Bioresource Technology 157 (2014) 231–239

Contents lists available at ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

Energy and exergy analysis of an ethanol reforming process for solid oxide fuel cell applications

Phanicha Tippawan, Amornchai Arpornwichanop *

Computational Process Engineering Research Unit, Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University, Bangkok 10330, Thailand

HIGHLIGHTS

- Energy and exergy analysis of ethanol reforming processes for SOFC are preformed.
- Steam reforming, partial oxidation and autothermal reforming are considered.
- The possibility of carbon formation in different ethanol reformings are examined.
- Use of ethanol reforming for fuel cell applications is discussed.
- The best ethanol reforming process for SOFC applications is identified.

ARTICLE INFO

Article history:
Received 5 December 2013
Received in revised form 25 January 2014
Accepted 27 January 2014
Available online 5 February 2014

Keywords:
Ethanol reforming
Solid oxide fuel cell
System performance
Energy analysis
Exergy analysis

ABSTRACT

The fuel processor in which hydrogen is produced from fuels is an important unit in a fuel cell system. The aim of this study is to apply a thermodynamic concept to identify a suitable reforming process for an ethanol-fueled solid oxide fuel cell (SOFC). Three different reforming technologies, i.e., steam reforming, partial oxidation and autothermal reforming, are considered. The first and second laws of thermodynamics are employed to determine an energy demand and to describe how efficiently the energy is supplied to the reforming process. Effect of key operating parameters on the distribution of reforming products, such as H_2, CO, CO_2 and CH_4, and the possibility of carbon formation in different ethanol reformings are examined as a function of steam-to-ethanol ratio, oxygen-to-ethanol ratio and temperatures at atmospheric pressure. Energy and exergy analysis are performed to identify the best ethanol reforming process for SOFC applications.

1. Introduction

A solid oxide fuel cell (SOFC) is considered the most promising technology for power generation for residential and stationary applications. Presently, hydrogen is a primary fuel for SOFC stacks. It can be produced from a wide range of fossil and renewable fuels via thermal-chemical and biological processes (Lin et al., 2013). Among the various renewable fuels, ethanol is a very attractive green fuel as it is produced by fermentation of agricultural products and easy to handle as a liquid fuel (Cardona and Sánchez, 2007). There are several methods to produce hydrogen rich gas from ethanol. A steam reforming is among the widely used processes due to its high hydrogen yield; however, this process involves a highly endothermic reaction and requires high energy supply. To minimize the external heat input, partial oxidation and autothermal reforming are alternative routes for hydrogen production (Rabenstein and Hacker, 2008). Because SOFC is operated at high temperatures and a waste heat recovery is generally included in the SOFC system to enhance its performance, a selection of appropriate fuel processing technology should also take an efficient energy usage into account.

Regarding the first law of thermodynamics, an energy balance can be used to determine the energy requirement in the forms of matter streams, heat and work, but fails to provide accurate information on how efficiently the supplied energy is used in a system. This is due to the fact that such an energy analysis cannot identify the real thermodynamic inefficiencies associated with the energy conversion system. On the other hand, an entropy balance determines entropy generation within the system, which is the indicator of its inefficient energy usage. However, since the entropy still fails to account for the quality of energy, the true thermodynamic value (quality) of an energy carrier is characterized by its exergy. Exergy destruction which is one of the exergy-based variables represents the exergy destroyed by an irreversibility (entropy generation) process within the system (El-Emam and Dincer,

* Corresponding author. Tel.: +66 2 218 6878; fax: +66 2 218 6877.
E-mail address: Amornchai.A@chula.ac.th (A. Arpornwichanop).

http://dx.doi.org/10.1016/j.biortech.2014.01.113
0960-8524/

2011). The irreversibility is caused by chemical reaction, heat transfer through a finite temperature difference, mixing of matter and unrestrained expansion and friction. In the past, there are few studies concerning about a comparison of hydrogen production from ethanol using different reforming processes. The investigation of the ethanol processing, i.e., steam reforming, partial oxidation and autothermal reforming, and the range of optimal operating conditions for each process was given. However, based on their results, it is difficult to determine exactly the suitable operational policy of the reforming processes. Furthermore, the process performance in terms of the energy demand was only focused (Rabenstein and Hacker, 2008). The thermodynamic analysis of different ethanol reforming processes was also studied (Sun et al., 2012). The optimal conditions for operating the ethanol reformer were proposed. It was found that the partial oxidation of ethanol provides the lowest H_2 yield with high possibility of coke formation, so it is not a suitable process for hydrogen production. However, the benefit of the partial oxidation process is to give useful heat, which can improve the system thermal management.

It is known that the first law of thermodynamics gives information about the conservation of energy within the process, whereas the second law of thermodynamics can be used to assess and improve the process, leading to a better understanding of the process energy usage. This meaningful information of the process operation cannot be attained by an energy analysis alone (Rosen et al., 2008). Even though, some researchers focused on an exergy analysis of the hydrogen production from ethanol (Douvartzides et al., 2004; Song et al., 2005; Casas et al., 2010), only the steam reforming process was chosen without comparing to other reforming processes. To date, exergatic information of each ethanol reforming process has not been clearly reported. The effect of the reforming factor on the exergetic efficiency of the solid oxide fuel cell (SOFC) power plant based on an external ethanol steam reforming was analyzed (Douvartzides et al., 2004). It indicated that the maximum exergy destruction rate is found in a combustion process. The study of the ethanol-fueled proton exchange membrane fuel cell for automobile applications can be concluded that the utilization of excess steam results in an increase of the overall exergy destruction and lowers the plant efficiency (Song et al., 2005). Recently, the model based energy–exergy analysis of the SOFC power plant was performed (Casas et al., 2010). The study suggested that the efficient use of waste heat in the SOFC combined cycle can reduce the irreversibility of the system, resulting in increases in the energy and exergy efficiencies.

In this study, the first and second laws of thermodynamics are applied to analysis of an ethanol reforming process to produce hydrogen fuel. Three different reforming methods, i.e., steam reforming, partial oxidation and autothermal reforming, are considered. Effects of key operating parameters, such as reactant feed ratio and operating reforming temperatures, on the equilibrium composition of reforming products are also presented. The performance assessment of each ethanol reforming process in terms of product yield, carbon-free operational region and energy usage is carried out in detail with the aim to optimize the process operation. Based on the second law of thermodynamics, the comprehensive analysis of an exergy destruction in different ethanol reforming processes is also discussed. Finally, the application of the ethanol reforming to produce hydrogen for SOFC is commented.

2. Methods

2.1. Ethanol reforming processes

Ethanol is regarded as a promising renewable resource for hydrogen production. Today, a fuel-to-hydrogen rich gas conversion technology has been received considerable interest according to the advancement of a fuel cell technology for power generation. In general, ethanol can be converted to hydrogen through different reforming processes: (i) steam reforming (SR), (ii) partial oxidation (POX) and (iii) autothermal reforming (ATR) (Rabenstein and Hacker, 2008). Each reforming process has its own operational method; thereby the composition and quality of the produced synthesis gas and the energy demand vary. Thus, finding the most suitable ethanol reforming process is important for commercialization. At present, ethanol steam reforming is the most widely used process because it provides a higher hydrogen yield and a lower rate of side reactions. This process, however, has some limitations, e.g., slow start-up time, high energy consumption and severe catalyst deactivation. Ethanol steam reforming is an endothermic process that combines ethanol and steam over catalysts at high temperatures as (Benito et al., 2005):

$$C_2H_5OH + H_2O \leftrightarrow 2CO + 4H_2 \tag{1}$$

However, there are several reaction pathways that could occur in the ethanol/water system, depending on types of catalyst used. Various kinds of intermediate by-products, such as acetaldehyde and ethylene, are usually formed (Vaidya and Rodrigues, 2006). In general, the feasible reactions of the ethanol/water system are ethanol dehydrogenation, acetaldehyde decomposition, ethanol dehydration, methane steam reforming and water gas shift reaction as shown in Eqs. (2)–(6), respectively.

$$C_2H_5OH \leftrightarrow CH_3CHO + H_2 \tag{2}$$

$$CH_3CHO \leftrightarrow CH_4 + CO \tag{3}$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \tag{4}$$

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \tag{5}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{6}$$

The steam reforming reaction, which gives the maximum hydrogen yield, is given by the following reaction:

$$C_2H_5OH + 3H_2O \leftrightarrow 2CO_2 + 6H_2 \tag{7}$$

The partial oxidation of ethanol is an exothermic process in which ethanol and oxygen are reacted in proportions to partially combust ethanol into a gaseous mixture of H_2 and CO. The advantages of the ethanol partial oxidation are fast start-up and less system complexity because it does not need an external heat source and a water balance. However, this process provides low hydrogen yield (Wang and Wang, 2008; Pereira et al., 2011). The ethanol oxidation reaction is shown in Eq. (8)

$$C_2H_5OH + \frac{3}{2}O_2 \leftrightarrow 2CO_2 + 3H_2 \tag{8}$$

The autothermal reforming of ethanol, also known as an oxidative steam reforming, is almost a thermoneutral process. This type of the reforming method combines the steam reforming and the partial oxidation reactions in a single process. The autothermal reforming reaction is shown in Eq. (9), which 0.61 mole of oxygen is needed to react with one mole of ethanol (Graschinsky et al., 2012).

$$C_2H_5OH + 1.78H_2O + 0.61O_2 \leftrightarrow 2CO_2 + 4.78H_2 \tag{9}$$

It is noted that in addition to the reforming products, carbon may be occurred under ethanol reforming environmental conditions, as shown in Eqs. (10)–(14). The formation of carbon causes catalyst deactivation, lowering hydrogen production efficiency.

$$2CO \leftrightarrow CO_2 + C \tag{10}$$

$$CH_4 \leftrightarrow 2H_2 + C \tag{11}$$