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Exergy analysis of hydrogen production via biogas dry reforming

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ABSTRACT

Among the alternative pathways for hydrogen production, the use of biogas from organic waste via dry reforming of methane (DRM), water gas shift reaction and pressure swing adsorption (PSA) is often seen as an interesting option. In this work, the thermodynamic performance of this type of biohydrogen energy system –additionally including a combined-cycle scheme that satisfies the electricity and steam requirements of the process– is evaluated through exergy analysis. The main data needed for the analysis are acquired from a predictive simulation model implemented in Aspen Plus®. The system shows an exergetic efficiency of 55%, with the DRM and the power generation subsystems arising as the main sources of irreversibility. Furthermore, given the significant influence found for the PSA off-gas on the thermodynamic performance of the system, two alternative process configurations based on the use of this stream are evaluated. In this regard, full recirculation of the PSA off-gas to the DRM reactor is found to improve the system's exergetic performance.

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Introduction

Within the current context of sustainability concerns about the energy sector, hydrogen is expected to play a key role as one of the most promising alternatives to fossil fuels. However, this is conditioned by the primary energy and the conversion technology used to produce hydrogen [1,2]. Unfortunately, hydrogen is currently produced mainly from fossil fuels: approximately 48% from natural gas via steam methane reforming (SMR), 30% as a fraction of the petroleum refining process, and 18% from coal gasification [3]. In this respect, urgency in global warming mitigation may result in a growing interest in hydrogen production from bioresources [4,5].

Biomass utilisation could contribute to the mitigation of greenhouse gas emissions, while enhancing energy security and promoting the economic development of rural regions [6,7]. Biomass is a versatile feedstock with different composition according to its origin (agricultural and forestry crops, animal residues, sewage, municipal solid waste, etc.). It can be converted into a wide range of products (biofuels, electricity, heat and/or chemicals) through different conversion pathways. In particular, biogas is an interesting product coming from waste valorisation. It is produced by fermentation processes or anaerobic digestion of organic residues from several origins, and can be used for energy purposes with potential advantages in terms of reduced air pollution [8].

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Among the alternative pathways for the production of hydrogen from bioresources, the use of biogas via dry reforming of methane (DRM) is especially interesting due to the involvement of methane and carbon dioxide as reactants ($CH_4 + CO_2 \leftrightarrow 2\ CO + 2H_2$) [9]. This DRM process produces syngas, which can be further processed to pure hydrogen through the water gas shift (WGS) reaction followed by pressure swing adsorption (PSA).

Given the interest in hydrogen production from biogas dry reforming, the evaluation of its technical feasibility is needed. This can be addressed from a thermodynamic perspective using exergy analysis [10], which is a useful methodology to optimise energy conversion processes by identifying and quantifying the sources of thermodynamic inefficiency in a thermal system [11]. Thus, exergy analysis can help to benchmark and improve the overall efficiency and cost effectiveness of a system [12].

In this article, the thermodynamic performance of a DRM-based biohydrogen energy system is evaluated through exergy analysis. The key units of the system include a DRM reactor, two WGS reactors, a PSA unit, and a power block (combined-cycle scheme) that satisfies the electricity and steam requirements of the process. The data required to perform the analysis are acquired from a predictive simulation model implemented in Aspen Plus®. When compared to other studies addressing exergy analysis of hydrogen energy systems [13,14], the main novelty of this study lies in the simulation and subsequent exergy analysis of hydrogen production via biogas dry reforming, which is an energy system [15] that had not yet been evaluated using these tools.

Material and methods

Case study

As shown in Fig. 1, the DRM-based biohydrogen energy system is divided into four sections: DRM, WGS –with high (HTS) and low (LTS) temperature steps–, PSA, and a power generation section. The main feedstock of the system is biogas, whose molar composition is defined as 65% (v/v) CH_4 and 35% (v/v) CO_2. The biogas capacity of the energy plant is assumed to be 4259 $Nm^3\ h^{-1}$, with biogas tentatively coming from a local landfill in the region of Madrid (Spain) [16]. It should be noted that biogas production and pre-treatment are outside the boundaries defined for the evaluated system.

The biogas (main CH_4 carrier) and the PSA off-gas (main CO_2 carrier) are fed to the dry reformer, where DRM reactions take place at 1 bar and 650 °C in the presence of a Ni/Al_2O_3 solid catalyst [9,17]. The target product of the DRM section is syngas, mainly composed of H_2 and CO, and minor species such as H_2O, coke and unreacted CH_4 and CO_2. Since the coke produced is deposited on the catalyst, a circulating bed reactor with a regenerator is used in order to avoid catalyst deactivation, as often done under these circumstances [18]. In this way, the coke deposited on the catalyst is burnt and eliminated while meeting the heat demand of the endothermic DRM reactions. Thus, continuous operation is enabled. The exhaust gases from the regenerator are sent to the heat recovery steam generator (HRSG) of the power generation section to produce steam.

The syngas produced is cooled down in COND-1 in order to remove water from the syngas stream, and then compressed to 23.5 bar in a multi-stage compressor with 3 intercooled stages. In order to increase the hydrogen content of the syngas stream, it is sent to the WGS section. This section involves an HTS reactor operating at 350 °C (Fe–Cr catalyst) and an LTS reactor operating at 220 °C (Cu–Zn catalyst), with a steam-to-carbon molar ratio of 3. As the WGS reaction is exothermic, the outlet stream from the HTS reactor is used to heat up the inlet one. Finally, the stream leaving the LTS reactor is condensed to remove water and introduced in a PSA unit operating at 21.0/1.5 bar to obtain pure hydrogen [19]. A fraction of the PSA off-gas –which contains carbon dioxide (70.05% v/v), hydrogen (14.99% v/v), methane (12.52% v/v), carbon monoxide (1.19% v/v), and water (1.25% v/v)– is recirculated to the DRM reactor, and the remaining fraction is sent to the power generation section with the aim of making the

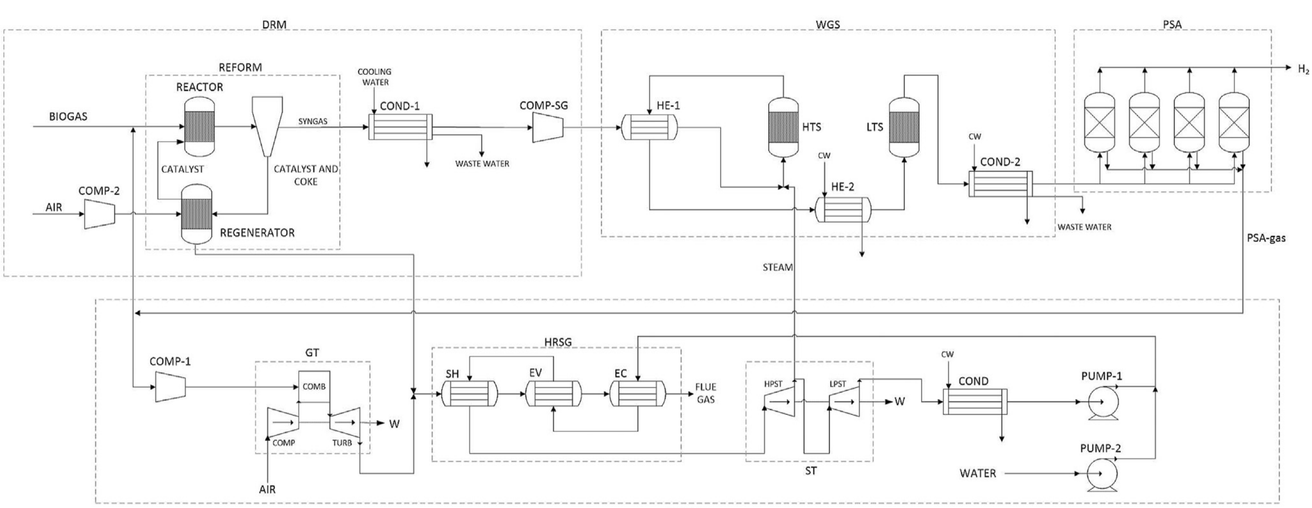

Fig. 1 – Simplified diagram of the DRM-based biohydrogen energy system.

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