction contribute the NO_x formation at typical 3000 K under stoichiomteric conditions (φ = 1.0) at moderate speed of 3000 rpm. ROP analysis shows the how much a particular reaction contributes in production or consumption of a specie/product. **Table 7** shows the important plausible reactions involved in NO_x formation due to CNG combustion in IC engine and normalized rate of production coefficients. The positive (+ve) value of Normalized ROP coefficient indicate the production or forward rate is dominant while negative (-ve) value means the consumption or backward rate of reaction is dominate.

In **Table 7**, it is clear that NO_2 is converted to NO via reaction; NO_2+M<=>NO+O+M where M is the third body molecular specie or radical (which may be OH). **Figure 8** shows the emission data NO and NO_2 from the tested engine data measured at various equivalence ratios. These figures indicate that the NO_x formation is greatly affected by Fuel/Air Equivalence Ratios. During the experiments, it was observed that as equivalence ratio is increased, the oxygen concentrations were lowered and in parallel burned gas temperature decreased. When mixture was leaned, increasing oxygen concentrations offset the lowered gas temperature and NO emissions get peak concentrations nearly at $\varphi \approx 0.97$ while highest concentrations reached at $\varphi \approx 0.85$.

The NO_x concentrations showed different character both under fuel lean and fuel rich conditions. Based upon both simulations results and experimental data, it can be concludes that;

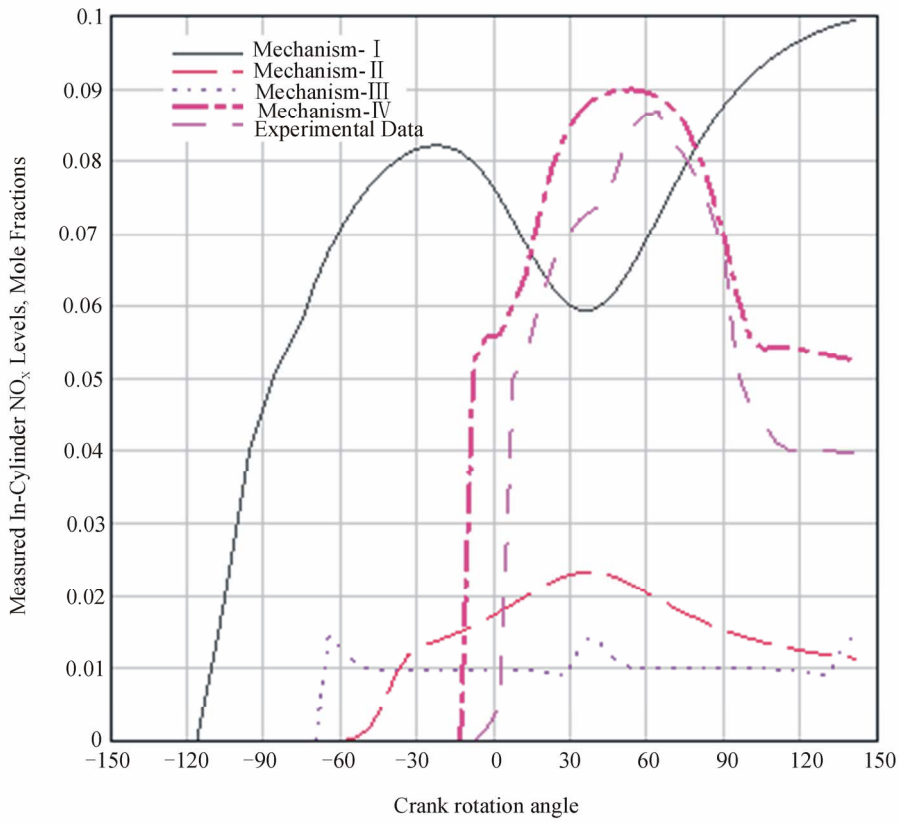

Figure 9. Comparison of NO_x profiles (with modeled data and experimental data).

Table 7. Reactions involved in formation and consumption of NO_x (NO & NO_2) in proposed four kinetic mechanisms with calculated normalized rate of production coefficients.

Mechanism	Reaction		Normalized Rate of Production Coefficient
Mechanism-I	1. NO REACTION		(–0.078)
	R-790	NO+H=>N+OH	**(1.000)**
	R-811	**NO+M<=>N+O+M**	**(0.916)**
	R-932	**HNO+M<=>H+NO+M**	
			(0.082)
	2. NO2 REACTION		(0.014)
			(–0.038)
	R-799.	$NO+HO_2<=>NO_2+OH$	(–0.617)
	R-814.	$NO_2+O<=>NO+O_2$	**(0.904)**
	R-818.	$NO_2+NH<=>N2O+OH$	
	R-819.	$NO_2+NH_2<=>N_2O+H_2O$	
	R-821.	**$NO_2+M<=>NO+O+M$**	
Mechanism-II	1) *NO-Reaction*		
	R-648.	NO+H=>N+OH	(–0.642)
	R-649	**N+OH=>NO+H**	**(0.870)**
	R-660	$NO+N=>N_2+O$	(–0.349)
	R-661	**$N_2+O=>NO+N$**	**(0.334)**
	R-746	O+NH<=>NO+H	(0.024)
	R-789	HNO+M<=>H+NO+M	(0.033)
	2) *NO_2 Reactions*		
	R-657	$NO+HO_2<=>NO_2+OH$	(–0.064)
	R-671	NO2+H<=>NO+OH	(–0.460)
	R-672	$NO2+O<=>NO+O_2$	(–0.475)
	R-679	**NO2+M<=>NO+O+M**	**(1.000)**
Mechanism-III	a) *NO Reactions*		
	R-704	O2+N<=>NO+O	(0.022)
	R-719	NO+H=>N+OH	(–0.267)
	R-720	**N+OH=>NO+H**	**(0.626)**
	R-731.	$NO+N=>N_2+O$	(–0.210)
	R-732	**$N_2+O=>NO+N$**	**(0.410)**
	R-743	$NO_2+O<=>NO+O_2$	(0.014)
	R-818	O+NH<=>NO+H	(0.012)
	b) *NO_2 Reactions*		
	R-728	$NO+HO_2<=>NO_2+OH$	(–0.086)
	R-742	**$NO_2+H<=>NO+OH$**	**(0.548)**
	R-743	$NO_2+O<=>NO+O_2$	(–0.913)
	R-750	**$NO_2+M<=>NO+O+M$**	**(0.452)**
Mechanism-IV	3. REACTION NO		(–0.742)
	R-61	NO+H=>N+OH	(0.063)
	R-62	N+OH=>NO+H	(–0.239)
	R-73	$NO+N=>N_2+O$	(0.028)
	R-74	$N_2+O=>NO+N$	**(0.905)**
	R-82	**NO+M<=>N+O+M**	(–0.015)
	R-84	$NO_2+H<=>NO+OH$	
			(0.789)
	4. REACTION NO_2		**(1.000)**
	R-84	**$NO_2+H<=>NO+OH$**	
	R-92	**$NO_2+M<=>NO+O+M$**	

- NO concentration become stable little early in the expansion process and a little conversion of NO may occur in lean fuel mixture conditions.
- In fuel rich mixture, the sharp decrease in NO concentrations occurs from peak values when maximum cylinder pressure is achieved.

The in-cylinder CO measurements were done through Rapid Sampling Valve. **Figure 10** shows the measurements of CO levels (measured in term of % while it is then converted to mole fraction and ppm units). The data is plotted against crank angle position. The CO data was recorded at nearly –8˚ (7.8˚ actual). The varying levels of CO after combustion process shows the occurring of some reactions CO consumption formed during the com-

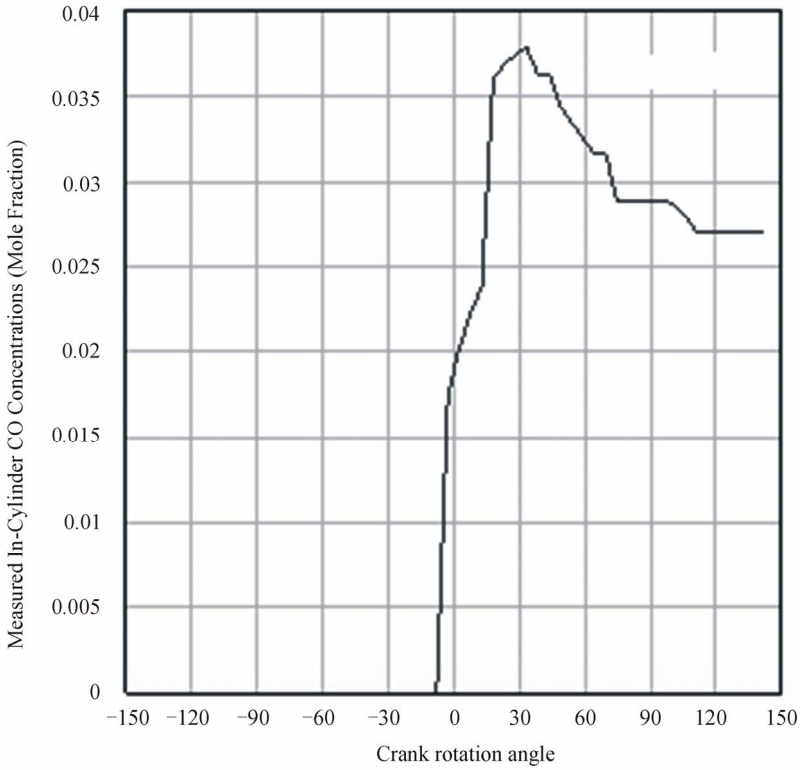

Figure 10. Measured CO concentrations (in-cylinder) for 3000 rpm, φ = 1.0 and P_{inlet} = 0.67 atm.

bustion phase and freezing of CO chemistry when used CNG

The experiments were conducted for various equivalence ratios and data was recorded when engine was operated at 3000 rpm and exit temperature was nearly 494 K. The molded data of CO data was also determined for the four proposed kinetic mechanisms using IC engine module of Chemkin 4.1.1 software. The simulation conditions were set as given in **Table 4** and fuels fractions were used as given for CNG in **Table 5**. The modeled data was compared with the experimental data (collected when engine was operated at 3000 rpm, φ = 1.0, P_{inlet} = 0.67 atm fired with CNG and **Figure 11** shows the comparison of modeled data for CO levels obtained for four proposed kinetic mechanisms. The CO profile for Mechanism-I, Mechanism-II and Mechanism III indicate that these mechanisms seem to be inappropriate for predicting the CO in IC engine. According to **Figure 11**, the molded data for Mechanism-IV exhibits closer agreement with experimental measurements.

The major reactions involved in formation and consumption of CO in the combustion chamber of the tested automobile (IC) engine for proposed kinetic mechanisms are given in **Table 8**. The reactions are listed according to the normalized rate of production coefficient determined by the ROP analysis of each mechanism.

According to **Table 8**, the following reaction were proposed to take part in the formation of CO and shows more contribution) during the combustion of CNG in tested IC engine;

HNCO+M<=>NH+CO+M,

NCO+M<=>N+CO+M

4. Conclusions

The proposed mechanisms were successfully implemented to predict the profiles of temperature, pressure and pollutant species in Chemkin 4.1.1. The average measured cylinder pressure varied from 0.61 atm to 32.62 atm for six consecutive engine cycles. The highest concentrations of NO_x were near the stoichiometric conditions and then become lower while CO level shows increasing trend. The modeled data was compared with the experimental data (measured when engine was operated at 3000 rpm, φ = 1.0, P_{inlet} = 0.67 atm) for each proposed mechanisms. The profile for Mechanism-I and Mechanism-II showed very early start of the combustion, which does not agree with the experimental data. Mechanism-III also shows far away behavior from the actual monitored data of the actual engine operation data. The predicted CO profiles for Mechanism-IV exhibits closer agreement with experimental measurements. Although there are some discrepancies exist in the CO profiles for Mechanism-IV and experimental data but on whole,

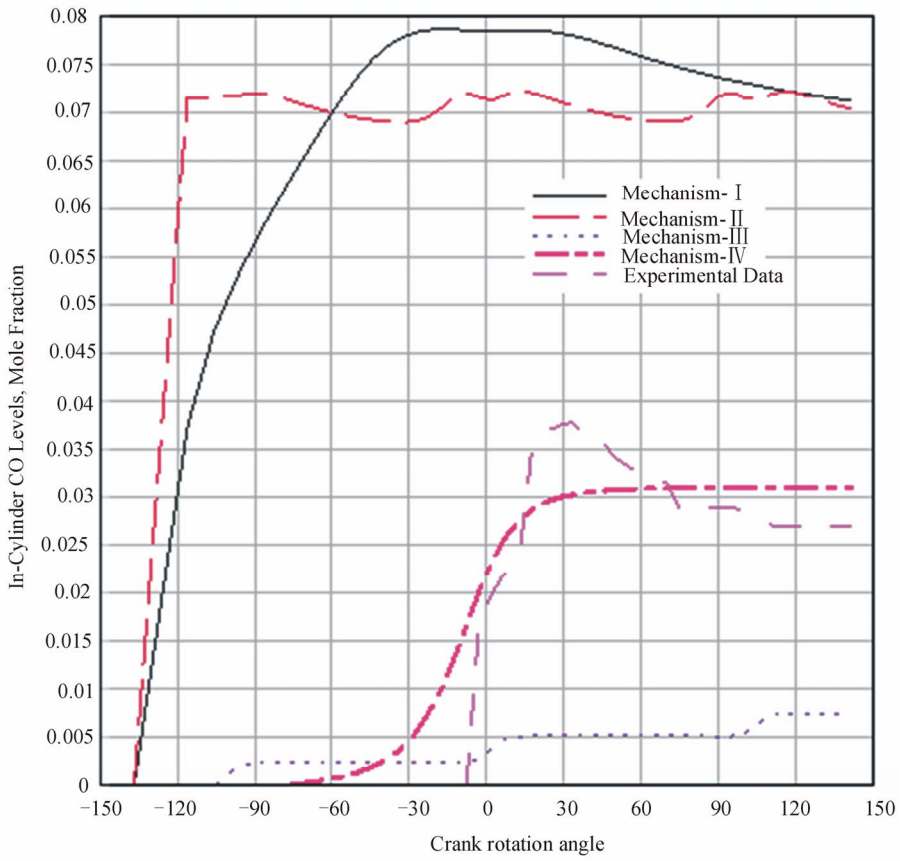

Figure 11. Comparison of CO profiles (with modeled data and experimental data).

Table 8. Reactions in four kinetic mechanisms (proposed) in CO formation and consumption.

Mechanism	Reactions	Normalized Rate of Production Coefficient
Mechanism-I	$CO+N_2O<=>CO_2+N_2$	–0.139
	$CO_2+N<=>NO+CO$	0.740
	HNCO+M<=>NH+CO+M	0.322
	NCO+M<=>N+CO+M	1.000
Mechanism-II	$CO+N_2O<=>CO_2+N_2$	–0.013
	$CO_2+N<=>NO+CO$	0.094
	HCN+O<=>NH+CO	0.044
	$NCO+H<=>NH_2+CO$	0.119
	HNCO+M<=>NH+CO+M	–0.025
	H+NCO<=>NH+CO	0.304
	O+CN<=>CO+N	–0.017
	O+NCO<=>NO+CO	0.290
	OH+NCO<=>NO+CO+H	0.138
	NCO+M<=>N+CO+M	–0.945
Mechanism-III	$CO+N_2O<=>CO_2+N_2$	–0.032
	CO2+N<=>NO+CO	–0.713
	HCN+O<=>NH+CO	0.020
	$HNCO+H<=>NH_2+CO$	0.056
	H+NCO<=>NH+CO	0.250
	O+NCO<=>NO+CO	0.383
	OH+NCO<=>NO+CO+H	0.285
	NCO+M<=>N+CO+M	–0.246
Mechanism-IV	HNCO+M<=>NH+CO+M	0.975
	OH+NCO<=>NO+CO+H	0.022
	NCO+M<=>N+CO+M	1.000

we can conclude the Mechanism-IV is representative scheme of reactions predicting the combustion in CNG fired IC engine.

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