CHEMICAL ENGINEERING TRANSACTIONS

VOL. 39, 2014

A publication of AIDIC
The Italian Association
of Chemical Engineering
www.aidic.it/cet

Guest Editors: Petar Sabev Varbanov, Jiří Jaromír Klemeš, Peng Yen Liew, Jun Yow Yong

ISBN 978-88-95608-30-3; **ISSN** 2283-9216

DOI: 10.3303/CET1439245

Theoretical Study on the Ethanol-Fueled SOFC System Integrated with Dehumidifier

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A solid oxide fuel cell (SOFC) fuelled by ethanol, an attractive green fuel that can be renewably produced from agricultural products, is regarded as a promising clean process to generate electricity with high efficiency. However, the direct feeding of ethanol to SOFC always causes a carbon formation problem. The use of an external steam reformer to convert ethanol into hydrogen for SOFC is another choice. In general, more steam is introduced to the reformer to obtain the hydrogen-rich gas product. This operational strategy may degrade the SOFC performance due to the dilution effect caused by the excess steam. In this study, the effect of removing steam from the reforming gas before it enters a cell stack on the electrical efficiency of SOFC is investigated. The minimization of total Gibbs free energy is employed to determine the equilibrium compositions of a hydrogen-rich gas from the ethanol steam reforming process. The electrical characteristics of the SOFC are evaluated by using the generalized, steady state electrochemical model taking all various voltage losses into account. An internal reforming of CH_4 and CO in the SOFC stack is also considered. Performance of the steam reformer and SOFC integrated system with and without a dehumidifying unit is compared and analysed with respect to key operating parameters.

1. Introduction

Today, the energy demand continues to increase considerably because of rapid population growth and economic development. Among the developing technologies for power generation, a fuel cell has been accepted to be a potential alternative. It is an electrochemical device that can directly convert chemical energy in fuels to electrical energy via an electrochemical process. A solid oxide fuel cell (SOFC) is among the types of fuel cells that is operated at high temperatures (873-1,273 K), allowing internal conversion of a wide range of fuels in SOFC itself and generation of high-quality by-product heat for cogeneration or trigeneration applications (Al-Sulaiman et al., 2010).

Ethanol is considered an attractive green fuel for use in SOFC because it can be produced renewably from various agriculture products. Regarding the cost effectiveness, only the utilization of renewable fuels from agricultural residues will allow SOFC be competitive potential in the near-term future. Compared with other fuels, ethanol presents several advantages, including a high heat of vaporization, a low photochemical reactivity, ease of storage and handling safety (Palma et al., 2013). However, the direct feeding of ethanol into SOFC always causes a carbon formation problem (Meusinger et al., 1998). The use of an external reformer to convert ethanol into hydrogen for SOFC is considered another choice.

Nowadays a steam reforming is the most commonly used process for hydrogen production from ethanol. Various aspects of hydrogen production for SOFC systems have been studied during the past decades. The effect of the reforming factors on the product yields and carbon deposits was analysed by Alvarado and Gracia (2010). The synthesis of suitable catalysts (Auprêtre et al., 2002), the reactor design (Bruschi et al., 2012), and even the energy and exergy analysis of hydrogen production from ethanol (Casas et al., 2010) are subjects of interest. To attain high hydrogen yield, the addition of more steam to the steam

Please cite this article as: Tippawan P., Assabumrungrat S., Arpornwichanop A., 2014, Theoretical study on the ethanol-fueled SOFC system integrated with dehumidifier, Chemical Engineering Transactions, 39, 1465-1470 DOI:10.3303/CET1439245

reformer is needed to promote the steam reforming reaction; however, it dilutes the hydrogen product stream, thereby degrading the fuel cell performance.

The aim of this study is to analyse the effect of removing steam from the reformate gas before it is fed to a cell stack by using a dehumidifier. The dehumidifier is conceptually designed and integrated with the SOFC system. The simulation of the ethanol steam reformer is performed to investigate its performance with respect to key operating parameters. A model of the SOFC integrated system is developed and employed to study its electrical and thermal energy performance. High-quality by-product heat form anode exhaust gas is recovered to be used in all requiring heat units. The SOFC integrated system with and without the dehumidifying unit is compared and analysed in terms of electrical and thermal efficiencies by using Aspen Plus.

2. SOFC system

A schematic diagram of the ethanol fuelled-SOFC system integrated with a dehumidifier is shown in Figure 1, which consists of three sections: (1) an ethanol steam reformer to convert ethanol into H_2-rich gas via the steam reforming process, (2) a dehumidifier to remove portion of steam from H_2-rich gas, and (3) the SOFC stack to generate electricity from the electrochemical reaction of hydrogen and oxygen.

2.1 Ethanol steam reformer

The ethanol steam reformer is a fuel processor for producing hydrogen-rich gas from ethanol by using steam as an agent. Ethanol and water at the temperature of 298 K are firstly fed to heaters where they are vaporised and preheated to the reforming temperature. Table 1 shows the reactions occurred under the steam reforming environment.

In this study, the thermodynamic analysis of the ethanol reforming reformer is performed using Aspen Plus simulator based data reported by Lima da Silva et al. (2009). The equilibrium composition of the reforming products is determined by the minimization of a total Gibbs free energy, known as a non-stoichiometric approach. It is assumed that the reformer is run at atmospheric pressure and a pressure drop is neglected; heat required for the reforming process is supplied by an anode exhaust gas and there are no heat losses to the surrounding; Peng-Robinson equation of state is employed to compute the thermodynamic properties of substances in the process. The primary components involved the ethanol reforming processes are C_2H_5OH, H_2O, O_2, CH_3CHO, C_2H_4, H_2, CH_4, CO_2, CO and C. To analyse the carbon formation, it is assumed that pure carbon is present in the graphitic form.

2.2 Dehumidifier

The dehumidifier is used to reduce the level of moisture in the H_2-rich gas. It is assumed that a compressor based on the dehumidifier draws the gas from the reforming process over a filter and passes it over some very cold coils where steam is condensed. The dehumidified gas is then reheated to the SOFC temperature and blown back out of the dehumidifier. It is noted that this approach may faces some difficulties in operation owing to the extreme environment and corrosion problem (Harriman, 1990). Using the dehumidifying system can eliminate the unnecessary steam and improve the quality of hydrogen fuel.

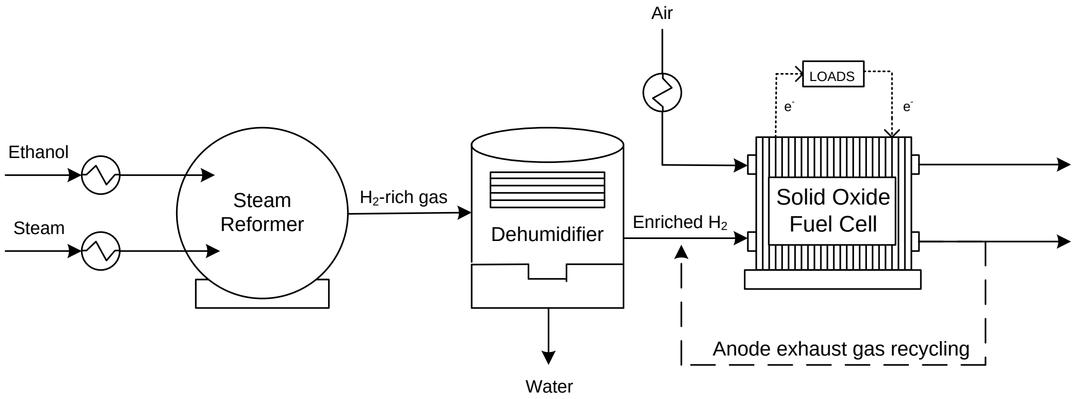

Figure 1: Schematic diagram of the ethanol-fuelled SOFC system integrated with a dehumidifier

Table 1: Possible reactions in the ethanol-fuelled SOFC system (Llorca et al., 2013)

Ethanol steam reformer			
$C_2H_5OH + H_2O \leftrightarrow 2CO + 4H_2$	$\Delta H^0_{298K} =$	+255.5	kJ/mol
$C_2H_5OH \leftrightarrow CH_3CHO + H_2$	$\Delta H^0_{298K} =$	+68.4	kJ/mol
$CH_3CHO + H_2O \leftrightarrow 2CO + 3H_2$	$\Delta H^0_{298K} =$	+187.1	kJ/mol
$CH_3CHO \leftrightarrow CH_4 + CO$	$\Delta H^0_{298K} =$	-18.8	kJ/mol
$C_2H_5OH \leftrightarrow C_2H_4 + H_2O$	$\Delta H^0_{298K} =$	+45	kJ/mol
$C_2H_4 + 4H_2O \leftrightarrow 6H_2 + 2CO_2$	$\Delta H^0_{298K} =$	+127.6	kJ/mol
$CH_4 + H_2O \leftrightarrow CO + 3H_2$	$\Delta H^0_{298K} =$	+205.5	kJ/mol
$CO + H_2O \leftrightarrow CO_2 + H_2$	$\Delta H^0_{298K} =$	-40.4	kJ/mol
$2CO \leftrightarrow CO_2 + C$	$\Delta H^0_{298K} =$	-171.5	kJ/mol
$C_2H_4 \leftrightarrow [\text{polymers}] \leftrightarrow 2C + 2H_2$	$\Delta H^0_{298K} =$	-52.1	kJ/mol
$CO + H_2 \leftrightarrow H_2O + C$	$\Delta H^0_{298K} =$	-131	kJ/mol
$CO_2 + 2H_2 \leftrightarrow 2H_2O + C$	$\Delta H^0_{298K} =$	-89.8	kJ/mol
SOFC stack			
$0.5O_2 + 2e^- \rightarrow O^{2-}$			
$H_2 + O^{2-} \rightarrow H_2O + 2e^-$			
$H_2 + 0.5O_2 \rightarrow H_2O$	$\Delta H^0_{298K} =$	-286	kJ/mol

Table 2: Material properties and kinetic parameters for the SOFC model (Aguiar et al., 2004; Petruzzi et al., 2003)

	Cathode	Electrolyte	Anode
Material	$La_{1-x}Sr_xMnO_3$	YSZ	Ni-YSZ
Layer thickness (µm)	50	20	500
Pre-exponential factor of exchange current density ($\Omega^{-1}m^{-2}$)	2.35×10^{11}	-	6.54×10^{11}
Activation energy of exchange current density (kJ mol^{-1})	137	-	140
Diffusion coefficient (m^2s^{-1})	1.37×10^{-5}	-	3.66×10^{-5}
Electronic conductivity ($\Omega^{-1}m^{-1}$)	8.4×10^3	-	80×10^3
Ionic conductivity ($\Omega^{-1}m^{-1}$)	-	$3.34 \times 10^4 \exp(-10,300/T)$	-

Table 3: Design specification and operating conditions for the SOFC system

Ethanol steam reformer	
Operating temperature (K)	980
Operating pressure (atm)	1
Molar flow rate of ethanol (kmol h^{-1})	1
SOFC stack	
Area (m^2)	100
Operating temperature (K)	1,073
Operating pressure (atm)	1
Fuel utilization (%)	70
Air composition	21 % O_2, 79 % N_2

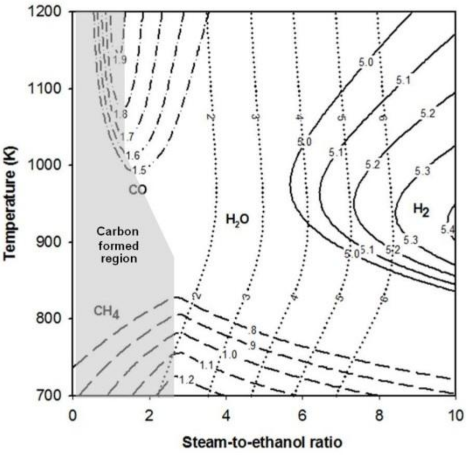

Figure 2: Effect of temperature and steam-to-ethanol ratio on the product yields (a number on the line is the amount of gaseous products (mole/mole of ethanol feed))

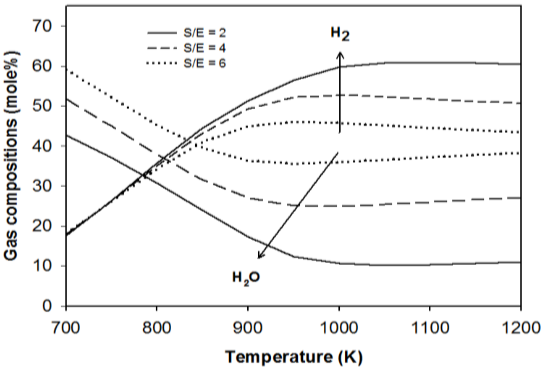

Figure 3: Effect of reforming temperature on product gas composition at different steam-to-ethanol ratios

2.3 SOFC

The SOFC is a power generator device that converts the chemical energy in fuel into electric power via an electrochemical reaction (Table 1). The electrochemical model of SOFC proposed by Aguiar et al. (2004) is used in this study. Simulation of the SOFC unit is performed based on input parameters given in Table 2. The anode and cathode of the SOFC are represented by an equilibrium reactor module and a separator module, respectively. Although SOFC is operated at high temperatures, allowing the feasibility of the direct oxidation of CO and CH_4 without a catalyst, it is assumed in this study that only the electrochemical reaction of hydrogen is present because the kinetic of the hydrogen oxidation on the anode is faster than that of the CO and CH_4 oxidations significantly.

3. Results and discussion

3.1 Effect of temperature and steam-to-ethanol ratio on the product gas composition

Simulation of the ethanol steam reforming process is performed to investigate the effect of key operating parameters, such as, temperature and steam-to-ethanol ratio (S/E). For each water feed ratio, the hydrogen yield reaches the highest value when the reforming temperature is in the range of 900-1,000 K. However, the more steam feed the more reforming performance can be enhanced. For example, when the reformer is operated at the steam-to-ethanol ratio of 10, the highest hydrogen yield of 5.4 mole/mole ethanol is obtained. It is noted that in practice, the reformer can be run at a lower S/E ratio to save energy demand because the remaining CH_4 and CO can be used as fuel in SOFC; at low S/E ratio, these reforming products are more produced under the thermodynamic control. A carbon formed region under the reformer operation is also presented in the Figure 2, so that it will be easy to choose the reforming operational conditions without the formation of carbon. Effect of temperatures on the H_2 and H_2O compositions at different steam-to-ethanol ratios is shown in Figure 3. The results show that the concentration of H_2 increases with the increased temperature and is kept content when the reforming temperature is higher than 980 K. Under this operating temperature, the synthesis gas obtained contains H_2 around 45-60 %, depending on the used excess steam.

3.2 SOFC performance

The dehumidifier is employed to keep the humidity of the synthesis gas product at a desired limit. The dehumidification ratio (DR) is defined as the ratio of steam removed from the gas product to the total amount of steam in the synthesis gas feed. The SOFC system is operated based on design specification and conditions given in Table 3. The results show that the DR affects the SOFC performance in term of cell voltage as shown in Figure 4. An increase in DR increases the voltage of the SOFC. High removal of steam improve the quality of hydrogen feed to SOFC and the electrochemical reaction in the SOFC is more pronounced along with the decreased concentration loss.

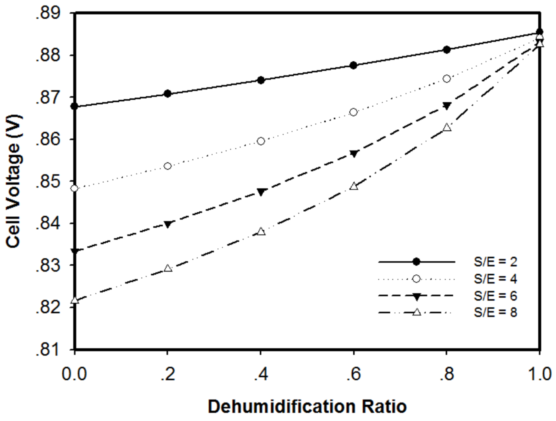

Figure 4: Effect of dehumidification ratio (DR) on the fuel cell voltage at different steam-to-ethanol ratios

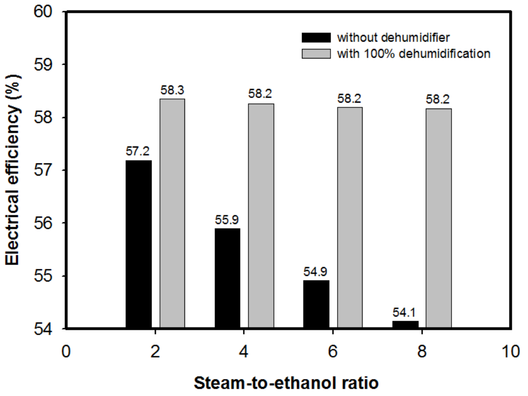

Figure 5: Electrical efficiency of the SOFC systems with and without dehumidifier at different steam-to-ethanol ratios

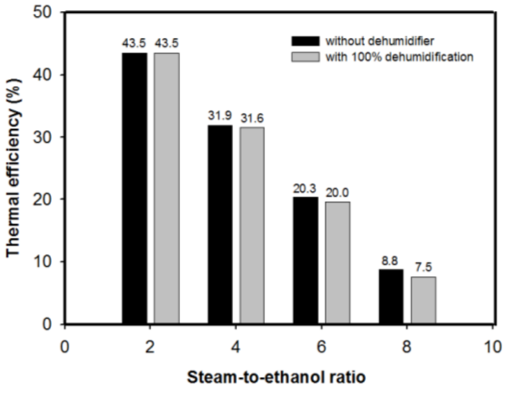

Figure 6: Thermal efficiency of the SOFC systems with and without dehumidifier at different steam-to-ethanol ratios

3.3 Efficiencies of SOFC system

The comparison of the SOFC efficiencies with and without a dehumidifier is analysed at various steam-to-ethanol ratios as shown in Figures 5 and 6. It is found that the electrical performance of the SOFC system without the dehumidifier decreases when increasing the steam-to-ethanol feed ratio. This can be explained by a dilution of the fuel fed to the SOFC. When the steam and ethanol are fixed at the ratio of 8, the electrical efficiency of the SOFC system with 100 % dehumidification is 58.2 %, which is higher than that without the dehumidifier (54.1 %) as shown in Figure 5. However, it is observed that the SOFC system without the dehumidifier unit can achieve its high efficiency when it is operated at a lower steam-to-ethanol ratio. Moreover, it is better if the least amount of water is added to the reformer in order to keep its high thermal efficiency as shown in Figure 6. When the SOFC system is run at low steam-to-ethanol ratio, heat obtained from the anode gas is higher than that required by the reformer and heaters. To further improve the system efficiency, the remaining useful heat can be applied to other heat requiring components in cogeneration or trigeneration applications. Figure 6 also shows that the addition of the dehumidifier in the SOFC system has less impact on its thermal efficiency.

4. Conclusions

In this study, the performance of an ethanol-fuelled SOFC system integrated with a dehumidifier was analysed. Simulation of the ethanol steam reformer was first performed to study the effect of key operating parameters on product distribution. It was found that the highest hydrogen yield can be achieved when operating the ethanol steam reformer at the operating temperature of 980 K with any steam-to-ethanol ratios. The installation of the dehumidifier at the outlet of the ethanol steam reformer to eliminate unnecessary steam can improve the actual cell voltage and electrical efficiency. Operating the reformer at low level of steam with the dehumidification provides the better SOFC system performance. The use of the dehumidifier has less effect on the thermal system efficiency; thus, the ethanol-fuelled SOFC system integrated with the dehumidifier is the attractive approve to improve the SOFC system performance.

Acknowledgements

Support from the Ratchadaphiseksomphot Endowment Fund of Chulalongkorn University (RES560530168-EN) is gratefully acknowledged. P. Tippawan would like to thank the Dutsadiphiphat Scholarship, Ratchadaphiseksomphot Endowment Fund, Chulalongkorn University.

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