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Model biogas steam reforming in a thin Pd-supported membrane reactor to generate clean hydrogen for fuel cells

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HIGHLIGHTS

- A Pd/Al_2O_3 membrane reactor generates concentrated H_2 (96%) via biogas reforming.
- The H_2/N_2 ideal perm-selectivity of the Pd/Al_2O_3 membrane is higher than 4000.
- The composite membrane reactor recovered 70% of H_2 during biogas reforming.

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ABSTRACT

Steam reforming of a model biogas mixture is studied for generating clean hydrogen by using an inorganic membrane reactor, in which a composite Pd/Al_2O_3 membrane separates part of the produced hydrogen through its selective permeation. The characteristics of H_2 perm-selectivity of the fresh membrane is expressed in terms of H_2/N_2 ideal selectivity, in this case equal to 4300. Concerning biogas steam reforming reaction, at 380 °C, 2.0 bar $H_2O:CH_4 = 3:1$, GHSV = 9000 h^{-1} the permeate purity of the recovered hydrogen is around 96%, although the conversion (15%) and hydrogen recovery (>20%) are relatively low; on the contrary, at 450 °C, 3.5 bar $H_2O:CH_4 = 4:1$, GHSV = 11000 h^{-1} the conversion is increased up to more than 30% and the recovery of hydrogen to about 70%. This novel work constitutes a reference study for new developments on biogas steam reforming reaction in membrane reactors.

1. Introduction

In the last decades, owing to a huge exploitation of fossil fuels to produce power, the rise of environmental pollution due to greenhouse gases (GHGs) and other harmful emissions has driven to the development of new technologies and to the utilization of renewable sources. Thus, hydrogen has been considered as a new and alternative energy carrier for several applications, making possible the development of the so called hydrogen economy [1,2]. Today, hydrogen generation comes from various feedstocks such as hydrocarbons, water and derived of biomass, involving several chemical processes and, consequently, energy requirements. Based on the nature of the chemical process and/or energy needs, hydrogen production can be realized mainly via thermochemical, electrochemical and/or biological methods [3]. However, nowadays the dominant process for producing hydrogen at large scale is represented by the reforming of natural gas [4,5]; therefore, to solve the issues related to the formation of GHGs and to limit the exploitation of fossil fuels, it is expected that alcohols such as ethanol, methanol, glycerol or other bio-fuels as acetic acid, biogas etc. could have a major impact in the future applications.

1.1. Biogas as a renewable source for hydrogen generation

Biogas represents a versatile raw material for reforming processes, which can be used as an alternative to natural gas as fossil fuels source. Then, hydrogen generation from biogas could help to largely lower the GHGs emission. Commonly, the composition of biogas is based mainly on methane and carbon dioxide, besides traces of H_2S, NH_3, hydrogen, nitrogen, oxygen and steam [6]. The composition of each compound is not fixed and can vary depending on which kind of residual biomass among animal waste, sewage treatment plants or industrial wastewater, landfills, etc. is used during the anaerobic digestion process [7]. As reported in the open

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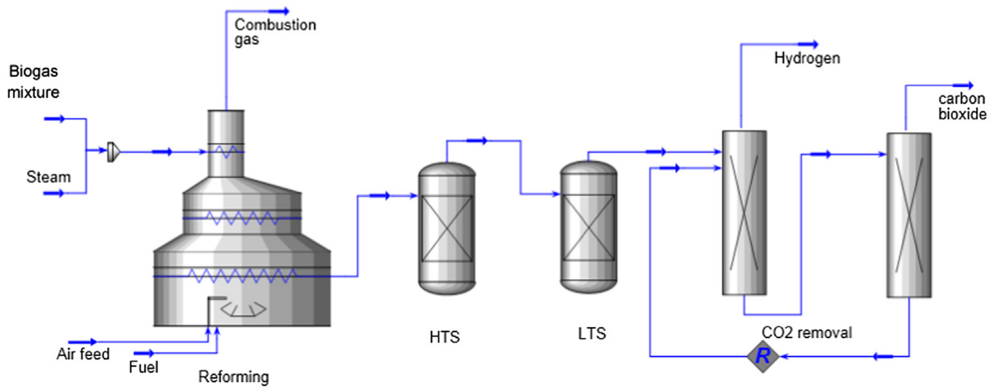

Fig. 1. Conceptual scheme of a conventional system for high grade hydrogen generation (HTS = high temperature water gas shift reactor; LTS = low temperature water gas shift reactor).

literature [8,9], in a biogas mixture methane can pass from 55% to 70%, carbon dioxide from 30% to 45%, H_2S from 500 to 4000 ppm, NH_3 from 100 to 800 ppm, while hydrogen, nitrogen, oxygen and steam can show percentage lower than 1% (vol.) with each one.

The biogas can be used in a wide range of applications [10], particularly because its chemical energy can be transformed into mechanical energy through combustion process. Furthermore, biogas can be useful to co-generate thermal energy, by producing hot water and steam through engines exercised at high temperature, or it can be burned to generate heat energy in boilers. Last but not least, it can be utilized directly as a fuel for automotive applications. However, even if at moment several types of biogas applications can be noticed, new and alternative routes of biogas exploitation could be followed. As a special case, biogas could be used to generate hydrogen to be further supplied to fuel cells [11,12], which reached remarkable progress in the last decade in the sector of transportation, for power generation and in stationary or portable installations [13–15].

1.2. Biogas reforming processes

Conventionally, in order to generate hydrogen the most common reforming processes involving methane (as a main product of biogas) are based on steam reforming, partial oxidation reforming, autothermal reforming, dry reforming and dry oxidation reforming [16]. Furthermore, in the open literature such non-conventional processes as solar reforming or thermal plasma reforming are noticed as further ways to produce hydrogen from methane [17,18]. Nevertheless, most of the scientific studies on biogas reforming for hydrogen generation deals with the utilization of model biogas mixtures in which only methane and carbon dioxide are present, whereas high purity methane (higher than 99%) is generally used to perform reforming reactions at bench scale. Indeed, to the best of our knowledge only few studies in the open literature regard the reforming of biogas directly coming from digestion process of residual biomass [19,20]. Therefore, as stated by Alves et al. [6], in a general subdivision when approaching to reforming of biogas, three different compositions of biogas should be taken into account: 1) *in natura*, with 55–70% of methane inside the mixture, 30–45% of CO_2 and 500–4000 ppm of H_2S; 2) biogas partially treated to remove H_2S; 3) purified biogas for “biomethane” enrichment (93–96% of methane, 4–7% of CO_2 and less than 20 ppm of H_2S).

However, hydrogen can be produced conventionally by methane or biogas reforming in a wide range of temperature between 600 and 1000 °C, which can be carried out at low pressure in fixed-bed (FBR) or fluidized bed reactors [21–24]. In this field, the combination of biogas reforming processes and fuel cells represents an interesting route for generating clean energy, with added high-energy efficiency [6,25–27].

Commonly, most of the scientific articles from literature about steam reforming of biogas deals with the utilization of Ni-based catalyst [28–32] owing to its lower cost than Pt, Rh or Pd as noble metals-based catalysts [33–35]. Nevertheless, Ni shows a strong deactivation susceptibility to coke formation owing to the high temperatures normally used during steam reforming reaction, while Pt and Pd catalysts seem to be more adapt concerning the catalytic stability [6] as well as Rh showing greater catalytic activity than Ni associated to a lower coke formation tendency [36].

To produce high-grade hydrogen from biogas steam reforming, such formed products as CO and CO_2 besides other by-products should be separated. Typically, the purification of hydrogen in conventional processes is performed in, at least, three stages (Fig. 1): conventional reformer, water gas shift reactors (high and low temperature) and different separating units [37].

As a special field of interest, various scientific studies in literature deal with the benefits obtained by using hydrogen-selective membrane reactors (MRs), owing to the possibility of integrating the reaction and the hydrogen purification stage in a single processor, Fig. 2, with the further possibility of directly supplying fuel cells [37–44].

In this contest, Pd-based MR technology has been applied often to steam reforming of methane to produce high grade hydrogen [40,41,45–47], but – to the best of our knowledge – only one time directly to a biogas mixture [48]. Therefore, the aim of this manuscript is to investigate the production of high grade hydrogen from the steam reforming of a model biogas mixture by means of a supported Pd-based MR packed by a commercial Ni-based catalyst chosen for its low cost. The novelty of this work consists of the combination within the application of a composite membrane based on a thin Pd-layer deposited on a porous ceramic support and the exploitation of a renewable source as biogas mixture to generate clean hydrogen for fuel cells and, meanwhile, to decrease the emission of pollutants. In particular, the utilization of a composite Pd-based membrane, having quite high hydrogen perm-selectivity with respect to all other gases and lower cost than dense unsupported Pd-based membranes (owing to the lower content of palladium) could make possible to match the aforementioned objectives.

2. Experimental

The experimental setup consists mainly of the MR module in which a porous Al_2O_3 supported Pd-based membrane is allocated, Fig. 3. The producer of the composite Pd-based membrane is the Nanjing University of Technology, while the porous Al_2O_3 support