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Energy and exergy analysis as tools for optimization of hydrogen production by glycerol autothermal reforming

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ABSTRACT

In this work, various assessment tools were comprehensively applied to investigate hydrogen production via glycerol autothermal reforming. These tools are used to study the chemical reactions, design and simulate the entire hydrogen production process, investigate the energetic and exergetic performances of the processes and perform parametric analyses (using intuitive and design of experiment-based methods).

Investigating the chemical reactions of autothermal reforming (ATR) of glycerol reveals that the optimal conditions, based on maximizing the hydrogen production, minimizing the methane and carbon monoxide contents and eliminating coke formation at thermoneutral conditions, can be achieved at a water–glycerol feed ratio (WGFR), reforming temperature (T) and oxygen–glycerol feed ratio (OGFR) of 9, 900 K and 0.35, respectively. The energetic study of the resulting process indicates that approximately two-thirds of the energy fed to the process is recovered in the useful product (H_2) and that the remaining incoming process energy is exhausted in the off-gas. The exergetic investigation reveals that the exergetic efficiency of the ATR process is 57% and that 152 kJ are destroyed to generate 1 mol of hydrogen. The process operating conditions recommended by the chemical reaction investigation suffers from low performance because energetic and exergetic efficiencies are comparatively lower than values previously reported in literature for other reformates. The parametric investigation indicates that more accurate conditions are needed to convert glycerol–hydrogen. These conditions ensure the lowest consumption of energy to generate a given amount of hydrogen. This paper recommends WGFR = 5.5, T = 900 K and OGFR = 0.96 as the optimum conditions for the entire glycerol-to-hydrogen process. For this configuration, the thermal and exergetic efficiencies are 78.7% and 67.8%, respectively.

1. Introduction

In recent decades, energy consumption has increased significantly to satisfy the lifestyle demands of the rapidly and steadily increasing population. However, approximately 80% of the world's energy demand is still supplied by non-renewable fossil fuels [1]. Consequently, the continued depletion of fossil fuel reserves and the threat of climate change caused by excessive emissions of anthropogenic greenhouse gases such as CO_2 have become serious issues for mankind. Therefore, the last several years has seen an increase in the search for alternative energy sources, which can decrease the worldwide dependence on fossil fuels.

Currently, hydrogen is considered one of the most promising candidates to substitute for conventional fuels. The advantages of using hydrogen are abundant availability and the utilization of a variety of feedstocks and production technologies [2]. Although the transition to the so-called "hydrogen economy" has been postulated to have already begun, significant technical challenges need to be addressed. According to Romm [3], the H_2 economy rests on two important pillars: pollution-free feedstocks for H_2 production and fuel cells for efficiently converting H_2 to useful energy. However, in fact, approximately 48% of hydrogen comes from natural gas steam reforming (SMR), 30% from naphtha/oil reforming in the chemical industry and 18% from coal gasification [4]. Accordingly, 96% of the hydrogen produced in the world comes from fossil fuels (FF), with a non-negligible amount of CO_2 emissions produced in these processes. For instance, the global warming potential (GWP) of hydrogen production via the SMR process is estimated as 13.7 kg

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eq. CO_2 per kg of net H_2 produced [5]. A typical SMR H_2 plant with the capacity of one million m^3 of H_2 per day produces approximately 0.3–0.4 million standard m^3 of CO_2 per day, which is normally vented into the atmosphere [5]. This huge amount of GHG emissions raises questions about the environmental sustainability of hydrogen production via FF. Moreover, H_2 demand is expected to increase in the near future when this fuel will begin to be used in fuel-cell applications [6], with demand anticipated to reach 3.1 million tons/year by the year 2023 [7]. The CO_2 emissions that accompany this hydrogen demand undoubtedly will intensify environmental problems if no preventive measures are applied. In brief, the FF-to-hydrogen system appears to have limited horizons, and the development and implementation of new methods for eco-friendly H_2 production, especially from biorenewable feedstocks, are required. Clearly, the benefits of a true hydrogen economy can only be achieved if the hydrogen is derived from biorenewable and carbon-neutral resources like biomass [8].

In this context, glycerol ($C_3H_8O_3$) has emerged as a promising source of hydrogen. Glycerol is the main by-product of biodiesel production from the transesterification of vegetable oils extracted from biomass [9]. Currently, large amounts of glycerol are obtained as waste products from biodiesel production, with approximately 1 ton of glycerol produced for every 10 tons of biodiesel. By the year 2020, crude glycerol production is projected to be approximately 3 Mton [10]; however, less than 500 kton of glycerol is used in pharmaceutical, food and cosmetics applications each year [11]. This surplus has created a worldwide oversupply crisis [12]. Due to presence of a large amount of impurities, crude glycerol cannot be directly used in the pharmaceutical or food industries, and its purification remains expensive [13]. Furthermore, if directly released without proper treatment, glycerol may be hazardous to the environment [14,15]. Therefore, employing glycerol in hydrogen production would be advantageous from both an economic and environmental point of view. Consequently, numerous studies have been conducted in recent years on converting glycerol–hydrogen by different routes such as catalytic steam reforming (SR) [16], autothermal reforming (ATR) [17], gasification [18], pyrolysis [19] and aqueous phase reforming [20]. Among these technologies, glycerol SR is the most commonly used method [21], providing high yields of hydrogen production. However, it operates at relatively high temperature and requires a large amount of external heat source [21,22]. Currently, ATR process has been suggested to ameliorate the difficulties associated with steam SR. Specifically, ATR overcomes the limitations of high temperature operations and fast dynamic responses typical of SR processes. Additionally, an autothermal reformer can reduce the size, weight, and start-up, shut-down, and other dynamic response times [23–25]. Therefore, ATR of glycerol has been extensively investigated and reported in the literature in the past several years [26–28]. To date, most of the efforts in this field have concentrated on thermodynamic investigations of the glycerol-to-hydrogen reaction and/or researching catalysis in this system. In this context, many catalysts have been developed and tested to enhance H_2 productivity and also to suppress undesired by-products in the reforming process. Lin and co-workers [17] studied glycerol autothermal steam reforming over a $Ni/CeO_2/Al_2O_3$ catalyst in a packed-bed reactor and in a Pd/Ag membrane reactor. These authors showed that, in the packed-bed runs, the best hydrogen yield was 85.26% at the followings conditions: a temperature of 773 K, weight hourly space velocity (WHSV) of 5 h^{-1}, water–glycerol feed ratio (WGFR) of 9 and oxygen–glycerol feed ratio (OGFR) of 0.15. In the Pd/Ag membrane reactor experiments, the results show that glycerol conversion increased with increasing pressure, but the hydrogen yield declined. Dauenhauer et al. [29] investigated glycerol autothermal steam reforming on a $Rh\text{-}Ce/Al_2O_3$ catalyst and found that within autothermal conditions, the carbon monoxide selectivity can be controlled from 80% to 50%, while the hydrogen selectivity was 79%.

On the other hand, most reported thermodynamic analyses aimed to identify suitable operation conditions, i.e., temperature, pressure, WGFR and OGFR, which maximize H_2 production and minimize CO and CH_4 contents without carbon formation in the synthesis gas (SG) [22–24,26]. Yang et al. [30] performed a thermodynamic analysis of the oxidative steam reforming of glycerol (OSRG) for hydrogen production. These authors showed that higher WGFRs and lower OGFRs favor the production of hydrogen from glycerol, and the highest hydrogen selectivity was obtained at 600–700 °C. From the viewpoint of thermodynamics, glycerol reforming is more resistant to carbon deposition. Thermodynamic analysis of hydrogen production from ATR of glycerol has also been investigated by Wang et al. [28]. The authors showed that the most favorable conditions for hydrogen production are achieved with the temperature, WGFR and OGFR of 900–1000 K, 9–12 and 0.0–0.4, respectively.

It should be noted here that little attention has been devoted to the design of an entire system that includes all of the steps involved in the production of hydrogen via ATR of glycerol. In fact, these aforementioned investigations consider hydrogen productivity of a chemical reaction system a key measure of performance. Hence, a system is efficient when the hydrogen productivity of the system is high. This approach does not emphasize energy consumption, i.e., the energy required to generate a given amount of hydrogen. Indeed, in an entire glycerol-to-hydrogen plant with heaters, reactors, steam generators, and so forth, the overall energy balance could be very endothermic, and hydrogen production becomes energy intensive. Therefore, an energy analysis should be established to determine the energy consumption and thereby the energetic performance of such a process.

Recently, there has been an increasing interest in using both energy and exergy analysis modeling techniques for energy-utilization assessments to maximize the energy savings and therefore the environmental and financial savings. Whereas energy analysis is based on the first law of thermodynamics, 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 of imperfection in the system and to quantitatively estimate the magnitude of these imperfections in a thermal or chemical process [31]. Moreover, exergy analysis leads to a better understanding of the influence of the thermodynamic parameters on the process efficiency and can help determine the most effective solutions to improve the process under consideration [32].

In this research, various assessment tools are applied to comprehensively investigate a hydrogen production system via ATR of glycerol. These tools are used to investigate the glycerol–hydrogen chemical reactions, design and simulate the entire hydrogen production process and study the energetic and exergetic performances. The combination of these tools has not been considered in the past and constitutes a key aspect of this research. Another relevant aspect of this study is a supporting parametric investigation. In fact, the process operating parameters are varied to illustrate the energetic and exergetic sensitivity of the process and to provide guidance for future research and development efforts in process design. This variation was performed using 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 Experiments (DOE) method.

This paper comprises (1) an investigation of the ATR 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