



A sorptive reactor for CO₂ capture and conversion to renewable methane



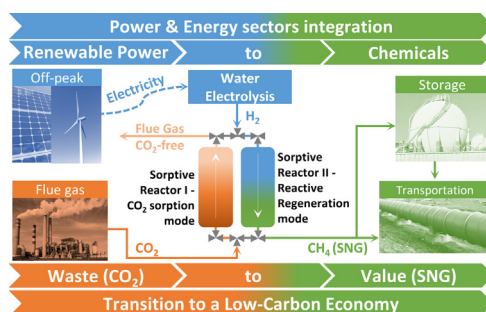
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HIGHLIGHTS

- Concept of integrating CO₂ capture and its conversion in the same unit is proved.
- A multifunctional reactor for CO₂ capture and conversion to CH₄ is tested.
- Captured CO₂ could be completely converted to CH₄.
- Reactive regeneration improves sorbent sorption capacity and desorption kinetics.
- The maximum CH₄ productivity obtained under cyclic operation is 2.36 mol/(kg·h).

GRAPHICAL ABSTRACT



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ABSTRACT

The aim of this work is to contribute for the scientific advancement of carbon capture and utilization technologies (CCU), while exploring the integration of intermittent renewable electricity production and substitute natural gas (SNG) production, the so-called “Power-to-Gas” concept. In this regard, a sorptive reactor for carrying in the same unit both CO₂ capture and conversion to SNG using renewable H₂ was studied, in a perspective of process intensification. The sorptive reactor containing a layered bed of a K-promoted hydrotalcite to capture CO₂ by sorption (step 1) and a nickel-based catalyst for CO₂ hydrogenation (step 2) is operated at 300–350 °C and low pressure (≤ 2.5 bar). Integration of CO₂ capture and conversion in the same unit leads to enhanced sorption capacities and desorption kinetics promoted by the steam produced *in situ* during the reactive regeneration stage (methanation reaction).

The sorptive reactor working under continuous operation mode allows to: i) capture *ca.* 0.30 mol of CO₂ per kilogram of sorbent and per sorption cycle, at 350 °C and $p_{\text{CO}_2} = 0.2$ bar; ii) completely convert the captured CO₂ into CH₄; iii) reach a productivity of *ca.* 2.36 mol_{CH₄} · kg_{cat}⁻¹ · h⁻¹; iv) avoid CO formation at 300 °C and 1.34 bar and v) reach a CH₄ purity of 35% at 350 °C after N₂ purge.

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1. Introduction

Curbing CO₂ concentration in the atmosphere requires considering simultaneously a diversity of approaches, such as the development and adoption of carbon capture and sequestration (CCS) or utilization (CCU) technologies, and growing policy support towards the development and penetration of energy from renewable

sources across the power market [1–3]. Regarding the adoption of end-pipe solutions for CO₂ emissions mitigation, CCU has relevant advantages compared to CCS because it avoids the (critical) cost of CO₂ transportation to a storage site and CO₂ is seen as a feedstock available at zero cost from which valuable products can be obtained [4,5].

Among the options for CO₂ utilization, its conversion to methane can offer a way to simultaneously avoid CO₂ emissions and chemically store, in the form of methane, the surplus energy from renewable sources which is produced during off-peak periods

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Nomenclature

Parameter Description, Units

C	carbon molar balance, %
E_{sorb}	heat of chemical reaction of CO ₂ with the sorbent, kJ·mol ⁻¹
F_{CO_2}	CO ₂ molar flow rate, mol·s ⁻¹
F	total molar flow rate, mol·s ⁻¹
ΔH_{sorb}	heat of physical sorption, kJ·mol ⁻¹
k_0^C	Arrhenius pre-exponential factor of CO ₂ sorption equilibrium constant through chemical reaction, bar ⁻¹
k_0^P	Arrhenius pre-exponential factor of CO ₂ sorption equilibrium constant through physical adsorption, bar ⁻¹
L	sorptive reactor length, cm
m_{ads}	sorbent mass, kg
m_{cat}	catalyst mass, kg
$n_{CO_2}^{sorbed}$	quantity of sorbed CO ₂ , mol
$n_{CO_2}^{desorbed/unconverted}$	quantity of desorbed and unconverted CO ₂ , mol
$n_i^{produced}$	quantity of carbon-containing produced species “i”, mol
p_{CO_2}	CO ₂ partial pressure, bar
P_{out}	total pressure at the outlet of the sorptive reactor, bar
$Prod$	CH ₄ productivity, mol·kg ⁻¹ ·h ⁻¹
Pur	CH ₄ purity, %
q_{CO_2}	CO ₂ sorption capacity (experimental), mol·kg ⁻¹

$q_{CO_2}^*$	CO ₂ sorption capacity (bi-Langmuir model), mol·kg ⁻¹
$q_{CO_2}^{max, C}$	maximum CO ₂ sorption capacity for endothermic chemical reaction, mol·kg ⁻¹
$q_{CO_2}^{max, P}$	maximum CO ₂ sorption capacity for exothermic physical adsorption, mol·kg ⁻¹
R	Ideal gas constant (8.314 × 10 ⁻³) kJ·mol ⁻¹ ·K ⁻¹
T	temperature in the sorptive reactor, K
t_R	time during regeneration step, s
$t_{R,f}$	duration of regeneration step, s
t_S	time during sorption step, s
$t_{S,f}$	duration of sorption step, s
X_{CO_2}	CO ₂ conversion, %
Y_{CO_2}	CO ₂ molar fraction,

Subscripts & Superscripts

i	carbon-containing species formed: CH ₄ and CO
in	inlet of the sorptive reactor
j	species N ₂ , H ₂ , CO ₂ , CH ₄ and CO
k	sorption-reaction cycle
out	outlet of the sorptive reactor
R	regeneration step
S	sorption step
z	axial position of the sorptive reactor (1–4)

[6]. This concept, also known as “Power-to-Gas”, relies on the production of H₂ making use of the excess electric power for the electrolysis of water. Further conversion of hydrogen to methane through the Sabatier reaction (Eq. (1)) is envisaged because it benefits from a well-established transmission, distribution and storage infrastructure that was developed for natural gas, a fossil fuel which consists primarily of methane in a concentration up to 70–90 mol% [7,8].



Consequently, the Power-to-Gas concept brings the possibility of connecting the power grid to the natural gas grid, thereby facilitating the integration between the power and energy sectors. Moreover, since methane is a low-carbon hydrogen carrier and produces the lowest amount of CO₂ upon combustion compared to other hydrocarbons, it provides a secure and efficient way of store and supply energy from renewable sources, while simultaneously reducing the dependence on fossil fuels and supporting the transition towards a low-carbon economy [3,6,7,9].

Direct methanation of CO₂ from flue gas has been addressed in the literature in catalytic studies using Ni-based catalysts [10] and in thermodynamic studies [11], which showed the necessity to previously separate CO₂ from other co-existent species in the flue gas, particularly O₂ (which consumes H₂) and SO₂ (that causes catalyst deactivation). Sorption-enhanced methanation processes relying on the Le Chatelier principle provide also an interesting way of producing high grade methane through the *in situ* capture of H₂O by an adsorbent (e.g. zeolite 4A) during the reaction, this way shifting the reversible Sabatier reaction (Eq. (1)) towards the products side [12,13]. However, it requires a unit for previous capture of CO₂ and its transport to the sorption-enhanced methanation reactor.

In this perspective, there is a clear advantage on integrating CO₂ capture from flue gas and its conversion in the same unit. This concept was recently addressed using a dual function material (DFM) that contains 10% of nanodispersed CaO (adsorbent) and 5% of Ru metal (catalyst) dispersed on different commercial Al₂O₃ carriers

[14]. However, the reported sorption capacity per sorption cycle (11.18 g_{CO₂}/kg_{DFM}, i.e. 0.025 mol_{CO₂}/kg_{CaO}), and CH₄ productivity (3.27 g_{CH₄}/kg_{DFM}, i.e. 7.66 × 10⁻³ mol_{CH₄}/kg_{Ru}·h) obtained during 10 cycles (T = 320 °C; p_{CO₂} = 0.075 atm; t_{cycle} = 80 min) were very low [14]. In this work, a mixed bed made of a commercial K-promoted hydrotalcite as CO₂ sorbent and a commercial Ni-based methanation catalyst were employed. This sorbent was chosen since hydrotalcites are the most suitable CO₂ sorbents at intermediate temperatures (200 °C–400 °C), showing good sorption stability under cyclic operation, reasonable kinetics and easy regeneration by pressure swing [15–21]. Besides, hydrotalcites are also cheap materials as compared to other available options (e.g. CaO sorbents). A nickel catalyst was selected because it is suitable for operation at this temperature range; moreover, Ni-based catalysts are the most widely used materials for CO₂ methanation at the industrial scale due to their good activity and lower price when compared to noble-based catalysts (e.g. Ru or Rh) [22,23]. The use of a sorptive reactor for CO₂ capture and methanation is studied assessing the performance of continuous cyclic operation, controlling the CO₂ sorption capacity, CO₂ conversion, CH₄ productivity and CH₄ purity. Given the complexity related to processes integration, the flue gas composition is simplified to CO₂ and N₂, although a pure H₂ stream is used for regenerating the sorbent, as expected to occur in real applications. Overall, this work shows the advantages of using such a reactor for CO₂ capture and utilization.

2. Experimental

2.1. Experimental setup and hybrid unit

A stainless-steel column with 15 cm length and 2.08 cm internal diameter was placed inside a tubular oven (model Split from Termolab, Fornos Eléctricos, Lda.) equipped with a 3-zone PID temperature controller (model MR13 from Shimaden). The type-K thermocouples used to measure and control the oven temperature

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