

Sorption Enhanced Steam Methane reforming on catalyst-sorbent bifunctional particles: a CFD fluidized bed reactor model



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Simulations are presented of **Sorption-Enhanced Steam Methane Reforming (SE-SMR)** in a pilot scale fluidized bed reactor with bifunctional particles containing: CaO (sorbent), Ni (catalyst) and calcium aluminate (inert phase). A chemical model is coupled to a CFD model.

1. Introduction

Pachauri and Meyer, 2014 evaluated different approaches and scenarios to limit CO₂ emissions and global warming:

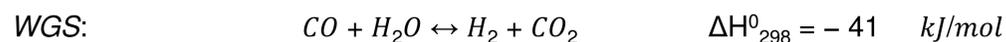
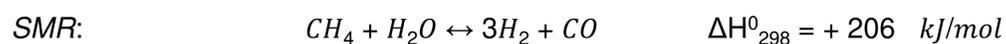
- coupling carbon capture and storage (CCS) with fossil energy sources.
- increasing energy efficiency and the use of nuclear, wind, solar, and bioenergy.

When combined together, global warming could be limited to 2°C.

Without CCS, less than half of the studied scenarios would be feasible, although 138% more expensive, on average.

Thus, CCS is critical to limit atmospheric CO₂ concentrations in a cost-effective manner.

Hydrogen is considered a clean energy carrier. It is mainly produced by natural gas reforming. Carbon dioxide generation is a necessary, undesired side effect. SE-SMR is a potential, convenient technology to reduce the environmental footprint while increasing methane conversion to hydrogen:



Conversion of CO₂ into a solid carbonate allows shifting the reversible SMR and WGS reactions beyond their conventional thermodynamic limits up to a hydrogen concentration higher than 95%.

To avoid mass transfer inter-particle resistances and allow a more intimate connection between endothermic and exothermic reaction processes catalyst-sorbent bi-functional materials were synthesized and tested (OP-IV-8).

2. CFD reactor model

The hydrodynamic behaviour of a 500 μm particle bed contained in a 250 mm ID, 2000 mm high cylindrical vessel is simulated by means of two-fluid Eulerian-Eulerian approach (Gidaspow, 1994).

The bed is composed of bi-functional particles: the calcined particles are composed of 10%wt Ni (catalyst), 60% CaO (sorbent for CO₂ capture) and calcium aluminate as inert support. The density of a completely calcined particle is 2000 kg/m³, the static bed void fraction is 0.4: the weight of the bed is about 24 kg.

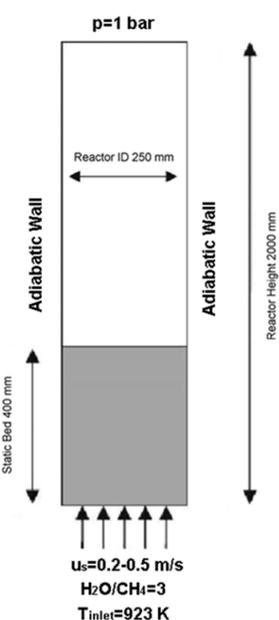
Simulations were carried out on a 2D diametric slice of the reactor.

Hydrodynamic Model (Eulerian-Eulerian approach)

- Gas and solid phases are present simultaneously in the computational volume: gas void fraction, ϵ_g ; particle solid fraction, $\epsilon_s = 1 - \epsilon_g$.
- Transport equations are solved for each phase.
- Particle phase viscosity and pressure are derived as functions of granular temperature. Particles are considered smooth, spherical, and undergoing binary, inelastic collisions.
- Granular temperature is predicted by an additional transport equation for the fluctuating kinetic energy of the particles.
- More details are available in Gidaspow, 1994.

Chemical Model

- The kinetics of SMR and WGS are described by the model of Numaguchi and Kikuchi, 1988.
- The CBN heterogeneous reaction is modelled by the *shrinking core approach* with first order surface reaction and *product layer diffusion coefficient* decreasing exponentially as a function of CaO conversion (Stendardo and Foscolo 2009).
- The bi-functional particle grain model (PGM) developed by Aloisi et al., 2016 is used to estimate overall effectiveness factors



2D-schematic view of the pilot scale fluidized bed reactor, together with boundary conditions

To estimate the carbonation kinetics, the CaO grain diameter in the PGM was set to 300 nm. In agreement with values assuring reliable simulations for TGA carbonation/calcination of the bi-functional material after 50 cycles (OP-IV-8).

Different initial carbonation conversion of the particles in the bed were considered ($X_{CaO,in} = 0 \dots 0.5$).

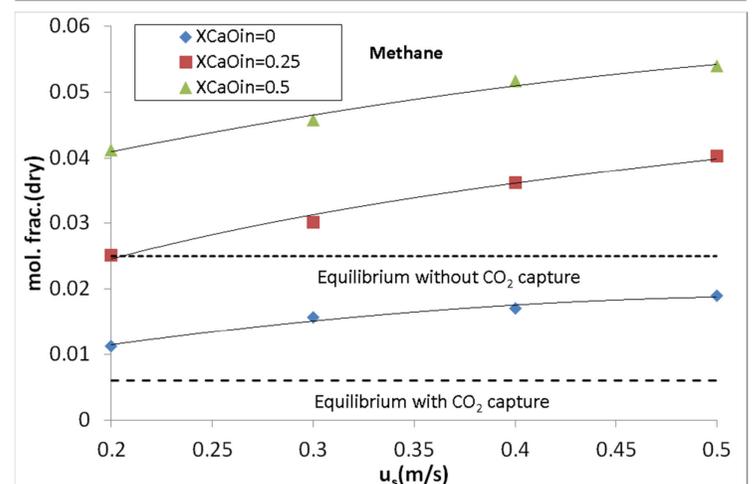
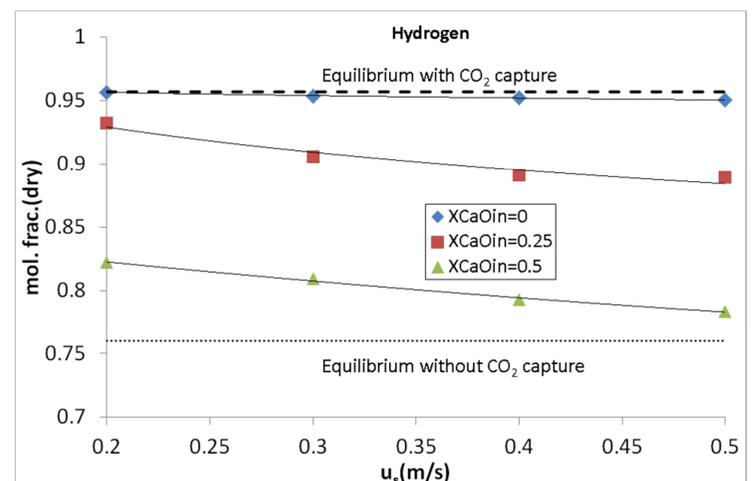
Model equations are reported in the additional sheets available below.

2.2 CFD main Inputs

Simulations are presented:

- for a static bed height of 400 mm at an initial temperature of 923 K.
- for a CH₄-H₂O feed stream with steam to carbon ratio S/C=3 and an inlet gas temperature of 923 K:
- at different superficial gas velocity (within the bubbling regime), between 0.2 and 0.5 m/s;
- The overall effectiveness factors calculated by PGM resulted close to 1 in each operating condition (>0.9) because:
 - small particle size (500 μm);
 - high particle porosity in the range of X_{CaO} considered here.

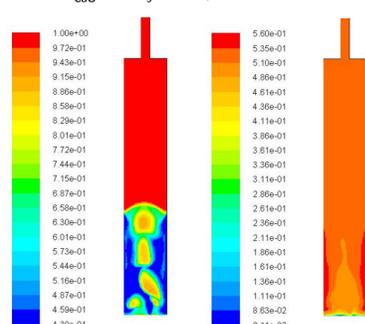
3. Results and Discussion



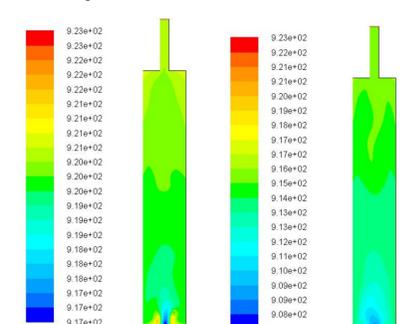
Dry molar fraction of H₂ and CH₄ at the reactor outlet at different u_s and $X_{CaO,in}$

- H₂ and CH₄ molar fractions are close to SER equilibrium (0.95 and 0.006, respectively) with a completely calcined bed.
- H₂ molar fraction is higher than 0.9 for a bed with $X_{CaO} \leq 0.25$ and for $u_s < 0.4$ m/s
- Even at $X_{CaO} = 0.5$, the hydrogen molar fraction is higher than that obtainable at equilibrium without sorption enhancement.

Void fraction and H₂ mass fraction for $X_{CaO}=0.5$ $u_s=0.5$ m/s time=13.8 s



Temperature for $X_{CaO}=0$ and $X_{CaO}=0.5$ $u_s=0.5$ m/s time=13.8 s



For $X_{CaO}=0$, T is more uniform and close to the initial value (923 K) with a better thermal balance between exothermic CBN and endothermic SMR

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