Methanol synthesis in a fluidized bed reactor with continuous addition/removal of sorbent

R. Ciércoles, J. Lasobras, J. Soler*, J. Herguido, M. Menéndez

Catalysis and Reactor Engineering Group (CREG) - Aragon Institute of Engineering Research (I3A) - Department of Chemical and Environmental Engineering. Universidad Zaragoza, 50018 Zaragoza (Spain).
**Corresponding author: jsoler@unizar.es*

Highlights

- Catalysts preparation and characterization for methanol synthesis reaction
- Experiments in a fluidized bed reactor system
- Segregation tests with a binary mixture of solids
- Simulation of reaction with continuous addition/removal of sorbent

1. Introduction

One of the main drawbacks of the direct conversion of CO_2 to methanol is the low yield of methanol per step, due to the thermodynamic limitations in conventional reactors. Sorption-enhanced reactors (SER) technology involves adding a sorbent to the reaction medium, which removes some of the products by their adsorption from the reacting atmosphere. A wide review on reactors based in the removal of steam has been published by van Kampen et al. [1]. A recent patent [2] has proposed to take advantage of the segregation phenomenon in fluidized beds to achieve continuous feeding and removal of sorbent, and thus to operate in a steady state. This work aims to verify, using real catalyst and sorbent mixtures, the feasibility of obtaining suitable segregation of catalyst and sorbent in a fluidized bed. To this end, the flotsam/jetsam concentration profiles will be experimentally determined in a fluidized bed at several operating conditions. In addition, the feasibility of operating with continuous feeding and removal of sorbent in a fluidized bed will be verified, studying operation variables that may affect the undesired catalyst content in the sorbent outlet stream.

2. Methods

The experiments for the study of the segregation of the solids are carried out in a system that consists of a fluidized bed reactor in which a binary mixture of both, i) a catalyst for methanol synthesis, $CuO/ZnO/Al_2O_3$ (CZA) and ii) a sorbent capable of adsorbing water, SiOLITE® 13-X zeolite, is introduced in order to shift the reaction balance towards the formation of products.

Figure 1 shows the layout of the reactor scheme in which the segregation experiments is carried out. The water-saturated sorbent is removed from the "jetsam" zone while unsaturated sorbent will be introduced simultaneously from the top of the reactor, maintaining the segregation of the solids.

The tests that were carried out lasted one hour. We took samples of the solids leaving the system every 10 minutes, to analyze the amount of catalyst being lost from the bed by this stream (outlet jetsam).

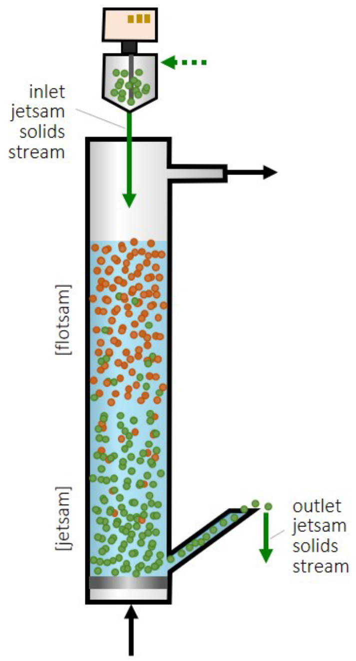

Figure 1. Scheme of the system where solids segregation studies are carried out.

3. Results and discussion

Once the u_{mf} of the binary bed had been studied, we analyzed the segregation of solids in the bed. For these tests the behavior of a 50% CZA – 50% SiOLITE® (v/v) bed mixture was experimentally checked at different nitrogen flow rates, q_0 (i.e., different u_0/u_{mf} ratios) to find the optimal segregation value, which will be the one with the lowest mixing index, *M.I.* The results obtained are shown in Table 1.

Table 1. Mixing index after binary bed segregation tests at several gas flow rates

Binary bed mixture	N_2 flow rate, q_0 (mL/min)	u_0 / u_{mf}	M.I.
50% CZA – 50% SiOLITE®	531	1.00	0.95
	664	1.25	0.55
	797	1.50	0.42
	929	1.75	0.38
	1062	2.00	0.91

The plots of the mixing index against u_0/u_{mf} is shown in Figure 2a. It can be seen that there is a minimum when working at a gas velocity around 1.75 times the u_{mf} of the mixture. That is, at those conditions the segregation will be maximum, so the rest of the segregation tests will be studied with this ratio u_o/ u_{mf}. Figure 2b shows the final solids profile obtained under these conditions.

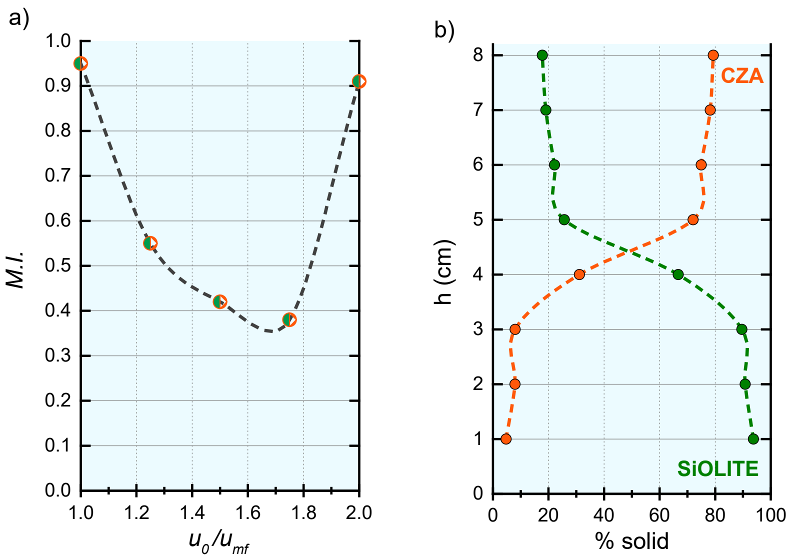

Figure 2. Results from the binary bed segregation experiments with a 50 vol% CZA – 50 vol% SiOLITE®. a) Distribution of mixing indices as a function of u_0/u_{mf}. b) Profile of solids percentage for u_0/u_{mf} = 1.75.

4. Conclusions

The study of the fluid dynamics and segregation of the catalyst-sorbent binary mixture, considered the key point in the development of the proposed concept, has been carried out successfully. Maximum bed segregation has been achieved, with a mixing index *M.I.* = 0.38. This favors the correct operation of the system with continuous addition/removal of sorbent, which, as indicated, had very few catalyst losses during the tests carried out. Indeed, under optimal conditions catalyst content in the exit solid stream less than 0.1% has been achieved.

References

[1] J. van Kampen, J. Boon, F. van Berkel, J. Vente, M. van Sint Annaland, Chem. Eng. J. 374 (2019) 1286–1303.

[2] M. Menéndez, J. Herguido, J. Soler, J. Lasobras, Reactor system for sorption-enhanced catalytic reactions with continuous regeneration of sorbent, and related methods, Europ. Patent Application EP23382685.8, (2023).

Keywords

Methanol synthesis; sorption enhanced reaction; process intensification: fluidization; segregation