SIMULATION OF A FLUIDIZED BED REACTOR FOR THE SORPTION-ENHANCED STEAM METHANE REFORMING PROCESS

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Abstract
In this work, ASPENplus was used to simulate a Sorption-Enhanced Steam Methane Reforming (SE-SMR) process in a fluidized bed reactor using a Ni-based catalyst supported on alumina and CaO particles to remove CO_2 from the reaction environment. The simulations investigated the performance of the process in terms of hydrogen purity at the outlet gas, degree of methane conversion, and hydrogen yield. The effect of the following reformer operating variables was studied: pressure, CaO/CH_4 feed ratio, temperature, and steam/methane feed ratio.

Introduction
Among the possible options for sustainable blue hydrogen production, sorption-enhanced steam methane reforming (SE-SMR) is a recent technology in which CH_4 reforming and CO_2 separation are integrated in a single reactor. The concept is based on the application of the Le Chatelier's principle, exploiting the removal of the produced CO_2 by a proper solid sorbent, to shift the reactions equilibrium towards a higher hydrogen yield. The steam reforming and CO_2 removal reactions occur in the reformer/absorber in the presence of a catalyst and a sorbent. The sorbent is then regenerated in another reactor [1]. This technology leads to a more compact process unit with the reduction of both capital and operating costs, in particular when a natural sorbent as CaO is used [1]. In the literature, steam reforming and water-gas shift reactions are reported to occur together with the in-situ CO_2 removal at temperatures between 550 and 650 °C and generally under atmospheric conditions. Fluidized bed experimental studies involving lab-scale reactors and using mostly traditional catalysts and natural dolomites as sorbents, reported outlet hydrogen concentrations up to 99 vol% on a dry basis [1]. In this work, the potential of the SE-SMR process in fluidized bed reactors was investigated, by mapping its performance through process simulations carried out with the ASPEN Plus software.

Modeling
The Aspen Plus FluidBed block was used to model the SE-SMR process in this preliminary work which was strictly focused on the sorption-enhanced effect in the reformer due to the utilization of a fresh CaO sorbent. It was chosen so far not to model the whole chemical looping configuration, i.e. the regeneration stage was not

considered in the simulations. The SMR process was modelled considering CH_4 steam reforming to CO and CO_2 and water gas shift, using the well-known Xu and Froment kinetic data [2]. As for the CaO carbonation reaction, the work of Bhatia and Perlmutter [3] was used to implement the reaction kinetics. The influence of temperature, pressure, steam to methane (S/C) feed ratio and CaO/CH_4 ratio on the process performance was assessed. Temperature was varied between 500 and 725 °C, in line with other studies [4], while for pressure a range of 1-20 bar was explored, to be close to possible industrial requirements. The S/C ratio was varied in the range 1-5. As for the molar CaO/CH_4 feed ratio, the range 0-1 was used, being negligible the effect of sorbent addition beyond the stoichiometric ratio [5]. The model results were analyzed in terms of the following performance indicators: H_2 purity (y_{H2}, dry basis), H_2 yield (η) and CH_4 conversion (X).

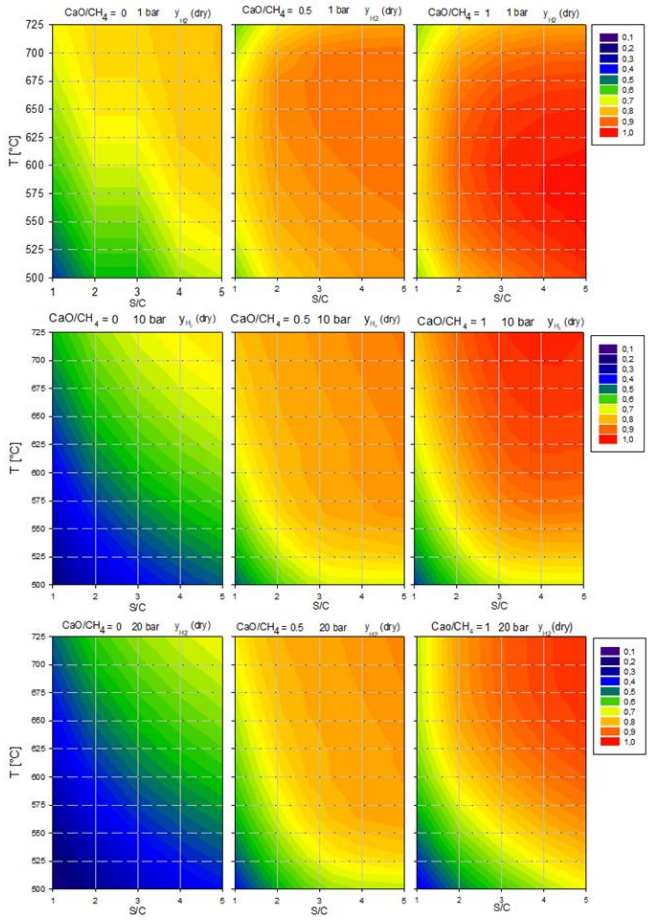

Figure 1. y_{H2} (dry basis) at varying temperature and S/C ratio, for CaO/CH_4 varying from 0 to 1 (from left to right) at three different pressures: 1 bar (upper maps), 10 bar (center maps), and 20 bar (bottom maps).

Results and Discussion

Figure 1 reports the dry H_2 concentration contour maps as a function of S/C and reaction temperature for three pressures (1, 10 and 20 bar) and for three CaO/CH_4 molar ratios (0, 0.5, 1). In general, as expected, the process showed a decrease in performance with the increase of pressure, but a clear improvement occurred, in terms of y_{H2}, X and η, when CaO was fed to the reformer due to the sorption-enhancement effect, compared to traditional SMR. However, it must be noted that the presence of CaO in the system could only partially balance the negative effect of a pressure increase. For example, when moving from traditional SMR at 1 bar to SMR at 10 bar an average decrease of y_{H2}, X and η by -16%, -44% and -41%, respectively, was recorded. However, when moving from SMR at 1 bar to SE-SMR at 10 bar only y_{H2} showed an increase by +20%, while X and η still showed a -14% and -4% decrease, respectively. Overall, under conditions less severe than in a conventional SMR process, the improvement induced by SE-SMR appears to be relevant to obtain performances of industrial interest.

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References

[1] Udemu C, Font-Palma C., "Modelling of sorption-enhanced steam reforming (SE-SR) process in fluidised bed reactors for low-carbon hydrogen production: A review", *Fuel* 340:127588 (2023).
[2] Xu J, Froment GF., "Methane steam reforming: intrisic kinetics", *AIChE J*. 35:88–96 (1989).
[3] Bhatia SK, Perlmutter DD., "Effect of the product layer on the kinetics of the CO2-lime reaction", *AIChE J.* 29:79–86 (1983).
[4] Antzaras AN, Lemonidou AA., "Recent advances on materials and processes for intensified production of blue hydrogen", *Renew. Sust. Energy Rev.* 155:111917 (2022).
[5] Luo Y, Chen J, Wang T., "Evaluation of the Effect of CaO on Hydrogen Production by Sorption-Enhanced Steam Methane Reforming" *ACS Omega* 9:5330–7 (2024).