SORPTION ENHANCED METHANATION IN FLUIDIZED BED REACTORS

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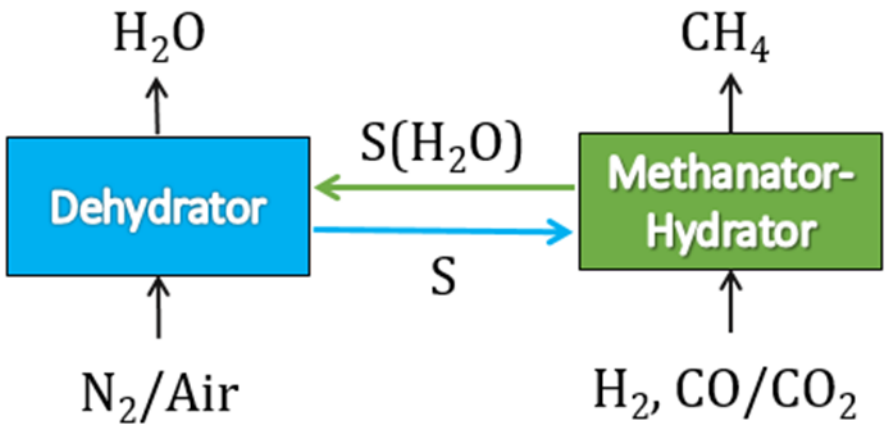
Although the climate change has become one of the most important issues of our time, the demand for energy is increasing worldwide. There are efforts to replace fossil resources by renewable energy. However, a major limitation must be overcome: its discontinuity. In order to achieve that, chemical storage seems to be the most suitable option and, in particular, there is an increasing interest towards the production of renewable methane. This is, clearly, an important energy carrier with an already developed infrastructure in many countries and a large public acceptance.
Methanation of CO_2 is known as a Power-to-Gas technology that converts surplus electric renewable energy into gaseous fuel using "renewable" hydrogen from water electrolysis and CO_2 which could be captured from industrial plants, thereby combining also a CCU (Carbon Capture and Utilization) process to the proposed Power-to-Gas solution. Similarly, CO methanation to "renewable synthetic natural gas" production consists in the methanation of syngas from biomass gasification.
Traditional methanation processes rely on adiabatic catalytic fixed bed reactors operated at temperatures up to 600°C, with intermediate cooling steps, recycles and high operational pressure. The most critical aspect is the difficult temperature control due to the high exothermicity of the reaction, with consequences also for the Ni-based commercially used catalysts, that may experience several types of deactivation.
In the last years, several research projects were directed to innovate the traditional methanation process: in particular, the application of Le Chatelier principle to shift the reaction equilibrium towards the products formation has been recently proposed through the so called Sorption Enhanced Methanation (SEM). This process involves the in-situ water removal using a suitable sorbent material and could be applied to overcome the thermodynamic limits at low pressure, which would favorably decrease the energy duty for compression work.
In order to overcome the complex industrial management of the thermicity of these reactions, fluidized bed reactors have been suggested as a possible alternative to the commercially used fixed bed ones. Through the solid-gas fluidization technique, the contact between granular solids with a gaseous stream fed from the bottom is achieved, ensuring a rapid and continuous movement of the solid and an intimate mixing of the two phases with highly efficient heat transport and rapid achievement of isothermal conditions. Secondly, the use of a fluidized bed reactor would be advantageous in a SEM process due to the ability of these reactors to easily transfer solid materials adsorbing water during steady operation.

This PhD thesis focuses on the study of a novel concept based on a chemical looping reactor arrangement where the catalytic methanation occurs simultaneously with the hydration of a sorbent in one reactor, i.e. performing SEM, while the sorbent, continuously circulated, is regenerated in another reactor.
The research activity started with the study of the behavior of selected water sorbents characterized by different sorption mechanisms: calcium oxide and commercial zeolites, giving, respectively, chemical and physical adsorption. The materials were tested during hydration-dehydration cycles at different temperatures and reaction environments relevant for methane production, investigating reaction rate, conversion and attrition which may represent a critical aspect in fluidized systems. The experimental apparatus is a specifically designed device for studying chemical looping processes and is made of two identical interconnected lab-scale bubbling fluidized beds. Moreover, still unexplored aspects, such as the thermodynamics of CO_2 methanation under SEM conditions, were analyzed by means of calculations carried out in MATLAB environment. This analysis was primarily carried out since under SEM conditions carbon formation can be much more extensive than in the absence of H_2O removal, due to the increased importance of the carbon-generating reactions, and an important target in a real plant is avoiding the catalyst deactivation due to carbon deposition.

Regarding the main paths to produce renewable methane, the research continued with a technical-economic assessment of the two main strategies considered in the study: the production of renewable methane from biomass and the Power-to-gas solution in the framework of the CCU technologies.
These two evaluated processes were of interest for the thesis project also because both relied on the Chemical Looping concept and on the utilization of the Dual Interconnected Fluidized Bed reactors arrangement in order to study the feasibility of carrying out SEM.
Aspen Plus software was used to simulate the processes and to obtain the material and energy balances. For these configurations, the Total Capital Investment, the Total Product Cost and the cost of methane were estimated.
A selective design analysis was carried out combining a full design analysis with a comparative method which estimates capital costs using known costs and performance of existing plants that use comparable technology, size and type.

In order to perform methanation, proper catalysts are being synthesized, the chosen active phase is Nickel, the metal which is mostly used for industrial application due to its good price-selectivity ratio. Several alumina supports, suitable for fluidization applications, are being impregnated with different Nickel loadings and then characterized.
Subsequently, the catalytic methanation with simultaneous hydration will be tested under different conditions. The performance indicators will be studied as a function of temperature, bed and feed gas composition.



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