

A comparative thermodynamic study on the CO₂ conversion in the synthesis of methanol and of DME

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ABSTRACT

A thermodynamic approach of the synthesis processes of methanol and DME from H₂+CO+CO₂ has been conducted, in order to compare the feasibility of incorporating CO₂ in the feed of both processes. The effects of reaction temperature (200-400 °C), pressure (10-100 bar) and CO₂/(CO+CO₂) ratio in the feed on the CO₂ conversion, yield and selectivity of oxygenates (methanol + DME), and heat released in each process have been studied. CO₂ conversion is strongly dependent on the CO₂ content in the feed and is higher in the DME synthesis for high CO₂ concentration values in the feed (CO₂/(CO+CO₂) > 0.75). The increase of reaction temperature has a favorable effect on the oxygenate yield and selectivity, while the increase of reaction pressure and the increase of CO₂ content in the feed have an unfavorable effect. Comparing both processes, higher oxygenate yield and selectivity values are obtained in the synthesis of DME, which is more relevant for CO₂ rich feeds. Moreover, feeding CO₂ lessens the exothermic nature of both processes which is a positive effect for protecting the metallic function of the catalyst, as the formation of hot spots is avoided.

KEYWORDS: CO₂; carbon dioxide; syngas; methanol synthesis; dimethyl ether synthesis

HIGHLIGHTS:

For CO₂/(CO+CO₂) ratio above 0.75, the equilibrium conversion of CO₂ is higher in the DME synthesis than in the methanol synthesis.

Oxygenate yield (methanol + DME) is higher in the DME synthesis than in the methanol synthesis, within 20-40 bar, 250-300 °C.

The addition of CO₂ lessens the yield of oxygenates, but also global reaction heat.

1. INTRODUCTION

It is well known that CO₂ is the most important greenhouse gas, and its accumulation in the atmosphere contributes to global warming, which could be a great threat to the environment and to the mankind. Consequently, the catalytic routes of CO₂ utilization as carbon source for the production of fuels like methanol or dimethyl ether (DME) have gained significant attention in the recent years [1-4].

Methanol is the simplest liquid hydrocarbon that can be regarded as a fuel, a hydrogen carrier, or a feedstock for producing other fuels or chemical compounds [5]. Methanol production has increased from 32 to 62 million metric tons annually between 2006 and 2012, and is expected to increase to 94 million metric tons annually in 2016 [6].

Besides, DME also has a huge market potential. Traditionally, it has been known as an environmentally friendly propellant, green coolant and fuel (for both domestic and automotive use) [7, 8]. However, it has other applications as H₂ source for fuel cells [9, 10] and key intermediate for producing high added-value products or raw materials [11].

Methanol and DME are mainly produced from syngas, which can be obtained with a low CO₂ amount (below 3 %) from natural gas and petroleum derivatives [12-14]. However, the most interesting innovative studies are focused on the methanol and DME synthesis using CO₂ rich streams as those derived from coal, biomass and wastes (by gasification) [4, 15-17].

The production of methanol and DME have different reaction schemes. Methanol is directly formed from the hydrogenation of CO or CO₂ (using Cu-ZnO based metallic catalysts) [18-21], whereas DME synthesis requires the subsequent dehydration of the methanol formed (using acid catalysts) [22]. However, nowadays, the single-step process has gained much attraction for the synthesis of DME, using a bifunctional catalyst (with a metallic function for methanol synthesis and an acid function for its subsequent dehydration to DME) [23-25]. In this process, the synthesis of methanol and its subsequent dehydration take place in the same reactor, therefore, a sole reactor is required, and apart from the cost savings, the thermodynamic limitations are lower than those of the two-step reaction, due to the rapid in situ dehydration of methanol, which allows working in the single-step synthesis of DME at higher reaction temperature and lower pressure than in the methanol synthesis [26, 27]. Moreover, improvements in the synthesis of DME are being studied, using membrane reactors (selective for removing H₂O from the reaction medium), in order to shift the thermodynamic equilibrium of methanol dehydration [28, 29].

The studies on the syntheses of methanol and DME have been habitually aimed at maximizing the yield of these products. However, the current focus is directed towards the conversion of CO₂ on a large scale, and consequently a better comprehension of this conversion from a thermodynamic and kinetic point of view is needed in order to establish appropriate reaction conditions. Chen et al. [30] have compared the thermodynamics of DME synthesis in two steps and in a single step (direct synthesis) co-feeding CO₂ together with syngas. The results confirm that while the co-feeding of CO₂ decreases DME yield (with both strategies), the direct synthesis of DME has lower thermodynamic limitations and enables attaining higher CO₂ conversion.

There is much literature reporting individually the thermodynamic behavior of methanol synthesis [31-33] and the synthesis of DME in a single step [34-36] from syngas. However the CO₂ conversion capability of each process has been scarcely studied in these works. Considering the interest to progress towards a strategy and optimal operating conditions for the conversion of CO₂, the thermodynamics of the synthesis of DME and the synthesis of methanol have been compared in this paper, focusing on the capacity of these processes for the valorization of the CO₂ co-fed with syngas (Figure 1). In this study the effects of reaction temperature, pressure and fed CO₂/(CO+CO₂) ratio on the conversion of CO₂, yield and selectivity of oxygenates (methanol and DME) and heat released in each process (relevant aspect for the design of the reactor) have been assessed.

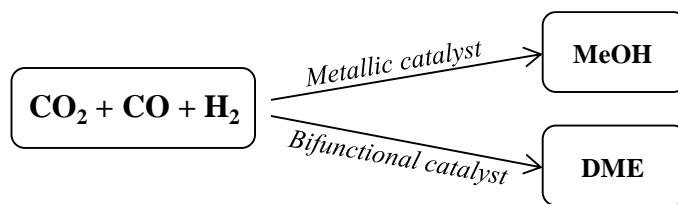


Figure 1. Graphical presentation of MeOH and DME synthesis processes.

On the other hand, the imperative need to reduce the net CO₂ emissions has motivated recent studies of strategy simulations combining CCU (ie carbon capture and utilization) strategies with CCS (i.e., carbon capture and sequestration) [37]. CCUs combined strategies (ie carbon capture utilization and sequestration) may be viable if CO₂ utilization benefits compensate carbon capture and sequestration costs. These studies take natural gas and CO₂ captured in power plants as complementary carbon sources, and CO₂ is used in two routes: i) for the intensification of natural gas extraction; and ii) co-fed with the syngas derived from the reforming of natural gas in

the synthesis of MeOH [38] or in the synthesis of DME [39,40]. These studies consider, by means of simulation, all the stages involved in the CCU strategy (generation, purification and capture of CO₂, extraction of natural gas, reforming through different alternative routes, synthesis of MeOH or DME, purification of currents, etc.). The consideration of criteria that quantify the production of oxygenates, the efficiency of the valorization of CO₂ and CH₄, and the energy efficiency, has given rise in these works to encouraging results for the progress towards the industrial implementation of these CCU strategies, in order to progressively replace CH₄ by CO₂ in the synthesis of methanol or DME. The environmental interest increases when the application of solar energy is considered to supply the required energy for the reforming of natural gas [40]. The present paper aims to be useful to focus attention on the possibilities of DME synthesis, which is a key step in the CCU strategy and whose complexity requires a detailed thermodynamic study.

2. METHODOLOGY

2.1. Simulation program

The study on the thermodynamic equilibrium of the set of reactions potentially involved in the synthesis of methanol and in the synthesis of DME has been conducted using a calculation program developed in MATLAB®, whose organization chart is described in Figure 2. The following steps have been explained in the supporting information: i) calculation of the composition in the thermodynamic equilibrium; ii) calculation of the fugacity coefficients; iii) calculation of the equilibrium constants; and iv) calculation of the heat generated in thermodynamic equilibrium conditions.

The main program, "*prin_equilibrium*", requires starting values of the temperature and pressure vectors, the reactions involved in the process and the composition in the feed, which are supplied by the "*start_values*" subroutine from a data file.

The calculation program considers the possibility of the existence of reactions that are linear combination of other reactions defined by the user. In this case, the linear combinations are removed, in order to perform the subsequent calculations with the minimum number of independent chemical reactions. Accordingly, the stoichiometric coefficients are redefined as a function of the selected reactions.

The Newton-Raphson method is used for the calculation of the composition of each species in the equilibrium. This method calculates the composition values that minimize (make equal to zero) the objective function defined in Eq. (2), using "*fun_NR*" subroutine.

This open method of finding zeros needs an adequate starting value to avoid divergence; hence, it is necessary to make a preliminary estimation of the initial searching value. Therefore, solving the differential equation set of the reaction extension as a function of space time is required, Eq. (1). The integration of the kinetic equations is performed using the proper function of MATLAB®, "*ode23s*" which solves ordinary differential equations by the Runge-Kutta method. The differential equations set is defined by the "*der_equilibrium*" calculation subroutine. Moreover, this subroutine also calculates the equilibrium constants as a function of temperature, Eq. (3). Since the fugacity values of the compounds are required for this calculation, the "*fugacity*" subroutine is called at the same time.

Once the composition values in the thermodynamic equilibrium are obtained, the extent of each reaction and the global heat generated in the process are calculated as a function

of the reaction temperature and composition in the feed. Finally, the main program returns the values of the equilibrium constants of each reaction together with the value of the global heat generated, and product yield and selectivity.

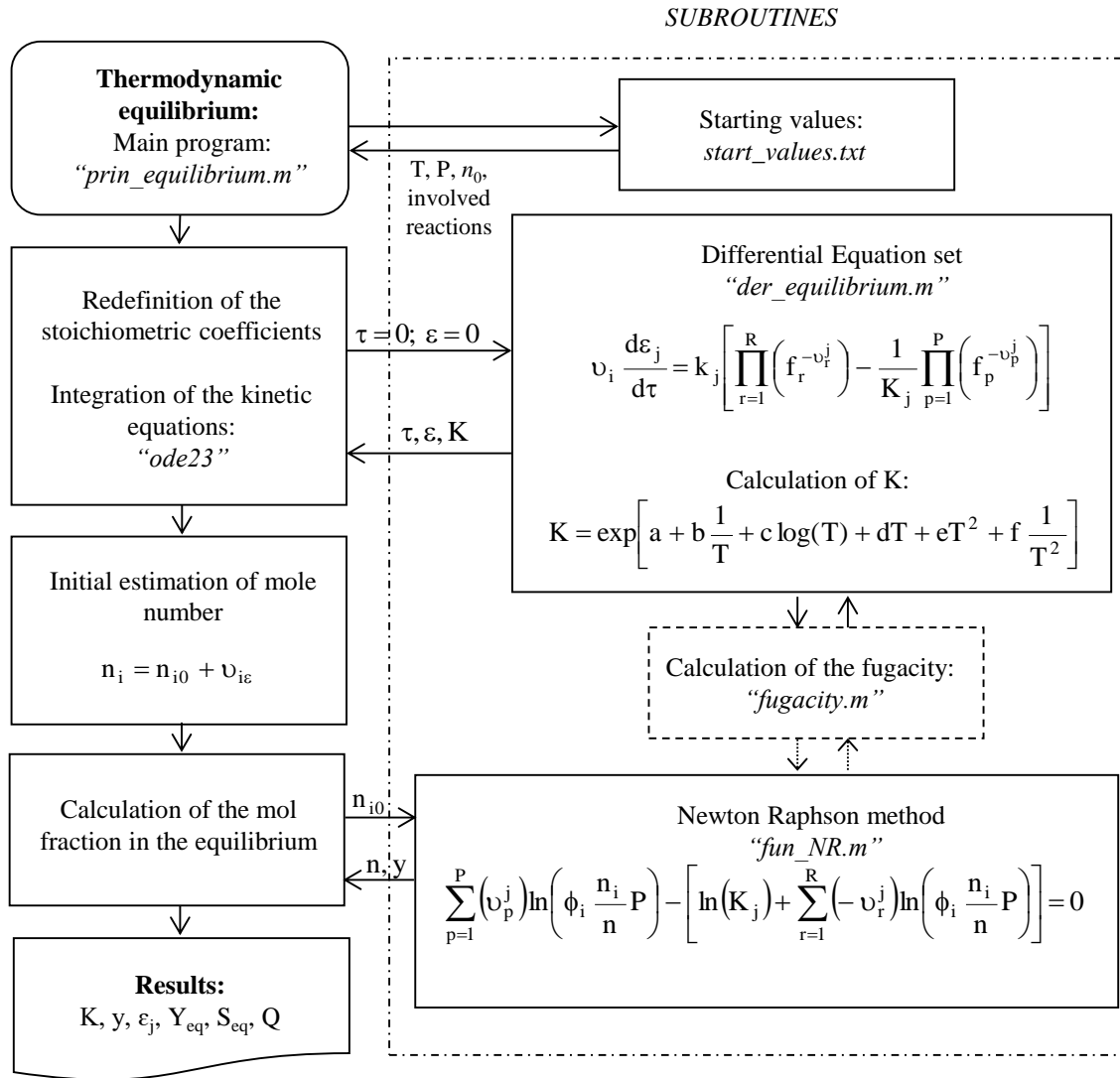


Figure 2. Procedure diagram of the calculation program.

2.2. Reaction indices

The CO₂ conversion has been defined as follows:

$$X_{CO_2} = \frac{F_{CO_2}^0 - F_{CO_2}}{F_{CO_2}^0} \cdot 100 \quad (4)$$

where $F_{CO_2}^0$ and F_{CO_2} are the molar flow rates of CO₂ in the feed and in the outlet stream, respectively, expressed in carbon units.

The yield of each product has been determined as:

$$Y_i = \frac{n_i \cdot F_i}{F_{CO_x}^0} \cdot 100 \quad (5)$$

where n_i is the number of carbon atoms of each i product, F_i is the molar flow rate of the i product in the outlet stream, and $F_{CO_x}^0$ is the molar flow rate of CO_x (CO+CO₂) in the feed.

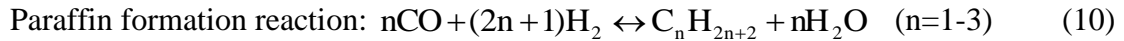
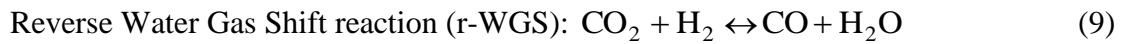
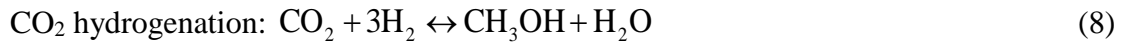
Product selectivity (by mass unit of carbon) has been calculated as the ratio between the molar flow rate of the i compound and the sum of the molar flow rates of the organic compounds (DME, MeOH and C₁-C₃) in the outlet stream:

$$S_i = \frac{n_i \cdot F_i}{\sum_i n_i \cdot F_i} \cdot 100 \quad (6)$$

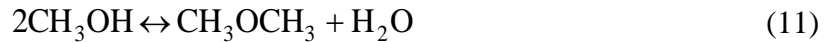
3. RESULTS AND DISCUSSION

3.1. Equilibrium constant

In the synthesis of methanol, the following reaction scheme has been considered:



In the synthesis of DME, along with the reactions described in Eqs. (7)-(10), which take place over the metallic function, the reaction of methanol dehydration to DME over the acid function does also take place:



The simulation of the thermodynamic equilibrium when considering the reactions of paraffin formation (Eq. (10)), predicts high paraffin yield values (of almost 100 % regardless the composition of the $\text{H}_2+\text{CO}+\text{CO}_2$ ternary mixture in the feed). This undesirable reaction has not been considered in this study and can be avoided by selecting suitable operating conditions. For this purpose it is convenient to limit reaction temperature and in particular to attenuate the acidity of the catalyst, in order to minimize the activity towards hydrocarbon formation by the hydrocarbon pool mechanism [41]. Consequently, the formation of coke by degradation of the hydrocarbons in the reaction medium has not been considered either. This formation is also attenuated by the co-feeding of CO_2 due to the higher concentration of water in the reaction medium as explained by Sierra et al. [42].

On the other hand, since the Eq. (8), is a linear combination of Eqs. (7) and (9), the equilibrium constant of the hydrogenation of CO₂ is calculated by means of combining the equilibrium constants of the CO hydrogenation to methanol and the reverse WGS reaction [32, 34, 43]. Table 1 sets out the coefficients reported in the literature [26] for the equilibrium constants of reactions (7), (9) and (11).

Table 1. Coefficients of the equilibrium constants of reactions Eqs. (7), (9) and (11).

Reaction	a	b·10 ⁻³	c	d·10 ⁴	e·10 ⁸	f·10 ⁻³
7	21.84	9.04	-7.66	54.07	-57.50	-6.75
9	18.01	-5.87	-1.86	2.70	0	58.20
11	-9.76	3.20	1.07	-6.57	4.90	6.05

3.2. CO₂ conversion

Figure 3 shows the effect of reaction temperature over the CO₂ conversion in the synthesis of methanol (MS) and in the synthesis of DME (DS), for different CO₂/CO_x molar ratios in the feed. The results correspond to a total operating pressure of 30 bar and feeds of H₂+CO+CO₂ ternary mixtures with H₂/CO_x ratio equal to 3. The results reveal that CO₂ valorization is feasible in both processes within the whole temperature range studied, for high CO₂ concentration feeds (CO₂/CO_x > 0.50). CO₂ conversion goes through a minimum between 250-300 °C (higher temperature when increasing CO₂ concentration), which is sharper in the synthesis of DME.

Comparing the results obtained for both methanol and DME synthesis processes, it is observed that the differences are strongly dependent on the concentration of CO₂ in the feed. On this regard, for pure CO₂ feeds (CO₂/CO_X= 1), the conversion of CO₂ is higher in the synthesis of DME below 300 °C. Furthermore, by decreasing the concentration of CO₂ in the feed the advantage of the DME synthesis process is achieved at progressively lower temperature (that is, at 275 °C for CO₂/CO_X= 0.75 and at 225 °C for CO₂/CO_X= 0.50). However, below CO₂/CO_X= 0.50 the conversion of CO₂ is higher in the synthesis of methanol in the whole temperature range.

In order to assess the relevance of these results, it should be taken into account that, on the one hand, 300 °C is considered to be the limiting temperature to avoid the sintering of Cu catalysts [44]; and on the other hand, the low reaction rate achieved below 250 °C [45]. On this regard, the 250-300 °C temperature range results interesting to attain remarkable values of conversion and reaction rate and CO₂ conversion is favored (higher in the synthesis of DME) when feeding high CO₂ concentration feeds under these conditions. On the other hand, the study has been extended to a wider range of operating conditions, since many efforts are focused nowadays on the continuous improvement of the activity and stability of these catalysts. Therefore, studying the thermodynamics of the process in the 200 - 400 °C range is interesting.

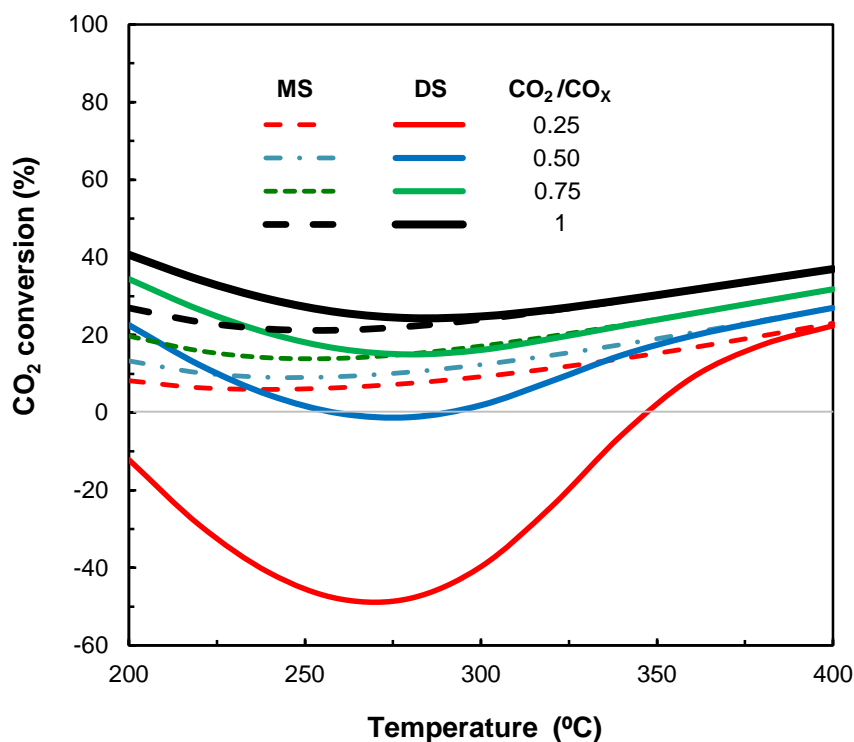


Figure 3. Comparison of the effect of temperature on the CO₂ conversion in the methanol synthesis (MS) and DME synthesis reactions (DS), for different CO₂/CO_x ratios in the feed. 30 bar, H₂/CO_x = 3.

Figure 4 compares the evolution of CO₂ conversion for both processes in a temperature vs fed CO₂ concentration (CO₂/CO_x) diagram. Figure 4a corresponds to methanol synthesis and Figure 4b to DME synthesis. These results allow evaluating in detail the suitable operating condition ranges for the valorization of CO₂ in each process. Furthermore, it should be noted that the conversion of CO₂ is remarkably higher in the synthesis of DME when the concentration of CO₂ in the feed is above CO₂/CO_x= 0.75.

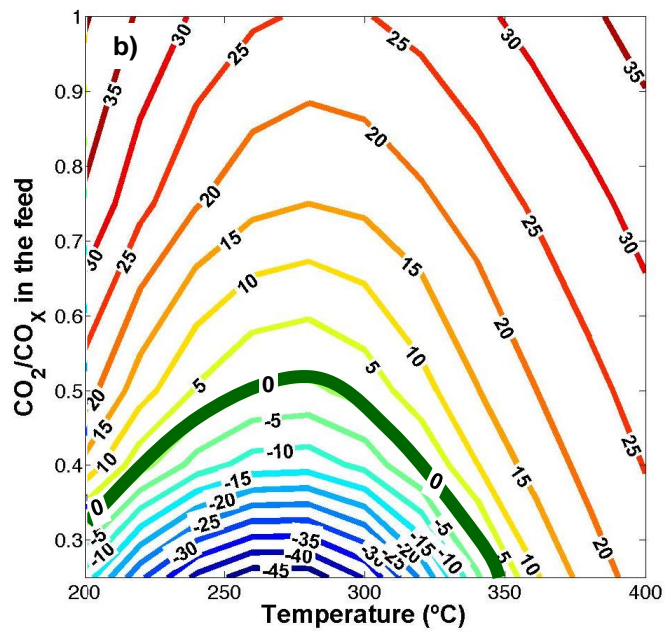
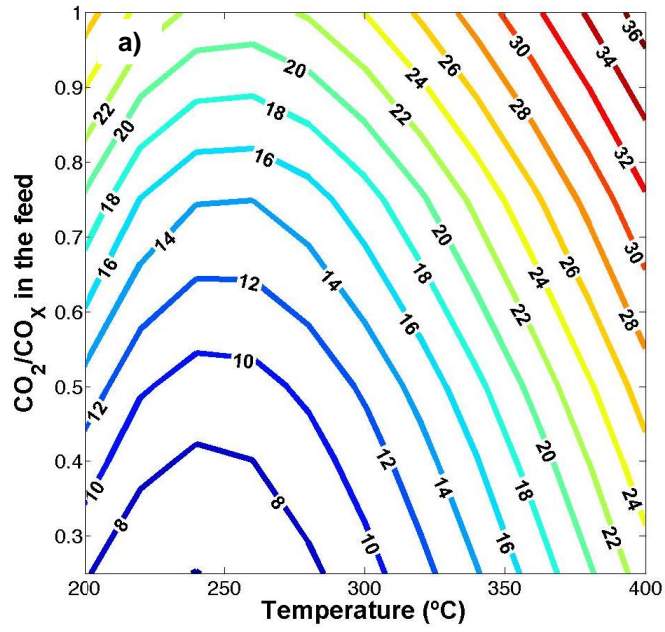


Figure 4. Maps of CO₂ conversion (in %) in a temperature vs fed CO₂ concentration (CO₂/CO_X ratio) diagram. (a) Methanol synthesis reaction; (b) DME synthesis reaction. 30 bar, H₂/CO_X= 3.

3.3. Yield of oxygenates

The effect of the operating conditions on the yield of oxygenates in each process has been studied in this section. In the MS process emphasis has been placed on the production of methanol, and in the DS process the formation of the two oxygenates has been studied, that is MeOH + DME, which are in equilibrium.

Figure 5 shows the effect of temperature on the yield of the corresponding oxygenates at different pressures, for the synthesis of methanol (dotted lines) and that of DME (continuous lines). Each graph corresponds to a different CO₂ concentration in the feed, maintaining the H₂/CO_x ratio equal to 3.

In light of the results obtained for the synthesis of methanol, reaction pressure has a favorable effect on the yield of methanol, whereas temperature is unfavorable, due to the exothermic nature of the reaction. Moreover, it can be observed that the increase of CO₂ concentration in the feed leads to an increase of the thermodynamic limitations of the reaction. The equilibrium constant of the methanol formation reaction is low for H₂+CO₂ feeds, and its formation is controlled by the reverse WGS reaction.

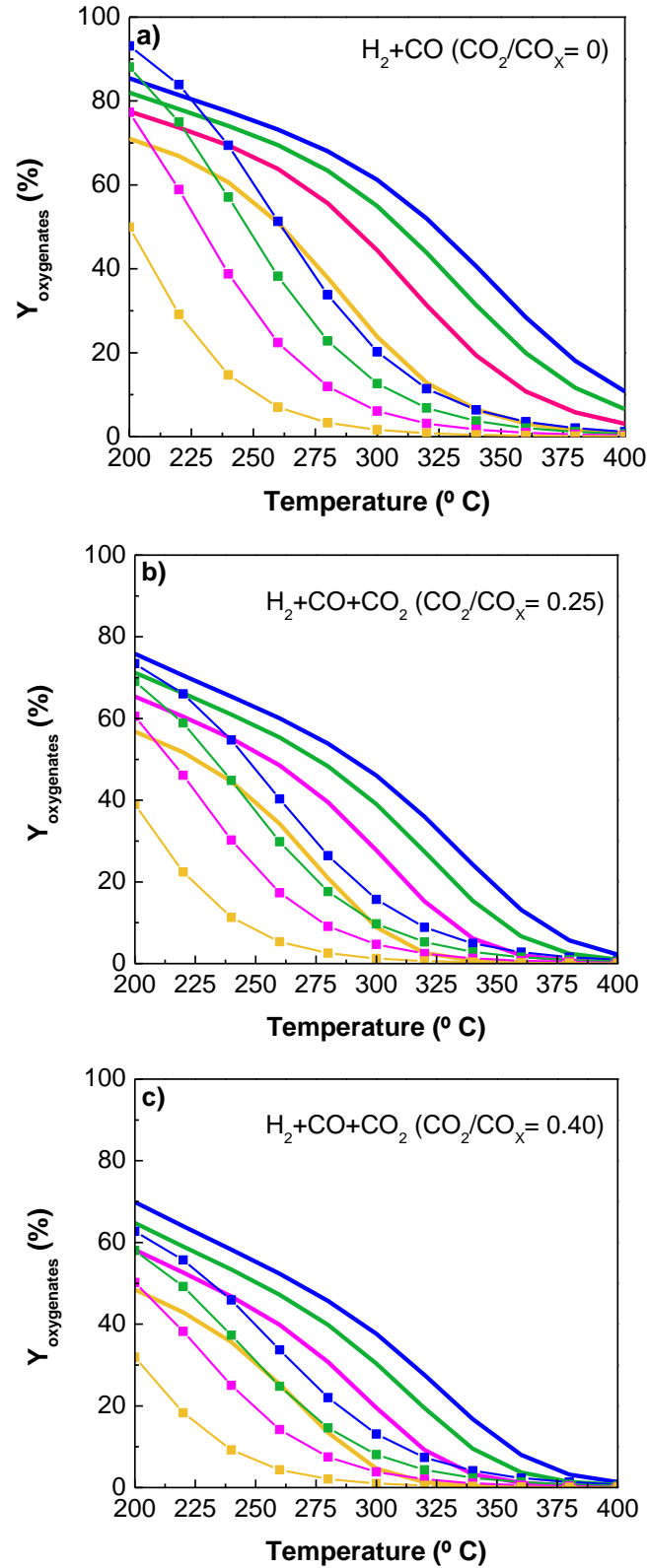
In the synthesis of DME (continuous lines in Figure 5), the favorable effect of pressure is also evident and a remarkable decay in the yield of oxygenates (DME and methanol) is observed when increasing reaction temperature. For CO₂ free feeds (Figure 5a), oxygenate yield decreases from around 80 to 60 %, when increasing temperature from 200 °C to 300 °C at 30 bar; and for feeds with a CO₂/CO_x ratio of 0.40 (Figure 5c), an increase of 25 °C in the reaction temperature (from 250 to 275 °C), leads to a decay of almost 10 % in the oxygenate yield, at 40 bar.

On the other hand, the co-feeding of CO₂ together with the syngas in the feed, decreases the yield of oxygenates, due to the thermodynamic restrictions of methanol synthesis described previously. Nevertheless, this decay is significantly less pronounced than in the methanol synthesis. It should be noted that the incorporation of a small amount of CO₂ in the feed (CO₂/CO_X = 0.25, Figure 5b), leads to a decrease in the oxygenate yield of above 20 % comparing to that obtained without CO₂ in the feed (Figure 5b). For feeds with a CO₂/CO_X ratio= 0.50 (Figure 5d) and therefore, doubling the CO₂ amount of that in Figure 5b, the oxygenate yield is 30 % lower than that obtained with syngas at 275 °C and 20 bar.

Figure 6 illustrates the results of DME selectivity corresponding to the same conditions as in Figure 5. It is observed that the effect of pressure and temperature over the selectivity of DME is similar to the aforementioned effect on the yield of oxygenates. Besides, for obtaining the maximum values of oxygenate yield and DME selectivity, low temperature and high reaction pressure are required, and both indices decrease when increasing CO₂ concentration in the feed.

In light of the results in Figures 5 and 6, it is concluded that the synthesis of DME is thermodynamically more favored than the synthesis of methanol. The oxygenate yield obtained in the DME synthesis process is significantly higher (Figure 5). Moreover, DME selectivity is noticeable (Figure 6), above 90 % in all cases for CO₂ free feeds (Figure 5a) and also for H₂+CO+CO₂ ternary mixture feeds (Figures 6b to 6d) below 300 °C, regardless the reaction pressure. Furthermore, more suitable oxygenate yields are obtained at higher temperature (faster reaction) and lower pressure, hence, reducing operating cost.

In order to assess the aforementioned results in further detail, the study has been completed with the results of the effect of reaction pressure and temperature on the yield of DME (Figure 7).



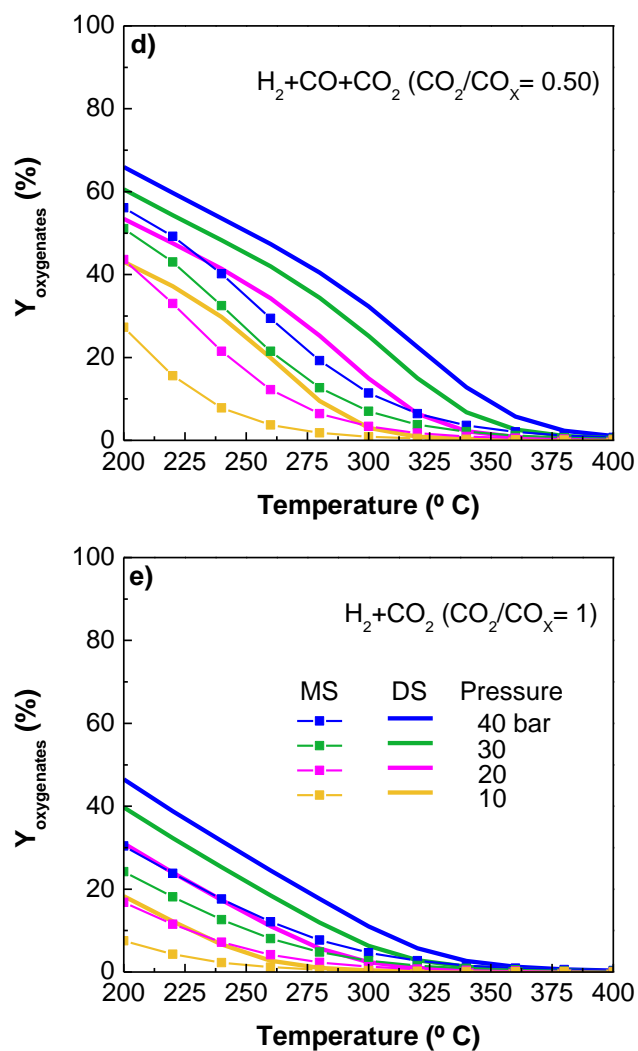
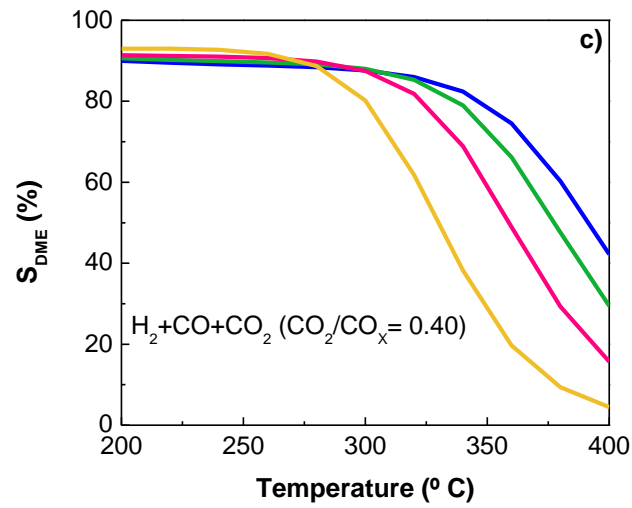
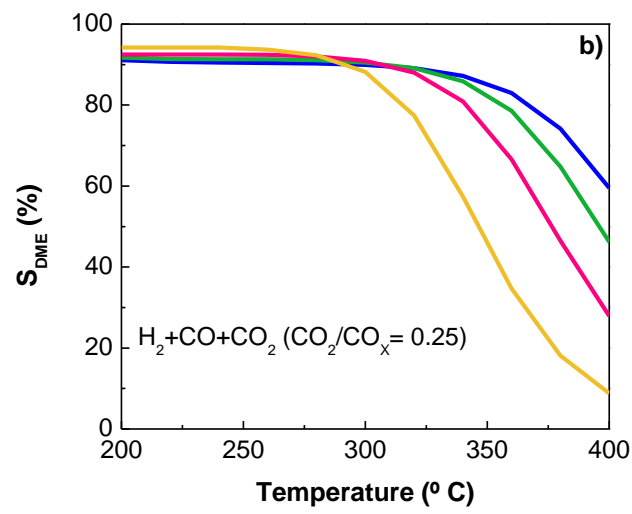
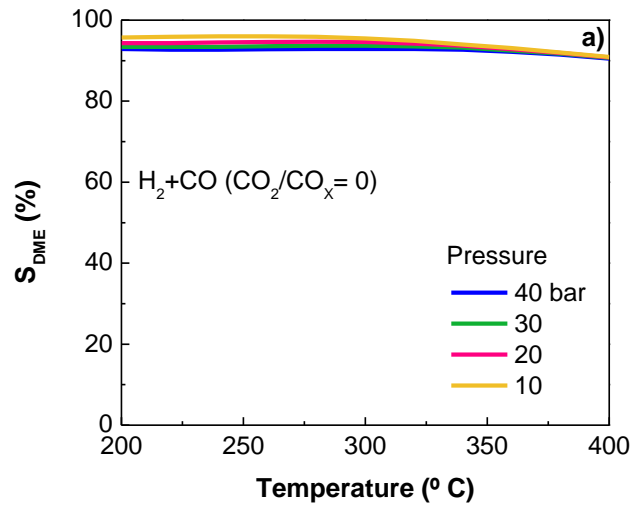


Figure 5. Effect of temperature and pressure on the yield of oxygenates (in %) in the thermodynamic equilibrium of the synthesis of methanol (MS, dotted lines) and for the synthesis of DME (DS, continuous lines). Each graph corresponds to a different CO_2 concentration in the feed; (a) $CO_2/CO_X=0$; (b) $CO_2/CO_X=0.25$; (c) $CO_2/CO_X=0.40$; (d) $CO_2/CO_X=0.50$; (e) $CO_2/CO_X=1$. $H_2/CO_X=3$.



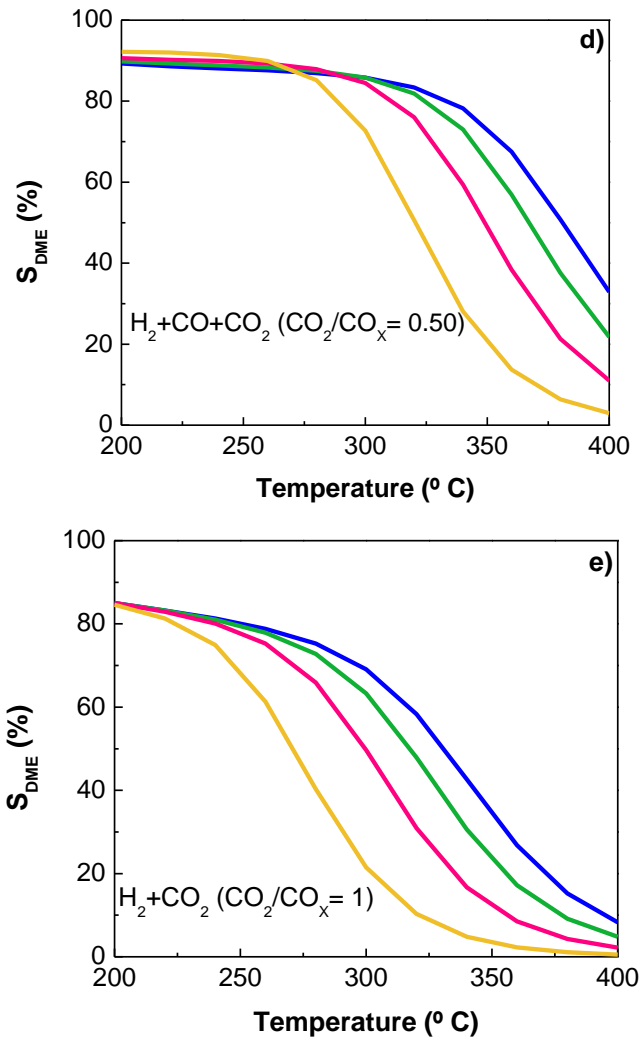


Figure 6. Effect of temperature and pressure on the selectivity of DME in the thermodynamic equilibrium of the synthesis of DME. Each graph corresponds to a different CO_2 concentration in the feed; (a) $CO_2/CO_x = 0$; (b) $CO_2/CO_x = 0.25$; (c) $CO_2/CO_x = 0.40$; (d) $CO_2/CO_x = 0.50$; (e) $CO_2/CO_x = 1$. $H_2/CO_x = 3$.

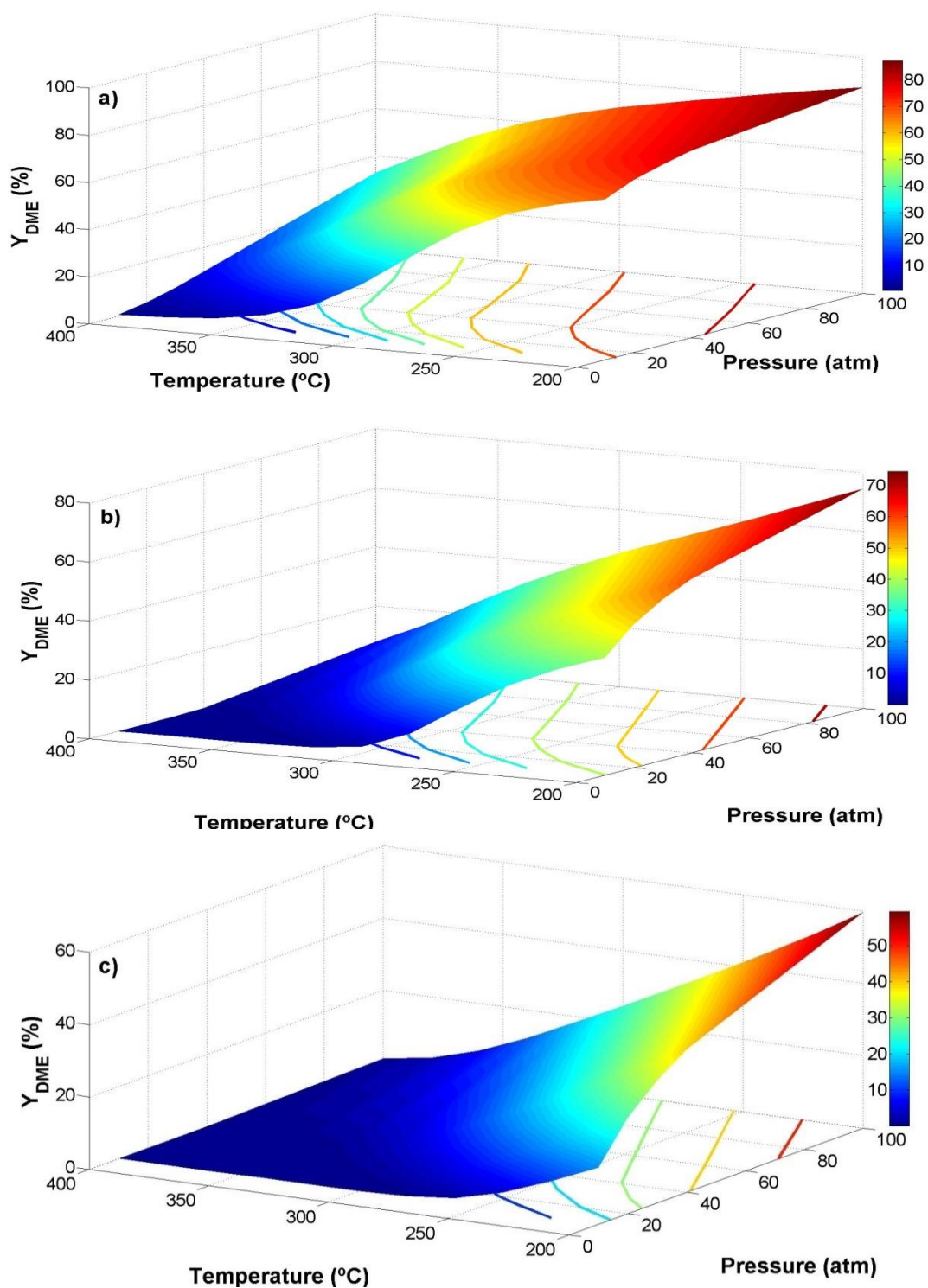


Figure 7. Maps of DME yield in a temperature vs pressure diagram in the DME synthesis reaction. Each graph corresponds to a different CO_2 concentration in the feed; (a) $\text{CO}_2/\text{CO}_x = 0$; (b) $\text{CO}_2/\text{CO}_x = 0.50$; (c) $\text{CO}_2/\text{CO}_x = 1$. $\text{H}_2/\text{CO}_x = 3$.

3.4. Reaction heat

Bearing in mind the exothermic nature of the CO and CO₂ hydrogenation reactions and the DME dehydration reaction, together with the endothermic nature of the r-WGS reaction, the feasibility of reaching a thermo neutral regime when co-feeding CO₂ with the syngas in the feed has been analyzed. These conditions are a key point for the design of the reactor.

Figure 8a illustrates the heat generated in the methanol synthesis reaction, for various CO₂/CO_x ratios in the feed and different reaction temperatures, and Figure 8b the heat released in the synthesis of DME in the same operating condition ranges. It is observed that for both processes, both reaction temperature and CO₂ concentration in the feed have a remarkable effect on the reaction heat. Therefore, for a fixed reaction temperature, increasing CO₂/CO_x ratio in the feed leads to a remarkable decrease on the generated heat. In the case of methanol synthesis, the heat generated in the overall reaction decays from around 80 to 45 kJ/mol_C when comparing CO₂ free feeds with feeds composed of a CO₂/CO_x ratio= 0.50 (Figure 8a), and from near 90 to 60 kJ/mol_C in the case of the synthesis of DME (Figure 8b). This fact is a key point for the methanol synthesis and for the synthesis of DME from the experimental point of view, since it helps to avoid the formation of hot spots in the reactor and the active sites of the catalyst, responsible for the Cu sintering.

Overall, the results predict that methanol synthesis process is slightly less exothermic than the DME synthesis process. Thermo neutral conditions, where energy formation or consumption is zero, is obtained over 330 °C for methanol synthesis process and over 360 °C for the DME synthesis process. In light of these results, regardless the temperature in the former is lower than in the latter, working at thermo neutral

conditions does not seem to be possible with the Cu catalysts commonly used nowadays, which would suffer severe Cu sintering at these temperatures. From the point of view of catalyst stability, the addition of CO₂ together with the syngas in the feed, helps lessening the heat released in the process (both in the methanol and DME syntheses), and therefore this co-feeding helps protecting and preserving the catalyst.

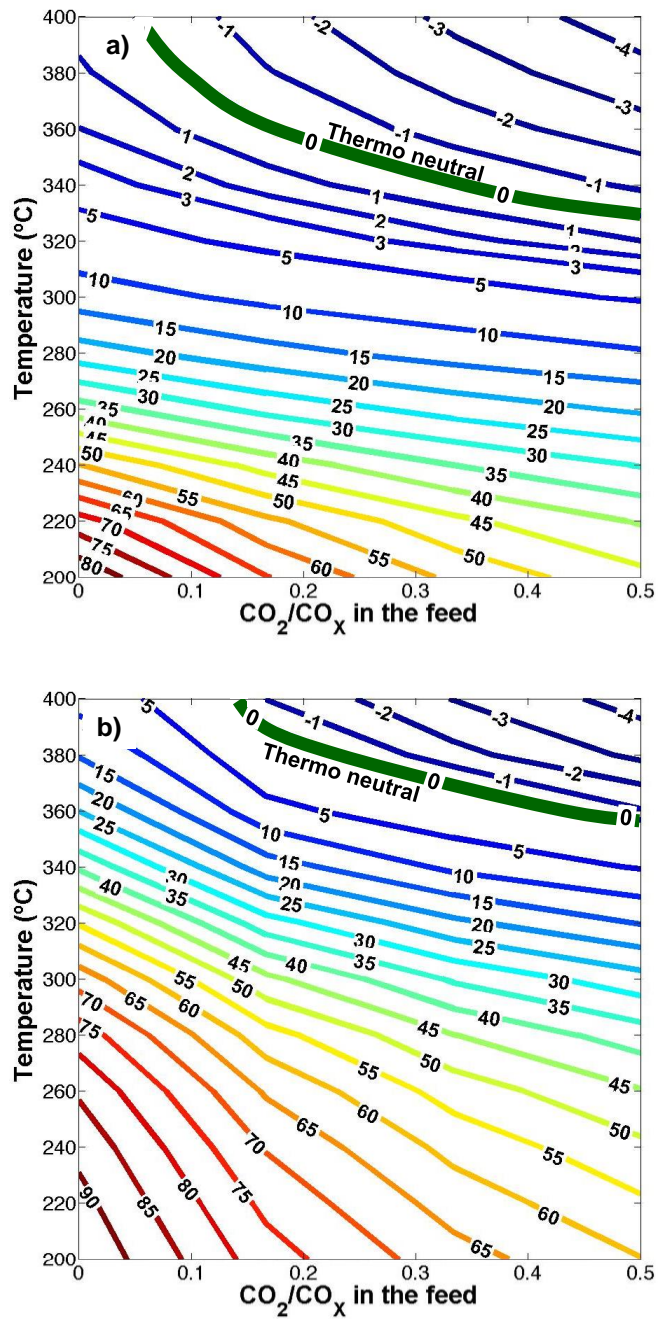


Figure 8. Map of heat generated (kJ/mol) in a temperature vs CO_2/CO_x ratio in the feed diagram. (a) Methanol synthesis reaction; (b) DME synthesis reaction. 30 bar, $\text{H}_2/\text{CO}_x=3$.

4. CONCLUSIONS

The thermodynamic capacity for the valorization of CO₂ is higher in the synthesis of DME than in the methanol synthesis when CO₂ concentration in the feed is higher than that corresponding to a CO₂/(CO+CO₂) ratio= 0.75, and this trend reverses for lower CO₂ concentrations in the feed. Under these conditions of high CO₂ concentration in the feed, the conversion of CO₂ in both processes goes through a minimum at 250-300 °C, which is more pronounced in the synthesis of DME, and takes place at slightly higher temperature when increasing reaction pressure.

Moreover, the yield of oxygenates (methanol and DME) is greater in the synthesis of DME than the yield of methanol in the synthesis of the latter. The yield of the corresponding oxygenates decreases in both processes with increasing CO₂ concentration in the feed, which is an opposite effect to that aforementioned regarding CO₂ conversion.

Co-feeding CO₂ has a favorable effect on the reaction heat, both in the methanol and in the DME synthesis processes, since a higher content of CO₂ in the feed favors the r-WGS reaction, and consequently, diminishes the exothermic nature of the overall process, which is important for an appropriate control of the temperature inside the reactor, avoiding the formation of hot spots (> 300 °C) responsible for Cu sintering in the metallic function of the catalysts used in these processes.

NOMENCLATURE

a, b, c, d, e, f	Equilibrium constant coefficients.
CO _x	CO+CO ₂ .
DME	Dimethyl ether.
F _i ⁰ , F _i	Molar flow rate of compound i in the feed and reactor outlet, respectively, mol _C h ⁻¹ and mol h ⁻¹ .
f _r , f _p , f _i	Fugacity of reactants, products and compound i, respectively, atm.
K _j	Equilibrium constant, bar ^{Δn} .
k _j	Kinetic constant of reaction j.
MeOH	Methanol.
n _i	Mol number of i component.
P	Pressure, bar.
Q	Heat generated in the reaction, kJ (mol _C) ⁻¹ .
Y _i , S _i	Yield and selectivity of the lump i, (mol _i mol ₀ ⁻¹) _C .
T	Temperature, °C.
X _{CO2}	CO ₂ conversion, %.
y	Mol fraction.

Greek symbols

ε	Extention of the reaction, mol.
τ	Space time, g _{cat} ·h (mol _C) ⁻¹ .

$\nu_{i,j}$ Stoichiometric coefficient of compound i in the reaction j .

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Supplementary information

**A comparative thermodynamic study on the CO₂ conversion in
the syntheses of methanol and of DME**

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1. THEORETHICAL ANALYSIS

A calculation program written in MATLAB® has been developed to systematically determine the parameters of thermodynamic equilibrium based on the steps described below.

1.1. Calculation of the composition in the thermodynamic equilibrium

For a chemical reaction in gas state of type:



the mole variation of the species is directly dependent on its stoichiometric coefficients, v_i . Therefore, the extent of the reaction, ε , is defined as:

$$d\varepsilon = \frac{dn_A}{v_a} = \frac{dn_B}{v_b} = \frac{dn_R}{v_r} = \frac{dn_S}{v_s} \quad (\text{S.2})$$

In order to obtain the composition of each species at the equilibrium, the reaction rate of i species in the j reaction is defined as follows:

$$v_i^j \frac{d\varepsilon_j}{d\tau} = k_j \left[\prod_{r=1}^R (f_r^{-v_r^j}) - \frac{1}{K_j} \prod_{p=1}^P (f_p^{v_p^j}) \right] \quad (\text{S.3})$$

where r refers to the reactants and p to the products of the reaction; f_r and f_p are the fugacity values of the reactant and products respectively; k_j is the kinetic constant of the reaction j ; τ is the space time; and K_j is the equilibrium constant of the reaction j .

The composition of each species in the equilibrium has been calculated considering the reaction rate in the equilibrium is zero:

$$v_i^j \frac{d\varepsilon_j}{d\tau} = k_j \left[\prod_{r=1}^R (f_r^{-v_r^j}) - \frac{1}{K_j} \prod_{p=1}^P (f_p^{v_p^j}) \right] = 0 \quad (\text{S.4})$$

In order to simplify the calculations required for the resolution, Eq. (S.4) is linearized:

$$\ln(K_j) + \ln \left[\prod_{r=1}^R (f_r^{-v_r^j}) \right] = \ln \left[\prod_{p=1}^P (f_p^{v_p^j}) \right] \quad (\text{S.5})$$

Eq. (S.5) can be reordered, leading to the objective function to be minimized:

$$\text{OF} = \sum_{p=1}^P (v_p^j) \ln(f_p) - \left[\ln(K_j) + \sum_{r=1}^R (-v_r^j) \ln(f_r) \right] \quad (\text{S.6})$$

1.2. Calculation of the fugacity coefficients

Since the DME synthesis reaction takes place at high pressure conditions, the non ideal behavior of the compounds in the reaction medium must be considered. Therefore, the thermodynamic equilibrium expressions and the reaction equations to be set in the subsequently, must consider the fugacity values of each compound instead of partial pressure values.

The fugacity of a compound (f_i) in a mixture, is a function of the fugacity coefficient (Φ_i) and the partial pressure (p_i), as well as a result of the mol fraction and the total pressure of the system (P), where y_i is the molar fraction and n_i is the mole number:

$$f_i = \Phi_i p_i = \Phi_i y_i P = \Phi_i \frac{n_i}{n} P \quad (\text{S.7})$$

The fugacity coefficient of each species has been determined by the Soave-Redlich-Kwong method [S1]:

$$\Phi_i = \exp \left[(Z-1) \frac{B_i}{B'} - \ln (Z-B'P) - \frac{A'^2}{B'} \left(\frac{2A_i}{A'} - \frac{B_i}{B'} \right) \ln \left(1 + \frac{B'P}{Z} \right) \right] \quad (\text{S.8})$$

The compressibility factor Z is given by the expression:

$$Z^3 - Z^2 + (A' - B' - B'^2)Z - A'B' = 0 \quad (\text{S.9})$$

Where the parameters A' , B' , A_i and B_i for a multi-compound system are calculated

as:

$$A' = \frac{a' P}{R^2 T^2} \quad (\text{S.10})$$

$$B' = \frac{b' P}{RT} \quad (\text{S.11})$$

$$A_i = \frac{a_i P}{R^2 T^2} \quad (\text{S.12})$$

$$B_i = \frac{b_i P}{RT} \quad (\text{S.13})$$

For a system with C compounds in the equilibrium, the values of the coefficients a' and b' are determined using original mixing rules with interaction coefficients:

$$a' = \sum_{i=1}^C \left[\sum_{i'=1}^C y_i y_{i'} (a_i a_{i'})^{0.5} \right] \quad (\text{S.14})$$

$$b' = \sum_{i=1}^C y_i b_i \quad (\text{S.15})$$

where y_i and $y_{i'}$ are the mol fractions of the i and i' compound pair. Coefficients a_i (or $a_{i'}$) and b_i are a function of the critical temperature and pressure (T_c , P_c) and the acentric factor (ω):

$$a_i = \frac{0.42748R^2T_c^2[1 + f_\omega(1 - T_r^{0.5})]^2}{P_c} \quad (\text{S.16})$$

$$b_i = \frac{0.08664RT_c}{P_c} \quad (\text{S.17})$$

$$f_\omega = 0.480 + 1.574\omega - 0.176\omega^2 \quad (\text{S.18})$$

being T_r the reduced temperature, related to the critical temperature:

$$T_r = \frac{T}{T_c} \quad (\text{S.19})$$

1.3. Calculation of the equilibrium constant

The equilibrium constant of a chemical reaction is calculated from the variation of the standard Gibbs free energy (ΔG°) by means of the following expression [S1]:

$$K = \exp\left(-\frac{\Delta G^\circ}{RT}\right) \quad (\text{S.20})$$

where ΔG° is a function of the standard enthalpy (ΔH°) and entropy (ΔS°), given by:

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (\text{S.21})$$

ΔH° and ΔS° values are calculated on the basis of a thermodynamic state at T_0 temperature as follows:

$$\Delta H^{\circ} = \Delta H_0^{\circ} + R \int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} dT \quad (\text{S.22})$$

$$\Delta S^{\circ} = \Delta S_0^{\circ} + R \int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} \frac{dT}{T} \quad (\text{S.23})$$

$$\Delta S_0^{\circ} = \frac{\Delta H_0^{\circ} - \Delta G_0^{\circ}}{T_0} \quad (\text{S.24})$$

therefore, ΔG_0° , ΔS_0° and ΔH_0° are the standard free Gibbs energy, entropy and enthalpy variations at the T_0 reference temperature. Combining Eqs. (S.21)-(S.24), the following expression is obtained:

$$\frac{\Delta G^{\circ}}{RT} = \frac{\Delta G_0^{\circ} - \Delta H_0^{\circ}}{RT_0} + \frac{\Delta H_0^{\circ}}{RT} + \frac{1}{T} \int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} dT - \int_{T_0}^T \frac{\Delta C_p^{\circ}}{R} \frac{dT}{T} \quad (\text{S.25})$$

being:

$$\Delta G_0^{\circ} = \sum_i \nu_i \Delta G_{fi}^{\circ} \quad (\text{S.26})$$

$$\Delta H_0^{\circ} = \sum_i \nu_i \Delta H_{fi}^{\circ} \quad (\text{S.27})$$

$$\Delta C_p^{\circ} = \sum_i \nu_i C_p^{\circ} \quad (\text{S.28})$$

where ν_i is the stoichiometric coefficient, positive for products, negative for reactants and equal zero for the inert compounds. ΔG_{fi}° , ΔH_{fi}° and $\Delta C_{p_{fi}}^{\circ}$ are, the free Gibbs formation energy, the formation enthalpy and the heat capacity of the i compound at a constant pressure in its standard state and T_0 reference temperature, respectively. The heat capacity is a function of temperature, given by:

$$\frac{C_p^o}{R} = A + BT + CT^2 + DT^{-2} \quad (\text{S.29})$$

where A, B, C and D are the parameters of the heat capacity equation. It should be noted that depending on the compound, the values of C or D might be zero.

Integrating Eqs. (S.26)-(S.29) in Eq. (S.25), it can be concluded that K equilibrium constant is a function of temperature as expressed in Eq. (S.30), where a, b, c, d, e and f are the coefficients of the equilibrium constant in each reaction involved in the process:

$$K = \exp \left[a + b \frac{1}{T} + c \log(T) + d T + e T^2 + f \frac{1}{T^2} \right] \quad (\text{S.30})$$

1.4. Calculation of the heat generated in thermodynamic equilibrium conditions

For a given chemical reaction, the standard reaction properties, such as ΔG_0 and ΔH_0 , vary with temperature as follows:

$$\frac{d(\Delta G^0/RT)}{dT} = -\frac{\Delta H^0}{RT^2} \quad (\text{S.31})$$

The variation of the standard free energy, ΔG_0 , can be expressed as a function of the equilibrium constant as:

$$\Delta G^0 = -RT \ln K \quad (\text{S.32})$$

consequently,

$$\Delta H^0 = RT^2 \frac{d \ln K}{dT} \quad (\text{S.33})$$

The derivate is conducted analytically from the relationship between the equilibrium constant and the temperature, Eq. (S.30).

The heat generated in a j reaction, is calculated from the standard reaction enthalpy, given by Eq. (S.33), considering the extent of the reaction, ε_j . In a chemical process where several reactions take place simultaneously, the total generated heat will be the sum of that corresponding to each reaction j , given by the following expression:

$$Q = \sum_j \varepsilon_j \Delta H_i^\circ \quad (\text{S.34})$$

The extent to which a j reaction has taken place, as defined in Eq. (S.35), determines the mol number of each i compound present in the reaction j at a certain moment, as expressed in Eq. (S.35):

$$n_i = n_{i_0} + \nu_i \varepsilon_j \quad (\text{S.35})$$

when various reactions occur simultaneously, the mole number of the i species is determined as follows:

$$n_i = n_{i_0} + \sum_j \nu_{i,j} \varepsilon_j \quad (\text{S.36})$$

Once the mole number of each i compound in the equilibrium for a each j reaction has been determined, the extent of each reaction j is calculated with Eq. (S.36), and the global heat generated or released is calculated by Eq. (S.34) from the corresponding values of ε_j and generated heat.

NOMENCLATURE

A, B, C, D, E, F Constants in Eq.S.29.

P_c Critical pressure, bar.

p_i Partial pressure of lump or compound i, bar.

R Universal gas constant, kJ (mol K)^{-1} .

T_0 Reference temperature, K.

T_c Critical temperature, K.

y_i, y_i' Mol fraction of i and i'.

Z Compressibility factor.

Greek symbols

ΔC_p° Variation of the heat capacity of the reaction at constant pressure in standard state and reference temperature, J (K mol)^{-1} .

$\Delta G^\circ, \Delta G_0^\circ$ Variation of the free Gibbs standard energy and its value at reference temperature, respectively, J mol^{-1} .

$\Delta G_{fi}^\circ, \Delta H_{fi}^\circ$ Free Gibbs energy and formation enthalpy at constant pressure of the compound i in its standard state at reference temperature, J mol^{-1} .

$\Delta H^\circ, \Delta H_0^\circ$ Variation of the standard reaction enthalpy, and its value at reference temperature, respectively, J mol^{-1} .

$\Delta S^\circ, \Delta S_0^\circ$ Variation of the standard entropy and its value at reference temperature, respectively, J (K mol)^{-1} .

Φ_i Fugacity coefficient of compound i.

ω Acentric factor.

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