Comparative Study of Kinetic Mechanisms for Natural Gas Combustion in an Internal Combustion Engine

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ABSTRACT

This study mainly focused on the combustion mechanisms of natural gas (of major constituent were methane, ethane, etc) in an ice (Internal Combustion Engine). Both detailed and reduced mechanisms were implemented in CHEMKIN 4.1.1 for 0-D closed IC (Internal Combustion) engine module. In present study, two detailed (GRIMECH 3.0 and UBC MECH) and two reduced (One step and four step) kinetic mechanisms were tested on three engine geometries. The combustion due to these mechanisms was characterized by plotting various parametric profiles like temperature, pressure and major species. Three mechanisms (4-step, GRIMECH3.0, & UBC MECH) successfully showed combustion while one step global mechanism was unable to predict any combustion reaction. Detailed mechanisms predicted the maximum pressure (atm) of 70, 40 and 30 for each of Designs I-III, respectively. The maximum chamber temperature with these mechanisms was predicted above 2000K. Four step reduced mechanism predicted maximum cylinder pressure of 90 atm for Design-II and III and 300 atm for Design-I. Maximum cylinder temperature was of 7000K for Design I and 5000K for each of Design-II and III, respectively. GRIMECH successfully predicted the formation of pollutants like CO (Carbon Monoxide) and NO_x while 4-step mechanism only predicted CO and unable to predict NO_x formation.

Although, there were some discrepancies among the simulation results for each of the engine design but on the whole it can be concluded that GRIMECH3.0 mechanism was favorable and successfully predicted the pollutants formation during combustion in the IC engine chamber.

Key Words: **Reduced Mechanism, Detailed Mechanism, Combustion, Methane, IC Engine.**

1. INTRODUCTION

The combustion of hydrocarbon fuel removes O_2 from the atmosphere and releases equivalent amount of H_2O and CO_2 always with trace amounts of numerous other compounds including hydrocarbons (CH_4, C_2H_2, C_6H_6, CH_2, CHO, .. . etc.), CO, nitrogen oxides (NO, N_2O), reduced nitrogen (NH_3 and HCN), sulfur gases (SO_2, OCS, CS_2), halo-carbons (CHC_l and CH_3Br), and particles [1].

The kinetics of the combustion process in an internal combustion engine can be understood easily if we know how it work during its operation. Heywood [2] elaborated the engine operation briefly. Fig. 1 show a light duty 4-stroke engine in which a premixed fuel-air mixture CNG-Air) enters the engine during the intake stoke, which starts when the piston is at TC (Top Center) and ends with the piston at BC (Bottom Center), and draws fresh mixture

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into the cylinder. To increase the mass inducted, the inlet valve open shortly before the intake stroke starts and closes after it ends. The mixture is compressed to small fraction of its volume in the compression stroke. Towards the end of the compression stroke, combustion is initiated by the spark plug typically. As the combustion progresses, the cylinder pressure rise more rapidly when both intake and exhaust valves closed. The power stroke, or expansion stroke starts with the piston at TC and ends at BC as high temperature, high pressure, gases push the piston down and force the crank to rotate. During an exhaust stroke, the remaining burned gases exit the cylinder; first because the cylinder pressure may be substantially higher than the exhaust pressure; then as they are swept out by the piston as it, moves towards TC. When the piston approaches the TC, the inlet valve opens. Just after TC, the exhaust valve closes and the cycle starts again.

Fig. 2 shows the sequences of events as function of crank angle. Literature dictates that the crank angle is useful independent variable because most of the engine processes occupy almost constant crank angle intervals over a wide range of engine speeds. It is clear from the Fig. 2 that the combustion started between 10 and 40 degree. During this event, a turbulent flame develops from the spark discharge which propagates across the mixture of air, fuel and residual gas in the cylinder and extinguishes at the combustion chamber wall. The duration of this burning process varies with engine design and operation, but is typically 40-60 crank angle degrees.

Fig. 3 shows the path by how the flame propagates. Thin zone of intense chemical reaction propagates through the unburned fuel-air mixture and this thin reaction zone is commonly referred to as a flame. Behind the flame, there are the hot products of combustion and front of this flame are the hot mixture of reactants. As the flame moves across the combustion space, the temperature and pressure rises in the unburned gas. Under certain conditions, rapid oxidation reactions occur at many locations within the unburned gas leading to very rapid combustion throughout the volume [3]. When the selected fuels is CNG (Compressed Natural Gas) containing methane as major component. This CNG containing fuel mixture (CNG + unburned residues from previous cycle) promises the good thermal efficiencies comparable to those accomplished by the high compression ratios, maintaining the smoke free operation of SI (Spark Ignition) engines and producing slightly lower NO_x emissions [4]. In recent years, CNG

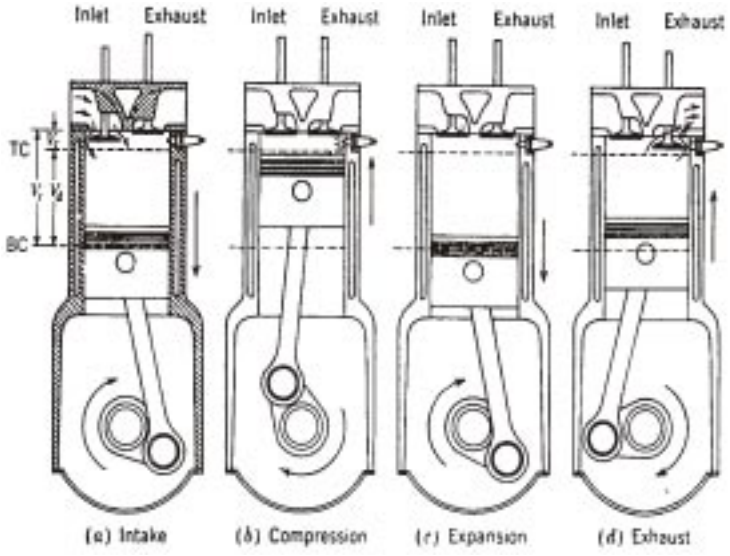


FIG. 1. SI ENGINE 4-STROKE OPERATING CYCLE (A) INTAKE (B) COMPRESSION (C) EXPANSION (D) EXHAUST

has been promoted as a promising clean fuel alternative to SI engines because of its relatively higher octane level. The growing concerns about the harmful effects of conventional fossil fuel emissions have also made the natural gas a very attractive alternative fuel to ICE due to its advantages to be environmental friendly, clean burning, economical and efficient fuel. Lean burning of CNG in SI engines has the potential to improve thermal efficiency and reduce emissions compared with the burning of gasoline. Due to its high research octane number (RON>130), CNG allows the combustion at higher compression ratio without knocking. It also offers much lower greenhouse gas emissions than those from the burning of other hydrocarbons as a result of its higher hydrogen to carbon ratio [5].

Methane, the major constituent of the CNG fuels, exhibits some unique combustion characteristic because of the unique tetrahedral molecular structure with large C^{-H} bond energies. For example, it has high ignition temperature, low flame speed and it's essentially uncreative in photochemical smog chemistry. Chemical kinetics of methane is the most widely researched and most well understood. Kaufman [6], in a review of combustion kinetics indicated that the methane combustion mechanism evolved in period of 1970-1982 from less than 15 elementary steps with 12 species to 75 elementary steps, plus the 75 reverse reactions, with 25 species. Recently, several research groups have collaborated in the creation of an optimized methane kinetic mechanism [7]. The designated mechanism is

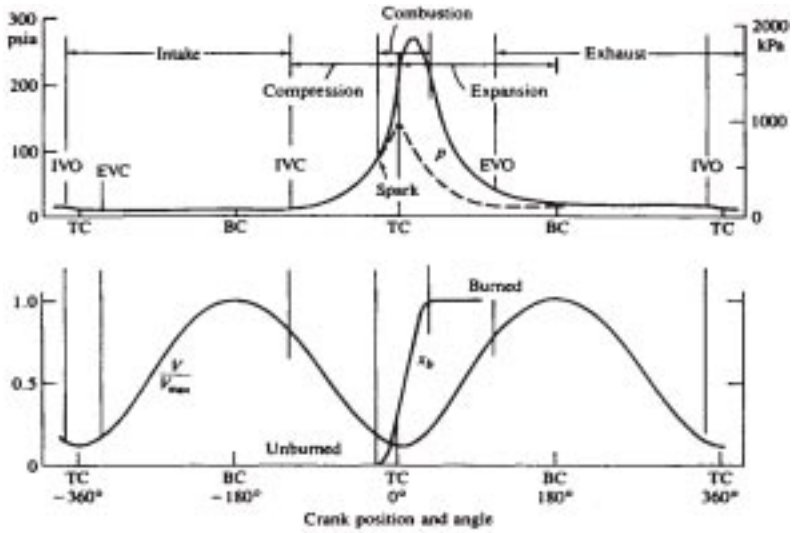


FIG. 2. SEQUENCES OF SI ENGINE CYCLE EVENTS AS FUNCTION OF CRANK ANGLE

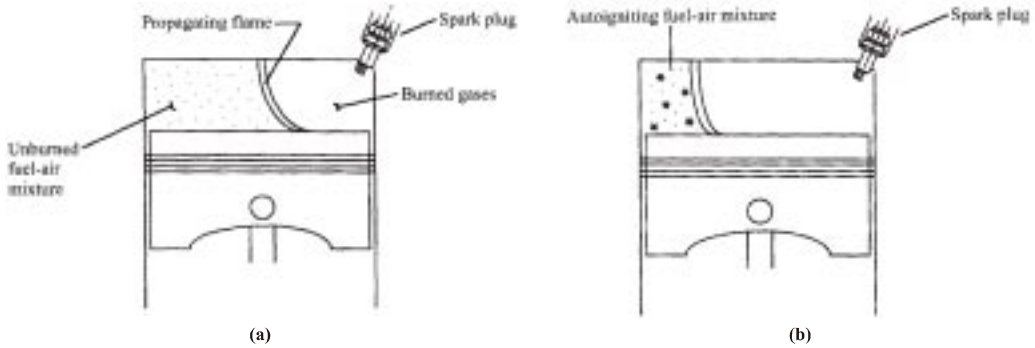


FIG. 3. CHEMICAL REACTIONS ZONES THROUGH (A) UNBURNED FUEL-AIR MIXTURE (B) AUTO-IGNITION FUEL-AIR MIXTURE

GRIMECH3.0 which is based on the optimization techniques of Frenklach, et. al. [8]. Due to versatility of this mechanism, this has been used to study oxidation of methane in an IC engine in current study and its capability of prediction of pollutants formation was investigated.

Various detailed reaction mechanisms are reported in literature [9]. They can be divided into full mechanisms, skeletal mechanisms, and reduced mechanisms. The various mechanisms differ with respect to the considered species and reactions. [10]. In literature, several mechanisms of methane combustion exist. For e example,

- For detailed mechanisms: Westbrook [11], Glarborg, et. al. [12], Miller and Bowman [13], and recently, Konnov [14], Huges, et. al. [15], and the standard GRIMECH [16].

- For reduced mechanisms: Westbrook and Dryer [17], Duterque, et, al. [18] (1-2 global reactions), Peters [19], Hutmann, et. al., [20], and Jones and Lindstedt [21] (more than 2 global reaction), Edelman and Fortune [22], and Edelman and Harsha [23] (1 global reaction with many elementary reactions; these mechanisms are called quasi-global mechanisms). All chemical models used in combustion share the same description of elementary chemical reactions, based on an Arrhenius law, leading to a rate coefficient ex pressed as $k = AT^{\beta} e^{-\frac{Ea}{RT}}$.The values of A, Ea (or Ta=Ea/R) and of the temperature-dependence coefficient β are thus reaction dependent. Based on this expression, different levels of approximation can be defined to describe the kinetics.

Both detailed and reduced methane combustion mechanisms were simulated to study the combustion phenomena in ICE. Four mechanisms were implemented in IC module of CHEMKIN software. Various profiles for temperature, pressure and major species produced as a result of combustion were successfully generated by simulation tool to characterize the process. Based upon the simulation profiles, an appropriate mechanism which predicts the formation of pollutants like NO_x, CO in engine cylinder was identified.

2. MATERIALS AND METHOD

2.1 Over View of Simulation Software

CHEMKIN is a powerful set of software tools for solving complex chemical kinetics problems. It is used to study reacting flows, such as those found in combustion, catalysis, chemical vapour deposition, and plasma etching. CHEMKIN 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 (Fig. 4).

CHEMKIN provides a broad capability that addresses needs of both non-expert and expert users [26]. The IC module of the software is based upon as:

$$\frac{d\left(\frac{V}{Vc}\right)}{dt} = \Omega\left(\frac{C-1}{2}\right)\sin\theta\left[\frac{1+\cos\theta}{\sqrt{R^2-\sin^2\theta}}\right]$$

where V is the cylinder volume and θ is the crank angle.

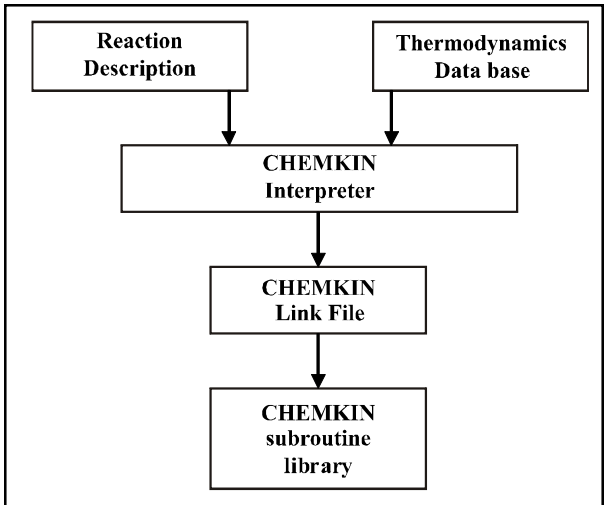


FIG. 4. CHEMKIN PACKAGE WORKING FLOW DIAGRAM

The IC model is for 0-D closed system, the simulation is only valid within the time period when both intake and exhaust valves are closed. Conventionally, engine cylinder events are expressed in crank rotation angle relative to the TDC (Top Dead Center). The IVC (Intake Valve Close) time of our test engine is 142 degrees (crank angle) before TDC (BTDC).

In this study, we set our simulation starting crank angle to -142 degrees in the software. Other simulation parameters we used in the software simulation were cylinder cycles end time as 0.043 sec or for 257 degrees crank angle to 115 degrees after TDC. The gas mixture pressure and temperature at IVC are 107911 Pa (or 1.065 atm) and 550 K, respectively.

2.2 Tested Kinetics Mechanisms

Following four mechanisms were investigated for methane combustion in ICE (Table 1).

$$k = AT^{\beta} e^{-\frac{E_a}{RT}}$$

Where, A, β, Ta (Ta= Ea/T) are the parameters for Arrhenius Law defined .

Two of these mechanism are the Detailed mechanism (GRIMECH 3.0 and UBC Mech) and other two (Duterque & Jones and Lindstedt) are reduced ones. Remember that two types of data files are required to run Chemkin, Mechanism data files and thermodynamics data files. The details of mechanism and thermodynamics files can found in references at [7, 18, 27].

2.3 Tested Engine Specifications

The above mentioned mechanisms were simulated and tested using Chemkin Kinetic simulation module for methane combustion study in ICE. Three different engines designs were selected in this study. These designs were selected to study the effect of engine geometrical parameters on the combustion. The other IC engine standard designs may be suggested to be studied. Following three reference engines design with the given specifications were tested given in Table 2.

These engine designs were selected only because these were tested in the similar studies [5, 26, 28]. This was the only simple criteria for selection of these designs for this study.

2.4 General Input Parameters

The heat transfer correlation coefficients (denoted by a, b and c) and Woschni Correlation coefficients (dented by C_{11}. C_{12} and C_2), wall temperatures etc. were the additional parameter to be defined to run the software and were taken from reference at [2] Table 3.

2.5 Composition of Initial Gas Mixture

The composition of the initial gas mixture is a combination of natural gas, air, and EGR (Exhaust Gas Recirculation) gas and is given in Table 4.

TABLE 1. TESTED MECHANISMS OF METHANE COMBUSTION

No.	Mechanism Type	Reactions	Arrhenius Parameters		
			A	β	Ta(K)
1.	Global One-Step Reaction [18]	$CH_4+2O_2 = CO_2+2H_2O$	1.50E+13	0.0	20000.0
2.	Four Step Reaction Mechanism of Jones and Lindstedt [21]	(i) $CH_4+1/2O_2 = CO+2H_2$	4.40E+14	0.0	24000.0
		(ii) $CH_4+H_2O = CO+2H_2$	3.00E+1	0.0	24000.0
		(iii) $H_2+1/2O_2 <=> H_2O$	2.50E+1	-1.0	32000.0
		(iv) $CO+H_2O <=> CO_2+H_2$	2.75E+12	0.0	16000.0
3.	Standards Detailed mechanism GRIMECH 3.0 (53 Species and 325 Reactions) [7]				

3. RESULTS AND DISCUSSION

In this study, four kinetic mechanisms (listed above) of methane combustion in engine cylinder were studied. Theses mechanisms were simulated for various engine designs (Table 1) having different like geometrical parameters (displacement volume, clearance volume, bore diameters, connecting rod to crank radius ratio etc.), operating parameters crank speed, gas mixture inlet temperature, pressure etc. GRI 3.0 thermodynamic data was used for the reaction mechanisms of Global One-Step Reaction (Duterque), 4-step of Jones and Lindstedt, and GRIMECH 3.0 in each simulation design.

In this section, four chemical kinetics schemes for predicted temperature, pressure, species and possible pollutants CO and NO_x were compared and discussed for each selected engine design.

3.1 Temperature and Pressure Profiles

Fig. 5(a-c) show the pressure profiles for engine Design-I, II and III for the selected reaction mechanisms (Duterque, Jones and Lindstedt, UBC Mech and GRIMECH 3.0), respectively versus crank angle. Each profile clearly show that the peak cylinder pressure occur close to TC. At TC, this build up of pressure is closely related to the rate of burning of the premixed fuel mixture. There is early built up of pressure with reduced mechanism (Duterque, Jones and Lindstedt) than detailed mechanisms (UBC MECH and GRIMECH 3.0). This difference shows that there is early start of combustion with reduced mechanisms. If we look at the crank rotation angle on X-axis of each graph, the combustion with reduced mechanism start 10-13° before TC than the

TABLE 4. COMPOSITION OF INITIAL GAS MIXTURE

Species	Mole Fraction
CH_4	0.035
C_2H_6	0.0018
C_3H_8	0.0012
O_2	0.1824
CO_2	0.0326
H_2O	0.0609
N_2	0.6861

TABLE 2. TEST ENGINES SPECIFICATIONS

Parameters	Design-1	Design-II	Design-III
Compression Ratio	16.5	10.3	10.0
Cylinder Clearance Volume (cm^3)	103.3	-	1530
Engine Speed (rpm)	1000	1000	1000
Connecting Rod to Crank Radius Ratio	3.714286	-	2.97729
Cylinder Bore Diameter (mm)	120.65	80	102
Displacement (cm)	-	1679	-

TABLE 3. GENERAL INPUT PARAMETERS

Parameters		Values
Heat Transfer Correlation Coefficients	Coefficient-a	0.035
	Coefficient-b	0.71
	Coefficient-c	0.0
Woschni Correlation Coefficients	C11	2.28
	C12	0.308
	C2	3.24
Wall Temperature (K)		400

detailed ones. The cylinder pressure for Design-II and III looked close due to nearly similar engine for geometrical parameters and maximum pressure generated up to 80 atm (for 4-step reduced mechanism) in the chamber whiles in case of Design-I, it built up to 300 atm for 4-step mechanism. This looks over predicted pressure for combustion chamber. This difference for design I is because of high compression ratio. This high pressure for 4-step mechanism results in the maximum conversion of the fuel and ultimately high combustion efficiency.

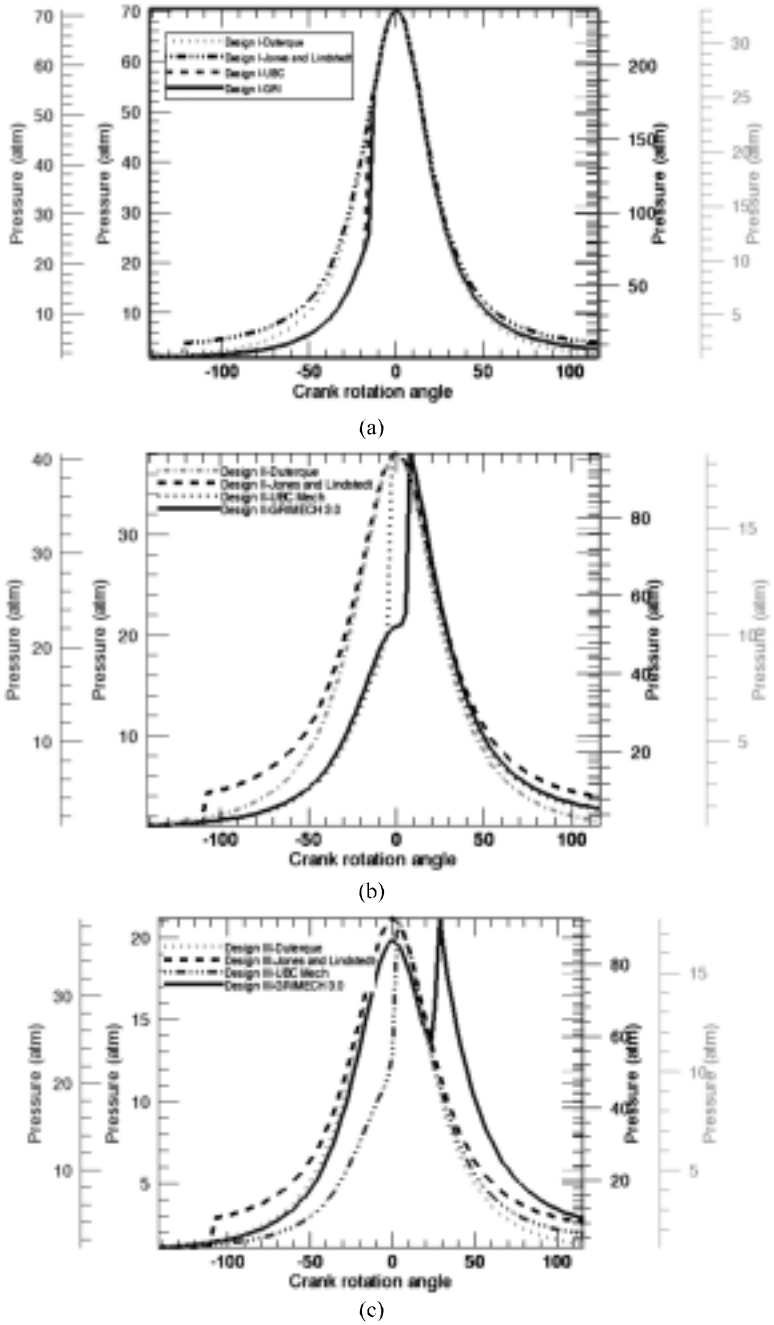


FIG. 5. PREDICTED PRESSURE PROFILES OF DESIGN-I (A) DESIGN-II (B) AND DESIGN-III (C)

Each pressure profile clearly show that global one step mechanism fails to predict the appropriate cylinder pressure. The detailed mechanisms show similar prediction of pressure in case of Design-I and show some discrepancies for Design-II and III as in Fig. 6(b-c). In Fig. 5(c), there were unexpected trend of curve with GRIMECH 3.0 mechanism of there is decrease of pressure after TC and at nearly, 20° of crank angle, again pressure increases. This might be correlated with the occurrence of the knocking during the combustion and unexpected chemical reactions due to formation or destruction of secondary radicals or molecules.

Temperature profiles, as shown in Fig. 6(a-c) support the argument that there is early start of combustion with reduced mechanisms than with detailed mechanisms. When we look at curves for detailed mechanisms like GRIMECH 3.0 and UBC Mech in Fig. 7(c), combustion with UBC Mech mechanism starts earlier than GRIMECH 3.0. The combustion with 4-step mechanism of Jones & Lindstedt start too earlier during compression after IVC (Inlet Valve Close) and peak temperature reaches nearly 5000K for Design-II and III while model predicts the temperature of nearly 7000K for Design-I.

Each of Fig. 6(a-c) shows that there is close variation behavior of temperature profiles for detailed mechanisms in Design-I and II and wide difference profiles between reduced mechanisms of One-step Global mechanism of Duterque and 4-step mechanism of Jones & Lindstedt. The reason of this difference is that the chemistry in reduced mechanisms is infinitely abrupt. If we look the over all behavior of profiles for each engine geometry, nearly similar trend can be observed for each of the considered kinetic mechanism.

3.2 Major Combustion Species Profiles

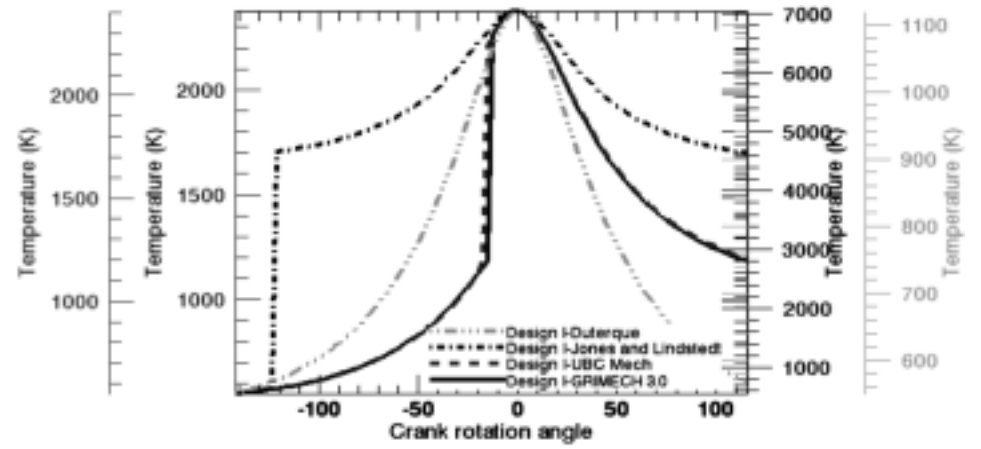
Figs. 7-9 illustrates the major species profiles of CH_4, CO_2, O_2 and H_2O for the stoichiometric condition for Design-I, II and III, respectively. Each of the plots is of mole fraction vs crank angle.

If we look at the profiles of CH_4, CO_2 and H_2O, 4-step mechanism predicts early reactions for each engine Design-I, II and III. There is some discrepancies of CO_2 and H_2O profiles between detailed and reduced mechanism. The detailed mechanisms show similar behaviors for design I and there is the indication little early burning with UBC MECH detailed mechanism with engine Design-II and III. In Design-I, CO_2 and H_2O profiles with reduce mechanism (Jones & Lindstedt) indicate that both species are produced suddenly, declining trend indicate the consumption in intermediate reaction paths and then produced as combustion products. We can see similar trend of H_2O profile for engine Design-II and III. CO_2 profile of Design-I deviate from those of Design-II and III during the initial stages of combustion.

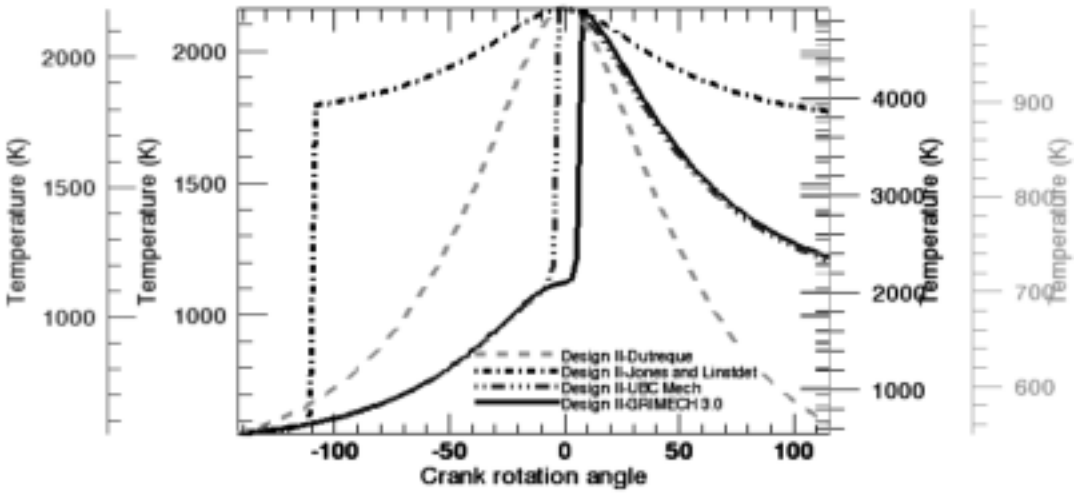
3.3 Pollutants Emissions Profiles

It is clear from Fig. 10 that, both detailed mechanisms (GRIMECH 3.0 and UBC Mech) and 4-steps mechanism predict CO in each design of IC engines. Each profile also proves the evidence that reduced mechanisms give early start of ignition. Reduce mechanism show similar trend for each engine design. CO profiles due to detailed mechanism for Design-II and III indicate suddenly formation of CO and show similar behavior with little difference of early combustion with UBC Mech mechanism.

Fig. 11 shows that detailed mechanism (GRIMECH 3.0) predicts the formation of oxides of nitrogen (N_2O, NO and NO_2). Each profile illustrate that N_2O is formed immediately during the combustion and then its fraction decreased. The reason for this production of N_2O production is oxidation N_2 with O_2 and the further conversion into NO_2 and N_O. There is rapid formation of N_O than NO_2.



(a)



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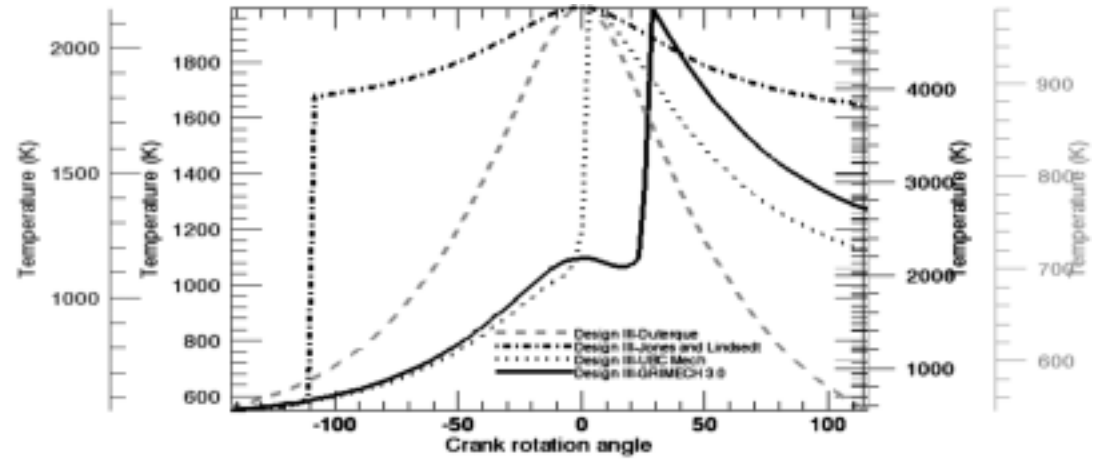


(c)

FIG. 6. PREDICTED TEMPERATURE PROFILES OF DESIGN I 0, DESIGN-II (B) AND DESIGN-III (C)

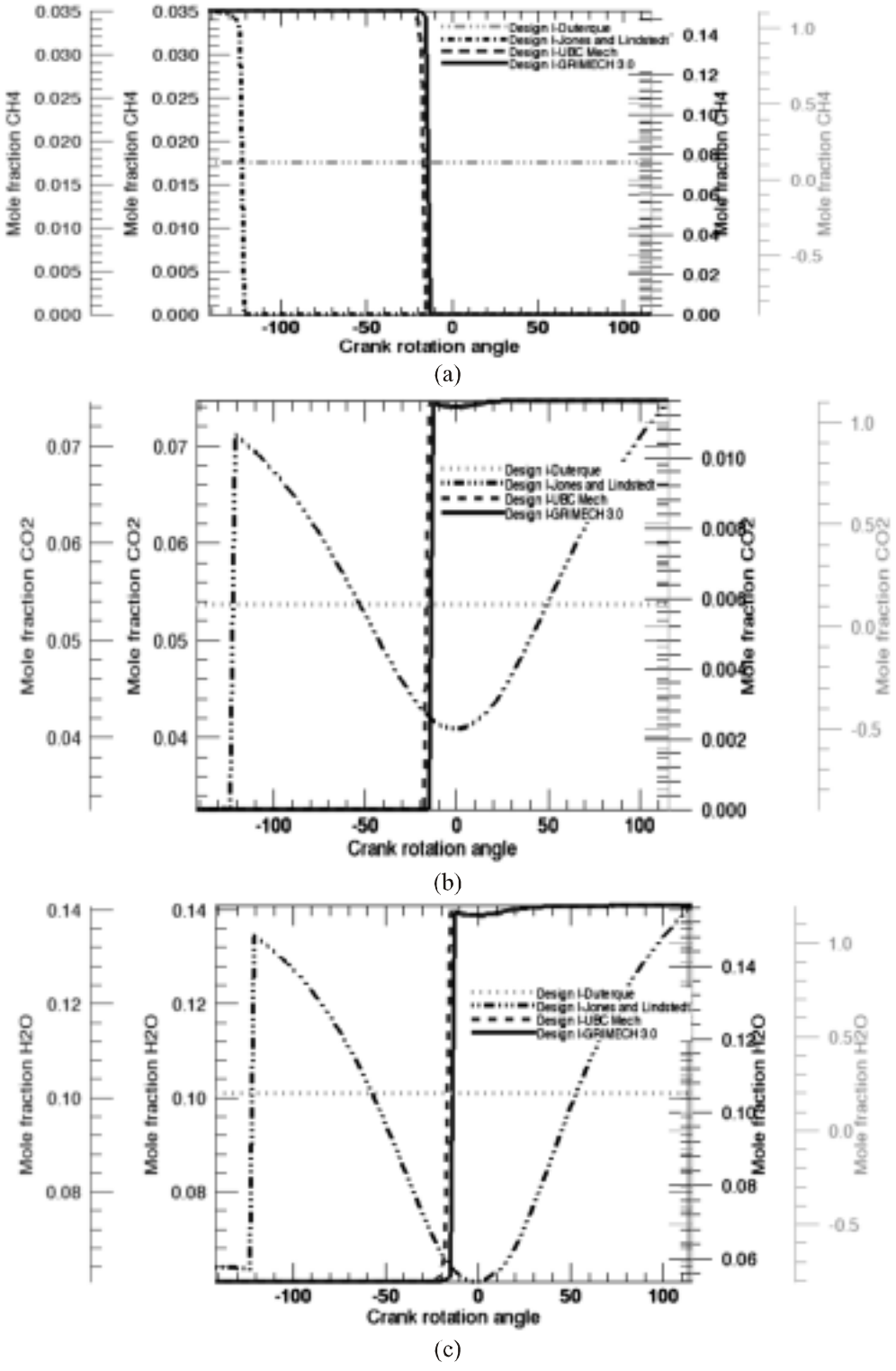
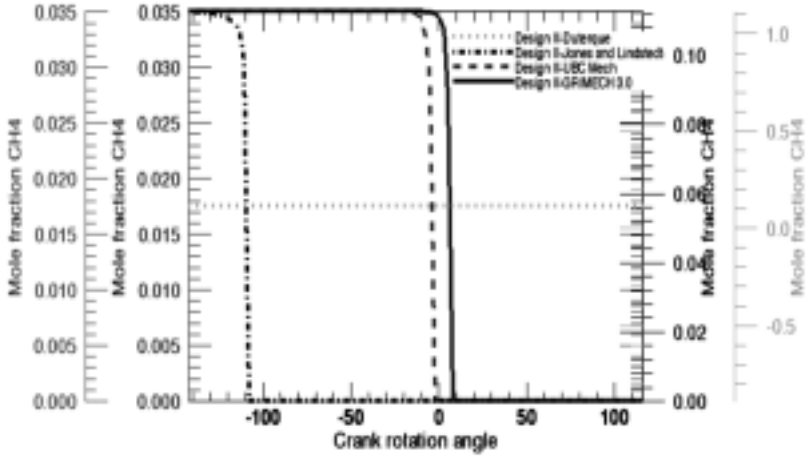


FIG. 7. COMBUSTION PRODUCTS PROFILES FOR DESIGN-I AT STOICHIOMETRIC CONDITION (Φ=1)



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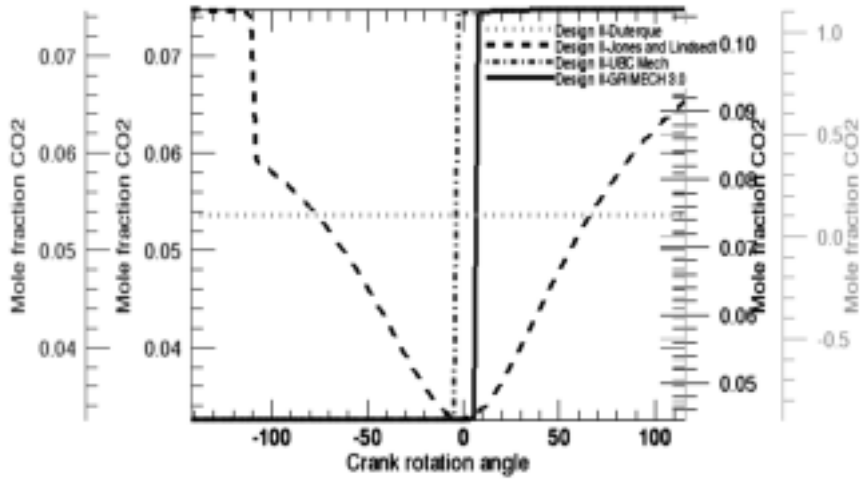

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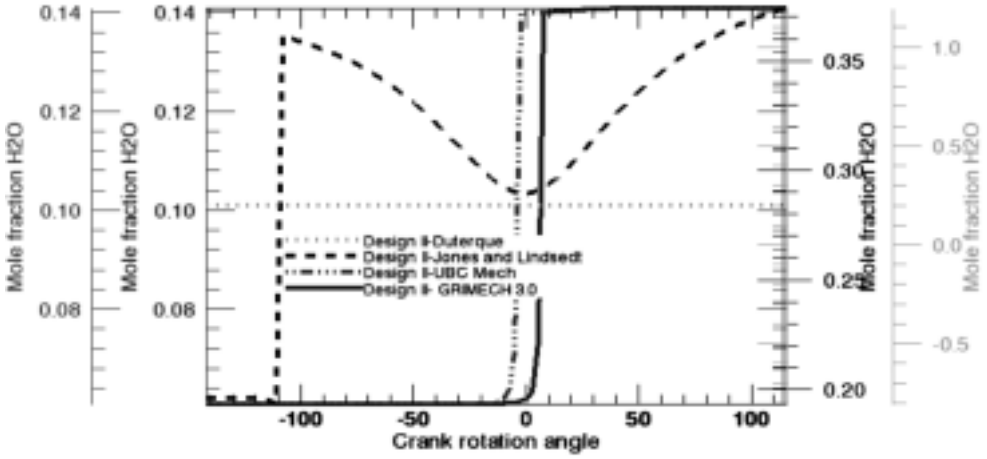
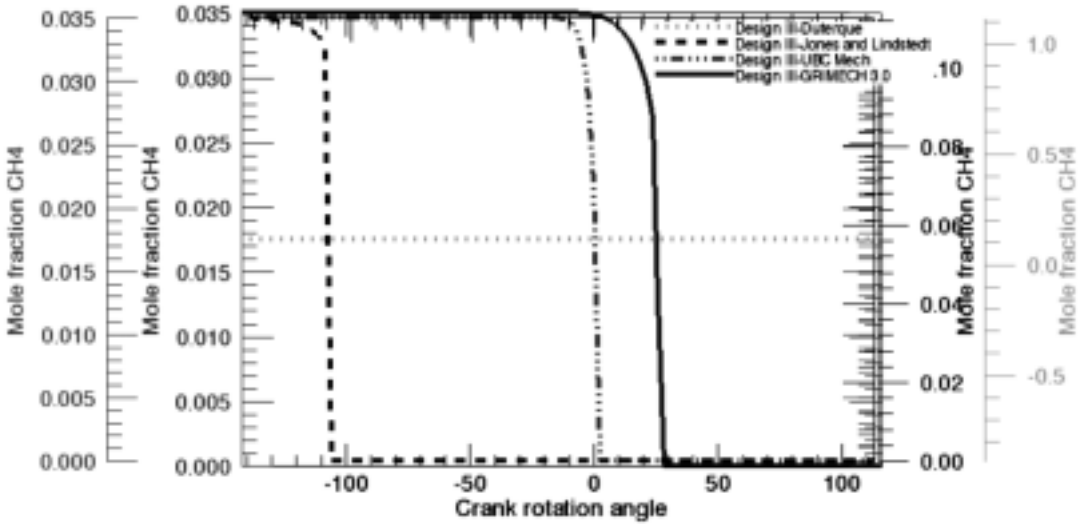


(c)

FIG. 8. COMBUSTION SPECIES PROFILES FOR DESIGN-II AT STOICHIOMETRIC CONDITION (Φ=1)



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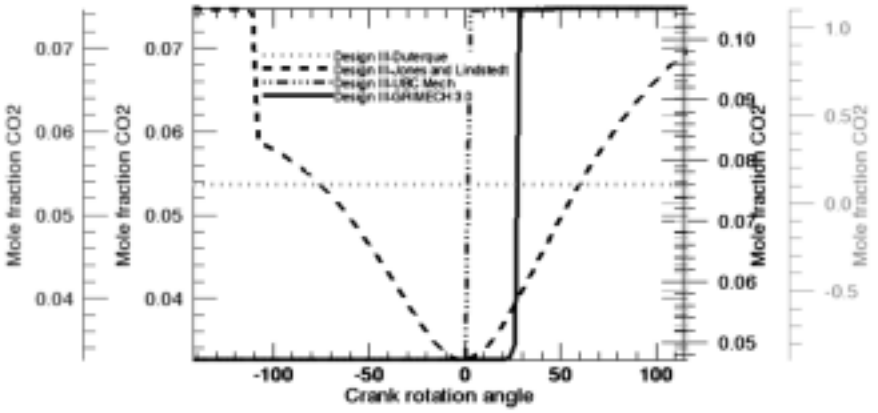

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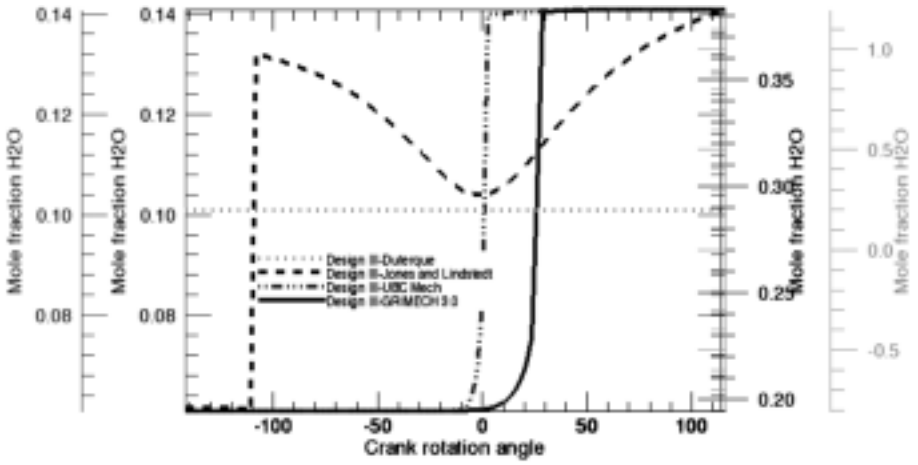

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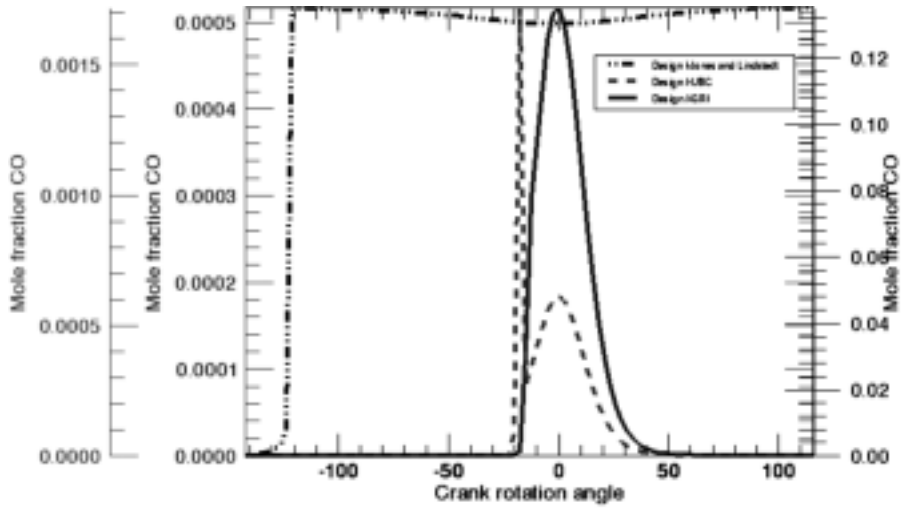
FIG. 9. COMBUSTION PRODUCTS PROFILES FOR DESIGN-III AT STOICHIOMETRIC CONDITION (Φ=1)



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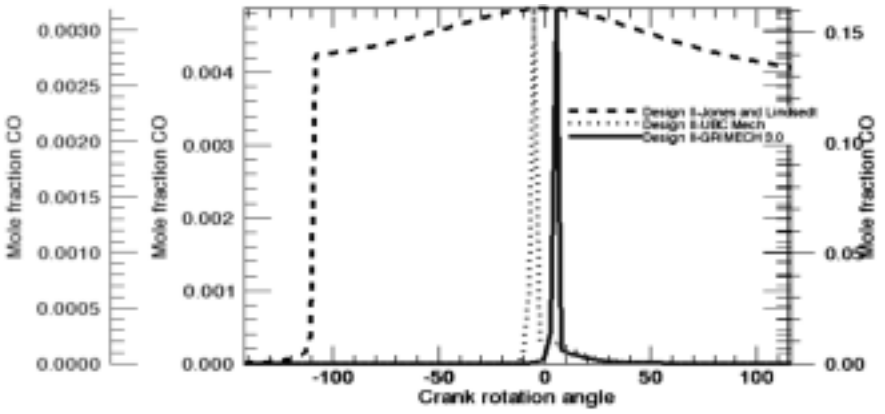

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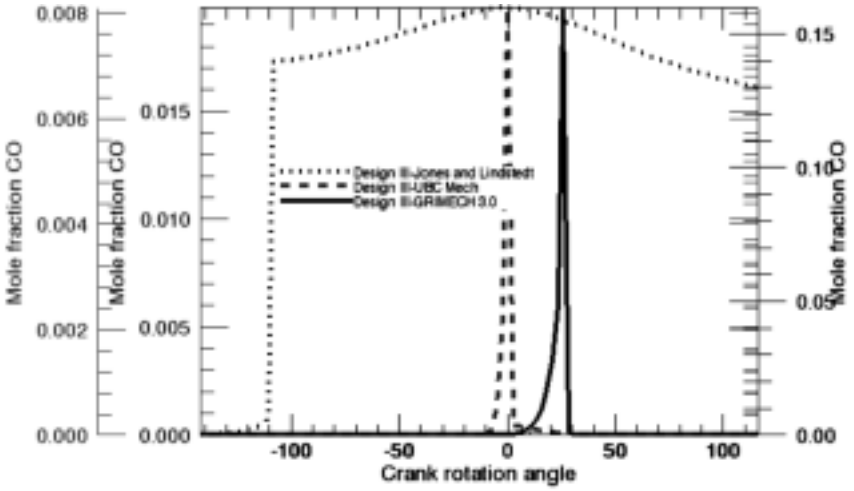

(c)

FIG. 10. COMPARISON OF CO EMISSION PROFILES OF (A) DESIGN-I (B) DESIGN-II AND (C) DESIGN-III

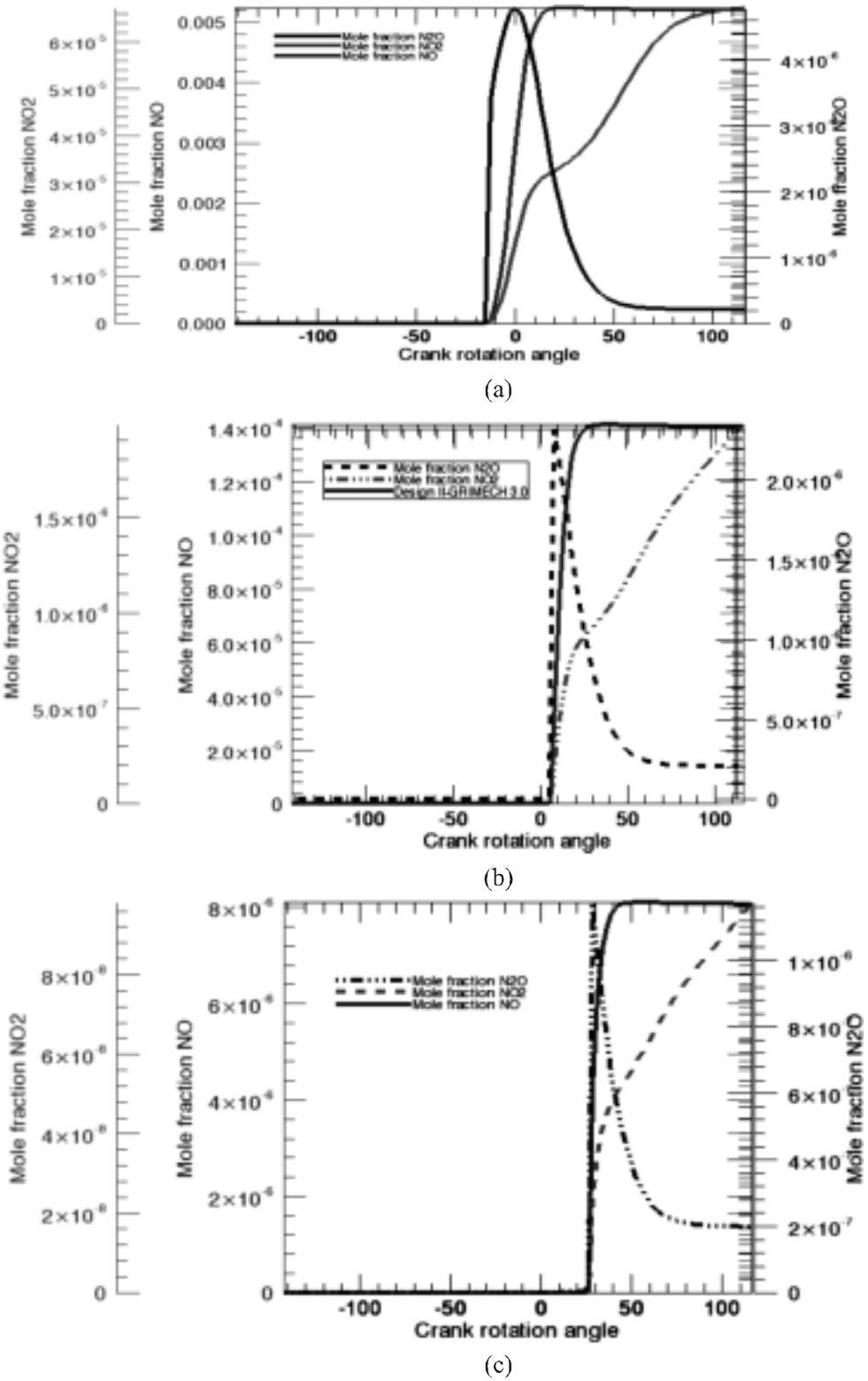

FIG. 11. NO_x FORMATION WITH GRIMECH 3.0 FOR (A) DESIGN-I (B) DESIGN-II AND (C) DESIGN-III

4. CONCLUSION

Four combustion mechanisms (two detailed and two reduced mechanisms) were implemented in the CHEMKIN simulation tool. Three mechanisms (One reduced; 4-step, Two detailed; UBC MECH and GRIMECH 3.0) successfully showed combustion reaction. The simulation profiles, for chamber pressure, temperature, and major combustion species, studied to characterize the combustion in IC engine chamber. Species profiles (due to each of mechanism) exhibited the similar trend for each of the engine geometry. Based upon these simulation profiles, it can be concluded that reduced mechanism (4-step) predicts only CO and failed in NO_x formation. Out of the detailed mechanisms, only GRIMECH 3.0 predicted the CO and NO_x formation. Besides the discrepancies (due to change in engine design), we can also conclude that GRIMECH 3.0 was the most favorable & representative mechanism for combustion in the IC engine chamber which added its versatility. Moreover, it can also be conclude that it has the capability to predict the pollutants formation like CO and NO_x.

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