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Thermodynamic analysis of sorption-enhanced hydrogenation for methane production from anthropogenic greenhouse gas

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Abstract

The thermodynamic perspective on CO₂ methanation using hydrogen was explored by minimizing total Gibbs free energy, employing a methodology incorporating in-situ water removal via sorption-enhanced systems. This investigation utilized a diverse representation of the solid phase, encompassing graphite, nanotubes, and amorphous carbon. The study contemplates a temperature range of 100-900 °C, with a constant pressure of 1 bar and an H₂/CO₂ ratio of 4, while varying water removal from 0 to 100%. Assessing the impact of temperature on species yields, with and without water removal, revealed the thermodynamic constraints of CO₂ methanation. Results indicated that in-situ water removal could enhance CO₂ conversion, particularly at lower temperatures (<400 °C) under the evaluated stoichiometric conditions. However, increasing water removal also correlated with higher total carbon deposits. Incorporating in-situ water removal proves valuable in reducing CO selectivity, thereby enabling compliance with quality specifications for injecting synthetic methane into the natural gas grid. The findings suggested that the sorption-enhanced system could enhance process efficiency without excessive H₂ overfeeding, offering adsorption scientists and researchers valuable insights.

Keywords: Methanation; In-situ water removal; Gibbs free energy minimization.

1. Introduction

Recently, a growing focus has been put on CO₂ methanation as a viable pathway for utilizing anthropogenic CO₂ alongside hydrogen [1]. The primary product of this reaction, methane, lends itself to easy storage, providing a pathway to power-to-gas technology [2], which utilizes hydrogen produced using renewable energy.

Alongside the beneficial use of CO₂, the development of dual-functioning materials [3] and H₂O-sorption enhanced process [4] turns possible pathways for process intensification. Within this scope, the thermodynamic analysis of methanation systems has been a matter of study in an extensive literature [5,6]. Still, only a few studies [4] considered the case of CO₂ methanation with in-situ water removal by sorption-enhanced systems using Gibbs free energy minimization algorithm. Indeed, no study has explored multiple representations of the solid phase by more than one species, which is this study's main novelty.

A multiple approach for representing solid carbon formation is of crucial interest because different species, such as amorphous, graphite, and nanotubes, can form depending on the process parameters [7,8].

2. Methodology

This study obtained the equilibrium composition using the Gibbs free energy minimization methodology [9]. The first step was to obtain the optimal composition of the system for 1 bar (CO₂ hydrogenation to CH₄ is more selective at atmospheric pressure [10]), stoichiometric conditions of H₂/CO₂ = 4, and varied temperatures [5] to cover low and high-temperature cases (100-900 °C). The former results derived from the prior step served as input to recalculate the new equilibrium composition by removing a % of water formed by sorption-enhanced systems (from 0 to 99%) [11]. Therefore, the new input will be handled by manipulating the water content of the prior output



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algorithm as the other remains constant. As a result, a two-step algorithm using Gibbs free energy minimization was constructed to evaluate the sorption-enhanced system using thermodynamic data derived from classical literature [7,12].

The gaseous phase comprised the main species in methanation reaction systems: water, carbon monoxide, carbon dioxide, and methane [5]. In this work, the solid phase was considered to be formed of amorphous, graphite, and nanotube carbon, given the enhanced flexibility of the proposed algorithm rather than the stoichiometric [7].

The ideal gas law was used to represent the gaseous phase, and the Pitzer coefficient [13] was employed to calculate their fugacity coefficient, which was set to 1 for the carbon deposits.

A custom algorithm was crafted and integrated into MATLAB software. This algorithm utilizes a constrained nonlinear optimization approach, combining the native *fmincon* function with a sequential quadratic programming algorithm to minimize the objective function effectively. This choice of optimization method resulted from the presence of polynomial terms to describe the chemical potential of each compound [7]. The system composition is thermodynamically optimal when the objective function reaches its minimum.

$$G^t = \sum_{i=1}^N n_i \mu_i$$

Where G^t is the system's total Gibbs free energy calculated by the chemical potential (μ_i) of all the N species (n_i).

3. Results and discussion

Fig. 1 shows the thermodynamic equilibrium composition of CO₂ methanation at 1 bar, with the stoichiometric ratio between CO₂ and H₂ equal to 4. This is the starting point for understanding how water removal through sorption-enhanced systems could affect this reaction. The reaction is thermodynamically restricted at this feeding condition, decreasing the CO₂ conversion until 600 °C, when it reaches c.a. 80%.

Fig. 2 shows the simultaneous effects of temperature and in-situ water removal on the equilibrium conversion and yield composition for CO₂ methanation at 1 bar and the relationship of H₂/CO₂ equal 4. This study is crucial since water is one of the leading products of this reaction and can promote undesired reaction pathways. Therefore,

removing water through sorption-enhanced systems can promote or intensify the CO₂ methanation process by increasing synthetic methane production and the final stream's lower heating value.

As the increase in temperature promotes a decrease in CO₂ conversion (see **Fig. 1**), water removal can potentially increase the overall conversion of CO₂. This was experimentally observed by Desgagnés and Iliuta (2023) [14], who evaluated the CO₂ methanation reaction with in-situ water removal using a series of hydrophilic adsorbents alongside Cu/UGSO catalysts as an innovative approach to improve this conventional process restricted by thermodynamics. The hybrid materials composed of the catalyst (Cu supported in mixed spinel oxides of Fe, Al, and Mg) and 13X zeolite adsorbent were optimal at 250 °C to obtain non-negligible water adsorption and a significant reaction rate [14]. At this same temperature, relative CO₂ conversion is up to 94% higher concerning equilibrium without removing water from the medium for a feed composition of H₂/CO₂ = 3.

As can be observed in **Fig. 2 (a)** and **Fig. 2 (e)**, in-situ water removal by sorption-enhanced systems minimizes the overall production of CO. This makes the synthetic methane produced more likely to meet the specifications for injection into the natural gas grid [11].

Without water removal, at 1 bar, H₂/CO₂ = 4, and around 600 °C, the total carbon deposits are formed within the range of 0.2 mol/mol CO₂ feed (see **Fig. 1**). This amount tends to increase gradually until ~0.4 mol/mol CO₂ feed is reached, see **Fig. 2 (c)**. At the same time, at temperatures lower than 400 °C, the sorption-enhanced methanation provides increased conversion without severe coke yields; at this temperature, the conversion can be thermodynamically improved from 90% to 100%.



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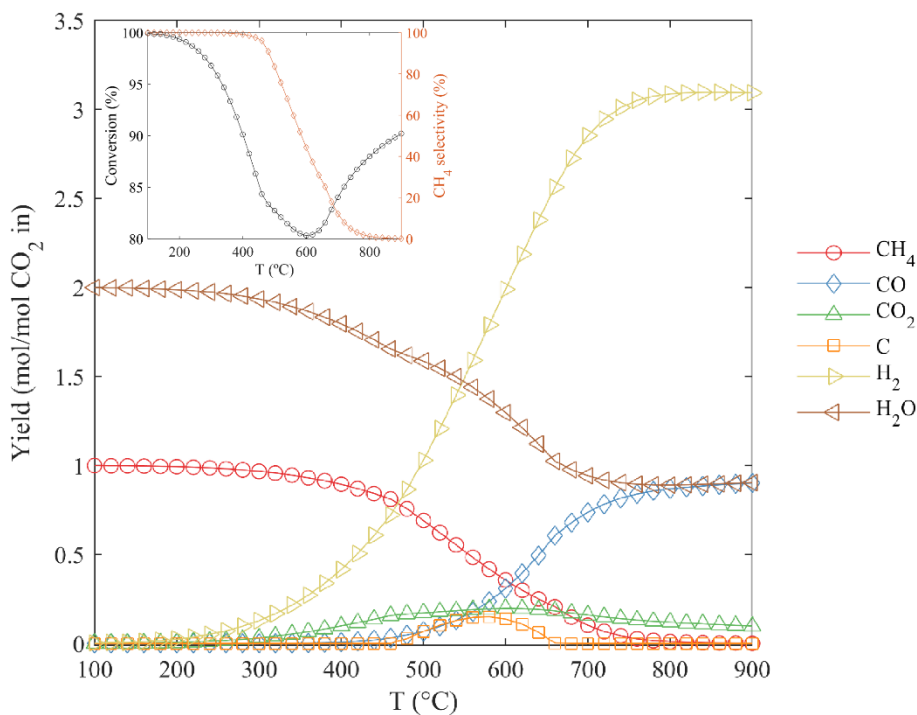


Fig. 1. Yield equilibrium thermodynamic composition of CO₂ methanation at 1 bar and H₂/CO₂ = 4 obtained by the Gibbs free energy minimization algorithm developed in this work.

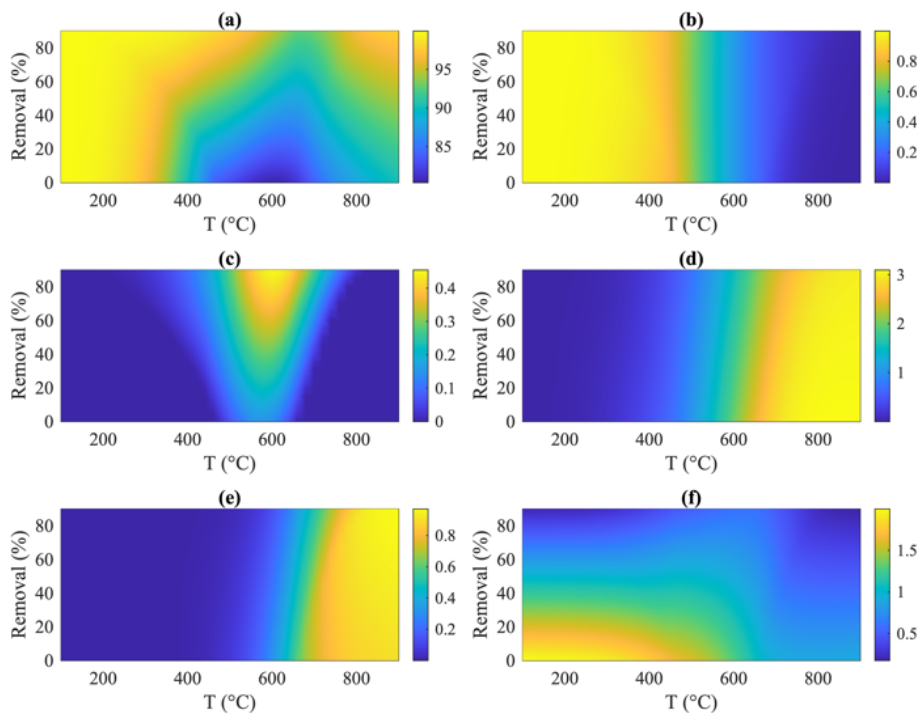


Fig. 2. Heat map of in-situ water removal impacts on equilibrium (a) CO₂ conversion (%), (b) CH₄ yield, (c) carbon deposits yield, (d) H₂ yield, (e) CO yield, and (f) H₂O yield. The H₂/CO₂ ratio was fixed at 4 and 1 bar. In (b)-(f), yields are reported as the total amount of the different species formed by mol of CO₂ feed. Carbon deposit yield is the sum of amorphous, graphite, and nanotubes.



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4. Conclusion

Removing water through sorption-enhanced systems can promote and intensify the CO₂ methanation process, although it can increase carbon deposition in the temperature range analyzed. Reducing water content in the final stream increases the lower heating value of the resulting methane, making it a more valuable and energy-dense fuel. Therefore, the increase in synthetic methane production and the enhancement of its lower heating value contribute to the overall improvement in the efficiency and effectiveness of the CO₂ methanation process.

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