Simulation Study on the Production of Hydrogen/Syngas via Partial Oxidation in a Natural Gas-Fueled Engine

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Abstract

The automotive industry is considered as one of the biggest industries worldwide. On this field, continuous research and development are performed to improve efficiencies of cars and trucks. Increasing efficiencies of automotives not only lead to cost reduction but also to reduced pollution, which is very important in today's society. Therefore, each country in the world is carrying out research on developing alternative energy sources. Therefore, it is essential to develop the environment-friendly alternative energy urgently considering the limitation of fossil fuel and the global warming caused by environmental destruction. In this research, the new technology to produce hydrogen and syngas from natural gas with a homogeneous charge compression ignition reforming engine was studied. The simulation tool used was CHEMKIN 3.7, using the GRI natural gas combustion mechanism. This simulation was conducted on the changes in hydrogen and syngas concentration according to the variations of equivalence ratio, intake heating temperature, and oxygen enrichment with partial oxidation. Through the parametric screening studies, optimum conditions in this study were found: The equivalence ratio was 2.5; The inlet temperature was 530 K, and the oxygen contents in air was 0.3.

NOMENCLATURE

A Area, m^2
B Cylinder bore, m
C Constant
h_c Heat transfer coefficient, $W/m^2 K$
l Connecting rod length, m
L Crank radius, m
N Engine speed, rpm
P Cylinder pressure, kPa
Q_{ht} Heat loss, W
r_c Compression ratio
$\bar{S}_p$ Mean piston speed, m/s
t Time, s
T Temperature, K
V Volume, m^3
w Gas velocity, m/s

Greek symbols
θ Crank angle, degree

Subscripts
c Clearance
d Displacement
IVC Intake valve close

1. INTRODUCTION

Hydrocarbon fuels, especially natural gas, can be thought of as a means of storing hydrogen until the fuel is broken down or reformed into a syngas consisting of hydrogen, carbon monoxide, and other gases. Worldwide distribution of natural gas reserves is well established. Utilizing this potential, hydrogen could be produced from natural gas in distributed locations such as automotive fuelling stations. Although such an approach is not without thermodynamic penalties, it does represent a potential interim solution for transition to a hydrogen economy for the transportation sector.

With extensive use of this approach, much of the heavily subsidized oil that is consumed domestically and amounts to nearly 25% of the total annual oil production would either be exported, creating much larger revenue, or redirected to the manufacture of petrochemical products that have an even greater added value while creating a positive impact on the environment in. The production of syngas, from natural gas (mainly methane, CH_4) can be carried out by steam (wet) reforming, carbon dioxide (dry) reforming and partial oxidation reforming (POX) [1].

Steam reforming and carbon dioxide reforming are an endothermic reaction that involves the conversion of a fuel into another fuel with a higher heating value [2-6,7]. However, they occur under high temperature and pressure that requires an external heat source and most often occurs in the presence of suitable catalysts. Moreover, soot formation during reforming process leads to degradation of the catalyst [8]. Also CO_2 sequestration on-board is difficult to perform.

Hydrogen production from fossil fuel resources can be obtained also via partial oxidation processes where much thermal energy is produced (ΔH^O_{298K} = -35.9 kJ/mol) with some presence of complete combustion products such as carbon dioxide and water vapor as well as carbon monoxide with the hydrogen [3]. Such partial oxidation approaches are attractive, particularly when suitable catalysts are employed.

There are two ways to reform CH_4 into syngas by partial oxidation, i.e., catalytic and non-catalytic

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reforming. Traditionally, syngas production has been achieved by using catalytic reformers [9–12]. However, in addition to its high economic investment cost [13–16], this conventional technology presents several drawbacks. The catalyst device can be poisoned by sulfur or halogen-containing compounds [17–18] and catalyst surface performances can be reduced by solid carbon adsorption or deposition [14,19–21]. The treatment or maintenance required to remove the contaminated catalytic equipment can represent a major drawback with respect to current environmental regulations [13–16]. Moreover, catalytic sites need to be activated by heating at high temperature [13–16,19,21-22].

There is a need to develop means to produce hydrogen rich gas promptly on demand including in small supply rates. The types of reforming reactors are changing this days; from wet type to dry type, from endothermic to exothermic reaction, from reaction that takes a few seconds to one that takes milliseconds and from large and complicated reactors to small and simple ones [23].

The reciprocating internal combustion engine, whether of the spark ignition or compression ignition types, can be viewed as effective commonly available high temperature and pressure chemical reactors of widely different designs and sizes that can be operated without the need for the use of catalysts [3]. It is associated with very short residence times and responds promptly to changes in the control variables. Accordingly, in principle, conventional engines can be suitably modified to operate on very rich mixtures of methane and oxygen or oxygenated air to produce promptly on demand hydrogen rich products and syngas simultaneously with power [3].

Previous work with spark-ignited natural gas POX engines has shown significant H_2 production while providing from 6.5% to 10% thermal efficiency [3,24–25]. Equivalence ratios as high as 2.5 have been achieved using oxygen enrichment in dual fuel (diesel pilot with homogeneous natural gas combustion) operation [24–25]. When producing syngas, the maximum power output of the engine is higher than that when operating conventionally whether in diesel or dual fuel engine modes [3]. The corresponding thermal efficiency remains very high and its values were comparable with those obtained with the engine operating with diesel.

The aim of this research is to perform a theoretical investigation on the reforming characteristic of natural gas (CNG) to produce hydrogen/syngas through uncatalyzed partial oxidation using an internal combustion engine reformer. In this regard, a detailed chemical kinetic mechanism for CNG combustion coupled to the Closed Homogeneous Reactor model from the CHEMKIN 3.7 [26] software has been adopted and the effect of equivalence ratio, intake temperature, and oxygen contents in air on the hydrogen/syngas yield is studied.

2. MODELING APPROACH

The Closed Homogeneous Reactor model from the CHEMKIN 3.7 [26] software for internal combustion engines coupled with the hydrocarbon reaction mechanism GRI Mech 3.0 [27] that considers 53 species and 325 reactions was used to simulate engine combustion and observe H_2 and CO exhaust compositions. In this study, the composition of natural gas (on the volumetric basis) used in the simulation is as follows: methane (CH_4) = 94.8%, ethane (C_2H_6) = 3.28%, propone (C_3H_8) = 1.2%, carbon dioxide (CO_2) = 0.53%, nitrogen (N_2) = 0.19%.

Table 1 Specifications of modeled engine.

Engine Type	Single Cylinder, 4 stroke
Bore / Stroke	85.5 mm / 110 mm
Displacement	631.56 cm^3
Compression Ratio	17
Connecting Rod	267 mm
Aspiration	Natural
Rated Power	6 HP@ 1500 rpm

The present analysis considers a single zone model that ignores spatial variations in the combustion chamber, treating heat loss as a distributed heat transfer rate, proportional to the temperature difference between the average gas temperature and a time-averaged wall temperature. The simulation is started at IVC where fresh charge at specified pressure, temperature, and equivalence ratio is inducted into the cylinder and stopped at the end of the expansion stroke. All tests were carried out at a constant speed of 1000 rpm. The CHEMKIN model accounts for changes in pressure, volume, and temperature. The effect of equivalence ratio, oxygen contents in air and intake temperature on the hydrogen/syngas yield is studied. The engine specifications assumed in the present work are shown in Table 1.

The simulation data represents a homogeneous mixture which is ignited via piston compression. This type of simulation represents homogeneous charge compression ignition (HCCI) combustion.

2.1.Modeling the HCCI Engine

To appropriately model the combustion event in an HCCI engine, it is necessary to describe the evolution of heat release via a detailed chemical kinetic mechanism, and a well-matched, stiff chemical kinetic solver. For this work, CHEMKIN 3.7 package [26] was selected due to the fact that it is widely accepted and used kinetic solver in a range of combustion studies.

The simulation is currently written in a single cylinder version, primarily because fundamental studies lend themselves to this configuration. A premixed charge at uniform temperature and pressure is compressed and expanded at a rate that depends on the engine speed and

geometry. The model is described briefly below and it is based on the assumptions that the mixture is a perfect gas with the temperature and species concentrations are uniformly distributed.

The piston motion is represented by the following formula [28]:

$$\frac{V}{V_c} = 1 + \frac{1}{2}(r_c - 1)\left(\frac{2l}{L} + 1 - \cos\theta - \left(\left[\frac{2l}{L}\right]^2 - \sin^2\theta\right)^{1/2}\right)$$

(1)

where V_c is the clearance volume, r_c is the compression ratio, l is the connecting rod length, L is half of the stroke (crank radius), and θ is the crank angle. A transition from time to crank angle and vise versa could be made as:

$$\theta = \frac{2\pi N}{60} t + \theta_{IVC}$$

(2)

where N is the engine speed in rpm and θ_{IVC} is the crank angle at intake valve close (IVC) in radians.

2.2. Heat Transfer Model

To calculate the heat exchange between gas and cylinder walls, the Woschni's heat transfer correlation [29], which has been widely used in the HCCI studies, was used.

$$Q_{ht} = h_c A_{total}(\theta)[T(\theta) - T_{wall}]$$

(3)

In this correlation, the heat loss Q_{ht} is a function of the heat transfer coefficient h_c, the cylinder heat transfer area A_{total} and the difference between the mixture temperature T and the time-averaged wall temperature T_{wall}. In this expression, the area, the gas temperature and the heat transfer coefficient vary with the crank angle. The heat transfer coefficient changes with the crank angle because it is a function of pressure p, temperature and the average cylinder gas velocity w, which vary with crank angle [28]:

$$h_c = 3.26 \cdot B^{-0.2} \cdot p^{0.8} \cdot T^{-0.55} \cdot w^{0.8}$$

(4)

where B is the cylinder bore in meters. The pressure, temperature and gas velocity have units kPa, Kelvin and m/s respectively. The units of h_c are W/m^2 K. The combustion chamber area is calculated as follows:

$$A_{liner} = \frac{\pi BL}{2}\left(\frac{2l}{L} + 1 - \cos\theta - \left(\left[\frac{2l}{L}\right]^2 - \sin^2\theta\right)^{1/2}\right)$$

(5)

$$A_{total} = A_{liner} + A_{head} + A_{piston}$$

(6)

where A_{liner}, A_{head}, A_{piston} and A_{total} are the liner, head, piston and total areas, respectively. The average cylinder gas velocity was described by the following expression [28]:

$$w = \left[C_1\bar{S}_p + C_2\frac{V_d T_{IVC}}{P_{IVC}V_{IVC}}(p - p_{motored})\right]$$

(7)

where $p_{motored}$ is the motored cylinder pressure at the same crank angle as p, C_1 and C_2 are constants with values as follows:

For the compression period:

$$C_1 = 2.28, \qquad C_2 = 0$$

For the combustion and expansion period:

$$C_1 = 2.28, \qquad C_2 = 0.00324$$

$\bar{S}_p = 2LN$ is the mean piston speed and N is the rotational speed.

3. RESULTS and DISCUSSION

The production of hydrogen/syngas, from natural gas (mainly methane, CH_4) depends mainly on the oxygen/fuel ratio. The oxygen/fuel ratio was represented as a ratio between oxygen, which was supplied as the most important impact factor for partial oxidation reforming, and methane fuel.

$$CH_4 + 2O_2 = CO_2 + 2H_2O$$
$$\Delta H^O_{298K} = -802.6 \text{ kJ/mol}$$
(8)
$$CH_4 + 0.5O_2 = CO + 2H_2$$
$$\Delta H^O_{298K} = -35.9 \text{ kJ/mol}$$
(9)
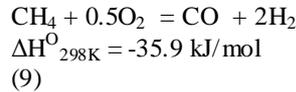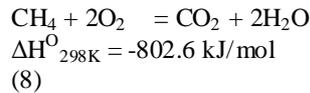
Equation (8) represents the reaction for the complete oxidation of methane and equation (9) indicates partial oxidation. If the oxygen/fuel ratio was greater than 2 as in equation (8), complete combustion occurred and only H_2O and CO_2 were generated as the final product. As shown in equation (9), when oxygen/fuel ratio is 0.5, a weak exothermic reaction occurs and hydrogen production reaches its maximum when $H_2/CO = 2$.

3.1 Effect of Equivalence Ratio

Figure 1 shows the main equilibrium products as a function of equivalence ratio. For these results, composition moles are normalized by mole of CNG at the inlet as the concern is on the efficient conversion of CNG to hydrogen/syngas. The plot suggests that CNG conversion to hydrogen peaks near an equivalence ratio

of $\phi = 2.5$, with roughly 60% of the H in the initial CH_4 (the main component in CNG) converted to H_2. The other main product which peaks near an equivalence ratio of $\phi = 2.5$ is CO. As equivalence ratio is increased (ϕ greater than 2.5), the unreacted CH_4 fraction increases, and the H_2 and CO yields decrease. Water vapor and CO_2 yields decrease as equivalence ratio is increased. The processes of the partial oxidation of methane were observed to take place in two consecutive stages where near complete combustion (Eq. 8) of part of the methane and much of the oxygen is followed by a reforming stage (Eq. 9) when much of the CO and H_2 are produced [3].

In general, increasing the mixture equivalence ratio well beyond the stoichiometric value results in an increase in the relative production of H_2 and CO in comparison to those of H_2O and CO_2 with product H_2/CO ratio increases as the equivalence ratio is increased as shown in Fig. 2.
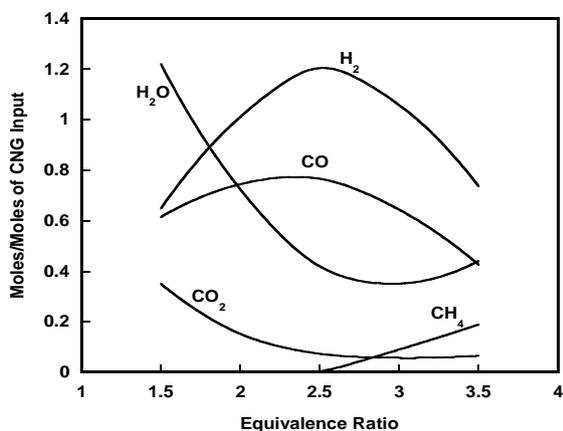
Fig. 1. Equilibrium products of CNG/air combustion with fuel-rich equivalence ratios.
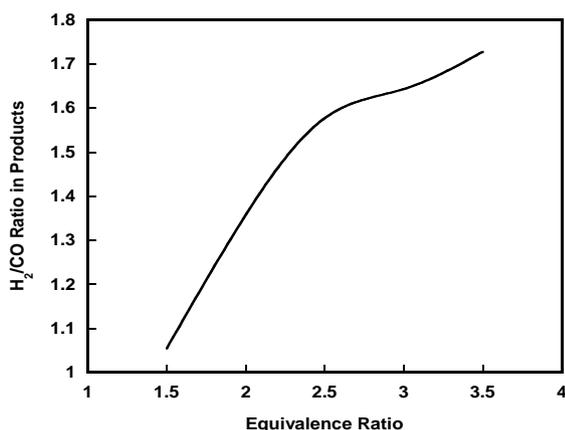
Fig. 2. H_2 to CO ratios with respect to equivalence ratio.

Engine exhaust mass fractions of H_2 and CNG fuel input are plotted as a function of equivalence ratio in Fig. 3. In these results, the inlet temperature was fixed at 530 K. It can be noted that the yield of H_2 increases as the equivalence ratio (ϕ) is increased until a certain value of $\phi = 2.5$ after which the yield of H_2 is decreased. This behavior could be due to erratic engine combustion near the rich misfire limit.

Figure 4 shows the effect of equivalence ratio on the mass and mole fractions of H_2 per mass and mole of fuel input. A maximum value of about 18.1% of the mass of CNG fuel has been reformed into H_2 at an optimum value of equivalence ratio equal to 2.5. Furthermore, in a mole basis at the same value of equivalence ratio, a maximum value of about 1.2 mole of H_2 has been produced from one mole of CNG fuel, as shown in Fig. 4.
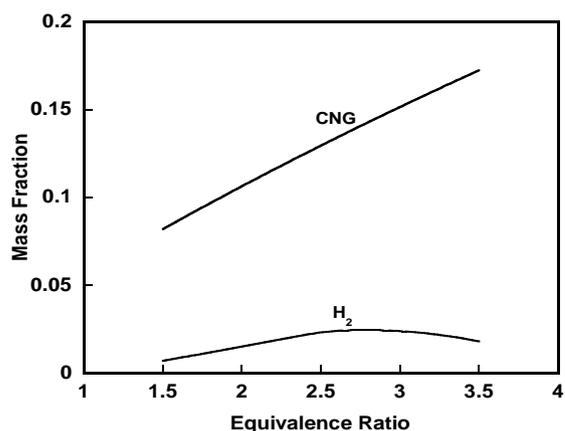
Fig. 3. Exhaust mass fractions of H_2 and fuel input versus equivalence ratio.

If the desired output is syngas which consists of mainly H_2 and CO, the effect of equivalence ratio on the yield of syngas is shown in Fig. 5. It is shown that the equivalence ratio has an effect similar to that on H_2 production and a maximum value of about 2 moles of syngas could be produced from one mole of CNG fuel at an optimum value of $\phi = 2.5$.
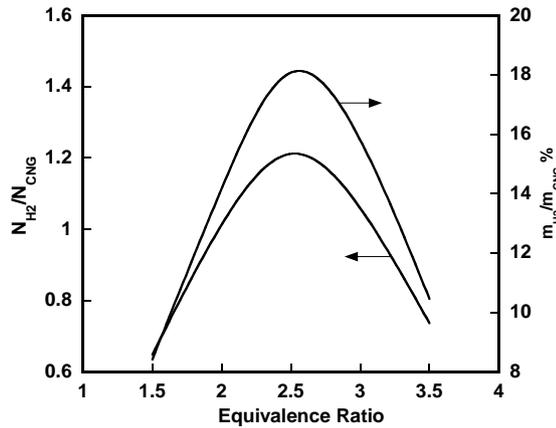
Fig. 4. Exhaust mass and mole fractions of H$_2$ per fuel input versus equivalence ratio.
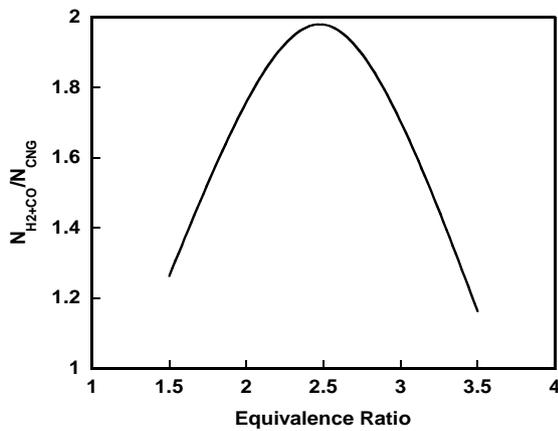
Fig. 5. Exhaust mole fraction of syngas per mole of fuel input versus equivalence ratio.

3.2. Effect of Inlet Temperature

In order to use CNG as a reforming fuel for an engine, high pressure and intake preheating are required as the CNG is hard to auto-ignites [23]. The previous results of equivalence ratio effect on hydrogen/syngas production indicate that an optimum value of approximately $\phi = 2.5$ is exist and the minimum yield is achieved with an equivalence ratios of 3.5. Therefore, following results reflect the effect of inlet temperature on hydrogen/syngas production at these two values of equivalence ratio.

Figure 6 presents the composition moles of H$_2$ and CO normalized by mole of CNG at the inlet according to the variation of intake preheating temperature up to 560 K at equivalence ratios of 2.5 and 3.5, respectively. It is to be noted that it was hard to obtain auto-ignition below 465 K with $\phi = 2.5$ and below 490 K with $\phi = 3.5$ of preheating temperature of the mixed gas with this HCCI reforming model. When partial oxidation is carried out, temperature for the reforming reaction is very important. If the reaction temperature is low, CNG conversion is incomplete and the concentration of the produced H$_2$ decreases. It is clearly shown that (Fig. 6a at $\phi = 2.5$) the

yield of hydrogen/syngas increases with an increase in the inlet temperature until a certain value after which any more increase in inlet temperature has no effect on the mass fraction of hydrogen produced. When the intake preheating temperature was 490 K, H$_2$ concentration was approximately 1.2 moles and at higher levels of temperature, it increased slightly. When the intake preheating temperature was below 490 K, the hydrogen/syngas concentration was weakened due to incomplete combustion of CNG.

The increase of intake temperature resulted in the increase of hydrogen/syngas production in the exhaust gas as shown in Fig. 6. As a result, the oxygen concentration in exhaust gases is expected to be decreased as the intake temperature increased. This is because the entropy in the engine was increased by the intake preheating, resulting in the acceleration of the reforming reaction of CNG and oxygen. Though the yield of hydrogen/syngas is expected to increase at higher temperature, as shown in Fig. 6b, the engine operation is expected to be hard above certain temperature because the volumetric efficiency of cylinder will drop due to decrease of specific gravity amount of intake air and CNG.
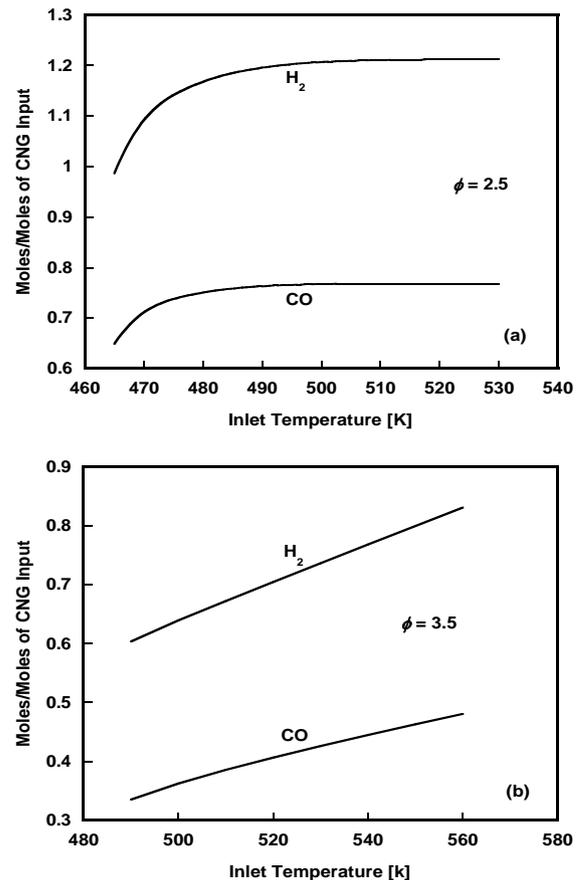
Fig. 6. Effect of inlet temperature on the exhaust moles of H$_2$ and CO with respect to input fuel.

3.3 Effect of Oxygen Contents in Air

To increase the relative yield of hydrogen/syngas in the products, it is suggested that pure oxygen or highly oxygenated air needs to be employed [3]. The effects of oxygen contents (by volume) in air on the exhaust mass fractions of H_2 and CO with various equivalence ratios are shown in Fig. 7. It can be seen that the mass fractions of H_2 and CO increase with an increase in oxygen contents in air. The increase in the mass fractions of H_2 and CO is more pronounced in a mixture of $\phi = 3$. It is to be noted that these simulation has been done with an inlet temperature of 540 K due to misfire occurred with the mixture of equivalence ratio of 3.5 when oxygen contents in air was increased.
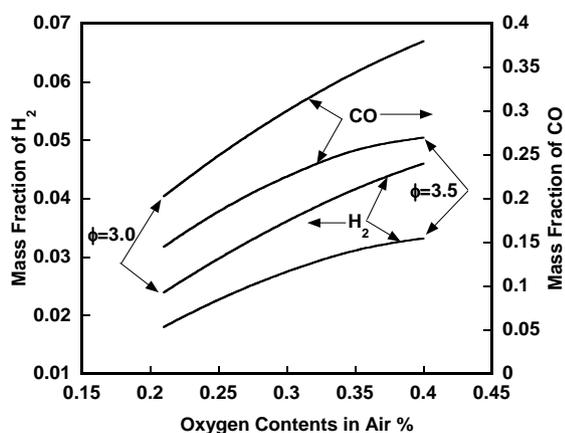
Fig. 7. Effect of oxygen contents in air on the exhaust mass fractions of H_2 and CO.
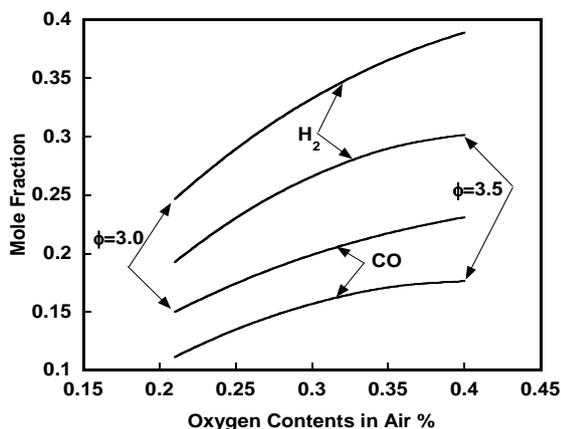
Fig. 8. Effect of oxygen contents in air on the exhaust mole fractions of H_2 and CO.
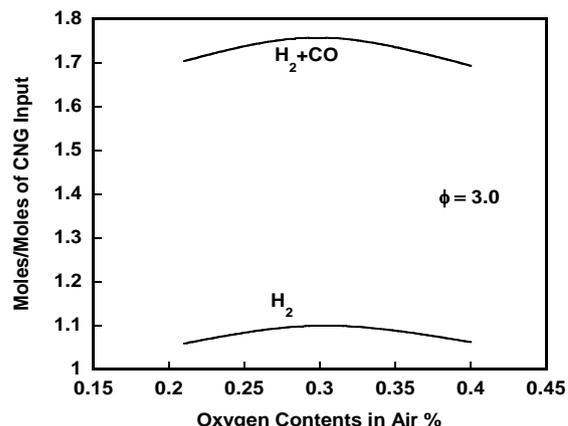
Fig. 9. Exhaust mole fractions of H_2 and CO per mole of fuel input versus oxygen contents in air.

In a mole basis, similar trends have been obtained for both H_2 and CO, as shown in Fig. 8, that oxygen enrichment resulted in increased H_2 and CO concentrations. The optimum quantity of oxygen in air in producing higher hydrogen/syngas yields is found to be around 0.3, as shown in Fig. 9. The increase of oxygen as an oxidizer causes the decrease of nitrogen and hence the increase of total entropy in the cylinder to supply sufficient thermal energy for reforming reaction, resulting in the increase of the yield of both H_2 and CO [3,23].

4. CONCLUDING REMARKS

A computer simulation is used to investigate the reforming characteristics of natural gas in a HCCI engine to show the possibility of producing hydrogen/syngas. The used simulation tool is CHEMKIN 3.7, using the GRI natural gas combustion mechanism. The operation characteristics are studied through the simulation with the variables affecting the yield of hydrogen rich gas. It is shown that partial oxidation engine operation can produce significant levels of exhaust hydrogen/syngas.

The following concluding remarks may be drawn from the results of the present study:

a) The concentration of hydrogen and syngas increase along with the increase of equivalence ratio until it peaked to the maximum at $\phi = 2.5$, and decrease afterward.

b) H_2/CO ratio increases as the equivalence ratio is increased.

c) Hydrogen yield increases as the inlet temperature is increased until a certain value after which the inlet temperature has no effect in the hydrogen production.

d) There is a good potential for producing gas mixtures containing hydrogen/syngas through the partial oxidation of natural gas with oxygenated air.

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e) The optimum quantity of oxygen in air in producing higher hydrogen and CO yields is found to be around 0.3.

f) This hydrogen/syngas production method will be accompanied simultaneously with efficiently produced power.

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