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Using multi-criteria and thermodynamic analysis to optimize process parameters for mixed reforming of biogas

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Abstract

Syngas is a gas mixture that can be obtained from a variety of raw materials and used as source of hydrogen. Biogas is an interesting raw material from which to produce syngas via thermocatalytic reforming because it is abundant, can be obtained from low-cost feedstock, and is potentially carbon-neutral. However, difficulties arise because biogas composition changes from source to source, the reforming process can be quite energy-intensive and there is associated catalyst deactivation through carbon deposition. Mixed reforming of biogas with steam and/or air shows benefits in terms of carbon deposition and energy requirements, but the reaction network is complicated and finding the optimal operating conditions is not trivial. Although several analytical techniques have been used in the literature to find the optimal process conditions, a direct comparison is difficult due to the different criteria and/or boundaries considered. This paper aims to develop a novel and comprehensive methodology for identifying the optimal thermodynamic operating conditions (temperature and feed ratios) for mixed reforming of biogas with air and steam, based on equilibrium data manipulated via two multi-criteria decision making (MCDM) techniques in series, namely the entropy and the TOPSIS methods. The optimal scenario is when biogas made of 50-60 % CH₄ in CO₂ is reacted in the reforming reactor at CH₄/CO₂/O₂/H₂O = 1/1-0.67/0-0.1/3-2.4 and 790-735 °C, resulting in a product stream composed of 66-65 % H₂, 0.8-1 % CO and 33-28 % CO₂ on a dry basis after the water-gas shift section. At these conditions the hydrogen yield and the conversion of methane in the biogas can be simultaneously maximized, while the yield of solid carbon and the net energy requirement of the overall process can be minimized. In conjunction with the numerical results, the main outcome of this paper is the development of a novel method based on MCDM techniques for the optimization of the operating conditions in a network of reactions.

Keywords Biogas, reforming, optimization, multi-criteria, entropy, TOPSIS

1. Introduction

1.1 Hydrogen production via biogas

Hydrogen is considered by many as the fuel of the future, with its best use in terms of energy efficiency being in fuel cells [1, 2]. Any improvement in the fuel cell field depends on developments in hydrogen production, storage and delivery technologies [3]. Nowadays hydrogen is obtained mainly through steam reforming (SRM) (Equation 1) or partial oxidation (PO_x) of methane/natural gas (Equation 2), followed by the water-gas shift (WGS) reaction (Equation 3) [4-6]. Biomass-derived gas through anaerobic digestion (AD), or simply biogas, represents a sustainable alternative to natural gas [7-11], since its utilization can result in a neutral carbon balance, depending on the feedstock [12], and it can displace fossil fuels [13], which are the main contributors to greenhouse gas (GHG) emissions [14, 15].

Biogas has a typical composition of 50-70 % CH₄, 30-50 % CO₂ and minor amount of H₂O, H₂S, NH₃, H₂, N₂ and O₂ depending on the source [16]. Once contaminants have been removed, biogas can be used as raw material in the dry reforming of methane (DRM) with CO₂ (Equation 4) to produce hydrogen; compared to SRM, the reaction is slightly more endothermic (247 vs. 209 kJ mol⁻¹) and the product stream has a lower H₂/CO ratio (H₂/CO = 1 vs. 3). The main problem associated with the SRM and DRM reactions is solid carbon (also known as coke) formation via methane cracking (Equation 5) and CO disproportionation (Equation 6).

The combination of endothermic reactions ($\Delta H > 0$) with PO_x ($\Delta H < 0$) is called autothermal reforming (ATR), because a fraction of the heat required by the process is generated by combustion of part of the feed with oxygen [17, 18]. The combination of SRM, DRM and PO_x is known as mixed reforming or tri-reforming (TRI-R). It has gained attention lately [19-23] because of the advantage of lowered carbon deposition and energy requirement, however, this is at the expense of the loss of some valuable CO (Equation 7) and H₂ (Equation 8) via oxidation.

Steam reforming of methane	$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	$\Delta H^0_{298} = 208.813 \text{ kJ mol}^{-1}$	Equation 1
Partial oxidation of methane	$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$	$\Delta H^0_{298} = -36 \text{ kJ mol}^{-1}$	Equation 2
Water-gas shift	$CO + H_2O \rightleftharpoons CO_2 + H_2$	$\Delta H^0_{298} = -41.166 \text{ kJ mol}^{-1}$	Equation 3
Dry reforming of methane	$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	$\Delta H^0_{298} = 246.979 \text{ kJ mol}^{-1}$	Equation 4
Methane cracking	$CH_4 \rightleftharpoons C + 2H_2$	$\Delta H^0_{298} = 74.52 \text{ kJ mol}^{-1}$	Equation 5
CO disproportionation	$2CO \rightleftharpoons CO_2 + C$	$\Delta H^0_{298} = -172.459 \text{ kJ mol}^{-1}$	Equation 6
Oxidation of CO	$CO + 0.5O_2 \rightarrow CO_2$	$\Delta H^0_{298} = -282.984 \text{ kJ mol}^{-1}$	Equation 7
Oxidation of H ₂	$H_2 + 0.5O_2 \rightarrow H_2O$	$\Delta H^0_{298} = -241.818 \text{ kJ mol}^{-1}$	Equation 8

1.2 Review of the literature

Considering that two thirds of the overall cost of hydrogen production are for feed, fuel and utilities [24], benefits in the process can be obtained by lowering the operating costs (e.g. through better control of carbon limits to extend catalyst lifetimes), by selecting catalysts which allow flexibility by using low-cost feedstock (e.g. biogas), and by selecting optimum process conditions giving low energy consumption. Given the various combinations of possible reactions for the production of hydrogen from methane/biogas (Equation 1 - Equation 8), the optimization of the operating conditions represents a trade-off between multiple criteria, whose relationships are not always clear. A direct comparison of the results of previous research on the optimization of mixed reforming of methane/biogas is difficult because of the different techniques, criteria, boundaries, and combinations of reactions considered (Table 1).

Seo et al. [25] studied the equilibrium values during SRM, PO_x and autothermal reforming, together with the energy required by the system, in order to maximize the conversion of methane and minimize the yield of solid carbon (biogas was not considered in the feed). The maximum allowable temperature was assumed to be 800 °C, and the results showed that, in terms of energy cost, the PO_x reforming system is more efficient than other systems for the production of the same amount of hydrogen from CH₄. The results, however, are not readily comparable with other studies because of the different configurations used during the simulation of the processes. The consumption of thermal energy is a key issue in the design of a reforming system, as demonstrated by Avila-Neto et al [26], whose thermodynamic analysis was focused on the maximization of hydrogen yield by using the equilibrium constant and Lagrange's multipliers method. The authors studied steam, dry, oxidative and autothermal reforming of methane. The analysis comprised a complicated system of non-linear algebraic equations to be solved numerically. Jarungthammachote [27] studied the combination of SRM, DRM and PO_x, by analysing the equilibrium data via a parametric study in order to find the operating conditions which maximize solely the hydrogen yield. A fixed composition of biogas was assumed in this analysis, which excluded a WGS stage. An energy assessment of the different processes was not included. Vita et al. [28] and Effendi et al. [29] performed experimental optimization of biogas reforming using a Ni/CeO₂ and Ni/Al₂O₃ catalyst, a fixed CO₂/CH₄ ratio, and quite narrow experimental conditions. The study focused on the reforming step alone, and did not include energy considerations. Larentis et al [30] investigated process optimization for the combined dry reforming and partial oxidation process of natural gas (79 % CH₄, 17 % C₂H₆, 4 % C₃H₈), through a combination of experimental results obtained with a

Pt/Al₂O₃ catalyst, mathematical and phenomenological modeling. The study did not consider steam in the feed, and the concentration of CO₂ in methane was fixed at 27 %.

While previous studies have investigated aspects of the optimisation of hydrogen production, there is a lack of existing research using a comprehensive approach to take the relevant criteria (i.e. energy requirements, carbon formation and the equilibrium composition of hydrogen-rich gas), their mutual relationships, all reaction stages, and the range of possible combinations of network reactions into account. MCDM techniques are used in engineering, business and many other fields [31-33] to assist in ranking available alternatives when complex multiple criteria have to be considered simultaneously [34], and present a possible solution to the problem. However, to the authors' knowledge, MCDM techniques have never been used before for the optimization of the process conditions in a chemical reaction network. Recent recommendations for best practice are to use MCDM techniques like the entropy method in series with Technique for Order Preference by Similarity to the Ideal Solution (TOPSIS) [35]. The combination of the two techniques has been used for safety evaluation of coal mines [36], information system selection [37], ecological-economic efficiency evaluation of green technologies [38], and building energy performance benchmarking [39], amongst others. The advantages of these techniques are that TOPSIS evaluates alternatives simultaneously considering all the criteria of interest with straightforward computation [39] [40], while the entropy method overcomes subjectivity when assigning the weights to the evaluation criteria [41] [42].

The aim of this paper is to fill the knowledge gap by developing a clear and comprehensive methodology which considers various compositions of biogas, combinations of reactions, and process conditions in order to make recommendations for optimizing the operating conditions of mixed reforming of methane/biogas. Along with the numerical results, the main novelty is the development of a methodology for the analysis of a chemical reaction network.

Table 1 - Optimization of methane/biogas reforming from literature

CH ₄ /CO ₂ /O ₂ /H ₂ O_range	T(°C)_range	P(atm)	CH ₄ /CO ₂ /O ₂ /H ₂ O_optimal	T(°C)_optimal	Target	Methodology	Ref.
1/0/0/0.6-3	<800	1	1/0/0/1.9	800	Maximize x _{CH₄} ; minimize Y _C	Thermodynamic analysis	[25]
1/0/0-1.2		1	1/0/0.6	800			[25]
1/0/0-1/0-1.2		1	1/0/0.58/0.35	800			[25]
1/0/0/0-4	100-1000	1	1/0/0/4	846.85	Maximize Y _{H₂}	Thermodynamic analysis via Lagrange's multipliers and equilibrium constant method	[26]
1/0-3	100-1000	1	1/1	700			[26]
1/0.54/0.46-0.92/0.77-12.3		1	1/0.54/0.66-0.7/6.15-7.69	800	Maximize Y _{H₂}	Thermochemical equilibrium study	[27]
1/0.67/0.05-0.1/0.3-0.7	800-900	1	1/0.67/0.1/0.3	800	Maximize activity and stability	Experimental (Ni/CeO ₂)	[28]
1/0.67/0/0-5	627-927	1	1/0.67/0/2.5	750	Low CO concentration	Experimental (Ni/Al ₂ O ₃)	[29]
1/0.37/0.25-0.55	600-1100	1	1/0.37/0.55	950	Maximize x _{CH₄} , S _{CO} ; minimize H ₂ /CO, Y _{H₂O}	Experimental (Pt/Al ₂ O ₃) + empirical and phenomenological modelling	[30]
1/0.33-1	400-1400	1	1/1	1100	Maximize Y _{H₂} ; minimize energy usage	Minimization of Gibbs free energy	[43]
1/1/0/2-6	400-1400	1	1/1/0/2	850			[43]
1/0/0/1-3	400-1400	1	1/0/0/1	900			[43]
1/1/0-0.5	327-1027	1	1/0.8-1/0.1-0.2	926.85	Maximize Y _{H₂}	Lagrange's undetermined multiplier method	[44]
1/0/1-5	500-1000	1	1/0/2-3	700-800	Maximize x _{CH₄} , x _{H₂O} , Y _{H₂} ; minimize Y _C	Minimization of Gibbs free energy	[45]
1/0.5-3/0.1-0.5/0.5-3	500-1000	1	1/0.8-1/0.1-0.2	>800			[45]
1/0.7/0.06	500-1000	1	1/0.7/0.06	850	H ₂ /CO = 1.6-1.7	Parameter sensitivity analyses	[46]
1/0.25-4	300-1100	1	1/1-2	800-1100	Maximize Y _{H₂} ; minimize Y _C	Numerical simulation model	[47]

2. Methodology

2.1 Overview

In order to develop the MCDM methodology with four variables (temperature, CO_2/CH_4 , O_2/CH_4 , $\text{H}_2\text{O}/\text{CH}_4$), initial testing of two- and three-variable methods was undertaken to explore the functionality of the method and the relevance of the model outputs. ASPEN Plus v7.3 by AspenTech [48] was used to generate thermodynamic equilibrium data, which was then analysed using MCDM techniques to find the trade-off between costs and benefits and thus identify optimum operating conditions for hydrogen production from biogas (Fig. 1). The overall MCDM technique, consisting of the entropy and TOPSIS methods running in series, was executed via a Matlab code written in-house, interfaced with ASPEN Plus via a local COM automation server (Fig. 1). This choice was taken because the gradient-based optimization routine of ASPEN struggles to determine the solution when there is a large number of decision variables [49]. The Matlab code employed is reported in the supporting information (SI2), while a description of each stage of the process (Fig. 1) is given in the following sections.

Fig. 1 – Graphical representation of the methodology. The orange box represents the Matlab code, whose inputs and outputs are the set of conditions (CH₄/CO₂/O₂) and the closeness to the associated ideal solution (C*), respectively

2.2 ASPEN Plus simulations

The thermodynamic data relating to the mixed-reforming of biogas were obtained via ASPEN Plus, using the Peng-Robinson equation of state and the RGibbs block [50], which is based on the minimization of the Gibbs free energy. The model biogas comprised solely of methane and carbon dioxide. The Model Analysis Tool of ASPEN Plus was used to run sensitivity analyses on the temperature inside the reforming reactor. The step sizes chosen for the analysis (Table 2) provide sufficient resolution, with reasonable computational workload.

The simulations were run at atmospheric pressure, assuming air comprising 79 % N₂ and 21 % O₂, while all the heat and mass balances were based on 1 mol s⁻¹ of CH₄ entering the system.

Regarding the flowsheet used in ASPEN Plus (Fig. 2), biogas with different percentages of methane, water and air (Table 2) enters the reforming block at room temperature and atmospheric pressure. Water is vaporized at 120 °C in block HX1, mixed with the other gases in the mixer M1, and fed to the reformer block SRM. Here the reforming takes place at T = 300-1200 °C, with all the components of the simulation considered as possible products (i.e. CH₄, H₂O, CO, H₂, C (graphitic carbon), CO₂, O₂, N₂). Even during pure SRM, there are secondary reactions taking place, such as WGS, CH₄ cracking, and CO disproportionation, the extent of which depends on the availability of reactants and on the temperature inside the block. Endothermic reactions are favoured as temperatures increase, while exothermic reactions are favoured as temperatures decrease. Products and unconverted reactants from the SRM block are assumed to leave the reactor at the reaction temperature.

Table 2 – Conditions for the sensitivity analyses (100 % CH₄ in the biogas refers to pure methane)

	Range	Step size
CH ₄ in the biogas (%)	50-100	10
T (°C)	300-1200	5
H ₂ O/CH ₄	0-5	0.05
O ₂ /CH ₄	0-0.5	0.05

Fig. 2 – ASPEN Plus flow sheet: reformer reactor (SRM), high-temperature shift reactor (HTS), low-temperature shift reactor (LTS), heat exchangers (HX1, HX2, HX3), mixer (M1), ideal separation block (SEP1). Reforming block (red line, - · -), water-gas shift block (blue line, - · -), overall block (yellow line, - - -)

To simulate a process/catalyst which is only selective towards WGS, only CO, H₂O, CO₂, and H₂ were allowed as possible products in the HTS and LTS blocks of ASPEN Plus. This is to avoid reverse-SRM and reverse-DRM (both exothermic) which would otherwise happen when the temperature inside the WGS block approaches lower temperature ranges,

leading to the undesirable formation of CH₄ from CO and H₂ [51]. Additionally, the other species were separated in the ideal separator block SEP1 and recovered through line 8. In fact, the simultaneous presence of CH₄ and O₂ in the equilibrium reactors of the WGS block would lead to the oxidation of unconverted methane, which is exothermic and thermodynamically favoured at any temperature.

The high-temperature shift (HTS) and low-temperature shift (LTS) blocks work at 380 and 225 °C, respectively [6]. The operating conditions of the WGS blocks are fixed, therefore the performance of the overall system is optimized by acting solely on the SRM block variables.

After the WGS stages, the concentration of CO in real reforming units is usually lower than 1 % [25]. No heat integration is assumed between blocks. The results arising from the thermodynamic modelling of the mixed reforming of biogas in ASPEN Plus are stored in a raw data matrix, before being manipulated into two MCDM techniques in series, namely the entropy [52] and the TOPSIS [53] methods.

2.3 Entropy method

The entropy method can be used to determine objective weights or the relative importance of criteria within MCDM problems. The weights are a measurement of the uncertainty in the information (disorder degree) formulated using probability theory, and therefore can be used to evaluate the effectiveness of the information for a particular system. In other words, the method measures the quantity of useful information provided by the data itself [54]. The method is based on entropy as defined by Shannon [55], who demonstrated that a broad distribution is associated with more ambiguity than one with a sharp peak. The greater the entropy weight, the more useful is the information carried by the criterion [56]. Compared with other synthetic evaluation methods for determination of weights, the entropy method shows a decrease in the calculation workload [57].

A MCDM problem can be expressed in a matrix format (Fig. 3): the possible alternatives of the problem, A_i (i = 1,2,...,m), are reported in the columns, while the criteria or properties, C_j (j = 1,2,...,n), are shown in the rows. A generic element x_{ij} represents the rating of alternative i with respect to the criterion j.

	C ₁	...	C _n
A ₁	x ₁₁	...	x _{1n}
...	...	...	...
A _m	x _{m1}	...	x _{mn}
	w ₁	...	w _n

Fig. 3 - Matrix representation of an MCDM problem

The entropy method consists of the following steps:

STEP 1 – Normalize the decision matrix by calculating p_{ij} (Equation 9)

$$p_{ij} = \frac{x_{ij}}{\sum_{i=1}^m x_{ij}} \quad i = 1, 2, \dots, m; \quad j = 1, 2, \dots, n \quad \text{Equation 9}$$

Raw data are normalized to eliminate anomalies with different measurement units and scales.

STEP 2 – Compute the entropy h_j (Equation 10). The constant λ (Equation 11) guarantees that $0 \leq h_j \leq 1$, assuming that when $p_{ij} = 0$, $\ln(p_{ij}) = 0$.

$$h_j = -\lambda \sum_{i=1}^m p_{ij} \ln(p_{ij}) \quad i = 1, 2, \dots, m; \quad j = 1, 2, \dots, n \quad \text{Equation 10}$$

$$\lambda = 1/\ln(m) \quad \text{Equation 11}$$

STEP 3 – Calculate the degree of diversification of the average information contained in each criterion, d_j (Equation 12)

$$d_j = 1 - h_j \quad j = 1, 2, \dots, n \quad \text{Equation 12}$$

STEP 4 – Determine the degree of importance (weight of entropy) of criterion j , w_j (Equation 13, Equation 14)

$$w_j = \frac{d_j}{\sum_{s=1}^n d_s} \quad j = 1, 2, \dots, n \quad \text{Equation 13}$$

$$\sum_{j=1}^n w_j = 1 \quad \text{Equation 14}$$

2.4 TOPSIS method

The TOPSIS method is a goal-based decision-making technique which needs information about the criterion weights in order to find which alternative is as close as possible to the positive-ideal solution (PIS), which is where all the benefit criteria are maximized and all the costs are minimized simultaneously. The negative-ideal solution (NIS) occurs when benefits are minimized and costs maximized. The distance between an alternative and the PIS is called closeness to the positive-ideal solution (C^*), and it varies from 0 to 1 when the alternative corresponds to the NIS or PIS, respectively (Fig. 4) [53]; a C^* value equal to 0 or 1 is an ideal case, and never happens in reality. The TOPSIS method is one of the most famous MCDM techniques, and its main advantages are: it is rational and understandable; the computational steps are straightforward; and the weights are incorporated into the comparison procedure. The steps in the TOPSIS method are shown in the supporting information, SI1.

Fig. 4 – Illustration of the TOPSIS method with two variables. The grey dashed line (---) indicates the criteria boundaries, while the red dashed and dotted line (- · -) indicates the distance between alternative i and the ideal solutions (NIS and PIS)

2.5 Running the simulation

The percentages of CH_4 , CO_2 and air entering the block diagram (Fig. 2) were fixed. The conversion of methane in the reformer (Equation 15) and total yield of hydrogen (Equation 16) were set as benefits, while the total yield of coke (Equation 17) and the net energy requirement for the process (Equation 18) were set as costs. The net energy requirement is the sum of the energy required or released by the blocks indicated as SRM(kW), HTS(kW), LTS(kW), HX1(kW), HX2(kW) and HX3(kW) (Fig. 2).

Methane conversion in the reformer was maximized because (i) it is the main reactant, (ii) it is a GHG (flaring should to be avoided), and (iii) a low methane slip is often crucial for the economics of the process [6]. The total yield of hydrogen (Equation 16) was maximized because it represents the main product of the process and because hydrogen loss in the form of unconverted steam at the outlet of the system represents an exergy loss [58]. The total yield of coke (Equation 17) was set as a cost, because coke is highly detrimental to the catalyst and inhibits the reforming and oxidation reactions that lead to the production of hydrogen. Finally, the net energy input was minimized in order to maximize the thermal efficiency of the simulation, as poor process performance could arise from underutilized heat outputs [59]. It was assumed that there were no heat losses between a given block and the following one in the block diagram. Selectivity towards a certain species, which is the combination of the yield of that species and methane conversion, was not included in the analysis to avoid redundancy between criteria.

The ASPEN Plus simulation was run, considering two sensitivity analyses: one on the $\text{H}_2\text{O}/\text{CH}_4$ ratio of the feed stream, and the other on the temperature of the SRM block (Table 2). The equilibrium data were generated and then stored in a matrix before being processed in the MCDM block. As the equilibrium data only depend on the operating conditions (i.e.

temperature and feed ratios), the only degree of freedom left to influence the analysis, without modifying the flow sheet, is the choice of cost and benefit criteria. The raw data distributions were used in the entropy method to generate the objective weights, which in turn were used in the TOPSIS method to rank the different operating conditions according to the C^* values. The steps were then repeated considering biogas with different concentrations of CO_2 and air at the inlet (Table 2). The model was verified and debugged as described in the supporting information, SI2.

Conversion of methane	$x_{CH_4_{SRM}} = 100 \frac{(CH_{4(5)} - CH_{4(6)})}{CH_{4(5)}}$	Equation 15
Yield of hydrogen	$Y_{H_2_{tot}} = 100 \frac{2(H_{2(12)})}{4(CH_{4(5)}) + 2(H_2O_{(5)})}$	Equation 16
Yield of solid carbon/coke	$Y_{COKE_{tot}} = 100 \frac{(COKE_{(8)} + COKE_{(12)})}{CH_{4(5)}}$	Equation 17
Net energy requirement	$E_{net}(kW) = SRM(kW) + HTS(kW) + LTS(kW) + HX1(kW) + HX2(kW) + HX3(kW)$	Equation 18

3. Results

3.1 Two-variable MCDM

The two variables considered were T ($^{\circ}\text{C}$) and $\text{H}_2\text{O}/\text{CH}_4$. The composition of the biogas and the O_2/CH_4 ratio were fixed. The method found the optimal operating temperature at different values of $\text{H}_2\text{O}/\text{CH}_4$. For instance, when pure methane and no air were present in the feed, the method calculated a recommended temperature of 775°C and a $\text{H}_2\text{O}/\text{CH}_4$ ratio of 1.5 (Table 3). By working at these operating conditions during steam reforming of pure methane, the equilibrium composition of the product stream comprised around 78% H_2 and had a H_2/CO ratio equal to 7.4, without any coke deposition (Fig. 5), although methane conversion was not complete ($\sim 96.7\%$) and the reaction was more endothermic than pure SRM with a stoichiometric feed (274 vs. 208 kJ s^{-1}). The results correspond well with other findings in the literature ([25], Table 1), demonstrating the functionality of the method.

Table 3 – Optimal outcome for the criteria of interest, when running the two-variable MCDM method with pure methane as the feed. $\text{CH}_4/\text{CO}_2/\text{O}_2 = 1/0/0$, $C^*_{\max} = 0.9985$, $T_{\text{optimal}} = 775^{\circ}\text{C}$, $\text{H}_2\text{O}/\text{CH}_4_{\text{optimal}} =$

	1.5			
	$x_{CH_4_{SRM}}(\%)$	$Y_{H_2_{tot}}(\%)$	$Y_{COKE_{tot}}(\%)$	$E_{net}(kW)$
CH ₄ in the biogas (%)	O ₂ /CH ₄ = 0			
100	96.72	97.37	0.00	274.57

Fig. 5 – Molar fractions of the final stream, when running the two-variable MCDM method with pure methane as the feed. $\text{CH}_4/\text{CO}_2/\text{O}_2 = 1/0/0$, $C^*_{\max} = 0.9985$, $T_{\text{optimal}} = 775\text{ }^\circ\text{C}$, $\text{H}_2\text{O}/\text{CH}_4_{\text{optimal}} = 1.5$

3.2 Three-variable MCDM

The two-variable analysis was extended to three dimensions with T ($^\circ\text{C}$), $\text{H}_2\text{O}/\text{CH}_4$, and O_2/CH_4 as variables, by keeping CO_2/CH_4 constant while running a sensitivity analysis on the air concentration in the feed. Initially the CO_2/CH_4 ratio was fixed at 0 (pure methane in the feed), and the highest value for C^* (0.9988) obtained at $735\text{ }^\circ\text{C}$, with $\text{O}_2/\text{CH}_4 = 0.05$ and $\text{H}_2\text{O}/\text{CH}_4 = 1.45$ (Fig. 6). When considering pure methane, increasing the amount of air in the feed caused a decrease in both the optimal operating temperature for the reformer and the optimal $\text{H}_2\text{O}/\text{CH}_4$ ratio. The C^* values were not drastically affected (standard deviation equal to 0.004), because the decrease in the conversion of methane and in the yield of hydrogen with an increasing amount of air in the feed were compensated by the lower net heat required by the process; from $\text{O}_2/\text{CH}_4 = 0.35$ upwards, the $E_{\text{net}}(\text{kW})$ value was negative (i.e. the overall process becomes exothermic) (Fig. 7).

At each optimal operating condition the carbon yield was zero, reflecting the fact that the minimization of solid carbon formation was the highest weighted criterion in the simulation (Fig. 9). The molar fractions of CO and H_2 decreased with increasing O_2/CH_4 ratio, to a certain extent because the CO and H_2 were oxidized to produce thermal energy, but also because there was an increasing amount of inert N_2 in the system coming from air, which diluted the product stream (Fig. 8). In the optimal case of $\text{O}_2/\text{CH}_4 = 0.05$, the final product stream contained 73 % H_2 , 13 % CO_2 , 8 % CO, 4 % N_2 , 1 % CH_4 and 1 % H_2O . No solid carbon was deposited, and the O_2 in the feed was completely converted in all the alternative process conditions (Fig. 6), because it was always present in sub-stoichiometric amounts. Carbon dioxide was always

present in the final stream (8-15 %), with excess steam up to around 30 % at higher O_2/CH_4 values due to the oxidation reactions taking place.

The results show similar trends to those in the literature when different boundaries are taken into account. For example, in an analysis that considered a narrower range of steam-to-methane ratio (0-1.2), Seo et al [25] recommended a higher temperature and O_2/CH_4 ratio (800 vs. 735 °C, 0.58 vs. 0.05, in [25] and this paper respectively), which were needed to compensate for the lower steam-to-carbon ratio (0.35 vs. 1.45).

Fig. 6 – Optimal operating conditions, when running the three-variable MCDM method with pure methane as the feed. $CH_4/CO_2 = 1/0$, $C^*_{max} = 0.9988$, $T_{optimal} = 735^{\circ}C$, $O_2/CH_{4optimal} = 0.05$, $H_2O/CH_{4optimal} = 1.45$

Fig. 7 – Optimal outcome for the criteria of interest, when running the three-variable MCDM method with pure methane as the feed. $CH_4/CO_2 = 1/0$, $C^*_{max} = 0.9988$, $T_{optimal} = 735^{\circ}C$, $O_2/CH_{4optimal} = 0.05$, $H_2O/CH_{4optimal} = 1.45$

Fig. 8 – Molar fractions of the final stream, when running the three-variable MCDM method with pure methane as the feed. $\text{CH}_4/\text{CO}_2 = 1/0$, $C_{\text{max}}^* = 0.9988$, $T_{\text{optimal}} = 735^\circ\text{C}$, $\text{O}_2/\text{CH}_{4\text{optimal}} = 0.05$, $\text{H}_2\text{O}/\text{CH}_{4\text{optimal}} = 1.45$

3.3 Four-variable MCDM model for optimisation of mixed reforming of biogas

The full results of the MCDM methodology with four variables (supporting information SI3, with a sample plot for $\text{CH}_4 = 50\%$ in Fig. 10) were obtained considering T ($^\circ\text{C}$), $\text{H}_2\text{O}/\text{CH}_4$, O_2/CH_4 , and CO_2/CH_4 as variables (Table 4). The weights for the criteria from the entropy method at different biogas compositions are shown in Fig. 9.

Fig. 9 – Weights for the criteria evaluated via the entropy method at different values of methane concentration in the biogas

When the percentage of methane in the biogas was 60-70 %, the method suggested running tri-reforming at $735\text{-}750^\circ\text{C}$; a combination of dry and steam reforming at a higher temperature was preferred when the methane concentration in the biogas was 50, 80, and 90 %. In the case of pure methane, the best route is to couple steam reforming and partial oxidation, resulting in the lowest $\text{H}_2\text{O}/\text{CH}_4$ operating value; the optimal steam-to-methane ratio

suggested by the method increased almost exponentially with increasing concentration of carbon dioxide in the biogas.

When working at the optimal conditions suggested by the method, the conversion of methane increases by 6.5 % with the percentage of carbon dioxide in the biogas going from 0 to 50 % (Table 5). The hydrogen yield first reached its peak at $\text{CH}_4 = 90\%$ and then decreased with the increase of CO_2 in the biogas (because methane is the source of hydrogen). When using pure methane, the hydrogen yield was slightly lower than that obtained when using biogas with $\text{CH}_4 = 80\text{--}90\%$, because the O_2/CH_4 ratio of 0.05 in the feed leads to the combustion of a small percentage of the hydrogen previously produced (Table 4). Because minimization of coke yield was the most important criterion in all the options analysed (Fig. 9), there was no solid carbon formation for any of the operating condition suggested by the method. The net energy requirement was minimal when using pure methane and oxygen in the feed, because (i) of the oxidation reactions occurring, (ii) it had the lowest steam-to-carbon ratio of all options (meaning less heat was required to vaporize the water), and (iii) there was no CO_2 in the feed (resulting in no DRM and a less endothermic overall reaction).

With an increasing concentration of CH_4 in the biogas, the hydrogen and carbon monoxide concentrations on a wet basis increased from 56 to 75 %, and 1 to 8 %, respectively (Fig. 11). On a dry basis, the hydrogen molar fraction was relatively constant at $70 \pm 5\%$ for the different feed conditions, showing that biogas can be a valid substitute for methane in the reforming process.

Table 4 – Optimal operating conditions, when running the four-variable MCDM method. $C^*_{\max} = 0.9999$, $T_{\text{optimal}} = 790\text{ }^\circ\text{C}$, $\text{CH}_4/\text{CO}_2/\text{O}_2/\text{H}_2\text{O}_{\text{optimal}} = 1/1/0/3$

$\text{CH}_4(\%)$ in the biogas	$T(^{\circ}\text{C})_{\text{optimal}}$	$\text{O}_2/\text{CH}_4_{\text{optimal}}$	$\text{H}_2\text{O}/\text{CH}_4_{\text{optimal}}$	$C^*_{\max}$
100	735	0.05	1.45	0.9988
90	770	0	1.6	0.9983
80	765	0	1.75	0.9992
70	750	0.05	2	0.9996
60	735	0.1	2.4	0.9997
50	790	0	3	0.9999

Fig. 10 – Distributions for the criteria at different values of temperature and $\text{H}_2\text{O}/\text{CH}_4$, when running the four-variable MCDM method. $\text{CH}_4/\text{CO}_2/\text{O}_2 = 1/1/0$, $C^*_{\text{optimal}} = 0.9999$, $T_{\text{optimal}} = 790\text{ }^\circ\text{C}$, $\text{H}_2\text{O}/\text{CH}_4_{\text{optimal}} = 3$

Table 5 – Optimal outcome for the criteria of interest, when running the four-variable MCDM method.

$C^*_{\text{max}} = 0.9999$, $T_{\text{optimal}} = 790\text{ }^\circ\text{C}$, $\text{CH}_4/\text{CO}_2/\text{O}_2/\text{H}_2\text{O}_{\text{optimal}} = 1/1/0/3$

CH_4 in the biogas (%)	$x_{\text{CH}_4_{\text{srm}}}(\%)$	$Y_{\text{H}_2_{\text{tot}}}(\%)$	$Y_{\text{COKE}_{\text{tot}}}(\%)$	$E_{\text{net}}(\text{kW})$
100	93.73	95.30	0.00	240.90
90	97.41	97.35	0.00	279.19
80	98.03	96.77	0.00	285.33
70	98.57	92.83	0.00	272.33
60	98.98	84.06	0.00	271.26
50	99.80	78.82	0.00	350.86

Fig. 11 – Molar fractions of the final stream on a wet basis, when running the four-variable MCDM method. $C_{\max}^* = 0.9999$, $T_{\text{optimal}} = 790$ °C, $\text{CH}_4/\text{CO}_2/\text{O}_2/\text{H}_2\text{O}_{\text{optimal}} = 1/1/0/3$

4. Discussion of results

The results compare reasonably well with the literature when the trade-off between temperature and steam- and/or air-to-methane ratio is considered (Table 6). The method recommended a low (<2.5) steam-to-methane ratio for all reforming processes. Although SRM is the most economical way to produce hydrogen, around 37 % of the exergy is not utilized and around 10 % is wasted in the exhaust stream [58]. Usually a high steam-to-methane ratio is advised during SRM [6], because it favours methane conversion, increases the production of H_2 via WGS, and inhibits the formation of carbon deposits on the catalyst [60]. However, a ratio below 2.5 would reduce the mass flow through the plant, decrease the size of the equipment and the operating costs [61], keep the formation of CO_2 in the WGS reaction low [62], and minimize the energy required to vaporize water [24, 61, 63, 64].

The optimal scenario for maximum syngas production with minimal energy expenditure and solid carbon deposition (biogas with 50-60 % CH_4 , and reforming operating conditions of $\text{CH}_4/\text{CO}_2/\text{O}_2/\text{H}_2\text{O} = 1/0.67-1/0.1-0/2.4-3$ and 735-790 °C (Table 4)) relates well to existing practices in both the reforming and AD industries. At the optimal operating conditions, the final concentration of CO in the output stream is slightly lower than 1 %, which is the average target for hydrogen-rich streams produced in industrial reforming processes [25]. Biogas composition of 50-60 % is typical in operational AD plants [16, 65]. The results recommend minimizing the net energy required in order to have a more favourable process. As a consequence of the low-temperature conditions recommended, catalysts with higher resistance to carbon deposition would be required during real operation [65, 66].

Table 6 – Comparison of the optimal values between literature and this article (in parentheses)

CH ₄ in the biogas (%)	$T(^{\circ}\text{C})_{\text{optimal}}$	$\text{O}_2/\text{CH}_4_{\text{optimal}}$	$\text{H}_2\text{O}/\text{CH}_4_{\text{optimal}}$	Ref
50	850 (790)	0 (0)	2 (3)	[43]
60	750 (735)	0 (0.1)	2.5 (2.4)	[29]
100	800 (735)	0 (0.05)	1.9 (1.45)	[25]

The developed method is based on thermodynamic data and represents the ideal scenario. A low O_2/CH_4 is always recommended; if oxygen is present above the stoichiometric value in the feed, CO_2 and H_2O formation via total oxidation is favoured over partial oxidation, causing loss of CO and H_2 . A methodology based on a kinetic model consider the actual catalyst selectivity towards partial or total oxidation, hence exploring a larger range of O_2/CH_4 ratio. However, kinetic models often apply to narrow ranges of operating conditions, and are catalyst or reaction environment specific. Therefore the optimal operating conditions based on thermodynamics in this model are adequately realistic and provide the basis for experimental catalysis research. The model could be improved by including the furnace used to maintain the reformer temperature, and considering heat integration and actual heat losses between blocks.

5. Conclusions

The aim of this paper was to develop a clear and comprehensive methodology to consider various compositions of biogas, combinations of reactions, and process conditions in order to make recommendations for optimizing the operating conditions of mixed reforming of methane/biogas. The outcome of this paper is quite powerful, because it considers (i) the reforming of methane/biogas with different compositions, (ii) the possible combinations of reactions obtained by adding air and/or steam to the feed, (iii) a wide range of operating conditions with reasonably small step sizes, and (iv) the simultaneous optimization of four criteria (methane conversion, hydrogen yield, carbon yield, energy requirement). The analysis showed that the optimal way to convert pure methane into hydrogen is at 735 °C, with O_2/CH_4 and $\text{H}_2\text{O}/\text{CH}_4$ equal to 0.05 and 1.45, respectively. For biogas, the ideal case is CH_4 of 50-60 %, with reforming reactor conditions at $T = 790\text{-}735$ °C, $\text{O}_2/\text{CH}_4 = 0\text{-}0.1$ and $\text{H}_2\text{O}/\text{CH}_4 = 3\text{-}2.4$. The method shows that biogas can theoretically be exploited to produce hydrogen as efficiently as methane/natural gas over an effective range of operating conditions. The research also developed a novel methodology where two MCDM techniques in series were used to optimize the operating conditions for a chemical reaction network. The method is based on thermodynamics, requires low computational workload, can maximize or minimize several criteria simultaneously, and is transferable to different scenarios for the optimization of

complicated networks. The results represent a starting point for experimental research on catalysts at the identified optimal operating conditions.

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Supporting information

Please refer to the supplementary data associated with this article.

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