MARIE SKŁODOWSKA-CURIE POSTDOCTORAL FELLOWSHIPS 2021

EXPRESSION OF INTEREST FOR HOSTING MARIE CURIE FELLOWS

HOST INSTITUTION

NOVA University Lisbon | School of Science and Technology
Associated Laboratory for Green Chemistry

RESEARCH GROUP AND URL

Bio(chemical) Process Engineering
https://laqv.requimte.pt/research/research-groups/106-bio_chemical_process_engineering

SUPERVISOR (NAME AND E-MAIL)

Fernando J.A.L. Cruz
fj.cruz@fct.unl.pt

SHORT CV OF THE SUPERVISOR

Dr. Fernando Cruz completed his PhD at Instituto Superior Técnico (Portugal, 2006) with a thesis entitled "Planetary Applications of Thermodynamics" under the supervision of Prof. Jorge Calado, after which was invited to conduct post-doctoral research at Imperial College London (UK, 2006-2008). The PI has participated in several research projects, both in Portugal (FCT/MCTES, CPCA/A2/2613/2020 (2021), UIDB/50006/2020 (2020-), UID/QUI/50006/2019 (2019), UID/QUI/50006/2013 (2015-2018), EXCL/QEQ-PRS/0308/2012 (2013-2015) and PTDC/CTM/104782/2008 (2009-2012)) and in the U.K. (EPSRC EP/D035171/1, (2006-2008) https://gow.epsrc.ukri.org). Dr. Cruz has an h-index of 13 and a track record of 41 communications presented at international conferences, 24 papers published in international peer reviewed journals and 1 invited paper, almost all of them as first and/or corresponding author; he has been a referee for international journals (*Nanoscale, J. Phys. Chem., Carbon, Phys. Chem. Chem. Phys., J. Mater. Chem. B, Coll. Surf. A*, etc.). The PI has a proven track record of collaborative work and dissemination expertise, both inside the host institution and at the national and international level where he has been a visiting scholar at the Univ. Wisconsin-Madison (U.S.A., 2010-2011) and at the Ruhr-Universität Bochum (Germany, 2003). Dr. Cruz has demonstrated excellent ability to conduct novel and independent research, in experimental physical-chemistry, molecular simulations and thermodynamics and, has published in such prestigious journals as *J. Chem. Phys., ACS Earth Space Chem., Phys. Rev. B, J. Phys. Chem. B & C, Carbon, J. Chem. Thermod. and Fluid Phase Eq.*

https://sites.google.com/site/fernandojalcruz

5 SELECTED PUBLICATIONS

[1] E.D. Sloan and C.A. Koh, *Clathrate Hydrates of Natural Gases*, 3rd ed.; CRC Press 2008.

[2] K. Ohgaki *et al. J. Chem. Eng. Jpn.* 29 (1996) 478.

[3] K.C. Hester and P.G. Brewer, *Annu. Rev. Mar. Sci.* 1 *(*2009) 303.

[4] K.A. Kvenvolden, *Terra Nova* 14 (2002) 302.

[5] F.J.A.L. Cruz, S. Alavi, J.P.B. Mota, *ACS Earth Space Chem.* 3 (2019) 789. F.J.A.L. Cruz and J.P.B. Mota, *Phys. Chem. Chem. Phys.* (2021) submitted.

PROJECT TITLE AND SHORT DESCRIPTION

CO2 Capture and Storage using Naturally Occurring H2O Ices

It is well known that CO_2 concentration in the atmosphere has surged from 280 ppm (pre-industrial level) to 387ppm today, raising major concerns regarding the corresponding greenhouse effect; such a global climate crisis requires atmospheric carbon dioxide levels to be reduced (at least) to 350 ppm. One idea currently under consideration to address this problem is the replacement of CH_4 in naturally-occurring clathrate hydrates (CHs) [1] with CO_2, in order to simultaneously combine clean energy production (methane "mining") with CO_2 sequestration and storage [2]. Favourable CHs formation conditions (high p, low T) exist over much of the margins of continental shelves (oceans) and permafrost sediments, where CH_4 is the dominating guest species, along with minor quantities of other hydrocarbons, CO_2 and H_2S. To date, more than 90 such sites have been identified, both offshore and onshore. Some estimates indicate $1-100$ Pm_3 of CH_4 at standard temperature and pressure (STP) stored in natural CHs [3], others, that the amount of such trapped methane (10000 Gt C) is twice the worldwide fossil fuel estimate of 5000 Gt C [4].

The approach seems promising because: I) the hydrate is left in its original place, reducing the risk of geomechanical failure, whilst forming a solid layer that prevents leakage of the stored gas back into the sea/atmosphere, and also II) the heat of CO_2 capture via enclathration (exothermic reaction) exceeds the heat of CH_4 hydrate dissociation (endothermic reaction), that is, CO_2 sequestration provides a heat supply for CH_4 production [2]. Nonetheless, the p–T diagram of methane CHs has a data scarcity in the region bellow 273 K, which is avoided industrially due to problems associated with ice formation; the latter is frequently responsible for pipeline blockage in the oil and natural gas industries, when explored hydrocarbons (methane, ethane, etc) react with H_2O to form plugs of solid clathrate hydrates and ice.

In order to access future industrial viability and ecological impact, the p and T equilibrium conditions of $CH_4/CO_2/H_2O$ mixtures (vapour, liquid, solid) need to be studied regarding the corresponding thermodynamical landscapes, at temperatures well bellow ice formation. Classical experimental techniques are usually rather expensive, and time consuming, owing to the cryogenic nature of the temperatures involved and the slow kinetics of the sequestration/release mechanism (~2000 USD & 1 week/data point). Necessary, nevertheless, experiments can be complemented with theoretical approaches, employing a unified framework that combines both while reducing time and funds necessary for research. Here we propose to address these issues in a self-consistent fashion, using theoretical tools derived from thermodynamics. We have already probed the empty CHs regarding their thermodynamics and mechanical features, under conditions including permafrost and deep sea-floor temperature and pressure ($T > 100$ K, $p < 5000$ bar) [5]. The next step is to expose those empty CHs to substances such as CO_2 and CH_4, and their mixtures, *e.g.*, gases which are particularly relevant in the oil and natural gas industries, and study their dynamics and equilibrium properties. The main variables to be measured/obtained include: *I)* enthalpies and potential energies, *II)* mixed hydrates substitution dynamics, *III)* overall crystalline volumes, *IV)* isobaric expansivities, *V)* CH_4 recovery rates and CO_2 storage capacities.

SCIENTIFIC AREA WHERE THE PROJECT FITS BEST*

Chemistry (CHE)
Environment and Geosciences (ENV)