**Modelling and simulation of a sorptive reactor unit for Power-to-Gas applications featuring CO2 capture and utilization (CCU)**

Carlos V. Miguel1, Jonathan C. Gonçalves2, Alírio E. Rodrigues2, Luís M. Madeira1

*1LEPABE - Laboratory for Process Engineering, Environment, Biotechnology and Energy, Faculty of Engineering, University of Porto, Portugal; 2* *Laboratory of Separation and Reaction Engineering - Laboratory of Catalysis and Materials (LSRE-LCM), Faculty of Engineering of University of Porto, Portugal*

*\*Corresponding author: mmadeira@fe.up.pt*

**Highlights**

* The proof-of-concept of a sorptive reactor for CCU was performed.
* Process intensification improves CO2 desorption capacity and kinetics.
* A model for reactor simulation and optimization was proposed.

**1. Introduction**

Power-to-Gas concept (PtG) relies in the chemical storage of electrical energy surpluses in the form of a gas, with hydrogen and/or methane commonly considered the most suited options [1]. The electricity generated powers H2O electrolysis to produce H2 (and O2) which, in turn, can be further converted to CH4 through the CO2 methanation reaction (Eq. 1).

CO2 + 4H2 ⇌ CH4 + 2H2O Δ*H*298K= - 165 kJ·mol-1 (1)

A sorptive reactor for PtG applications able to capture and convert CO2 to methane in the same unit is presented and modeled to describe its operation.

**2. Methods**

**2.1. Experimental**

The sorptive reactor consists in a tube with *L*=15 cm and ID=2.07 cm, packed with alternating layers of a K-promoted hydrotalcite and a Ni-based catalyst with a sorbent/catalyst ratio of 3.15. A synthetic flue gas stream (15 mol % of CO2 in N2) was fed to the bed and CO2 retained by the sorbent. The sorption step ended when the feed was switched to pure H2 for the reactive regeneration step, where CO2 desorbs and is converted to CH4 (and H2O) at the catalyst layers (cf. Eq. 1). Experiments were performed at low pressure (≤2.5 bar) in a range of *T*=300-350 ˚C.

**2.2. Reactor model assumptions**

 Reactor model assumptions are: 1) ideal gas behavior, 2) axially dispersed plug flow, 3) absence of radial profiles, 4) presence of heat and mass resistances between gas and solid phases and the reactor wall, 5) CO2 sorption occurs only at the hydrotalcite material, 6) CO2 sorption equilibrium is described by the dual-site Langmuir model [2], 7) CO2 sorption kinetics described by the linear driving force model [2], 8) CO2 methanation kinetics described by the rate equation given in [3], 9) mass transfer in the radial direction of catalyst spheres is described by pore diffusion, 10) pressure drop follows Ergun equation, 11) constant porosity assumed within each layer. Model validation against experimental is ongoing and the gProms software used to solve model equations.

**3. Results and discussion**

Fig. 1a shows the CO2 desorption curves during cycle 5 and 6, where N2 or H2 were used as purge gas, respectively. Fig. 1a highlights that the desorption kinetics was faster when H2 was used (i.e. cycle 6) because the reaction of desorbed CO2 with H2 at the catalyst layers produces H2O (cf. Eq. 1), that is known for its ability to regenerate hydrotalcites [2]. Besides faster desorption kinetics, the *in situ* H2O formation leads also to the complete reestablishment of the initial CO2 sorption capacity (i.e. cycle 0 vs. cycle 7 in Fig. 1b).

a)

The proof-of-concept of the sorptive reactor concept was successfully performed; the sorbent retained 0.30 moles of CO2­ per each kg (with *T*=350 ˚C and *p*­CO2=0.20 bar), and the catalyst was able to convert 99 % of captured CO2, mostly into CH4 (nCH4/nCO≈25,000).

b)

**4. Conclusions**

The performance of a sorptive reactor for PtG applications was presented. The experimental data highlights that the CO2 capture step benefits from process intensification. Ongoing modelling and simulation work will provide the key to optimize and boost the reactor performance, while reducing the experimental effort, particularly to find the best operation conditions and bed configurations to enhance the CH4 purity at the reactor outlet and comply with the natural gas grid specifications (data not shown).

**Figure 1.** a) CO2 desorption curves during regeneration in cycles 5 (with N2) and 6 (with H2) and b) CO2 sorption capacity with cycling. *T*=350 ˚C and *P*=1.34 bar.

**Acknowledgments**

This work was financially supported by: i) Project UID/EQU/00511/2019 - LEPABE funded by national funds through FCT/MCTES (PIDDAC); ii) Project POCI-01-0145-FEDER-030277, funded by ERDF through COMPETE2020 – Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES; iii) Project POCI-01-0145-FEDER-006984 – Associate Laboratory LSRE-LCM – funded by ERDF through COMPETE2020 - (POCI) – and by national funds through FCT; iv) Project “LEPABE-2-ECO-INNOVATION” – NORTE‐01‐0145‐FEDER‐000005, funded by Norte Portugal Regional Operational Programme (NORTE 2020), under PORTUGAL 2020 Partnership Agreement, through ERDF; v) Project “AIProcMat@N2020 - Advanced Industrial Processes and Materials for a Sustainable Northern Region of Portugal 2020”, with the reference NORTE-01-0145-FEDER-000006, supported by NORTE2020, under the Portugal 2020 Partnership Agreement, through ERDF. The authors also acknowledge Clariant and Sasol for supplying, respectively, the catalyst and sorbent materials used.

**References**

1. C.V. Miguel, A. Mendes, L.M. Madeira, Energies 11 (2018) 3259-3279.
2. E.L.G. Oliveira, C.A. Grande, A.E. Rodrigues, Sep. Purif. Technol. 62 (2008) 137-147.
3. C.V. Miguel, A. Mendes, L.M. Madeira, J. CO2 Util. 25 (2018) 128-136.