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Original Article

Comparison of automatically generated reaction mechanism for oxidation of simple hydrocarbons in IC engine

Muhammad Mansha* and Hassan Javed S.

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

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Abstract

In this work, a detailed kinetic reaction mechanism, consisting of 208 reactions and 79 species, has been developed to describe the oxidation of simple hydrocarbon fuel (natural gas) in IC engine. The performance of the proposed mechanism is tested using simulation, tool CHEMKIN 4.1.1, and experimental measurements. The simulation results of the proposed reaction scheme were compared with those of reference mechanisms (GRI v3.0 and Konnov 0.5 version) as well as experimental data. Based upon simulation results, it can be concluded that the proposed mechanism shows good concordances with GR I3.0 mechanism especially in the prediction of temperature, pressure, and major product species (H_2O, CO_2) profiles at stoichiometric conditions ($\varphi = 1.0$). Although, there are some discrepancies among each predicted profile, the proposed detailed mechanism is good to describe the oxidation of natural gas in IC engine. The experimental data also showed favorable results for prediction of major product species (CO_2, H_2O & CO) at various engine operating speeds in idle mode.

Keywords: IC Engine, mechanism, simulation, stoichiometric conditions

1. Introduction

The understanding of oxidation kinetics of simple hydrocarbons such as methane (CH_4), ethane (C_2H_6), propane (C_3H_8), and mixture of these (natural gas) is a key objective of combustion chemistry. To achieve this understanding, a detailed mechanism is required. The detailed mechanisms involved hundreds of chemical species and thousands of reaction steps. Detailed combustion mechanisms are based on measurements of elementary gas phase reaction coefficients. The measurements have provided the temperature and pressure dependencies of the over overall rate coefficient. The mechanisms of Warnatz and Walker (Warnatz, 1983, 1993; Walker *et al.,* 1997) have been used by many people, but were mainly created as illustrations in combustion model ing papers. Another widely used mechanism is the Miller-Bowman NO mechanism (Miller and Bowman, 1989), which, like the Warnatz mechanism, is now out of-date in many respects. The GRI mechanism (Gregory *et al.*, 2011) is used for study of oxidation of methane. This mechanism is based on elementary reactions, where combinations of experimental and theoretically determined values are assigned to the rate parameters. One of the pioneering ideas of the GRI mechanism was that the mechanism, its testing, and related information are available through Internet (http://www.me.berkeley.edu/gri_mech/). Other combustion mechanisms also available through Internet were developed by Konnov (2000) and the Leed's mechanisms (http://www.chem.leeds.ac.uk/Combustion/Combustion.html). These mechanisms were used to understand the various combustion phenomenon like flame speed, oxidation of fuel mixture of simple hydrocarbon, flame structure, etc.

EXGAS is an automatic tool for kinetic reaction mechanism for hydrocarbon fuels (developed at Nancy, France). It also generates allied data (thermo chemical) automatically using its associated components, i.e., THERGAS

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* Corresponding author.
Email address: muhammad_mansha@uet.edu.pk

and KINGAS (Muller *et al.*, 1995; Glaude *et al.,* 2000). EXGAS was utilized for the generation of oxidation mechanism for mixture of species (Come *et al.*, 1996; Glaude *et al.*, 1997; Glaude *et al.*, 1998; Warth *et al.*, 1998; Barbé *et al.*, 1995). The reacting mixture species have special 1D notation. The software has built-in-notations for methane and ethane species as base species. These one dimensional (1D) notations were linked by the computer to an internal representation, which allows species reactants and products to be stored in a unique format using a canonicity algorithm. A detailed primary mechanism by EXGAS contains the following types of reactions primary required to understand the oxidation mechanism of hydrocarbons (Battin *et al,*, 2004);

1) Unimolecular and bimolecular initiation steps
(e.g. $C_3H_8 \leftrightarrow {\bullet}CH_3 + {\bullet}C_2H_5$; $C_3H_8 + O_2 \leftrightarrow {\bullet}C_3H_7 + {\bullet}OOH$),

2) Reactions leading to alkenes from alkyl and hydroperoxyalkyl radicals

- Decompositions by beta-scission
  (e.g. ${\bullet}C_3H_7 \leftrightarrow {\bullet}CH_3 + C_2H_4$),
- Oxidations to form the conjugated alkene and ${\bullet}OOH$
  (e.g. ${\bullet}C_3H_7 + O_2 \leftrightarrow C_3H_6 + {\bullet}OOH$),

3) Additions of alkyl and hydroperoxyalkyl radicals to a molecule of oxygen
(e.g. ${\bullet}C_3H_7 + O_2 \leftrightarrow C_3H_7OO{\bullet}$, ${\bullet}C_3H_6OOH + O_2 \leftrightarrow {\bullet}OOC_3H_6OOH$),

4) Isomerizations of alkyl and peroxy radicals involving cyclic transition state
(e.g. $CH_3CH_2CH_2OO{\bullet} \leftrightarrow {\bullet}CH_2CH_2CH_2OOH$),

5) Decompositions of hydroperoxyalkyl and dihydroperoxyal alkylradicals to form cyclic ethers, alkenes, aldehydes or ketones (oxohydroperoxyalkanes),
(e.g. ${\bullet}CH_2CH_2CH_2OOH \leftrightarrow$ Cyclic-$C_3H_6O + {\bullet}OH$),
(e.g. $CH_2OOHC{\bullet}OOHCH_3 \leftrightarrow CH_2OOHC(=O)CH_3 + {\bullet}OH$),

6) Metathesis reactions to abstract an H atom from the initial reactant
(e.g. ${\bullet}OH + C_3H_8 \leftrightarrow H_2O + {\bullet}C_3H_7$),

7) Termination steps:

- Combinations of two free radicals
  (e.g. $CH_3{\bullet} + CH_3{\bullet} \leftrightarrow C_2H_6$),
- Disproportionations of peroxy radicals with ${\bullet}OOH$
  (e.g. $C_3H_7OO{\bullet} + {\bullet}OOH \leftrightarrow C_3H_7OOH + O_2$).

2. Materials and Methods

2.1 Generation of detailed primary kinetic mechanism by EXGAS

We generated kinetic mechanisms of simple hydrocarbon fuel (natural gas; a mixture of methane, ethane, propane, and butane) combustion in an internal combustion engine using EXGAS software. It generates the reaction scheme automatically and has built in 1D notations for molecules of methane, ethane in reaction base, and we input the formulas in form of ch3/ch2/ch3, ch3/ch2/ch2/ch3, and //(o)2 for propane, butane, and oxygen molecule, respectively. Initially, the software generated a mechanism with 502 reaction steps and this mechanism has been reduced automatically to 69 reaction pathways by chemical lumping technique. Thermodynamics data (JANAF format) necessary for CHEMKIN is produced by THERGAS (built-in-module in EXGAS) automatically. This model contains 60 reactions of various types such as initiation, beta-scission, oxidation, branching, termination, and others, and has 79 species. The reaction is further simplified by chemical lumping method and about 33% reaction steps are reduced.

2.2 Coupling of EXGAS mechanism and leeds NO_x mechanism

The reaction by EXGAS was coupled with Leeds NO_x mechanism (version 2.0 available at http://www.chem.leeds.ac.uk/Combustion/nox.htm) using a software OPENCHEM WORKBENCH (http://openchemwb.sourceforge.net/OpenChemWB_Home.html).The purpose of this coupling was to develop a comprehensive reaction scheme (model) that describes CH_4/NO_x chemistry for oxidation of simple hydrocarbon fuel (natural gas) at high temperature (above 2,000 K).

The major objective of this study is to develop a reaction kinetic model, which is capable of predicting the formation of major gaseous pollutants from engine exhaust. The results were evaluated by comparing with profiles of in-cylinder temperatures, pressures, major species, and pollutant emissions (only CO, NO_x as NO and NO_2 and NH_3) of GRI 3.0 and that of A. Konnove's detailed reaction (Konnov, 2000) for small hydrocarbons.

2.3 General simulation inputs

Inputs of the simulation are

- Chemical reaction mechanisms with Arrhenius coefficients.
- Thermodynamic and transport data.
- Mole fraction of reactive species (in our case of natural gas: CH_4, C_2H_6, C_3H_8, N_2, CO_2, Air-O_2) for various equivalence ratio and geometrical parameters of ICE.

Through theses inputs, we can extract information from simulation such as

- Temperature profiles
- Pressure profiles
- Main species profiles, and
- Total rate-of-production.

3. Results and Discussions

The performance of this newly proposed (developed by coupling EXGAS mechanism and Leed's NO_x mechanism version 2.0) kinetic mechanism was investigated using Internal Combustion Engine (ICE) module of CHEMKIN 4.1.1

Table 1. Menu for generation of primary mechanisms by EXGAS.

Types of Primary Reactions	Options Selected for Generation of Primary Reaction Mechanism	
	Yes/No	No. of Reactions
Unimolecular initiations	Yes	3
Bimolecular initiations	Yes	3
Additions with oxygen	No	0
Isomerizations	No	0
Beta-scissions	Yes	7
Decompositions to o-rings	No	0
Oxidations	Yes	3
Branching	No	0
Metatheses	Yes	43
Combinations	Yes	10
Dismutations	No	0
Number of Reactions in Lumped Primary Mechanism	69	
Total Number of reactions (after Coupling with Lead's NO_x Mechanism)	208	
No of Species	79	
Number of primary molecules	23	
Number of free radicals	22	
Number of lumped molecules	34	

(Kee *et al.,* 2007). The combustion of natural gas mixture was simulated in an engine cylinder with the proposed kinetic reaction scheme (Table 2). In this simulation, various engine parameters (crank rotary speed, compression ratio, cylinder displacement volume, etc.) and initial inlet gas composition were utilized (Table 3). The other necessary simulation input data are thermodynamic data, which for proposed kinetic reaction scheme was automatically generated by THERGAS module of EXGAS software. The simulation with the proposed kinetic model produces about 46 species in the product mixture, which are purely dependent on the reacting and product species in the pathway reaction steps.

Figure 1 shows the simulation results of molar conversion of inlet natural gas mixture and oxidizer for the three mechanisms. The simulation is carried out at stoichiometric condition (φ=1.0) at P=1.0 atm and T=2,000°C. During the simulation, it was observed that the maximum (nearly 100%) conversion of reacting species could be achieved under fuel rich conditions (i.e. $\varphi>1.0$). The major fuel components (i.e. CH_4 and C_2H_6) show nearly complete conversion to products at an equivalence ratio of $\varphi \geq 1.3$ (at rich conditions). The profile of propane conversion indicates that complete conversion could be achieved at an equivalence ratio of far greater that 1.3. It can be concluded that maximum conversion of natural gas occurs under rich conditions ($\varphi>1.0$).

Figure 2 shows that the pressure and temperature profiles obtained with the three detailed kinetic models for adiabatic and stiochiometric condition (T_{ini}=500°C, P_{ini}=1.0 atm and φ =1.0). The reference mechanisms (GRI version 3.0 and Konnov version 0.5) predict the maximum engine pressure of about 40.7 atm, while the proposed mechanism predicts the P_{max} of nearly 39.4 atm. With the proposed kinetic mechanism, the predicted pressure is about 3% lower than the reference mechanisms (GRI 3.0 and Konnov 0.5). As shown in this figure, there is some discrepancy in the temperature profiles between the proposed mechanism and both referenced detailed mechanisms. The proposed mechanism shows a later start of combustion and lower engine cylinder peak temperature (about 234 K).

Figure 3 illustrates the fuel species (natural gas components; CH_4, C_2H_6 C_3H_8) and oxidizer (air-O_2) profiles for the adiabatic and stoichiometric conditions. The proposed mechanism shows closer consumption pattern with GRI 3.0 mechanism especially for methane (CH_4) and atmospheric oxidizer (O_2) profiles under the similar simulation conditions. All species profiles indicate that the proposed mechanism exhibits complete combustion of natural gas in the IC engine and depicts that the reactions proposed represents the combustion of the natural gas. Figure 4 illustrates the two major combustion product species (CO_2 and H_2O). This figure also shows that Konnov 0.5 mechanism exhibits some earlier start of combustion and later end of the combustion in H_2O profiles. The proposed detailed mechanism and GRI 3.0 mechanism exhibit similar combustion behaviors, but during the ending of the combustion process, the proposed mechanism illustrates the earlier completion of the combustion. There is some discrepancy in the species profiles near the completion of combustion. The proposed mechanism predicts

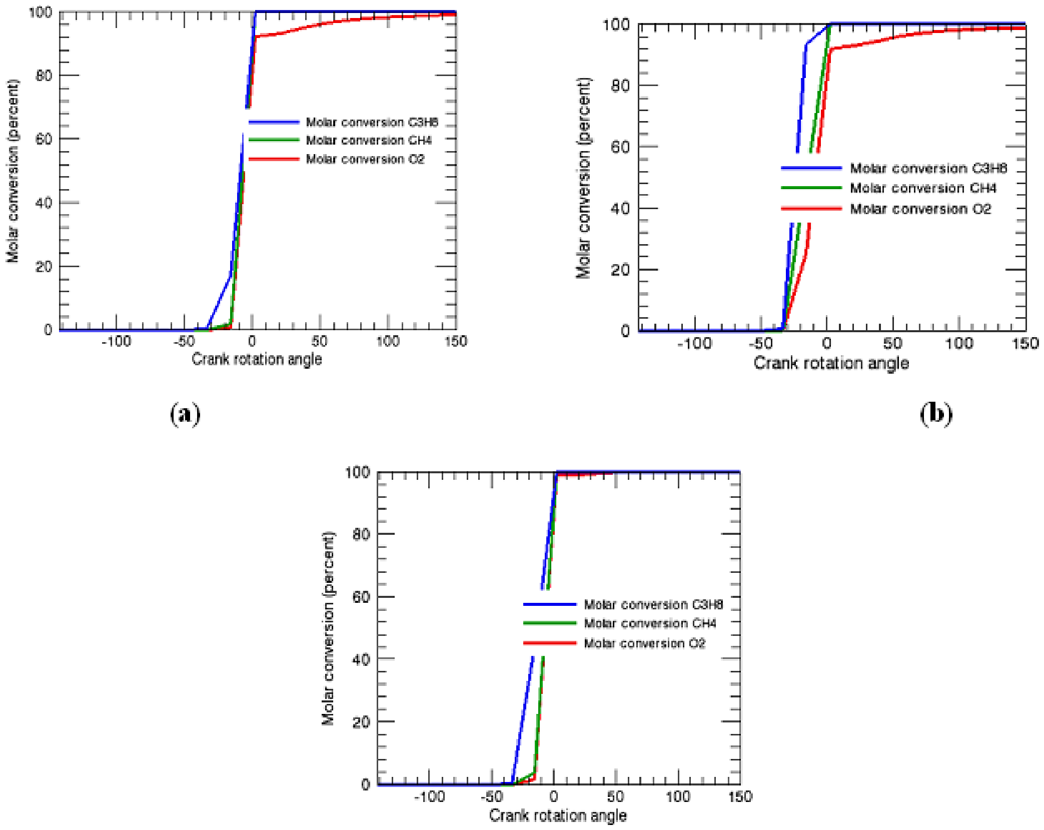
Table 2. Pressure dependent reactions in the proposed kinetic reaction mechanism for oxidation of simple hydrocarbon fuels at high temperature (above 2,000 K).

Sr. No	Reactions Considered	k = A T**b exp(-E/RT)		
		A	b	E
1	$C_3H_8+R_1H=>H_2+R_{21}C_3H_7$	9.00E+06	2	5000
2	$C_4H_{10}+R_1H=>H_2+R_{20}C_4H_9$	5.70E+07	2	7700
3	$C_3H_8+R_2OH=>H_2O+R_{21}C_3H_7$	2.60E+06	2	-765
4	$C_4H_{10}+R_2OH=>H_2O+R_{20}C_4H_9$	5.40E+06	2	450
5	$C_4H_{10}+R_4CH_3=>CH_4+R_{20}C_4H_9$	6.00E-01	4	8200
6	$C_3H_8+R_5CHO=>HCHO+R_{21}C_3H_7$	1.00E+07	1.9	17000
7	$C_4H_{10}+R_5CHO=>HCHO+R_{20}C_4H_9$	2.00E+05	2.5	18500
8	$C_3H_8+R_6CH_2OH=>CH_3OH+R_{21}C_3H_7$	6.00E+01	3	12000
9	$C_4H_{10}+R_6CH_2OH=>CH_3OH+R_{20}C_4H_9$	2.00E+02	3	14000
10	$C_3H_8+R_{21}C_3H_7=>C_3H_8+R_{19}C_3H_7$	8.40E-03	4.2	8700
11	$C_4H_{10}+R_{21}C_3H_7=>C_3H_8+R_{22}C_4H_9$	5.60E-03	4.2	8000
12	$H_2+CN=HCN+H$	1.93E+04	2.9	6.8
13	$CH_4+CN=HCN+CH_3$	9.03E+04	2.6	-1.2
14	$O_2+N=NO+O$	9.03E+09	1	27.2
15	$O_2+NH_2=HNO+OH$	1.51E+12	-0.4	151
16	$O_2+NH_2=H_2NO+O$	1.10E+18	-1.3	140.6
17	$NO_2+NH=HNO+NO$	1.00E+11	0.5	16.6
18	$NO_2+NH_2=N_2O+H_2O$	2.03E+17	-1.7	0
19	$NH_3+H=NH_2+H_2$	5.42E+05	2.4	41.5
20	$NH_3+NH_2=N_2H_3+H_2$	7.94E+11	0.5	90.2
21	$N_2H_2+O=NNH+OH$	1.00E+11	0.5	0
22	$N_2H_2+NH_2=NH+N_2H_3$	1.00E+11	0.5	141.3
23	HCN+O=NCO+H	8.45E+05	2.1	25.6
24	HCN+O=NH+CO	3.19E+05	2.1	25.6
25	HCN+O=CN+OH	2.22E+05	2.1	25.6
26	HCN+OH=HOCN+H	5.85E+04	2.4	52.3
27	HCN+OH=HNCO+H	1.98E-03	4	4.2
28	$HCN+CN=C_2N_2+H$	3.80E+07	1.6	0.4
29	$HNCO+H=NCO+H_2$	2.05E+14	-0.3	84.7
30	$O+NH_2=NH+OH$	6.90E+11	0.3	-0.8
31	$O+NH_2=HNO+H$	8.93E+14	-0.5	1.4
32	O+NNH=NH+NO	1.65E+14	-0.2	-4.2
33	O+HNO=OH+NO	5.01E+11	0.5	8.3
34	OH+NH=HNO+H	1.00E+12	0.5	8.3
35	$OH+NH=N+H_2O$	5.01E+11	0.5	8.3
36	$OH+NH_2=>O+NH_3$	1.99E+10	0.4	2.1
37	$OH+NH_2=NH+H_2O$	5.01E+11	0.5	8.3
38	$N+NH=N_2+H$	6.31E+11	0.5	0
39	N+NCO=NO+CN	2.77E+18	-1	72.2
40	$NH+NH_2=N_2H_2+H$	1.51E+15	-0.5	0
41	$NH+NNH=N_2+NH_2$	2.00E+11	0.5	8.3
42	$NH_2+M=NH+H+M$	7.91E+23	-2	382.4
43	$NH_2+HNO=NH_3+NO$	5.01E+11	0.5	4.2
44	$NNH+M=N_2+H+M$	2.50E+13	0.5	12.8

Note: Formulas with notation R in above reactions means they are radicals and obtained in the primary mechanism. For example; R_1H is a hydrogen radical, R_{21}C3H7 is 1-propyle radical and $R_{20}C_4H_9$ is the 1-butyle radical etc. M is third body component and formulas with Z denotes the alkene leading by metathesis to an allylic radical which can decompose by breaking a (C-C) bond)

Table 3. Simulation inputs for combustion analysis.

Test Engine Specification *(Installed in 4-Stroke 3-wheeler Automobile)*		Initial Reactants (Natural Gas) Composition	
Parameters	Values	Component	Mole Fraction
Compression Ratio	10.0	CH_4	0.888
Engine Displaced Volume (cm^3)	63	C_2H_6	0.012
Engine Speed (rpm)	5000	C_3H_8	0.003
Connecting Rod to Crank Radius Ratio	1.632	CO_2	0.026
Cylinder Bore Diameter (cm)	63	N_2	0.071



(a)

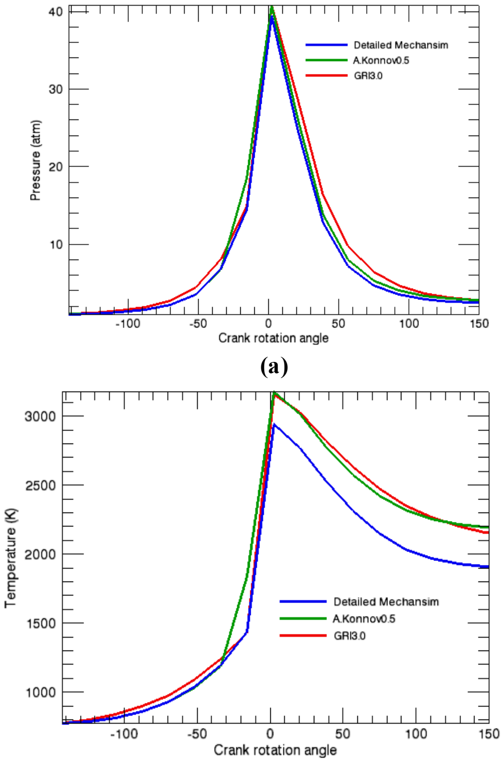
(b)

(c)

Figure 1. Comparison of Molar Conversion of Inlet Gas Mixture at P_{in}=1.0 atm, T_{in}=2,000°C and φ=1.0 for mechanism (a) GRI 3.0, (b) Konnov 0.5 and (c) proposed detailed Mechanism.

the lower species fractions. During the expansion and exhaust strokes, profiles show the occurrence of equilibrium in the product species of CO_2 and H_2O. The product species profile predict that the proposed mechanism exhibit the closer combustion cycle behavior with the GRI 3.0 and predicts lower fraction of the species than both reference mechanisms (GRI 3.0 and Konnov 0.5). Each mechanism dictates that CO_2 and H_2O are formed as rapidly as fuel and oxygen are consumed. The deviation in reactants and products profiles occurs because of the number of reaction steps and intermediates in each mechanism. Although there is a discrepancy in the species profiles, the proposed mechanism produces acceptable agreement with GRI 3.0 mechanism (reference detailed mechanism).

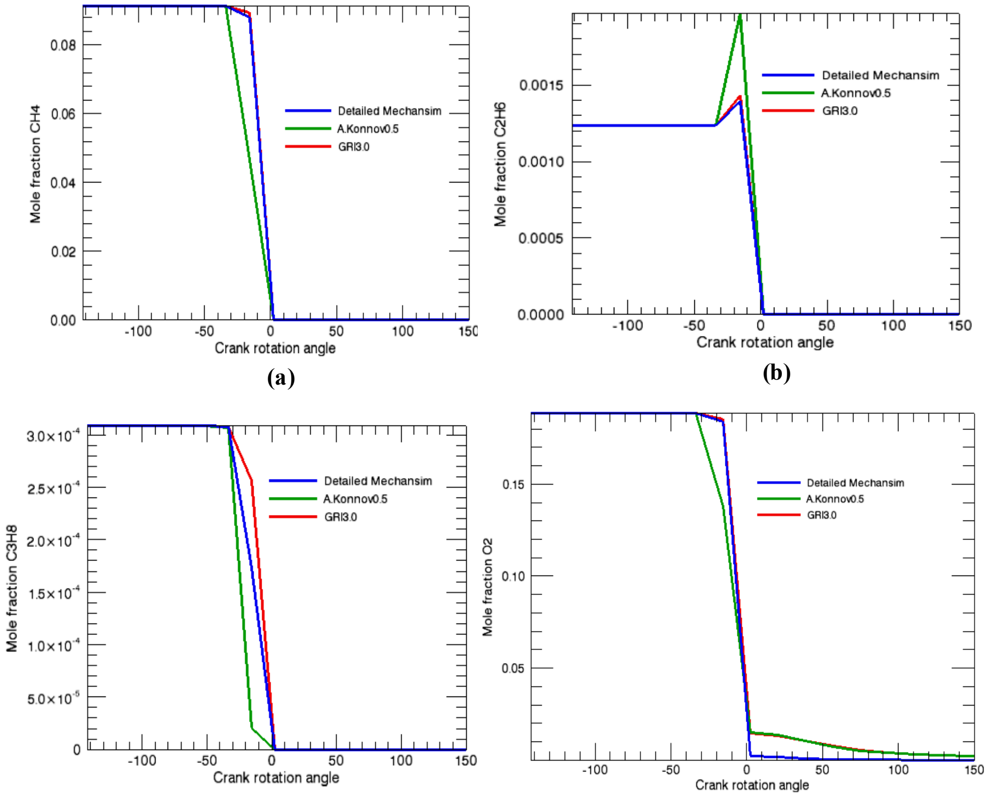
Figure 5 compares the prediction of emissions of major pollutant species (CO, NH_3, NO, NO_2, etc.) for each mechanism. The proposed mechanism produces lower fraction of CO than both GRI 3.0 and Konnov 0.5 mechanism.



(a)

(b)

Figure 2. Predicted pressure and temperature profiles for P_{ini}= 1.0 atm T_{ini}=500°C and Equivalence Ratio φ =1.0.



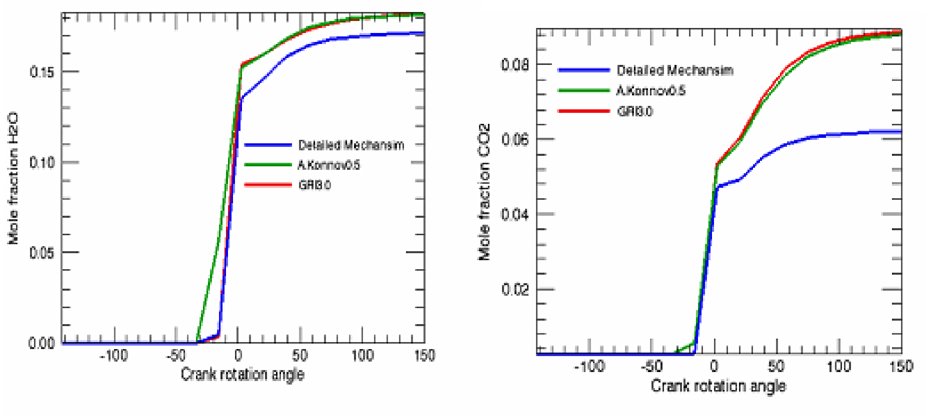
(a)

(b)

(c)

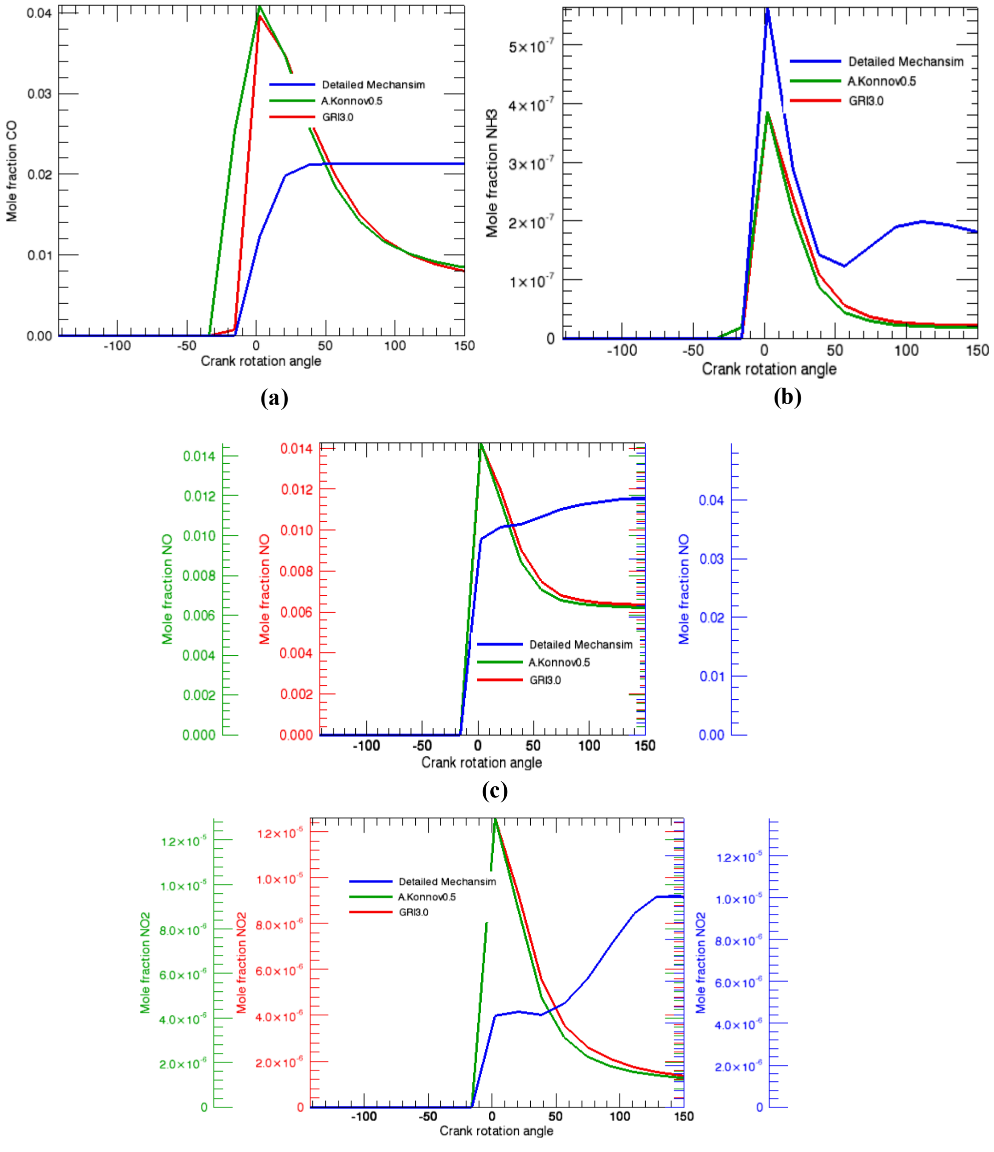
(d)

Figure 3. Comparison of fuel species and oxidizer profiles for adiabatic and stoichiometric conditions (P_{ini}= 1.0 atm T_{ini}=500°C and equivalence ratio φ =1.0).



(a) (b)

Figure 4. Major combustion product species profiles for equivalence ratio of φ =1.0.



(a) (b)

(c)

(d)

Figure 5. Pollutants formation (CO, NH_3, NO, and NO_2) profiles for stoichiometric conditions (φ =1.0).

The predicted NO and NO_2 profiles show the formation after the combustion of fuel by the proposed mechanism and deviate significantly from those of the reference mechanisms. On whole, the mean fractions of each pollutant for the proposed mechanism is overpredicted but peak fraction are lower than the reference detailed mechanism (GRI 3.0 and Konnov 0.5). This could be due to the fact that in the proposed mechanism CO reacts by more multitude pathways than GRI 3.0 and Konnov 0.5 mechanisms.

In our experimental setup, exhaust composition and pressure were measured. The cylinder pressure was measured directly by the using a pressure transducer (Kistler, Model 603B1) combined with a charge amplifier (Kistler, Model 5004). Pressure data was recorded using NUDAC-TK version 2.0, a program for data acquisition and processing. The original data files contained cylinder pressure at crank angles 0°–720°. Each of three large files, about 969 mega bites each, contained about 9,000 combustion cycles. The engine speed, air/fuel ratio, and throttle setting were all held constant throughout the data collection period. The collected pressure data was plotted at various engine speeds. During pressure measurements, intake air pressure had a value of 38 kPa. The data for major species like CO_2, CO, H_2O were measured using online emission analyzer (Testo 350XL Model).

From the experimental data, the fraction of exhaust species (CO_2, H_2O, and CO) is determined at various operating engine speeds (Figure 6). Each plot show close agreement between measured data and simulation results obtained by CHEMKIN 4.1.1 for proposed mechanism. The simulation predicts the closer cylinder pressure at lower engine speed.

Correlation coefficient of simulation data of each of three mechanisms with the experimental data was calculated. The simulation data of proposed mechanism shows a strong relation with experimental results for major combustion products (CO_2, H_2O, and CO) and resulting values of correlation coefficients were 0.9353, 0.9776, and 0.9756, respectively, as shown in Table 4. Based upon the results, it can be concluded that the proposed mechanism predicts well correlated results with the experimental data for the species profiles of H_2O, CO_2, and CO except the pressure profile, which could be due the reaction involvement in the formation of the species. The referenced mechanisms show the greater deviation with the experimental results.

4. Conclusions

A major focus of this study was to develop a detailed kinetic mechanism to study the oxidation at in IC engine. The performance of this proposed reaction scheme was studied at both fuel lean (φ<1.0) and rich conditions (φ>1.0) with a range of fuel inlet condition of temperature (T_{ini}=400-5,000°C) and pressure (P_{ini}=1.0 to 12 atm). Although discrepancies in various simulation profiles exist, the proposed kinetic mechanism showed good concordance with the GRI 3.0

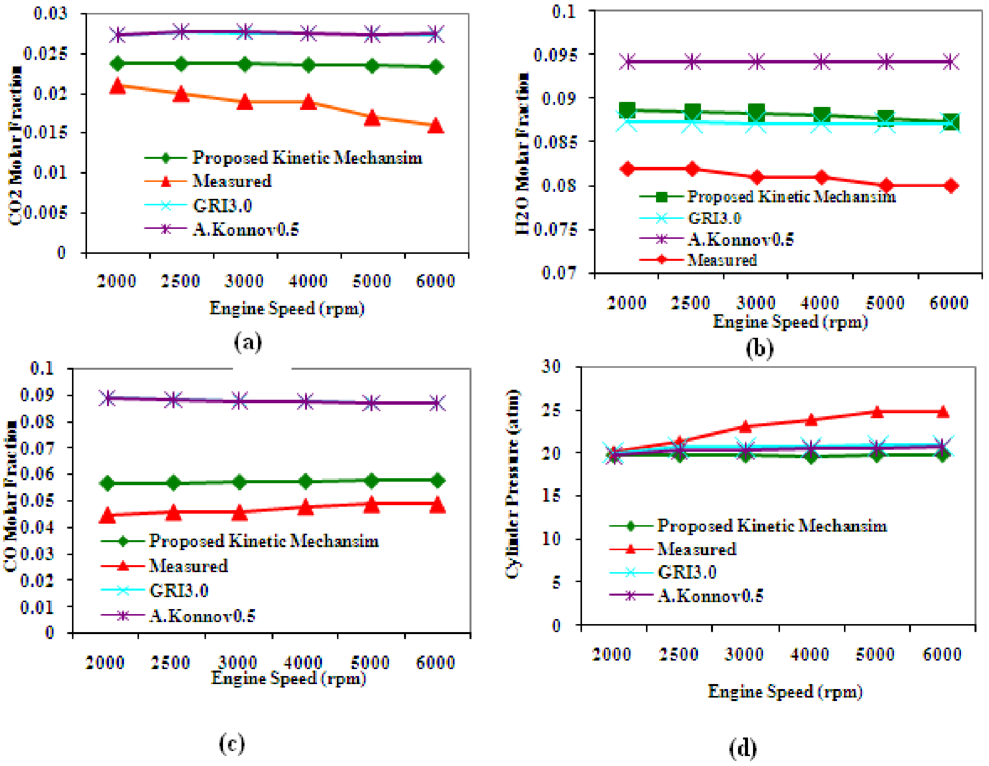


Figure 6. Effect of engine speed (rpm) on major product species fractions (CO_2, H_2O, CO) and cylinder pressure.

Table 4. Correlation coefficients of kinetic mechanisms with experimental data.

Mechanism Type	Correlation Coefficient			
	H_2O	CO_2	CO	Pressure
Proposed kinetic mechanism	0.9367	0.9753	0.9775	0.1616
GRI 3.0	0.8817	0.1933	-0.963	0.8476
Aknnov 0.5	0.6324	0.1988	-0.9658	0.9192

mechanism. The experimental results especially in prediction of combustion pressure, temperature and major species profiles showed close agreement with the both reference mechanisms. Higher pollutants molar fractions (mean) are predicted using the proposed mechanism compared to both reference mechanisms (GRI 3.0 and Konnov 0.5). Based upon the simulation results and limited experimental data, the proposed kinetic model is a competitive candidate of natural gas combustion in IC engine.

Acknowledgement

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Nomenclature

T_{ini} = Initial Temperature [°C]
P_{ini} = Initial Pressure [atm]
CO = Carbon monoxide
CO_2 = Carbon dioxide
NO_x = Oxide of nitrogen (as NO, NO_2, N_2O)
k = Reaction rate coefficient
A = pre-exponential factor [mol-cm-sec-K]
Ta = Activation temperature [K]
b = temperature exponent of pre-exponential factor
E = activation energy of chemical reaction [cal/mole]
R = ideal gas constant [J-$mol^{-1}K^{-1}$]
Φ = equivalence ratio

References

Barbé, P. Battin-Leclerc, F. and Côme, G.M. 1995. Experimental and Modelling Study of Methane and Ethane Oxidation between 773 and 1573 K, Journal of Chemical Physics. 92, 1666-1692.

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

Côme, G.M., Warth, V., Glaude, P.A., Fournet, R., Battin-Leclerc, F. and Scacchi, G. 1996. Twenty-Sixth International Symposium on Combustion. The Combustion Institute, Pittsburgh, U.S.A.

Glaude, P. A., Warth, V. R., Fournet, F. Battin-Leclerc, G. M. Coˆme, and G.Scacchi, 1997. Bulletin des Sociétés Chimiques Belges, 106, 343

Glaude, P. A., Warth,V. R., Fournet, Battin-Leclerc, F. Scacchi, G. and Coˆme, G. M. 1998. Modeling of the Oxidation of *n*-octane and *n*-decane using an Automatic Generation of Mechanisms, International Journal of Chemical Kinetics, 30, 949.

Glaude P.A., Batttin-Leclerc, F. Fournet, R., Warth, V.and Come,G.M. 2000. Construction and Simplification of a Model for Oxidation of Alkanes, Combustion and Flame, 122, 451-462.

Gregory P. Smith, M. David 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, and Zhiwei Qin. 2011 http://www.me.berkeley.edu/gri_mech/

Kee R. J., F. M. Rupley, J. A. Miller, M. E. Coltrin, J. F. Grcar, E. Meeks, H. K. Moffat, A. E. Lutz, G. Dixon-Lewis, M. D. Smooke, J. Warnatz, G. H. Evans, R. S. Larson, R. E. Mitchell, L. R. Petzold, W. C. Reynolds, M. Caracotsios, W. E. Stewart, P. Glarborg, C. Wang, C. L. McLellan, O. Adigun, W. G. Houf, C. P. Chou, S. F. Miller, P. Ho, P. D. Young, D. J. Young, D. W. Hodgson, M. V. Petrova, and K. V. Puduppakkam, 2007. CHEMKIN Release 4.1.1, Reaction Design, San Diego, CA.

Konnov, A. 2000. Detailed reaction mechanism for small hydrocarbons combustion, Release 0.5. http://homepages.vub.ac.be/~akonnov/(2000)

Miller, J. A., and C.T Bowman, 1989. Mechanism and Modeling of Nitrogen Chemistry in Combustion, Progress in Energy and Combustion Science, 15, 287-338.

Muller, C., Michel V., Scacchi, G. and Côme,G.M. 1995. A Computer Program for the Evaluation of Thermochemical Data of Molecules and Free Radicals in the Gas Phase, Journal of Chemical Physics, 92, 1154.

Warnatz, J. 1983. The Mechanism of High Temperature Combustion of Propane and Butane, Combustion Science and Technology. 34, 177-200.

Warnatz, J. 1993. In Reduced Kinetics Mechanisms for Applied in Combustion Systems; Peters, N. and B. Rogg Eds., Sringer-Verlag, New York.

Walker R.W. and C. Morley, 1997. Basic Chemistry of Combustion in Comprehensive Chemical Kinetics; Low-Temperature Combustion and Auto-Ignition, (M.J. Pilling ed.), Vol.35, Elsevier, Amsterdam.

Warth, V., N. Stef, P. A. Glaude, F. Battin-Leclerc, G. Scacchi, and G. M. Côme, 1998. Computer-Aided Derivation of Gas-Phase Oxidation Mechanisms: Application to the Modeling of the Oxidation of *n*-Butane, Combustion and Flame, 114, 81-102.