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Catalytic propane dehydrogenation in a two zone fluidized bed reactor with hollow fibre palladium membrane

J.A. Medrano¹, I. Julian¹, F.R. Garcia-Garcia², K. Li², J. Herguido¹, M. Menendez^{*1} ¹University of Zaragoza, Spain, ²Imperial College-London, UK

Membrane reactors have been proposed as a process intensification method for propane dehydrogenation, increasing the conversion because the removal of hydrogen by the membrane. However the lower hydrogen partial pressure increases the rate of catalyst deactivation by coke. This adverse effect is relieved with the Two-Zone Fluidized Bed Reactor (TZFBR) [1] complementing the hydrogen selective membrane. The two zones inside the reactor allow carrying out the reaction and catalyst regeneration at same time as shown in Fig.1.

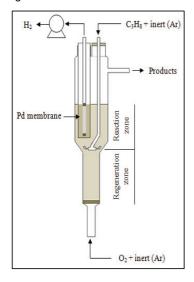


Fig.1 TZFBR + M diagram

In the TZFBR propane is fed in the middle of the bed creating a reactive atmosphere above this feed point. Simultaneously, another reactant (oxygen) is fed to the bottom of the reactor, creating an oxidative atmosphere between two feed points. Then, reaction takes place in the reaction zone and deactivated catalyst descends to the regeneration zone, in which is regenerated. A hollow fiber palladium membrane removes hydrogen and thus shifts equilibrium to products. This reactor provides a high level of process intensification (reaction, regeneration and separation in one single reactor). The TZFBR has been previously tested in propane dehydrogenation using a Pt-Sn/Al₂O₃ catalyst, but it had a high coke formation tendency [2].

In this work Pt-Sn/MgAl₂O₄ catalyst has been employed, which has the advantage of lower coke formation than Pt-Sn/Al₂O₃ [3]. We compared the performance of TZFBR with a traditional fluidized bed reactor and the TZFBR with membrane. In addition, two different sections were employed to optimize the feed flows in each feed point, because the oxygen flow necessary in regeneration zone is smaller than the propane flow in the upper zone.

Oxygen flow in the regeneration zone was optimized, because if it was larger than the optimum, oxygen reached the reaction zone and combustion between propane and oxygen happened causing an important decrease in propylene selectivity. On the contrary if the oxygen feed flow was less than the optimum, it was not enough to regenerate the deactivated catalyst in the regeneration zone and the coke accumulation caused a continuous decrease in propane conversion.

The comparative results between the three different reactor types are shown in Fig.2. In a traditional fluidized bed reactor catalyst deactivation is very pronounced due to coke deposition and conversion decreased along the time. With the TZFBR this limitation was solved, because catalyst was continuously regenerated in the regeneration zone inside the reactor, which not only solves this problem, also provides heat by coke combustion to the endothermic propane dehydrogenation reaction. Finally, palladium membrane allows removing hydrogen from the reaction zone, thus shifting the thermodynamic equilibrium to products. This action increases propylene yield in comparison with the TZFBR and traditional reactors. Additional experiments were carried out employing other reaction temperatures and longer reaction times.

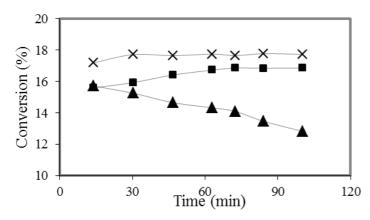


Fig.2 Propane conversion with different reactors: (\blacktriangle) Traditional fluidized bed reactor; (\blacksquare) TZFBR; (\star) TZFBR + M. T_R = 500°C; W_{cat}/F_{C3H8}= 20.1 kg·s/mol

In conclusion, two features for process intensification have been integrated in this work: Firstly, adding a selective hydrogen membrane to the TZFBR improves propylene yield; secondly, the TZFBR provides an important improvement with respect to traditional reactors, because reaction and regeneration take place in the same physical space and maintains the steady state because catalyst deactivation is counteracted by continuous regeneration inside the reactor.

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