

Modeling fluidized bed reactors for thermochemical storage systems based on calcium looping.

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Highlights

- FBRs represent an interesting solution for thermochemical storage.
- Gas flow rate affects several aspects of reactor performance.
- Heat transfer, fluidization regimes, reaction time depend on gas flow rate.

1. Introduction

The significant growth in renewable energy capacity in the past few years evidences the need for energy storage technologies to integrate these intermittent sources of energy with the continuous demand from the grid. Energy storage technologies may be roughly divided into three categories: (i) sensible heat storage systems, (ii) latent heat storage systems, and (iii) thermochemical storage systems. The latter are based on gas-solid reactions characterized by high enthalpy changes to store and release energy through a cyclic process. These systems could potentially provide higher operating temperatures and energy densities, compare to other storage system [1] and provide the possibility to be coupled with concentrated solar power systems, as discussed in detail in [2]. An interesting cycle among thermochemical energy storage systems is based on the calcium looping (CaL) process (Eq. (1))



characterized by high reaction temperatures for the exothermic (calcination) reaction (650-850°C), low hysteresis, and high energy density (approximately 690 kWh/m³). In addition, it has been found that one of the main drawbacks of this process, namely its low cyclability, may be overcome by doping the material with an inert solid, such as a mayenite [3]. With regards to the rate of the process, it has been found that the calcination step is very fast in the entire temperature range of interest, whereas the carbonation step is slower. In terms of modelling, the calcination step does not therefore pose significant issues. The carbonation step has instead been described through a multigrain shrinking-core model assuming a first order kinetic reaction and a conversion-dependent diffusivity of CO₂ inside the porous CaCO₃ layer [4].

The use of fluidized bed reactors (FBRs) for these processes has been gaining significant interest because of their efficiency in heat transfer and their capability of maintaining almost isothermal conditions in the entire reactor volume. On the other hand, the operating conditions of FBRs are less flexible than traditional flow reactors because the gas flow rate needs to be chosen to achieve the desired fluidization regimes, which also depend on the density and size of the solid particles participating in the process. This entails that the identification of the adequate gas velocity is not a "one-size-fits-all" solution, but must be carried out carefully for the specific reactive system.

2. Methods

The aim of the present work has been the development of a preliminary model that may serve as a tool for the design of fluidized bed reactors applied to thermochemical energy storage reactions. More specifically, the first step consists in the evaluation of the minimum fluidization and minimum bubbling velocities through the theoretical correlations of Eqs. (2) and (3)

$$\frac{u_{mf}\rho_f d}{\mu} = 150 \frac{1 - \varepsilon_{mf}}{\varepsilon_{mf}^3} \frac{u_{mf} d \rho_f}{\mu} + \frac{1.75}{\varepsilon_{mf}^3} \left(\frac{u_{mf} d \rho_f}{\mu} \right)^2 \quad (4)$$

$$\frac{u_{mb}}{u_{mf}} = \frac{2300\rho_f^{0.13}\mu^{0.52}\exp(0.72P_{45\mu m})}{\bar{d}_p^{0.8}(\rho_s - \rho_f)^{0.93}} \quad (5)$$

taking into account typical size and density of the CaO/mayenite and CaCO₃/mayenite solid particles, i.e. the properties at the beginning and end of the carbonation step, in order to determine the range of values that these characteristic velocities may take on. Subsequently, the residence time required for the conversion of solid particles has been estimated from the results reported in [4]. Regarding the carbonation step, two conditions have been considered: (i) full conversion of CaO, and (ii) CaO conversion of 20%. This value was selected because higher degrees of conversion have been found to be achievable only after very long reaction times, as the process enters in the regime in which the rate is limited by CO₂ diffusion through the solid product (CaCO₃) layer. The model was developed under the assumption that isothermal conditions are achieved in the reactor, that the solid is perfectly mixed and that the gas is under plug flow conditions.

3. Results and discussion

The minimum fluidization and bubbling velocities at 800°C are reported in Table 1. The solid particles were considered to have a diameter of 200 μm, an apparent density of 1448 kg/m³ for the CaO/mayenite particles and of 2512 kg/m³ for the CaCO₃/mayenite particles. It is interesting to note that the gas composition, and therefore density, has very little effect on the characteristic velocities; on the other hand, the solid density has a significant effect. This means that care must be taken in avoiding significant changes in the fluidization regime as the reaction progresses. The results summarized in Table 1 were used as starting points for the design of the FBR reaction.

Table 1. Minimum fluidization and bubbling velocities under the conditions of interest

	pure CO ₂		50% CO ₂ /50% air	
	CaO/mayenite	CaCO ₃ /mayenite	CaO/mayenite	CaCO ₃ /mayenite
u_{mf} [m/s]	0.017	0.030	0.017	0.030
u_{mb} [m/s]	0.207	0.214	0.206	0.209

4. Conclusions

The design of FBRs requires the choice of operating conditions adequate for reaction time and fluidization conditions. The application of FBRs to thermochemical energy storage processes is gaining significant interest; however, the different solid materials that may be employed and, consequently, the different solid properties and temperature conditions, entail the need to design reactors specifically for the reactive system being considered. Here, a preliminary model was developed with the aim of determining the height and diameter of a lab-scale reactor to be employed for the CaL cycle.

References

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Keywords

Fluidization regimes, thermochemical storage, calcium looping.