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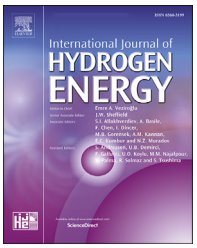

Using multi-criteria and thermodynamic analysis to optimize process parameters for mixed reforming of biogas

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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 thermo-catalytic 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% CH_4 in CO_2 is reacted in the reforming reactor at $CH_4/CO_2/O_2/H_2O$ = 1/1–0.67/0–0.1/3–2.4 and 790-735 °C, resulting in a product stream composed of 66–65% H_2, 0.8–1% CO and 33-28% CO_2 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.

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Introduction

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) (Eq. (1)) or partial oxidation (PO_X) of methane/natural gas (Eq. (2)), followed by the water-gas shift (WGS) reaction (Eq. (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% CH_4, 30–50% CO_2 and minor amount of H_2O, H_2S, NH_3, H_2, N_2 and O_2 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 CO_2 (Eq. (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 H_2/CO ratio (H_2/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 (Eq. (5)) and CO disproportionation (Eq. (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 (Eq. (7)) and H_2 (Eq. (8)) via oxidation.

Steam reforming of methane

$$CH_4 + H_2O \rightleftarrows CO + 3H_2 \quad \Delta H^0_{298} = 208.813 \text{ kJ mol}^{-1} \tag{1}$$

Partial oxidation of methane

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2 \quad \Delta H^0_{298} = -36 \text{ kJ mol}^{-1} \tag{2}$$

Water-gas shift

$$CO + H_2O \rightleftarrows CO_2 + H_2 \quad \Delta H^0_{298} = -41.166 \text{ kJ mol}^{-1} \tag{3}$$

Dry reforming of methane

$$CH_4 + CO_2 \rightleftarrows 2CO + 2H_2 \quad \Delta H^0_{298} = 246.979 \text{ kJ mol}^{-1} \tag{4}$$

Methane cracking

$$CH_4 \rightleftarrows C + 2H_2 \quad \Delta H^0_{298} = 74.52 \text{ kJ mol}^{-1} \tag{5}$$

CO disproportionation

$$2CO \rightleftarrows CO_2 + C \quad \Delta H^0_{298} = -172.459 \text{ kJ mol}^{-1} \tag{6}$$

Oxidation of CO

$$CO + 0.5O_2 \rightarrow CO_2 \quad \Delta H^0_{298} = -282.984 \text{ kJ mol}^{-1} \tag{7}$$

Oxidation of H_2

$$H_2 + 0.5O_2 \rightarrow H_2O \quad \Delta H^0_{298} = -241.818 \text{ kJ mol}^{-1} \tag{8}$$

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 (Eq. (1) - Eq. (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 CH_4. 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/CeO_2 and Ni/Al_2O_3 catalyst, a fixed CO_2/CH_4 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% CH_4, 17% C_2H_6, 4% C_3H_8), through a combination of experimental results obtained with a Pt/Al_2O_3 catalyst, mathematical and phenomenological modelling. The

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