Energy 64 (2014) 473–483

Contents lists available at ScienceDirect

Energy

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

A comprehensive energy–exergy-based assessment and parametric study of a hydrogen production process using steam glycerol reforming

Noureddine Hajjaji [a,*], Amna Chahbani [a], Zouhour Khila [a,b], Marie-Noëlle Pons [b]

[a] Unité de Recherche Catalyse et Matériaux pour l'Environnement et les Procédés URCMEP (UR11ES85), Ecole Nationale d'Ingénieurs de Gabès, Université de Gabès, Rue Omar Ibn Alkhattab, 6029 Gabès, Tunisia

[b] Laboratoire Réactions et Génie des Procédés – CNRS, Université de Lorraine, 1, rue Grandville, BP 20451, 54001 Nancy cedex, France

ARTICLE INFO

Article history:
Received 2 May 2013
Received in revised form
2 October 2013
Accepted 5 October 2013
Available online 1 November 2013

Keywords:
Hydrogen
Glycerol
Simulation
Energy–exergy assessment
Design of experiment

ABSTRACT

Various assessment tools are applied to comprehensively investigate a glycerol-to-hydrogen production system. These tools investigate the chemical reactions, design and simulate the entire hydrogen production process, study the energetic and exergetic performances and perform parametric analyses (using intuitive and design of experiment-based methods).

Investigating the chemical reaction of steam glycerol reforming reveals that the optimal conditions, determined based on maximizing the hydrogen production while minimizing the methane and carbon monoxide contents and coke formation, can be achieved at a reforming temperature and a water-to-glycerol feed ratio (WGFR) of 950 K and 9, respectively. The thermal and exergetic efficiencies of the resulting process are 66.6% and 59.9%, respectively. These findings are lower than those cited in the literature and relative to other reformates (methane, ethanol and methanol). The parametric investigation indicates that the performance of the process (energetic and exergetic) could be ensured by using an appropriate and judiciously selected combination of the reactor temperature and WGFR. Based on the parametric energetic and exergetic investigation, WGFR = 6 and T = 1100 K appear to be the most accurate parameters for the entire glycerol-to-hydrogen process. For this recommend configuration, the thermal and exergetic efficiencies are 78.1% and 66.1%, respectively.

1. Introduction

The limited oil reserves on Earth, increasing price of a barrel of oil and need to reduce CO_2 emissions and environment pollution have resulted in an intensive search for new technologies that can produce new types fuels and new efficient devices for energy conversion. We are, consequently, now in a critical era and need to address energetic and environmental issues to overcome worldwide problems.

Hydrogen energy systems appear to be one of the most effective solutions and can play a significant role in improving the environment, as they are sustainable [1]. This is for several reasons. First, hydrogen is the simplest element, consisting of atoms that contain only one proton and one electron, and is the most abundant element in the universe. Second, hydrogen is equally distributed around the world, mostly bound with oxygen in water, and is therefore essentially limitless. Third, hydrogen has a high energy content, the main advantage of which is that the burning of hydrogen fuel is clean, as its oxidation yields only water [2]. Despite its simplicity and abundance, hydrogen cannot be extracted in the same way as natural gas or oil; it must be recovered by applying energy. Hydrogen is, consequently, an energy carrier but not an energy resource, and thus, hydrogen must be produced first. Actually, hydrogen can be generated from many energy sources using a range of processes, including reforming of natural gas, gasification of coal, electrolysis of water, and thermochemical decomposition of water. The conventional methods for industrially producing hydrogen, such as steam reforming of methane and partial oxidation of fossil fuels, are energy intensive and require high temperatures (>850 °C), resulting in the release of carbon dioxide and other greenhouse gases and pollutants as by-products [3].

To establish a sustainable and eco-friendly hydrogen production process, hydrogen should be produced from renewable resources. Renewable resource-based technologies to generate hydrogen for fuel cells applications are attractive options for the future due to the

* Corresponding author. Tel.: +216 24 04 04 00; fax: +216 75 29 00 41.
E-mail address: Hajjaji.nour@gmail.com (N. Hajjaji).

0360-5442/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.energy.2013.10.023

carbon neutral nature of these technologies and their lesser effects on the environment. Therefore, the USA, Japan, India, China, and several European countries have established research and development programs focused on renewable hydrogen production and fuel cell technology to solve the energy problem and the high dependence on fossil fuels [4].

Glycerol ($C_3H_8O_3$) is the main by-product of biodiesel production, with approximately 1 kg of glycerol being generated per 10 kg of biodiesel [5], and the production of glycerol is expected to grow dramatically in the coming years. By the year 2020, the crude glycerol production is projected to be approximately 3 megatons [6]; however, less than 500 kilotons of glycerol is used in pharmaceutical, food, and cosmetics applications each year [7]. This surplus has created a worldwide oversupply crisis [8]. Therefore, it is crucial to find useful and efficient applications for this by-product.

Currently, glycerol has emerged as a promising and attractive source of hydrogen for several reasons. First, glycerol is a safe, non-toxic and renewable resource with high hydrogen content [9]. Second, crude glycerol produced during biodiesel production generally contains impurities, such as soap, methanol, oils, salts and solid organic materials [10–12]. However, due to presence of a large amount of impurities, crude glycerol cannot be directly used in the food or pharmaceutical industries, and its purification is also expensive [13]. Furthermore, if directly released without proper treatment, glycerol may be hazardous to the environment [14,15]. Consequently, numerous studies have been conducted in recent years to convert crude glycerol to hydrogen by different routes such as gasification [16], pyrolysis [17], supercritical water reforming [18] and catalytic steam reforming [19]. Up to now, most of the efforts in this field have been focused on investigating the glycerol-to-hydrogen reaction and/or researching the catalysis of the system, but little attention has been devoted to the design of an entire system that includes all of the steps involved in the production of hydrogen from glycerol. Lin et al. [20] recently investigated hydrogen production by steam reforming glycerol in conventional and membrane reactors and reported that 5.82 mol-H_2/mol-$C_3H_8O_3$ could be produced, which is an attractive value and should stimulate research on full experimental setups. In their investigation, 5 mol of water was used per mole of glycerol in the reforming reactor operating at 800 °C. In an entire glycerol-to-hydrogen plant with heaters, steam generators, and so forth, the overall energy balance could be very endothermic. Therefore, the energy balance should be established to determine the energy consumption and thereby the energetic performance of such process. This was a prime motivation behind the present study, which comprehensively investigated hydrogen production via the steam glycerol reforming (SGR) process. The performance of the SGR process is evaluated in terms of the hydrogen productivity, energy efficiency, exergy destruction, exhaust exergy and exergetic efficiency.

There has been increasing interest in using modeling techniques to analyze both the energy and exergy for energy-utilization assessments to maximize energy savings and hence environmental and financial savings. The traditional way to evaluate the performance of the process is based on the energy efficiency, which is defined as the ratio of the energy produced (output) to the energy supplied (input), but an exergetic analysis provides a more accurate measure of the process performance. Whereas an energy analysis is based on the first law of thermodynamics, an exergy analysis is based on both the first and the second laws of thermodynamics. The main purpose of an exergy analysis is to identify the causes and quantitatively estimate the magnitude of the thermodynamic imperfection of a thermal or chemical process [21]. Therefore, an exergy analysis provides a better understanding of the influence of the thermodynamic parameters on the process efficiency and can help determine the most effective ways to improve the process being considered [22].

In this investigation, the process operating parameters are varied to illustrate the energetic and exergetic sensitivity of the process and to guide future research and development efforts to improve the process. This variation is performed by two methods: (1) the intuitive method, where the level of all factors except one is fixed and the response is measured for several values of the varied factor, and (2) a factorial Design of Experiment (DOE) method. A notable aspect of this research is that it was carried out using a DOE method, which is a well-established statistical approach used in various engineering fields. DOE methods are more satisfactory than the intuitive methods because an increase in efficiency can be gained by studying several parameters simultaneously. DOE methods involve the following general advantages [23]: (1) More information is obtained per experiment than unplanned (intuitive) approaches. (2) The number and cost of experiments are reduced. (3) It is possible to calculate the interactions among variables within the range studied, leading to a better knowledge of the problem being considered. (4) It helps determine the operating conditions necessary for the scale-up of the process.

This paper comprises (1) an investigation of the SGR reforming reaction to identify the best operating conditions to optimize the hydrogen production, (2) a simulation of the full process to evaluate the thermodynamic properties at different process locations, (3) an energetic study and an exergetic analysis and (4) a parametric energetic and exergetic analysis (using intuitive and DOE methods) to illustrate the system's performance sensitivity and to provide guidance for future research and development efforts for the process design.

2. Steps for the glycerol-to-hydrogen production processes

A typical reforming based processor is constituted by a reforming unit coupled by a CO cleanup section introduced to guarantee hydrogen production with a CO content compatible with fuel cell specifics. The cleanup of CO is performed by the water–gas shift (WGS) reactors and the CO preferential oxidation reactor (COPROX) [24]. The conventional hydrogen production system for fuel cell applications is demonstrated in Fig. 1.

The first step of the steam reforming process involves reacting glycerol with steam to produce a synthesis gas, a mixture primarily made up of H_2, CO, CO_2, CH_4 and H_2O.

The SGR reaction can be modeled to reflect the following relationship:

$$\text{Glycerol}\ (C_3H_8O_3) + \alpha H_2O \rightarrow \text{Synthesis Gas}(H_2,\ CO,\ CO_2,\ CH_4,\ H_2O) \quad (1)$$

where α is the stoichiometric coefficient of water.

Reforming glycerol to produce hydrogen can be summarized by two main reactions [25].

First, the steam reforming of glycerol:

$$C_3H_8O_3 \xrightarrow{H_2O} 3CO + 4H_2 \quad \Delta H^{\circ}_{298\ K} = 251\ \text{kJ mol}^{-1} \quad (2)$$

This reaction is followed by the water–gas shift (WGS) reaction:

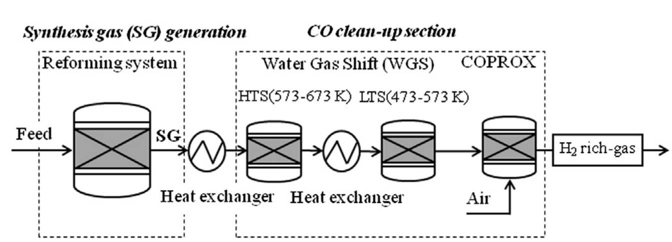

Fig. 1. Simplified flow diagram of glycerol-to-hydrogen production system.