Assessment of CO_2 Conversion in a Biorefinery Concept: a Biomethane Plant Case Study

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One of the main challenges imposed by the climate crisis is to reduce the greenhouse gases emissions while keeping high levels of social and economic development. Therefore, the deployment of process alternatives that use residues as raw materials and integrate the conversion of by-products in added value products of interest is mandatory and integrated biorefineries play a major role in this context. In this work, thermodynamic analyses were performed to assess the conversion of a residual CO_2 stream captured from the flue gases of a biomethane-based thermal power plant into syngas or methane. Results showed that the syngas production from CO_2 is favored at high temperatures (>700 ˚C), low pressures (1 bar) and low H_2/CO_2 ratios (e.g. 1). Conversely, methane formation is favored at lower temperatures and higher H_2/CO_2 ratios. Simulations were also carried out considering the conversion of an off-gas stream from a biomethane plant, with different concentrations of CH_4. Considering the syngas formation, the presence of CH_4 in the feed stream enhances the CO_2 conversion and increases the production of CO and H_2 (desired products), while decreasing H_2O formation (unwanted side product), possibly due to the simultaneous occurrence of the methane bi-reforming, RWGS and methanation reactions. Therefore, from the thermodynamic point of view, the use of the off-gas from a biomethane plant for syngas production could be a potential alternative for the destination of this residual stream, converting it into interesting chemical platforms and intermediates for fuels and chemicals production.

1. Introduction

The climate crisis and its associated targets and restrictions urgently demand the development of technological alternatives for industrial production that allows the human development in a socially and environmentally responsible way. Among the greenhouse gases (GHGs), CO_2 is of major importance since large amounts of this gas are released into the atmosphere daily by anthropogenic activities (IPCC, 2021). As such, the use of CO_2 as a raw material for the production of highly demanded added value products represents a potential alternative for GHGs mitigation.

Integrated biorefineries play a major role in this context, promoting the production of a wide variety of products, utilizing the maximum as possible the by-products and consequently generating less residues compared with conventional processes, employing renewable sources of raw materials or even residues. Biogas production from organic matter is a sustainable approach for residue recycling, as it can be produced from multiple sources such as wastewater sludge (Cortez et al., 2022) and industrial (Donkor et al., 2021) and agricultural residues (Caiardi et al., 2021). As an example, the generated biogas (or the purified biomethane) can be destined to chemical conversion, heat or electricity generation (Caiardi et al., 2021). The biomethane could be used as a fuel in a thermal power plant (TPP), generating the required (or part of the) electricity demanded in a biorefinery, which could be fed with CO_2 captured from the TPP flue gases as the process raw material. This work aimed to perform a thermodynamic assessment of CO_2 conversion to CO (or CH_4) in this biorefinery context. Besides the captured CO_2 stream, the chemical conversion of an off-gas stream from biogas purification containing different amounts of CH_4 was also considered.

2. Materials and methods

The integrated biorefinery model is represented in Figure 1. It considers the utilization of biomethane in a TPP, in which electricity is generated and the flue gases are further purified to CO_2, which is processed to fuels and chemicals. The off-gas stream from biogas purification, consisting of CO_2 and CH_4, was also considered in the process simulations. The H_2, necessary for conversion and purification, is considered to be generated by water electrolysis with renewable electricity. Thus, organic residues could be transformed into fuels and chemicals with *in situ* renewable electricity generation and minimum input of raw materials and residue generation.
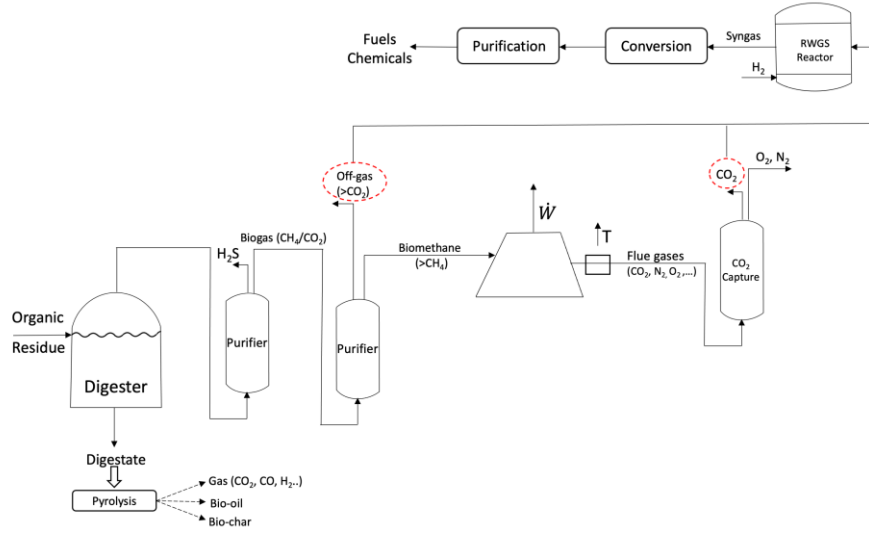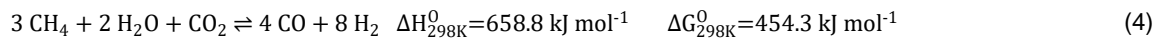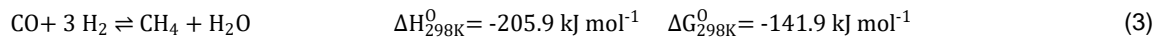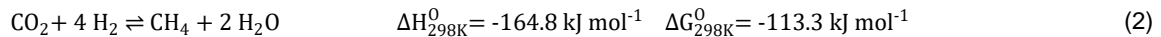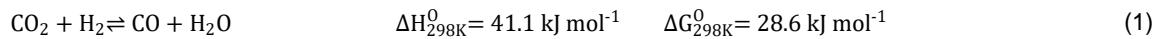

Figure 1: Integrated biorefinery process model

The process simulation was performed in the Aspen Plus® software, using the Peng-Robinson equation of state to calculate the system properties. The RGibbs reactor model, based on Gibbs free thermodynamic equilibrium energy minimization, was chosen to model and evaluate the thermodynamic equilibrium. No reaction was specified, and the following components were considered: CO, CO_2, H_2, H_2O, CH_4 and C (graphite). Among the reactions taking place, it is expected the occurrence of two competing side reactions, the RWGS and CO_2 methanation, represented by Eq(1) and Eq(2), respectively. As the RWGS reaction produces CO, the CO methanation (Eq(3)) can also take place. The CH_4 produced by the methanation reactions may also be converted to syngas in the presence of water by the methane bi-reforming reaction (Eq(4)). Solid carbon formation (reactions equations presented in the literature (Xing et al., 2020)) may also occur. The ΔH_{298K}^0 and ΔG_{298K}^0 values for each reaction were calculated with data taken from the Aspen Plus® databank.

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \qquad \Delta H_{298K}^0 = 41.1 \text{ kJ mol}^{-1} \quad \Delta G_{298K}^0 = 28.6 \text{ kJ mol}^{-1} \qquad (1)$$

$$CO_2 + 4 H_2 \rightleftharpoons CH_4 + 2 H_2O \qquad \Delta H_{298K}^0 = -164.8 \text{ kJ mol}^{-1} \quad \Delta G_{298K}^0 = -113.3 \text{ kJ mol}^{-1} \qquad (2)$$

$$CO + 3 H_2 \rightleftharpoons CH_4 + H_2O \qquad \Delta H_{298K}^0 = -205.9 \text{ kJ mol}^{-1} \quad \Delta G_{298K}^0 = -141.9 \text{ kJ mol}^{-1} \qquad (3)$$

$$3 CH_4 + 2 H_2O + CO_2 \rightleftharpoons 4 CO + 8 H_2 \quad \Delta H_{298K}^0 = 658.8 \text{ kJ mol}^{-1} \quad \Delta G_{298K}^0 = 454.3 \text{ kJ mol}^{-1} \qquad (4)$$

The influence of temperature (50 to 1100 °C), pressure (1 to 20 bar) and H_2/CO_2 molar feed ratio (1:1 to 1:4) on the CO_2 conversion (Eq(5)) and CO global selectivity (Eq(6)) was assessed. In these equations, $\dot{n}$ represents the molar flow rates and the suffixes in and out are related to inlet and outlet reactor streams. Furthermore, the effect of temperature and H_2/CO_2 ratio on the product composition (H_2/CO ratio) was also considered.

$$CO_{2\,Conversion}(\%) = \frac{\dot{n}_{CO_2in} - \dot{n}_{CO_2out}}{\dot{n}_{CO_2in}} \times 100 \qquad (5)$$

$$CO_{Selectivity}(\%) = \frac{\dot{n}_{COout}}{(\dot{n}_{CH_{4,out}} - \dot{n}_{CH_{4,in}})} \times 100 \qquad (6)$$

Different compositions were analyzed for the off-gas stream, with the molar CH_4 content varying between 1 % and 20 %. When considering this stream, the methane conversion (Eq(7)) was also analyzed. For the off-gas stream the feed ratio of H_2/CO_2 was fixed at 1.

$$CH_{4Conversion}(\%)=\frac{\dot{n}_{CH_4 in}-\dot{n}_{CH_4 out}}{\dot{n}_{CH_4 in}}\times 100 \tag{7}$$

3. Results and discussion

3.1 Pure CO_2 stream

3.1.1 Pressure effect

Firstly, the pressure effect on the analyzed responses was evaluated for a purified residual gas stream, comprising only CO_2. Examples of results obtained regarding pressure, temperature and CO_2 conversion or CO selectivity are presented in Figure 2a, 2b and 2c.
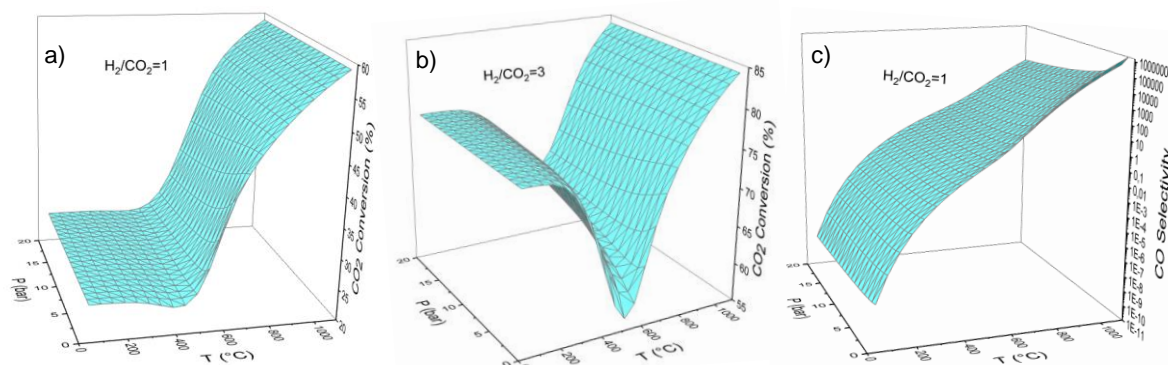

Figure 2: CO_2 conversion and CO selectivity as a function of temperature and pressure. a) CO_2 conversion with $H_2/CO_2=1$; b) CO_2 conversion with $H_2/CO_2=3$; c) CO selectivity with $H_2/CO_2=1$

In general, it was observed that pressure increases lead to a reduction in CO selectivity, which can be related to the displacement in the methanation reactions equilibria towards the products according to the Le Chatelier's principle (higher pressures favor methane formation). Consequently, CO selectivity is reduced. It should be noted that the RWGS reaction equilibrium is not affected by pressure variations since Eq(1) is equimolar.

In most of the studied reaction conditions, the conversion is not significantly affected by the pressure, and in the cases that it is affected, it occurs in the intermediate temperatures analyzed (450-750 ˚C). Since the main focus of this work is to study the syngas generation from CO_2 (that is favored, by its turn, at higher temperatures) and since the CO selectivity is benefited by lower pressures, the pressure effect in the studied variables will no longer be considered in the analysis, and from this point the results will be reported at the pressure of 1 bar.

3.1.2 Temperature and H_2/CO_2 ratio effects

Figure 3 depicts the results of CO_2 conversion, CO selectivity and product H_2/CO ratio as a function of temperature and H_2/CO_2 ratio, at 1 bar. A temperature increase causes a reduction in conversion at lower temperatures (until approx. 500˚C) and a conversion increase at higher temperatures. The CO selectivity is benefited with a temperature increase. The methanation reactions are exothermic while the RWGS is endothermic. Thus, the formers are favored at lower temperatures while the latter benefits from higher temperatures, which may explain the observed results.

At conditions of $H_2/CO_2=1$ (Figure 2a), low conversions of CO_2 are obtained at low temperatures. However, when H_2/CO_2 ratio is increased (Figure 2b), the simulations indicate higher conversion of CO_2 with a minimum valley around 500 ˚C. When the H_2/CO_2 ratio is increased the CO_2 conversion increases (Figure 3a) and the methane formation is favored over the CO formation (the CO selectivity is reduced (Figure 3b)). This can be partially explained by the fact that the CO_2 and CO methanation reactions require 4 and 3 mols of H_2, respectively, for each mol of CO_2, and thus methanation reactions are favored with higher H_2 concentrations.

It should be noted that despite the fact that higher H_2 initial concentrations cause an increase in CO_2 conversion, at all the evaluated temperatures less CO and more CH_4 are formed when increasing the H_2/CO_2 ratio. Accordingly, if the aim of a process is to produce syngas, lower H_2/CO_2 feed ratios (e.g. 1) are recommended. If one aims to feed the RWGS product in a FT reactor (after water condensation), it is important to consider the

amount of CH_4 generated by the methanation reactions, using reactional conditions that generate the desired syngas composition and avoiding an additional step of syngas purification. It is noteworthy that even with higher H_2/CO_2 ratios (e.g. 3 or 4), at elevated temperatures (>~800-850 ˚C) and low pressures (e.g. 1 bar) the amount of generated CH_4 is considerably lower than the amount of CO, and high CO selectivity is obtained.
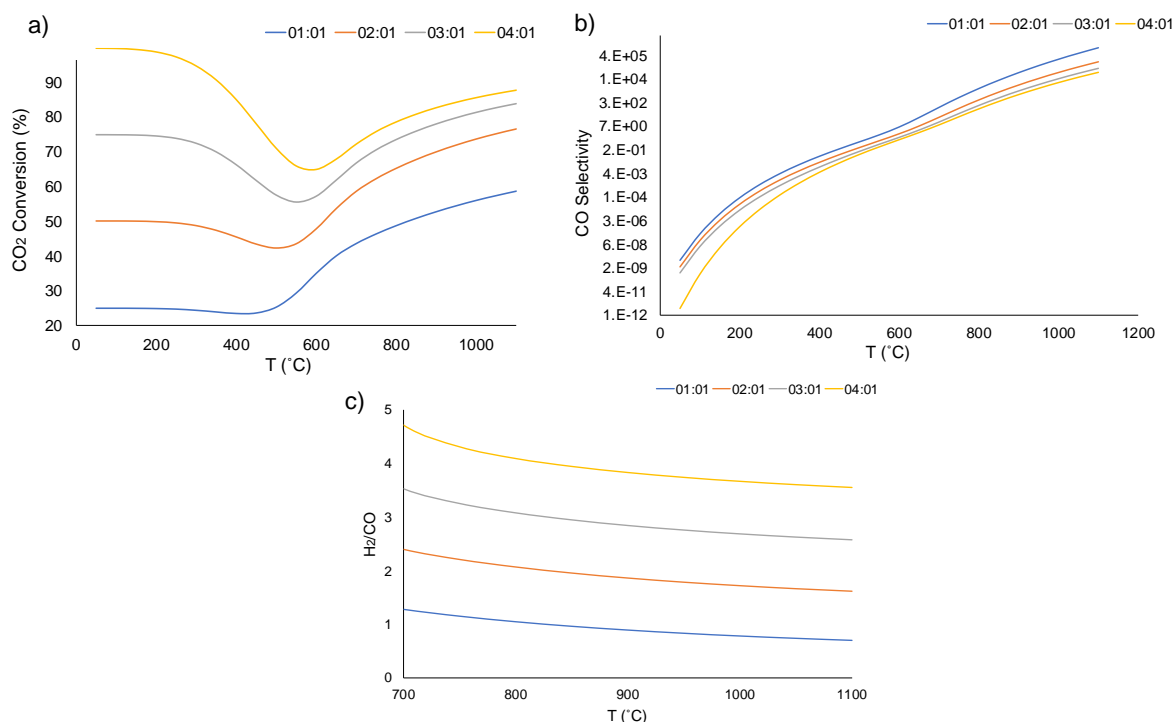

Figure 3: CO_2 conversion, CO selectivity and H_2/CO ratio as a function of temperature for different H_2/CO_2 feed ratios (P=1 bar). a) CO_2 conversion; b) CO selectivity; c) H_2/CO ratio

To analyze the syngas composition (H_2/CO product ratio), only temperatures above 600 ˚C were considered, since at lower temperatures small amounts of CO are formed. The higher the H_2 concentration in the feed stream the higher the H_2/CO product ratio (Figure 3c). Thus, if the syngas stream is destined to a FT reactor, for example, it is possible to adjust the H_2/CO_2 feed ratio to obtain a syngas with the appropriate composition. A H_2/CO ratio of 2 is usually recommended in the literature for cobalt catalyzed FT synthesis (Ghogia et al., 2021; Hannula et al., 2020). In summary, from a thermodynamic equilibrium perspective, if the process focus is syngas generation for a FT process, high temperatures (>700 ˚C) and low pressures (1 bar) should be used, and the appropriate H_2/CO_2 ratio must be chosen so high CO_2 conversions, small amounts of CH_4 and the desired H_2/CO product ratio are obtained. It is important to mention that the considerations about the process operating conditions apply only to the reactor, and when a whole process is considered other reactor operating conditions may imply in a better overall process performance. In this case, optimization should be carried out considering the integrated process (Adelung et al., 2021). The amount of solid carbon ($C_{graphite}$) formed was negligible and thus no coke formation was detected at the thermodynamic equilibrium in the evaluated conditions.

3.2 Off-gas

The qualitative behavior of the CO_2 conversion and CO selectivity as a function of pressure and temperature was the same as the observed in the previous analysis. However, at temperatures above approximately 500 ˚C negative values for the CO selectivity are observed, once the amount of CH_4 in the product stream is lower than in the feed stream (the denominator of Eq(5) becomes negative), that is, there is a global consumption of CH_4. As the amount of CH_4 in the feed stream is increased, higher CO selectivity is obtained, and again the higher the temperature the higher CO selectivity. When the CH_4 concentration is increased in the off-gas, higher CO_2 conversions at high temperatures (T>~500 ˚C) are obtained (Figure 4a), higher amounts of CH_4 are present in the product stream (Figure 4c), and more CO is present in the resulting product (Figure 4d). The product H_2/CO ratio (Figure 4b) is also increased with the amount of CH_4 in the feed stream. These results can be partially related with the fact that when increasing the CH_4 content in the system, the methanation reactions equilibria are displaced towards the reactants, implying that more reactants are available for the RWGS reaction.

Furthermore, the higher presence of CH_4 in the system (once it is present also in the feed stream) may imply in a greater occurrence of the methane bi-reforming reaction (Eq(6)), favoring even more the CO formation.
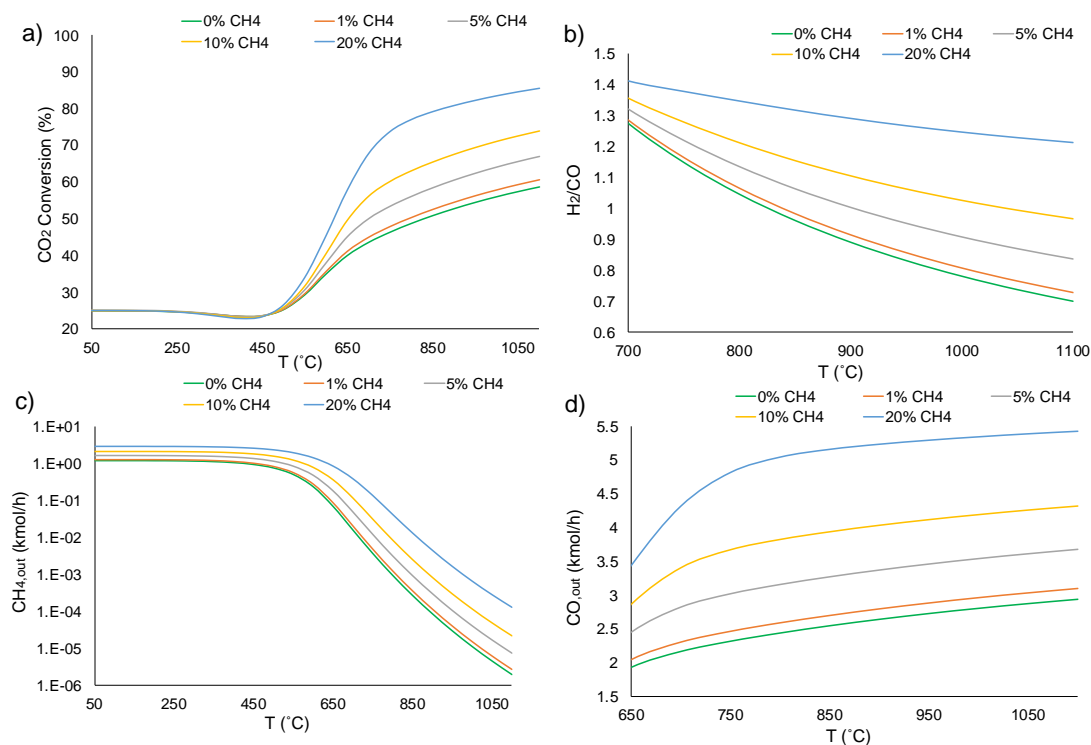

Figure 4: Results for the off-gas stream
($H_2/CO_2=1$). a) CO_2 conversion; b) H_2/CO ratio; c) CH_4 flow in the product; d) CO flow in the product
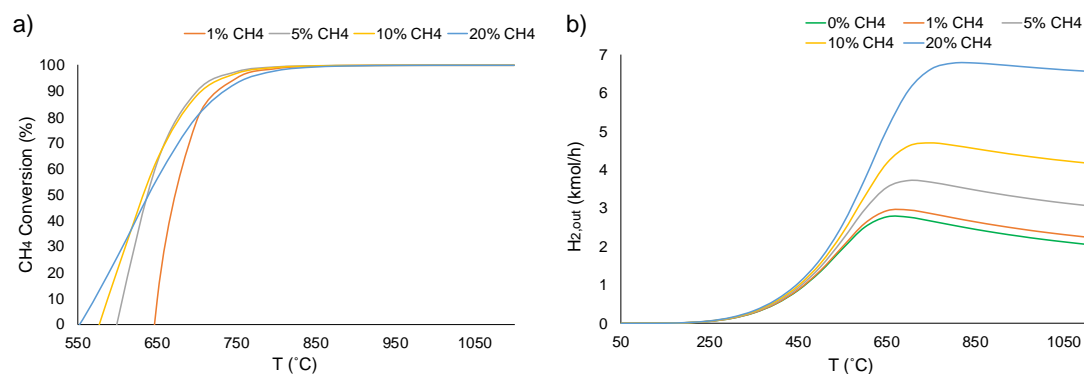

Figure 5: CH_4 conversion and H_2 flow in the product stream ($H_2/CO_2=1$). a) CH_4 conversion; b) H_2 product flow

Negative methane conversion (Figure 5a) are obtained until approx. 550 ˚C, indicating a global production of this species ($\dot{n}_{CH_4 out} > \dot{n}_{CH_4 in}$ in Eq(7)). From 800-850 ˚C, CH_4 conversions close to 100 % are obtained, reinforcing that methane bi-reforming reaction may simultaneously occur with the RWGS reaction, once methane reforming reactions are endothermic and temperatures above 800-900 ˚C are recommended (Kumar et al., 2015). The presence of CH_4 in the reactants contributes with higher amounts of H_2 in the product (Figure 5b), and the higher the CH_4 concentration the higher the H_2 amount in the product, explaining the enhancement of the H_2/CO product ratio. The results of the product water flow obtained in the simulations supported again the simultaneous occurrence of the RWGS and methane bi-reforming reactions when the CO_2 stream contains CH_4. The higher the amount of CH_4 in the feed stream, the lower the product H_2O content. As an example, when increasing the CH_4 content in the feed stream from 0 to 10 % at 900 ˚C (1 bar, $H_2/CO_2=1$), the CO_2 conversion is increased from 52.9% to 67.5%, the CO flow is increased from 2.6 to 4.0 kmol/h, the CH_4 flow is increased from $8.9.10^{-5}$ to $8.3.10^{-4}$ kmol/h, the H_2 flow increases from 2.4 to 4.5 kmol/h and the water flow decreases from 2.6 to 2.0 kmol/h. Considering the thermodynamic analysis results, using an off-gas stream from a biomethane

plant (or a CO_2 stream doped with CH_4) could be a potential alternative for syngas production, once the possible simultaneous occurrence of the RWGS and the methane bi-reforming reactions allows higher CO_2 conversions and the production of higher amounts of CO and H_2, while consuming H_2O, an unwanted RWGS by product, reducing the need of water condensation before syngas conversion.

4. Conclusions

The CO_2 conversion presents technical thermodynamic feasibility, and its application in an integrated biorefinery plant could be an interesting approach for the production of highly demanded products with potential GHGs mitigation. The CO formation is favored at high temperatures (>700 ˚C) and low pressures (1 bar). The ideal H_2/CO_2 feed ratio must be selected so high CO_2 conversions can be obtained with adequate product CH_4 content as well as the desired H_2/CO product ratio. Alternatively, if a certain process is destined for methane production from CO_2, the reaction must be carried out at lower temperatures and higher H_2/CO_2 ratios (e.g. 3) allowing higher CO_2 conversions. A complete economic feasibility analysis integrated with optimization techniques must be performed when selecting the operational parameters, considering the whole process. In this way it is possible to find the best operating conditions that matches both overall performance and economic criteria. Experimental testing and catalyst selection are also necessary to certify whether the thermodynamic equilibrium is achievable at feasible time intervals, and if other molecules than the considered ones are present in the product. The utilization of a biogas upgrading off-gas stream (or a CO_2 stream doped with CH_4) showed itself as a potentially interesting alternative for syngas production from a thermodynamic equilibrium perspective, since the presence of CH_4 in the reactants allows higher CO_2 conversions, higher CO and H_2 production as well as smaller H_2O production when compared to a pure CO_2 stream. For example, when CH_4 content in the feed stream is increased from 0 to 10 % at 900 ˚C (1 bar, H_2/CO_2=1), the CO_2 conversion and CO flow are increased from 52.9% to 67.5% and from 2.6 to 4.0 kmol/h, respectively. The operating conditions must be carefully chosen to comply with syngas composition limitations, considering, for example, the concentration of CH_4 in the final stream. In this way, this residual off-gas stream could be applied to generate added value products. In a biorefinery scenario, this can represent smaller residue output and higher amounts of the desired products.

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