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Advances and trends in two-zone fluidized-bed reactors

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Two-zone fluidized bed reactors, devices to carry on two reactions in a single reactor, have been widely studied in our group. This work summarizes the developments achieved after a previous review published in 2005 and shows how this technology can be applied in a wide variety of reactions. The advantages for each kind of process are discussed, as well as several proposals for improvement of the reactor aimed to achieve new functions or to improve the process performance. Finally, the possibilities of this kind of reactors at industrial scale are discussed.

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Introduction

A two-zone fluidized bed reactor (TZFBR) is a device in which two chemical reactions are made simultaneously: one of the reactions is carried in the upper zone and other reaction in the lower zone. The formation of two zones with different reaction environment is achieved by feeding two streams with different composition, one of them to the bottom of the fluidized bed and the other to an intermediate point of the fluidized bed. The difference with the conventional fluidized bed reactor is shown as the comparison of Figure 1a,b. The gas bubbles, as is usual in fluidized beds, transport solid between the two zones, in such a way that each particle alternatively remains some time in each zone. Although other systems have been described in literature where there is a transport of solid between fluidized beds, as reviewed in Ref. [1], the TZFBR is different because it creates two zones, making a different reaction in each zone, in a single vessel.

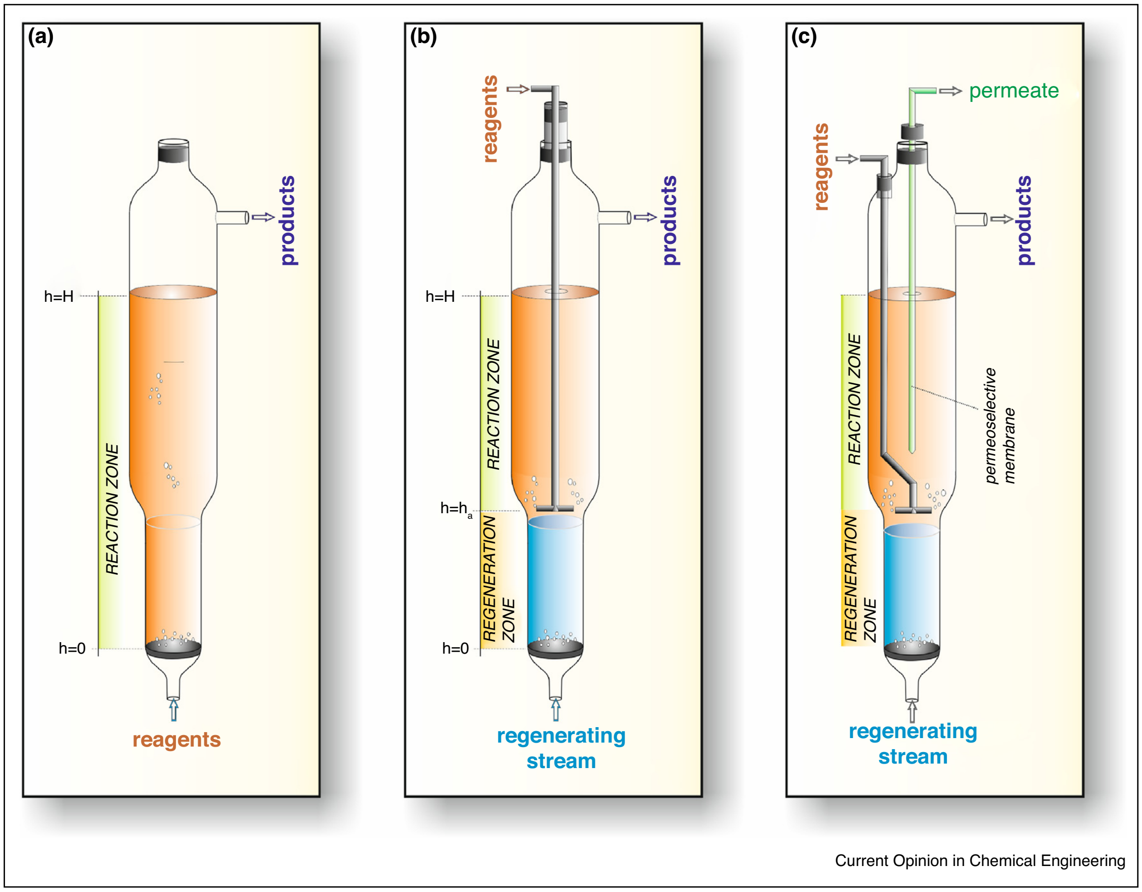
In a previous review [2••] we presented the developments made in our group in the field of TZFBRs. The different kinds of reactions to which the TZFBR was applied, as was described in that review, are shown in Table 1. These reactions can be divided in two groups: (a) Reactions in which the catalyst acts as oxygen carrier, for example oxidative coupling of methane. In that case the catalyst is oxidized with oxygen in the lower part of the reactor and the catalyst transports oxygen in the crystalline lattice to the upper part of the reactor, where a desired catalytic oxidation is carried out using the oxygen from the solid structure (thus reducing the solid). (b) Reactions in which the catalyst is deactivated by coke during the desired reaction, for example alkane dehydrogenation. In that case the catalyst is regenerated by an oxidizing gas in the lower zone of the reactor. The catalyst transports coke from the reaction zone to the regeneration zone.

The articles included in that revision showed how the use of a TZFBR can provide significant advantages over conventional reactors. In some cases it was possible to counteract the catalyst deactivation and achieve steady state operation in the TZFBR, while conversion continuously decreased in a conventional reactor. In other cases the TZFBR allowed the operation with higher oxygen/hydrocarbon ratio than a conventional reactor with cofeeding of reactants, because it avoided the premixing of reactants that could generate explosive mixtures. In some cases the TZFBR provided higher selectivity to the desired product for a given degree of conversion than the conventional reactor.

The modelling of this type of reactors was started using a simple mathematical model [3] based on the Kunii–Levenspiel model [4] for fluid dynamics of fluidized beds, but accounting for the reaction kinetics for the main reaction, the catalyst deactivation, the kinetics for the coke removal and the solid transport between the reaction and the regeneration zones.

Although most of the work in TZFBR has been developed at the University of Zaragoza, several groups have started to test this kind of reactor and have confirmed that the TZFBR can sometimes provide advantages over conventional reactors. Talebizadeh *et al.* [5] have shown the use of this reactor for oxidative coupling of methane. These authors found improved selectivity to the desired products in the TZFBR over the conventional reactor. This is interesting because in our previous work [6] such improved selectivity was not achieved with another catalyst, although it was possible to have separate zones for the catalyst oxidation and the oxidative coupling reaction.

Figure 1



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FBR **(a)**, TZFBR **(b)** and TZFBR + MB **(c)** configurations.

Also Rischard *et al.* [7,8] have found that with one of the tested catalysts the TZFBR provides improved selectivity in oxidative dehydrogenation of butane to butadiene. It is remarkable that the improved selectivity was not obtained with all the tested catalysts, which shows the need to test for each specific application and catalyst if the TZFBR improves the yield to the desired product. Finally, the use of TZFBR has also been proposed [9] for the decomposition of maleic anhydride.

The next section will show the developments made by our group in the field of TZFBR, both checking the feasibility of its use in new reactions and reactor configurations, and in new contributions to the modelling of this kind of reactors.

Recent developments

New reactions

Methane steam reforming

Methane steam reforming (MSR) is currently the main industrial process for hydrogen production. Coke formation may be a problem in this process if it operated with low steam/carbon ratio. Although some procedures have been proposed to reduce carbon formation [10,11], the

Table 1

First developments on fluidized bed catalytic reactors where reduction and oxidation zones are present simultaneously [2••]

Reaction	Catalyst	Main finding	Reference
Oxidative coupling of methane	MnP/SiO_2	Separation of oxidation and reaction zones	[6]
Oxidative dehydrogenation of butane and propane	V/MgO	Increased butadiene yield	[46]
		Confirmation in larger diameter reactor	[47]
Oxidation of butane to maleic anhydride	VPO	Feasibility of operation with high butane content in the feed	[48]
Dehydrogenation of propane	Cr_2O_3/Al_2O_3	Stable operation	[49]
Dehydrogenation of butane			[50]