The Numerical Exergy Analysis of H₂/Air Combustion with Detailed Chemical Kinetic Simulation Model

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Article Info

Article history:
Received 19 November 2011
Received in revised form 13 May 2012
Accepted 14 June 2012

Keywords:
Air-fuel Ratio
Combustion
Exergy
Energy
Irreversibility
Chemical Kinetics

Abstract

Energy and exergy concepts come from thermodynamics laws and are applicable to all fields of science and engineering. This study considers numerical simulations of combustion of hydrogen with air in a constant pressure environment and exergy terms according to first and second laws analysis using homemade code. Chemical kinetic model includes 20 reactions and 9 species. At the first stage of present study, the effects of airl-fuel ratio (φ) on energy and exergy terms are investigated for different φ (from 0.6 to 1.4) at constant temperature 1000 (K). The predictions show that the increase of φ from 0.6 to 1 increases average temperature, thermo-mechanical and chemical exergys and irreversibility, while increase of φ from 1 to 1.4 decreases them, except for chemical and total exergys. Also second-law efficiency increases with increasing of φ. At the second stage, at φ=1.4, in which the second-law efficiency is maximum, initial temperature of mixture (T) is varied from 1000 to 1400 (K) by 100 (K) step. The predictions show that increase of T from 1000 to 1100 (K) increases average temperature, thermomechanical, total exergy and irreversibility while decreases the chemical exergy and second-law efficiency. Also, the increase of T from 1100 to 1400 (K) increases the thermo-mechanical, chemical total exergys and second-law efficiency, while irreversibility decreases. It was found that second-law efficiency reaches a maximum value in the case of higher airl-fuel ratio and initial temperature.

doi: 10.5829/idosi.ije.2012.25.03c.08

Nomencalature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tr>
<td>B</td>
<td>constant coefficient</td>
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<tr>
<td>Cp</td>
<td>specific heat at constant pressure</td>
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<td>R</td>
<td>universal gas constant</td>
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<tr>
<td>R</td>
<td>reaction rate</td>
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<td>S</td>
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<td>time</td>
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<td>constant coefficient or pre-exponential factor</td>
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<td>x</td>
<td>concentration of species</td>
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<td>kk</td>
<td>number of species</td>
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<tr>
<td>I</td>
<td>irreversibility</td>
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<tr>
<td>η</td>
<td>second law efficiency</td>
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<tr>
<td>ō</td>
<td>Rate of production</td>
</tr>
</tbody>
</table>

Subscript

- i: relating to species 'i'
- j: relating to reaction step 'j'
- f: relating to fuel
- t: relating to backward reaction
- work: associated with work transfer
- destroyed: associated with work destruction
- 0: dead state, or environment state
- gen: relation to generation
- ch: relating to chemical
- ox: relating to oxidation
- heat: relating to heat
- tm: relating to thermomechanical
- red: relating to reduction
- Il: relating to second law

Greek Letters

- µ: chemical potential
- ρ: density

Superscript

- 0: restricted dead state

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1. INTRODUCTION

In view of the decreasing energy sources, optimization of thermal processes has initiated vigorous research worldwide. In order to analyze combustion performance, second-law analysis can be a useful alternative for first-law, being able to shed more light and provide better insight into the combustion processes. For the second-law analysis, the key concept is exergy; exergy is a special case of the more fundamental concept, available energy, introduced by Gibbs [1]. The exergy content of a process represents its potential to do useful work, thus, a quantitative measure of the quality or usefulness of the process. Unlike energy, exergy can be destroyed as a result of phenomena such as combustion, friction, mixing or throttling. Details about the relevant relationships can be found in some articles [2-5]. From the second-law analysis point of view, hydrogen combustion was found qualitatively different from the combustion of hydrocarbon fuels since hydrogen oxidation is the combination of two simple diatomic molecules, which yields a triatomic one with significantly larger structure than any of the reactants. For this reason, a monotonic decrease in combustion irreversibilities with increasing hydrogen component was calculated for the combustion of CH$_4$-H$_2$ mixtures burning in an engine cylinder; this decrease in combustion irreversibilities translates also into an increase in second-law efficiency [6].

Dunbar and Lior [7] studied the irreversibility of constant pressure combustion in an adiabatic chamber with hydrogen and methane as fuels. They showed that the major cause of irreversibility during the combustion was due to the internal thermal energy exchange process. Cohce et al. [8] presented a novel biomass-based hydrogen production plant. The system used oil palm shell as a feedstock. The plant, with modifications, was simulated and analyzed thermodynamically using the Aspen Plus process simulation code. Exergy analysis was used throughout the investigation, in addition to energy analysis. The overall performance of the system was evaluated, and its efficiencies were 19% for exergy efficiency and 22% for energy efficiency while the gasifier cold gas efficiency was 18%.

Nieminen and Dincer [9] carried out the comparative exergy analysis of gasoline and hydrogen fuelled internal combustion engines (ICE). Their numerical results showed that the hydrogen fuelled engine had a greater proportion of its chemical exergy converted into work exergy, indicating higher second-law efficiency than the gasoline fuelled engine due to significantly lower irreversibilities and lower specific fuel consumption associated with a hydrogen fuelled ICE. Fathi et al. [10] studied the influence of initial charge temperature under various injection timings on the second-law terms in a direct injection SI engine fuelled with hydrogen. They showed that the indicated work availability is more affected by varying injection timing in comparison with other second-law terms. Also, with increase of initial temperature, heat loss and exhaust gas availabilities increased while work availability, combustion irreversibility and entropy generation decreased. Zhiquan et al. [11] carried out systematical analysis of the fuel exergy of hydrogen and other ideal gases. Through the comparison of the fuel exergy of hydrogen and other ideal gases, it was shown that hydrogen combustion was different for different fuels. The differences between the various fuels appeared to be related to the complexity of the fuel molecule and the presence (or absence) of an oxygen atom.

At the present work, energy and exergy analyses are carried out for hydrogen combustion in a constant pressure environment using thermodynamic homemade code with developed chemical kinetics. Comparative energy and exergy analyses at various air-fuel ratio ($\phi$) with constant initial temperature of 1000 K and various initial temperatures at $\phi$=1.4, in which the second-law efficiency is maximum, are carried out and the numerical results are graphed and commented.

2. MODEL DESCRIPTION

In this research a single-zone analytical transient chemical kinetic model is employed to investigate combustion characteristics of mixture gaseous fuel and air.
The scheme consisted of the following 20 chemical reactions and the 9 chemical species [13]:

1) \( \text{H}_2 \), (2) \( \text{H} \), (3) \( \text{OH} \), (4) \( \text{O} \), (5) \( \text{H}_2\text{O} \), (6) \( \text{O}_2 \), (7) \( \text{N}_2 \), (8) \( \text{HO}_2 \) and (9) \( \text{H}_2\text{O}_2 \)

and reactions [13]:

1) \( \text{H}_2+\text{O}_2=2\text{OH} \),
2) \( \text{OH}+\text{H}=\text{H}_2+\text{H} \),
3) \( \text{O}+\text{OH}=\text{O}_2+\text{H} \),
4) \( \text{O}+\text{H}_2=\text{OH}+\text{H} \),
5) \( \text{H}+\text{O}_2=\text{M}=\text{HO}_2+\text{M} = \text{H}_2\text{O}/18.6\text{H}_2/2.86/\text{N}_2/1.26^\circ \),
6) \( \text{OH}+\text{HO}_2=\text{H}_2\text{O}+\text{O}_2 \),
7) \( \text{H}+\text{HO}_2=\text{OH} \),
8) \( \text{O}+\text{HO}_2=\text{O}_2+\text{OH} \),
9) \( 2\text{OH}=\text{O}_2+\text{H}_2 \),
10) \( \text{H}+\text{H}+\text{M}=\text{H}_2+\text{M}+\text{H}\text{H}_2/0.0/\text{H}_2/0.0/\text{H}_2/0.0^\circ \),
11) \( \text{H}+\text{H}+\text{H}+\text{H} \),
12) \( \text{H}+\text{H}+\text{O}_2=\text{H}_2+\text{H}_2\text{O} \),
13) \( \text{H}+\text{OH}=\text{M}+\text{H}_2\text{O}/5/, \)
14) \( \text{H}+\text{O}=\text{M}+\text{H}_2\text{O}/5/, \)
15) \( \text{O}+\text{O}=\text{O}_2+\text{M} \),
16) \( \text{H}+\text{HO}_2=\text{H}_2\text{O}_2 \),
17) \( \text{HO}_2+\text{HO}_2=\text{H}_2\text{O}_2+\text{O}_2 \),
18) \( \text{H}_2\text{O}_2+\text{M}=\text{OH}+\text{H}_2\text{O} \),
19) \( \text{H}_2\text{O}_2+\text{H}=\text{HO}_2+\text{H}_2 \),
20) \( \text{H}_2\text{O}_2+\text{OH}=\text{H}_2\text{O}+\text{HO}_2 \).

To construct a thermodynamic model for working fluid inside a constant pressure environment, following assumptions are made:

1) The system is closed.
2) All components of working fluid are modeled as an ideal gas.
3) Heat loss is assumed to be negligible.
4) The total pressure is assumed to be constant and equal to 1 bar.
5) Start time for simulation is equal to zero.
6) End time for simulation is equal to 2E - 4 s.

2. 1. First-Law Analysis For the reaction scheme, the intermediate reaction steps may be represented as follows [13]:

\[
\sum_{i=1}^{k} \alpha_{ij} A_i \leftrightarrow \sum_{j=1}^{k} \alpha_{ij} B_j = 1,2,...
\]

(1)

For the j-th reaction, the forward rate constant \( k_{fj} \) can be expressed by the following Arrhenius expression [13]:

\[
k_{fj} = A_{fj} \exp \left( \frac{E_{fj}}{RT} \right)
\]

(2)

where the pre-exponential factor \( A_{fj} \), the temperature exponent \( B \) and the activation energy \( E_{fj} \) are specified. These three parameters are required input for each reaction. While the backward rate constant \( k_{bj} \) is of similar form to that of \( k_{fj} \).

The reaction rates for the j-th reaction in the forward and backward directions can be expressed, respectively, in terms of the concentrations as follows [13]:

\[
R_{fj} = k_{fj} \prod_{i=1}^{n} x_i^{\alpha_{ij} j=1}
\]

(3)

\[
R_{bj} = k_{bj} \prod_{i=1}^{n} x_i^{\alpha_{ij} b j=1}
\]

(4)

where \( x_i \) is the mole fraction of specie \( i \), \( \rho \) is the density and is equal to ratio of the mass content of the cylinder to its time-dependent volume.

\[
\rho = \frac{\rho_0}{T}
\]

(5)

The net rate of production of each species will be a function of the rate of all reaction steps involved that are proceeding simultaneously and are given by a relation of the following form [13]:

\[
-\rho \frac{\partial x_i}{\partial t} = \sum_{j=1}^{k} (\alpha_{ij} a_{ij} - \alpha_{ij} b_{ij} ) (R_{fj} - R_{bj} ) , i = 1, ..., k
\]

(6)

Assuming caloriically perfect gases, the energy equation becomes [13]:

\[
\frac{dT}{dt} = \frac{1}{\rho c_p} \sum_{i=1}^{k} \sum_{j=1}^{k} \left( \mu_i \right) \text{H}_k \delta_k
\]

(7)

where \( T \) is the temperature, \( C_p \) represents the mean specific heat, \( H_k \) is the molar species enthalpies, and \( \delta_k \) represents the species molar production rates.

Thus, the energy Eq. (7) and the simultaneous set of non-linear first-order differential equations that were solved by the ChemKin code [13] in order to determine mole fraction of each species, average pressure and temperature in cylinder. The second-law analysis is carried out numerically by home code and using the results of the calculations which are performed with the first-law of thermodynamic.

2. 2. Second-Law Analysis Exergy of a system in a given state is defined as the maximum useful work that can be produced through interaction of the system with its surroundings, as it reaches thermal, mechanical and chemical equilibrium. Usually, the terms associated with thermo-mechanical and chemical equilibration is calculated separately. For a closed system experiencing heat and work interactions with the environment, thermo-mechanical and chemical exergys are given as [14]:

\[
\text{Ex}_{tm} = (u-u_0) + P_0 (v - v_0) - T_0 (s - s_0)
\]

(9)

\[
\text{Ex}_{ch} = \sum_i x_i (\mu_i - \mu_i^0) = T_0 \sum_i x_i \ln \frac{\mu_i}{\mu_i^0}
\]

(10)

with \( \mu_i \) and \( \mu_i^0 \) are the chemical potential of species \( i \), and \( x_i \) and \( x_i^0 \) represent the mole fractions of species \( i \) in the mixture at restricted dead state (thermal and mechanical equilibrium) and the true dead state in environment (thermal, mechanical and chemical equilibrium), respectively. This chemical exergy is a
measure of the maximum work when the system comes to equilibrium with the environmental composition. In general, chemical exergy can be divided into oxidation, reduction and diffusion exergies [14-15]. The species number 1-4 can be burned and converted to environmental species and includes chemical exergy. The reduction term concerns the species number 8-9 and species number 5-7 concerns diffusion term. Therefore, the total chemical exergy is:

\[ \Delta \text{Ex}_{\text{ch}} = \Delta \text{Ex}_{\text{Red}} + \Delta \text{Ex}_{\text{Diff}} \]  

(11)

Total, i.e., thermo-mechanical plus chemical exergy is then given by:

\[ \Delta \text{Ex}_{\text{sys}} = \Delta \text{Ex}_{\text{ch}} + \Delta \text{Ex}_{\text{tm}} = uP_0 - T_0S - \sum_i x_i (\mu_i^0) \]  

(12)

the nature of exergy is opposite to that of entropy in that exergy can be destroyed, but it cannot be created. Therefore, the exergy change of a system during a process is less than the exergy transfer by an amount equal to the exergy destroyed during the process within the system boundaries. Therefore, exergy balance in a close system can be expressed as [14-15]:

\[ \Delta \text{Ex}_{\text{heat}} - \Delta \text{Ex}_{\text{destroyed}} - \Delta \text{Ex}_{\text{work}} = \Delta \text{Ex}_{\text{sys}} \]  

(13)

with \( \Delta \text{Ex}_{\text{heat}} \), \( \Delta \text{Ex}_{\text{work}} \) showing the exergy transfer by heat, work, and \( \Delta \text{Ex}_{\text{destroyed}} \) denoting exergy destruction due to irreversibility and \( \Delta \text{Ex}_{\text{sys}} \) representing exergy change of the system. The destroyed exergy is proportional to the generated entropy and is expressed as [11-12]:

\[ \Delta \text{Ex}_{\text{destroyed}} = T_0s_{\text{gen}} \]  

(14)

The internal energy of the mixture was determined to be a function of temperature at two temperature ranges. There are seven coefficients for each of the two temperature ranges. Thus, for each species there are 14 coefficients overal [13]. The common temperature connecting the two ranges is 1000 K.

\[ u = RT(1 - 1 + \frac{2}{3}T + \frac{2}{5}T^2 + \frac{11}{10}T^3 + \frac{7}{20}T^4 + \frac{1}{4}T^5) \]  

(15)

\[ s = R(\frac{a_1\ln(T)}{T} + a_2T + \frac{2}{5}T^2 + \frac{11}{40}T^3 + \frac{7}{200}T^4 + \frac{1}{400}T^5 + a_3) - Rlnx_i \]  

(16)

The second-law efficiency is intended to serve as a measure of approximation to reversible operation, and thus its value should range from zero in the worst case (complete destruction of exergy) to one in the best case (no destruction of exergy). With this in mind, the second-law efficiency of a system is defined during a process as:

\[ \eta = \frac{\text{Energy recovered}}{\text{Energy supplied}} = 1 - \frac{\text{Energy destroyed}}{\text{Energy supplied}} \]  

(17)

here, each term of exergy equation can be evaluated as long as the corresponding properties of working fluid have been obtained by simultaneously solving of species and energy equations.

3. RESULTS AND DISCUSSION

At the present work, simulations have been performed to investigate the effect of air-fuel ratio and initial temperature on combustion of hydrogen fuel in constant pressure environment with detailed chemical kinetic simulation model.

Figures 1 and 2 show the variation of mole fraction of \( \text{H}_2 \) and temperature in the combustion chamber for all cases (from \( \phi = 0.6 \) to 1.4), respectively. As shown at these figures, as the values of \( \phi \) decrease, the start of combustion is earlier. However, the study show that the increase of \( \phi \) (or the decrease of \( \lambda \)) significantly reduces the reaction rate levels [16].

Figures 3 shows the variation of thermo-mechanical exergy with time. At times before start of combustion, thermo-mechanical exergy remain constant while at time of start of combustion and combustion duration increases considerably. Similar behaviors can be observed between thermo-mechanical exergy and temperature (Figure 1). At whole, thermo-mechanical exergy increases with rising pressure and temperature of the cylinder charge. At \( \phi = 0.8 \) and 1 because of complete combustion, the values of thermo-mechanical exergy is higher than others states.

Figures 4 and 5 show the variation of chemical and total exergies with time. It can be seen that, at times before start of combustion, the chemical and total exergies of the mixture remains constant. This situation continues until ignition starts. During ignition, the chemical exergy decreases due to the conversion of unburned species into combustion products. At this time, chemical exergy of the fuel is converted to thermo-mechanical exergy and decrease of chemical exergy compensate with the increase of thermo-mechanical exergy.

Figures 6 shows the variations of irreversibility with time at various air-fuel ratios. Before the ignition, exergy destruction is observed as irreversibilities are insignificant. With the start of combustion and during the combustion, irreversibility increases and this increase at \( \phi = 0.8 \) and 1 because of complete combustion, is more than other air-fuel ratios.

Figure 7 shows the variations of irreversibility with air-fuel ratio at constant initial temperature and pressure. As it is shown in this figure, when air-fuel ratio increases from 0.6 to 1, because of more complete combustion, irreversibility increases while the increase of air-fuel ratio from 1 to 1.4, decreases it.

Comparison of the second-law efficiency for different cases of air-fuel ratio is presented in Figure 8. It shows that the second-law efficiency reaches its maximum amount at \( \phi = 1.4 \). From \( \phi = 0.8 \) to \( \phi = 1 \), because of the same irreversibility (as shown in Figure 7) and complete combustion, second-law efficiency
remain unchanged. At air-fuel ratios 0.8 and 1 second-law efficiencies are the same because of equal irreversibilities.

**Figure 1.** Variation of hydrogen mole fraction with time for various air-fuel ratios at initial temperature 1000 K

**Figure 2.** Variation of hydrogen mole fraction with time for various air-fuel ratios at initial temperature of 1000 K

**Figure 3.** Variation of in-cylinder thermo-mechanical exergy for various air-fuel ratios

**Figure 4.** Variation of in-cylinder chemical exergy for various air-fuel ratios

**Figure 5.** Variation of in-cylinder total exergy with time for various air-fuel ratios

**Figure 6.** Predicted irreversibility for various air-fuel ratios

**Figure 7.** Predicted irreversibility for various air-fuel ratios
Figure 8. Variation of second-law efficiency with air-fuel ratio.

Figure 9. Variation of mole fraction of $H_2$ with time at $\varphi = 1.4$ and various initial temperatures.

Figure 10. Variation of temperature with time at $\varphi = 1.4$ and various initial temperatures.

Figure 9 indicates variations in the calculated mole fraction of hydrogen with time for different cases of initial temperatures at $\varphi = 1.4$. It can be seen that combustion takes place faster when initial temperature increases. When initial temperature increases, duration of combustion and average temperature in cylinder increases.

Figure 10 indicates variations in the calculated temperature with time for different cases of initial temperatures at $\varphi = 1.4$. It can be seen that at high initial temperature because of earlier start of combustion, in-cylinder temperature more increases than that of low temperature.

Figure 11 shows the variations in the calculated thermo-mechanical exergy with time for different cases of initial temperatures at $\varphi = 1.4$. It can be seen that, with increase of initial temperature, the thermo-mechanical exergy increases. The main reason for this trend is arising from increasing temperature of the in-cylinder mixture according to Figure 10. This increasing is more considerable because of fast start of combustion when the initial temperature increases from 1000 to 1100 K.

Figure 12 indicates variations in the calculated chemical availability with time for different cases of initial temperatures. As shown in this figure, with increase of initial temperature, combustion takes place faster and the chemical exergy decreases fast because of decreasing of hydrogen mole fraction with start of combustion. When the chemical exergy decreases, thermo-mechanical exergy increases. As shown in this figure, the increasing of initial temperature from 1000 to 1100 K decreases the chemical exergy while increasing of temperature from 1100 to 1400 K increases the chemical exergy at end time of combustion. At higher initial temperature as shown in Figure 9, the mole fraction of $H_2$ increases after main combustion because of reverse reaction occurring, chemical exergy of mixture increases.

Figure 13 shows the variations in the calculated irreversibility with time for different cases of initial temperatures. As indicated in this figure, the irreversibility increases with the increase of initial temperature from 1000 to 1100 K because of decreasing of chemical exergy (as shown in Figure 12) and complete combustion. With increase of initial temperature from 1100 to 1400 K, irreversibility decreases because of increasing the chemical exergy and longer duration of combustion process.

Sum of thermo-mechanical and chemical exergies is shown in Figure 14. Before combustion process, total exergy remains constant. At the time of combustion because of the decrease of chemical exergy, total exergy also decreases. At the next times, the effect of chemical exergy reduction is compensated by increasing the thermo-mechanical exergy and then total exergy increases.

Comparison of the second-law efficiency for different cases of initial temperatures is presented in Figure 15. It shows that the second-law efficiency reaches its minimum amount at 1100 K. As shown in Figure 15, irreversibility increases with initial temperature to reach a maximum value at 1100 K, and thereafter decreases. Therefore, this maximum value of irreversibility at 1100 K causes that second-law efficiency reach to minimum value.
4. CONCLUSION

The combustion of hydrogen with air in a constant pressure environment was considered to numerically determine the amount of energy and exergy terms and second-law efficiency in a cylinder at different conditions. The effects of various equivalence ratios at constant initial temperature (1000 K) and various initial temperatures at $\varphi = 1.4$, on the energy, exergy terms and second-law efficiency were investigated. Also, the resulting irreversibly due to combustion process was computed. The specific conclusions derived from this study can be listed briefly as follows:

The increase of $\varphi$ reduces the reaction rate levels and causes that the start of combustion delayed. This result is in good agreement with the corresponding data in literature [16].

- The increase of $\varphi$ from 0.6 to 1 increases peak temperature while the increase of $\varphi$ from 1 to 1.4...
decreases it. This result is in good agreement with the corresponding data in literature [17].

- The increase of $\phi$ from 0.6 to 1 increases thermo-mechanical and chemical exergies, and irreversibility while increase of $\phi$ from 1 to 1.4 decreases them except for chemical exergy.
- The increase of $\phi$ from 0.6 to 1.4 increases the second-law efficiency.
- The increase of initial temperature from 1000 to 1100 K at $\phi=1.4$ increases thermo-mechanical, irreversibility and decreases chemical exergies at end time, while the increase of it from 1100 to 1400 K increases thermo-mechanical and chemical exergies except for irreversibility.
- The increase of initial temperature from 1000 to 1400 K at $\phi=1.4$ increases total exergy.
- The increase of initial temperature from 1000 to 1100 K at $\phi=1.4$ decreases the second-law efficiency, while increase of it from 1100 to 1400 K increases second-law efficiency.
- The results indicate that hydrogen can be a good alternative fuel in combustion systems at higher air-fuel ratio and initial temperature.

5. REFERENCES

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doi: 10.5829/idosi.ije.2012.25.03c.08