

Optimization studies of hydrogen production via biogas steam reforming

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Keywords: Hydrogen, Optimization, Biogas, Bayonet reactor, Membrane reactor

1. Introduction

Although hydrogen is produced from many different raw materials and using diverse methods, hydrogen production from biogas/biomethane is identified as an interesting alternative in a process with low/zero fossil CO₂ emissions. Anaerobic conversion of organic raw materials into biogas provides not only a clean and renewable fuel, that consists almost exclusively of a mixture of methane and carbon dioxide (50-70% CH₄), but also a nutrient-rich digestate for land applications. Biomethane with up to 97% CH₄ can be obtained through biogas purification [1].

In order to maximize H₂ production, catalytic steam reforming of natural gas is preferred as it leads to the highest H₂/CO ratio. This reaction is strongly endothermic and presents equilibrium limitations, which determines that the choice of the reactor results highly dependant on the process scale. For large-scale operations, a reactor with radiant heat transfer is preferred, while, at smaller scales, convective-type designs become convenient. In the latter reactors, heat is supplied through a stream of hot gases from a combustion chamber. The temperature of the hot gases is preferably selected under 1300 °C to preserve the mechanical integrity of the reformer tubes assuring long life operation. The combustion chamber could be fed by fuel cell output stream, PSA stage rejection or the retentate stream of H₂ purifying membranes [2].

In order to improve energy integration and reduce reactor volumes, the implementation of two reactors showing different types of process intensification are proposed: biomethane steam reforming is conducted in a bayonet-type reactor while the water shift reaction is performed in parallel with H₂ purification in a membrane reactor.

As shown in Figure 1 (see insert for more details), the design of bayonet reactors provides internal countercurrent heat recovery [3]. Although the using of convective heating implies lower heat fluxes when compared with radiant heating, the internal heat recovery and the absence of the radiant box lead to an overall simpler and smaller reactor design, with enhanced dynamics [3]. These facts point out the preference of this compact design for small-scale installations, specially where a suitable fuel is available.

Membrane reactors are an interesting intensification strategy as they combine in the same unit, the reaction and separation process. The membrane selectively removes one of the products of reaction and shifts the equilibrium towards products in equilibrium-limited reactions. In particular, if the removed product is H₂, constitutes a method to purify the desired product.

In the present study, an autothermal process to produce ultrapure hydrogen from biogas is presented and analyzed. In order to maximize pure H₂ production, optimization studies were performed over the integrated process.

2. Methods

2.1 Process description

The process flow diagram under study is presented in Fig. 1. As stated before, the design process includes a bayonet-type reactor (BR) to produce syngas (reactions 1 to 3), and a WGS membrane reactor (MR) to enhance hydrogen yield while it is purified by a selective Pd membrane (reaction 2). A membrane separation module (PMBG) to purify biogas (BG, 60 % CH₄/40 % CO₂) to biomethane (BM, 96 % CH₄/4 % CO₂) is included upstream of RB [4]. A heat exchanger network to preheat and evaporate streams and to recover heat from the hot effluents is also added. Water boilers are also considered since all remaining calorific power available might be used to generate steam as sub-product. Both the biogas stream (BG), previously desulfurized, and the process water enters at 25 °C and 10 bar, whereas the combustion air is fed at 25 °C and 1 bay.

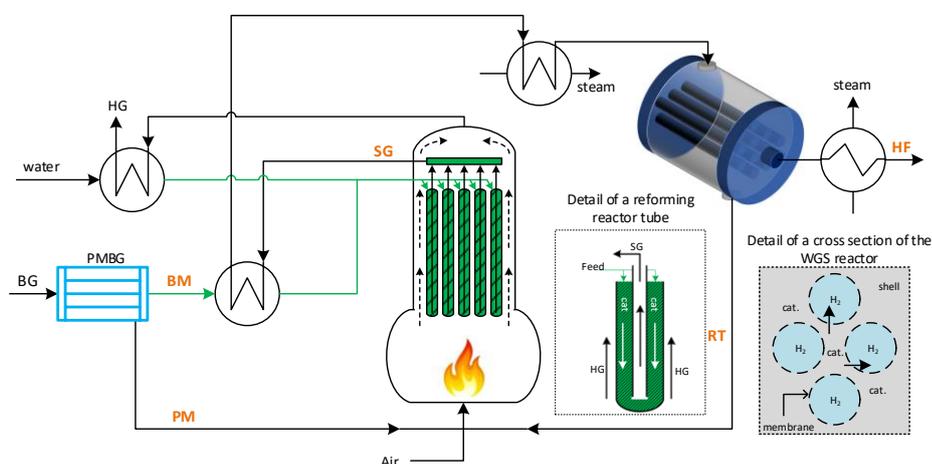


Fig. 1. Process flow diagram.

Reaction	ΔH°_{298K}	
$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3 \text{H}_2 + \text{CO}$	206 kJ/mol	(1)
$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO}_2$	-41 kJ/mol	(2)
$\text{CH}_4 + 2 \text{H}_2\text{O} \rightleftharpoons 4 \text{H}_2 + \text{CO}_2$	165 kJ/mol	(3)

Both the retentate stream (RT) from the MR and the permeate stream (PM, up to 15 % CH₄) from biogas PMBG are used as fuel in the combustion chamber of the bayonet reformer.

2.2 Process modelling and optimization

For the bayonet-type reactor (BR), a pseudo-homogeneous 1-D model is adopted [5]. The BR contains outer and inner tubes an annulus between them. The dimension of the tubes is 5/8" external diameter of the internal tube, and 2" external diameter of the external tube, both BGW 14. The catalyst adopted: Ni/MgO/Al₂O₃ (spherical pellets with a diameter of 5 mm), is arranged within the annular section of the tubes. As can be seen in Fig. 1, the input streams to the process are the biogas stream, the water input to the reformer and the air stream required for the combustion chamber. The heating gas circulates from the combustor located directly below the reformer in the shell (see Fig. 1).

The kinetic model proposed by Xu and Froment [6] is selected to evaluate the reaction rate and the global effectiveness factors reported by De Groote and Froment [10] are used. A pseudo-homogeneous 1-D model is adopted for WGS membrane reactor as reported by Adrover [7]. A multitubular configuration is selected to carry out the WGS reaction (Eq. 2) with H₂-selective membranes (0.7/1.4 cm in/out diameter, in a triangular arrangement). The catalyst (Fe₃O₄/Cr₂O₃) [8] is packed in the shell and the permeated H₂ is collected inner side of the membrane tubes. The operation is without sweep gas a co-current configuration is assumed. (see Fig. 1). H₂ permeates through a 4.5 μm thick layer of Pd/Ag deposited on multilayer porous ceramic tubes (permeation parameters from Marcoberardino et al. [9]).

A nonlinear optimization problem is set here in order to maximize the process performance in terms of ultrapure hydrogen flowrate (HF) and minimize both reactors' areas taking into account the number of tubes as well as the reactors length. The objective function (F_{obj}) is a weighted sum as shown in Eq. (4) [10]. The optimization problem must be solved for each unit (x: reactors, heat exchangers, mixing points, etc.), under the restriction of mass (M(x)) and energy (E(x)) balances closure, applying the properties (P(x)) of each species or mixture. Moreover, constraints (C(x)) must accomplish the imposed lower and upper bounds (C_{LB} and C_{UB}, respectively).

Both reactor's geometric parameters (L/D_s) and operative variables (temperatures) are considered as control variables. Then, the problem can be represented as follows:

$$F_{obj} = w_1 \cdot \max F_{H_2}^s + w_2 \cdot \min A_{BR} + w_3 \cdot \min A_{MR} \quad (4)$$

s.t.:

$$M(x) = 0 \quad (5)$$

$$E(x) = 0 \quad (6)$$

$$P(x) = 0 \quad (7)$$

$$C_{LB} \leq C(x) \leq C_{UB} \quad (8)$$

The selected constraints are:

$$1000 \text{ } ^\circ\text{C} \leq T_{HG} \leq 1300 \text{ } ^\circ\text{C} \quad (9) \quad \Delta T_{HX} \geq 10 \text{ } ^\circ\text{C} \quad (12)$$

$$T_{w,BR} \leq 920 \text{ } ^\circ\text{C} \quad (10) \quad T^{\circ}c \geq 100 \text{ } ^\circ\text{C} \quad (13)$$

$$300 \text{ } ^\circ\text{C} \leq T_{MR} \leq 550 \text{ } ^\circ\text{C} \quad (11) \quad \xi \geq 5 \text{ } \% \quad (14)$$

The temperature of the hot gas stream leaving the combustion chamber (T_{HG}) as well as the tube-skin temperature ($T_{w,BR}$) are limited in order to enlarge the service life of reactor materials. The operating temperature inside the MR (T_{MR}) is limited to guarantee the integrity of both the membrane and the WGS catalyst. The minimum temperature difference (ΔT_{HX}) between the hot and cold streams in each heat exchanger is defined at 10°C. The fluegas temperature ($T^{\circ}c$) leaving the process should exceed 100 °C to avoid steam condensation. The minimum combustion oxygen excess (ξ) is fixed to assure complete combustion.

2.3 Implementation

The differential equations of each unit are discretized by means of second order central finite differences. The final system of equations is composed of a total of 66807 algebraic equations. The generated system of equations is solved with the solver BDNL SOL of gPROMS 4.0. [11] Physicochemical and thermodynamic properties for the involved species and mixtures are evaluated according to Yaws [12].

3. Results

Figure 2 summarizes the values of both reactors' areas and ultrapure hydrogen flowrate obtained after solving the optimization problem considering different weights of the optimization function (Eq. 4). Case I: $w_1 = 0.8$; $w_2 = w_3 = 0.1$, Case II: $w_1 = 0.7$; $w_2 = 0.1$ $w_3 = 0.2$ and Case III: $w_1 = 0.7$; $w_2 = 0.2$ $w_3 = 0.1$. It is worth noting that in all three optimization scenarios the hydrogen production (HF) reaches the limit imposed by thermodynamics. In Case II, when more weight to minimize the membrane reactor area is adopted, the BR almost duplicates its size while a drop of 20% in MR size is observed, with respect to Case I. This implies that more hydrogen is generated in BR at expenses of less hydrogen separated in the MR. On the other hand, and with reference to Case I, when a size minimization of BR is sought (case III), the reformer area is reduced by 67% whereas the size of the MR only increases 21%. In all three cases, the tube-skin temperature is equal to the maximum value imposed by the restriction, i.e., $T_{w,BR} = 920^\circ\text{C}$. In this sense, designs that promote greater heat exchange between the flue and process streams in the reformer should be developed in order to reduce $T_{w,BR}$.

Figure 3 shows the axial temperature profiles corresponding to the BR for all three cases. It can be seen that the reaction mixture enters the reactor at 550°C (see T profiles) and suffers a slight drop due to the endothermic nature of the reforming reaction and the high reaction rates in the inlet zone of the reactor. Then, further along the axial coordinate, T increases due to the countercurrent heat exchange with both the combustion gases (see T_{HG}) and the exiting synthesis gas (T_{SG}). This behaviour is similar for all three optimization scenarios.



Fig. 2. Reactor areas (MR and BR) and hydrogen production (HF) after process optimization for the three cases under study.

The synthesis gas (T_{SG}) shows a temperature drop of ca. 200°C along the inner tube, thus demonstrating good heat recovery for all three cases. In Case III, where a minimization of the BR's size is intended, a higher thermal level of the combustion gases is required to compensate a diminished reactor size. Nevertheless, the temperature of the gases exiting the catalyst bed is the lowest among the three cases, implying a lower H_2 production in the BR and, consequently, higher areas of MR to compensate this fact.

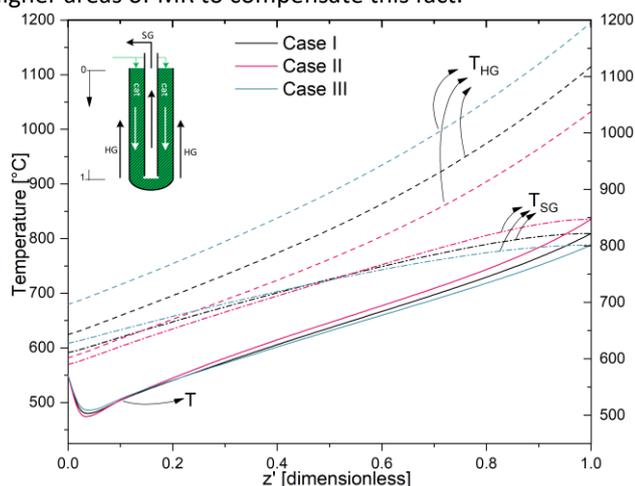


Fig. 3. Temperature axial profiles of the BR for the three cases under study.

Results related to CO conversion (X_{CO}) and hydrogen recoveries ($R_{H_2}^{MR}$, $R_{H_2}^G$) in the MR are presented in Table 1. $R_{H_2}^{MR}$ is calculated as the ratio between the H_2 flowrate in the permeate stream to the sum of H_2 flowrates in both permeate and retentate streams. Complementary, $R_{H_2}^G$ is calculated as the quotient between the permeated hydrogen flowrate and the hydrogen flowrate generated in the reformer (i.e., the H_2 fed to the MR). Considering all three CO conversion and the two recoveries, Case III appears as the preferable choice. It's worth remarking that in this situation a complete recuperation of the H_2 produced in the reactor is achieved as pure H_2 , while the overall energetic balance is satisfied. Nevertheless, this scenario points the need of higher membrane areas, which would imply higher costs for this unit.

Table 1. CO conversion and hydrogen recoveries for the MR.

	Case I	Case II	Case III
X_{CO} (%)	84	81	88
$R_{H_2}^{MR}$ (%)	84	81	89
$R_{H_2}^G$ (%)	99	94	100

4. Conclusions

The present contribution presents optimization studies regarding an autothermal process to produce pure H_2 from biogas. After purification, biomethane steam reforming is proposed in a bayonet-type convective reformer. The process includes as well a membrane reactor where the WGS reaction is carried out in parallel with ultrapure hydrogen separation from the syngas. Three different optimization scenarios are studied where the hydrogen production is maximized and reactor areas minimized differently weighted. Optimization studies show that the BR and MR areas compensate each other to maintain H_2 production as well as to assure the heat integration in the process. The MR appears to impact with higher weight in the total area required summing both reactors to maintain the hydrogen production flowrate. An economical analysis appears relevant to contribute in the final design.

Acknowledgements

The authors thank funding from CONICET [PIP 0912CO], ANPCyT [PICT 2018-01603] and UNS [PGI 24/M162].

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