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Direct CO₂ hydrogenation to methane or methanol from post-combustion exhaust streams - a thermodynamic study

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Abstract

The conversion/utilization of waste carbon dioxide is seen as a complementary option to the well-known capture, sequestration and storage strategies (CSS) to substantially reduce atmospheric CO₂ (environmental concern). This approach is attractive regarding CCS strategies because CO₂ can be transformed into a valuable chemical (economic benefit). Among the options available, methane and methanol are important chemicals that could be obtained from CO₂ hydrogenation and used for energy production/storage or as intermediaries to other chemicals.

A thermodynamic analysis regarding the hydrogenation of CO₂ into CH₄ or CH₃OH was carried out. The analysis was performed to check the limitations and optimal conditions when converting CO₂ from flue gas exhaust streams without previous removal of unnecessary species present in significant amounts (e.g. N₂, H₂O and O₂). The present analysis supports that, from the thermodynamic point of view, the conversion of CO₂ into

CH₄ is favoured in comparison to the CH₃OH valorisation strategy, for the considered pressure and temperature ranges.

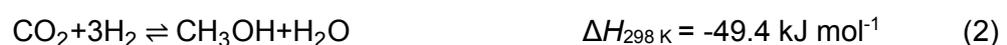
Keywords:

Carbon dioxide, methane, methanol, methanation, thermodynamic analysis.

1 Introduction

Carbon dioxide is the end-product of the largest-volume and most globally applied chemical reaction, the combustion of hydrocarbons and biomass, and it is well known the growing concern about reducing CO₂ emissions due to its enormous contribution to the greenhouse effect [1]. The Kyoto Protocol has created the market for carbon credits, a crucial mechanism for valuating CO₂ emissions and thus incorporating the pollution effect in the cost structure of the corporation's economy [2]. However, top-polluting countries such as Canada and USA are out of the agreement; moreover, according to the International Energy Agency, the top 10 polluting countries represent around 2/3 of world CO₂ emissions [3]. This means that any solution to solve the carbon dioxide problem will always depend on the compromise of these countries. So, economic benefits should be considered together with environmental concerns. In this regard, in recent years there has been a focus on developing different possibilities for CO₂ recycling as complement of the well-known capture, sequestration and storage approaches, particularly, its conversion into added value products [4-6]. This new paradigm considers CO₂ as chemical feedstock (value) and not only as a waste that needs to be treated (cost) [7].

Recent works provide together a comprehensive state-of-the-art of the options available for CO₂ valorisation and utilization, including the necessary timeframe for development, the time of sequestration, the economic perspectives, etc. [4-7]. Among the options presented in those works are CO₂ hydrogenation into methane (Eq.1) or methanol (Eq.2), the first being also known as Sabatier reaction or CO₂ methanation.



These two options, however, require expensive H₂ which, in turn, is preferentially produced worldwide using non-renewable feedstock's, being the steam methane reforming the most

developed and commercialized technology [8]. In this regard, these routes should be viable in view of CO₂ emissions abatement only when H₂ is produced from renewable resources, such as water electrolysis. Moreover, the energy required for the electrolysis should be also renewable for the global process to truly allow reducing CO₂ emissions [5, 9]. So, in this case, important chemicals such as methane or methanol could be produced using renewable resources (for H₂ production) and waste CO₂.

The conversion of CO₂ into methanol (reaction 2) has, compared to the methanation process, the advantage of consuming less hydrogen (see also the stoichiometry of reaction 1). Moreover, methanol has a higher energy density, is easier to store and can be used, for example, in the synthesis of important chemicals such as formaldehyde, methyl tertiary-butyl ether (MTBE), among others [10]. These advantages are pointed by various personalities as the driving force for the conversion/recycling of CO₂ into methanol, thus alleviating the dependence on fossil fuels while simultaneously reducing the emission of greenhouse gases. Among such personalities is the winner of the Nobel Prize in Chemistry in 1994, Prof. Olah, who clearly supports a strategy of "Methanol Economy" [11]. On the other hand, the "Power-to-Gas" concept can be a very interesting way to chemically store the off-peak electricity generated in wind power stations in the form of methane, which can be further integrated with the already existing natural gas infrastructures [12-14], as long as the exit process stream properties complies with the specifications required for natural gas transport in pipelines.

The necessary CO₂ is available from a large variety of emission sources. However, the International Energy Agency reported that the majority of the world CO₂ emissions arise from post-combustion sources related to electricity and heat production (41 % in 2010), particularly, from coal-fired power plants and the combustion of oil or gas, respectively 43 %, 36 % and 20 % of the electricity related CO₂ emissions. Previous works addressed, from the thermodynamic standpoint, the CO₂ valorisation into CH₄ [15] or CH₃OH [16]; in particular, Gao et al. [15] studied the effect of species present in syngas produced by coal or biomass gasification, where CO is the major species present (rather than CO₂). In this work, however, CO₂ valorisation was assessed considering its direct conversion from a real coal-fired power plant exhaust stream. Moreover, the effect of pressure, temperature, H₂/CO₂ ratio and the presence of major co-existing species present in flue gas streams (N₂, O₂ and H₂O) was systematically assessed regarding CO₂ conversion, product yield and selectivity.

2 Methodology

Thermodynamic analysis was performed using the Gibbs reactor model (RGibbs) available in the Aspen Plus software from AspenTech. RGibbs models simultaneous phase and chemical equilibria minimizing the Gibbs free energy and does not require the specification of the reactions involved and their stoichiometry [17, 18].

The total Gibbs free energy of a system is given by the sum of the chemical potential of all the N species [15, 19, 20]:

$$G_T = \sum_{i=1}^N n_i \mu_i \quad (3)$$

where n_i is the number of moles of species i , which chemical potential, μ_i , is given by:

$$\mu_i = \Delta G_{f_i}^0 + RT \ln \left(\frac{f_i}{f_i^0} \right) \quad (4)$$

where $\Delta G_{f_i}^0$ is the standard Gibbs function of species i formation, R is the ideal gas constant, T is the absolute temperature and f_i and f_i^0 stand for the fugacity and standard fugacity, respectively. For the reaction equilibrium in the gas phase:

$$f_i = y_i \phi_i P \quad (5)$$

$$f_i^0 = P^0 \quad (6)$$

where y_i is the mole fraction of species i , ϕ_i is the fugacity coefficient, P is the pressure of the system and P^0 is the standard pressure. So, combining equations 3-6 and applying Lagrange multipliers, used to incorporate the constraints related to conservation of the total amount of individual chemical elements into the body of the problem, the constrained function to be minimized, f_{obj} , is [18]:

$$\begin{aligned}
f_{\text{obj}} &= G_T + \sum_{j=1}^m \lambda_j \left(b_j - \sum_{i=1}^N n_i a_{ji} \right) \\
&= \sum_{i=1}^N \left[n_i \left(\Delta G_{fi}^0 + RT \ln \left(\frac{y_i \phi_i P}{P^0} \right) \right) \right] + \sum_{j=1}^m \lambda_j \left(b_j - \sum_{i=1}^N n_i a_{ji} \right)
\end{aligned} \tag{7}$$

where λ_j is the Lagrange multiplier, b_j the total amount of element j in the mixture, a_{ji} the number of atoms of element j in species i . Whenever the presence of solid carbon was considered in simulations, equation 7 should be changed to the following one [20]:

$$f_{\text{obj}} = \sum_{i=1}^N \left[n_i \left(\Delta G_{fi}^0 + RT \ln \left(\frac{y_i \phi_i P}{P^0} \right) \right) \right] + \sum_{j=1}^m \lambda_j \left(b_j - \sum_{i=1}^N n_i a_{ji} \right) + n_C \Delta G_{fC(s)}^0 \tag{8}$$

Fugacity was estimated using the Soave-Redlich-Kwong (SRK) equation of state contained in the Aspen Plus database, as suggested elsewhere for similar conditions [15].

The starting gas composition (mixture 1 in Table 1) was obtained from a typical coal-fired power station flue gas stream. The inlet gas compositions used for calculations (mixtures 2-10, Table 1) were established to independently analyse, in realistic scenarios, the effects of the H₂/CO₂ and H₂O/CO₂ molar ratios, as well as the influence of the presence of H₂O and/or O₂, which is discussed in section 3. One should take into account that H₂ is not originally present in flue gas streams (mixture 1 in Table 1) and should be added. So, the resulting feed stream (mixtures 2-10) has a composition different from the considered flue gas one.

Table 1. Inlet compositions (mol. %) of the Gibbs reactor used in simulations.

Mixture	CO ₂	H ₂ O	N ₂	O ₂	H ₂	H ₂ /CO ₂	N ₂ /CO ₂	H ₂ O/CO ₂	O ₂ /CO ₂
1 ^a)	13.0	20.5	63.0	3.5	0.0	0	4.8	1.6	0.3
2	10.2	0.0	49.2	0.0	40.6	4	4.8	0.0	0.0
3	11.3	0.0	54.8	0.0	33.9	3	4.8	0.0	0.0
4	12.8	0.0	61.8	0.0	25.5	2	4.8	0.0	0.0
5	8.8	13.8	42.4	0.0	35.0	4	4.8	1.6	0.0
6	9.9	0.0	47.9	2.7	39.5	4	4.8	0.0	0.3

7	8.6	13.5	41.4	2.3	34.2	4	4.8	1.6	0.3
8	9.6	15.1	46.4	0.0	28.9	3	4.8	1.6	0.3
9 ^{b)}	8.8	4.8	51.0	0.0	35.4	4	5.8	0.5	0.0
10 ^{b)}	9.7	5.2	56.0	0.0	29.1	3	5.8	0.5	0.0

a) Flue gas composition taken from [21].

b) Stream composition based on flue gas composition from [22].

Table 2 shows the main reactions considered for the analysis of our results (reactions 1-7) as well as other possible reactions that may occur in small extent.

Table 2. Reactions considered in the present thermodynamic study.

	Reaction formula	$\Delta H_{298\text{ K}}$ (kJ mol ⁻¹)	Reaction description
Main reactions			
1	$\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$	-165.0	CO ₂ hydrogenation to CH ₄
2	$\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-49.4	CO ₂ hydrogenation to CH ₃ OH
3	$\text{CO}_2 + 2\text{H}_2 \rightleftharpoons \text{C} + 2\text{H}_2\text{O}$	-90.1	CO ₂ reduction
4	$\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	41.2	Reverse water-gas shift
5	$\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O}$	-803.0	CH ₄ oxidation
6	$\text{CH}_4 + 1/2 \text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2$	-36.0	CH ₄ partial oxidation
7	$\text{H}_2 + 1/2 \text{O}_2 \rightleftharpoons \text{H}_2\text{O}$	-241.8	H ₂ oxidation
Other possible reactions			
8	$\text{C} + 1/2 \text{O}_2 \rightleftharpoons \text{CO}$	-110.5	Coke partial oxidation
9	$\text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2$	-393.5	Coke complete oxidation
10	$\text{CO} + 1/2 \text{O}_2 \rightleftharpoons \text{CO}_2$	-283.0	CO oxidation
11	$\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$	247.4	Reverse dry reforming of CH ₄
12	$\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$	74.9	CH ₄ cracking
13	$\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$	-206.2	CO hydrogenation to CH ₄

14	$\text{CO} + \text{H}_2 \rightleftharpoons \text{C} + \text{H}_2\text{O}$	-131.3	CO reduction
15	$2\text{CO} \rightleftharpoons \text{CO}_2 + \text{C}$	-172.5	Boudouard reaction

3 Results

3.1 Strategies for CO₂ valorisation: CH₄ or CH₃OH?

As stated before, thermodynamic analysis was performed using the continuous Gibbs reactor model. Carbon dioxide equilibrium conversion (equation 8) was determined for hydrogenation into methane or methanol as a function of pressure and temperature (Fig. 1),

$$X_{\text{CO}_2} (\%) = \frac{F_{\text{CO}_2}^{\text{in}} - F_{\text{CO}_2}^{\text{out}}}{F_{\text{CO}_2}^{\text{in}}} \times 100 \quad (9)$$

In this equation, F stands for the molar flow rate at the inlet (in) or outlet (out) of the Gibbs reactor. In this section only the main reactions (reactions 1 and 2, Table 2) were considered, which means that the occurrence of secondary reactions was, at this stage, discarded. Broad ranges of pressure and temperature were set for the calculations, including those found in industrial catalytic reactors operating these reactions.

As shown in Fig. 1, for either route of CO₂ valorisation its conversion decreases with reaction temperature, because both processes are exothermic. In addition, total pressure has a positive effect, because in either case there is a decrease in the total number of moles (from reactants to products – cf. equations 1 and 2). However, data presented in Fig. 1 clearly evidences that CO₂ conversion into CH₃OH (Fig. 1b) requires high pressures, particularly in the temperature range where active catalysts operate in industry (see dashed areas in Fig. 1) so that significant conversions can be achieved. Thus, since post-combustion flue gases are typically at the atmospheric pressure, the CH₃OH route requires compression of the feed stream, which increases operation costs, when compared to the methane route. For instance, at 250 °C the conversion of CO₂ in CH₄ production is almost complete at the atmospheric pressure while for the CH₃OH route it is practically null. Based on these evidences, in the following sections it was chosen to analyse into more detail only the valorisation strategy of CO₂ hydrogenation into CH₄.

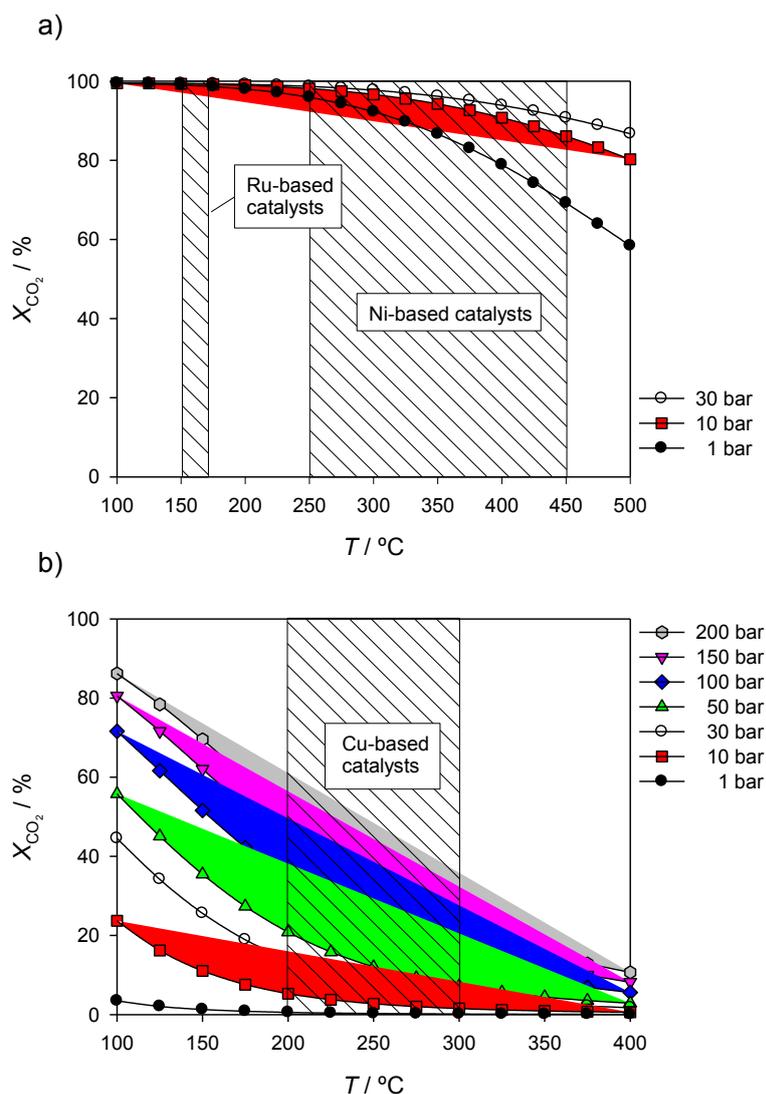


Fig.1 Carbon dioxide conversion obtained for hydrogenation reactions into: a) CH₄ and b) CH₃OH. Dashed areas show typical operation temperature ranges of industrial catalysts.

3.2 CO₂ methanation: effect of pressure, temperature and H₂/CO₂ ratio

The effects of pressure, temperature and H₂/CO₂ molar ratio on CO₂ conversion (equation 9), product selectivity (equation 10) and yield (equation 11) were investigated on CO₂ methanation. In this section, the methanation main reaction 1 and secondary reactions 3 and 4 (see Table 2) were considered. Reactions 5-7 (Table 2) were not accounted because O₂ was considered not to be present in the feed stream (this will be addressed in section 3.3); other reactions present in Table 2 occur in small/very small extent.

Selectivity to carbon-containing species (CH₄, CO and C):

$$S_i (\%) = \frac{F_i^{out}}{F_{CO_2}^{in} - F_{CO_2}^{out}} \times 100 \quad (10)$$

Yield of carbon-containing species (CH₄, CO and C):

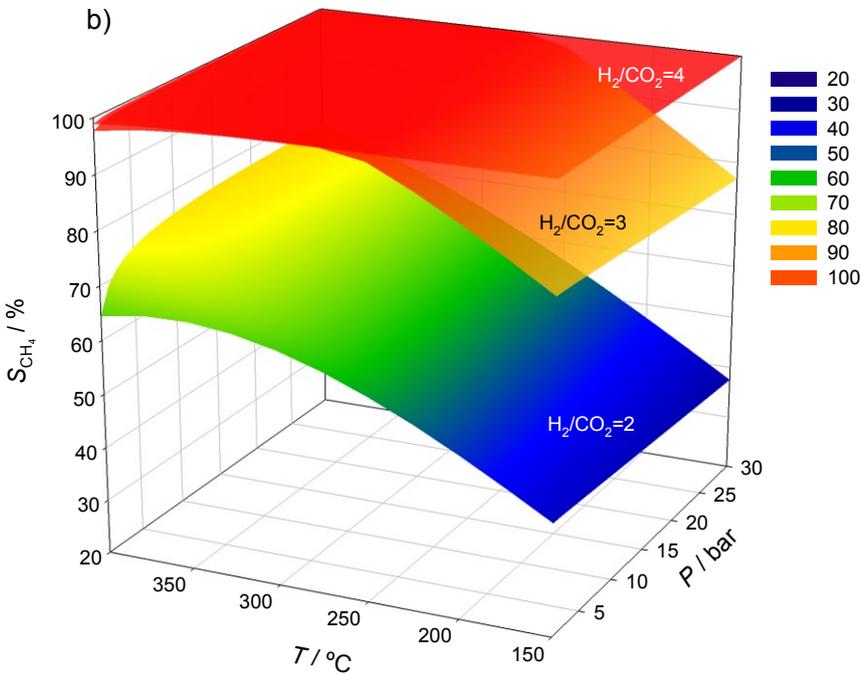
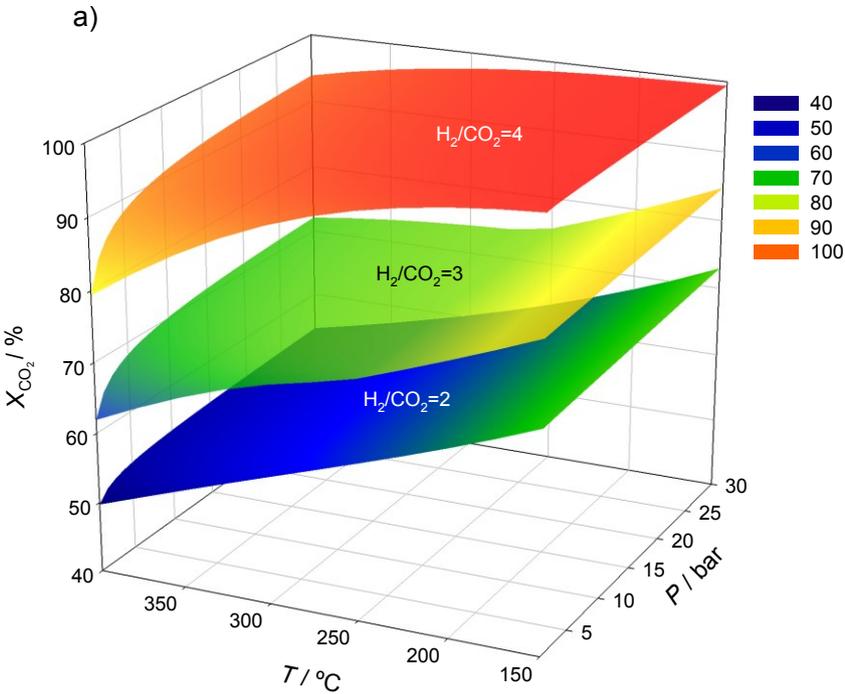
$$Y_i (\%) = \frac{F_i^{out}}{F_{CO_2}^{in}} \times 100 \quad (11)$$

Since H₂ is an expensive compound, the highest H₂/CO₂ ratio considered was 4, corresponding to the stoichiometry of the desired reaction (Eq. 1).

Fig. 2a shows that, for a given pressure, CO₂ conversion decreases with temperature but increases with the H₂/CO₂ ratio. In Fig. 2b it can be observed that CH₄ selectivity increases with both the temperature and the H₂/CO₂ ratio, except at low pressures and for H₂/CO₂=2. For a H₂/CO₂ ratio of 4 the selectivity is almost complete (Fig. 2b), except for low pressures and high temperatures where a small fraction of carbon monoxide is formed ($Y_{CO} < 1\%$) through the endothermic reverse water gas shift reaction. So, when a ratio of 4 is used, CO₂ methanation is the most favoured reaction. This is also supported by the fact that the outlet molar flow rate of H₂O is twice the value of CH₄, which obeys to the stoichiometry of the CO₂ methanation and means that these species are not being produced nor consumed through other reactions.

As mentioned above, when lower H₂/CO₂ ratios (i.e. 3 and 2) are used, CO₂ conversion decreases and a similar trend is observed for both ratios along the temperature and pressure values. This was somehow expected because more CO₂ will remain available (unconverted) since H₂ is not fed with the required stoichiometry for CO₂ methanation (Eq. 1). Interestingly, for a ratio of 3 it is observed that for temperatures below ca. 250 °C the conversion of CO₂ starts to increase (Fig. 2a), which is accompanied by a decrease of CH₄ selectivity (Fig.2b) and yield (Fig. 2c). This trend suggests that below 250 °C another compound is being produced using CO₂ as reactant; from Fig. 2d it becomes clear that such species is solid carbon (coke) through CO₂ reduction (reaction 3 in Table 2). Its exothermic nature also supports that carbon formation is favoured at lower temperatures, as observed. Moreover, this is also corroborated by the fact that the H₂O molar flow rate is higher than

twice the value of CH_4 , meaning that H_2O is produced not only through CO_2 methanation (Eq. 1) but also via the CO_2 reduction reaction.



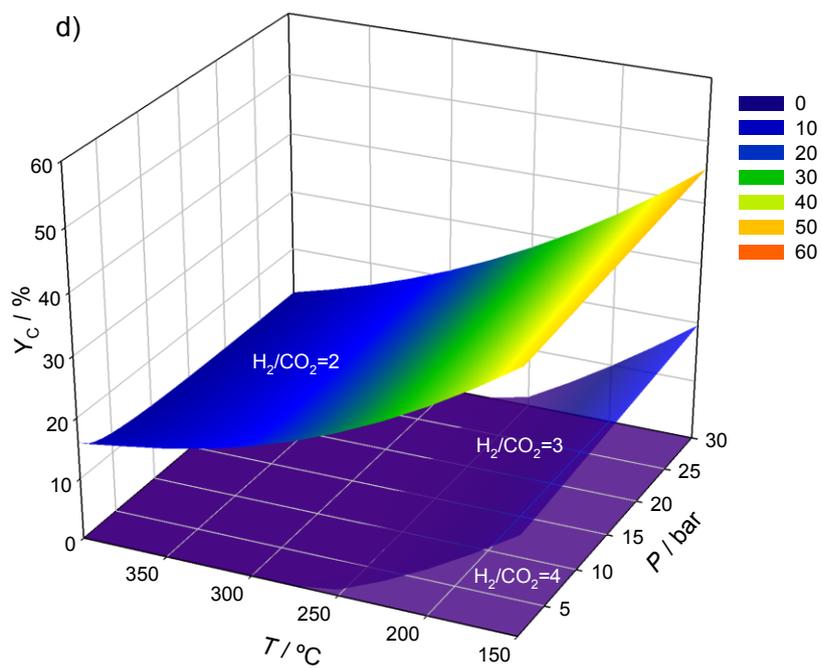
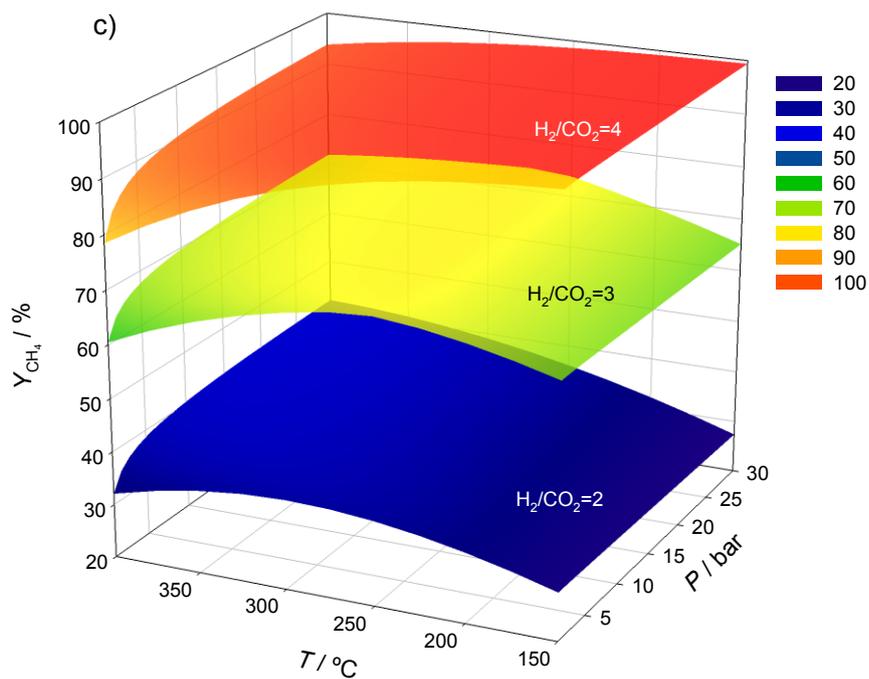


Fig.2 Effect of the H₂/CO₂ ratio (mixtures 2, 3 and 4 in Table 1), temperature and pressure on: a) CO₂ conversion, b) CH₄ selectivity, c) CH₄ yield and d) Carbon yield.

3.3 Direct CO₂ methanation from coal-fired power plant (CF-PP) flue gas streams

3.3.1 Effect of H₂O

Water vapour is an important component present in coal-fired power plant (CF-PP) flue gas streams. Herein, its effect was studied considering that H₂O is coming exclusively from the post-combustion stream. One should note that H₂ is not present in CF-PP flue gas streams (cf. mixture 1 in Table 1) and so it should be added. To observe the effect of H₂O in the methanation reaction it was considered that oxygen was absent. Still, in section 3.3.3 the simultaneous effect of H₂O and O₂ will be addressed.

Fig. 3 shows contour plots illustrating the effect of H₂O content on CO₂ conversion as a function of pressure, temperature and H₂/CO₂ ratio; H₂O content was varied to address realistic limits. For both H₂/CO₂ ratios of 4 and 3, the addition of H₂O decreases the equilibrium conversion, which was expected because H₂O is a product of the CO₂ methanation reaction (Eq. 1), thus limiting the forward reaction. The decrease of CO₂ conversion due to the presence of H₂O is more notorious for a H₂/CO₂ ratio of 3. Still more importantly, CH₄ was the only carbon-containing product formed (nearly 100 % selectivity was observed) in the presence of H₂O for the pressure and temperature ranges considered when a H₂/CO₂ ratio of 4 or 3 is used. In fact, in Fig. 4 it is shown that when a ratio of 3 is used, the presence of H₂O markedly inhibits carbon formation at temperatures below 250 °C. In this regard, industrial operation can be carried out using a H₂/CO₂ ratio of 3 without carbon formation as long as H₂O is present. Obviously, this option represents a CO₂ equilibrium conversion decrease of at least 25 % as compared to the situation of H₂/CO₂=4 without H₂O (cf. Figs. 3a and 3f). Moreover, due to the exothermic nature of the CO₂ hydrogenation into CH₄ ($\Delta H_{298\text{ K}} = -165.0\text{ kJ mol}^{-1}$), the addition/presence of H₂O can be also an interesting strategy to control the heat produced in a catalytic reactor, as suggested elsewhere [23].

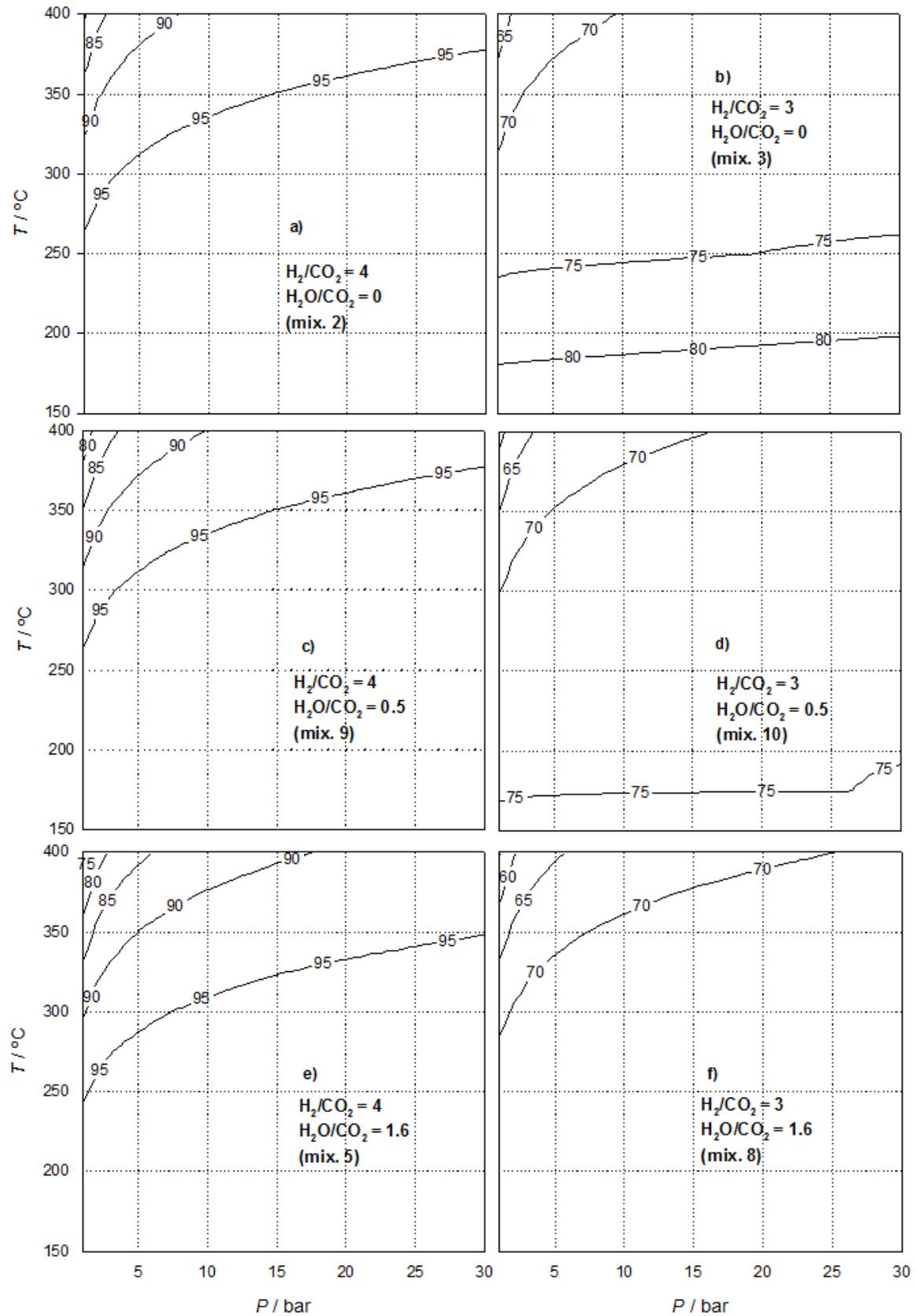


Fig.3 Contour plots showing the effect caused by H_2O content on CO_2 conversion considering different H_2/CO_2 ratios of 4 (left column) and 3 (right column). For the compositions of the different mixtures, please refer to Table 1.

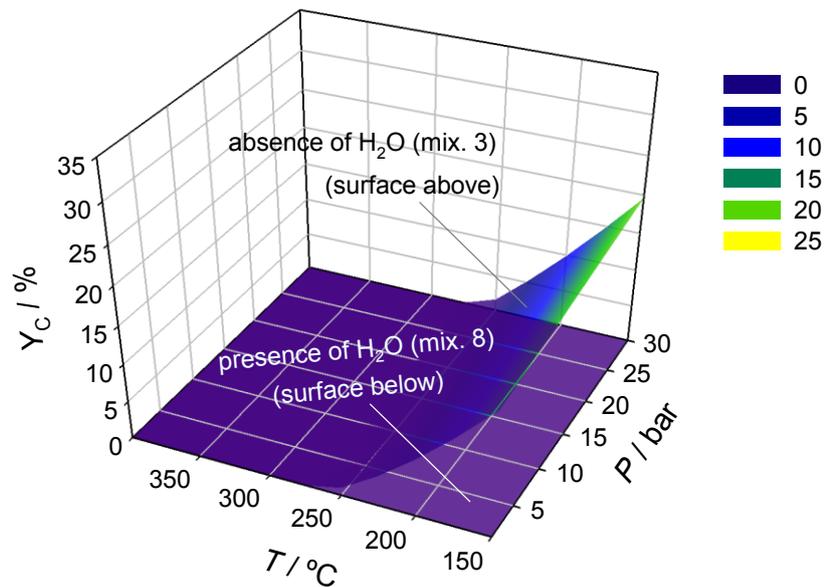


Fig.4 Carbon yield (Y_C) obtained in the absence (mixture 3) or in the presence of H₂O (mixture 8) considering a feed stream with a H₂/CO₂ ratio of 3. For the compositions of the different mixtures, please refer to Table 1.

3.3.2 Effect of O₂

Oxygen is commonly found in flue gas streams despite in small contents (< 5 %). In this regard it is important to assess its possible impact on CO₂ methanation. A stream with 2.7 mol % of O₂ (mixture 6 in Table 1) was considered at the inlet of the Gibbs reactor. The possible oxidations (reactions 5-7) are depicted in Table 2. Oxygen can react with H₂ and CH₄, both species participating in CO₂ methanation, the first as a reactant and the latter as a product. The presence of only 2.7 mol % of O₂ in the feed stream produces a significant decay of CO₂ conversion, as shown in Figure 5, which can be mainly explained by the formation of CO₂ and H₂O. In fact, in certain conditions the CO₂ conversion shifts from 95 % to ca. 82 %, while in the range of industrial nickel catalysts operation (i.e. at 400 °C and atmospheric pressure) the conversion can be as low as 70 %.

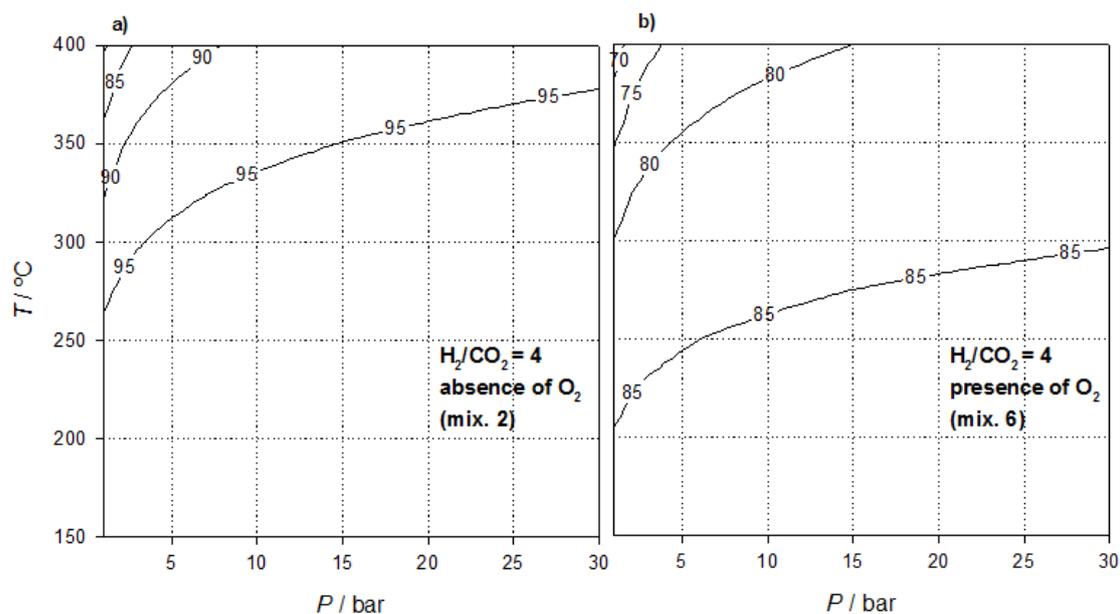


Fig.5 Contour plots showing the effect of the presence of O_2 on CO_2 conversion. For the compositions of the different mixtures, please refer to Table 1.

3.3.3 Simultaneous effect of H_2O and O_2

Fig. 6 shows that X_{CO_2} decreases when both H_2O and O_2 are present in the feed stream (trends for Y_{CH_4} are the same as for X_{CO_2} because methane selectivity was nearly 100 % in both plots – data not shown). The presence of H_2O , as mentioned in section 3.3.1, hinders CO_2 methanation in the forward direction (Eq. 1) because it is a product of the reaction. Additionally, the presence of O_2 promotes the oxidation of species such as CH_4 or H_2 (reactions 5-6 and 7 in Table2, respectively), leading to the formation of H_2O and CO_2 . Therefore, the presence of O_2 , although in a small percentage (2.3 mol % - cf. mixture 7 in Table 1) should be avoided because it leads to the parallel consumption of a reactant (H_2) and also of the desired product (CH_4). In fact, in the conditions tested, all the O_2 fed is consumed. Above 300 °C and at the atmospheric pressure a slight formation of CO ($Y_{CO} < 1\%$) through reverse water gas shift (reaction 4 in Table 2) is observed (data not shown for brevity reasons). However, CO formation can be suppressed increasing the pressure. In this case, CO_2 methanation (Eq. 1) is favoured and overlaps the reverse water-gas shift (reaction 4), which is not influenced by the pressure since the reaction takes place without change in the number of moles.

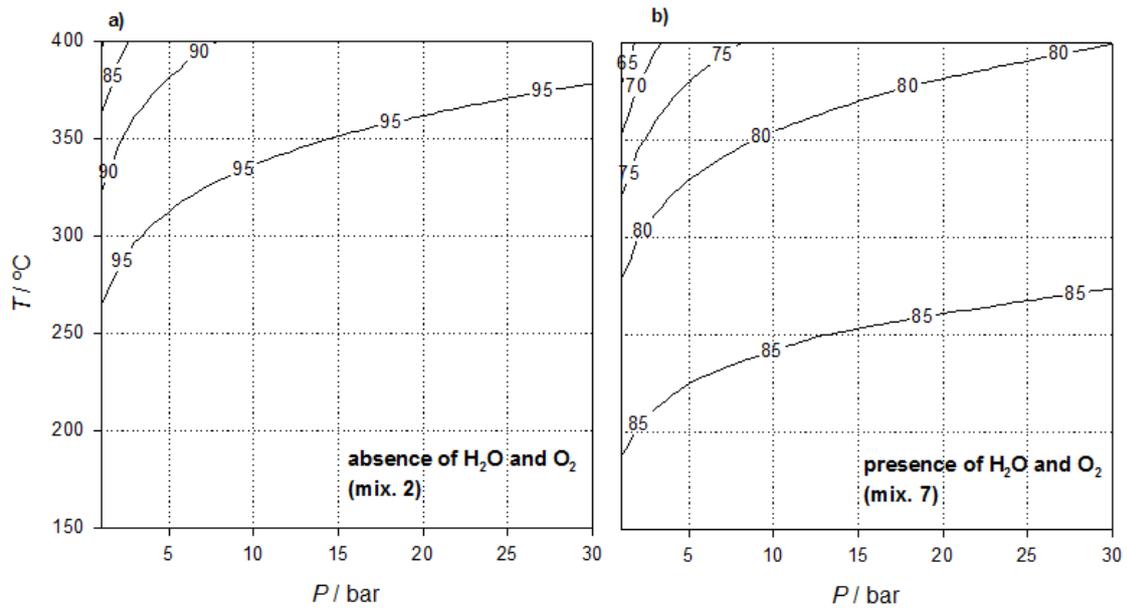


Fig.6 Contour plots showing the effect of simultaneous presence of H₂O and O₂ on CO₂ conversion for a H₂/CO₂ ratio of 4. For the compositions of the different mixtures, please refer to Table 1.

4 Technological implementation

From the technological point of view, i.e. for process implementation, two related problems are identified: i) the presence of substances in the flue gas, namely O_2 (as above-mentioned) and N_2 (that simply acts as diluents), and ii) the existence of un-reacted CO_2 in the reactor outlet, due to thermodynamic restrictions. Integration of a methanation catalyst with a CO_2 -selective sorbent in a single mixed bed is anticipated to allow overcoming all these drawbacks simultaneously. In a first stage, the unit (operating in sorption mode) is fed with the flue gas, so that CO_2 is selectively retained while the other species leave the bed, up to almost sorbent saturation (in fact up to CO_2 breakthrough from the column). In the second stage, (renewable) H_2 is fed to the bed, reacting with the previous concentrated CO_2 , in a so-called reactive regeneration approach. To operate on a continuous basis of CO_2 capture and conversion at least two beds are thus necessary operating in complementary stages: when one CO_2 -saturated bed is being regenerated (with a hydrogen-containing stream) and CH_4 is being produced, the other one is capturing carbon dioxide; after regeneration of the 1st column, the bed is able again to capture more carbon dioxide (cf. Figure 7). The reactive regeneration concept was already proved for other applications, namely in sorption-enhanced reactors for H_2 production through steam methane reforming [24], and the proof-of-concept towards CO_2 methanation is the goal of ongoing work. Finally, it should be mentioned that water must be removed from the exit stream to obtain a product with quality compatible with existing natural gas infrastructures.

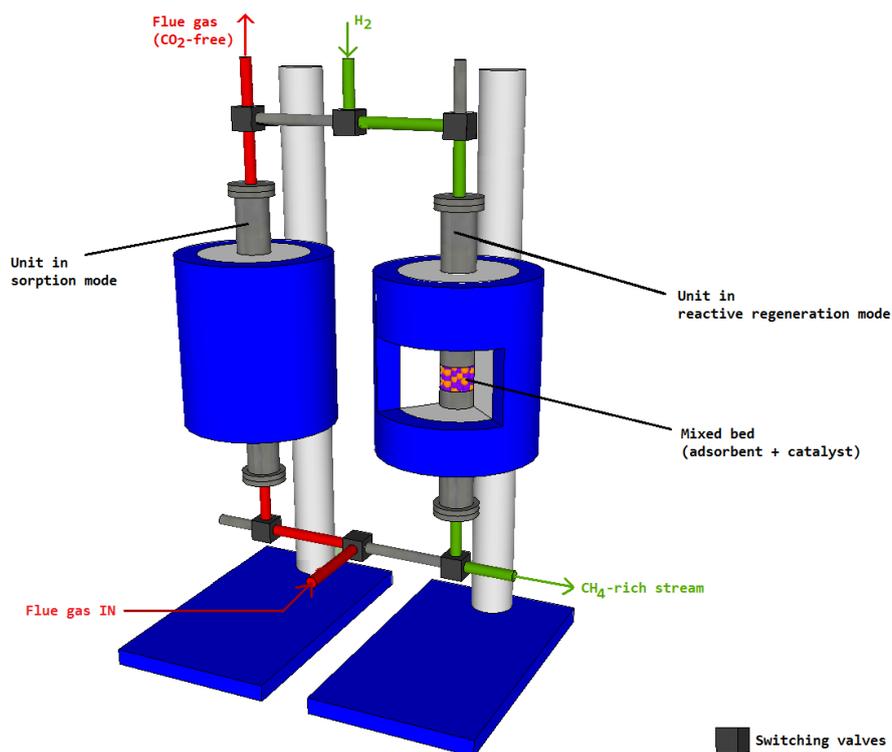


Figure 7 – Illustration of the integrated reactive regeneration process for CO₂ capture and conversion to CH₄ with two beds operating 180° out of phase with each other.

5 Conclusions

The present work compared, from the thermodynamic standpoint, the carbon dioxide valorisation to methanol and methane. The option for CO₂ conversion into CH₃OH requires harsh operation conditions when compared to the CH₄ route, namely in terms of pressure. Thus, in the near term, CO₂ methanation seems to be an easier pathway for CO₂ valorisation, while research on the development of active catalysts at lower pressures and temperatures for CO₂ hydrogenation to CH₃OH is required.

This study also allowed concluding that CO₂ methanation can take place with complete (~100%) methane selectivity and with high methane yields in the temperature and pressure ranges of industrial catalysts operation, as long as the H₂/CO₂ ratio is 4. A preliminary stage for O₂ removal from post-combustion exhaust streams is required due to its detrimental impact on CO₂ conversion, apart from security reasons. On the other hand, the effect caused by H₂O is not so pronounced as for O₂. In fact, water presence can substantially inhibit coke formation whenever a H₂/CO₂ ratio of 3 is used, thus opening a wider range of operation conditions available for the catalytic conversion of CO₂ into CH₄. Moreover, the

addition of water can bring additional advantages regarding temperature control of the methanation reactor due to the exothermic nature of the Sabatier reaction.

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