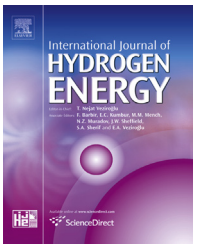
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2016) 1–7

Available online at www.sciencedirect.com

ScienceDirect

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



Thermodynamic evaluation of glycerol autothermal reforming in membrane reactors

Shuai Wang[*], *Xiaojiao Song*, *Qi Wang*, *Guodong Liu*, *Huilin Lu*

School of Energy Science and Engineering, Harbin Institute of Technology, Harbin, 150001, China

ARTICLE INFO

Article history:
Received 18 May 2016
Received in revised form
8 July 2016
Accepted 9 July 2016
Available online xxx

Keywords:
Glycerol
Thermodynamics
Autothermal reforming
Membrane reactor
Ethanol

ABSTRACT

The performance of glycerol autothermal reforming in membrane reactors with in situ hydrogen separation is investigated by means of thermodynamic analysis based on Gibbs free energy minimization method. The influence of operational parameters such as reaction temperatures and oxygen to glycerol ratios under different hydrogen separation fractions is evaluated. It is found that reaction temperatures have a more significant impact on hydrogen yield compared to other parameters. The hydrogen removal can promote the hydrogen production obviously and reduce the required temperature of the maximum hydrogen yield. The hydrogen separation effect on carbon formation is discussed. Meanwhile, the performance of ethanol–glycerol mixture autothermal reforming process is also analyzed.

Introduction

Biofuel has become a promising alternative energy source owing its low emission and high efficiency [1]. Whereas in recent years, a great deal of the byproduct glycerol has been generated with a rapid development of biodiesel industry, which leads to a saturated market and resource waste. It has become urgent to make effective use of biomass-derived fuel [2].

Hydrogen source application has been considered to be an important means of solving energy crisis. The glycerol reforming has wide prospects for hydrogen production industry and efficient utilization of biomass-derived glycerol [3]. A high hydrogen yield can be obtained via glycerol steam reforming under constant atmospheric pressure, which has attracted more and more attentions [4,5]. A thermodynamic analysis of glycerol steam reforming for hydrogen production was performed. The impacts of process variables including system pressure, steam to glycerol feed ratio and temperature were discussed on the basis of the criterion of Gibbs free energy minimization [6]. It was demonstrated that carbon formation can be inhibited at a higher water to glycerin feed ratio. The glycerol steam reforming using Ni–Mg–Al based catalysts was experimentally studied [7]. It was shown that carbon formation was serious under low temperatures although the catalysts exhibited a better hydrogen selectivity. The impacts of impurities on steam reforming process of glycerol were evaluated [8]. It was emphasized that the impurities had a little influence on the gas composition.

During the glycerol steam reforming process, carbon deposition has a great impact on catalyst stability. The autothermal reforming integrates the steam reforming with the partial oxidation. With the introduction of oxygen, the dependence of the reforming process on external energy is

* *Corresponding author*. Fax: +86 0451 8622 1048.
E-mail address: shuaiwang@hit.edu.cn (S. Wang).

http://dx.doi.org/10.1016/j.ijhydene.2016.07.062

decreased. Meanwhile, the carbon formation is restricted [9,10]. An autothermal glycerol steam reforming in a packed bed and a membrane reactor by means of partial oxidation was investigated [11]. The impacts of temperature and oxygen on glycerol conversion and hydrogen yield were analyzed. It can be found that the reaction showed a better stability with the introduction of oxygen. The carbon deposition during glycerol autothermal reforming process was estimated based on the Gibbs free energy minimization [12]. The thermoneutral conditions were obtained. The results demonstrated that the carbon formation was eliminated under the thermoneutral condition. The carbon dioxide sorption effects on hydrogen yield during autothermal reforming process were studied [13]. It was shown that a higher hydrogen yield was obtained using hydrotalcites as carbon dioxide sorbents.

During the glycerol autothermal reforming process, the hydrogen production is decreased as the oxygen is introduced. In order to weaken the adverse effect, the hydrogen separation via membrane reactors provides a possibility of promoting the hydrogen yield. The hydrogen separation can shift the reaction equilibrium in favor of hydrogen yield, which can be operated in membrane reactors [14,15]. Palladium-based membrane reactors have been widely applied to carry out hydrogen separation. The hydrogen permeation through a palladium-based membrane occurs following solution/diffusion mechanism [16]. Furthermore, a thermodynamic evaluation of glycerol steam reforming in situ hydrogen separation was conducted [17]. The impacts of operational parameters on hydrogen production and carbon deposition were evaluated. It was demonstrated that the hydrogen removal can promote the hydrogen yield approaching to stoichiometric value. The impacts of hydrogen separation and temperature on carbon formation and reforming process were examined [18]. It was concluded that the hydrogen extraction in situ can promote the hydrogen production and reduce the most favorable temperature for reforming process. The energetically neutral condition of the impure glycerol autothermal reforming system in situ carbon dioxide and hydrogen separation was investigated [19]. It was pointed out that carbon dioxide sorption reactions can provide the energy for glycerol reforming process.

Up to now, there have been few reports about the integrated effect of hydrogen separation fraction and added oxygen amount on glycerol autothermal reforming process in membrane reactors. In this work, the autothermal glycerol reforming process in membrane reactors is investigated by means of a thermodynamic analysis with the method of Gibbs free energy minimization. The reforming performance is analyzed under different operational parameters including reaction temperature, water to glycerol ratio and oxygen to glycerol ratio. Effects of the hydrogen separation fraction and added oxygen amount on hydrogen production and overall reaction heat during autothermal reforming process are evaluated. The carbon deposition distribution and the ethanol effect are also discussed.

Methodology

In the current work, the glycerol autothermal reforming process is chosen as the research object in this work. The main reaction is expressed as follows:

$$C_3H_8O_3 + 3H_2O \leftrightarrow 3CO_2 + 7H_2;\ \ \Delta H_{298K} = 127.67 kJ\ mol^{-1} \quad (1)$$

Due to the oxygen is introduced in the autothermal process, the glycerol oxidation will occur. The detailed reactions depend on the oxygen to glycerol ratio, which are written in the following forms:

$$C_3H_8O_3 + 0.5O_2 \leftrightarrow 2CO + CO_2 + 4H_2;\ \ \Delta H_{298K} = -31.79 kJ\ mol^{-1} \quad (2)$$

$$C_3H_8O_3 + O_2 \leftrightarrow CO + 2CO_2 + 4H_2;\ \ \Delta H_{298K} = -314.76 kJ\ mol^{-1} \quad (3)$$

$$C_3H_8O_3 + 1.5O_2 \leftrightarrow 3CO_2 + 4H_2;\ \ \Delta H_{298K} = -579.73 kJ\ mol^{-1} \quad (4)$$

$$C_3H_8O_3 + 3.5O_2 \leftrightarrow 3CO_2 + 4H_2O;\ \ \Delta H_{298K} = -1564.93 kJ\ mol^{-1} \quad (5)$$

From the above reaction equations, we can find that the energy is supplied by the glycerol oxidation at the expense of lowering the hydrogen yield. Hence, it is essential to balance the relationship between hydrogen production and energy consumption. The water gas shift reaction plays an extremely vital role in the hydrogen production via glycerol autothermal reforming and is expressed as:

$$CO + H_2O \leftrightarrow CO_2 + H_2;\ \ \Delta H_{298K} = -41.17 kJ\ mol^{-1} \quad (6)$$

Besides the above mentioned main reactions, there are some side reactions including the methanation and carbon formation reactions:

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O;\ \ \Delta H_{298K} = -206.11 kJ\ mol^{-1} \quad (7)$$

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O;\ \ \Delta H_{298K} = -164.94 kJ\ mol^{-1} \quad (8)$$

$$CO + H_2 \leftrightarrow C + H_2O;\ \ \Delta H_{298K} = -131.26 kJ\ mol^{-1} \quad (9)$$

$$CH_4 \leftrightarrow C + 2H_2;\ \ \Delta H_{298K} = 74.85 kJ\ mol^{-1} \quad (10)$$

$$2CO \leftrightarrow CO_2 + C;\ \ \Delta H_{298K} = -172.43 kJ\ mol^{-1} \quad (11)$$

The methanation and carbon formation reactions will result in the reduction of hydrogen yield and the deactivation of catalyst, which should be restricted as much as possible. In the next section, some influential factors are discussed.

The methodology of Gibbs free energy minimization is applied to the computation of thermochemical equilibrium species and the corresponding reaction heat. This approach can avoid the divergence during the solution and the selection of possible reactions [20]. The total Gibbs free energy in the system can be expressed by the sum of each composition:

$$G^t = nG = \sum_{i=1}^{N} n_i \overline{G}_i = \sum_{i=1}^{N} n_i \overline{\mu}_i = \sum n_i G_i^0 + RT \sum n_i \ln \frac{\widehat{f}_i}{f_i^0} \quad (12)$$

By employing the Lagrange's undetermined multiplier approach, the minimum Gibbs free energy of total system without consideration of solid species is written as follows:

Please cite this article in press as: Wang S, et al., Thermodynamic evaluation of glycerol autothermal reforming in membrane reactors, International Journal of Hydrogen Energy (2016), http://dx.doi.org/10.1016/j.ijhydene.2016.07.062