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Life cycle assessment of hydrogen and power production by supercritical water reforming of glycerol

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ABSTRACT

The environmental performance of hydrogen and electricity production by supercritical water reforming (SCWR) of glycerol was evaluated following a Life Cycle Assessment (LCA) approach. The heat-integrated process was designed to be energy self-sufficient. Mass and energy balances needed for the study were performed using Aspen Plus 8.4, and the environmental assessment was carried out through SimaPro 8.0. CML 2000 was selected as the life cycle impact assessment method, considering as impact categories the global warming, ozone layer depletion, abiotic depletion, photochemical oxidant formation, eutrophication, acidification, and cumulative energy demand. A distinction between biogenic and fossil CO_2 emissions was done to quantify a more realistic GHG inventory of 3.77 kg CO_2-eq per kg H_2 produced. Additionally, the environmental profile of SCWR process was compared to other H_2 production technologies such as steam methane reforming, carbon gasification, water electrolysis and dark fermentation among others. This way, it is shown that SCWR of glycerol allows reducing greenhouse gas emissions and obtaining a favorable positive life cycle energy balance, achieving a good environmental performance of H_2 and power production by SCWR of glycerol.

1. Introduction

The conversion of biomass into heat and electricity, biofuels and bio-based chemicals are gaining interest due to environmental and social problems associated with fossil fuels [1]. The production of chemicals and energy carriers from renewable sources are considered as carbon neutral products, because the CO_2 generated in the processing can be absorbed by plants during their growth. An example is the conversion of biomass into green hydrogen, an excellent energy carrier that is expected to acquire great importance in the next generation fuels [2].

Bioenergy technologies use renewable resources to produce a variety of energy related to products including electricity, fuels, heat and chemicals [3]. For example, glycerol is the main byproduct of the biodiesel industry and the increase in the production of this biofuel has led to a simultaneous increase in crude glycerol, causing prices to fall. Therefore, the identification of high value-added products derived from glycerol such as the production of energy carriers (H_2) has become a topic of active research and development area for increasing the biodiesel process economy [4].

One of the most promising options of glycerol valorization is the supercritical water reforming (SCWR), an emerging technology with some advantages over traditional thermochemical routes: a catalyst is not needed and the vaporization heat is saved in the supercritical state among others [5,6]. By this process it is possible to obtain not only hydrogen but also power by an expander just located at the outlet of the reformer. The expanded product gas should be conditioned by two water gas shift (WGS) reactors and a pressure swing adsorption unit (WGS) in order to obtain a hydrogen-rich gas stream [7]. To our knowledge, there is not a similar process, containing all of these units, performed at pilot scale, since SCW reforming is a relatively new technology and, so far, most of the experimental investigation has been carried out at lab scale [5]. Interest in SCW reforming steadily increasing in the last years as can be verified by the number of publications. Recently, we have published a techno-economic study on the SCW reforming process [8], but there are not studies on the environmental impact of this technology when used to produce hydrogen and electricity, and it is very important to identify environmental footprints of bioenergy systems before performing a scale-up. The aim of this paper is to quantify the environmental impacts of the SCWR of glycerol to produce hydrogen and electricity and identify the main environmental loads to suggest potential process improvements, thus promoting sustainable development policy. This way, the previous

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study [8] is completed. To achieve this objective, Life Cycle Assessment (LCA) was used. This is a useful tool to evaluate the environmental aspects of a product by considering potential impacts from all stages of a process [9]. The analysis allows comparing the sustainability performance of hydrogen production alternatives with each other as well as the identification of the critical elements of the process. In order to perform the study, Aspen Plus 8.4 [10] was used to simulate the process rigorously and solve material and energy balances, and SimaPro 8.0 [11] Life Cycle Assessment Software was utilized to collect, analyze and monitor the environmental performance of products, following the ISO 14040/44 recommendations.

2. Methodology

In this section, the design of supercritical water reforming (SCWR) process and the Life Cycle Assessment procedure are described.

2.1. SCWR process design

Fig. 1 shows a simplified flow-sheet of the SCWR process, where main operating conditions are included, designed with energy integration through a number of heat exchangers that were suitably located according to a '*from inside to outside*' approach, in which the high-temperature hot streams heat the high-temperature cold streams and the low-temperature hot streams warm up the low-temperature cold streams [7].

The feed to the process is pumped and heated as much as possible with hot process streams before entering the reformer. Supercritical water reformer has to operate above the critical point of water (374 °C and 221 bar). According to a previous study [6], optimal conditions to maximize the hydrogen production in SCWR are 800 °C and 240 bar. The product gas is a mixture of CO, CO_2, CH_4, H_2, and SCW at 800 °C and 240 bar. The syngas exiting the reformer with a high energy, pressure and temperature is expanded in a turbine to 15 bar, obtaining electrical power. Then, the gas is sent to two adiabatic WGS reactors to reduce the amount of CO and produce additional H_2. The water–gas shift reaction (WGS) is performed in the first reactor at 350 °C to promote the kinetics of the process, and in the second reactor at 200 °C to favor the thermodynamics, since the reaction is exothermic. Both reactors use Fe–Cr and Cu–Zn based catalysts, respectively [12].

To obtain pure hydrogen and a CO_2-rich gas stream that minimizes emissions, a PSA unit is used, which is suitable for small-to-medium scale plants [7]. PSA is based on adsorption beds that capture impurities at medium pressure, and desorbs them at lower pressure in the regeneration step. This unit operates at 15 bar and 35 °C, and it makes it possible to achieve hydrogen at 99.999% purity with a recovery of hydrogen of 80% [13] and to remove pure CO_2 for future sequestration by means of an additional bed [14]. Before entering the PSA unit, the stream is cooled to 35 °C condensing almost all of the water present in the gas. The condensate water is removed in a knock-out drum.

In order to achieve an energy self-sufficient process, the PSA off-gas (made up mainly of unrecovered hydrogen with the other gases removed) is sent to a furnace, providing the heat required by the reforming reactor. The flue gas leaving the furnace at 1000 °C is used to preheat the feed. The air enters the furnace by a fan with an excess to accomplish an O_2 content of 3 vol.% in the flue gas.

2.2. Life-Cycle Assessment (LCA)

LCA comprises four interrelated steps following ISO-14044 [15]:

1. Goal and scope definition: objective of the analysis, functional unit (FU) and system boundaries (SB) are clearly specified.

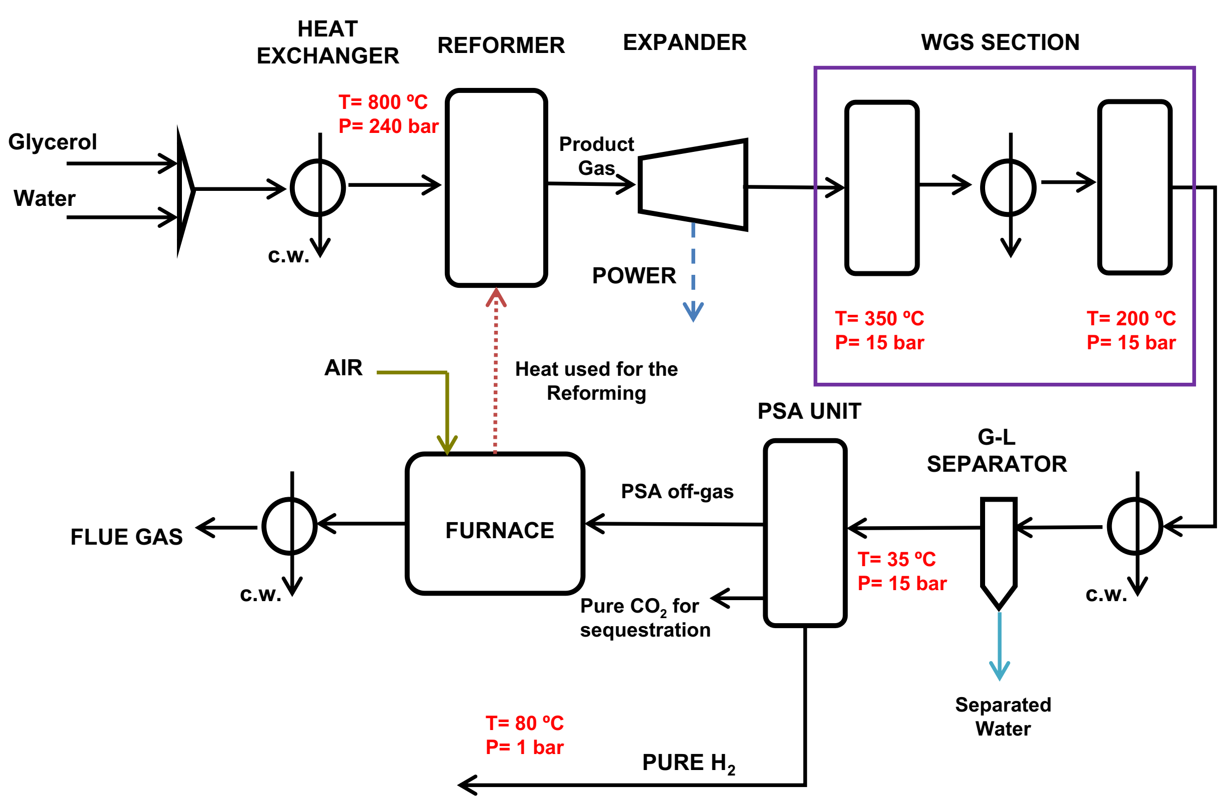

Fig. 1. Simplified flow-sheet of the supercritical water reforming process.