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TWO-ZONE FLUIDIZED BED REACTOR (TZFBR) AS A POTENTIAL TOOL FOR PROCESS INTENSIFICATION IN CATALYTIC REACTIONS

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ABSTRACT
The state-of-art of Two-Zone Fluidized Bed Reactor (TZFBR) technology is here reviewed. TZFBR potentials and hurdles are discussed. Recent advances in the TZFBR field and some experimental applications in gas-solid catalytic reactions are presented. These examples illustrate the reactor performance in processes where catalyst coking represents a thread for the process feasibility and in catalytic oxidations where the separation of the catalyst oxidation and the catalyst reduction can provide some advantage.

1. INTRODUCTION

Process intensification in chemical engineering aims to optimize safety, benefits, capital or energy costs by reducing the chemical plant size [1]. In this frame, the Two-Zone Fluidized Bed Reactor (TZFBR) represents a potential tool for process intensification in the field of heterogeneous catalysis since its design provides two simultaneous processes in one piece of equipment. In particular, the TZFBR has been proved to be effective to carry out gas-solid catalytic reactions where the catalyst suffers from fast deactivation due to coke deposition and those catalytic oxidations where the catalyst can be used as oxygen carrier [2].

Traditionally, processes that involve catalyst reduction and further regeneration (oxidation) are carried out in subsequent steps in a single unit or in different reactors. This is the basis of the circulating fluidized beds that have been implemented at industrial scale for fluid catalytic cracking, light alkanes dehydrogenation or catalytic butane oxidation [2]. In other cases, like the Houdry Catadiene^{TM} process, the two steps are carried out in the same unit, but separated in time [3]. The advantages of separating the red-ox steps include process safety and selectivity improvement and abetter control of the catalyst oxidation degree [2]. The separation of the two process steps avoids the risk of explosion since the gas hydrocarbon and oxygen are not mixed in a single vessel. Furthermore, undesirable reactions promoted by oxygen can be avoided. The cons of these systems are related to the control of the solid flow in the catalyst circulation and the need to carry out periodic red-ox operation, which leads to unsteady-state processes [2].

With the aim to offer process alternatives that keep the advantages of the above-mentioned traditional processes but being able to reach a steady-state operation and reduce size and energy resources, our group has been developing during

the last two decades the so called 'Two-Zone Fluidized Bed Reactor' (Figure 1.a). This reactor consists of a fluidized bed with a fractionated gas inlet. The oxidizer agent, e.g. diluted oxygen, is fed through the lower catalytic bed entrance whereas the reactant hydrocarbon enters the bed at an intermediate point of it [2]. Therefore, two different atmospheres (reactor zones) are induced inside the single vessel: the hydrocarbon oxidation (or catalyst reduction) takes place within the upper bed region whereas the catalyst re-oxidation (or 'regeneration') occurs within the lower bed zone. The solid circulation inside a fluidized bed, caused by bubbles, provides the catalytic process integration by transporting the catalyst between both zones. This allows a steady-state operation without net catalyst deactivation in reactions with coke formation or the separation of the reduction and the oxidation steps in catalytic oxidations.
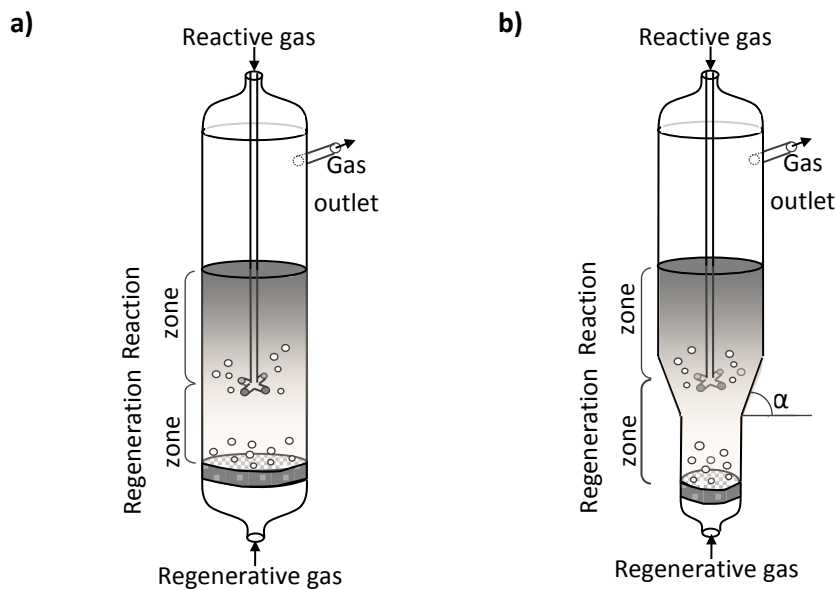

Figure 1. a) TZFBR reactor scheme, b) TS-TZFBR reactor scheme

The main advantages of the proposed reactor model are compactness, ability to reach a steady-state operation and reduction of energy consumption in comparison to traditional units [2]. In case of catalytic reactions affected by coking, the catalyst behaves as a heat carrier, since the heat needed to perform endothermic hydrocarbon conversions (e.g. alkane dehydrogenation) is partially provided by the coke combustion in the lower zone of the TZFBR.

Two critical issues concern the proper TZFBR performance: the fact that the oxygen flow must be consumed in the downer bed zone before reaching the upper region and the fact that the hydrocarbon back-mixing related to the solids mixing must be avoided. The first issue implies that the need to select the most suitable oxygen flow for each reaction condition. The second one deals with the need to control the fluid dynamic regime in every bed region separately. Both issues will be discussed in sections 3 and 4 respectively.

2. TZFBR APPLICATIONS
The proposed reactor configuration has been found to be especially useful to

perform reactions where the catalyst suffers from a fast deactivation due to coke deposition over the catalytic active surface or where a red-ox process takes place, using the catalyst as oxygen carrier between regions with different atmospheres. Some lab scale results of catalytic reactions performed in TZFBR are discussed below.

2.1 Catalytic oxidations

Several oxidative processes of interest have been tested to evaluate the behavior of the TZFBR carrying out simultaneous red-ox catalytic reactions. In a first step, a TZFBR system was applied to the oxidative coupling of methane [4 – 5]. This reaction towards ethane and ethylene resulted in a great interest during the decade of 1980s to make use of natural gas sources. Its main limitation is that reaction products are more reactive towards oxygen than methane. Experimental studies showed that the TZFBR concept was suitable to achieve stable operation with a low oxygen concentration in the reaction zone, using the oxygen transport capabilities of the catalyst.

Once proved that catalytic oxidations could have been carried out within TZFBR in the absence of gas phase oxygen, further target processes as oxidative dehydrogenation of butane and propane were performed at lab scale [6 – 9]. Alkanes dehydrogenation face several process limitations such coking, high endothermicity and low conversions at moderated reaction temperatures (thermodynamic equilibrium limitation). The use of a TZFBR provided a steady-state operation with increased selectivity to alkenes and, particularly, to butadiene which represents the most valuable product [7]. The oxidative butane dehydrogenation was even implemented at larger scale showing promising results when working with V/MgO based catalysts [10]. Catalyst deactivation problems were not observed after hundreds of hours of operation [10].

Butane was also the raw material to produce maleic anhydride via catalytic oxidation in the presence of VPO catalyst [11 – 13]. In this case, the use of a TZFBR allows working at higher butane-to-oxygen rates than the ones employed industrially in fixed bed reactors, which must be kept very low to avoid explosive mixtures. For high butane concentration, the TZFBR system leaded to higher yield and selectivity to maleic anhydride than the fixed bed reactor, while preserving similar butane conversions [11].

2.2 Catalytic reactions with catalyst deactivation by coking

Two catalytic reactions that lead to a fast catalyst deactivation due to coke deposition over the active catalytic surface have been studied in the last decade: a) methane aromatization, which is a quite new gas-to-liquid (GTL) conversion method, b) olefins production by means of light alkane (propane and butane) dehydrogenation.

Methane aromatization represents a challenging catalytic reaction that could improve the natural gas exploitation in remote sources. The purpose is to produce liquid BTX aromatics from CH_4 in order to ease the fuel transportation, freeing hydrogen that can be used as a clean energy source. Process limitations include catalyst coking, non-aromatic byproducts formation and low conversions at common operation temperatures (700ºC - 900ºC) [2, 14]. By using a lab scale TZFBR configuration with an on purpose zeolite based catalyst and low spatial

velocities, the above limitations could be strongly reduced, improving the this process feasibility. Experimental studies show how the system stability without deactivation can be achieved during hours and, furthermore, how the yield to benzene reaches values among the best reported in literature [14].

Catalytic alkane dehydrogenation represents an alternative method to selectively obtain light olefins. This process, that has been largely studied, has to face challenging limitations such as conversion limited by the thermodynamic equilibrium, the high endothermicity or the fast catalyst deactivation due to coke deposition over the catalytic active surface. Many efforts have been focused on obtaining a suitable catalyst that provides high selectivity to olefins and low tendency to coke formation [15 – 18]. The use of a TZFBR represents here an attractive system to overcome the process limitations [19]. On the one hand, this reactor configuration allows the in-situ catalyst regeneration via coke burning leading to a dynamic equilibrium between coke deposition and coke removal and avoiding the conversion decrease along the time on stream. On the other hand, the exothermic coke combustion generates a part of the heat needed for the endothermic dehydrogenation [16]. As previously discussed, the oxidizer concentration depends on the amount of generated coke within the reaction bed zone. The percentage of oxygen in the feed needed to reach full coke burning without alkane combustion depends on the reaction temperature, gas velocity and alkane concentration [2, 16]. By varying that percentage, the olefins production can be optimized avoiding net catalyst deactivation [20].

Both propane and butane dehydrogenations have been widely studied in different TZFBR configurations [20 – 23]. The experimental results improve those obtained at industrial scale (e.g. Oleflex semi-continuous process for propane dehydrogenation: S_{C3H6} = 90%, x_{C3H8} = 20%) and those performed at lab scale in other reactor configurations (Figure 2) [20].
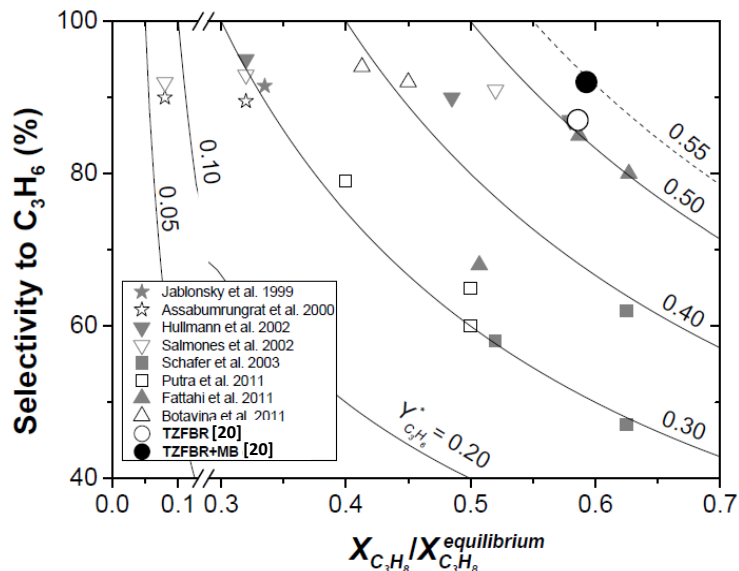

Figure 2. Performance of TZFBR and TZFBR+MB in comparison with results from literature. Diverse operating conditions [20].

3. REACTOR IMPROVEMENTS: TWO-SECTION TZFBR AND MEMBRANE REACTORS

Ongoing improvements to the TZFBR will be described in this section. All of them aim to achieve a better reactor performance, in one case by modifying the reactor shape and in the second case by including an additional element.

3.1. Two section TZFBR

A novel TZFBR configuration that incorporates different cross-sectional areas between zones has been recently proposed (Figure 1.b). This reactor emerges from the need to solve a fluid dynamic issue of the prior straight-column TZFBR: the gas flow needed in the regeneration section was much lower than that needed in the reaction section. The so called 'Two-Section Two-Zone Fluidized Bed Reactor' (TS-TZFBR) has been developed to control the bubbling regime and the solid circulation within the two bed zones separately [24]. The transition region geometry that connects the different bed cross-sections has a conical form, which angle has to be designed in order to avoid defluidized regions over the section change. The upper gas distributor location with respect to the transition section represents, thus, a new process variable to be considered [24]. Catalytic processes in TS-TZFBR provide higher gas-solid contact time in the reaction zone and low regenerative flows when required. Moreover, this configuration reduces the probability of finding gas-phase oxygen in the upper zone [14, 20].

3.2 Membrane TZFBR

New research efforts deal with a further process intensification coupling dense Pd based membranes and TS-TZFBR in order to remove hydrogen from the reaction media. This solution could move dehydrogenation thermodynamic equilibriums towards olefins production [20, 22], but coking effect would be enhanced by removing H_2 (e.g. [25 – 26]). This problem is solved in the TS-TZFBR system thanks to its in-situ regeneration characteristic. The membrane-integrated TS-TZFBR (M+TS-TZFBR) has been successfully applied to the propane dehydrogenation process. Excellent system stability and an increase in the yield to propylene have been experimentally achieved (Figure 3, black point). This new M+TS-TZFBR concept represents a dual process intensification system and further studies are now in progress to extend its application to other processes.

4. REACTOR MODELLING

Parallel to experiments on catalytic reactions of interest, the optimization and design of reactors needs to model and understand the fluid dynamic behaviour of the developed reactor, as well the kinetics of the different performed reactions.

The first steps to describe the solids axial circulation in a TZFBR were based on the 3-phase model suggested by Kunii and Levenspiel that considers three different phases within a bubbling fluidized bed: bubble, wake-cloud and emulsion. The upward wake velocity was assumed to be the same as the velocity of gas bubbles (u_b). Other model parameters such ascending solid fraction (f_1) or wake-emulsion solids transfer rate (k_w) were estimated from existing correlations [6, 27]. The gas-solid reaction kinetics was defined for each process from literature measurements [15, 17, 28].

In order to understand the solid axial mixing, fluid dynamic measurements have been recently conducted in cold pseudo-2D reactor facilities [24]. Both the gas bubbles hydrodynamics and the particles circulation have been studied by means of optical measuring techniques. Particle Image Velocimetry (PIV) has been used to describe the solids movement and to detect defluidized regions and preferential circulation paths. Optical tracers (phosphorescent particles) have been used to quantify the solids axial mixing between reactor zones. Gas bubbles have been detected and measured after image post-processing and image contrast enhancement to perform hydrodynamic statistical analysis concerning size distribution (Figure 3), aspect ratio, velocity or bubbling frequency. A new non-parametric bubble size correlation describes the hydrodynamic behaviour inside a TS-TZFBR as a function of the transition section angle, upper gas distributor position and gas velocity. The hydrodynamic data have been related to solids mixing and circulation results gaining insight into the fluid dynamics of a TS-TZFBR in order to optimize the reactor design.

CFD simulation studies based on the Eulerian-Eulerian model for multiphase flows have been recently performed to predict the fluid dynamic behavior inside the TS-TZFBR in different fluidization conditions. Simulations are in reasonable agreement with experimental results in terms of bubbling behavior (Figure 3) and defluidized regions detection. These results confirm that computational simulations represent a powerful tool for the scale-up of TZFBR.
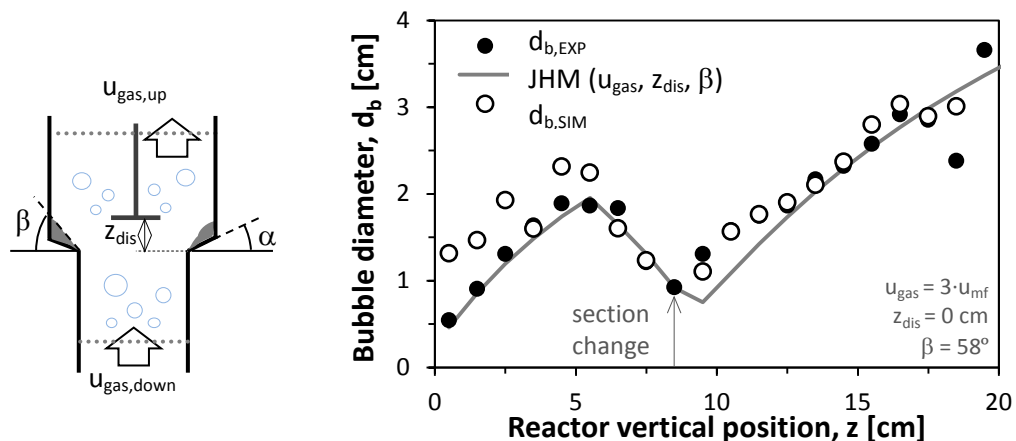

Figure 3. a) TZFBR bubbling set up, b) Comparison between experimental, simulated and modeled bubble size evolution for certain fluidization conditions

5. CONCLUSIONS
The TZFBR represents an interesting alternative system to face some process limitations in a wide range of heterogeneous catalytic applications. This reactor has been successfully tested in several alkane dehydrogenations, as well as in selective oxidation systems, reforming and aromatization reactions. In all cases, a steady-state operation has been achieved without net catalyst activity decrease along the reaction time and in a single multipurpose vessel. As an alternative for certain industrial processes, the TZFBR technology would report system compactness, savings in energy consumption, great stability (i.e. savings in catalyst replacement and reactor maintenance) and safety. Nevertheless, the

development of reliable scaling-up methods is necessary before this reactor might be employed at industrial level.

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