

A different take on dry reforming of methane in DBD: combining sorbents and plasma for single-stage carbon capture and utilization

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In the transition to a more sustainable society, it is crucial to decarbonize the industry through electrification and carbon capture, utilization, and storage (CCUS) [1,2]. One way to reduce the overall cost is to apply single-stage CCU and circumvent process steps [3]. For example, with adsorption-based carbon capture, the CO₂ is first captured from a dilute source such as flue gas (~ 15 vol% CO₂) or direct air capture (DAC) [4]. Second, the adsorbed CO₂ is converted *in situ*, while simultaneously regenerating the adsorbent. Plasma technology is a promising candidate to realize single-stage CCU. The plasma enables the desorption of CO₂ from a sorbent and the simultaneous conversion to CO. Li et al. [5] demonstrated CO₂ capture with a hydrotalcite sorbent and plasma-based desorption and conversion in a dielectric barrier discharge (DBD) plasma reactor.

In this study, we explore the flexibility of such a plasma-sorbent system, specifically for sorption-enhanced dry reforming of methane (DRM). The combined reaction of CO₂ and CH₄ is interesting for producing value-added gas mixtures, such as syngas and hydrocarbons. In addition, variable input streams, such as biogas and landfill gas, can be easily coupled to the plasma when using a sorbent system. To the best of our knowledge, no previous research has investigated DRM with a plasma-sorbent system for single-stage CCU.

A cylindrical DBD reactor was packed with zeolite 5A pellets (size 250-355 μm) as the sorbent material and compared to non-adsorbing quartz particles as a control measurement. The sorbent selectively adsorbs CO₂ to filter CH₄, in line with the literature for zeolite 5A [6]. In the adsorption stage, CO₂ with Ar as carrier gas was fed to the reactor until the sorbent material was saturated (flow rate of 20/20 mL_n/min). To clear the lines and remove non-adsorbed CO₂, the reactor was flushed with a high flow rate of CH₄ and Ar (50/50 mL_n/min). This also ensures we only measured surface desorption and conversion in the desorption step. Finally, in the desorption step with a CH₄/Ar flow (20/20 mL_n/min), the plasma was switched on to induce CO₂ desorption. We applied a frequency of 45 kHz and a constant plasma power of ca. 30 W. The time-dependent concentrations were determined with FTIR (Agilent Technology, Cary 630). Additional samples were taken with an in-line gas chromatograph (GC, Thermo Scientific® Trace 1300) equipped with two thermal conductivity detectors and a flame ionization detector. To study the influence of water, a simple humidity meter (Extech Instruments Humidity Alert II 445815) was installed in the line.

Figure 1 presents the concentrations as a function of time during the desorption step when the Ar/CH₄ plasma is ignited. The concentrations of CO₂ and CO exhibit similar profiles, indicating that the CH₄/Ar plasma is suitable to desorb CO₂ and convert it to CO at the same time. The concentration of CH₄ drops within the initial 200 seconds, due to three primary factors: (1) CH₄ is consumed via non-oxidative coupling into higher hydrocarbons induced by the plasma, which also explains the drop observed in CH₄ concentration in the blank experiments; (2) dilution of the relative concentration due to CO₂ desorption from the sorbent into the gas phase; (3) CH₄ consumption as a result of reactions with desorbed CO₂. Due to the latter two reasons, the CH₄ concentration decreases to a lower level in the case of zeolite 5A compared to the blank experiment. Subsequently, it begins to increase and reaches a plateau, corresponding to the declining CO₂ desorption over time.

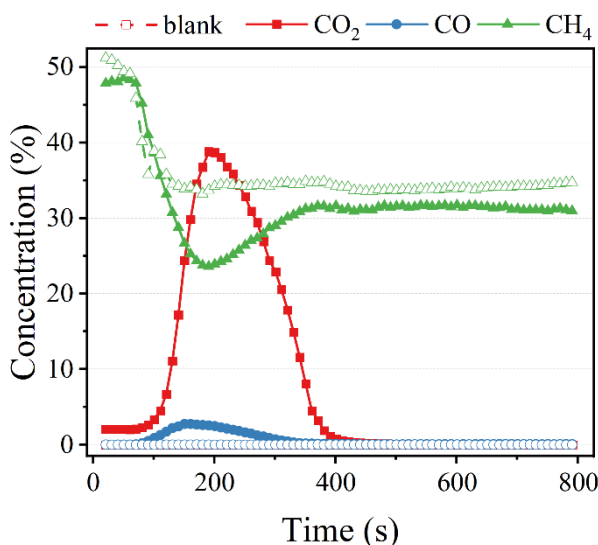


Figure 1 Concentration of CO₂, CO, and CH₄ in the outlet stream during the desorption stage when the Ar/CH₄ plasma is ignited.

Measurements with GC confirm the formation of H₂ and C₂₊ hydrocarbons, including C₂H₆, C₂H₄, C₂H₂, and C₃₊ products. Although most of these products (except CO) could also be formed by CH₄ non-oxidative coupling only, the presence of H₂O suggested possible DRM reactions. Notably, the zeolite showed potential for *in situ* removal of H₂O, shifting the equilibrium and possibly enhancing the conversion in the plasma. Material analysis revealed that the surface area and pore volume of zeolite 5A decreased after plasma exposure, caused by the carbon deposition on the sorbent. However, the material remained stable since we observed no significant morphological changes. Overall, this plasma-sorbent system is an interesting proof-of-concept for *in situ* CCU.

- [1] C. Hepburn, E. Adlen, J. Beddington, E.A. Carter, S. Fuss, N. Mac Dowell, J.C. Minx, P. Smith, C.K. Williams, The technological and economic prospects for CO₂ utilization and removal, *Nature* 575 (2019) 87–97. <https://doi.org/10.1038/s41586-019-1681-6>.
- [2] IEA Global Energy and Climate Model, (2023). <https://www.iea.org/reports/global-energy-and-climate-model> (accessed December 12, 2023).
- [3] S. Sun, H. Sun, P.T. Williams, C. Wu, Recent advances in integrated CO₂ capture and utilization: a review, *Sustain Energy Fuels* 5 (2021) 4546–4559. <https://doi.org/10.1039/D1SE00797A>.
- [4] M. Erans, E.S. Sanz-Pérez, D.P. Hanak, Z. Clulow, D.M. Reiner, G.A. Mutch, Direct air capture: process technology, techno-economic and socio-political challenges, *Energy Environ Sci* 15 (2022) 1360–1405. <https://doi.org/10.1039/D1EE03523A>.
- [5] S. Li, M. Ongis, G. Manzolini, F. Gallucci, Non-thermal plasma-assisted capture and conversion of CO₂, *Chemical Engineering Journal* 410 (2021) 128335. <https://doi.org/10.1016/j.cej.2020.128335>.
- [6] M. Mofarahi, F. Gholipour, Gas adsorption separation of CO₂/CH₄ system using zeolite 5A, *Microporous and Mesoporous Materials* 200 (2014) 1–10. <https://doi.org/10.1016/j.micromeso.2014.08.022>.