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Autothermal Operation of Catalytic Fixed-Bed Reactors by Periodical Flow Reversal Technique

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Abstract. An efficient technique for autothermal operation of catalytic fixed-bed reactors is the forced unsteady state operation by periodical flow reversal. This paper presents a mini review of the main investigations dedicated to the design and operation of this process, published over the past several decades. A case study is also presented, describing the particularities of process mathematical modelling and emphasizing the typical space and time evolutions of the main process variables. The case-study illustrates the use of packed beds of porous pellets with egg-shell type distribution of catalyst, which combines the high thermal capacity advantage of pellet packed beds with the minimal internal diffusion limitations on process kinetics typical for monolithic catalyst beds. A sensitivity analysis highlights the potential modelling errors that could be induced by the uncertainty in the evaluation of model parameters, using published correlations.

Keywords: reverse flow reactor, autothermal operation, catalyst, design, mathematical modelling.

1. Introduction

It is well known that initiating a chemical transformation in a reactor requires preheating the reactant mixture to a minimum temperature, commonly referred to as the ‘ignition temperature’. Frequently, the heat necessary for the reactants preheating is obtained by partial or total recovery of the sensible heat content of reaction products. The operation of a chemical reactor hosting an exothermal transformation is defined as *autothermal*, if the heat generated in reaction is used to preheat the feed stream [1]. In the case of endothermic reactions, similar operating regimes can be achieved by coupling the process with an exothermic transformation occurring within the same apparatus [2,3].

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The autothermal operation requires technical means to transfer the heat generated in reaction, towards the feeding reactants mixture. The simplest solution in this aim is to operate the reactor adiabatically and to interconnect it with an external heat exchanger, ensuring the heat transfer from the hot effluent to the cold reactant mixture (Fig. 1-A). More effective solutions for the design of autothermal reactors combine the reactor internals with the heat exchanger elements, in the same apparatus [4]. These techniques involving the recovery of the hot products sensible heat by transfer across a separating wall, are usually called *recuperative*.

In the case of gas-solid catalytic fixed bed reactors, an alternative solution for the realization of the autothermal regime is the forced unsteady state operation. The most investigated techniques in this class are the operation with periodical gas flow reversal (reverse flow reactor) and the sequence (network) of catalyst beds operated with periodical change of the feed point (the simulated moving bed reactor) [5]. These autothermal operation techniques, called *regenerative*, involve the storage of the heat generated in reaction into the solid bed contacted directly by the reaction mixture. Other unsteady-state techniques are described by Zagoruiko et al. [6]. From the practical point of view, the most investigated is the reverse flow reactor (RFR), the only unsteady-state technique implemented commercially. Note that the same principle can be applied for homogeneous (non-catalytic) reactions, by using a solid bed (inert) for heat storage (thermal RFR). Due to its high thermal efficiency, operating stability and relatively low investment cost, the reverse flow reactor principle is included in the class of process intensification methods [7]. As the subject of this work regards the catalytic RFR, the information that follows will be focused on this technique.

2. Functional principle of RFR

The principle of regenerative heat exchange was patented by the British reverend Robert Stirling as early as 1816 [8]. The application of this principle in the unsteady operation of a fixed bed catalytic reactor was patented in USA, in 1938, by Cottrell [9] and the first attempt to apply it in practice, for SO₂ reduction process, was reported by the company Allied Chemical Corp. (USA), around 1970. However, this endeavor was not entirely successful due to technical problems with the valves system [10]. It is also worth noting that the famous Eugene Houdry (the inventor of catalytic cracking technology) published, in 1956, a patent of a RFR reactor for catalytic treatment of gas streams containing relatively small amounts of oxidizable impurities [11].

In the last decades, the interest in the RFR principle has increased, particularly in applications involving the treatment of diluted gaseous mixtures by exothermal reactions (due to the RFR capability to maintain the auto-thermal regime at low feed concentrations). Important progresses in the practical implementation of RFR principle were achieved at the Russian Institute of Catalysis, Novosibirsk, under the coordination of the scientists Georgy Boreskov and Yurii Matros [12]. The most investigated processes were waste gas treatment (SO₂ oxidation, selective reduction of NO_x) and the purification of gas streams containing volatile organic compounds

by combustion [13]. It is recalled that the volatile organic compounds (VOC) are organic pollutants (commonly the hydrocarbons and their oxygenated or halogenated derivatives) having relatively low boiling points (conventionally less than 250 °C at 1 bar), which contribute to the formation of photochemical smog, when emitted into the atmosphere. The main sources of VOCs are oil refineries and most of the chemical industry's plants [14].

The constructive and operational principles of a fixed bed operated with periodic gas flow reversal (RFR), are depicted in the scheme given in Fig. 1-B. The periodical change of gas flow direction through the catalytic bed is possible using a pipe system on which the valves V1 to V4 are mounted. When the gas flows from the left to the right the valves V1 and V3 are open, and V2, V4 are closed, and vice versa when the gas flow direction is reversed. The working principle of a RFR can be explained by considering the solid bed sketched Fig. 1-B, heated at a sufficiently high temperature. At a given instant, one starts to feed the bed, from the left to the right, with a gaseous mixture containing reactants (at relatively low temperature). It is assumed that the reactant is chemically transformed (exothermic reaction) with significant rates, only on the catalyst surface. By contacting the solid, the gas is heated, achieving the ignition temperature of reactants, which begin to transform when contacting the catalyst, generating heat, that permits further gas and solid heating.

The calculated temperature evolutions along such a bed, at different moments of time, are shown in Fig. 2-A. Due to the solid-gas heat transfer, the solid on the first contacting zone is continuously cooled, whereas the solid beyond the exothermic reaction zone is heated. extend the gas feed, the cooled solid zone extends continuously in the direction of the gas flow, cooling completely the solid bed, at large gas feeding times.

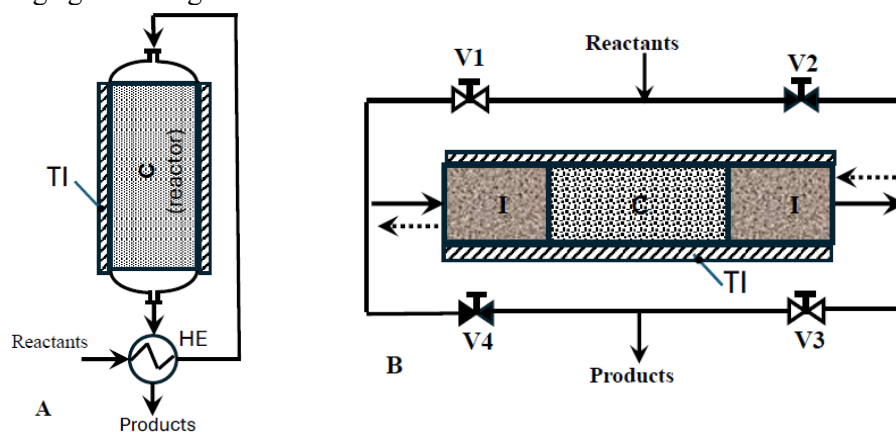


Fig. 1. Two autothermal operating techniques for a catalytic fixed bed reactor. A- Classical technique (recuperative); B- unsteady reverse flow operation (regenerative); HE- heat exchanger; I- inert material; C- catalyst; TI- thermal insulation; V1..V4- switch valves.

However, if the gas feed direction is changed after a duration suitable selected (t_{sc}), the process is progressing similarly in the opposite direction. During this second operation interval, the cold solid zone appeared previously on the left section of the bed, is reheated by the hot gas mixture. Thus, whilst one extreme zone of the reactor

is heating the gas feed, the other extreme zone is reheated (regenerated) by the high temperature gas mixture. So, when the flow direction is reversed, the role of bed extreme zones is swapped. By continuing to reverse periodically the gas flow direction, the heat is kept inside the solid bed, achieving temperature evolutions featuring maxima in the central zone, higher than the ignition temperature of reactant. It is worth noting that the maximum gas temperature increase in the bed is much higher than the adiabatic temperature rise (ΔT_{ad}) of the reaction system [15]. As illustrated in Fig. 2-B, the two marginal zones of the solid bed serve mainly for heat storage and gas heating, so they can consist of a solid inert, cheaper than the catalyst (Fig. 1-B). Thus, in the RFR, the role of the relatively expensive gas-gas heat exchanger is played by the two zones of inert solid, accommodated in the same reactor shell. In these zones, the heat transfer warranting the gas preheating takes place between solid and gas, across an interface characterized by a very high contact area (usually over $1000 \text{ m}^2/\text{m}^3$ of bed, much higher than that feasible in heat exchangers). Regularly, the lengths of the two inert zones at the bed borders are identical and the total volume of inert material is equal to the volume of catalyst [16]. The time interval between two successive flow reversals is called semi-cycle or semi-period (t_{sc}), two semi-cycles defining a cycle, or a period ($t_c = 2 t_{sc}$). Keeping identical feed conditions for both flow directions, after a sufficiently high number of flow reversals, the temperature and gas composition variations along the bed are stabilized: at same time durations in respect with flow reversal instant, the axial concentration and temperature profiles are identical in every cycle (cyclic stationary state). The axial evolutions corresponding to two successive semi-cycles are symmetrical relative to the cross midsection of the bed (Fig. 2-B).

The RFR (regenerative) autothermal technique has several advantages, as compared with the classical recuperative autothermal operation techniques (involving heat exchange across a solid wall): (a) The autothermal operation is possible, in practice, even at significantly low values of the adiabatic temperature rise (ΔT_{ad}), characterizing the reaction system, i.e. ΔT_{ad} even below 20°C according to Matros and Bunimovich [13], or ΔT_{ad} values of minimum $\sim 30^\circ\text{C}$, according to Zagoruiko [10].

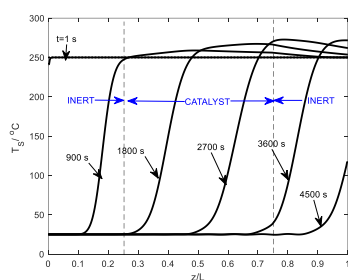


Fig. 2-A. Solid temperature evolutions in a (initially hot) fixed bed including a central zone of catalyst and two marginal zones of inert, when contacted by a colder flowing gas containing a reactant (exothermal reaction). The numbers on the curves represent the moments of time.

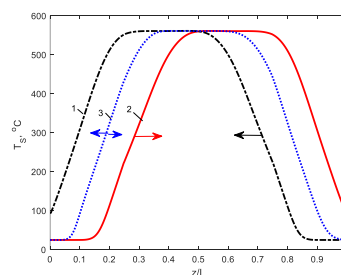


Fig. 2-B. Typical solid temperature evolutions in the fixed bed at the final moment of a semi-cycle (curves 1 and 2) and at the half of a semi-cycle (curve 3 identical for both gas flow directions). The arrows on the curves indicate the flow directions.

For comparison, recuperative reaction systems are practicable in autothermal mode, using usual heat exchangers, for reaction mixtures characterized by ΔT_{ad} values of minimum 50 °C. This permits a decrease of energy consumption for lean gas mixture processing, as compared with steady-state recuperative reaction systems.

(b) The RFR presents a higher stability at feed perturbations, as compared with steady-state reactors. The variations in the feed reactant concentration and/or feed temperature do not have a significant effect on the main RFR process parameters, i.e. values of reactant conversion and maximum solid temperature. This characteristic is explained by high thermal inertia of catalyst bed and high ratio of solid and gas heat capacities. However, numerical studies have evidenced that periodic perturbations in feed concentration or flow rate can induce reactor instability, for particular ratios between flow reversal cycle and the feed variation cycle [17, 18].

(c) The specific temperature profile along the bed, for the RFR, is advantageous for exothermal reversible reactions (the lower temperature on the last zone of the bed increases the equilibrium conversion).

(d) The processing plant including a RFR is characterized by a lower pressure drop, as compared with the traditional scheme, mainly due to elimination of heat exchangers.

However, a significant inconvenience of RFR is the elimination of small amounts of untransformed reactant mixture (confined in the voids of the inlet zone of the bed and adsorbed on the solid surface of this zone), into the exit gas stream, immediately after the moment of flow reversal. However, except for short reverse flow cycles (t_c), this inconvenience is tolerable in practice. An alternative construction principle, avoiding this disadvantage, is the rotary reverse flow reactor, in which the bed turns around its axis, the reagents feed and the product outlet being realized using segmented fixed heads. This construction needs a smaller number of valves and eliminates the emission of untransformed reactants, by an auxiliary gas circuit [19, 20, 21].

The bed of RFR can consist of randomly arranged solid pellets, of different geometries, or ordered structures (solid monoliths). Energetic performances of pellet beds and monolithic structures were compared by Kushwaha et al. [22, 23] respectively by Amelio and Morrone [24]. The results evidenced that the cheaper random solid pellet beds exhibit higher thermal efficiency but are inducing higher pressure drop of gas in the bed and significant diffusional kinetic limitations within the catalyst pellets. On the other hand, the use of monolith beds features a lower pressure drop and insignificant diffusional limitations but gives rise to faster temperature variations (due to a low thermal capacity). A practical compromise involves using a pellet bed, more cost-effective than a monolithic structure, with the catalyst confined to a thin outer layer at the pellet periphery, known as an egg-shell distribution. This type of catalyst distribution, which is readily achievable in practice, enables the use of relatively large pellets with minimal internal diffusion limitations, while also resulting in a relatively low gas pressure drop.

A drawback in the operation of the RFR is the occurrence of temperature spikes (hot spots) at catalyst bed extremities, in cases of frequent, positive feed concentration

perturbations. A proposed solution to this problem is the increase of solid bed thermal dispersity, by inserting metal rods inside the bed [25].

3. Published experimental studies of the catalytic RFR

The experimental setups necessary to investigate the RFR process are rather complex, requiring minimum amounts of solid catalyst and solid inert, adequate instrumentation and a suitable control system insuring the valve manipulations. Small scale experiments performed on laboratory or pilot setups (typical bed volume of 0.3-10 L) are useful in the identification of the working intervals of the main process variables ensuring the chemical transformation, the influence of the mass and heat transfer on the chemical kinetics, the dependence of switching time on the working conditions etc. However, small-scale thermally insulated RFRs present the inconvenience of a significant influence of thermal insulation on the thermal regime of the reactor, i.e. on the temperature evolutions in the bed [14].

An important number of published studies investigated the elimination of organic compounds from lean gaseous mixtures by catalytic combustion; many of these studies are focused on the performances of different catalysts usable in this aim. Methane, usually not considered as a VOC (being nontoxic and not contributing significantly to the formation of photochemical smog) is an important greenhouse gas, having a global warming potential over 20 times higher than that of carbon dioxide, so its emissions into atmosphere are subject to environment regulations. By methane oxidation to carbon dioxide (combustion), its greenhouse effect will be reduced by a factor of about 20. In addition, methane is a significant source of energy, so that capture and combustion of methane fugitive emissions could bring also economic benefits. Important methane fugitive emissions take place from coal mines, oil and gas sector, landfills etc. [26, 27]. Due to the low methane concentrations typical for these gas emissions (under 1.0 vol.%), catalytic combustion using the reverse flow technique is the most effective, allowing autothermal operation.

Similarly, other published works investigate the performances of RFR technique in the elimination of different VOC's (hydrocarbons, solvents etc.) by combustion on different catalysts. The main experimental studies published in the last two decades in this domain are systematized in Table 1. Further data regarding the performances of the VOCs catalytic combustion using RFR technique, over noble metal or non-noble metal oxides catalysts, are provided in references [6, 14, 15, 28]. Other RFR applications investigated include methanol synthesis, ammonia synthesis, methane reforming, SO₂ oxidation in diluted mixtures and reduction of nitrogen oxides by ammonia in the waste gases resulted from nitric acid production [10, 13].

The RFR technique has been implemented at commercial scale since the years 1980, the main applications being reported in the domain of SO₂ oxidation in diluted gas mixtures (0.5 % to 3.5 % SO₂ in moles) and catalytic removal of volatile organic compounds from lean residual gases. The first commercial scale RFR was implemented for SO₂ oxidation at a non-ferrous smelter in Krasnouralsk (Russia) in 1982. After this date, other similar installations were put into operation in Russia,

China and Bulgaria [10]. In the domain of VOC removal by catalytic combustion, the first RFR application was put into operation at a Novosibirsk Chemical Plant, Russia, in 1984.

Currently, hundreds of such plants are in operation worldwide. In 1989, a NO_x decontamination plant-based on the same RFR principle and employing ammonia for NO_x reduction-was commissioned at the Byisk Oleum Plant in Russia [10].

Table 1 Experimental studies of the catalytic RFR technique

Chemical transformation	Catalyst/bed type	Cycle duration, t _c (s)	Aim of the study	References
Methane to syngas (partial oxidation)	Rh/Al ₂ O ₃ ; - monolith	≤ 10	Modelling and simulation;	Pourghadiri and Sari [29]
VOC combustion (toluene)	Not specified; - catalyst pellets	>3000	Comparison of RFR with axial, side, or tangential gas inlet/outlet streams.	Zazhigalov et al. [30]
General schemes for first order reactions. Test for C ₂ H ₄ oxidation.	Pd/ γ- alumina; - catalyst pellets	100 ÷4000	Modelling and simulation. Test of internal diffusion effects.	Mastroianni et al. [15]
VOC combustion (methane)	Not specified	600	RFR control study (linearized model)	Aksikas [31, 32]
NH ₃ oxidation	Pt/support - catalyst pellets	4÷3600	Theoretical study of RFR with side feeding. Effect of feed position.	Budhi [33]
VOC combustion (methane-propane)	Pd/ γ- alumina;	840	Theoretical study of the instability generated by periodic oscillations in feed concentration.	Li et al. [34]
VOC combustion (benzene)	CuO/γ-alumina; - catalyst pellets	600÷3600	Modelling and simulation;	Sophiana et al. [35]
VOC combustion (ethanol and ethyl acetate mixture)	Mn and Cu oxides mixture; - monolith	≤ 400	Theoretical comparison between classical RFR and rotary RFR	Luzi et al. [36]

Economic estimations showed that the use of RFR technique in SO₂ oxidation allows a decrease in metal needed, by a factor of 1.5 to 5, a 30-50% lower pressure drop, 20-80% lower capital costs, and 5-20% lower operating costs. Similarly, by applying the RFR principle in catalytic VOC removal, the operating costs are reduced by a factor of 5, in comparison with a conventional unit using external heat exchangers [13].

4. Published theoretical studies of the catalytic RFR

The principles and particularities of RFR modelling are detailed by Matros and Bunimovich [13] and Matros [37]. The process occurring in a reverse flow reactor can be described by unsteady state (dynamic) mathematical models of different complexities. Due to the symmetry of the process in the cylindrical beds, the most

used mathematical models consider two directions of transport in the bed (axial and radial) particular for 2D models or a single direction (axial), specific for the simpler 1D models. The main phenomena taking place in the unsteady catalytic fixed bed reactor are gas-solid mass and heat transfer, intra-particle mass and heat transport, convective heat and mass transport in the gas phase, heat transport inside the solid by effective conduction, heat and mass transport in the gas phase by dispersion, loss of gas pressure, and heat and mass accumulation in the two phases.

The most popular are the 1D models, which are simpler and provide reasonably accuracy for reactor design, simulation or optimization calculations. In commercial applications, the relatively large bed diameters correspond to thermal regimes practically adiabatic and a gas velocity profile approximately flat, so that 1D models describe adequately the process. However, in the modelling of pilot or laboratory reactors, having relatively small diameters (typically lower than 0.18 m), the radial heat transfer should be taken into consideration [13, 14].

More complex three-dimensional modelling was used by Zazhigalov et al. [38] to calculate RFRs featuring design asymmetries (radial and tangential gas feeding), leading to significant radial gradients of temperature, concentration and fluid velocities in the catalytic bed.

The main theoretical studies published in the last two decades in this domain are outlined in Table 2.

5. Heat balance of the reverse flow reactor over a semi-cycle

5.1 Heat balance equations over a semi-cycle

The overall heat balance of the RFR over a semi-cycle (the time interval between two consecutive flow reversals) is described by the equation:

$$Q_r + Q_{S0} + Q_{IG} = Q_{EG} + Q_{Sf} \text{ or}$$

Table 2 Theoretical studies of the catalytic RFR technique

Chemical transformation	Catalyst/bed type	t_c (s)	Reactor characteristics	References
VOC combustion (toluene)	Mn/cordierite; - monolith	480 ÷ 960	Li=100 mm; Lc=50 mm; dt=29 mm;	Liang et al. [39]
VOC combustion (methane)	Pt / γ - Al ₂ O ₃ - catalyst pellets	1200	dt=60 mm; Li=2x0.5 m; Lc=0.4 m; dp=3÷5 mm	Chen et al. [40, 41] See also [42]
Methane combustion	Zr-Cu-Ce-Mn/ alumina/ monolith	600 ÷ 1200	Lc=1.5 m (monolith); Li=2x2.4 m (monolith);	Li et al. [43]
VOC combustion (methane with H ₂ S impurity)	CuO-MnO ₂ / γ - Al ₂ O ₃ pellets; mol. sieve 5A as H ₂ S adsorbent	400 ÷ 800	Lc=200 mm; dt=50 mm; Li=2x 100mm (inert and adsorbent)	Urbani et al. [44]

Chemical transformation	Catalyst/bed type	t_c (s)	Reactor characteristics	References
NO _x reduction with NH ₃	- V/TiO ₂ /cordierite; - monolith	100 ÷ 600	L _c =0.5 m; dt=57 mm Li= 2x0.2 m (pellets)	Muñoz et al. [45]
VOC combustion (methane)	- Pd/cordierite; commercial monolith (CPO-5 M BASF)	200 ÷ 1200	L _c =0.2 m; dt=50 mm; Li=2x 0.1 m (monolith)	Fernandez et al. ([46, 47] See also [48,49]
Oxidative reforming of tar components	- dolomite; - catalyst pellets	Not provided	L=L _c =0.620 m; dt=0.152 m (outer);	Tuna et al. [50]
SO ₂ -CO mixture oxidation	-Pt (Zr)/glass fibers and V ₂ O ₅	900	Not provided	Zagoruiko and Vanag [51]
VOC combustion (isopropyl alcohol)	-Cu/molecular sieve; - catalyst pellets	240 and 600	L=2 m; L _c =0.5 m; Li=2x0.75 m; Bed section 0.15x0.15 m	Huang et al. [52] See also [53]
VOC combustion (methane)	Pd/ CeO ₂ -ZrO ₂ / cordierite monolith (Engelhard)	200 ÷ 1800	L _c =0.25 m; Li=2x0.125 m (monolith); dt=50 mm	Marin et al. [54]
VOC combustion (hexane-toluene)	- Pt / γ- alumina; - catalyst pellets	600 and 1200	L _c =0.25 m; Li=2x0.125 m; dt=50 mm	Marin et al. [55]
Autothermal reforming of methane	Rh/Al ₂ O ₃ (Engelhard) - pellets	100 ÷ 2400	L _c = 20 mm; Li=2x60 mm;	Simeone et al. [56]
VOC combustion (methane)	Mn oxide / γ- Al ₂ O ₃ ; - catalyst pellets	1200	L= 0.496 m; L _c =0.246 m; Li=2x0.125 m; dt=51.7 mm;	Fissore et al. [57] See also [58,59]
Autothermal reforming of methane	Pt-Rh/alumina; - monolith	30	L _c =10 mm; Li=2x110 mm (monolith); dt=18 mm,	Neumann and Vesper [60]; See also [61-64]
VOC combustion (methane)	Non-noble metal/alumina; - catalyst pellets.	120 ÷ 700	Li=2x 0.65 m (ceramic monolith); L _c ≈ 0.60 m (Raschig rings) dt=0.2 m;	Kushwaha et al. [22,23] See also [26, 27, 65]
VOC combustion (methyl ethyl ketone and toluene)	- Precious metal on a monolith structure (7.5 cm ² × 20 cm height).	7200	Li=2x2 m (granite gravel, dp=12.5 mm as inert); dt=0.2 m; catalyst bed.	Chou, Cheng and Lee [66]

$$Q_r + Q_{cs} = Q_p \quad (1)$$

In the above equations:

Q_{s0} , Q_{sf} the sensible heat content of the solid bed at the beginning and at the end of a semi-cycle, respectively;

Q_{IG}, Q_{EG} - the sensible heat fed and respectively removed from the reactor by the gas flow;

Q_r - the heat released by the VOC combustion reaction;

Q_p - the amount of sensible heat accumulated in the gas phase crossing the bed:

$$Q_p = Q_{EG} - Q_{IG} = \int_0^{t_{sc}} D_m c_{pg} [T_G(t, L) - T_{G0}] dt \quad (2)$$

Q_{cs} -the amount of sensible heat transferred from the solid phase:

$$Q_{cs} = Q_{S0} - Q_{Sf} = \int_0^L S \rho_s c_s (1 - \varepsilon) [T_s(0, z) - T_s(t_{sc}, z)] dz \quad (3)$$

$$Q_r = \int_0^{t_{sc}} D_{MA,0} X_A(t, L) (-\Delta H_{RA}) dt \quad (4)$$

Due to the symmetry of the solid temperature profiles at the beginning and the end of a semi-cycle, the heat contents of the bed, Q_{Sf} and Q_{S0} are identical, so $Q_{cs}=0$, and the equation (1) becomes:

$$Q_r = Q_p \quad (5)$$

This result signifies that, at thermal regime stabilization, the amount of heat released in the VOC combustion during a semi-cycle, is entirely removed from the bed, by the gas phase. Consequently, after the thermal regime stabilization, the sensible heat content of the bed at the beginning and the end of a semi-cycle are the same, the main phenomenon taking place during a semi-cycle, being the displacement of the sensible heat by the gas phase, inside the solid bed.

5.2 The thermal recovery efficiency

A parameter proposed to characterize the autothermal reactor operation is the *thermal recovery efficiency* achieved in the system, η , defined by the relations [14, 67]:

For the classic reactor-heat exchanger system:

$$\eta = \frac{Q_{st}}{Q_R + Q_{ph}} \quad (6)$$

Q_{st} - the heat that can be recovered in the heat exchanger, in Fig. 1-A (with external heat exchanger) or the heat accumulated in the solid bed, available for preheating the gaseous reactants in Fig. 1-B (RFR);

Q_{ph} - the heat consumed to preheat the reactant mixture to the ignition temperature, required by the reaction.

Considering a single reaction, for a recuperative scheme (Fig. 1-A) the amounts of heat appearing in relation (6) are reported to the unit of time ($Q_R = D_{MA,0} X_A (-\Delta H_{RA})$), whereas for the RFR (Fig. 1-B), these are reported to the

duration of a semi-cycle, t_{sc} (the time interval between two successive flow reversals), (Q_R is replaced in (6) by Q_r , defined by relation (4)).

For the RFR technique, Q_{st} has the expression:

$$Q_{st} = \int_0^L S(1-\varepsilon) \rho_s c_s (T_s(z) - T_{G0}) dz$$

An autothermal operation is possible when the amount of heat required to preheat the supplied gas is lower than the amount of heat accumulated in the bed (respectively that recovered in the heat exchanger).

$$Q_{ph} \leq Q_{st} \quad \text{or} \quad Q_{ph} \leq \eta(Q_{ph} + Q_r) \quad (7)$$

At constant reactant feed flowrate ($D_{MA,0}$), constant mass flowrate (D_m), and total reactant conversion ($X_A=1$), by approximating constant exit temperature and constant physical properties of the gas:

$$\begin{aligned} Q_{ph} &= D_m c_{pg} \Delta T_{ph} t_{sc}; \quad \Delta T_{ph} = T_{ign} - T_{G0} \\ Q_r &= D_m c_{pg} \Delta T_{ad} t_{sc}; \quad \Delta T_{ad} = \frac{-\Delta H_{RA} y_{A0}}{M_m c_{pg}} \end{aligned} \quad (8)$$

T_{ign} – ignition temperature; ΔH_{RA} - enthalpy variation in the combustion reaction, reported to one mole of reactant; y_{A0} - mole fraction of reactant in the feed; c_{pg} , M_m - the specific heat and average molar weight of the gaseous mixture; ΔT_{ad} - the adiabatic temperature rise in reactor.

Substituting in (7) one obtains the feasibility condition for the autothermal regime:

$$\Delta T_{ad} \geq \frac{1-\eta}{\eta} \Delta T_{ph} \quad (9)$$

The value of the parameter ΔT_{ad} is dependent on the reactant concentration in the feed and the value of reaction enthalpy respectively, while the value of ΔT_{ph} depends on the activity of the catalyst (ignition temperature) and the temperature at which the reactants are available.

Experimental and theoretical studies evidenced values of thermal recovery efficiency of approximately 70% ($\eta \approx 0.7$) for the classical system with external heat exchanger (Fig. 1-A), and between 90% and 95% ($\eta \approx 0.9 \div 0.95$) respectively for the reactor operated with periodic flow reversal [14]. The condition (9) is represented graphically in Fig. 3, for typical η values characterizing the two autothermal operation techniques [67]. The lines equations in this diagram correspond to equality sign in expression (9).

The upper area over each line corresponds to the domain on which the inequation (9) is fulfilled, i.e. on which the autothermal regime is achievable, for the corresponding technique. In situations where inequation (9) is not fulfilled (the area under each line), the heat released in the process is not sufficient to preheat the mixture fed into the reactor, an additional source of energy being required. For the reactor with periodic flow reversal (represented by the solid blue line), the ΔT_{ad} domain is more extended towards small values. This means that the reactor with flow reversal allows autothermal operation at lower values for ΔT_{ad} , as compared to the classical

technique (reactor-external heat exchanger system/ dashed red line). Consequently, the RFR offers more extensive possibilities for saving energy, the difference between the two techniques being represented by the region between the two lines.

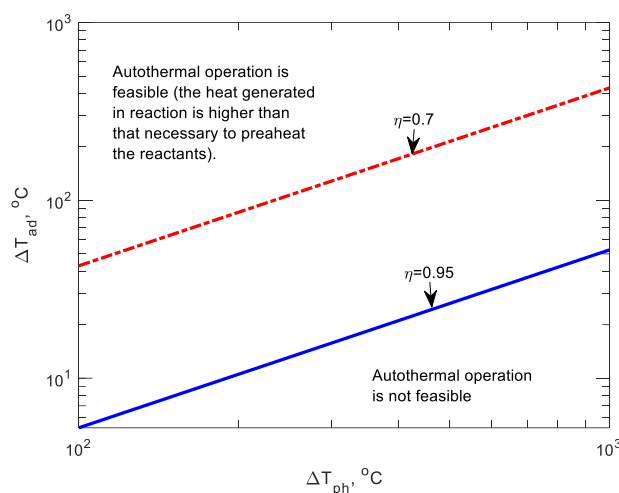


Fig. 3. Domains of autothermal operation represented in the ΔT_{ad} - ΔT_{ph} diagram (adapted from Barresi et al. [67])

6. Design principles of the RFR

As expected, the design procedures for unsteady state operated reactors are more complex, compared with the corresponding steady-state operated ones. Design principles for the RFR were formulated only in a relatively small number of published studies [17, 21, 67, 68]. These studies emphasize that the main parameters having to be considered in RFR design are the duration of a semi-cycle (t_{sc}), the feed reactant concentration (y_{A0}), the inlet gas superficial velocity (u) and the fixed bed zones lengths (L_c , L_i).

The feed reactant concentration and the gas velocity are the main parameters influencing the maximum temperature attained in the bed and the extension of the high temperature zone. In order to achieve the autothermal operation regime, the maximum temperature should be higher than the reactant ignition temperature. On the other hand, the length of the high temperature zone must be sufficient to achieve the required conversion of reactant (particularly important in pollutant combustion applications).

According to Barresi et al. [67] and Luzi et al. [21], the main steps in the design of the RFR (for a selected catalyst, a gas flow rate to be processed and a desired reactant conversion) are the following: a) Selection of the catalyst bed type (fixed bed of catalyst pellets or monolith structure). The criteria adopted in this selection are a good utilization of the catalyst (minimization of limitation effects induced by physical steps on catalytic process kinetics, particularly by internal diffusion), a high

thermal capacity of the solid bed and a low gas pressure drop in the bed. As shown above, the monolith bed provides a good utilization of the catalyst (thin catalyst layer), a low gas pressure drop but a relatively low thermal capacity (high bed porosity) and a higher manufacturing cost.

A fixed bed of relatively large catalyst pellets, with the catalyst distributed in a thin layer near the external surface (egg-shell distribution), permits to avoid the limiting influence of internal diffusion, assuring at the same time a relatively high thermal bed capacity and a relatively low gas pressure drop. An important decision to be taken in this step is also selection of the shape and size of the catalyst pellets. To ensure good gas-solid heat and mass transfer, the most advantageous are the shapes that maximize the ratio between external surface area and volume of the pellet, such as monoliths, wagon wheels, rings, trilobes [69]. However, due to their relatively lower manufacturing cost, the common spherical or cylindrical shapes are frequently preferred.

b) Selection of the reactor spatial velocity (WHSV or GHSV) value, in the interval recommended by the catalyst provider and calculation of necessary amount of catalyst for a steady state fixed bed reactor. In the case of RFR, a larger catalyst quantity (longer catalyst bed) is necessary, in order to keep the high temperature front inside the catalyst, to reach the required level of reactant conversion. In their RFR design study (VOC combustion), Barresi et al. [67] doubled the amount of catalyst calculated for steady state fixed bed reactor. In addition, two supplementary beds of inert solid should be placed before and after the catalyst bed, to ensure the regenerative heat storage and exchange. As already mentioned, the same authors suggest using a total volume of inert equal to the volume of catalyst bed. However, these are empirical assumptions. More rational is to determine the volumes of catalyst using optimization calculations based on economic criteria.

c) Calculate the diameter and length of the bed, assuming a value for gas velocity in the feed section. Large reactor diameters correspond to low gas velocities and low pressure drops. The presence of an inert bed before the catalyst guarantees a uniform gas distribution across the catalyst bed, even at low gas velocities. However, low gas velocities lead to high extra-particle concentration and temperature gradients, limiting the chemical transformation kinetics; therefore, the gas velocity should be carefully selected. Usually, the feed gas superficial velocity is chosen in the interval 0.1–0.5 m/s.

d) Determine, by successive reactor simulations, the duration of a semi-cycle (t_{sc}). An adequate mathematical model of the process is necessary in this aim. A one-dimensional heterogeneous model satisfies usually the accuracy demands for the reactor design. Two aspects should be taken into consideration in the selection of t_{sc} : (i) the decrease of t_{sc} increases the maximum temperature attained in the bed; (ii) the valves used to switch the gas flow direction are resisting to approximately 500 000 strokes [67], so the choice of t_{sc} will directly influence the life of the valves.

7. Case study: combustion of a volatile organic compound in a reverse flow reactor

7.1. The mathematical model

In what follows, will be presented a theoretical study of methyl methacrylate (MMA) catalytic combustion in a fixed bed reactor with periodic flow reversal. MMA is an important monomer included in the class of VOC. MMA combustion in air diluted mixtures, on Pt (0.5 wt %)/ γ -alumina, can be modelled as a first order reaction, due to the large excess of oxygen [70]:

$$v_{RA} = k p_A; k = k_0 \exp\left(-\frac{E}{RT}\right); k_0 = 17284 \text{ kmol kg}^{-1} \text{ s}^{-1} \text{ bar}^{-1}; E = 60.84 \text{ kJ/mol} \quad (10)$$

p_A - partial pressure of MMA.

The spatial distribution of Pt in the alumina pellet is considered of 'egg-shell' type, i.e. Pt is distributed only in a thin zone (having a thickness of 0.25 mm), situated in the proximity of external pellet surface. The Pt concentration in this active zone is considered 0.5 % (wt). The considered constructive and operational reactor characteristics are given in Table 3.

Table 3 The parameter values used in the simulation of the RFR for MMA combustion

Parameter	Notation	Value
Diameter of the catalyst bed (m)		0.3
Total length of the solid bed (inert and catalyst) (m)	L	1.34
Length of the catalyst bed (m)		0.67
Length of each inert solid zone at solid bed extremities (m)	L_i	0.335
Feed temperature of the gaseous reaction mixture (°C)	T_{G0}	25
Initial temperature of the solid bed (°C)	T_{S0}	210
Solid particle diameter (spherical), mm	d_p	6
Particle density, kg/m ³	ρ_s	1327
Thickness of catalytic zone in the catalyst pellet, mm		0.25
MMA molar fraction in the feed	y_{A0}	0.000185
Superficial velocity of the gas in the feed section of the bed (m s ⁻¹)	u	0.26
Reaction enthalpy (J mol ⁻¹)	ΔH_{RA}	-2600000
Adiabatic temperature rise (K)	ΔT_{ad}	16
VOC ignition temperature (°C)	T_{ign}	210

The simulation study is based on a one-dimensional, heterogeneous, axial dispersion model. This consists of the mass and heat balance equations for the gaseous and solid phases, (11)–(14), formulated in the following hypotheses: (i) adiabatic operation; (ii) negligible accumulation of gas components in the pores of catalyst pellet; (iii) isothermal catalyst pellet; (iv) external concentration and temperature gradients insignificant; (v) the limiting effect of intraparticle gas diffusion is characterized by the internal effectiveness factor concept; (vi) the transport of mass and heat in the gas phase take place essentially by convection and axial dispersion; (vii) the only

reaction of MMA is its oxidation to CO₂; (viii) isobaric operation (1 bar); (ix) the solid bed includes a central catalyst zone (pellets containing Pt/alumina) bounded by two identical zones of inert (γ -alumina pellets), as shown in Fig. 1-B.

$$\varepsilon \frac{\partial y_{AG}}{\partial t} = \varepsilon D_L \frac{\partial^2 y_{AG}}{\partial z^2} - u \frac{\partial y_{AG}}{\partial z} - k_G a_v (y_{AG} - y_{AS}) \quad (11)$$

$$k_G a_v C_t (y_{AG} - y_{AS}) = \rho_p (1 - \varepsilon) \eta_i v_{RA} (y_{AS}, T_S) \quad (12)$$

$$\varepsilon \rho_G c_{pG} \frac{\partial T_G}{\partial t} = \varepsilon \lambda_{LG} \frac{\partial^2 T_G}{\partial z^2} - u \rho_G c_{pG} \frac{\partial T_G}{\partial z} + \alpha a_v (T_S - T_G) \quad (13)$$

$$(1 - \varepsilon) \rho_S c_S \frac{\partial T_S}{\partial t} = \lambda_{LS} \frac{\partial^2 T_S}{\partial z^2} + (-\Delta H_{RA}) (1 - \varepsilon) \rho_p \eta_i v_{RA} (y_{AS}, T_S) - \alpha a_v (T_S - T_G) \quad (14)$$

The initial conditions:

$$t=0, \quad 0 \leq z \leq L, \quad y_{AG} = y_{Ai}, \quad T_G = T_{Gi}, \quad T_S = T_{Si} \quad (15)$$

The boundary conditions:

$$z=0, t>0: \quad u(y_{A0} - y_{AG}) = -\varepsilon D_L \frac{\partial y_{AG}}{\partial z}; \quad u \rho_G c_{pG} (T_{G0} - T_G) = -\varepsilon \lambda_{LG} \frac{\partial T_G}{\partial z}; \quad \frac{\partial T_S}{\partial z} = 0; \quad (16)$$

$$z=L, t>0: \quad \frac{\partial y_{AG}}{\partial z} = \frac{\partial T_G}{\partial z} = \frac{\partial T_S}{\partial z} = 0 \quad (17)$$

y_{AG}, y_{AS} – MMA molar fractions in the gas and solid respectively; T_G, T_S – gas and solid temperatures; k_G, α – gas to solid mass and heat transfer coefficients; ρ_p, ρ_G – catalyst pellet and gas densities; D_L, λ_{LG} – axial dispersion mass and heat transport coefficients; η_i – internal effectiveness factor; u – superficial velocity of the gas; a_v – gas to solid specific contact area; λ_{LS} – effective axial heat conduction of solid in the bed; C_{pS}, C_{pG} – specific heats of solid and gas respectively; C_t – total molar concentration in the gas; ε – interparticle porosity of the solid bed; t, z – time and axial coordinates.

Note that the differential balance equations (11) to (14) are valid also for the inert solid, by nullifying the reaction rate term (v_{RA}).

7.2 The expression of internal effectiveness factor

The MMA combustion on Pt/alumina is a fast reaction, the internal diffusion having a limitation effect on the MMA combustion, even at thin catalyst layers in the pellet. To include this effect, it is used the effectiveness factor concept.

The mass balance equation inside a spherical catalyst pellet with egg-shell type distribution (Fig. 4) and its solution for single reactions are presented in Table 4.

Using the expression of the MMA concentration inside the pores of the catalyst pellet, it is calculated the internal effectiveness factor, by the relation:

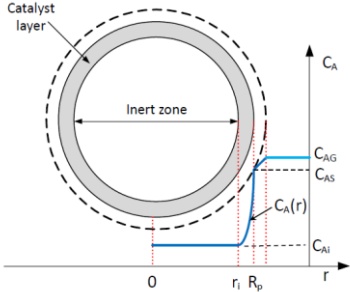
$$\eta_i = \frac{\bar{v}_{RA}^{(v)}}{v_{RA}^{(v)}(C_{AS})}; \quad \bar{v}_{RA}^{(v)} = \frac{1}{(1-x_i^3)V_p} S_{ext} D_{ef} \left(\frac{dC_A}{dr} \right)_{r=R_p} \quad (23)$$

By performing analytical calculations, the effectiveness factor expression is obtained:

$$\eta_i = \frac{3}{\phi^2(1-x_i^3)} \frac{(\phi^2 x_i - 1) \sinh[\phi(1-x_i)] + \phi(1-x_i) \cosh[\phi(1-x_i)]}{\sinh[\phi(1-x_i)] + \phi x_i \cosh[\phi(1-x_i)]} \quad (24)$$

In the above expressions are used the notations defined in Fig. 4. In addition: D_{ef} – effective diffusivity of reactant A inside the porous catalyst pellet, calculated by Bosanquet formula, considering both molecular and Knudsen diffusion mechanisms; S_{ext} and V_p are the external surface area and volume of the pellet. For a spherical pellet: $S_{ext}/V_p = 3/R_p$.

Table 4 The solution of mass balance equation in a spherical pellet with egg-shell type distribution of catalyst

$\frac{1}{r^2} \frac{d}{dr} \left(r^2 D_{ef} \frac{dC_A}{dr} \right) - v_{RA}^{(v)} = 0, \quad v_{RA}^{(v)} = \rho_p v_{RA} \quad (18)$ $\frac{d^2 y}{dx^2} - \phi^2 y = 0; \quad x = r/R_p; \quad y = C_A x \quad (19)$ $\phi^2 = R_p^2 \frac{k_v}{D_{ef}}; \quad k_v = \rho_p k RT$ Equation (19) has the general solution: $y = A_1 e^{\phi x} + A_2 e^{-\phi x} \quad \text{or} \quad C_A = \frac{1}{x} (A_1 e^{\phi x} + A_2 e^{-\phi x}) \quad (20)$ A_1 and A_2 are calculated from the boundary conditions (Fig. 4): $x=1, C_A = C_{AS}; \quad x=x_i = \frac{r_i}{R_p}, \quad \frac{dC_A}{dx} = 0 \quad (21)$ $A_1 = \frac{C_{AS}}{2} \frac{(1+\phi x_i) \exp(-\phi x_i)}{\sinh[\phi(1-x_i)] + \phi x_i \cosh[\phi(1-x_i)]}; \quad (22)$ $A_2 = \frac{C_{AS}}{2} \frac{(\phi x_i - 1) \exp(\phi x_i)}{\sinh[\phi(1-x_i)] + \phi x_i \cosh[\phi(1-x_i)]};$	 Fig. 4. Sketch of a spherical pellet with egg-shell type distribution of catalyst.
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The values of the interphase (gas to particle) mass and heat transfer coefficients and the ones of the effective axial transport coefficients were calculated using correlations published in the literature [71,72].

The system of nonlinear partial differential equations (11)–(14) was integrated numerically, using the method of lines, by an own code developed in Matlab

programming environment. This involves the approximation of spatial partial derivatives by the central difference method and the integration in time, of the ordinary differential equations system thus obtained.

It was considered that initially the bed has a uniform temperature and does not contain reactant ($y_{Ai}=0$). After the change of the feed point, the initial conditions are represented by the states at the moment of flow reversal. It should be also emphasized that the values $z=0$ and respectively $z=L$ are systematically assigned to the gas entry and exit positions respectively.

7.3. Reactor simulation results

Figures 5-A and 5-B presents the stabilized profiles of gas and solid temperatures along the reactor, at different moments of time, during a cycle (forward and reverse flow semi-cycles). Due to the relatively high interphase heat transfer, the gas and solid temperatures are very close, so the curves are superposed. From these diagrams one can observe the development of a cold zone of the bed (due to gas preheating) in the vicinity of the inlet section of the bed and its extension in time. Also, due to the heat evolved in the reaction, hot spot zones are developed, which displace continuously along the bed. The shift of these hot zones along the solid bed is also evidenced in the tridimensional diagram pictured in Fig. 6 and the corresponding heat transferred from the solid phase (calculated by relation (3)) is given in Fig. 7.

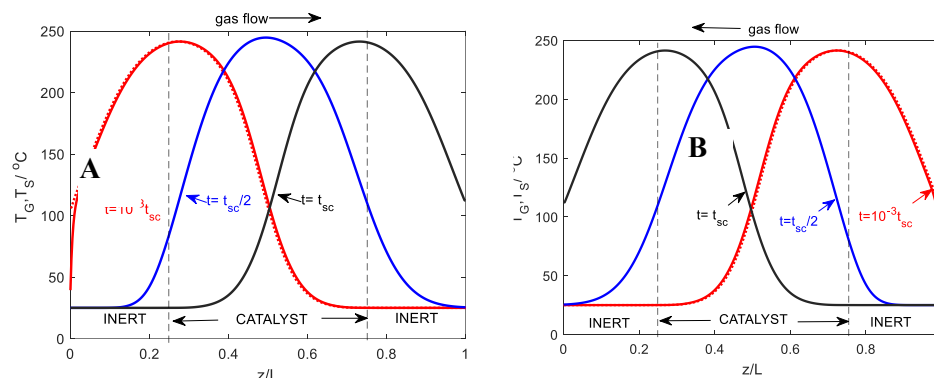


Fig. 5 Temperature evolutions along the bed, during a cycle: A-forward gas flow semicycle; B – reverse gas flow semicycle. Continuous lines: gas temperature; dotted lines: solid temperature. The vertical dashed lines represent the limits between the catalyst and inert zones of the bed.

Figures 8-A and 8-B illustrate the evolutions of VOC conversion (reacted VOC fraction) along the solid bed, corresponding to the temperature evolutions presented in Figures 5-A and 5-B. The conversion increase is relatively sharp, due to the fast combustion kinetics in the working conditions.

For the operation conditions given in Table 3 and the simulation results already presented, considering the ignition temperature $T_{ign}=210\text{ }^{\circ}\text{C}$, it was calculated a *thermal recovery efficiency* of the reactor, $\eta=0.93$. The ignition temperature was approximated as the temperature necessary to attain a VOC conversion of 50 % [73].

This was determined from the experimental conversion-temperature curves for MMA, published by Banu et al. [70].

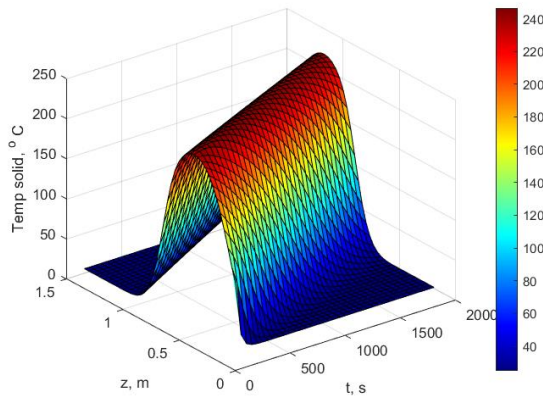


Fig. 6 Axial and time evolutions of the solid temperature in the RFR reactor.

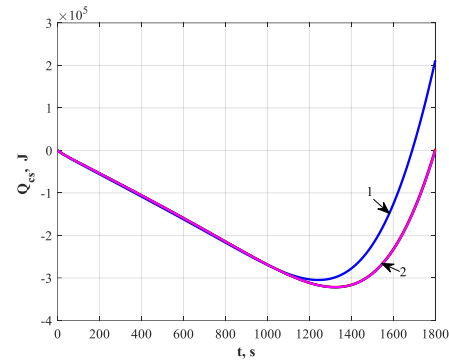


Fig. 7 Time evolution of the amount of sensible heat transferred from the solid phase (relation (3)). Forward gas flow. 1- a semi-cycle before stabilization; 2- at cyclic stationary state.

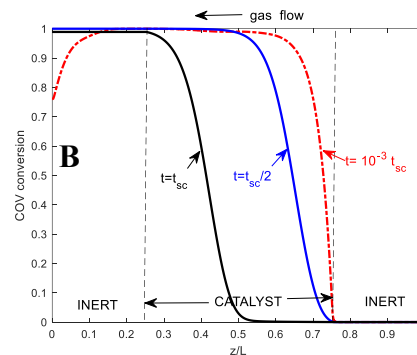
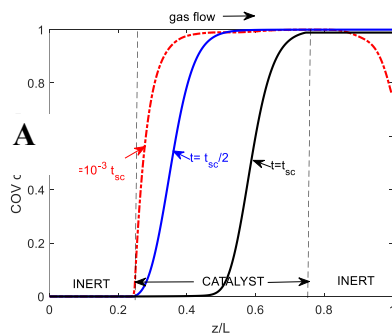


Fig. 8 VOC conversion profiles along the reactor bed: **A**-forward gas flow semicycle; **B** – reverse gas flow semicycle.

The RFR heat balance analysis shows that, when operating in a stabilized regime (cyclic stationary state), the autothermal operation mechanism consists in the displacement of solid sensible heat (essentially by the intermediate of gas phase), from the bed zone adjacent to the feed section, towards the bed zone preceding the gas exit. The heat transferred from the solid for preheating the gas in the first zone of bed is recovered from the heat generated in the reaction, which accumulates in the area adjacent to the gas exit [74]. So, the sensible heat content of the solid bed at the end of semi-cycle, is the same as that at the beginning of semi-cycle (Fig. 7), i.e. the profiles of solid temperature at $t=0$ and $t=t_{sc}$ are symmetrical as shown in Fig. 5.

The RFR reactor simulation studies led to the following observations:

- The increase of the gas flowrate leads to the expansion of the cooled zone of the solid and the contraction of the high temperature zone, having as consequences the decrease of VOC conversion and the flattening of the maximum temperature.
- The increase of VOC concentration in the feed leads to an increase in the temperature of the bed, as result of the increase of transformed VOC amount and the augmentation of heat released in the solid bed.
- The increase in the duration of the semi-cycle (t_{sc}), leads to the expansion of the cooled zone of the solid, with the contraction of the high-temperature front and its displacement towards the bed exit, with possible decrease of VOC conversion, if the high-temperature front leaves the catalytic zone. At given working conditions, there is a maximum value of t_{sc} , beyond which stabilization is no longer possible. The decrease of t_{sc} value leads to tighter cooled zones, higher reaction temperatures, and increased VOC conversions.

7.4. A sensitivity analysis of the RFR

The transport and transfer parameters involved in the process model (D_L , λ_{LG} , λ_{LS} , D_{ef} , α , k_G) are calculated, with inherent errors, using literature correlations. Therefore, in addition to RFR simulation, it is interesting to calculate the sensitivity of temperatures and reactant conversion profiles, in respect to the model parameters. The temperature and conversion *sensitivity coefficients*, in a point along the reactor axis, give information on the effect of potential errors in the parameter calculation, on the local temperature or reactant conversion.

The *normalized sensitivity coefficient*, of the variable y with respect to the variable θ , s_θ^y , is defined by the relation [75]:

$$s_\theta^y = \frac{\partial y}{\partial \theta} \frac{\bar{\theta}}{\bar{y}} \quad (25)$$

$\bar{y}$ and $\bar{\theta}$ are the corresponding nominal values, at which the sensitivity coefficient is calculated.

For the simulated RFR, the numerical calculations evidenced that the highest sensitivity values occur in respect to interphase heat transfer coefficient, α . The result is explicable, as the value of this parameter gives the intensity of interphase heat transfer (from the solid phase to the flowing gas in the reaction zone, and respectively from gas to solid in the zones of heating the solid), the essential phenomenon in the RFR process mechanism.

The sensitivities of gas temperature and reactant conversion respectively, in respect to gas-solid heat transfer coefficient α , are presented in Fig. 9. The results show that both conversion and gas temperature sensitivities feature zones of both negative and positive values. The zone of negative sensitivity of gas temperature (in the neighborhood of $x=0.4$, Fig. 9-A) corresponds to a potential extension of cooled zone of the bed, when increasing the interphase heat transfer coefficient. The temperature decrease leads to a decrease in reaction rate, and consequently to a negative conversion sensitivity (Fig. 9-B). The zone of positive temperature and conversion

sensitivities lies on the catalyst area of the bed, where the occurs VOC combustion. An increase of the interphase heat transfer coefficient leads to an increase of gas temperature and reactant conversion on this zone. Both sensitivities present a maximum around $x=0.55$, the point corresponding to the maximum of the VOC combustion rate. Around this point, the difference between the solid and gas temperatures (T_s-T_g) is maximum (Fig. 10). Beyond this point, the value of the difference T_s-T_g diminishes, and the gas temperature sensitivity with respect to α decreases, remaining positive. At a point close to the boundary between catalyst and inert region ($x \cong 0.75$), T_s-T_g passes from positive to negative values (T_g becomes higher than T_s), beginning the region of solid bed heating. The difference T_s-T_g continues to decrease ($T_g - T_s$ increases) stabilizing on the vicinity of the bed exit section. On this second inert zone of the bed, the gas temperature sensitivity presents a local maximum, around $x \cong 0.90$.

From the temperature sensitivity coefficient presented in Fig. 9-A, it can be estimated that, in the point of maximum sensitivity, an error of 10 % in the evaluation of α , typical for published correlations, leads to an error of approximately 8 K in the calculation of the gas temperature, and respectively 4% in the calculation of the VOC conversion [74,75]. These results emphasize the importance of using adequate values of the interphase heat transfer coefficient. However, in design studies, experimental data are often lacking, literature data being the single source of information. In these cases, it is suggested to use average values provided by two or more correlations, recommended for the working domain.

8. Conclusions

This work reviews the main research results in the field of RFR technique, published in the last decades. RFR principle is already used in commercial applications, particularly for purification of gaseous effluents by catalytic reactions.

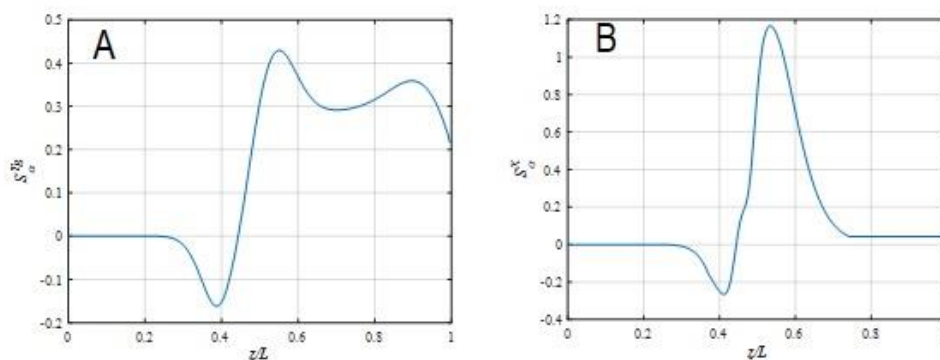


Fig. 9. Sensitivities in respect to the gas-solid heat transfer coefficient (A – Gas temperature sensitivity B– VOC Conversion sensitivity). Left-to-right flow; $t_{sc} = 1800$ s.

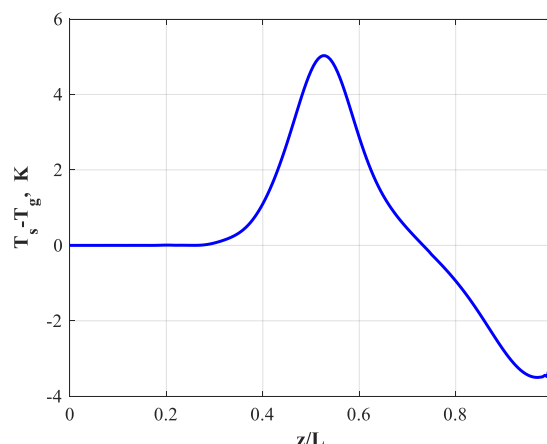


Fig. 10 The difference between solid and gas temperatures along the bed. Left-to-right flow; $t_{sc} = 1800$ s.

The fixed bed catalytic reactors with periodic reversal of the gas flow allows an efficient autothermal operation, particularly for the treatment of gaseous mixtures with low concentrations of reactants, such as the removal, by catalytic combustion, of volatile organic compounds from waste gases. Compared to the classic process including an adiabatic reactor and a heat exchanger, the RFR permits to achieve the autothermal regime of operation at significantly lower values of the adiabatic temperature rise, thus saving energy.

The fixed bed of the RFR can be constituted of solid pellets or monolithic structures. An advantageous option is to use catalyst pellets of relatively large dimensions, with the catalyst distributed in a thin layer at the external surface (e.g. egg-shell type). This provides a relatively low-pressure drop of the gas, a small pellet resistance to reactant diffusion inside the catalyst layer (the reaction zone) and a relatively large heat capacity of the bed.

To evidence the particularity of the RFR process modelling, a detailed case study is also presented. A sensitivity analysis evidenced potentially temperature calculation errors that could arise due to the uncertainty in the evaluation of interphase heat and mass transfer coefficients by the available correlations. Hence, the values of these parameters should be selected with caution in the RFR modelling applications.

References

- [1] Butt J. B., *Reaction kinetics and reactor design*, 2nd edition, Marcel Dekker, Basel, 2000.
- [2] Kolios G., Frauhammer J., Eigenberger G., *Autothermal fixed-bed reactor concepts*, Chem. Eng. Sci., **55**, 2000, p. 5945-5967.
- [3] Brown R. C., *Process intensification through directly coupled autothermal operation of chemical reactors*, Joule, **4**, 2020, p. 2268–2289.
- [4] Froment G. F., Bischoff K. B., De Wilde J., *Chemical Reactor Analysis and Design*, 3rd Edition, John Wiley & Sons, 2011.
- [5] Velardi S. A., Barresi A. A., *Methanol synthesis in a forced unsteady-state reactor network*, Chem. Eng. Sci., **57**, 2002, p. 2995 – 3004.

- [6] Zagoruiko A. N., Bobrova L., Vernikovskaya N., Zazhigalov S., *Unsteady-state operation of reactors with fixed catalyst beds*, Rev. Chem. Eng., **37**, 2021, p. 193-225.
- [7] Abdulrahman I., Masa V., Teng S. Y., *Process intensification in the oil and gas industry: A technological framework*, Chem. Eng. Process: Proc. Intensif., **159**, 2021, 108208.
- [8] <http://hotairengines.org/closed-cycle-engine/stirling-1816> (accessed June 2025).
- [9] Cottrell F. G., *Purifying gases and apparatus therefore*, US Patent 212173, 1938.
- [10] Zagoruiko A. N., *The reverse-flow operation of catalytic reactors: history and prospects*, Curr. Top. Catal., **10**, 2012, p. 113-129.
- [11] Houdry E. J., *Catalytic treatment of gas streams*, US Patent 2946651, 1956.
- [12] Boreskov G. K., Matros Y. S., *Unsteady state performance of heterogeneous catalytic reactions*, Cat. Rev.-Sci. Eng. **25**, 1983, p. 551-590.
- [13] Matros Yu. Sh., Bunimovich G. A., *Reverse-flow operation in fixed bed catalytic reactors*, Cat. Rev.-Sci. Eng., **38**, 1996, p. 1-68.
- [14] Marin P., Diez F. V., Ordonez S., *Reverse flow reactors as sustainable devices for performing exothermic reactions: Applications and engineering aspects*, Chem. Eng. Process., **135**, 2019, p. 175-189.
- [15] Mastroianni L., Di Serio M., Salmi T., Russo V., *Comprehensive reverse flow reactor model for fluid-solid systems*, Chem. Eng. Sci., **280**, 2023, Article 119019.
- [16] Barresi A. A., Baldi G., Fissore D., *Forced Unsteady-State Reactors as Efficient Devices for Integrated Processes: Case Histories and New Perspectives*, Ind. Eng. Chem. Res., **46**, 2007, p. 8693-8700.
- [17] Cittadini M., Vanni M., Barresi A. A., Baldi G., *Reverse-flow catalytic burners: response to periodical variations in the feed*, Chem. Eng. Sci., **56**, 2001, p. 1443-1449.
- [18] Li Q., Chen G., Zhu Y., Li X., Yao Y., *Resonance response in the catalytic combustion of methane and propane binary mixture in reverse-flow reactor*, Chem. Eng. J., **345**, 2018, p. 375-388.
- [19] Zhao Z., Chen T., Ghoniem A. F., *Rotary bed reactor for chemical-looping combustion with carbon capture. Part 1: Reactor design and model development*, Energ. Fuel., **27**, 2013, p. 327-343.
- [20] Zhao Z., Chen T., Ghoniem A. F., *Rotary bed reactor for chemical-looping combustion with carbon capture. Part 2: Base case and sensitivity analysis*, Energ. Fuel., **27**, 2013, p. 344-359.
- [21] Luzi C. D., Martinez O. M., Barreto G. M., *Autothermal reverse-flow reactors: Design and comparison of valve-operated and rotary systems*, Chem. Eng. Sci., **148**, 2016, p. 170-181.
- [22] Kushwaha A., Poirier M., Sapoundjiev H., Hayes R.E., *Effect of reactor internal properties on the performance of a flow reversal catalytic reactor for methane combustion*, Chem. Eng. Sci., **59**, 2004, p. 4081 - 4093.
- [23] Kushwaha A., Poirier M., Hayes R.E., Sapoundjiev H., *Heat extraction from a flow reversal reactor in lean methane combustion*, Chem. Eng. Res. Des., **83**, 2005, p. 205-213.
- [24] Amelio M., Morrone P., *Numerical evaluation of the energetic performances of structured and random packed beds in regenerative thermal oxidizers*, Appl. Thermal Eng., **27**, 2007, p. 762-770.
- [25] Keith J. M., *Controlling reverse-flow reactors via multiscale transient thermal Dispersion*, Adv. Environ. Res., **7**, 2003, p. 521-535.
- [26] Hayes R.E., *Catalytic solutions for fugitive methane emissions in the oil and gas sector*, Chem. Eng. Sci., **59**, 2004, p. 4073 - 4080.
- [27] Salomons S., Hayes R. E., Poirier M., Sapoundjiev H., *Modelling a reverse flow reactor for the catalytic combustion of fugitive methane emissions*, Comput. Chem. Eng., **28**, 2004, p. 1599-1610.
- [28] Zhang Z., Jiang Z., Shangguan W., *Low-temperature catalysis for VOCs removal in technology and application: A state-of-the-art review*, Catal. Today, **264**, 2016, p. 270-278.
- [29] Pourghadiri E., Sari A., *Theoretical Investigation on syngas production by catalytic partial oxidation of methane in a reverse-flow microchannel monolithic reactor*, Ind. Eng. Chem. Res., **62**, 2023, p. 9433-9452.
- [30] Zazhigalov S., Elyshev A., Zagoruiko A., *Catalytic reverse-flow oxidation process in reactors of various designs: Axial, side and tangential gas inlet*, Chem. Eng. Res. Des., **191**, 2023, p. 364-374.
- [31] Aksikas I., *Optimal output-feedback temperature regulation of a catalytic reverse flow reactor PDEs model*, J. Process Control, **103**, 2021 p. 1-7.
- [32] Aksikas I., *Error-feedback temperature regulation for a reverse flow reactor driven by a distributed parameter exosystem*, J. Process Control, **117**, 2022, p. 132-139.

- [33] Budhi Y. W., *Reverse flow reactor with side feeding as a novel strategy to create dynamic oxygen coverage and heat propagations in lean ammonia oxidation*, Chem. Eng. Process.: Process Intensif., **155**, 2020, Article 108064.
- [34] Li Q., Chen G., Zhu Y., Li X., Yao Y., *Resonance response in the catalytic combustion of methane and propane binary mixture in reverse-flow reactor*, Chem. Eng. J., **345**, 2018, p. 375–388.
- [35] Sophiana I. C., Topandi A., Culsum N. T. U., Budhi Y. W., *Design and simulation of a reverse flow reactor for catalytic oxidation of lean benzene emissions*, J. Phys.: Conf. Ser., 1772, 2021, paper 012018 (doi:10.1088/1742-6596/1772/1/012018).
- [36] Luzi C.D., Martínez M. O., Barreto G. F., *Rotary reverse flow reactor vs. adiabatic reactor with regenerative preheating - Design and comparison*, Chem. Eng. Sci., **166**, 2017, 246–261.
- [37] Matros Yu Sh., *Catalytic processes under unsteady-state conditions, Studies in surface science and catalysis*, **43**, Elsevier Science, Amsterdam, 1989.
- [38] Zazhigalov S., Elyshev A., Zagoruiko A., *Catalytic reverse-flow oxidation process in reactors of various designs: Axial, side and tangential gas inlet*, Chem. Eng. Res. Des., **191**, 2023, p. 364–374.
- [39] Liang W., Sun H., Shi X., Zhu Y., *Abatement of toluene by reverse-flow nonthermal plasma reactor coupled with catalyst*, Catal., **10**, 2020, 511 (doi:10.3390/catal10050511).
- [40] Chen Y., Chi Y., Yan J.-H., Ni M.-J., *Effect of periodic variation of the inlet concentration on the performance of reverse flow reactors*, Ind. Eng. Chem. Res., **50**, 2011, p. 5448–5458.
- [41] Chen G., Chi Y., Pan C., Yan J., Ni M., *Methane-benzene binary mixture destruction in a reverse flow catalytic reactor*, J. Mater. Cycles Waste Manag., **13**, 2011, p. 219–224.
- [42] Effendy M., Wardhono E. Y., Soeryanto K., Arsana I. M., *Effect of intraparticle diffusion-reactions at reverse flow reactors. Cases study: Methane catalytic oxidation*, IOP Conf. Series: Materials Science and Engineering, **673**, 2019, 012007 (doi:10.1088/1757-899X/673/1/012007).
- [43] Li Z., Wu Z., Qin Z. et al., *Demonstration of mitigation and utilization of ventilation air methane in a pilot scale catalytic reverse flow reactor*, Fuel Proc. Technol., **160**, 2017, p. 102–108.
- [44] Urbani C., Marin P., Diez F. V., Ordonez S., *Catalytic combustion of sulphur-containing methane lean emissions in a reverse-flow reactor with integrated adsorption*, Chem. Eng. J., **285**, 2016, p. 39–48.
- [45] Muñoz E., Marín P., Diez F. V., Ordóñez S., *Selective catalytic reduction of NO in a reverse-flow reactor: Modelling and experimental validation*, Appl. Energ., **138**, 2015, p. 183–192.
- [46] Fernandez J., Marín P., Diez F. V., Ordonez S., *Experimental demonstration and modeling of an adsorption-enhanced reverse flow reactor for the catalytic combustion of coal mine ventilation air methane*, Chem. Eng. J., **279**, 2015, p. 198–206.
- [47] Fernandez J., Marín P., Diez F. V., Ordonez S., *Coal mine ventilation air methane combustion in a catalytic reverse flow reactor: Influence of emission humidity*, Fuel Proc. Technol., **133**, 2015, p. 202–209.
- [48] Thompson C. R., Marín P., Diez F. V., Ordonez S., *Evaluation of the use of ceramic foams as catalyst supports for reverse-flow combustors*, Chem. Eng. J., **221**, 2013, 44–54.
- [49] Wang S., Gao D., Wang S., *Steady and transient characteristics of catalytic flow reverse reactor integrated with central heat exchanger*, Ind. Eng. Chem. Res., **53**, 2014, p. 12644–12654.
- [50] Tuna P., Bauer F., Hulteberg C., Malek L., *Regenerative reverse-flow reactor system for cracking of producer gas tars*, Biomass Conv. Bioref., **4**, 2014, p. 43–51.
- [51] Zagoruiko A.N., Vanag S.V., *Reverse-flow reactor concept for combined SO₂ and CO-oxidation in smelter off-gases*, Chem. Eng. J., **238**, 2014, p. 86–92.
- [52] Huang S.-W., Lou J.-C., Lin Y.-C., *Treatment of VOCs with molecular sieve catalysts in regenerative catalytic oxidizer*, J. Hazard. Mater., **183**, 2010, p. 641–647.
- [53] Lou J.-C., Huang S.-W., *Treating isopropyl alcohol by a regenerative catalytic oxidizer*, Separ. Purif. Technol., **62**, 2008, p. 71–78.
- [54] Marín P., Ordonez S., Diez F., *Monoliths as suitable catalysts for reverse-flow combustors: modeling and experimental validation*, AIChE J., **56**, 2010, p. 3162–3173.
- [55] Marín P., Ordonez S., Diez F. D., *Combustion of toluene–hexane binary mixtures in a reverse flow catalytic reactor*, Chem. Eng. Sci., **63**, 2008, p. 5003 – 5009.
- [56] Simeone M., Salemm L., Allouis C., Volpicelli G., *Temperature profile in a reverse flow reactor for catalytic partial oxidation of methane by fast IR imaging*, AIChE J., **54**, 2008, p. 2689–2698.

- [57] Fissore D., Barresi A. A., Baldi G., Hevia M. A. G., Ordonez S., Diez F. V., *Design and Testing of Small-Scale Unsteady-State Afterburners and Reactors*, *AIChE J.*, **51**, 6, 2005, p. 1654-1664.
- [58] Hevia M. A. G., Ordonez S., Diez F. V., Fissore D., Barresi A. A., *Design and Testing of a Control System for Reverse-Flow Catalytic Afterburners*, *AIChE J.*, **51**, 11, 2005, p. 3020-3027.
- [59] Hevia M. A. G., Ordonez S., Diez F. V., *Effect of the catalyst properties on the performance of a reverse flow reactor for methane combustion in lean mixtures*, *Chem. Eng. J.*, **129**, 2007, 1–10.
- [60] Neumann D., Vesper G., *Catalytic partial oxidation of methane in a high-temperature reverse-flow reactor*, *AIChE J.*, **51**, 2005, p. 210-223.
- [61] Mitri A., Neumann D., Liu T., Vesper G., *Reverse-flow reactor operation and catalyst deactivation during high-temperature catalytic partial oxidation*, *Chem. Eng. Sci.*, **59**, 2004, p. 5527 – 5534.
- [62] Neumann D., Kirchhoff M., Vesper G., *Towards an efficient process for small-scale, decentralized conversion of methane to synthesis gas: combined reactor engineering and catalyst synthesis*, *Catal. Today*, **98**, 2004, p. 565–574.
- [63] Neumann D., Gepert V., Vesper G., *Some considerations on the design and operation of high-temperature catalytic reverse-flow reactors*, *Ind. Eng. Chem. Res.*, **43**, 2004, p. 4657-4667.
- [64] Liu T., Temur H., Vesper G., *Autothermal reforming of methane in a reverse-flow reactor*, *Chem. Eng. Technol.*, **32**, 2009, p. 1358–1366.
- [65] Salomons S., Hayes R. E., Poirier M., Sapoundjiev H., *Flow reversal reactor for the catalytic combustion of lean methane mixtures*, *Catal. Today*, **83**, 2003, p. 59–69.
- [66] Chou M.-S., Cheng W.-H., Lee W.-S., *Performance characteristics of a regenerative catalytic oxidizer for treating VOC-contaminated airstreams*, *Journal of the Air & Waste Management Association*, **50**, 2000, p. 2112-2119.
- [67] Barresi A. A., Baldi G., Fissore D., *Forced unsteady-state reactors as efficient devices for integrated processes: Case histories and new perspectives*, *Ind. Eng. Chem. Res.*, **46**, 2007, p. 8693-8700.
- [68] Haynes T., Georgakis C., Caram H. S., *The design of reverse flow reactors for catalytic combustion systems*, *Chem. Eng. Sci.*, **50**, 3, 1995, p. 401-416.
- [69] Krishna R., Sie S. T., *Strategies for multiphase reactor selection*, *Chem. Eng. Sci.*, **49** (24A), 1994, p. 4029 4065.
- [70] Banu I., Manta C. M., Stoica I., Bercaru G., Bozga G., *Kinetics of methyl methacrylate combustion over a Pt/alumina catalyst*, *J. Serb. Chem. Soc.*, **8**, 6, 2018, 759-772.
- [71] Bozga G., Muntean O., *Chemical Reactors* (in Romanian), vol. 2, Ed. Tehnica, Bucuresti, 2001.
- [72] Manta C.M., Bozga G., Bildea C.S., *Simulation du procédé de depollution par combustion catalytique au niveau du grain de catalyseur poreux*, *U.P.B. Sci. Bull., Series B*, **74**, 4, 2012, p. 47-60.
- [73] Pecchi G., Jiliberto M.G., Delgado E.J., *Reaction kinetics of methane combustion over $\text{La}_{1-x}\text{Ca}_x\text{FeO}_3$ perovskites*, *J. Chil. Chem. Soc.*, **56**, 4, 2011, 895-900.
- [74] Stoica I., Banu I., Bozga G., *An analysis of the stabilization mechanism of reverse flow reactors with application in catalytic VOC combustion*, *Studia UBB Chemia*, **58**, 2013, p. 227-241.
- [75] Wu H., Rota R., Morbidelli M., Varma A., *Parametric sensitivity in fixed-bed catalytic reactors with reverse-flow operation*, *Chem. Eng. Sci.*, **54**, 1999 4579-4588.