

Carbon monoxide yield in natural gas autothermal reforming process

S.H. Chan^{*}, H.M. Wang

School of Mechanical and Production Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798, Singapore

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Abstract

This study presents the effect of natural gas (NG) composition on carbon monoxide (CO) yield in the products of an autothermal reforming (ATR) process. Since NG is a mixture without definite composition, a computer routine is coded, which is able to randomly generate various compositions whose individual constituents fall within the defined ranges. Then each NG is analyzed based on the ATR process within optimal ranges of the air-to-fuel ratio (AFR) and water-to-fuel ratio (WFR), which were obtained from a typical composition of NG under the constraints of maximum hydrogen production, minimum carbon monoxide yield, and free from solid carbon in the reformat. Finally, the correlation between NG composition and carbon monoxide yield is established. This provides valuable information for the development of methods for the clean-up of carbon monoxide. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Natural gas; Carbon monoxide (CO); Autothermal reforming process

1. Introduction

Fuel cell technology offers significant promise as an alternative energy conversion device due to its high energy efficiency and low pollution. Hydrogen (H₂), as an ideal fuel for the fuel cell, can be obtained in several ways, but the most effective and feasible method at present should be through fuel reforming. That is, H₂ can be derived from fossil fuel through catalytic reaction in a reactor/reformer. Historically, H₂ derived from liquid fuels has been used in H₂ engine applications in order to reduce exhaust emissions and increase thermal efficiency through lean-combustion technology [1,2]. Since 1990s, fuel reforming technologies for fuel cell applications have been the subject of extensive study. Chrysler's fuel processing technology [3] can convert gasoline, diesel fuel, methane and alcohol into H₂-rich fuel. Argonne National Laboratory [4] has proposed a reactor for the partial oxidation (POX) of methanol; a 7.5 cm diameter and 40 cm long reactor can generate sufficient H₂-rich gas to operate a 18 kW fuel cell. Johnson Matthey Technology Center [5] has developed the 'Hot Spot' methanol processor which provides a H₂ concentration in the reformat that can be as high as 58%. Little [6] has been involved in the development of a POX fuel processor since 1992. This multi-fuel processor can accept gasoline as well as various

alternative fuels. McDermott Technology, Inc. (MTI) and Catalytic Advanced Technologies (CAT) [7] have teamed up to produce a compact autothermal reforming (ATR) fuel processor for fuel cell electric vehicle applications. Northwest Power Systems [8] has developed a family of versatile fuel processors based on a novel design which combines steam reforming (STR), heat recovery and H₂ purification into a single device. The Los Alamos National Laboratory [8] has focused on contaminant control through modification of fuel processing conditions either to remove the contaminants or to convert them into less troublesome compounds.

Commonly used reforming methods include partial oxidation (POX), STR, catalytic decomposition (CDC), and ATR. Among these, ATR, which combines POX and STR to achieve an overall net heat balance, is favored because of its superior approach to producing syngas from hydrocarbon fuels. During the ATR process, the air-to-fuel ratio (AFR) and the water-to-fuel ratio (WFR) are two crucial parameters, for a fixed composition of the fuel, in determining not only the reaction temperature but also the reformat composition. The optimum AFR and WFR can be determined under the criteria of maximum H₂ production and minimum CO yield in the reformat, as well as free from solid carbon formation during the processing. When the composition of any kind of fuel is indefinite, however, the composition of the reformat will be quite different from one to another under specified AFR and WFR. For example, natural gas (NG) contains methane in the range 70–90% and many other paraffin compounds. In this case, fuel

^{*} Corresponding author. Tel.: +65-790-4862; fax: +65-791-1859.
E-mail address: mshchan@ntu.edu.sg (S.H. Chan).

Nomenclature

a	number of atoms in products
AFR	air-to-fuel ratio
A/F	molar air-to-fuel ratio
b^0	number of atoms in reactants
C_nH_{2n+2}	paraffinic hydrocarbon family in natural gas
CO	carbon monoxide mole numbers per mole of natural gas consumed or (COMN)
COMF	carbon monoxide mole fraction in products
COMN	carbon monoxide mole numbers per mole of natural gas consumed
C_xH_y	weighted sum of paraffinic hydrocarbon family in the natural gas
$f(\text{CO})$	parameter related to carbon monoxide production
FCO	carbon monoxide mole numbers in 1 mole of natural gas
FCO_2	carbon dioxide mole numbers in 1 mole of natural gas
G	Gibbs free energy (J)
H	total enthalpy (J)
HC	parameter related to natural gas composition
n	total mole number
n_j	mole number of specie j
p	pressure (N m^{-2})
\bar{R}	universal gas constant ($8314 \text{ J mol}^{-1} \text{ K}^{-1}$)
T	temperature (K)
WFR	water-to-fuel ratio
W/F	molar water-to-fuel ratio
λ	Lagrangian multiplier
$\bar{\mu}$	molar chemical potential (J mol^{-1})
Π	function

Subscripts

1	reactants
2	products
i	element index
j	constant
m	constant
n	constant
o	atmospheric pressure

composition has become another important parameter besides AFR and WFR in the ATR process.

A study of the effect of NG composition on H_2 production shows that the weighted sum of paraffinic hydrocarbon family compositions (C_xH_y) in NG determines the H_2 mole numbers per mole of NG consumed in an ATR process under specified AFR and WFR. The greater the number of carbon atoms (x) in C_xH_y , the greater the number of H_2 moles will be. Besides H_2 , however, CO is an important constituent in the reformat, especially for low-temperature fuel cells, e.g.

PEMFC, which will poison the catalyst when its concentration is greater than 10 ppm [9] in the feedstock. Thus, minimizing CO yield is an important consideration in any fuel reforming process.

To study the effect of NG composition on CO yield, a computer routine is coded which is able to generate randomly various compositions of NG. Each NG is then analyzed based on the ATR method in a 'single-bed' reactor under specified AFR and WFR. The relationship between CO mole numbers (COMN) per mole of NG consumed and NG composition can then be established.

2. Fundamentals

2.1. NG compositions

2.1.1. Generation of 100 compositions of NG

It is known that NG is a mixture without definite composition. Each component of NG may vary within the range given in Table 1 [10,11].

Based on the probabilistic method, a computer routine is coded to generate various compositions of NG with each component varying randomly within its allowable range. Ten main components were selected, namely: methane (CH_4), nitrogen (N_2), carbon dioxide (CO_2), ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), hexane (C_6H_{14}), hydrogen (H_2), carbon monoxide (CO). The compositions of these 10 components, except that for CO_2 , were randomly generated by the simulator within their valid ranges. The mole fraction of CO_2 was calculated by

Table 1
Composition of natural gas

Component	Formula	Mole fraction
Main components		
Methane	CH_4	≥ 0.70
Nitrogen	N_2	≤ 0.20
Carbon dioxide	CO_2	≤ 0.20
Ethane	C_2H_6	≤ 0.10
Propane	C_3H_8	≤ 0.035
Butane	C_4H_{10}	≤ 0.015
Pentane	C_5H_{12}	≤ 0.005
Hexane	C_6H_{14}	≤ 0.001
Heptane	C_7H_{16}	≤ 0.0005
Octane and above	C_{8+}	≤ 0.0005
Hydrogen	H_2	≤ 0.10
Carbon monoxide	CO	≤ 0.03
Helium	He	≤ 0.005
Water	H_2O	≤ 0.00015
Minor and trace components		
Ethylene	C_2H_4	≤ 0.001
Benzene	C_6H_6	≤ 0.0005
Toluene	$\text{C}_6\text{H}_5\text{CH}_3$	≤ 0.0002
Argon	Ar	≤ 0.0002
Hydrogen sulfide	H_2S	≤ 0.0002
Oxygen	O_2	≤ 0.0002
Total unspecified components		≤ 0.0001

subtracting the sum of the mole fractions of the other nine components from one. With this method, 100 compositions of NG, each with 10 components, were generated and were believed to cover all possible NG compositions available in the gas market.

2.1.2. Representation of NG composition

In NG, the component that has the dominant influence on the reforming products is the paraffinic hydrocarbon family (C_nH_{2n+2} , $n = 1-6$ are considered in this study), especially, CH_4 . In general, the variation in the composition of the paraffinic hydrocarbon family can typically represent the variation in the NG composition. To obtain a fuel formula which represents the mean average of the paraffinic hydrocarbon family in the NG, the weighted sum of the paraffinic hydrocarbon family compositions (C_xH_y) must be defined. The respective numbers of carbon atoms and hydrogen atoms contained in 1 mole of C_xH_y are

$$x = \sum_{n=1}^6 c_n n \quad (1)$$

$$y = \sum_{n=1}^6 c_n (2n + 2) \quad (2)$$

where c_n denotes the mole fraction of the component C_nH_{2n+2} . For 100 compositions of NG randomly generated by a computer simulator, a linear relationship between x and y can be obtained, namely: $y = 0.162 + 3.647x$. If x is equal to 1, the H-to-C ratio in C_xH_y becomes 3.809, which implicitly indicates that CH_4 is the major component present in NG.

2.2. Thermodynamics

2.2.1. Chemical equilibrium

There are two common ways to express a chemical equilibrium. One is based on an equilibrium constant [12] while the other is the minimization of free energy [13]. One of the disadvantages of using the former is that it is more difficult to test for the presence of some condensed species, e.g. formation of solid carbon, in the reaction products than in the latter. It is anticipated that solid carbon may be produced during the fuel reforming process and deactivate the catalytic reactions. Therefore, a method based on minimization of free energy is normally used in fuel reforming analysis. In this study, minimization of Gibbs free energy is used to calculate the equilibrium composition of the products at specified temperature and pressure. A detailed description of this method has been reported previously [14].

2.2.2. Equilibrium temperature



The product temperature from the reactor is calculated based on the following assumptions.

- A steady flow process with negligible change in kinetic and potential energies.
- Perfect insulation of the reactor with negligible heat loss.
- An equilibrium chemical reaction with specified reactant compositions.
- An isobaric reaction with reactants entering the reactor at 1 atm and 298 K.

Based on the above assumptions, the total enthalpy of reactants should be equal to the total enthalpy of the products. Thus,

$$H_1(p_1, T_1, n_{1,j}) = H_2(p_2, T_2, n_{2,j}) \quad (3)$$

where subscript 1 denotes the reactants and subscript 2 denotes the products. Based on the above assumptions, the adiabatic temperature of the products (T_2) can be determined.

When T_2 is known, chemical equilibrium is considered to be established at this temperature. Since the POX is exothermic and STR is endothermic, the POX can provide the heat required by STR. The advantage of this reforming system is that the reaction can be carried out automatically and requires no heat from the external source. This reforming process is an autothermal process. Therefore, the equilibrium temperature can be adjusted by the molar air-to-fuel ratio (A/F) and the molar water-to-fuel ratio (W/F). An increase of A/F or a decrease of W/F causes the equilibrium temperature to increase, and vice versa. The values of A/F and W/F determine both the reaction temperature and the reformat composition.

2.3. Effect of NG composition on reformat

Among all the reformed gases, H_2 is the most desirable product for fuel cell applications. Solid carbon, on the other hand, is the most undesirable product. Once produced, it will deactivate the catalyst of the reformer and, hence, degrade its performance. The presence of CO in reformed gas is harmful to the electrode (anode) of the fuel cell (for PEMFC, the concentration of CO should be less than 10 ppm). Similarly, too high a content of CO in atmospheric air will also cause the same problem of cathode poisoning. Therefore, the target should be placed on locating an optimum operating regime (optimal W/F and A/F) that can maximize H_2 production with lowest possible CO yield and free from solid carbon during the reforming process.

In this study, the optimum operating range of A/F and W/F ($A/F = 3.5$; and $W/F = 2.5-4.0$) was obtained from a typical NG reforming [14,15]. Then, 100 kinds of NG with different compositions, generated randomly by a computer simulator, were analyzed for CO yield under this optimum A/F and W/F range.

3. Results and discussion

The CO mole fraction (COMF) reformed from 100 compositions of NG under a A/F of 3.5 and a W/F of 2.5 is shown in Fig. 1. Cases with higher COMF are 1, 2, 10, 15, 29, 32, 45, 61, 63, 70 and 82. The corresponding CO contents in NG for these cases are 0.731, 2.809, 0.684, 1.721, 2.088, 1.668, 1.666, 0.337, 2.019, 1.751, 2.932%, respectively, and the corresponding CO_2 contents are 0.167, 10.173, 9.183, 8.443, 2.252, 9.946, 9.476, 15.985, 0.864, 11.871, 10.448%, respectively. All of these cases are considered as NG contains a low content of the paraffinic family (the sum varies from 79.70 to 83.35%), except for cases 15 (87.28%) and 29 (88.39%). It is noted that for all these cases, either the paraffinic family content is low, or the CO content is high, or the CO_2 content is high in the NG and may cause a higher COMF. Cases with low COMF (0.04046–0.04132) are 14, 22, 31, 53, 60, 62, 78 and 84. All of these cases have a high content of the paraffinic family (the sum varies from 98.9 to 100%) with the contents of methane in the range

97.8–99.9%. The corresponding CO contents (volume concentration) in the NG are 0, 0, 0, 0, 0, 0, 0.00001, 0.00046, respectively, and corresponding CO_2 contents (volume concentration) are 0, 0.00002, 0, 0, 0, 0, 0.00013, 0.00081. It can be seen that all the cases which cause lower COMF have higher paraffinic family contents, lower CO contents and/or lower CO_2 contents in NG. The effect of CO_2 and CO contents in NG on the COMF can be explained by the water–gas shift reaction ($CO + H_2O \rightarrow CO_2 + H_2$). From this reaction, it is known that when the concentration of CO_2 increases, the chemical equilibrium will move to the direction of an increase in CO concentration, which leads to a higher CO equilibrium concentration. Obviously, the higher the initial CO concentration, the higher the final CO equilibrium concentration will be, and vice versa. Therefore, a conclusion can be drawn that COMF is related to the composition of NG, in particular the contents of the paraffinic family, CO and CO_2 in NG. A higher paraffinic family content, a lower CO content or/and a lower CO_2 content may lead to a lower yield of CO, and vice versa. The deviation of

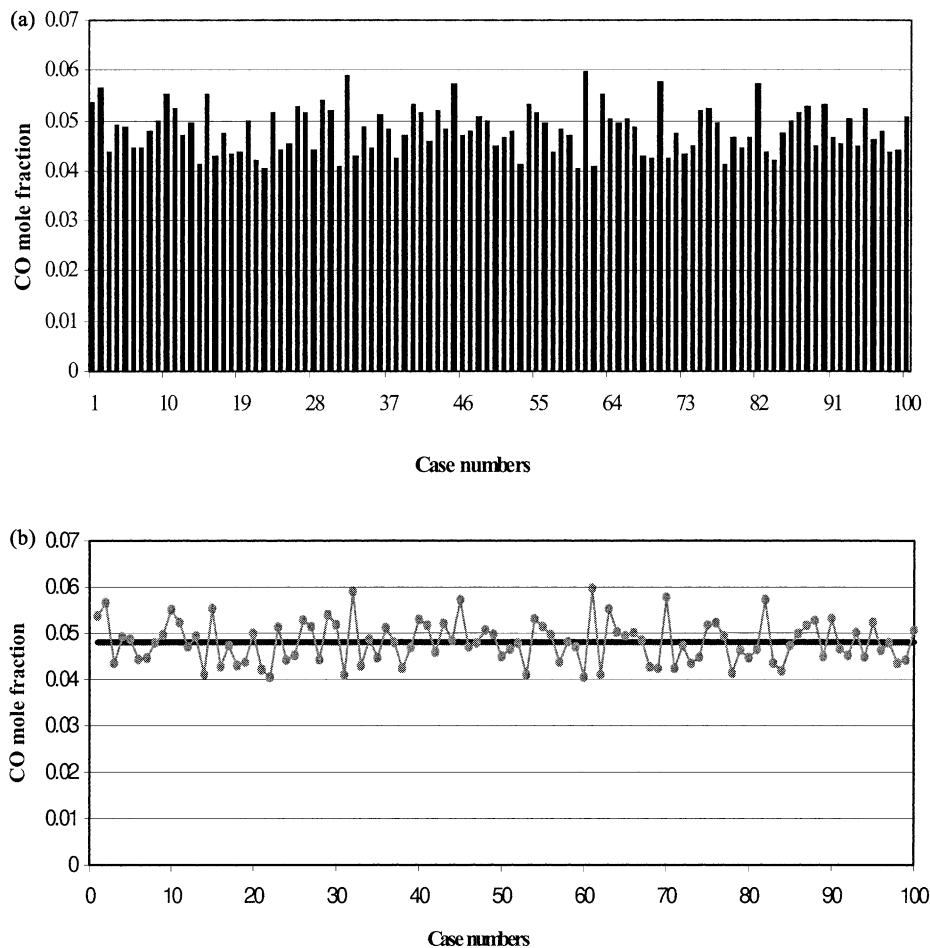


Fig. 1. (a) Carbon monoxide (mole fraction) reformed from 100 compositions of natural gas at $A/F = 3.5$ and $W/F = 2.5$. (b) Deviation of carbon monoxide (mole fraction) from case-to-case against average carbon monoxide yield at $A/F = 3.5$ and $W/F = 2.5$.

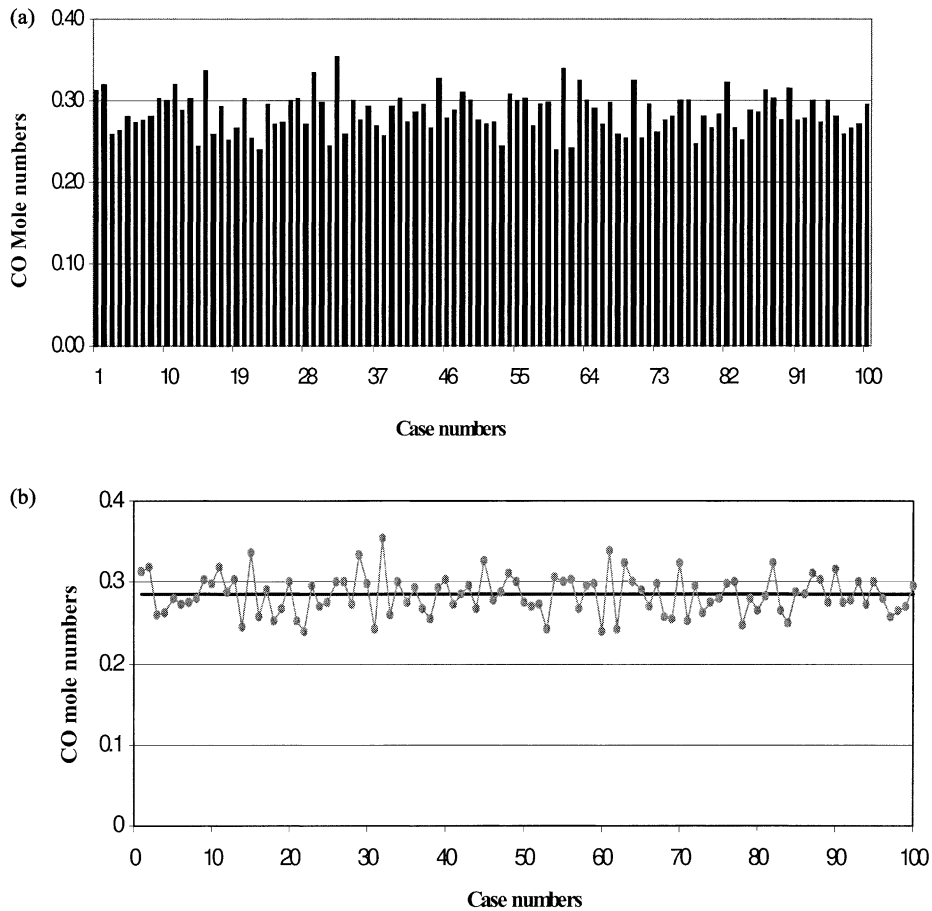


Fig. 2. (a) Carbon monoxide (mole numbers) reformed from 100 compositions of natural gas at $A/F = 3.5$ and $W/F = 2.50$. (b) Deviation of carbon monoxide (mole numbers) from case-to-case against average carbon monoxide yield at $A/F = 3.5$ and $W/F = 2.5$.

all COMF around the mean value of 0.04803 (or 4.803% in volume concentration) is shown in Fig. 1(b). The range of variation is between 4.046 and 5.967% in volume concentration.

The COMN produced by 1 mole NG for 100 kinds of NG with different compositions under a A/F of 3.5 and a W/F of 2.5 is shown in Fig. 2. Cases with low COMN (from 0.23883 to 0.24997) are 14, 18, 22, 31, 53, 60, 62, 78, 84. While, cases 1, 2, 11, 15, 29, 32, 61, 63, 70, 87 and 90 correspond to a relatively high COMN (>0.31). There is a similar profile for the COMN and COMF. Compared with COMF, COMN can be used as a criterion to identify the quality of any fuel processing technique in the context of generating low CO reformat. This is because the CO (in mole number) produced is based on 1 mole of NG used and the reforming process is self-supported. Unlike the steam-reforming process or thermal decomposition, heat is applied from the external source to drive the reaction. Though CO produced by these methods can be also based on 1 mole of NG consumed, COMN so obtained may not be a reflection of the quality of the processing technique if the external heat source is generated by a combustion process, which contributes to CO formation as well. The deviation of all

COMN around the mean value of 0.28449 is presented in Fig. 2(b). The range of variation is between 0.2388 and 0.3534.

From the above analysis, it can be concluded that COMN is related to the composition of the paraffinic family and the CO and CO_2 contents in the NG under specified A/F and W/F . In order to simplify the relationship between the composition of NG and COMN, an expression for $f(\text{CO})$ is established

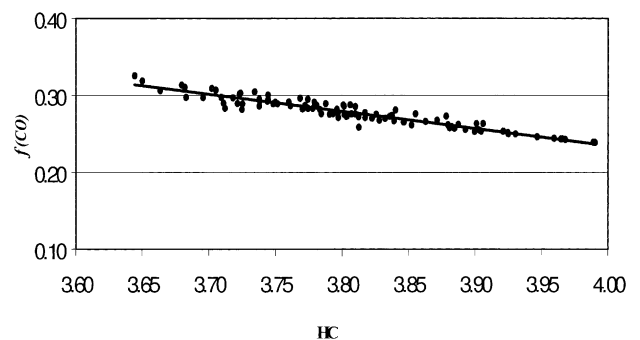


Fig. 3. $f(\text{CO})$ distribution as a function of HC at $A/F = 3.5$ and $W/F = 2.5$.

as a function of the H-to-C ratio, i.e.

$$f(\text{CO}) = \text{CO} - 0.5\text{FCO} - 0.2\text{FCO}_2 \quad (4)$$

where CO is the COMN produced by 1 mole of NG consumed or COMN; FCO the COMN in 1 mole of raw NG and FCO₂ is the carbon dioxide mole numbers in 1 mole of raw NG. Another parameter (HC) is defined as

$$\text{HC} = \frac{y}{x} \quad (5)$$

where x and y are defined in the Eqs. (1) and (2). The relationship between HC and $f(\text{CO})$ is shown in Fig. 3. It can be clearly seen that $f(\text{CO})$ decreases with increase in HC. In other words, when the CO and CO₂ present in the raw NG are fixed, an increase in HC will lead to a decrease in COMN. From the trend of this monotonic decreasing linear function, the lowest $f(\text{CO})$ is achieved when the paraffinic family of NG is pure methane gas. From the definition of HC, it is obvious that the value of HC is not only related to the sum of the paraffinic family in the NG, but is also related to the proportion of compositions among the paraffinic family. Therefore, these two parameters both exert an

influence on the yield of CO for the specified FCO and FCO₂. From curve-fitting of the data points as expressed in Eq. (5), the coefficient of FCO is 0.5, which is greater than 0.2 of FCO₂. This indicates that among all the compositions of NG, the CO content has a stronger impact on CO yield than that of CO₂.

The results of CO yield in the reforming process using the same 10 kinds of NG reformed under a A/F of 3.5 and a W/F of 4.0 are shown in Figs. 4–6. Compared with a A/F of 3.5 and a W/F of 2.5 in the previous case, both COMF and COMN have the same profile for the same 100 kinds of NG. That is, a higher composition of the paraffinic family (higher HC), a lower CO content, and/or a lower CO₂ content give rise to a lower CO yield in the reformat. For $A/F = 3.5$ and $W/F = 4.0$, the averaged COMF and COMN are 2.523% and 0.1510, respectively, and the range of variation of COMF and COMN are 2.837–3.343% and 0.1209–0.1699, respectively. The results show that when more water is added to the reforming process (i.e. W/F from 2.5 to 4.0), the CO content (either in COMF or COMN) is decreased for all kinds of NG. The variation of the parameter $f(\text{CO})$ against HG for $W/F = 4.0$ is similar to that for $W/F = 2.5$, but the absolute value of $f(\text{CO})$ is much less.

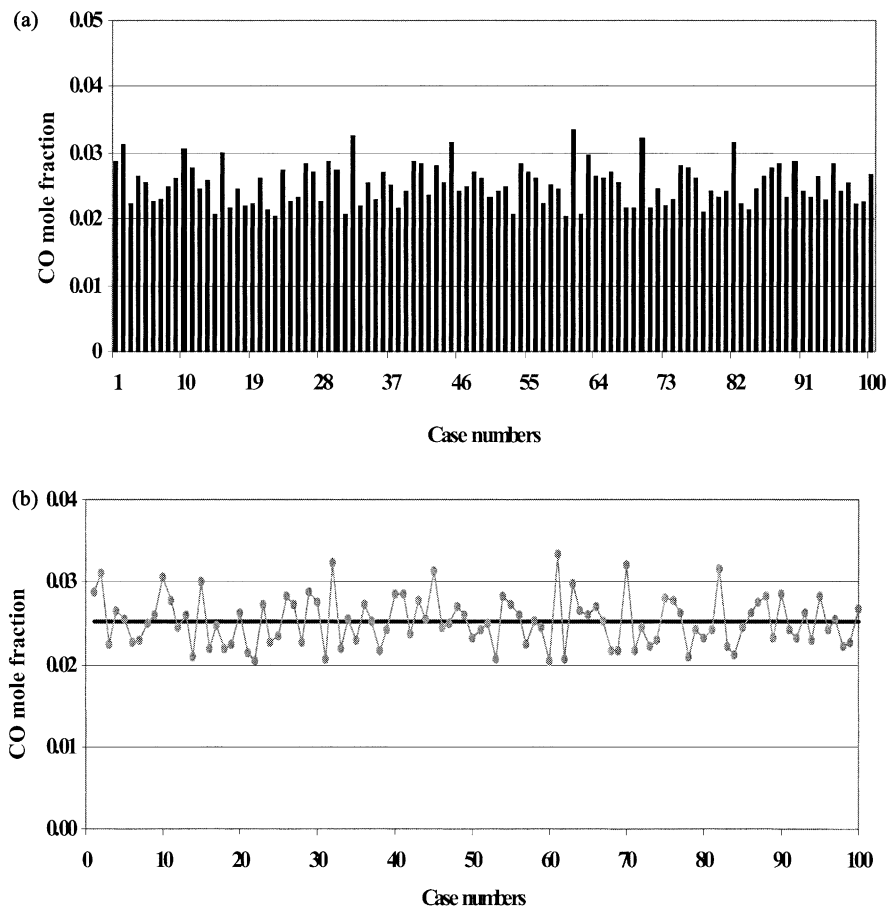


Fig. 4. (a) Carbon monoxide (mole fraction) reformed from 100 compositions of natural gas at $A/F = 3.5$ and $W/F = 4.0$. (b) Deviation of carbon monoxide (mole fraction) from case-to-case against average carbon monoxide yield at $A/F = 3.5$ and $W/F = 4.0$.

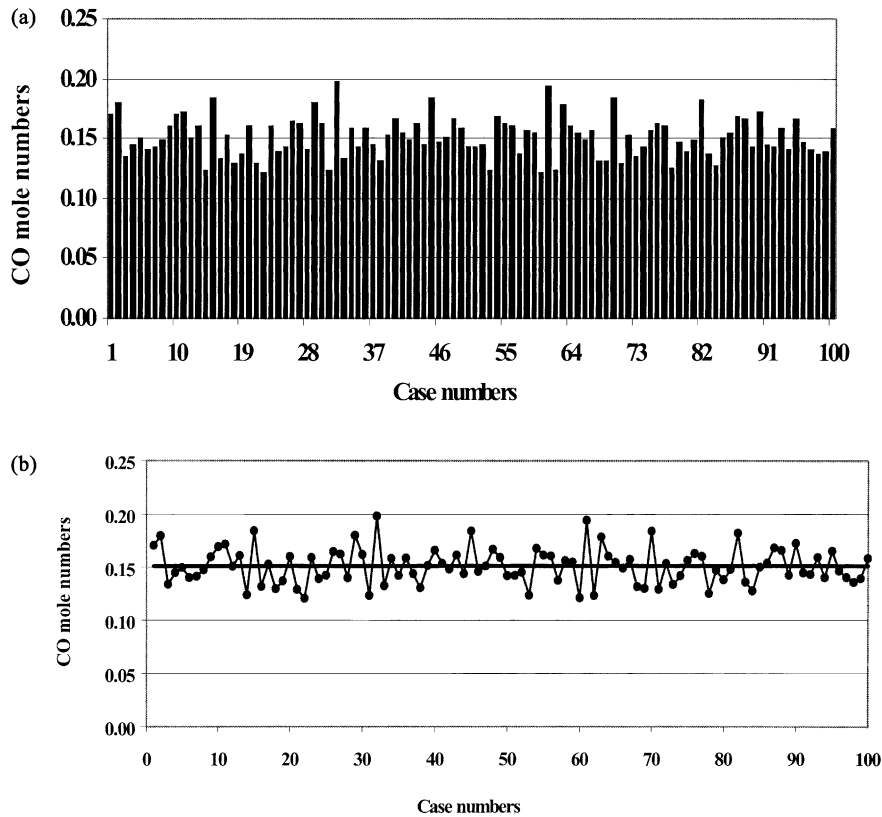


Fig. 5. (a) Carbon monoxide (mole number) reformed from 100 compositions of natural gas at $A/F = 3.5$ and $W/F = 40$. (b) Deviation of carbon monoxide (mole number) from case-to-case against average carbon monoxide yield at $A/F = 3.5$ and $W/F = 4.0$.

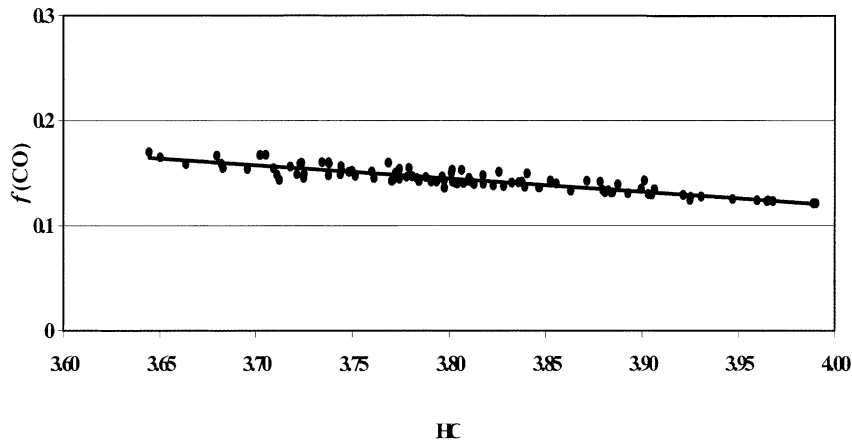


Fig. 6. $f(\text{CO})$ distribution as a function of HC at $A/F = 3.5$ and $W/F = 4.0$.

4. Conclusions

- A computer simulator has randomly generated 100 kinds of NG. The results of autothermal fuel reforming conducted for these 100 kinds of NG at molar A/F and W/F ratios of 3.5 and 2.5, respectively, show that the average COMN (per mole of NG consumed) is 0.2845, and the variation is in the range 0.2388–0.3534. This indicates

that the composition of NG has a great impact on the yield of CO.

- When the molar W/F ratio is increased to 4.0 while the other conditions remain the same, the average COMN decreases to 0.1510, and the variation falls within the range 0.1209–0.1981. It is, therefore, concluded that the higher WFR reduces the CO yield with an expected lower equilibrium temperature.

- For specified AFR and WFR ratios, COMN is determined by the composition of the paraffinic family, the proportions among the paraffin family, and the CO and CO₂ contents in NG. A higher paraffinic family content, a higher H-to-C, a lower CO content or/and a lower CO₂ content in NG can lead to a lower CO yield, and vice versa. The content of CO in the NG has a stronger influence on the COMN than that of CO₂.

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