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Pre-saturation in multiphase fixed-bed reactors as a method for process intensification/reactor minimization

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Abstract

The pre-saturated-one-liquid-flow (POLF) technology, in which multiphase reactions are carried out over a stationary (fixed-bed) catalyst in the presence of a single liquid phase previously saturated with gas, permits a significant increase in the reactor productivity (in some cases up to 100 times). The POLF technology can provide an exceptional decrease in the size of newly constructed plants as well as a remarkable enhancement of production by revamping the existing trickle-bed or bubble column reactors.

Keywords: POLF technology; Pre-saturation; Process intensification; Multiphase catalysis; Fixed-bed catalyst; Stationary catalyst

1. Introduction

Three-phase reactors with a stationary catalyst including trickle-bed, bubble column and multitubular reactors (TBR, BCR and MTR) are often encountered in industry in such multiphase catalytic processes as hydrogenation, oxidation, and hydrotreatment of refinery streams. In these reactors, different modes of gas and liquid flow and different interaction regimes between gas and liquid phases (co- and counter-current modes, film, pulse, bubbling flow, etc.) can be performed. Despite the complex pattern of hydrodynamics and physical and chemical processes, these reactors have the following common features: (a) the necessity of the heat removal; (b) the demand of intensive gas–liquid–solid mass transfer; (c) the requirement of the admissible, appropriate pressure drop. In many industrial applications, in order to satisfy criteria (a) and (b), the reactors are operated under conditions of gas recycling through the catalyst bed. To provide the permissible temperature and effective mass transfer, an enormous quantity of gas should pass through the reactor. For example in hydrogenation processes, the excess of the recycled hydrogen can be 400 times more than the need for the reaction itself, resulting in the consumption of a tremendous amount of energy [1].

To compress such great volumes of gas through the reactor, pipework, heat exchangers and other equipment installed on the gas loop, huge recycling gas compressors are used. Generally, the pressure drop that can be overcome by the existing industrial compressors is limited by 10–15 bar. This imposes a significant restriction upon the particle sizes that should be more than 1 mm (as a rule 3–5 mm), which in turn constrains the use of the full potential of the most active catalysts because of the intraparticle diffusion limitation.

One of the specific problems inherent in exothermic processes is a very high probability of runaways when the control system cannot cope with a sharp temperature increase. In some cases, such behavior can occur without any perceptible reason or malfunction of the process control and can sometimes lead to a damage of equipment and even to heat explosion.

It is especially necessary to note that in the framework of the existing three-phase reactors, it is impossible to enhance reactor productivity by several times. Any attempt to intensify the process by the more violent interaction of gas and liquid (intensification of gas–liquid–solid mass transfer) or by the utilization of small catalyst particles (increase in both catalyst effectiveness and mass transfer) will lead to such a pressure drop and to such an energy demand that can never be realized in industry [1].

Over the past decade, many attempts have been undertaken to make the conventional TBR and BCR operate more efficiently (e.g. [2]). The main method for process intensification is the

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periodic modulation of the liquid feed that can lead to a 50% growth in productivity [3].

In this paper, the comparatively new, so-called pre-saturated-one-liquid-flow technology (POLF) is presented. In this technology, only the liquid phase goes through the reactor, but this liquid phase is previously saturated with gas in a compact device outside the reactor [4]. The POLF technology provides extremely high productivity (in some cases up to 100 times) of a stationary (fixed-bed) catalyst at considerably low-energy consumption. The POLF technology is characterized by a simple equipment set and absolute process safety, excluding any accidents related to heat evolution.

Despite the fact that different applications of the POLF technology has recently been presented elsewhere [1,4,11–14], the descriptions devoted to it are still not complete. This paper is an additional attempt to elucidate some aspects omitted in earlier publications and focuses on the "process management", i.e. how to achieve high intensity of processes at far less energy consumption. It also shows why conventional technologies (TBR and BCR) have no potential for the process improvement in the light of the energy efficiency.

2. Mass transfer and effectiveness of energy consumption in the conventional TBR and BCR

Typical technological schemes of TBR and BCR with gas recycling are shown in Fig. 1. In order to analyze these reactors, it is necessary to bear in mind a very complex interplay between all physicochemical processes (Fig. 2). The attempt to comprehend all these phenomena in industrial TBR and BCR has recently been presented in [1]. What follow here are the most important features of the reactor performance.

The necessary heat regime is provided by recycling the cooled gas through the catalyst. Typical values of the gas recycle rates for different reaction classes are presented in Table 1.

The flow of an enormous quantity of gas and liquid through the reactor and some part of the pipework is very intricate from a hydrodynamic point of view. To give a complete phenomenology of the gas–liquid flow is always a challenging task. In industrial reactors, there is generally a very high grade of the interaction between gas and liquid phases. The velocity of gas can reach values of more than 40 cm/s, whereas liquid can move with velocities in the range of 0.1–5 cm/s or even higher.

The energy necessary for carrying out such a two-phase flow can be estimated as

$$E = N_{\text{gas}} RT \ln \frac{P_{\text{out}}}{P_{\text{in}}} \tag{1}$$

or

$$E \approx N_{\text{gas}} RT P_{\text{in}}^{-1} \Delta P \quad \text{if} \quad \frac{\Delta P}{P_{\text{in}}} < 0.3 \tag{2}$$

where E is the energy expenditure for gas recycling, N_{gas} the molecular flow rate of the recycled gas, R the gas constant, T the temperature of the gas in the compressor, P_{out} and P_{in} are the pressures at the outlet and inlet of the recycle compressor, and $\Delta P = P_{\text{out}} - P_{\text{in}}$. It is noteworthy that the gas recycling is the most cost-consuming part of all energy expenditures related to the reactor plant.

Naturally, the value of the energy for gas recycling varies in different processes (see Table 1). The greater the reaction heat, the higher the gas recycle and, therefore, the energy demand for it.

If the maximum pressure difference produced by the recycle compressor is taken as 100%, then the pressure drop related to the catalyst is about 20–30% (or less) and the rest (70–80%) is the pressure drop in lines, heat exchangers, valves, etc. According to Eq. (2), the same proportion is also true for the energy dissipation. It is necessary to point out that the energy expenditure, which can be regarded as expedient and useful for reaction purposes, is the energy that dissipates in the catalyst bed, where the moving gas provides mass and heat transfer

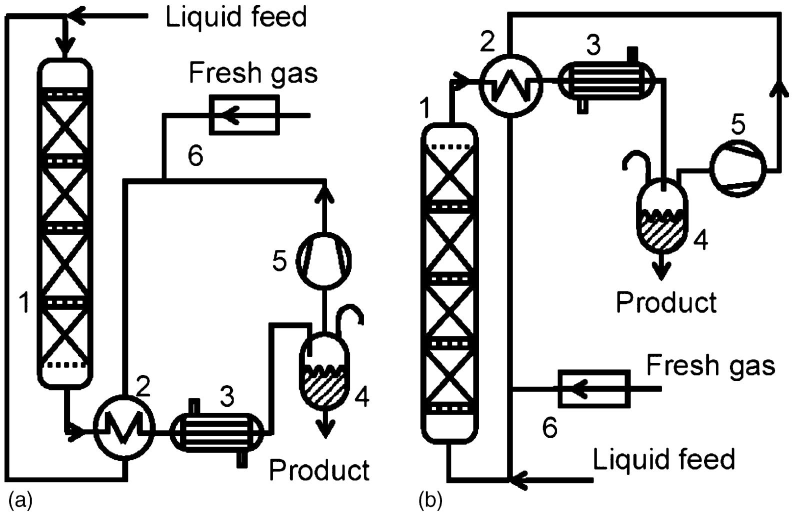

Fig. 1. Schematic technological schemes of TBR and BCR with gas recycling: (1) reactor with a catalyst and liquid/gas distributors; (2) recuperative heat exchanger; (3) cooler; (4) phase separator; (5) recycle compressor; (6) feed compressor.

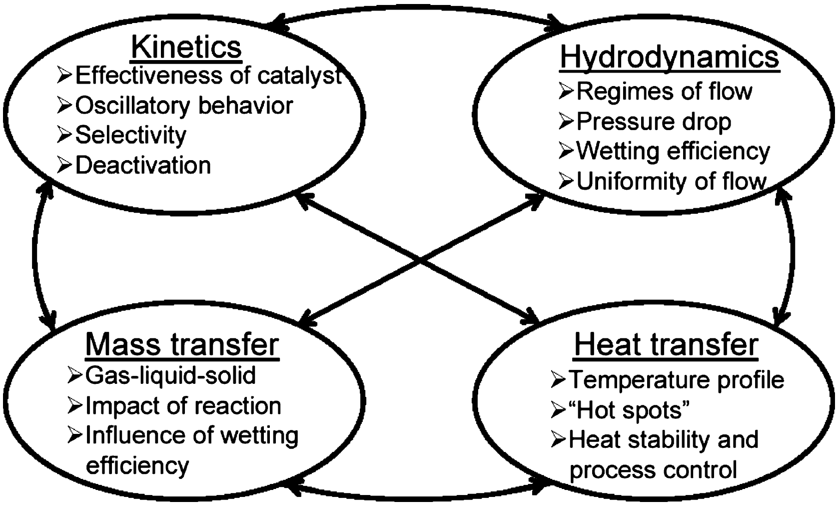

Fig. 2. Network of physicochemical processes in TBR and BCR.

between the gaseous, liquid, and solid phases and, therefore, promotes the reaction. Thus, from the point of view of the process management, energy dissipation in conventional technologies is very ineffective because 70–80% of the total energy is expended on the transportation of recycling gas through the pipework, whereas only a small part of energy consumption serves the reaction.

Another aspect of the TBR and BCR performance is the effectiveness of mass transfer. Most reactions carried out in multiphase reactors can be expressed as

$$\mathrm{A\ (liquid)} + n\mathrm{B\ (gas)} \rightarrow \mathrm{product(s)\ (liquid)} \quad (3)$$

where n is a stoichiometric coefficient.

Available literature often states that the rate of chemical processes is limited by mass transfer of the gaseous compound, particularly, in the case of hydrogenation or oxidation, because the solubility of hydrogen and oxygen in most solvents and organic compounds is very low [5–8]. However, as will be shown below, this is correct only to a point.

The ideal situation for the reaction is when the concentrations of gas and liquid compounds on the catalyst surface $C_{\mathrm{B,s}}$ and $C_{\mathrm{A,s}}$ are related as $C_{\mathrm{A,s}} \approx C_{\mathrm{B,s}}/n$. In the initial part of the reactor where, as a rule, the concentration of the liquid compound considerably exceeds the equilibrium concentration of the gas in the liquid phase, the concentration of the liquid compound at the catalyst surface is also far more than that of the gas: i.e. $C_{\mathrm{A,s}} \gg C_{\mathrm{B,s}}/n$ and, as a result, $C_{\mathrm{B,s}} \approx 0$ (Fig. 3). So the conclusion about the mass transfer limitation of the gaseous compound in the initial part of TBR and BCR is correct. But since the industrial reactors perform a high degree of conversion, the concentration of the liquid compound at the reactor outlet in many practical applications is so low that beginning from some point L_{cr}, the concentration of the saturated gas becomes more than the concentration of the liquid compound so that $C_{\mathrm{B,s}}/n > C_{\mathrm{A,s}}$ and $C_{\mathrm{A,s}} \approx 0$ (Fig. 3). That means that in the final part of the reactor, the reaction is carried out under the condition of the mass transfer limitation of the liquid compound, not the gas compound. The estimation made in [1] shows that the initial part of the reactor L_{cr} takes less than 20% of the whole catalyst length; in some processes, e.g. hydrodesulfurization, the initial part of the reactor where the reaction rate is limited by mass transfer of the gas compound can be absent altogether.

In conventional TBR and BCR, there are only two ways for process intensification: either the velocity of gas flow is increased or small catalyst particles are used.

It is important that gas–liquid mass transfer coefficients are proportional to gas velocity to the power of 0.2–0.4 and to liquid velocity to the power of 0.7–1.0, whereas liquid–solid

Table 1
Process characteristics of TBR and BCR with gas recycling

Reaction	ΔT_{ad}[a] (K)	Permitted ΔT[b] (K)	Gas recycle rate[c]	Energy expenditure related to the initial liquid feed
Nitrile-, nitro- and nitrosocompounds to amines	Up to 2000 °C	~15	Up to 420	Up to 780 kJ/mol
Ketones, aldehydes to alcohols	Up to 1200 °C	~20	Up to 140	Up to 120 kJ/mol
Hydrotreatment of oil	Up to 140 °C	~10	10–20	$\sim 15 \times 10^6$ J/m^3 oil

[a] ΔT_{ad}: adiabatic temperature warming related to the goal reaction.
[b] ΔT: permitted temperature warming necessary for an appropriate selectivity.
[c] The ratio of the flow rate of the recycling gas to the flow rate of make-up gas.

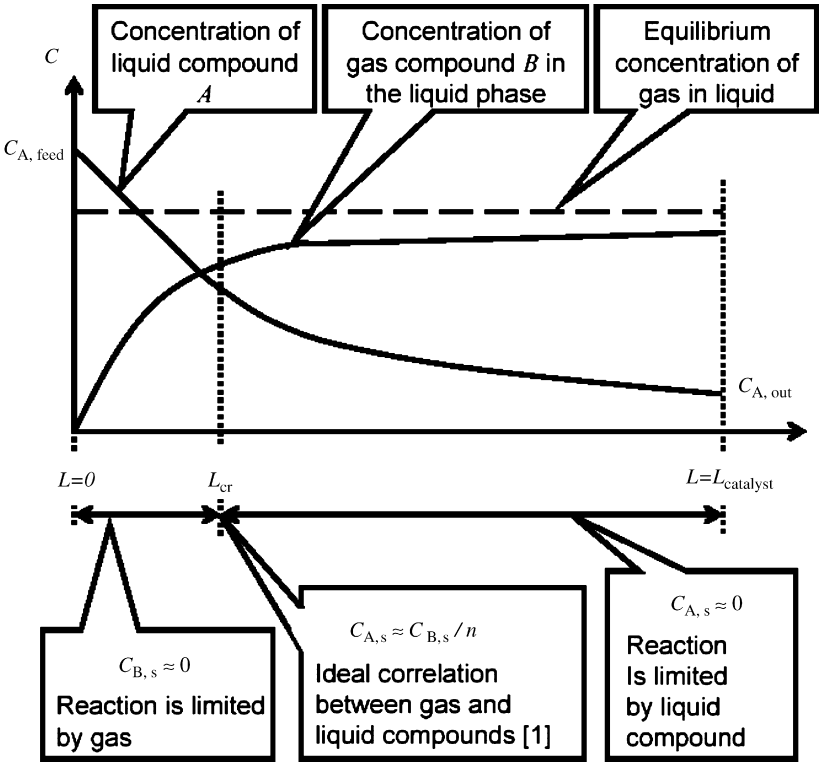

Fig. 3. Concentration profiles of liquid and gas vs. the reactor length.

mass transfer coefficients are proportional to liquid velocity to the power of 0.5–0.7 and are practically not dependent on gas velocity [9]. Thus, in order for gas–liquid mass transfer to be enhanced 2 times, the velocity of gas should be increased 6–30 times. Driving such a huge volume of gas through the reactor can result in a 40–900-fold increase in pressure drop [1,10], which can never be realized in industry, because even if there were available compressors, there is a problem with the mechanical strength of the catalyst, not to mention the non-productive energy expenditure. Small catalyst particles cannot be used because of the same problems with pressure drop and energy demand.

This analysis indicates that in the framework of the old technological paradigm (the use of gas recycling for mass transfer purposes and heat removal), conventional reactors with a stationary (fixed-bed) catalyst have no potential for further process development.

3. Pre-saturation as a method for process intensification/reactor minimization

In conventional reactors, the final part of the reactor (see Fig. 3) operates under the conditions of the mass transfer limitation of the liquid compound. In this part, the concentra-

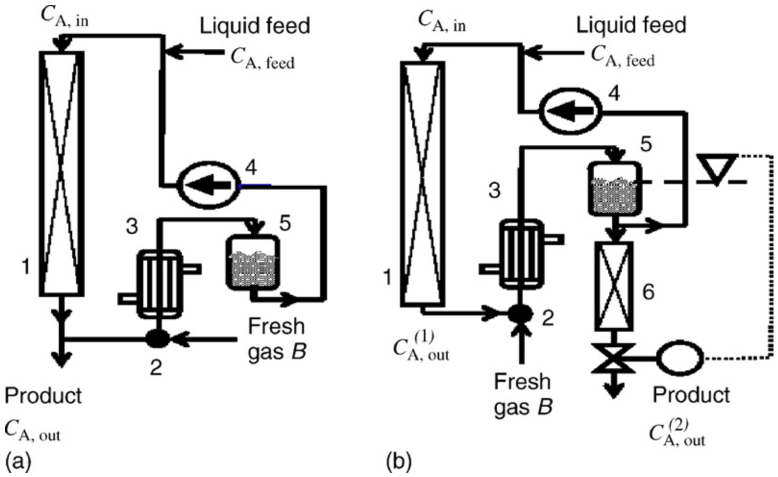

Fig. 4. Simplified schemes of the POLF technology: (a) one stage and (b) two stage processes. (1) Reactor; (2) saturator; (3) cooler; (4) recycle pump; (5) phase separator; (6) second reactor.

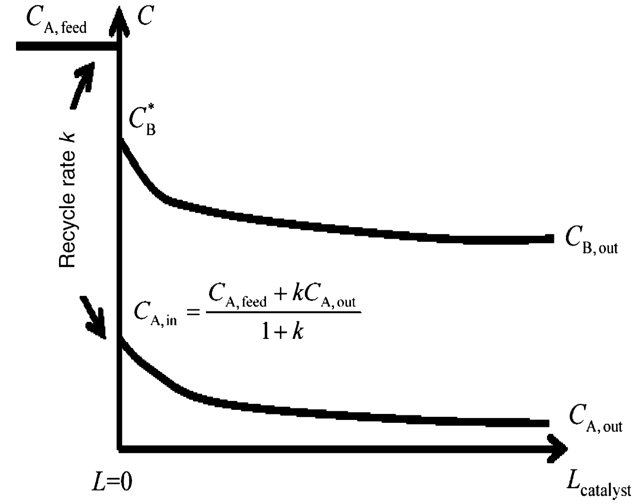

Fig. 5. Concentration profiles of gas and liquid compounds in the POLF reactor.

tion of the gas compound in the liquid phase is enough to provide the reaction without any additional gas flow or any gas input. Hypothetically, if the gas gave up going through the catalyst bed after the point L_{cr}, the reaction rate would remain the same because, on one hand, the gas–liquid mass transfer stage is not necessary there at all and, on the other hand, the gas flow has no particular effect on liquid–solid mass transfer.

In the POLF technology, in order to avoid mass transfer of gas–liquid in the reactor, this mass transfer stage is realized outside the reactor in a highly intensive device called a saturator, and only the liquid phase previously saturated with gas is fed into the reactor. Because the single liquid phase is pumped through the catalyst, the pressure drop related to the reactor, pipework, and other equipment becomes incredibly low. This means that the velocity of the liquid flow can be significantly increased, resulting in significant improvement of liquid–solid mass transfer, or small catalyst particles can be used. Since, as a rule, the concentration of the initial liquid compound at the reactor inlet is more than the equilibrium concentration of gas, in order to deliver the necessary quantity

Table 2
Comparison of TBR/BCR with the POLF reactor

Reaction	TBR/BCR		POLF technology[a]	
	Pressure (bar)	Productivity[b] (kg/(dm^3 cat h))	Pressure (bar)	Productivity[b] (kg/(dm^3 cat h))
Acetone to isopropanol	50	0.4	10	3.5
Furfurol to tetrahydrofurfuryl alcohol	150	0.1	50	0.25
4-Nitrosophenol to 4-aminophenol (solvent, ethanol)	50	0.2	50	0.3
Furfurol to furfuryl alcohol	100	0.15	50	0.45
Nitroparaffins (C12–C14) to aminoparaffins (solvent, methanol)	50	0.15	50	0.45
Dinitrotriethylbenzene to diaminotriethylbenzene (solvent, methanol)	50	0.15	50	0.3
Dinitrotriethylbenzene to diaminotriethylbenzene (without solvent)	50	~0	50	0.15
1,5-Dinitronaphthalene to 1,5-diaminonaphthalene (10% suspension)	This type of the reactor cannot function		50	0.1
Nitrobenzene to aniline	50	0.15	50	0.4
3,4-Diclornitrobenzine to 3,4-dicloraniline (solvent, toluene)	200	0.2	50	0.4
2,4/2,6-Dinitrotoluene to 2,4/2,6-diaminotoluene	50	0.15	50	0.4
1-Octene to octane (1.0 mm particles)	25	5	25	32
1-Octene to octane (0.6 mm particles)	This type of the reactor cannot function		25	65
1-Octene to octane (0.35 mm particles)	This type of the reactor cannot function		25	500 [11]
Ultra hydrodesulfurization[c]	30	0.5	30	1.25 [13]

[a] The energy consumption for liquid recycling in the POLF technology is 100–1500 times less than that for gas recycling in TBR and BCR [1].

[b] Mass of an initial material converted by 1 dm^3 of a catalyst per hour. Conversion (usually more than 99%) is the same for both reactors; selectivity in the POLF process is, as a rule, higher.

[c] The outlet concentration of sulfur compounds is 50 ppm.

of gas into the reaction zone, the liquid phase should be recycled. This permits reaction heat to be removed in an external heat exchanger installed on the recycle line. The simplified schemes of the POLF technology are depicted in Fig. 4; Fig. 5 represents the concentration runs of the compounds in the POLF reactor. In this technology, a comparatively compact recycle pump is used instead of a huge recycle compressor.

The recycle rate k, the ratio of the volumetric rate of the liquid recycle to the volumetric rate of the liquid feed, can be calculated from the mass balances:

$$C_{\mathrm{A,in}}(1+k) = C_{\mathrm{A,feed}} + kC_{\mathrm{A,out}} \tag{4}$$

and

$$\frac{C_{\mathrm{B}}^{*} - C_{\mathrm{B,out}}}{n} = C_{\mathrm{A,in}} - C_{\mathrm{A,out}} \tag{5}$$

as

$$k = \frac{n(C_{\mathrm{A,in}} - C_{\mathrm{A,out}})}{C_{\mathrm{B}}^{*} - C_{\mathrm{B,out}}} \tag{6}$$

where $C_{\mathrm{A,feed}}$, $C_{\mathrm{A,in}}$, and $C_{\mathrm{A,out}}$ are the concentrations of A compound in the liquid feed, at the reactor inlet and outlet correspondingly, and C_{B}^{*} and $C_{\mathrm{B,out}}$ are the concentrations of the gas compound B at the reactor inlet (equilibrium concentration) and outlet.

$C_{\mathrm{B,out}}$ can in principle be set equal to zero, but from a technological point of view, it should always be kept more than zero in order to prevent catalyst aging and by-reactions. This value should be set as much as 60–80% of the equilibrium concentration C_{B}^{*} by the appropriate liquid recycle rate (Eq. (6)).

A comparison of the POLF technology with conventional TBR and BCR is given in Table 2, which shows that at the same or less pressure, the reactor productivity in the POLF technology is several times more than in TBR and BCR. Only the POLF technology can use small catalyst particles in the fixed-bed reactor, so the productivity can be increased up to 100 times (hydrogenation of 1-octene). Apart from reactions presented in Table 2, there are other examples of successful utilization of the POLF technology in the regeneration of spent lubricants and transformer oils [12], in hydrodesulfurization [13] and in the production of a fragrance [14].

Energy for liquid recycling can be estimated as

$$E = Q_{\mathrm{recycle}} \Delta P \tag{7}$$

where Q_{recycle} is the volumetric rate of the recycled liquid and ΔP is the pressure drop. It is especially noteworthy that energy demanded for liquid recycling in the POLF technology is 100–1500 times less than the energy needed for gas recycling in TBR and BCR.

One of the most important features of the POLF technology is a great potential for the further process intensification [1]. The revamping of existing TBR and BCR plants allows a significant increase in the productivity of old equipment and an extreme decrease in energy consumption. In the case of new construction, the POLF technology remarkably lessens the reactor size. An industrial reactor can look like a pilot-plant one while a pilot-plant unit can be as small as a laboratory reactor.

Apart from high productivity and low-energy demand, there are other advantages of the POLF technology. It is absolutely safe because the quantity of soluble gas in the liquid phase is so low that there is no possibility of any dangerous temperature increase. The equipment set of the POLF plant is very simple; the reactor itself has no liquid–gas distributors inside. That makes reconstruction of existing TBR and BCR very easy and cheap because many pieces of the old equipment and control systems can be used. In the case of new construction, the investment costs are very low.

4. Conclusion

The POLF technology is characterized by high productivity, absolute process safety, and low-energy demand. It has an uncomplicated process control, and simple, cheap equipment. This technology can be regarded as a universal industrial method allowing the construction of extremely small industrial plants.

It is necessary to point out that similar approaches to carrying out some special reactions [15–17] have been made by excellent researchers long before us. Unfortunately, at that time, those narrow applications did not allow the scientific community of the time to evaluate the importance of the pre-saturation technique for industry.

Despite the fact of the successful applications considered above and elsewhere [15–17], it should be underlined that that the POLF technology (especially, the one-stage process (Fig. 4a)) cannot be recommended for all reactions. Since the flow pattern due to the liquid recirculation is close to that in continuous stir tank reactor (CSTR), the POLF reactor cannot be appropriate for the processes where the goal product can form by-products with considerable reaction rates.

It should also be mentioned that the POLF technology does not result in the process intensification if the catalyst has a comparatively low activity (i.e. there is no mass transfer limitations). Nevertheless, in this case, the implementation of the POLF technology lessens essentially the consumption of energy.

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