

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 of 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 and the increase of the CO₂ content in the feed have an unfavorable effect on the oxygenate yield and selectivity, while the increase of reaction pressure has a favorable 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.

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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

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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 (Fig. 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.

On the other hand, the imperative need to reduce the net CO₂ emissions has motivated recent studies of strategy simulations combining CCU (i.e. carbon capture and utilization) strategies with CCS (i.e., carbon capture and sequestration) [37]. CCUs combined strategies (i.e. 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.

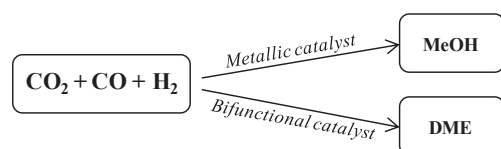


Fig. 1. Graphical presentation of MeOH and DME synthesis processes.

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 Fig. 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. (3), 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. (2). 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.

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.

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