

**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<sub>2</sub>/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 biogas 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.

## **Keywords:**

Tri-reforming  
Hysys simulator  
Exergy analysis  
Syngas

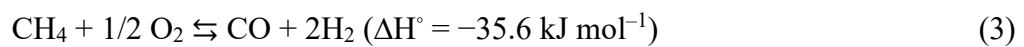
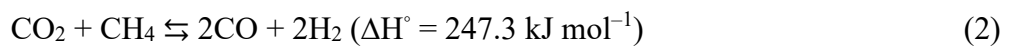
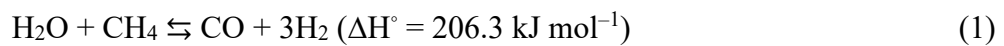
## **Highlights**

- Energetic and exergetic analyses were applied to the methane tri-reforming process.
- A sensitivity analysis was carried out in order to select the best feed composition.
- The reactor was the component where most of the exergy was destroyed.

## 1. 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 biogas 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 biogas 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.



The strengths 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 ( $\text{H}_2/\text{CO}$ ) 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 biogas, 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 biogas 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 was 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 biogas streams to obtain syngas.

## 2. 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):

$$\eta_{Therm} = \frac{(m_{H_2} \cdot LHV_{H_2} + m_{CO} \cdot LHV_{CO})}{(m_{CH_4} \cdot LHV_{CH_4} + W_{compressors} + W_{pump})} \quad (5)$$

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.

$$Ex_W = W \quad (6)$$

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

$$Ex_M = Ex_{phys} + Ex_{chem} + Ex_{mix} \quad (8)$$

Where Q is the heat transferred, T is the temperature and T<sub>0</sub> is the reference temperature. The exergy associated with mass flow (EX<sub>M</sub>) is divided into physical (EX<sub>phys</sub>), chemical (EX<sub>chem</sub>) and mixing exergies (EX<sub>mix</sub>).

The physical exergy (EX<sub>phys</sub>) is the total amount of work that can be obtained using a reversible processes when the system is brought from its initial state (temperature T and pressure P) to the state determined by the temperature T<sub>0</sub> and P<sub>0</sub> of the environment. This parameter was calculated as follows:

$$Ex_{phys} = \Delta_{actual\ state-ref\ state} \left\{ D \cdot \left( x_i \cdot \left( \sum_{i=1}^n x_i \cdot H_i^l - T_0 \cdot \sum_{i=1}^n x_i S_i^l \right) + x_v \cdot \left( \sum_{i=1}^n y_i H_i^v - T_0 \cdot \sum_{i=1}^n y_i S_i^v \right) \right) \right\} \quad (9)$$

Where n is the number of chemical species' in a material stream; D is the molar flow rate; x<sub>l</sub> and x<sub>v</sub> are the liquid mole fraction and vapor mole fraction in the material stream, respectively; x<sub>i</sub> and y<sub>i</sub> are the mole fraction of species i in the liquid phase and vapor phase, respectively; and H<sub>i</sub> and S<sub>i</sub> 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):

$$Ex_{chem} = D \cdot (x_{0,l} \cdot \sum_{i=1}^n x_{0,i} \cdot \varepsilon_{chem,i}^{0,l} + x_{0,v} \cdot \sum_{i=1}^n y_{0,i} \cdot \varepsilon_{chem,i}^{0,v}) \quad (10)$$

Where  $\varepsilon_{chem,i}^{0,l}$  and  $\varepsilon_{chem,i}^{0,v}$  denote the standard chemical exergy of any species  $i$  in the liquid and vapor phase, respectively. These parameters are explained in the paper by Hinderink [18] and were calculated using the reference state model defined by Szargut [17]. The reference state used in this work was  $T_0 = 25$  °C and  $P_0 = 1$  atm.

The mixing exergy, which always has a negative value, is given by Eq. (11).

$$Ex_{mix} = \Delta_{mix}H - T_0\Delta_{mix}S \quad at \quad (T, P) \quad (11)$$

With

$$\Delta_{mix}H = D \cdot (x_l \cdot (H^l - \sum_{i=1}^n x_i H_i^l) + x_v \cdot (H^v - \sum_{i=1}^n y_i H_i^v)) \quad (12)$$

$$\Delta_{mix}S = D \cdot (x_l \cdot (S^l - \sum_{i=1}^n x_i S_i^l) + x_v \cdot (S^v - \sum_{i=1}^n y_i S_i^v)) \quad (13)$$

$H^{l(v)}$  and  $S^{l(v)}$  denote the enthalpy and the entropy of the mixture in liquid phase (vapor).

The aim of the exergy analysis is to identify where the thermodynamic losses are produced by studying where the exergy is destroyed. The amount of exergy destroyed is calculated as:

$$Ex_{destroyed} = Ex_{in} - Ex_{out} \quad (14)$$

Where  $Ex_{in}$  and  $Ex_{out}$  are the total input and output exergy flows of the system, respectively.

The unused exergy is defined as the sum of the destroyed exergy and the exergy wasted in the exhaust stream. In this study, the exhaust stream is the sum of the stream of the reactants that did not react in the reactor and the energy stream of the reactor.

$$Ex_{unused} = Ex_{destroyed} + Ex_{exhaust} \quad (15)$$

The exergetic efficiency of the system is given by Eq. (16):

$$\eta_{exergy} = 1 - \left( \frac{Ex_{unused}}{Ex_{in}} \right) \quad (16)$$

### 3. Tri-reforming process simulation

The tri-reforming process, which is depicted in Figure 1, was simulated under stationary conditions using a flowsheet simulator (Aspen HYSYS V8.4 licensed by Aspen Technology, Inc.). The description of the different materials and process energy included in the flow scheme are summarized in Table 1.

The following conditions were selected in order to draw the flow sheet of the plant:

- The different reactants (methane, carbon dioxide, air and water) were added to the system at atmospheric pressure and temperature (1 atm and 25 °C).
- The pressure was increased up to 20.52 bar in the case of gases using compressors (K-01, K-02 and K-03) and up to 21.04 bar in the case of the liquid water using a pump (P-01).
- Liquid water was transformed into steam in the first heat exchanger (HE-01) with the heat transferred from the products stream (C-09).
- All of the feed streams were mixed (MIX-01).
- Prior to entering the reactor, the feed stream was heated in the second heat exchanger (HE-02) with the heat transferred from the out-reactor stream (C-08).
- The reactor was modeled using a Plug Flow Reactor with the kinetic expressions and parameters obtained experimentally in a previous study by our group [8]. The kinetic equations, kinetic expressions and the parameters obtained are listed in Table 2. The reactions that were considered to make a contribution to the



global kinetic of the tri-reforming process were the steam reforming, the dry reforming and the water gas-shift reaction. It was assumed that the partial oxidation was close to full conversion whenever oxygen was not practically detected in the effluent gas.

- The final step was the separation of the synthesis gas (CO and H<sub>2</sub>) from the rest of the compounds that did not react (CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O, N<sub>2</sub>, O<sub>2</sub> and traces of argon). The process units used to carry out this separation are not considered in this work.

The assumptions made are as follows:

- The thermodynamic data and phase behavior predictions were calculated using the Peng–Robinson equation of state, which is suitable for hydrocarbons and light gases and for high temperatures and pressures.
- The reference environmental temperature is 25 °C and the pressure is 1 atm, with these values applied to every inlet flow.
- The composition of air is summarized in Table 3.
- Heat transfer occurs ideally in reactors and heat exchangers.
- The minimum temperature difference considered in the heat exchangers is 15 °C.
- There is a pressure drop of 0.52 atm in every heat exchanger, while in the rest of the units the pressure drop was neglected.
- The possible deactivation of the catalyst is not taken into account.
- The reactor works at 20 atm because the synthesis gas produced will be used at this pressure.

#### **4. Sensitivity and energetic analysis**

The sensitivity analysis was carried out in order to determine the best feed composition to carry out the tri-reforming process. The methodology applied in the optimization of the feed stream was to vary the inlet molar flow of one of the reactants while the rest of the molar flows were kept constant. The influence of the feed composition with respect to temperature was analyzed in the range 600 °C to 1200 °C. The methane molar flow was the only molar flow that was kept constant throughout the sensitivity analysis and this was maintained at  $100 \text{ kmol}\cdot\text{h}^{-1}$ .

The parameters studied to select the most appropriate molar flows were:

- $\text{H}_2/\text{CO}$  molar ratio of the synthesis gas produced in the tri-reforming process. The target molar ratio was 2, which is the most suitable value for methanol synthesis and the Fischer–Tropsch process.
- Conversion of methane. The conditions that lead to conversions higher than 90% would be selected.
- Thermal efficiency. This parameter was studied in order to include the energetic analysis in the study. Thermal efficiencies as high as possible would be selected.

The first molar flow studied was that of carbon dioxide (Figure 2). For this study the methane, water and air molar flows were kept constant at  $100 \text{ kmol}\cdot\text{h}^{-1}$ ,  $50 \text{ kmol}\cdot\text{h}^{-1}$  and  $49.14 \text{ kmol}\cdot\text{h}^{-1}$  ( $10 \text{ kmol}\cdot\text{h}^{-1} \text{ O}_2$ ), respectively.

The way in which the thermal efficiency increases as the temperature increases is shown in Figure 2. A similar trend was found for the methane conversion. A significant influence of  $\text{CO}_2$  on the methane conversion was not observed as all of the molar flows showed similar conversions above 900 °C. Therefore, higher molar flows lead to higher thermal efficiencies and conversions. However, the limiting factor in the case of  $\text{CO}_2$  is the  $\text{H}_2/\text{CO}$  ratio, which is only around 2 at high temperatures, where higher conversions

and thermal efficiencies were found for a molar flow of  $25 \text{ kmol}\cdot\text{h}^{-1}$ . The most appropriate temperatures for this molar flow were in the range  $850\text{--}950 \text{ }^\circ\text{C}$ .

The water molar flow was studied next (Figure 3). In this case the feed composition was kept constant at  $100 \text{ kmol}\cdot\text{h}^{-1}$  for methane,  $25 \text{ kmol}\cdot\text{h}^{-1}$  for  $\text{CO}_2$  and  $49.14 \text{ kmol}\cdot\text{h}^{-1}$  for air ( $10 \text{ kmol}\cdot\text{h}^{-1}$  of  $\text{O}_2$ ). Increases in thermal efficiency and conversion were obtained when the temperature was increased and an appropriate  $\text{H}_2/\text{CO}$  molar ratio was also obtained for a molar flow of  $100 \text{ kmol}\cdot\text{h}^{-1}$ . In order to assess whether molar flows greater than  $100 \text{ kmol}\cdot\text{h}^{-1}$  would lead to higher conversions and thermal efficiencies, a molar flow of  $150 \text{ kmol}\cdot\text{h}^{-1}$  was included in the study. Although the thermal efficiency and conversion did increase, a value of 2 for the  $\text{H}_2/\text{CO}$  molar ratio was only obtained at very high temperatures ( $1050\text{--}1150 \text{ }^\circ\text{C}$ ), which are not commonly used in the reforming processes. For this reason, a molar flow of  $100 \text{ kmol}\cdot\text{h}^{-1}$  was selected. The temperatures that gave the best results (conversion,  $\text{H}_2/\text{CO}$  molar ratio and thermal efficiency) were in the range  $900\text{--}1000 \text{ }^\circ\text{C}$ .

Finally, the influence of the oxygen molar flow on the selected parameters was studied (Figure 4). Although the values that appear in Figure 4 are related to oxygen, it should be noted that the molar flow of oxygen depends on the air molar flow. For this reason the thermal efficiency decreases when the oxygen molar flow increases, because when the  $\text{O}_2$  molar flow increases the rest of the air gases are also increased. The nitrogen included in the air stream decreases the thermal efficiency because it does not participate in the reaction and it increases the energy required in the compressors and the energy to heat the streams.

In this case, in order to select the most appropriate oxygen molar flow, some previously mentioned restrictions were considered:  $\text{H}_2/\text{CO}$  molar ratio of 2, conversion

higher than 90% and thermal efficiency higher than 70%. The molar flow that fulfills these conditions was  $50 \text{ kmol}\cdot\text{h}^{-1}$  while the temperature was kept in the range 850–950 °C.

## 5. Exergetic analysis

Once the best feed composition for the tri-reforming process had been selected, an exergy analysis was carried out in order to identify the temperature that gave the best process performance. The different temperatures studied were 850, 900, 950 and 1000 °C. These temperatures were selected on the basis of the temperature ranges that were used in the sensitivity analysis and because they are temperatures that are frequently used in the reforming processes.

The amount of exergy destroyed in each component of the plant and the unused exergy for each component in the system are shown in Table 4 and Figure 5, respectively. It can be observed that the majority of the exergy destruction occurs in the reactor, which contributes three-fifths of the exergy destroyed in the entire process. This finding is due to a combination of the high irreversibilities of the chemical reactions and the difference in temperature between the reactants and the products in the reformer. The component in which the second highest exergy is destroyed is the heat exchanger (HE-01). This is due to the high temperature difference between the fluids in the exchanger. Finally, the third highest exergy loss occurs in the mixer, where the exergy destroyed is unavoidable and is already minimized in this model because it is assumed to occur adiabatically and at constant pressure. The amount of exergy destroyed in each component does not show a large dependence on the temperature when the temperature of the reactor is above 900 °C. However, the same behavior is not found for the unused exergy in the exhaust stream, which continuously decreases as the reactor temperature

increases. This exhaust stream is the sum of the exergy of stream C-11, which is composed of the gases that do not react, and the exergy of the energy stream of the reactor. It was observed that higher reactor temperatures yield a higher methane conversion (Table 5), which means that there is a smaller proportion of reagents that do not react at higher temperatures and, therefore, the exergy of stream C-11 decreases, thus decreasing the unused exergy of the exhaust stream in Figure 5.

The most important parameters studied are listed in Table 5. The methane conversion was similar at temperatures above 950 °C. H<sub>2</sub>/CO molar ratios with values of 2±0.1 and similar destroyed exergies were found at temperatures above 900 °C. Finally, the exergy efficiency clearly increases as the temperature increases, albeit more slowly at temperatures around 950 °C.

A design engineer could use these results to make design improvements that could decrease the amount of unused exergy and increase the exergy efficiency. The unused exergy (Eq. (15)) is composed of the exergy destroyed and the exergy exhaust. The former could be reduced by incorporating optimal designs. In the case of the reactor these optimal designs could reduce the thermodynamic irreversibility of the chemical reactions. Such designs may require a loss of exergy in the separation and recycling of the reagents but optimal conversions could be achieved; this means that minimal exergetic losses per unit of useful reaction products would be obtained [15, 19]. In the case of the heat exchangers, where the destroyed exergy is due to the high temperature difference between the fluids in the exchangers, one way to minimize the exergy destroyed is to reduce this difference between the streams. This could be achieved with larger heat transfer surfaces in the heat exchangers. In this respect, there is a tradeoff between the investment cost (system size) and the operating cost (exergetic efficiency). These design recommendations based on exergy analysis would not be identified by

first-law analysis alone. The exhaust exergy could also be reduced. The exergy of the energy stream of the reactor could be reduced using this energy stream in some process in the plant. The exergy of the C-11 stream is separated into two forms: thermo-mechanical (T-M) and chemical. The T-M exergy is due to fact that the temperature of the stream is higher than the environmental temperature. This T-M exergy could be transformed into work by adding a bottoming cycle to the system. The chemical exergy of the exhaust stream is the amount of work that could be extracted from the stream if it was brought into chemical equilibrium with the environment. If all the exhaust exergy were used, the exergy efficiency would be similar for reactor temperatures above 900 °C, as can be seen in Table 5. Last, but not least, the total unused exergy in the system could be reduced by using pure oxygen as the reactant or the inclusion of an air separator.

Based on the results described above, the temperature selected as the most appropriate for the tri-reforming process was 950 °C, which combines higher conversions (~98%) with the production of synthesis gas with a suitable H<sub>2</sub>/CO molar ratio for many applications and a good exergy efficiency value.

## 6. Conclusion

A thermodynamic analysis was conducted to investigate the characteristics of the tri-reforming process for methane. The most important conclusions obtained were:

- The optimal feed composition was identified: 100 kmol·h<sup>-1</sup> methane, 25 kmol·h<sup>-1</sup> CO<sub>2</sub>, 100 kmol·h<sup>-1</sup> H<sub>2</sub>O and 50 kmol·h<sup>-1</sup> O<sub>2</sub> (245.7 kmol·h<sup>-1</sup> of air). This feed composition was selected because it combined high thermal efficiency (>70%), methane conversion (>90%) and the production of synthesis gas with a desirable H<sub>2</sub>/CO molar ratio of 2.

- The reactor was the component where most of the exergy was destroyed. This is mostly due to the high irreversibility of the chemical reactions that occur.
- A reactor temperature of 950 °C combines higher conversions (~98%) with a desirable H<sub>2</sub>/CO molar ratio and a good exergy efficiency value.
- Based on the results, research and development efforts should be focused on reducing the exergy destruction within the reactor and heat exchangers as well as recovering part of the exhaust stream exergy.

### **Acknowledgements**

The authors would like to thank the Spanish government (grant FPU13/00727) for their financial support.

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## **Figure captions**

**Figure 1.** Detailed flowsheet for the methane tri-reforming process.

**Figure 2.** CO<sub>2</sub> sensitivity analysis: Effect of the CO<sub>2</sub> molar flow on the thermal efficiency, methane conversion and H<sub>2</sub>/CO ratio at different temperatures.

**Figure 3.** H<sub>2</sub>O sensitivity analysis: Effect of the H<sub>2</sub>O molar flow on the thermal efficiency, methane conversion and H<sub>2</sub>/CO ratio at different temperatures.

**Figure 4.** O<sub>2</sub> sensitivity analysis: Effect of the O<sub>2</sub> molar flow on the thermal efficiency, methane conversion and H<sub>2</sub>/CO ratio at different temperatures.

**Figure 5.** Unused exergy per mole of syngas obtained in the equipment and in the exhaust stream.