HGtS – Gas Hydrates Technology

KEYWORDS: Gas Hydrates / Carbon Dioxide Capture / NETmix / Heat and Mass Transfer

Gas hydrates are solid crystalline water-based compounds that can capture gas in their lattice, allowing their use for carbon capture from syngas or flue gas. The major difficulty of hydrates-based processes is related to mass and heat transfer limitations. Using NETmix to produce hydrates drastically reduces these transport limitations, reducing the reaction time to less than 1 second (as opposed to the hours usually required), forming a slurry with a solid concentration of 20% wt. The obtained solid possesses about 18-20% wt. of carbon dioxide in its framework. Previously, it was shown that NETmix can be applied for a continuous process to capture CO2 from a gas stream using a pilot installation at LSRE-LCM. In the period of this report, this promising technology has been implemented at higher TRLs, and the research work has been done in collaboration with a collaborative laboratory between FEUP and Petrogal, the major Portuguese oil company that is exploiting the technology.

Introduction

Hydrate-based CO_2 capture (HBCC) is a process approach involving precipitation of CO_2 hydrates, concentrating large amounts of gas in solid crystals. Hydrates consist of a lattice of water that traps guest gas molecules. Gas hydrates are formed when water is in contact with a hydrate-forming guest molecule, such as carbon dioxide, nitrogen or many other hydrocarbon molecules (both gas or liquid), in favourable thermodynamic conditions, including supersaturation of the medium. The PT conditions at which hydrates are formed depend on the gas and hydrate structure but usually comprise relatively high pressures and low temperatures. Furthermore, the process of hydrate crystallisation is highly exothermic and an inefficient heat removal results in a temperature increase that slows down or hinders the production of hydrates. This is one of the major difficulties in producing hydrates since low heat transfer rates result in large reaction times and, therefore, low productivity. The continuous production of hydrates was a breakthrough that paved the way for a major contribution of LSRE-LCM to society, CoLab NET4CO2, a dedicated collaborative laboratory with Petrogal for developing carbon-neutral industrial processes with integrated carbon capture. Fig. 1 shows the vision of a neutral carbon economy based on NETmix technologies: HGTs for the capture and sequestration of carbon dioxide in a solid lattice, NET4Syn for hydrogen production from methane, and NETGtL for the production of synthetic fuels from carbon dioxide and hydrogen.

The portfolio of technologies supporting this vision requires research to adapt NETmix to the new processes, using CFD and process integration. This cooperation with NET4CO2 is explained in the Highlights topic: Industrial Process Design.

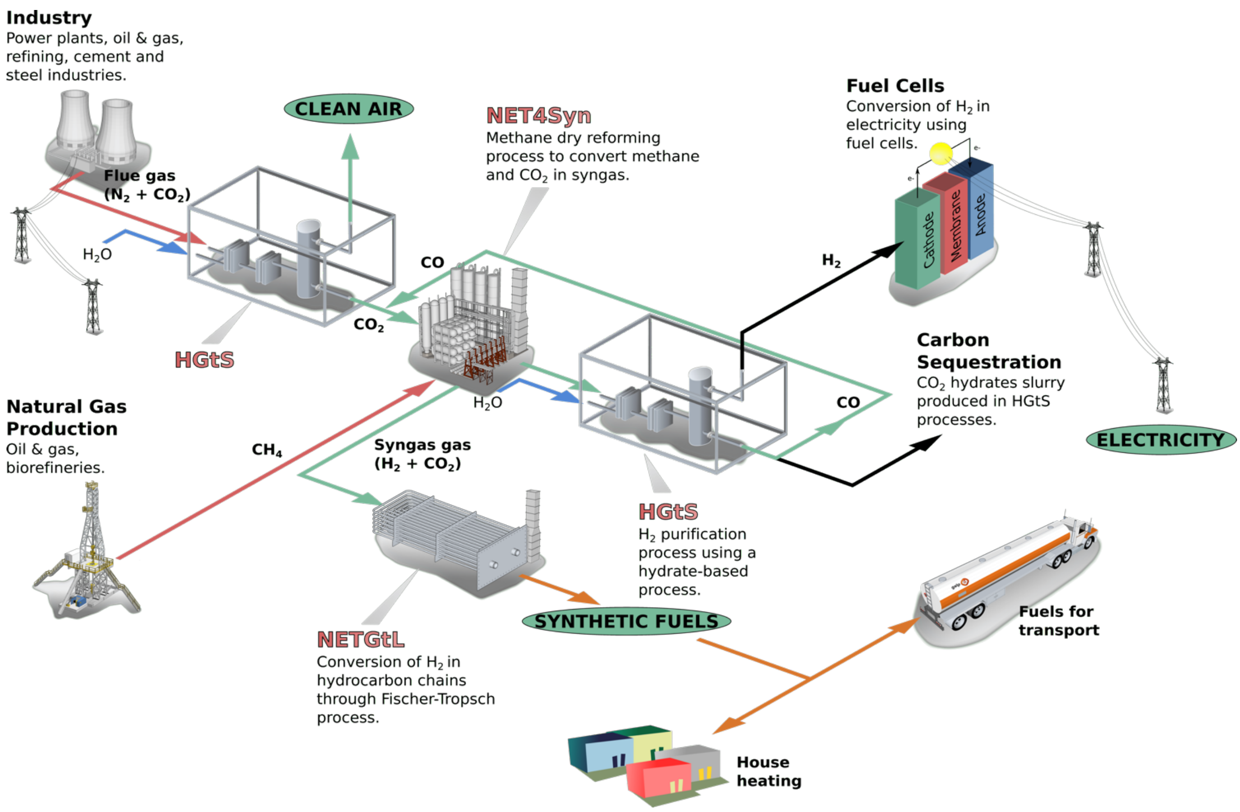

Fig 1. NET4CO2 vision of a neutral carbon enconomy from NETmix based technologies.

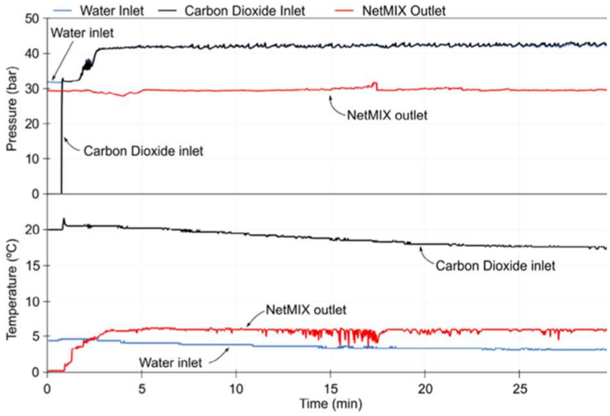

Fig 2. Dynamic data records of temperature and pressure in the pilot HGtS installation of through the continuous carbon dioxide enclathration process.

In the period of this report, the main challenge regarding the gas hydrate technology was the stable operation of the HGtS pilot unit and the search for crystallisation paths that reveal less demanding in terms of process pressure and temperature. The hydrates technology viability relies heavily on these operational conditions.

Current Development

Process simulation showed that hydrate-based Carbon Capture and Sequestration (CCS), even at an early mature level, were already competitive with the best available technologies. This justified to further development of the process and tune NETmix operation to enable long runs of continuous hydrate production without clogging. Fig 2. shows the stable operation of the HGtS pilot installation during the continuous production of CO_2 hydrates for 30 min. This breakthrough represented months of experimental work developing technical solutions to make the operation of the HGtS machine more stable. Currently, the HGtS operation runs for consecutive hours without operational hurdles. The heart of this process is mixing water and CO_2 in NETmix at a passage time of less than 2s, resulting in a space–time yield of about 200 tonne h^{-1} m^{-3} of CO2, much larger than any of the available continuous technologies. Fast crystallisation in NETmix results from its unparalleled capacity to remove heat from the medium, in addition to the chaotic laminar mixing attained in the mixing chambers, that can enable CO_2 enclathration. High CO_2 conversion rates are attained, which is clear from the very small number of gas microbubbles observed in the hydrates' slurry visualisation window at the outlet of the NETmix.

The hydrate slurry stability and CO_2 content, which are important parameters regarding the application of this technology for CO_2 transport and sequestration, were assessed. About 20% of the solid hydrates mass is composed of carbon dioxide, as determined by a gravimetric method, representing a volume reduction of about 110-fold compared to gaseous CO2 at NPT. XRD analysis was used to characterise the crystalline structure of hydrates produced in NETmix. This process produces sI hydrate, with no ice phase, when the material is dried with pressurised gas (carbon dioxide or air). CO2 dissolution experiments revealed that the overall liquid mass transfer coefficient in NETmix ranges from 1000 to 12 000 h^{-1}, which is one to two orders of magnitude larger than most of the technologies industrially used for gas–liquid mass transfer, namely, in processes based on amines for carbon capture, such as stirred tanks, or bubble or packing columns. Additionally, it is shown that when the system's pressure increases above the equilibrium pressure, the driving force of the process changes, thus allowing further dissolution of carbon dioxide that enables medium supersaturation and hydrate formation.

The showcase process designed for the technology assessment demonstrates the CO2 hydrate formation in NETmix as an industrial technology for CCS. In particular, the modular characteristic of NETmix, where production scale-up is done by increasing the NETmix network number, underlines the potential of the development of a modular process/device based on NETmix for CO2 capture, enabling the direct application of laboratory data from this work to large-scale plants. Patents were granted for this process in Europe (2021), Brazil (2022), and the USA (2023).

HGtS depends on very narrow control parameters in the NETmix (pressure and temperature) and large heat transfer rates. This is made with chillers and compressors, which make this process energy-intensive. Thermodynamic and kinetic promotors enable the widen the operation window for HGtS, resulting in large energy savings per tonne of captured CO_2. In this period, some promotors were assessed with good results, which enabled to decrease the operation pressure. Another significant result was the separation of gases with hydrates technology. One of the cases that was demonstrated was the separation of hydrogen from carbon dioxide.

Future Perspectives

The HGtS reached a high maturity level, with large pilots being constructed for on-site testing in an FSO (Floating Storage and Offloading unit) in Brazil. Further work in this field will be made to attend to specific requests from technology stakeholders.

Related Sustainable Development Goals

Outputs

Master Dissertations

[1] Francisco Dias, Gas separation via hydrate-based process: experimental, modelling, validation and optimization of a microscale HGtS unit for continuous carbon capture, MIEQ, FEUP, 2021

Patents

[1] Lopes et al., Continuous production of clathrate hydrates from aqueous and hydrate-forming streams, methods and uses thereof, EP3845290A1 (filed 2019, granted 2021), BR112022013216 (filed 2020, granted 2022), and US2023040153 (filed 20, granted 2023)

Selected Publications

[1] M.F. Costa et al., Energy Technology, 10, 2100950 (2022)
[2] M.A.L. Fernandes et al., Computer Aided Chemical Engineering, 51, 337 (2022)

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Funding

HXmeso, POCI-01-0145-FEDER-030445, 2018-2022
LSRE-LCM Base Funding, UIDB/50020/2020, 2020-2023
LSRE-LCM Programmatic Funding, UIDP/50020/2020, 2020-2023
LA LSRE-LCM Funding, UID/EQU/50020/2019, 2019
LA LSRE-LCM Funding, POCI-01-0145-FEDER-006984,2013-2018
AIProcMat@N2020, NORTE-01-0145-FEDER-000006, 2016-2019
FCT Scholarships: SFRH/BD/143958/2019 (I. Fernandes)