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Optimization of power and hydrogen production from glycerol by supercritical water reforming

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HIGHLIGHTS

- ▶ A process design is proposed and simulated for reforming glycerol using supercritical water.
- ▶ The product gas is conditioned to obtain a hydrogen-rich gas stream, which is sent to a fuel cell.
- ▶ The process includes energy integration and it is energy self-sufficient by burning the off-gas.
- ▶ The process is assessed by an energy and exergy analysis.
- ▶ Maximum power generation is obtained by an expander and a fuel cell.

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ABSTRACT

A process design is proposed and simulated for reforming glycerol using supercritical water aimed to produce maximum power and hydrogen in an energy self-sufficient system. The selected route takes advantage of the huge pressure energy of product gas just at the outlet of the reformer converting that into power by a turbine. The expanded product gas is conditioned by two water gas shift reactors and a pressure swing adsorption unit, so a hydrogen-rich gas stream is sent to a proton exchange membrane fuel cell to be converted into electrical energy and the pressure swing adsorption off-gas stream is used as fuel gas to provide the thermal energy required by the reforming process. The evaluation of the global efficiency of the process is carried out by energy and exergy analysis. Required glycerol feed concentration in aqueous solution was obtained for a self-sufficient process, both for pure and pretreated crude glycerol, at reforming temperatures from 600 to 1000 °C and 240 atm. Thus, reforming and preheating at 800 °C and 240 atm, it was obtained a power of 1592 kW per ton/h of glycerol, with exergy and energy efficiencies of 33.8% and 35.8%, respectively.

1. Introduction

The rising surplus of biodiesel-derived crude glycerol from the transesterification process requires a further processing. The crude glycerol stream leaving the homogeneous base-catalyzed transesterification reactor normally contains glycerol, methanol, alkalies (catalyst and soap), methyl esters and water. Normal refining of glycerol involves an acid treatment to split the soaps into free fatty acid and salts. Fatty acids are not soluble in glycerol and are separated from the top and recycled to the process; then, if methanol is recovered by vacuum distillation, some salts remain with the glycerol, which is in aqueous solution and its purity is about 85 wt.%; if methanol is present, glycerol purity may be reduced to about 75 wt.%.

A great deal of research has been carried out following a thermochemical route of glycerol valorization to obtain H_2 or synthesis gas, by steam reforming [1–4], autothermal reforming [5,6] and aqueous phase reforming [7–10]. Many of these studies are centered on the development and characterization of catalysts.

Supercritical water (SCW) is an emerging and promising medium to obtain hydrogen by reforming of glycerol, due to its relevant thermophysical properties such as a high capability to solubilize gaseous organic molecules and high diffusivity, among others [11–14] with only a few papers published regarding with the glycerol [15–17]. SCW is extremely reactive and, it may be possible to perform the process in the absence of a catalyst, although this premise requires to be experimentally verified.

Hydrogen is very attractive as a clean fuel for proton exchange membrane fuel cells (PEMFCs), which are more efficient than combustion engines and have zero carbon emissions. In order to lessen the CO content and to increase the hydrogen content in the reformate stream, two water gas shift reactors (WGS), at two

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