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Kinetic, energetic and exergetic approach to the methane tri-reforming process

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ABSTRACT

Energetic and exergetic analyses were applied to the methane tri-reforming process in order to assess the suitability of this reaction for the production of syngas with a desirable H_2/CO molar ratio for the Fischer–Tropsch process and methanol production. The kinetic equations used in the simulated plug flow reactor were obtained experimentally in a previous study using typical feed compositions of a landfill gas produced in a landfill site. A sensitivity analysis was carried out in order to select the best feed composition for the tri-reforming process. Moreover, the thermodynamic losses were identified and it was found that the exergy destruction occurs mainly in the reactor due to the high irreversibility of the chemical reactions. Finally, possible improvements were proposed in an effort to increase the exergy efficiency.

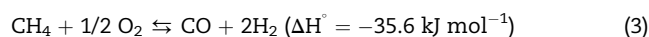
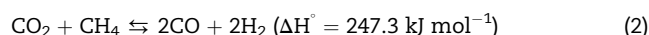
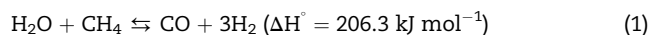
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Introduction

The shortage of fossil fuels and the increasing rates of contamination are major concerns for society today. As a consequence, a great deal of effort is made by the scientific community to identify new sources of energy, to optimize existing processes from an energetic point of view and to develop applications for energy streams that are currently not exploited. One such energy source is represented by landfill gas streams generated in landfills during the biodegradation of organic waste by microorganisms [1–3].

The tri-reforming process is one of the most interesting options for the exploitation of these landfill gas streams, which are usually composed of methane (50–25%), carbon dioxide (25–7%), water (20–3%) and oxygen (3–0.6%). The

reactants used in this process represent a synergetic combination of the steam reforming (Eq. (1)), the dry reforming (Eq. (2)) and the partial oxidation of methane (Eq. (3)). The water–gas shift reaction (Eq. (4)) also participates in the tri-reforming process.

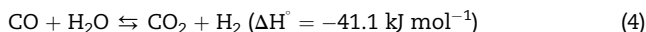


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The advantages of the tri-reforming process compared with those of the other well-known reforming processes are:

- Higher energy efficiency because it combines endothermic and exothermic reactions.
- The synthesis gas ratio (H_2/CO) can be controlled varying the feed composition.
- The presence of water and oxygen minimizes coke formation, thus increasing the catalyst stability.
- In the case of the landfill gas, the stream can be used without prior separation of any of its components.

The above process could be used to obtain synthesis gas with an H_2/CO molar ratio of 2, which is suitable for the production of methanol and the Fisher–Tropsch process [4].

In previous studies by our research group [5–7] the tri-reforming process was extensively investigated and it was concluded that a Ni–Mg/SiC catalyst was the most appropriate due to its excellent catalytic performance. A kinetic study was carried out [8] with 36 experiments using the typical feed compositions of landfill gas in order to obtain a kinetic model that was statistically meaningful. In the work described here, a simulation of the tri-reforming process using the kinetic expressions was carried out. The performance of the process is studied by an energetic and exergetic approach.

The performance of a system has been studied by an energetic analysis [9] based on the first law of thermodynamics. The main drawbacks of this kind of analysis are that it does not provide any information about the degradation (quality) of energy that occurs in the process and it cannot identify the real thermodynamic inefficiencies associated with irreversible processes in the energy conversion system [10]. Therefore, an exergetic analysis, based on the first and the second laws of thermodynamics, could provide very useful information when evaluating an industrial process for the design, optimization and performance evaluation of a system [11–13]. The aim of an exergy analysis is to identify where thermodynamic losses occur, to identify the equipment in which the exergy is destroyed and to pinpoint the area where a process engineer has to focus their efforts to improve the process, thus increasing the exergy efficiency and therefore reducing the operating cost of the industrial plant. Some exergetic analyses have been applied to different reforming systems [14–16], mainly in plants dedicated to the production of hydrogen. In the work described here the simulation and performance evaluation of the methane tri-reforming process using real kinetic expressions was developed. The viability of the process was analyzed in order to treat landfill gas streams to obtain syngas.

Energetic and exergetic parameters

One of the main parameters considered in the energetic analysis of a system is the thermal efficiency, which is defined as the ratio of the energy produced (output) to the energy supplied (input). In the case of the tri-reforming process this thermal efficiency is given by Eq. (5):

$$\eta_{\text{Thermal}} = \frac{(m_{\text{H}_2} \cdot \text{LHV}_{\text{H}_2} + m_{\text{CO}} \cdot \text{LHV}_{\text{CO}})}{(m_{\text{CH}_4} \cdot \text{LHV}_{\text{CH}_4} + W_{\text{compressors}} + W_{\text{pump}})} \quad (5)$$

Where m_i and LHV_i correspond to the mass flow and lower heating value of the component 'i', respectively, and W_i is the mechanical work of engine 'i'.

As discussed above, the energetic analysis based on the first law of thermodynamics is not sufficient to carry out a performance evaluation of a system. As a result, an exergetic analysis was introduced in order to complete the evaluation. The exergy of a system is defined as the maximum work that can be obtained from a system during a process that brings this system into thermodynamic equilibrium with its surroundings using a reference state characterized by a temperature T_0 and a pressure P_0 [17]. In this study, an exergetic analysis was carried out by considering three exergy transfers: with work (Eq. (6)), with heat interaction (Eq. (7)) and with the mass flow (Eq. (8)) [14,15]. The exergies associated with potential and kinetic energy were not considered.

$$\text{Ex}_W = W \quad (6)$$

$$\text{Ex}_Q = Q \left(1 - \left(\frac{T_0}{T} \right) \right) \quad (7)$$

$$\text{Ex}_M = \text{Ex}_{\text{phys}} + \text{Ex}_{\text{chem}} + \text{Ex}_{\text{mix}} \quad (8)$$

Where Q is the heat transferred, T is the temperature and T_0 is the reference temperature. The exergy associated with mass flow (Ex_M) is divided into physical (Ex_{phys}), chemical (Ex_{chem}) and mixing exergies (Ex_{mix}).

The physical exergy (Ex_{phys}) is the total amount of work that can be obtained using a reversible process when the system is brought from its initial state (temperature T and pressure P) to the state determined by the temperature T_0 and P_0 of the environment. This parameter was calculated as follows:

$$\text{Ex}_{\text{phys}} = \Delta_{\text{actual state-ref state}} \left\{ D \cdot \left(x_L \cdot \left(\sum_{i=1}^n x_i \cdot H_i^L - T_0 \cdot \sum_{i=1}^n x_i S_i^L \right) + x_v \cdot \left(\sum_{i=1}^n y_i H_i^V - T_0 \cdot \sum_{i=1}^n y_i S_i^V \right) \right) \right\} \quad (9)$$

Where n is the number of chemical species' in a material stream; D is the molar flow rate; x_L and x_v are the liquid mole fraction and vapor mole fraction in the material stream, respectively; x_i and y_i are the mole fraction of species i in the liquid phase and vapor phase, respectively; and H_i and S_i are the molar enthalpy and molar entropy of pure component i , respectively. The superscripts l and v refer to liquid and vapor phase, respectively.

The chemical exergy is defined as the maximum amount of work obtainable when the substance under consideration is brought from the environmental state, defined by the parameters T_0 and P_0 , to the reference state by processes that involve heat transfer and exchange of substances only with the environment. This is given by Eq. (10):

$$\text{Ex}_{\text{chem}} = D \cdot \left(x_{0,i} \cdot \sum_{i=1}^n x_{0,i} \cdot \epsilon_{\text{chem},i}^{0,i} + x_{0,v} \cdot \sum_{i=1}^n y_{0,i} \cdot \epsilon_{\text{chem},i}^{0,v} \right) \quad (10)$$

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