Journal of Power Sources 267 (2014) 104–116

Contents lists available at ScienceDirect

Journal of Power Sources

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

Purge gas recovery of ammonia synthesis plant by integrated configuration of catalytic hydrogen-permselective membrane reactor and solid oxide fuel cell as a novel technology

Fakhteh Siavashi [a, b], Majid Saidi [a], Mohammad Reza Rahimpour [a, *]

[a] Department of Chemical Engineering, School of Chemical and Petroleum Engineering, Shiraz University, Shiraz 71345, Iran
[b] National Iranian Oil Products Distribution Company (N.I.O.P.D.C), HSE Department, Tehran, Iran

HIGHLIGHTS

- A new configuration is proposed for purge gas recovery of ammonia synthesis plant.
- A membrane reactor is used to generate pure hydrogen as feed of SOFC.
- An electrochemical model for SOFC is developed.
- Parametric analysis of the membrane reactor and SOFC performance is done.

ARTICLE INFO

Article history:
Received 8 January 2014
Received in revised form
5 May 2014
Accepted 10 May 2014
Available online 22 May 2014

Keywords:
Purge gas
Catalytic reactor
Pd–Ag membrane
Solid oxide fuel cell
Methane steam reforming

ABSTRACT

The purge gas emission of ammonia synthesis plant which contains hazardous components is one of the major sources of environmental pollution. Using integrated configuration of catalytic hydrogen-permselective membrane reactor and solid oxide fuel cell (SOFC) system is a new approach which has a great impact to reduce the pollutant emission. By application of this method, not only emission of ammonia and methane in the atmosphere is prevented, hydrogen is produced through the methane steam reforming and ammonia decomposition reactions that take place simultaneously in a catalytic membrane reactor. The pure generated hydrogen by recovery of the purge gas in the Pd–Ag membrane reactor is used as a feed of SOFC. Since water is the only byproduct of the electrochemical reaction in the SOFC, it is recycled to the reactor for providing the required water of the reforming reaction. Performance investigation of the reactor represents that the rate of hydrogen permeation increases with enhancing the reactor temperature and pressure. Also modeling results indicate that the SOFC performance improves with increasing the temperature and fuel utilization ratio. The generated power by recovery of the purging gas stream of ammonia synthesis plant in the Razi petrochemical complex is about 8 MW.

1. Introduction

Nowadays environmental and energy challenges facing humanity are becoming two important factors that limited social and economic development. To satisfy the ever-increasing global energy demand, application of new environmentally friendly and highly economical approaches is necessary [1]. Hydrogen-based energy systems appear as an attractive alternative to common fossil fuel-based energy systems in the future. Hydrogen is an environmentally friendly replacement for other fuels in both industrial application and transportation [2]. Although hydrogen storage is difficult because of its low density, it has the largest energy of combustion per unit of mass. Its combustion with oxygen produces water and heat. So energy conversion devices using hydrogen are highly efficient and produce very little or no harmful emissions.

Fuel cells are electrochemical devices which convert the chemical energy of hydrogen to electricity power directly and produce pure water as the only byproducts. Among the various types of fuel cells, solid oxide fuel cell (SOFC) is more efficient [3]. SOFC is a kind of fuel cell contains two porous electrodes, which are separated by a nonporous oxide ion-conducting ceramic electrolyte. SOFC operates at temperatures about 800–1000 °C and uses hydrogen containing gas mixtures as a feed and oxygen in the air as

* Corresponding author. Tel.: +98 711 2303071; fax: +98 711 6287294.
E-mail address: rahimpor@shirazu.ac.ir (M.R. Rahimpour).

http://dx.doi.org/10.1016/j.jpowsour.2014.05.072
0378-7753/

an oxidant [4]. Although the high operating temperature of SOFC leads the flexibility of using various fuel types (i.e. methane, methanol, ethanol, biogas, etc.), SOFCs operate best on pure hydrogen. Since the concentration of pure hydrogen in the atmosphere is less than 1 ppm, hydrogen should be produced from other hydrogen containing fuels. Gasification of coal, reforming of hydrocarbons and electrolysis of water are several approaches for hydrogen production [5–12].

Since ammonia has high hydrogen content, it is introduced as an important source to generate hydrogen. Ammonia has many industrial applications, is commercially manufactured with Haber–Bosch process at temperature 450 °C and pressure about 250 atm [13]. Since the conversion per pass is not 100%, the reactor operates in loop mode. Ammonia is continuously condensed out of the loop and fresh synthesis gas is added. The synthesis gas contains small quantities of impurities such as methane and argon and also some impurities build up in the loop, so they must be continuously purged to atmosphere to prevent them from exceeding a certain concentration [14]. This purge gas stream which contains valuable hydrogen can be proposed as an appropriate feed for SOFC, but due to the presence of ammonia in this stream, direct application of this feed degrades the performance of anode electrode. Different studies considered pure ammonia as the feed of SOFC directly [15–18]. When oxygen ion conducting electrolyte is used in the SOFC, the presence of ammonia in the feed of SOFC increases the risk of producing NO_x compounds over anode catalyst as Eq. (1) [19]. Hence for preventing NO_x compounds, proton conducting electrolyte should be used when ammonia is fed to the fuel cell. Ammonia is decomposed as Eq. (2) at the cell temperature over anode that is consisting Ni-based material. As is shown in Eq. (2), ammonia is converted to hydrogen and nitrogen. The generated hydrogen undergoes electrochemical reaction at the anode-electrolyte interface and is converted to hydrogen ions and electrons. The protons pass the electrolyte and react to oxygen molecules and water is generated at the cathode-electrolyte interface [20].

$$2NH_3 + 5O^{2-} \rightarrow 2NO + 3H_2O + 10e^- \quad (1)$$

$$NH_3 \leftrightarrow \frac{3}{2}H_2 + \frac{1}{2}N_2 \quad (2)$$

Many researchers studied ammonia decomposition rate [21,22]. They found that dilute ammonia kinetic decomposition is slightly different from pure ammonia. For pure ammonia feed, the decomposition rate was found first order respect to ammonia partial pressure. But the inhibition effect of the hydrogen partial pressure is significant at low ammonia concentration (about ppm level) [23]. As reported in Table 1, the composition of ammonia in the purge gas of ammonia synthesis plant is not significant. So, not only the ammonia existing in the purge gas of ammonia synthesis plant is not decomposed over the anode, but also it is possible the reaction reverses and ammonia is produced in the cell. Hence the ammonia should be removed from the gas stream before entering to the cell.

Table 1
Characteristics of ammonia plant in the Razi petrochemical complex [37].

Ammonia plant specifications	Value
Number of ammonia units	2
Plant capacity	1000 (ton day^{-1})
Purge gas flow rate	285 (kg mol h^{-1})
Total ammonia in purge gas	1600 (ton year^{-1})
Purge gas stream pressure	108.9 (bar)
Gas composition (mol %)	
NH_3	2.3
H_2	58.2
N_2	19.3
Ar	6.0
CH_4	14.2

Ammonia absorption by using water is a common approach to remove ammonia from the purge gas. In this way ammonia is scrubbed with water in an absorption tower at pressure about 75.5 bars. At this condition ammonia cannot remove perfectly and about 400 ppm ammonia remains in the purge gas stream [24]. Another approach is decomposition of ammonia in a catalytic reactor as Eq. (2). But the main challenge of this method is that due to high concentration of hydrogen and nitrogen in the purge gas stream, the decomposition reaction is limited thermodynamically, therefore ammonia conversion does not occur completely. The equilibrium limitation issue can be solved by using hydrogen-selective membrane which removes hydrogen from the reaction zone and shift the equilibrium of reaction toward right and as a result the conversion will increase. Rahimpour and Asgari studied the decomposition of ammonia over Ni/Al_2O_3 catalyst in a hydrogen-permselective membrane reactor to increase the conversion of ammonia in the purge gas stream and hydrogen production [25,26]. Their proposed model can be used for the design of an industrial catalytic membrane reactor for the removal of ammonia from the purge gas and production of hydrogen as a fuel of SOFC.

In addition to ammonia, there is an amount of methane in the purge gas. Methane is a greenhouse gas and has the most effect on the global warming [27]. It is usually burned in the flares to decrease its effect. Its reaction with steam is one of the most important processes to produce hydrogen. The methane steam reforming reaction is strongly endothermic and is conducted over Ni catalysts at high temperature conventionally. The reactions which occur during the methane steam reforming are as follows:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad (3)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad (4)$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad (5)$$

According to Eqs. (3)–(5), an amount of carbon dioxide and carbon monoxide are produced as well as hydrogen. So the application of hydrogen-selective membrane reactor can produce pure hydrogen with high conversion of methane. Since the thermodynamic conditions of methane steam reforming reaction and decomposition of ammonia are similar, Eqs. (2)–(5) can be occurred simultaneously by adding required steam to purge gas in the catalytic membrane reactor.

Many researchers have investigated the methane steam reforming in a membrane reactor [6–9]. Due to good surface properties, high permeability and selectivity, high resistance to temperature and corrosion, palladium-based thin wall tube membranes are used extensively as hydrogen-permeable membranes in many hydrogen-related reaction systems [28–30]. Khademi et al. proposed a novel reactor configuration for simultaneous methanol synthesis, cyclohexane dehydrogenation and hydrogen production [31,32]. In their study, methanol synthesis took place in the exothermic side and dehydrogenation of cyclohexane to benzene took place in the endothermic side. Also they used sweep gas flow across the permeate side for selective removal of permeated hydrogen through the Pd/Ag membrane. In other related work, Rahimpour and Bayat investigated the production of hydrogen by utilizing fluidization concept from the coupling of methanol and benzene synthesis in a hydrogen-permselective membrane reactor [33]. Their reported results indicated that combining reaction and