Hydrogen production for PEM fuel cell by gas phase reforming of glycerol as byproduct of bio-diesel. The use of a Pd–Ag membrane reactor at middle reaction temperature

A. Iulianelli [a,*], P.K. Seelam [b], S. Liguori [a,c], T. Longo [a], R. Keiski [b], V. Calabrò [c], A. Basile [a]

[a] Institute on Membrane Technology of Italian National Research Council (ITM-CNR), Via P. Bucci, c/o University of Calabria – Cubo 17/C, 87036 Rende (CS), Italy
[b] Department of Process and Environmental Engineering mass and heat transfer process Laboratory, P.O. Box 4300, FI-90014, University of Oulu, Finland
[c] Department of Engineering Modeling, Via P. Bucci, c/o University of Calabria, Cubo 39/C, 87036 Rende (CS), Italy

ARTICLE INFO

ABSTRACT

Glycerol as a byproduct of biodiesel production represents a renewable energy source. In particular, glycerol can be used in the field of hydrogen production via gas phase reforming for proton exchange membrane fuel cell (PEMFC) applications. In this work, glycerol steam reforming (GSR) reaction was investigated using a dense palladium–silver membrane reactor (MR) in order to produce pure (or at least CO-free) hydrogen, using 0.5 wt% Ru/Al_2O_3 as reforming catalyst. The experiments are performed at 400 °C, water to glycerol molar feed ratio 6:1, reaction pressure ranging from 1 to 5 bar and weight hourly space velocity (WHSV) from 0.1 to 1.0 h^{-1}. Moreover, a comparative study is given between the Pd–Ag MR and a traditional reactor (TR) working at the same MR operating conditions. The effect of the WHSV and reaction pressure on the performances of both the reactors in terms of glycerol conversion and hydrogen yield is also analyzed. The MR exhibits higher conversion than the TR (~60% as best value for the MR against ~40% for the TR, at WHSV = 0.1 h^{-1} and 5 bar), and high CO-free hydrogen recovery (around 60% at WHSV = 0.1 h^{-1} and 5 bar). During reaction, carbon coke is formed limiting the performances of the reactors and inhibiting, in particular, the hydrogen permeation through the membrane with a consequent reduction of hydrogen recovery in the permeate side.

1. Introduction

Sustainability in energy production is the key factor in the contemporary world. In the last decades, the consumption of fuel and energy sources is raised due to population growth. Moreover, depletion of fossil fuels, environmental pollution and climate change represent serious problems. According to EU energy and climate policy, 20% as a reduction of greenhouse gas emissions and 10% as an increase of the biofuels in the transports represent the targets for 2020 [1]. Today, many initiatives have been taken to implement alternative technologies and use renewable sources such as bioethanol, biodiesel and biogas [2]. In particular, EU is the largest producer of biodiesel, targeting its use at 5.75% by the end of 2010 [1]. Generally, biodiesel is obtained via transesterification of vegetable (edible) or non-edible oils using

methanol as solvent, where glycerol is the main byproduct. Moreover, the use of biodiesel as a direct replacement for traditional diesel is increasing every year [3]. Nevertheless, it presents a negative aspect: the cost of biodiesel production is expensive and makes it uncompetitive in the market. Therefore, taking into account that the production of glycerol is rapidly growing, biodiesel production could be more economical viable using glycerol as value added product. Glycerol is a natural organic building block [3] and it can be used in many applications: production of pharmaceutical, polymer products and also in the synthesis of 1, 2-propanediol and 1, 3-propanediol. The crude glycerol consists of many impurities and its purification is an expensive distillation process [4]. Thus, it could be directly utilized in aqueous or gas phase reforming reactions for producing hydrogen [5–7]. At the moment, to the best of our knowledge, glycerol steam reforming (GSR) reaction is carried out conventionally in fixed bed reactors and hydrogen is produced with other byproduct gases like CO, CH_4 and CO_2 [8–12]. With the aim of producing hydrogen for feeding a PEMFC system, the GSR reformed stream going out from a TR needs to be purified. In fact, a concentration of CO >10 ppm is able to poison the anodic catalyst of a PEM fuel cell device. Using a dense palladium-based MR, pure or at least CO-free hydrogen can be obtained without requiring any further separation/purification process. Furthermore, the benefits of using a dense palladium-based MR consist of the possibility of simultaneously coupling the reaction process with the hydrogen separation/purification step in only one device.

Palladium-based membrane reactors are widely studied for carrying out several kind of reforming reactions such as methane, ethanol, methanol and acetic acid steam reforming, oxidative steam reforming and/or partial oxidation and so on in order to produce pure or at least CO-free hydrogen [13–19].

The aim of the present study is to investigate the GSR reaction performed at middle temperature (400 °C) in a dense Pd–Ag MR packed with a Ru-based catalyst in order to produce pure (or at least CO-free) hydrogen. The influence of parameters like WHSV and reaction pressure on the performances in terms of glycerol conversion, hydrogen yield and gas selectivity (as well as CO-free hydrogen recovery for only the MR) of both the MR and a TR (exercised at the same MR operating conditions) is presented.

2. Experimental section

2.1. Experimental setup

Fig. 1 illustrates the MR consisting of a dense, tubular pin-hole free Pd–Ag membrane, having wall thickness of 50 μm, outer diameter 10 mm, length 150 mm. It is inserted in a tubular stainless steel (SS) module, length 280 mm and internal diameter of 20 mm. The dense Pd–Ag membrane is produced by cold-rolling and diffusion welding technique [20] and presents an upper working temperature limit around 450 °C. It is joined to two stainless steel tube ends for the membrane housing, whose one of them is closed. In order to avoid the mixing of retentate and permeate streams, a graphite gasket is used. The MR is heated by means of heating filaments connected to a temperature-controller with a three points thermocouple placed inside MR. The sweep gas (31.3 ml/min) is fed into the permeate side in counter current flow configuration with respect to the reactants by means of mass-flow controller (Brooks Instruments 5850S). Liquid water and glycerol are mixed in a solution with a feed molar ratio $H_2O/C_3H_8O_3 = 6/1$ and it is pumped ($Q_{TOT-reactants} = 3.9 \cdot 10^{-3}$ mol/min) into reaction side by means of a HPLC pump (Dionex). The MR is operated at 400 °C and the absolute reaction pressure ranges between 1.0 and 5.0 bar, regulated by means of a back pressure controller placed at the retentate outlet stream pipeline. WHSV is varied from $0.1\ h^{-1}$ to $1.0\ h^{-1}$.

A constant nitrogen molar rate (28.5 ml/min) as internal standard gas is fed with the reactants into MR reaction side. The retentate stream is passed over a cold-trap in order to condensate unreacted products (glycerol, water, etc.). Thus, dry outlet streams from permeate and retentate sides are analyzed using a temperature programmed HP 6890 GC with two thermal conductivity detectors at 250 °C and Ar as carrier gas. The GC is equipped by three packed columns: Porapack R 50/80 (8 ft × 1/8 in) and Carboxen™ 1000 (15 ft × 1/8 inch) connected in series, and a Molecular Sieve 5 Å (6 ft × 1/8 inch).

The MR is packed in the membrane lumen with 3 g of a commercial 0.5 wt% $Ru–Al_2O_3$ reforming catalyst, furnished by Johnson Matthey. The catalyst is placed between glass spheres (<2 mm diameter) layers. Before reaction, the catalytic bed was pre-heated using nitrogen up to 400 °C under
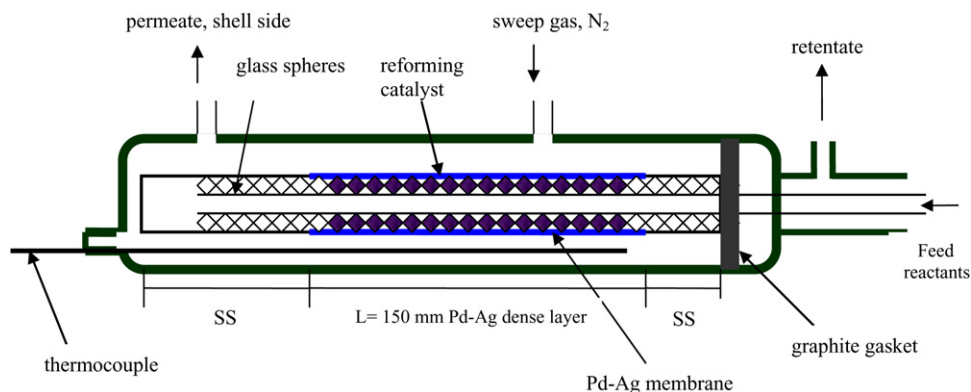

Fig. 1 – MR scheme.