Kinetics-free process intensification: from semi-batch to series of continuous chemical reactors

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Abstract

A kinetics-free procedure is developed to transform a reaction recipe carried out in an isothermal discontinuous semi-batch reactor into one based on a series of continuous tubular or tank reactors. Using a suitable number of reactors and a correct feeding policy, it is possible to reproduce any discontinuous recipe in flow reactors without knowing the kinetics of the system. The developed procedure allows to determine the number of reactors in series (either tubular or stirred tank) able to reproduce the performance of a semi-batch recipe in terms of selectivity, keeping the same productivity of the original semi-batch process. It was found that using 15 reactors in series allows to keep unchanged the performance of a large number of semi-batch processes once a correct policy of intermediate reactant feeding is implemented. This large number of reactors in series with intermediate feeding can be easily implemented using tubular reactors instead of stirred tank ones. Finally, the synthesis of an amine/epoxy resin was investigated as a case study, fully supporting the reliability of the proposed procedure.

Keywords: Semi-batch to continuous, Process Intensification, Kinetics-free, Flow chemistry

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1. Introduction

Process intensification (PI) is a widely-studied multidisciplinary topic which aims at increasing the efficiency of a given system by means of novel equipment designs, processes, or material [1]. PI techniques can be adopted in the chemical/petrochemical industry to develop better processes, e.g., for productivity enhancement, safety and environmental reasons, or cost reduction [2].

One very effective PI method is to switch form discontinuous to continuous processes. According to the equipment scale, there are many different ways to improve a process. For example, small scale (and

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production) equipments can adopt the methods of flow chemistry, using milli- and micro-reactors [3, 4]. These small-scale systems can also be designed to enhance mixing of species by passive devices without energy input [5]. Larger scales can take advantage from scale-out (numbering-up) of small reactors [6], or use larger (but simpler and cheaper) equipments as modular units [7]. In this last case, the transformation of semi-batch reactors (SBRs, as a generalisation of batch systems) to continuous reactors can be performed using systems at an intermediate scale between a micro-reactor and the original SBR. This is generally possible thanks to PI techniques, which allow a volume reduction keeping the productivity unchanged. By reducing the volume, one increases the intrinsic safety of the reactor, as less material is held-up. Operations are also safer as the smaller scale allows more efficient heat exchange [8, 9], when running exothermic reactions. Continuous systems also allow simple solvent separation and recycle, thus reducing its use in the plant with environmental advantages [10].

The main types of reactors used in PI are the traditional stirred tanks and tubular reactors. Novel configurations still take advantage of these two main classes of reactors, mainly aiming at approximating the ideal plug-flow reactor (a reactor with a sharp-step residence time distribution and even cross-sectional distribution of species concentration). Examples are the oscillatory baffled reactor [11], which reproduces a series of mixed vessels (thus approximating a plug-flow reactor [12, 13]), and tubular reactors in laminar conditions equipped with static mixers [14], which guarantee a well defined residence time and efficient radial mixing.

However, intensifying a process using these techniques requires a deep understanding of chemical phenomena involved in the system. Kinetic studies are thus frequently required to properly design a safe continuous process with acceptable throughput for industrial application. Recently, a procedure to switch from SBR to a continuous lateral injection reactor (LIR) was developed [15, 16] such that no chemical kinetics information is required, that is, the procedure is kinetics-free. The LIR is able to reproduce the SBR performance with a substantial decrease in volume at constant productivity. However, a continuous lateral feed can be difficult to realise in practice at a reasonable cost. Therefore, an approximation of this reactor can be obtained using simpler configurations, i.e., a series of continuous stirred tank reactors (s-CSTR) with intermediate feed or a discrete lateral injection reactor (d-LIR).

In principle, an infinite number of discrete injections (both for s-CSTR and d-LIR) perfectly reproduces the LIR (and equivalently the original SBR) behaviour. However, this is not realisable in practice. Therefore, the aim of this work is to find a finite number of injections able to approximate the LIR behaviour up to a desired extent for typical organic chemistry reaction classes. The developed approach should be used when a reaction is preferentially run in a SBR rather than a batch reactor. This happens when the concentration of a co-reactant is desired to be kept low throughout the reaction process, either because of quality (possible loss in selectivity) and/or safety (exothermic reactions) reasons. The case in which a possible loss of selectivity can happen in the reactor is considered in this work for stoichiometric addition of reactants. This method developed is general and would therefore allow moving any reaction belonging to a given class (e.g., nitrations, alkylations, aminations, ...) from a SBR recipe to a continuous reactor series (either s-CSTR or d-LIR), without knowing its kinetics.

2. Methods

A generic isothermal LIR configuration is sketched in Figure 1. This tubular reactor is equivalent (in terms of selectivity and yield) to the original isothermal SBR recipe from which it can be derived through the procedure discussed in detail elsewhere [15]. Using this procedure the continuous length-specific feed policy along the axial coordinate for species i, $f_i(x)$, can be obtained without requiring any information on the chemical reaction run in the system. Therefore, in the following $f_i(x)$ will be considered as an input (known) information, since it can be derived from the original SBR recipe.

Moreover, even if not strictly required, uniform cross-sectional area and constant density are assumed for the LIR to make the mathematics simpler. This means that the diameter (for circular pipes) is uniform throughout the length of the reactor, as well as the density. The latter is usually a reasonable approximation for organic chemistry syntheses.

2.1. LIR approximations

Many different methods can be adopted to discretise the continuous lateral feed of the LIR. In this work the LIR is divided into N_d portions of equal length, thus of equal volume. This volume is then equated to that of a single mixed vessel of the s-CSTR (Figure 2) or to that of a single tubular reactor of the d-LIR (Figure 3). This will guarantee the same total volume for both the discrete configurations, therefore retaining the same hold-up reduction with respect to the original SBR. The s-CSTR is then a series of continuous

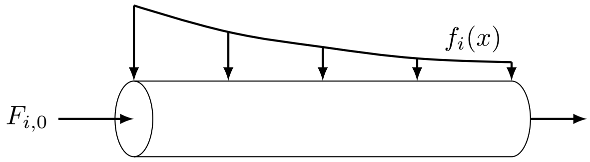

Figure 1: Generic isothermal LIR configuration.

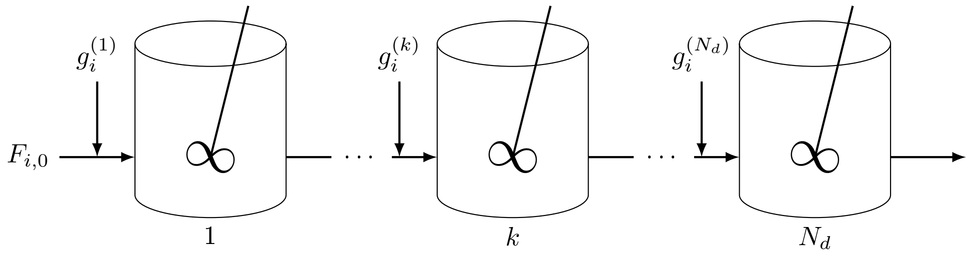

Figure 2: s-CSTR configuration. The volume of each reactor is equal to the overall LIR volume divided by N_d.

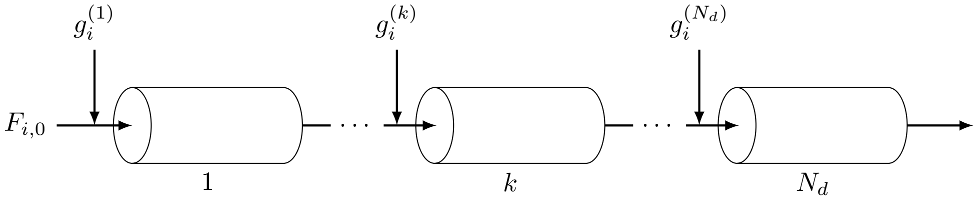

Figure 3: d-LIR configuration. The volume of each reactor is equal to the overall LIR volume divided by N_d.

stirred tank reactors of the same volume, while the d-LIR is a series of tubular reactors (assumed behaving as plug-flow reactors, PFRs), both with intermediate feed injections. This means that each reactor in the series has a volume equal to:

$$V_d = \frac{L\mathscr{A}}{N_d} \tag{1}$$

where L is the LIR length and $\mathscr{A}$ the (uniform) LIR cross-sectional area. Each reactor represents a portion of the LIR of length $\delta_L = L/N_d$.

The continuous feed pertaining each portion of the LIR is fed as a discrete injection before the single reactor (mixed vessel or pipe). For the generic k-th reactor of the series (either s-CSTR or d-LIR), the discrete injected massive flowrate for the species i is therefore computed as:

$$g_i^{(k)} = \int_{(k-1)\delta_L}^{k\delta_L} f_i(x)\, dx \tag{2}$$

for all portions $k = 1, \ldots, N_d$ and all species $i = 1, \ldots, NC$, being NC the total number of species.
The LIR inlet massive flowrate for each species, $F_{i,0}$, is fed to the first reactor for both discrete configurations. These feed policies will ensure that the same quantity of material is fed to both the LIR and its discretised configurations.

The total residence time in the s-CSTR is defined as:

$$\tau_{\text{s-CSTR}} = \sum_{k=1}^{N_d} \frac{V_d \rho}{F_0 + \sum_{l=1}^{k} g^{(l)}} \tag{3}$$

being ρ the (constant) density, $F_0 = \sum_i F_{i,0}$ the total inlet massive flowrate, and $g^{(l)} = \sum_i g_i^{(l)}$ the total injected flowrate at the l-th reactor of the series.

Similarly, the total residence time in the d-LIR is defined as:

$$\tau_{\text{d-LIR}} = \sum_{k=1}^{N_d} \int_0^{\delta_L} \frac{\rho \mathscr{A}}{F_0 + \sum_{l=1}^{k} g^{(l)}} \, dx = \sum_{k=1}^{N_d} \frac{V_d \rho}{F_0 + \sum_{l=1}^{k} g^{(l)}} \tag{4}$$

which means that $\tau_{\text{s-CSTR}} = \tau_{\text{d-LIR}} = \tau$. The total flowrate in the LIR at a given coordinate, x, is given by [15]:

$$F(x) = F_0 + \sum_{i=1}^{NC} \int_0^x f_i(\xi) \, d\xi \tag{5}$$

Thus, by Equation (2):

$$F_0 + \sum_{l=1}^{k} g^{(l)} = F_0 + \sum_{i=1}^{NC} \int_0^{k\delta_L} f_i(x) \, dx = F(k\delta_L) \tag{6}$$

This allows recasting Equations (3) and (4) as:

$$\tau = \sum_{k=1}^{N_d} \frac{V_d \rho}{F(k\delta_L)} = \frac{\rho \mathscr{A} L}{N_d} \sum_{k=1}^{N_d} \frac{1}{F(k\delta_L)} = \rho \mathscr{A} \delta_L \sum_{k=1}^{N_d} \frac{1}{F(k\delta_L)} \tag{7}$$

In the LIR the residence time corresponds to the outlet elapsed time $\theta(L)$ [15]:

$$\theta(L) = \int_0^L \frac{\rho \mathscr{A}}{F(x)} \, dx \tag{8}$$

Therefore, the overall residence time in the s-CSTR/d-LIR is the same as in the LIR when

$$\delta_L \sum_{k=1}^{N_d} \frac{1}{F(k\delta_L)} = \int_0^L \frac{1}{F(x)} \, dx \tag{9}$$

that is, when the integral of $1/F(x)$ is correctly described by its discrete approximation over N_d equal intervals. This trivially happens when $F(x)$ is constant (no lateral injections – batch reactor). As $F(x)$ is a non-decreasing function of x, then $1/F(x)$ is strictly non-increasing. Consequently, the RHS of Equation (9) is necessarily lower than the LHS. This means that every LIR approximation with these assumptions will decrease the overall residence time in the reactor series.

For $N_d \to \infty$ both mixed vessels and tubular reactors become of infinitesimal volume $\mathscr{A}dx$. In this case $g_i^{(k)} \to f_i(x)dx$ and $\tau = \theta(L)$, meaning that both configurations can approximate the LIR behaviour provided that a sufficiently high number of reactors is used.

It should be noted that this procedure is independent on the chemical reaction kinetics since all the involved quantities are parameters ($\mathscr{A}$, N_d, ...) or kinetics-free terms (L, $f_i(x)$, ...).

However, the minimum number of reactors required (both in the d-LIR and s-CSTR discretisation) to approximate the LIR (and therefore the SBR) performance to a given extent obviously depends on the kinetics of the specific process considered. This makes the application of the aforementioned procedure to a specific SBR process not kinetics-free.

To overcome this problem a large number of simulations were carried out by changing the kinetic parameters in a range characteristic of organic reactions and (for each set of kinetic parameters) by looking for the minimum number of reactors required to approximate satisfactorily the LIR behaviour. Using the highest value of these minima will guarantee the d-LIR and s-CSTR performance to be close enough to the LIR ones regardless the reaction kinetics of the specific chemical process considered.

The following sections discuss the results of this approach.

2.2. Investigated class of reactions

The generic liquid-phase irreversible reaction

$$A + B \to C \tag{10}$$

with reaction rate r_1 is considered as a case study. This reaction scheme can represent a large number of organic syntheses classes, such as nitrations, alkylations, aminations, and so forth [17]. Different classes obviously differ because of kinetic parameters and operating conditions (e.g., kind of solvents, temperature, reaction time). Several processes also have additional undesired side reactions (e.g., di-nitration), which is represented by the generic irreversible reaction:

$$C + B \to D \tag{11}$$

with reaction rate r_2.

The overall reaction rate for the j-th reaction, r_j, can be usually expressed with a power law:

$$r_j = k_j \prod_{i=1}^{NC} c_i^{\alpha_{ij}} \tag{12}$$

where k_j is the j-th reaction rate constant, c_i the molar concentration of species i, and α_{ij} the reaction order of species i in reaction j.

Let us consider a chemical process carried out in an isothermal SBR where A is pre-loaded into the vessel and B is fed over the whole reaction time with a constant feedrate, Q_0. The reaction time is such that it guarantees a stoichiometric addition of B with respect to A and no solvent is used.

The SBR can be modelled through the material balance equations. By using suitable dimensionless variables it is possible to recast these equations in the following form (see Appendix for the mathematical details):

$$\begin{cases} \dfrac{d\hat{n}_i}{d\hat{t}} = \dfrac{\hat{Q}(x_i^f - \hat{n}_i)}{\hat{V} + \gamma - 1} + \displaystyle\sum_{j=1}^{NR} \left(\nu_{ij} \kappa_j \left(\dfrac{\hat{V} + \gamma - 1}{\hat{V}} \right)^{\sum_{k=1}^{NC} \alpha_{kj} - 1} \prod_{k=1}^{NC} \hat{n}_k^{\alpha_{kj}} \right) \\ \dfrac{d\hat{V}}{d\hat{t}} = \hat{Q} \\ \hat{n}_i(0) = x_i^0 \\ \hat{V}(0) = 1 \end{cases} \tag{13}$$

where $\hat{n}_i = n_i / n_{ref}$ is the dimensionless mole number of species i, $\hat{t} = t/t_{ref}$ the dimensionless time, $\hat{V} = V/V_{ref}$ the dimensionless volume, x_i^f the molar fracion of species i in the feed stream, x_i^0 the molar fraction of species i in the reactor at the initial time, γ the ratio between the dosed stream and initial mixture molecular weights, NR the number of reactions, ν_{ij} the stoichiometric coefficient of species i in reaction j, $\hat{Q} = H(\hat{t}_d - \hat{t})$ the dimensionless volumetric feedrate (H is the Heaviside step function being $\hat{t}_d$ the dimensionless dosing time), and

$$\kappa_j = \frac{V_0 k_j}{Q_0} c_{tot}^{f\ \sum_{k=1}^{NC} \alpha_{kj} - 1} \tag{14}$$

is the dimensionless reaction rate constant. All dimensionless quantities are obtained by dividing the dimensional quantity by a reference value (see Appendix for details).

For the analysed reaction scheme, in the case of stoichiometric addition of species B over the dosing time, it is possible to show that (see Appendix for details):

$$\hat{t}_d = \gamma \frac{\nu_{A1} x_B^0 - \nu_{B1} x_A^0}{\nu_{B1} x_A^f - \nu_{A1} x_B^f} = \frac{\gamma}{\eta_{0f}} \tag{15}$$

where η_{0f} physically represents the ratio between the total number of moles initially present into the reactor and the number of moles to be fed in the whole dosing time.
Note that the system of equations (13) also describes the behaviour of a batch reactor (BR).

The set of Equations (13) is characterised by some parameters which are related to the reactive system itself (i.e., κ_j, ν_{ij}, α_{ij}, and γ) and others related to the recipe (i.e., x_i^f and x_i^0). In the following, $\gamma = 1$ is assumed since the following results are quite insensitive to this parameter. Furthermore, $x_A^0 = x_B^f = 1$ as no solvent is used and species B is fed as pure species into the reactor. Therefore, the performance of the SBR will be affected by the values of the remaining parameters. In particular, conversion of species A, X_A, yield of species C with respect to species A, $Y_{C/A}$, and selectivity of species C with respect to A, $s_{C/A}$, can be computed for $\hat{t} \leq \hat{t}_d$ as (see Appendix):

$$X_A = 1 - \frac{\hat{n}_A(\hat{V} + \gamma - 1)}{x_A^0\gamma + x_A^f\hat{t}} \tag{16}$$

$$Y_{C/A} = \frac{\hat{n}_C(\hat{V} + \gamma - 1) - x_C^0\gamma - x_C^f\hat{t}}{x_A^0\gamma + x_A^f\hat{t}} \tag{17}$$

$$s_{C/A} = \frac{Y_{C/A}}{X_A} \tag{18}$$

These quantities depend only on the dimensionless parameters and variables found via integration of the ODE system (13). The advantage of using dimensionless quantities is the possibility to represent an infinite number of reactive systems with very different values of the kinetic and process parameters leading to the same set of dimensionless parameters. In other words, the solution of the dimensionless system of equations represents an infinite number of different chemical processes, whose dimensional kinetic and recipe values lead to the same dimensionless parameters values.

2.3. Minimum number of reactors

Even if the kinetic parameters may widely differ between the various classes of the industrial processes represented by reactions (10) and (11), the aim of this work is to identify the minimum number of reactors (both for a s-CSTR and a d-LIR configuration) able to guarantee a reasonable approximation of the LIR (and therefore of the original SBR) performance in terms of conversion and selectivity. Consequently, this leads to a kinetics-free transformation of an industrial SBR process into a s-CSTR or d-LIR one. This was done by carrying out a large number of simulations evaluating the performance of both s-CSTR and d-LIR as a function of the number of reactors used to discretise the LIR in very different conditions.

Considering the typical values of the kinetic constants of organic syntheses [17], the dimensionless reaction rate constants κ_j range between 10^{-3} and 10^3 and the reaction orders range between 0.5 and 2.0 for reactants, while they are zero for products.
The total number of parameters changed in the large number of simulations is then equal to 6, namely: κ_1, κ_2, α_{A1}, α_{B1}, α_{B2}, and α_{C2}. The choice of a set of parameter values was based on the Latin Hypercube Sampling (LHS) [18] which grants statistical accuracy with a sufficiently small number of samples.

The main focus of the selected class of reactions is on selectivity, which may be lost due to the side reaction (11). However, depending on the particular values of a set of parameters, it can happen that the selectivity obtained using a BR would be higher than that obtained in a SBR. These cases are not of interest (since we are considering the transformation of a SBR into a LIR) and they were not considered in the following analysis. The choice criterion used to include or exclude a set of parameters is then based on the selectivity ratio between SBR and BR, $s_R \overset{\text{def}}{=} s^{SBR}/s^{BR}$. If $s_R > 1$, then the SBR outperforms the BR, otherwise the case is excluded. For completeness, also yield and conversion ratios are computed as $Y_R \overset{\text{def}}{=} Y^{SBR}/Y^{BR}$ and $X_R \overset{\text{def}}{=} X^{SBR}/X^{BR}$, respectively.

For any included set of parameters, the discontinuous reactor is transformed into a LIR, which exactly reproduces the original SBR [15]. Every LIR is then approximated with a d-LIR or a s-CSTR with a different number of units in series, looking for the minimum number of reactors able to reach at least 95 % of the selectivity of the LIR (and then of the original SBR).

3. Results

The analysis based on LHS was performed with 5000 samples of the parameters in the aforementioned range. The distribution of samples is verified to be log-uniform for the dimensionless rate constants and uniform for the reaction orders over the respective ranges of values.

For every parameter set, SBR and BR were compared by calculating conversion, selectivity and yield ratios to exclude the sets of parameters leading to $s_R < 1$. Figure 4 reports the three performance indexes dependency on selected parameters and their interdependency. It can be noted from Figures 4a and 4b that the majority of excluded parameters sets (126 out of 5000, indicated with crosses) belongs to the region of high reactivity (large rate constants). Furthermore, the higher the reactivity is, the higher the conversion ratio is, approaching unity from below, as from Figure 4c. It is also possible to note from Figure 4d that a dependency between yield and selectivity ratios exists, presenting an almost linear trend on a bi-logarithmic plane:

$$\log_{10} Y_R = 1.0131 \log_{10} s_R - 0.0663 \tag{19}$$

This means that increasing the selectivity in a SBR has a similar effect on yield (both with respect to the BR). From the low number of excluded points it is evident that a SBR is generally more selective than a BR for this class of reactions. The selectivity ratio is particularly high for systems with low reactivity (see Figure 4a), while there is obviously no selectivity problem for system with a low value of κ_2 (see Figure 4b).

Figure 5a depicts the interdependency of the two dimensionless rate constants, κ_1 and κ_2, while Figure 5b the one between the main reaction rate constant, κ_1, and the reaction order of species B in the main reaction, α_{B1}. We can see that the excluded sets are not randomly distributed on these plot (as for the other parameter couples), since they lie on the regions:

$$\begin{cases} \log_{10} \kappa_2 \geq -1.329 \log_{10} \kappa_1 + 1.866 \\ \alpha_{B1} \leq 0.5843 \log_{10} \kappa_1 + 0.5937 \end{cases} \tag{20}$$

This means that extremely fast main and side reactions are not conveniently (in terms of selectivity) run in an isothermal SBR. Analogously, increasing the reaction order of species B in the main reaction allows the SBR to be more efficient than the BR for faster main reactions. Equation (20) thus provides a conservative approximation of the regions where a BR can overperform an SBR.

For all the parameter sets defined by Equation (20), the corresponding SBR process was transformed in a LIR process as discussed elsewhere [15]. Therefore, the LIR configuration was approximated, as previously discussed, with a finite number of reactors in series. By varying parametrically the number of reactors, N_d, it is possible to compute (for each set of parameters and for several different number of reactors in the series) the deviation of the selectivity in the series of reactors (d-LIR and s-CSTR) with respect to the LIR through a selectivity ratio now defined as the ratio between the selectivity computed for each series of reactors and the LIR selectivity. The kinetic parameters were again chosen randomly according to the LHS method and some of them were excluded according to Equation (20).

From each set of parameters and each value of N_d, a value of the selecitivity ratio is obtained for both d-LIR ($s_{R,d-LIR} = s^{d-LIR}/s^{LIR} = s^{d-LIR}/s^{SBR}$) and s-CSTR ($s_{R,s-CSTR} = s^{s-CSTR}/s^{LIR} = s^{s-CSTR}/s^{SBR}$). Considering the whole set of results, a distribution of selectivity ratios between d-LIR/s-CSTR and LIR (and equivalently between d-LIR/s-CSTR and SBR) is obtained for each value of N_d. Figure 6a reports the cumulative distribution function of selectivity ratios for the d-LIR for several values of N_d.

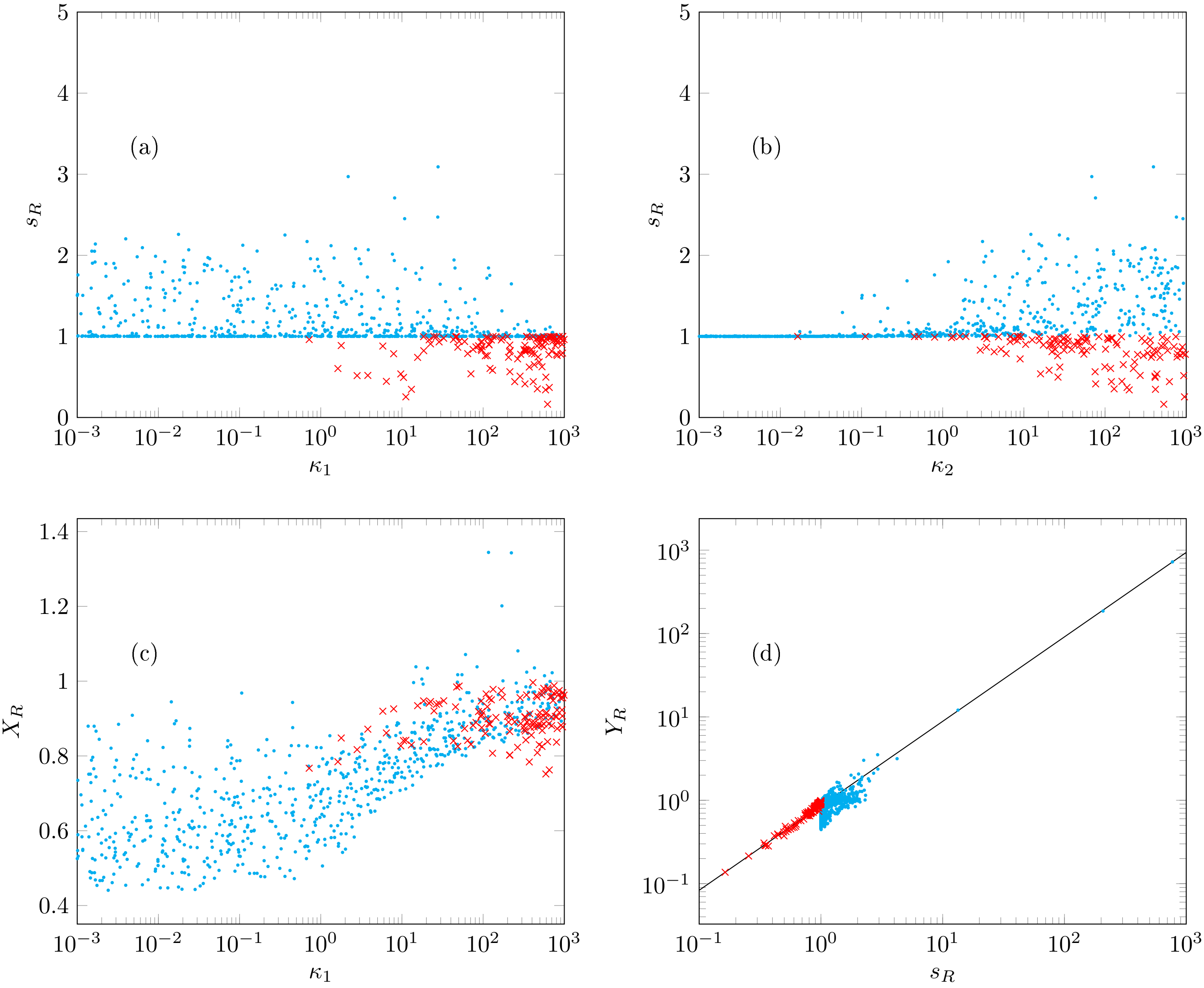

Figure 4: Conversion, yield and selectivity ratios dependency on some selected dimensionless parameters of the sensitivity analysis and their interdependency. Crosses represent excluded points. (a) Dependency of the selectivity ratio on the first dimensionless reaction rate constant. (b) Dependency of the selectivity ratio on the second dimensionless reaction rate constant. (c) Dependency of the conversion ratio on the first dimensionless reaction rate constant. (d) Interdependency of yield and selectivity ratios. The line is represented by Equation (19).

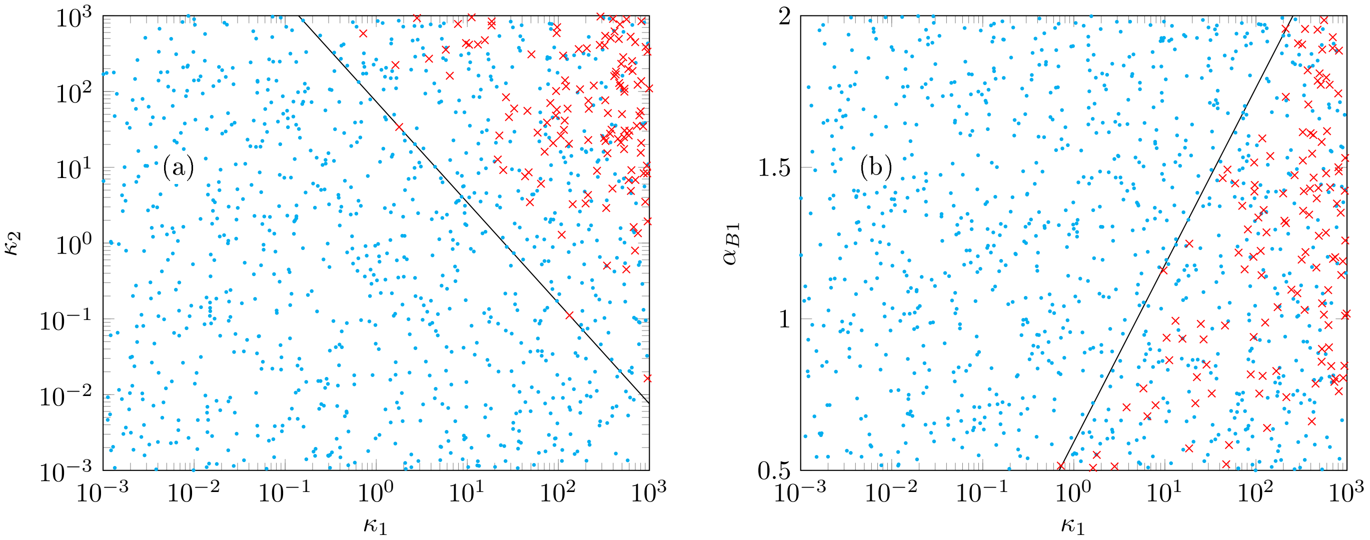

Figure 5: Interdependency between some of the dimensionless parameters. Crosses are excluded points. (a) Relationship between the two dimensionless kinetic constants. The line is represented by the equality in (20). (b) Relationship between the first dimensionless kinetic constant and the reaction order of species B in the first reaction. The line is represented by the equality in (20).

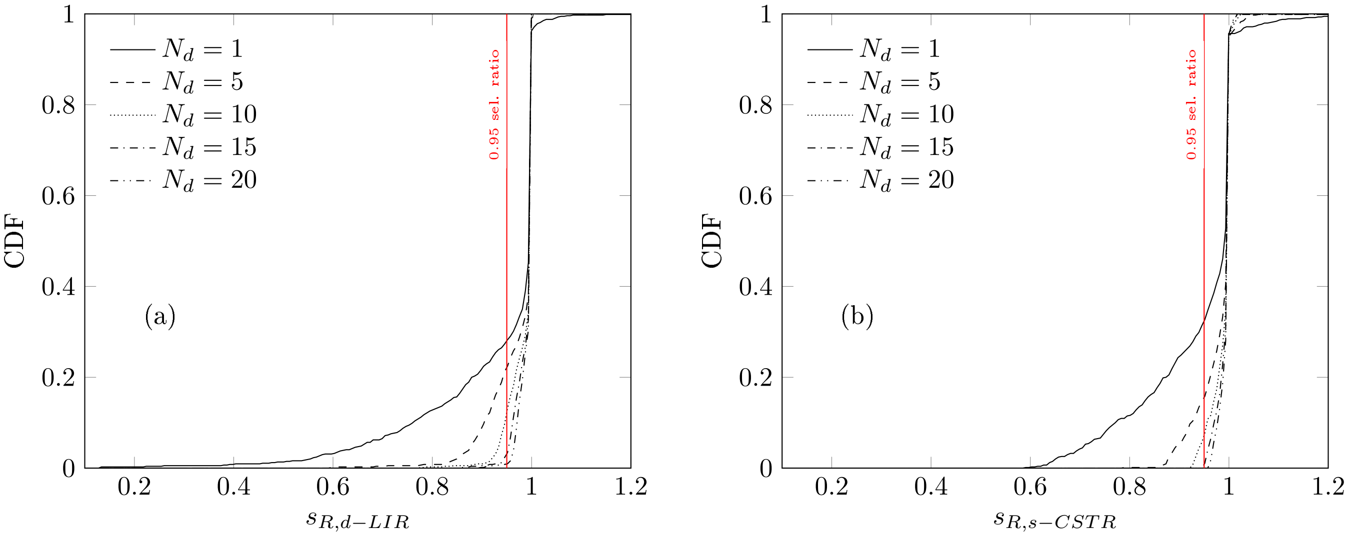

Figure 6: Cumulative distribution function for the selectivity ratio of the (a) d-LIR and (b) s-CSTR with respect to the LIR at varying number of reactors in series, N_d.

Since each curve represents the fraction of cases leading to selectivity ratio values lower than a given abscissa value for a given value of N_d, increasing the number of reactors in the series makes the distribution shift to the right. This means that the approximation of the selectivity is more and more accurate at increasing N_d values. For instance, for the value $s_{R,d-LIR} = 0.95$, we can see that using 1 reactor ($N_d = 1$) about 30 % of the investigated cases result in selectivity values lower than the SBR selectivity multiplied by 0.95. This percentage reduces to about 1 % when $N_d = 20$. Figure 6b depicts the same variable for the s-CSTR, with a similar qualitative behaviour.

These results can be recast in Figure 7, which reports the percentage of cases with a selectivity ratio larger than 0.95 for both d-LIR and s-CSTR. It can be noted that at least 15 reactors in series are required to reduce the loss of selectivity below 5 % for more than 97 % of all the investigated scenarios. This means that for the analysed class of reactions, regardless the value of the kinetic parameters, almost any SBR process can be reproduced (in terms of selectivity) in a continuous system by computing the LIR configuration and then discretising it with 15 reactors (either PFRs or CSTRs) in series with intermediate injections. However, it is worthwhile noting that the d-LIR configuration is more convenient than the s-CSTR one as series involving a large number of tubular reactors (possibly equipped with static mixers) are cheaper and simpler to realise than series involving a large number of mixed vessels.

Moreover, another advantage of using a d-LIR/s-CSTR instead of a SBR is the reduction of the hold-up of the system. Using this procedure, the overall volume of the d-LIR/s-CSTR is always reduced by more than 40 % keeping the same productivity as the original SBR process.

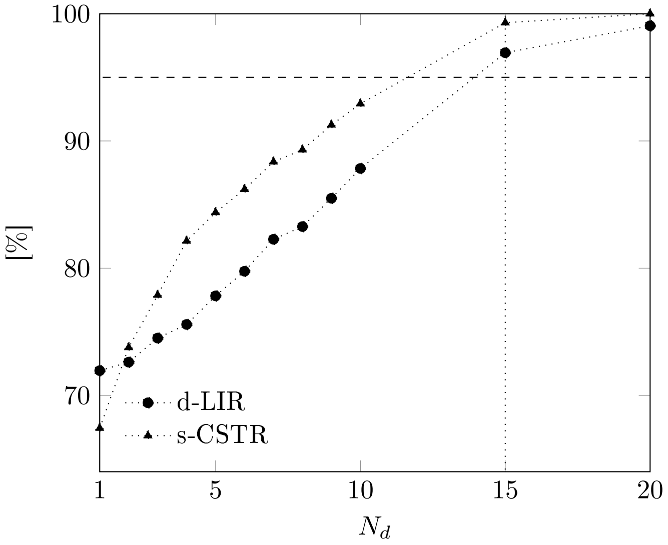

Figure 7: Percentage of cases with selectivity ratio greater than 0.95 for the d-LIR and the s-CSTR with respect to the LIR.

4. Case study

To verify the reliability of the proposed approach, a transition from a SBR process to a d-LIR/s-CSTR one was simulated using kinetic information available in the literature. In particular, the synthesis of amine/epoxy resins was considered as a case study. The selected case involves the addition of phenyl glycidyl ether (B, PGE) to aniline (A) in a isothermal SBR with a constant feed rate. The reaction mechanism follows the scheme described by Equations (10) and (11) as shown in Figure 8. Polymerisation of the epoxide is neglected as the reaction is run without a Lewis acid/base catalyst [19].

The product (C) of the first reaction is the desired species and the side reaction product (D) is undesired. Both reactions can be described via second order reaction rates with unitary reaction orders for each reactant; the reaction rate constants are $2.8 \times 10^{-4}\,\mathrm{L\,mol^{-1}\,min^{-1}}$ and $2.0 \times 10^{-4}\,\mathrm{L\,mol^{-1}\,min^{-1}}$ at 110 °C for the main and side reactions, respectively [19]. The starting material in the SBR is pure aniline (300 kg) and a stoichiometric quantity of PGE is constantly added over 8 h. Density is assumed to be constant and equal to $1060\,\mathrm{kg\,m^{-3}}$, leading to a reaction volume at theend of the dosing time equal to 739 L. The performance of this SBR process was computed using known kinetics, resulting in a selectivity value equal to about 0.90.

Using the procedure detailed elsewhere [15], the SBR process is transformed into a LIR one having the same productivity (considering 2.4 h of dead times in the discontinuous process) and a diameter of 7.26 cm. The resulting reactor length is 95 m and perfectly reproduces the SBR in terms of conversion and

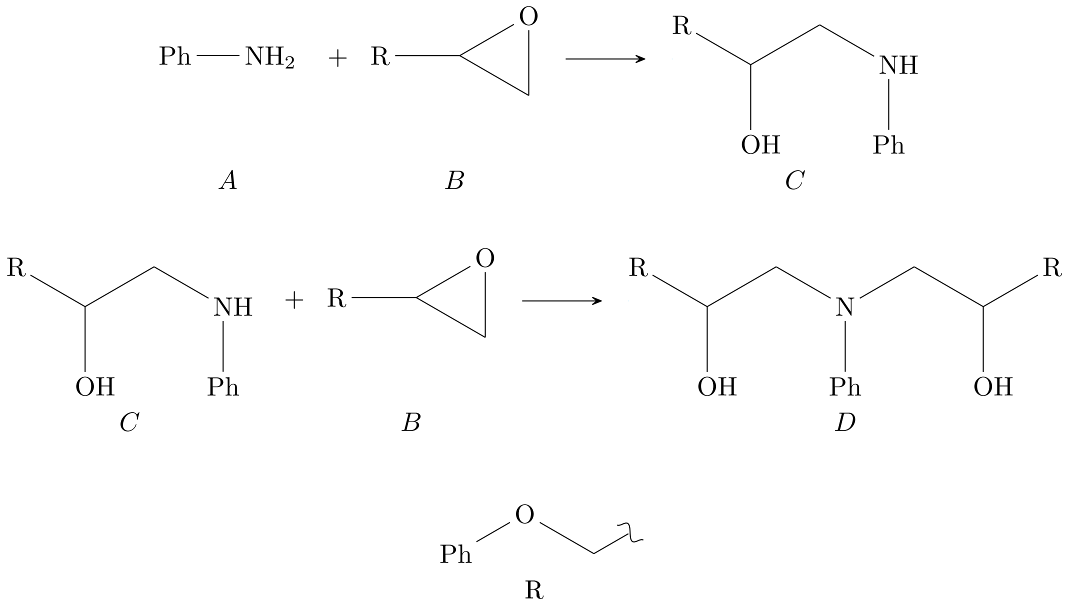

Figure 8: Reaction mechanism for the reaction of aniline and PGE.

selectivity. Note that this quite large reactor can be built in a very compact shape with an hindrance of about 1 m × 1 m × 1 m by bending the tube. It should also be noted that the reaction volume is reduced by more than 45 % with respect to the discontinuous process. This result was expected, as generally the transition from a SBR to a LIR reduces the volume by a factor of 2, thus achieving a good degree of process intensification.

The required feed policy of PGE along the axial coordinate was also computed [15] and it is reported in Figure 9 as a continuous line. Notably, the feed policy is non-trivial, even if the feedrate is constant for the SBR.

The aforementioned discretisation procedure (Equation 2) is then applied using 15 reactors in series with intermediate feed injections. The computed discrete feedrates are reposted in Figure 9 as dots, showing a trend along the axial coordinate (or volume) similar to that of the continuous lateral injection of the LIR.

The resulting d-LIR and s-CSTR were simulated with the known kinetic parameters, leading to the species mass fractions profiles shown in Figure 10. We can see that such profiles show excellent overlap of the LIR/SBR trends. Accordingly, the selectivity ratio for the desired product between d-LIR/s-CSTR and LIR (or SBR) is above 99 %. This means that the recipe of the discontinuous process was transformed into a continuous one using a kinetics-free procedure (note that kinetic information was used solely to compute the selectivity values in the SBR and s-LIR/s-CSTR configurations and not to design the continuous reactors)

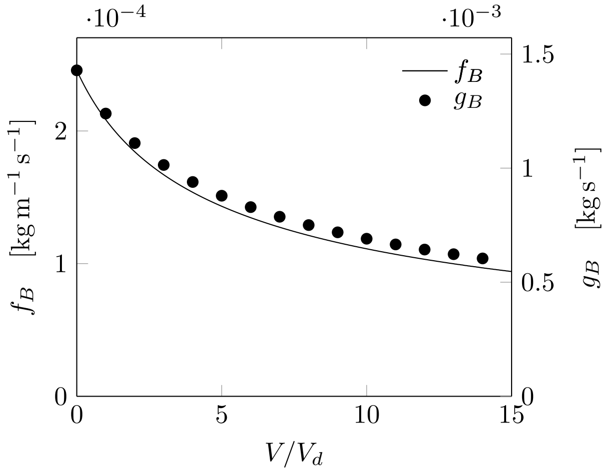

Figure 9: Continuous lateral feed policy in the LIR (solid line) and discretised injections in the d-LIR/s-CSTR (dots).

and 15 reactors in series with a clear reduction of the hold-up, while keeping the productivity unchanged.

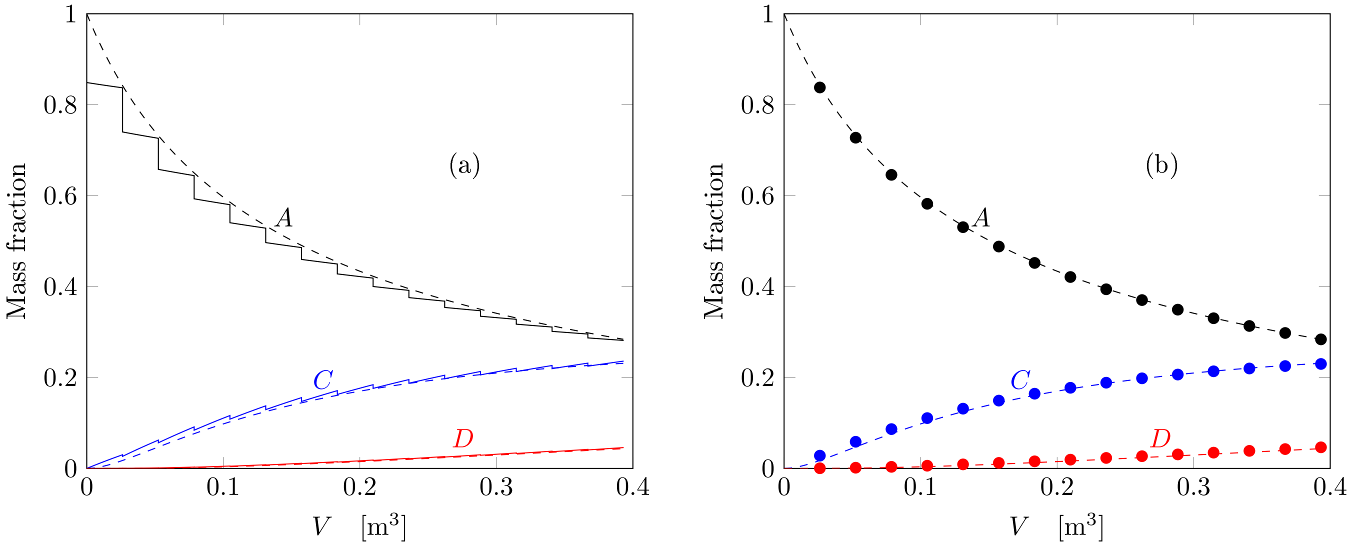

Figure 10: Comparison of species mass fractions for the (a) d-LIR (solid lines) and (b) s-CSTR (dots) with respect to the LIR (dashed lines).

5. Conclusions

SBRs are used for a large number of chemical processes that could be more efficiently carried out in continuous reactors. For a wide class of chemical processes involving selectivity problems due to consecutive side reactions, a general procedure was developed to identify a-priori the number of reactors (either tank or tubular) to be connected in series with intermediate feed injections in order to obtain, for any chemical process of this class, selectivity values not lower than 95 % of the original SBR selectivity. This number is equal to about 15 for both s-CSTR and d-LIR. Given this number of reactors, it is possible to transform a known recipe carried out in an isothermal SBR into one carried out in a d-LIR or a s-CSTR without knowing the kinetics of the reactions involved. The proposed procedure is therefore fully kinetics-free, which is an important point when the kinetic characterisation of the process is not available, as usual when dealing with multi-purpose processes of the fine-chemical or pharmaceutical industries.

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Appendix - Dimensionless SBR model

Governing equations

A given isothermal homogeneous SBR can be modelled through molar balance equations as:

$$\frac{dn_i}{dt} = Qc_i^f + \sum_{j=1}^{NR} \nu_{ij} k_j \prod_{k=1}^{NC} c_k^{\alpha_{kj}} V \tag{21}$$

with the initial condition

$$n_i(0) = n_i^0 \tag{22}$$

being $i = 1 \ldots NC$, NC the number of species, n_i the number of moles of species i, Q the volumetric flowrate of species added to the reactor, c_i^f the (constant) concentration of species i in the fed stream, NR the number of reactions, ν_{ij} the stoichiometric coefficient of species i in reaction j, k_j the j-th reaction rate constant, c_k the k-th species molar concentration, α_{kj} the reaction order of species k in reaction j, V the reaction volume, and n_i^0 the initial number of moles of species i.

Q_0 is defined as the integral average of the volumetric flowrate over the dosing time, t_d. In the simplest case the volumetric flowrate can be assumed constant over the dosing time and thus equal to $Q_0 H(t_d - t)$ being H the Heaviside function. In this simple case Q_0 also represents the initial flowrate. The following derivation is valid for non-constant volumetric flowrate.

By assuming constant density, ρ, and equal for both fed stream and reaction vessel contents, it is possible to write the total mass balance equation in terms of volume as:

$$\frac{dV}{dt} = Q \tag{23}$$

with initial condition

$$V(0) = V_0 \tag{24}$$

being V_0 the initial reaction volume.

It is possible to define a quantity, n^*, which corresponds to the total number of moles in the reactor when no reaction takes place, through its conservation equation as:

$$\frac{dn^*}{dt} = Q \sum_{i=1}^{NC} c_i^f \overset{\text{def}}{=} Qc_{tot}^f \tag{25}$$

with initial condition

$$n^*(0) = \sum_{i=1}^{NC} n_i^0 \overset{\text{def}}{=} n_{tot}^0 \tag{26}$$

This equation is easily solved by comparison with Equation (23) as:

$$n^* = (c_{tot}^0 - c_{tot}^f)V_0 + c_{tot}^f V \tag{27}$$

being $c_{tot}^0 = n_{tot}^0 / V_0$.

The total number of moles dosed into the reactor is

$$n_{tot}^f = \int_0^{t_d} Q(t) c_{tot}^f \, dt = Q_0 t_d c_{tot}^f \tag{28}$$

as c_{tot}^f was assumed constant by exploiting the definition of Q_0.

By now defining the following dimensionless quantities:

$$\begin{aligned}
\hat{t} &\overset{\text{def}}{=} \frac{tQ_0}{V_0} \\
\hat{V} &\overset{\text{def}}{=} \frac{V}{V_0} \\
\hat{Q} &\overset{\text{def}}{=} \frac{Q}{Q_0} \\
\hat{n}_i &\overset{\text{def}}{=} \frac{n_i}{n^*} \\
\eta_{0f} &\overset{\text{def}}{=} \frac{n_{tot}^0}{n_{tot}^f} \\
\gamma &\overset{\text{def}}{=} \frac{c_{tot}^0}{c_{tot}^f}
\end{aligned} \tag{29}$$

it is possible to recast the aforementioned equations in dimensionless and general terms.

Equation (23) now becomes:

$$\frac{d\hat{V}}{d\hat{t}} = \hat{Q} \tag{30}$$

with initial condition $\hat{V}(0) = 1$.

γ can also be rewritten in terms of the dimensionless dosing time as:

$$\gamma = \frac{c_{tot}^0}{c_{tot}^f} = \frac{n_{tot}^0 Q_0 t_d}{n_{tot}^f V_0} = \eta_{0f} \hat{t}_d \tag{31}$$

It should be noted that the total initial concentration and the total concentration of the fed stream can be rewritten by using the initial and dosed stream molecular weights, MW^0 and MW^f respectively, as:

$$c_{tot}^0 = \frac{\rho}{MW^0} \tag{32}$$

$$c_{tot}^f = \frac{\rho}{MW^f} \tag{33}$$

thus

$$\gamma = \frac{MW^f}{MW^0} \tag{34}$$

which makes this parameter fixed by the chosen recipe.

Equation (27) can be rewritten as:

$$n^* = c_{tot}^f V_0(\hat{V} + \gamma - 1) \tag{35}$$

and therefore Equation (21) is recast, exploiting (29) and (25), as:

$$\frac{d\hat{n}_i}{d\hat{t}} = \frac{V_0}{Q_0 n^*}\left(-\hat{n}_i \frac{dn^*}{dt} + \frac{dn_i}{dt}\right) = \frac{V_0}{Q_0 n^*}\left(-\hat{n}_i Q c_{tot}^f + Q c_i^f + \sum_{j=1}^{NR} \nu_{ij} k_j \prod_{k=1}^{NC} c_k^{\alpha_{kj}} V\right) \tag{36}$$

By definition, the molar fraction of species i in the dosed stream is $x_i^f = c_i^f / c_{tot}^f$, and the molar concentration of species k is

$$c_k = \frac{n_k}{V} = \frac{n^* \hat{n}_k}{V_0 \hat{V}} = \frac{c_{tot}^f(\hat{V} + \gamma - 1)\hat{n}_k}{\hat{V}} \tag{37}$$

These quantities allow rewriting the last balance equation as:

$$\frac{d\hat{n}_i}{d\hat{t}} = \frac{\hat{Q}(x_i^f - \hat{n}_i)}{\hat{V} + \gamma - 1} + \frac{V_0}{Q_0}\sum_{j=1}^{NR} \nu_{ij} k_j \left(\frac{c_{tot}^f(\hat{V} + \gamma - 1)}{\hat{V}}\right)^{\sum_{k=1}^{NC} \alpha_{kj} - 1} \prod_{k=1}^{NC} \hat{n}_k^{\alpha_{kj}} \tag{38}$$

With the definition of dimensionless reaction rate constant

$$\kappa_j \overset{\text{def}}{=} \frac{V_0}{Q_0} k_j (c_{tot}^f)^{\sum_{k=1}^{NC} \alpha_{kj} - 1} \tag{39}$$

the final form of the equation is obtained:

$$\frac{d\hat{n}_i}{d\hat{t}} = \frac{\hat{Q}(x_i^f - \hat{n}_i)}{\hat{V} + \gamma - 1} + \sum_{j=1}^{NR} \nu_{ij} \kappa_j \left(\frac{\hat{V} + \gamma - 1}{\hat{V}}\right)^{\sum_{k=1}^{NC} \alpha_{kj} - 1} \prod_{k=1}^{NC} \hat{n}_k^{\alpha_{kj}} \tag{40}$$

The initial condition is $\hat{n}_i = n_i^0/n^*(0) = n_i^0/n_{tot}^0 = x_i^0$, by definition of molar fraction.

Stoichiometric addition of species

If species k is desired to be added stoichiometrically to species i according to reaction R, then it must be:

$$\frac{n_i^0 + n_{tot}^f x_i^f}{\nu_{iR}} = \frac{n_k^0 + n_{tot}^f x_k^f}{\nu_{kR}} \tag{41}$$

from which a constraint on one of the dimensionless parameters arises:

$$\eta_{0f} = \frac{\nu_{kR} x_i^f - \nu_{iR} x_k^f}{\nu_{iR} x_k^0 - \nu_{kR} x_i^0} \tag{42}$$

Since γ is fixed by the recipe according to Equation (34), this is equivalent to imposing a constraint on the dimensionless dosing time, in fact

$$\hat{t}_d = \frac{\gamma}{\eta_{0f}} = \gamma \frac{\nu_{iR} x_k^0 - \nu_{kR} x_i^0}{\nu_{kR} x_i^f - \nu_{iR} x_k^f} \tag{43}$$

Performance parameters

Conversion of a given reactant i can be computed from its definition in a SBR:

$$X_i = \frac{n_i^0 + c_i^f \displaystyle\int_0^t Q(\tau)\, d\tau - n_i}{n_i^0 + c_i^f \displaystyle\int_0^t Q(\tau)\, d\tau} \tag{44}$$

and by substituting the dimensionless variable definitions, one obtains:

$$X_i = 1 - \frac{\hat{n}_i(\hat{V} + \gamma - 1)}{x_i^0 \gamma + x_i^f \displaystyle\int_0^{\hat{t}} \hat{Q}(\hat{\tau})\, d\hat{\tau}} \tag{45}$$

Similarly, from the definition of yield of species j with respect to reactant i

$$Y_{j/i} = \frac{n_j - n_j^0 - c_j^f \displaystyle\int_0^t Q(\tau)\, d\tau}{n_i^0 + c_i^f \displaystyle\int_0^t Q(\tau)\, d\tau} \tag{46}$$

with dimensionless variables it is possible to obtain:

$$Y_{j/i} = \frac{\hat{n}_j(\hat{V} + \gamma - 1) - x_j^0\gamma - x_j^f \displaystyle\int_0^{\hat{t}} \hat{Q}(\hat{\tau})\, d\hat{\tau}}{x_i^0\gamma + x_i^f \displaystyle\int_0^{\hat{t}} \hat{Q}(\hat{\tau})\, d\hat{\tau}} \tag{47}$$

By definition the selectivity of product j with respect to reactant i is:

$$s_{j/i} = \frac{Y_{j/i}}{X_i} \tag{48}$$

In the simplest case of constant volumetric flowrate the aforementioned equations simplify as:

$$\int_0^{\hat{t}} \hat{Q}(\hat{\tau})\, d\hat{\tau} = \int_0^{\hat{t}} H(\hat{t}_d - \hat{\tau})\, d\hat{\tau} = \begin{cases} \hat{t} & \hat{t} \le \hat{t}_d \\ \hat{t}_d & \hat{t} > \hat{t}_d \end{cases} \tag{49}$$

BR simulation

Similar balance equations can be obtained for the BR considering no addition of species. The same equations of the SBR can be used anyway with the formal substitution of $\hat{Q}^{BR} = 0$, thus $\hat{V}^{BR} = 1$, and $\gamma^{BR} = 1$. The dimensionless rate constant is defined now as:

$$\kappa_j^{BR} \overset{\text{def}}{=} \frac{V_0^{BR}}{Q_0^{BR}} k_j (c_{tot}^{0,BR})^{\sum_{k=1}^{NC} \alpha_{kj} - 1} \tag{50}$$

and Q_0^{BR} is an arbitrary flowrate.

When it is desired to compare a SBR with the corresponding BR, some constraint must be supplied. In fact, the BR corresponding to a SBR is that reactors where all dosed reactants are initially charged together with the initial charge of the SBR. This means:

$$n_i^{0,BR} = n_i^0 + n_{tot}^f x_i^f \tag{51}$$

and thus

$$n_{tot}^{0,BR} = n_{tot}^0 (1 + \eta_{0f}) \tag{52}$$

$$x_i^{0,BR} = \frac{x_i^0 + \eta_{0f} x_i^f}{1 + \eta_{0f}} \tag{53}$$

In terms of volumes:

$$V_0^{BR} = V_0 + Q_0 t_d \tag{54}$$

The initial total concentration in the BR is thus

$$c_{tot}^{0,BR} = \frac{n_{tot}^{0,BR}}{V_0^{BR}} = c_{tot}^0 \frac{1 + 1/\eta_{0f}}{1 + \hat{t}_d} \tag{55}$$

The arbitrary Q_0^{BR} is set as to guarantee the formal equivalence of dimensionless times in the two systems:

$$\hat{t}^{BR} = \hat{t} \tag{56}$$

from which

$$Q_0^{BR} = (1 + \hat{t}_d) Q_0 \tag{57}$$

Finally, the same reaction should be run in the two reactors, meaning

$$k_j = \kappa_j \frac{Q_0}{V_0} (c_{tot}^f)^{1-\sum_{k=1}^{NC} \alpha_{kj}} = \kappa_j^{BR} \frac{Q_0^{BR}}{V_0^{BR}} (c_{tot}^{0,BR})^{1-\sum_{k=1}^{NC} \alpha_{kj}} \tag{58}$$

from which

$$\kappa_j^{BR} = \kappa_j \left(\frac{\gamma + \hat{t}_d}{1 + \hat{t}_d} \right)^{\sum_{k=1}^{NC} \alpha_{kj} - 1} \tag{59}$$

meaning that overall-first-order reactions and reactions where $\gamma = 1$ share the same dimensionless rate constant in both BR and SBR. The difference in the two dimensionless kinetic constants becomes relevant only if γ is far from unity, which does not happen in diluted systems or when mixing reactants of similar or high molecular weight.

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