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# Techno-economic assessment of hydrogen and power production from supercritical water reforming of glycerol

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## HIGHLIGHTS

- The supercritical water reforming (SCWR) of glycerol was assessed techno-economically.
- Electrical power by an expander and hydrogen were the products.
- An autothermal (ASCWR) version of the process was also assessed.
- The break-even price of hydrogen was 5.36 \$/kg $H_2$ for SCWR and 5.75 \$/kg $H_2$ for ASCWR.
- The competitiveness of the technology seems to be promising versus other renewable processes.

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## ABSTRACT

Hydrogen and power production from supercritical water reforming of glycerol was techno-economically assessed, considering future states of technology because there is no demonstration plant using this technology. Two different configurations were proposed: supercritical water reforming (SCWR) and autothermal supercritical water reforming (ASCWR). A plant size of 1000 kg/h of glycerol was considered on a process flow-sheet simulated by Aspen Plus with the criterion of being energy self-sufficient. The results reveal that, although ASCWR presents better performance than SCWR in terms of energy efficiency, the investment capital and operational difficulties of ASCWR process leads to higher hydrogen production costs. The levelized production cost of hydrogen was evaluated using a discounted cash flow analysis with a discount rate of 10% and 100% equity financing. Thus, the minimum hydrogen selling price (achieved when net present value is zero) is 5.36 \$/kg for SCWR and 5.75 \$/kg for ASCWR. These values are somewhat higher than in a few conventional technologies, such as steam methane reforming, although lower than other renewable processes, such as wood gasification. In a future scenario, possible improvements in SCW reforming performance may lead to a decrease in the estimation of renewable hydrogen price.

## 1. Introduction

Although glycerol has many commercial applications as an additive or raw material, its price is decreasing in an accelerating mode due to the progressive increase in biodiesel production (catalytic transesterification of fatty acids) from vegetable oils [1]. Thus, around 10% of the vegetable oil is converted into glycerol. This glycerol was initially considered a by-product that gave an added value to the process, but right now it is beginning to be a waste because glycerol market is becoming saturated. The prices for crude glycerol have fallen down to zero, and even negative, as producers of glycerol are forced to pay to take it away from their plants [2]. Therefore, it is necessary to find high value-added products based on glycerol.

One of the most promising options is the thermo-chemical valorisation of glycerol to produce hydrogen [3]. Many alternatives have been studied, such as steam reforming [4], autothermal reforming [5] and aqueous-phase reforming [6]. However, supercritical water reforming (SCWR), and its autothermal version (ASCWR), are emerging technologies with some advantages over the other technologies: a catalyst is not needed, the heat required when reforming at supercritical conditions is lower in than others, such as steam reforming [7,8], and the huge pressure energy of the products can be converted into electrical energy by an expander.

Autothermal reforming of glycerol, which is a combination of classic steam reforming (endothermic) and partial oxidation (exothermic), is a very capable technology. The great advantage of

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**Nomenclature**

| | |
|---|---|
| $\dot{m}$ | mass flow-rate (kg/s) |
| $T$ | temperature (°C) |
| $\dot{W}$ | power (kW) |
| $LHV$ | lower heating value (kJ/kg) |
| $\eta$ | efficiency (%) |

*Acronyms*

| | |
|---|---|
| SCWR | supercritical water reforming |
| ASCWR | autothermal supercritical water reforming |
| PSA | pressure swing adsorption |
| WGS | water gas shift |
| PEMFC | proton exchange membrane fuel cell |

autothermal reforming is that there is no need to supply or dissipate thermal energy to or from the reaction. ASCWR take the energy from the partial oxidation of glycerol and no syngas is wasted.

Hydrogen, as an energy vector, represents a serious alternative to fossil fuels in the medium term [9]. This is because the energy stored in hydrogen can be easily converted into electricity with a high efficiency (60–65%) by fuel cells (PEMFC and SOFC type). This process has also the advantage of not increasing greenhouse gases (GHG) concentration in the atmosphere, unlike what happens in an internal combustion engine fuelled with Diesel with an efficiency of energy conversion of only 27% and generating hazardous pollutants besides GHG [10].

To date, there are no demonstration plants of supercritical water reforming of glycerol to produce hydrogen, so it is necessary to develop an extensive research on this technology.

The aim of this paper is to perform a techno-economic analysis of the SCWR of glycerol process to produce hydrogen and electrical power, and it is autothermal alternative ASCWR, in order to estimate the total capital to invest, the production costs and the price of the products, and to assess the feasibility of the full process in a hypothetical plant.

## 2. Methodology

In this section, the process design and modeling for both SCWR and ASCWR of glycerol are described, as well as the way in which the process economics was performed.

### 2.1. Process design

Fig. 1 shows a simplified flow-sheet of the SCW reforming process. The main difference with autothermal process is an air stream entering the reformer (by a compressor, as shown in Fig. 1) to oxidize a part of the glycerol so as to achieve an autothermal process. Commercial process units have been included downstream from the reformer, such as two water–gas-shift reactors (WGS), PSA unit (pressure swing adsorption) and a proton exchange membrane fuel cell (PEMFC).

As a design basis, a feed of 1000 kg/h of glycerol was selected. The glycerol concentration in the aqueous feed solution must be that necessary to obtain an energy self-sufficient process [11,12].

In addition, a number of heat exchangers were strategically arranged to maximize heat transfer among the streams to avoid energy losses. The approach used for arranging the heat exchanger network was systematic, and the methodology and results were published in our previous papers [11,12,14,15].

Aspen Plus software was used to solve mass and energy balances of the two reforming processes. The thermodynamic method selected was the predictive Soave–Redlich–Kwong (PSRK) EoS for supercritical water zone, because it is the best method to characterize the properties of the supercritical fluids involved in the process. For the rest of the plant, the Peng–Robinson (PR) EoS was selected [8,13].

Figs. 2 and 3 show the process flow diagram of SCWR and ASCWR used in Aspen Plus. The results of mass and energy

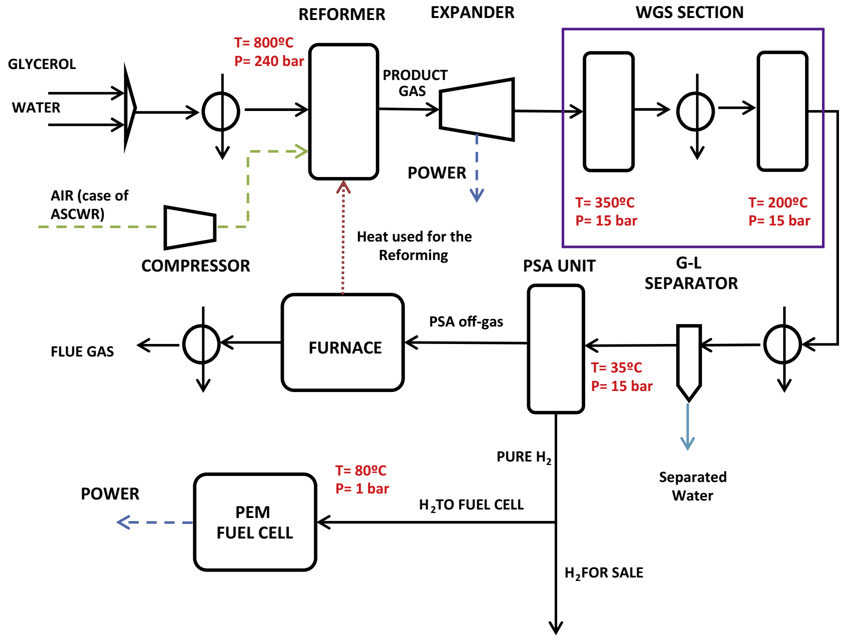

**Fig. 1.** Block diagrams of supercritical water reforming (SCWR) and autothermal supercritical water reforming (ASCWR) of glycerol.