Kinetic-free selectivity control of chemical reactions leading to non volatile products.

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Abstract

A number of reaction processes of the fine chemical and pharma industry undergo selectivity losses, since the target product (often a low volatility compound) can be further consumed by a non selective reactant, according to a mixed series/parallel kinetic scheme.

In these cases, performing the reaction in a semibatch recycle reactor (SBRR) allows achieving both a high process selectivity and productivity even in a non continuous plant, since the target product concentration in the reactor can be limited adopting a relatively low excess of the selective reactant.

In the literature, on the basis of a mass balance approach, a number of boundary diagrams have been developed that allow to predict selective and productive operating conditions for SBRRs in which (1,1) order reactions occur.

However, when dealing with fine chemical and pharma reaction processes, the estimation of the kinetic parameters is often not practicable, due to the huge variety of productions encountered.

In this work a criterion has been developed that allows for identifying the optimal operating conditions of SBRRs without knowing the kinetics of the reactions involved.

The criterion has been applied to a reaction process of industrial interest performed in a SBRR, that is the production of ethylene glycol from ethylene oxide, with further ethoxylation of the desired product to diethylene glycol.

Keywords:

Semibatch recycle reactor (SBRR); Kinetics; Selectivity; Energy balance; Dynamic criterion; Process control; ethylene oxide; ethylene glycol.

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1. Introduction

A number of reaction processes of the fine chemical and pharma industry undergo selectivity losses with respect to a target product.

Such a behavior can be due to consecutive consumption reactions of the target product, in series to the main one, or to parallel consumption reactions of a non selective reactant, yielding an undesired by-product (Westerterp et al., 1984; Levenspiel, 1998; Froment et al., 2010).

More in general the selectivity loss can arise from a mixed series/parallel reaction scheme, according to which a target product, C, is consumed by its further reaction with a non selective reactant, A:

$$\begin{gathered} A + B \xrightarrow{k_1} C \\ A + C \xrightarrow{k_2} D \end{gathered} \tag{1}$$

The undesired consecutive reaction is typically of the same class as the main one: therefore, the enthalpies of the two reactions are normally close to each other.

Several reaction classes of the type (1) can be found in the fine chemical and pharma industry (Smith and March, 2007): as a relevant example the nucleophylic substitution of amines on alkyl halides can be mentioned, for the production of polyamines, that can further react with the alkyl halide to yield undesired olygomeric species; moreover, dealing with electrophylic substitution reactions on activated aromatic rings, the electrophylic reactant can further react with the mono-substituted target product, yielding undesired poly-substitution species; finally, epoxydation reactions of various nucleophylic substrates can be cited, in which a strongly reactive (and hence non selective) reactant such as ethylene oxide can further react with the target product to yield undesired poly-ethoxylated compounds.

In these cases the target product concentration in the reactor must be kept at sufficiently low values, in order to limit the selectivity loss.

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For high volume productions such a result can be achieved performing the reaction in continuous reactors operated at a low single pass conversion, with further separation of the target product and recycle of the unreacted reactants.

However, when dealing with low volume multipurpose productions, such as those encountered in the fine chemical and pharma industry, the adoption of a continuous reaction process is often not practicable.

Moreover, performing the reaction in a standard semibatch reactor (SBR) a huge excess of one reactant (that is, the selective one, B) could be required in order to limit the selectivity loss, which however lowers the process productivity.

In these cases adopting the SBRR process configuration shown in Figure 1 (Maestri and Rota, 2013), both a satisfactory process selectivity and productivity can be achieved, even in a non continuous plant.

The SBRR process configuration consists of a top stirred tank reactor, to which the non selective reactant, A, is fed and of a separation unit, at the bottom of which the target product, C (typically a low volatility species) accumulates, whereas the selective reactant, B (which excess can effectively be limited) is continuously recycled to the reactor: in this way, performing the main reaction under quick onset, fair conversion conditions (Steensma and Westerterp, 1988 and 1990) and adopting a sufficiently high recycle rate of the reactant B through the system, the non selective reactant, A, accumulation in the reactor can be limited and an effective segregation between such a reactant and the target product, C, can be achieved, hence minimizing the extent of the undesired reaction.

In Maestri and Rota (2013), on the basis of a mass balance approach, a number of boundary diagrams have been developed allowing to easily identify the target operating conditions of SBRRs in which (1,1) order reactions of the type (1) occur.

Under such conditions the characteristic time of the target species production is close to the non selective reactant dosing time as well as much higher than the average residence time in the reactor.

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However, the application of the criterion presented in Maestri and Rota (2013) requires the knowledge of the kinetic parameters of the reactions involved and the development of a number of boundary diagrams for different reaction order kinetics as well as the identification of rules of thumb for their simplified and safe use, along the line presented elsewhere in the literature (Maestri and Rota, 2005 a, 2005 b and 2006 a).

However, in this case such an approach is rather complicated, since more than one reaction occurs in the system (at least, the main one and an undesired one) and different combinations of the involved kinetic parameters should be considered.

Aim of this work is to develop a simple and general selectivity criterion for SBRRs that, on the basis of the macroscopic energy balance for the system, allows to discriminate at the industrial scale the optimal SBRR operating regime with respect to the target conditions, without knowing the kinetics of the reactions involved.

The criterion has been finally validated analyzing a reaction process of industrial interest that can be performed in a SBRR: the production of ethylene glycol from ethylene oxide. Such a reaction process typically undergoes selectivity losses, since the reaction product is likely to further react with ethylene oxide to yield poly-ethoxylated species, the main of which is diethylene glycol.

2. Mathematical model

The development of a selectivity criterion based on the energy behavior of the SBRR requires a detailed modeling of the system concerning both the macroscopic mass and energy balances, as well as a discussion about the physical meaning of the parameters introduced.

According to the process configuration represented in Figure 1, in which a reaction scheme of the type (1) occurs, a given amount of component B is initially loaded in the system and recycled through it at a constant rate, so that the same heat duty is supplied at the bottom reboiler and removed at the top condenser.

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At time equal to zero the feed of the non elective reactant, A, to the reactor is started at a constant flowrate.

It is assumed that the dosing stream temperature is lower or equal to the reaction temperature, and that the reaction temperature is lower than the temperature at which the component B reflux occurs.

A simple mathematical model of the SBRR can be developed assuming that:

1) a negligible amount of unreacted A reaches the bottom reboiler;
2) the whole amount of products C and D coming from the reactor accumulates in the bottom reboiler, where their complete separation from the recycled reactant, B, occurs;
3) the change of the amount of species B in the reboiler vessel can be neglected in comparison with its initial holdup, so that the mass increase in the reboiler vessel is due to the C and D accumulation;
4) the characteristic time of the heat removal from the system is much lower than that of the conversion of the reactants (and hence of the exothermic effects related to it). Under forced reflux conditions, in fact, such exothermic contributions are balanced at a much lower time scale by a corresponding decrease of the duty demand at the bottom reboiler, to which an increase of the net duty removed from the system corresponds;
5) the chemical reactions occur only in the top reactor vessel under homogeneous adiabatic conditions, being the reaction heat entirely removed through the top condenser; in this equipment the condensate recycled back to the reactor is subcooled at a temperature (below the reaction one) such that the desired reaction temperature is reached in the reactor;
6) any mixing enthalpy contribution can be neglected with respect to the reaction enthalpy;
7) the reaction volume is constant;
8) the holdup of the separation unit is negligible with respect to that of the top reactor and of the reboiler vessel.

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These requirements are typical also of batch reactive distillation (e.g., Sundmacher et al., 1994; Bollyn and Wright, 1998; Gadewar et al., 2000; Qi and Malone, 2010; Edreder et al., 2011; Kao and Ward, 2014).

However, since the reaction occurs in the top reaction vessel at a suitable temperature, through the SBRR plant configuration even thermally unstable products can be dealt with: in this case, a continuous single pass bottom reboiler can be adopted (such as a width film evaporator), operated at relatively low residence times, through which the B component is vaporized and recycled back to the reactor, and the C product concentrate fraction is accumulated in a bottom vessel kept at a proper temperature.

As discussed in Maestri and Rota (2013), the selectivity behavior of the SBRR can be described solving the following ODE problem, involving the expressions of the macroscopic mass balance for the selective reactant, B, to the whole SBRR system, of the macroscopic mass balance for the target product, C, to the whole SBRR system and of the macroscopic mass balance for the target product, C, to the reactor, respectively (see the Appendix for the details about the derivation of the main equations reported in the paper):

$$\frac{d\chi}{d\vartheta} = \frac{Ex\, t_{dos}}{C_{B0,r}} r_1 \tag{2}$$

$$\frac{d\sigma_C}{d\vartheta} = \frac{Ex\, t_{dos}}{\chi C_{B0,r}} \left(r_1 - r_2\right) - \frac{\sigma_C}{\chi} \frac{d\chi}{d\vartheta} \tag{3}$$

$$\frac{d\gamma_{C,r}}{d\vartheta} = \frac{t_{dos}}{C_{B0,r}} \left(r_1 - r_2\right) - \frac{t_{dos}}{\tau} \gamma_{C,r} \tag{4}$$

These equations involve three dependent variables, that is the normalized conversion, $\chi=(n_{B0}-n_B)/n_{A1}$; the overall selectivity with respect to the target product C, $\sigma_C=n_C/(n_{B0}-n_B)$, and the dimensionless concentration of C in the reactor, $\gamma_{C,r}=C_{C,r}/C_{B0,r}$. The parameter $Ex=\alpha/\beta=n_{B0,r}/n_{A1}$ is referred to as the *effective excess number*, that is the ratio between the initial reactant B molar amount in the reactor and the dosed molar amount of reactant A.

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The initial conditions for solving the ODE system above are: $\chi=0$, $\sigma_C=1$ and $\gamma_{C,r}=0$.

A general power law rate expression is assumed for the two reactions involved:

$$r_1 = k_1 C_A^n C_B^m \tag{5}$$

$$r_2 = k_2 C_A^p C_C^q \tag{6}$$

Equations (2) to (4) can be expressed in the following dimensionless form (Maestri and Rota, 2013):

$$\frac{d\chi}{d\vartheta} = Da_1 \frac{1}{Ex^{n-1}}\left[\vartheta - \chi\left(2-\sigma_C\right)\right]^n \left(1-\frac{\chi}{Ex}\right)^m \kappa_1 \tag{7}$$

$$\begin{aligned}\frac{d\sigma_C}{d\vartheta} &= Da_1 \frac{1}{Ex^{n-1}}\frac{1}{\chi}\left[\vartheta - \chi\left(2-\sigma_C\right)\right]^n \left(1-\frac{\chi}{Ex}\right)^m \kappa_1 + \\ &- Da_2 \frac{1}{Ex^{p-1}}\frac{1}{\chi}\left[\vartheta - \chi\left(2-\sigma_C\right)\right]^p \gamma_{C,r}^q \kappa_2 - \frac{\sigma_C}{\chi}\frac{d\chi}{d\vartheta}\end{aligned} \tag{8}$$

$$\begin{aligned}\frac{d\gamma_{C,r}}{d\vartheta} &= Da_1 \frac{1}{Ex^{n}}\left[\vartheta - \chi\left(2-\sigma_C\right)\right]^n \left(1-\frac{\chi}{Ex}\right)^m \kappa_1 + \\ &- Da_2 \frac{1}{Ex^{p}}\left[\vartheta - \chi\left(2-\sigma_C\right)\right]^p \gamma_{C,r}^q \kappa_2 - R_x \gamma_{C,r}\end{aligned} \tag{9}$$

where $Da_1 = k_{1,R} t_{dos} C_{B0,r}^{n+m-1}$ and $Da_2 = k_{2,R} t_{dos} C_{B0,r}^{p+q-1}$ are the Damköhler numbers for the main and the side reactions, equal to the ratio of the non selective reactant dosing time to the characteristic times of the main and side reaction respectively; $\kappa_1=\exp[E_1/R(1/T_R-1/T_r)]$ and $\kappa_2=\exp[E_2/R(1/T_R-1/T_r)]$ are the dimensionless reaction rate constants; $R_x=t_{dos}/\tau$ is referred to as the *recycle number*, that is the ratio of the non selective reactant dosing time to the average residence time in the reactor (Maestri and Rota, 2013).

After the supply period (that is, at $\vartheta>1$), the ϑ terms in Equations (7) to (9) must be replaced with unity.

The energy behavior of the SBRR can be described by the macroscopic energy balance for the system, which dimensional form is (see the Appendix for more details):

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$$\begin{aligned}\left(n\tilde{C}_P\right)_b \frac{dT_b}{dt} = {} & F_A \tilde{C}_{P,A}\left(T_{dos} - T_r\right) + \\ & + r_1 V_r\left(-\Delta\tilde{H}_1\right) + r_2 V_r\left(-\Delta\tilde{H}_2\right) + \\ & -\left(C_{C,r}\tilde{C}_{P,C} + C_{D,r}\tilde{C}_{P,D}\right) Q\left(T_b - T_r\right) + \\ & + \dot{Q}_b - \dot{Q}_t\end{aligned} \tag{10}$$

where $\dot{Q}_b$ and $\dot{Q}_t$ are the heat duties supplied at the bottom reboiler and removed at the top condenser respectively.

Equation (10) can be rewritten in dimensionless form as follows:

$$\begin{aligned}\left(1+\varepsilon\vartheta\right)\frac{d\breve{T}_b}{d\vartheta} = {} & \varepsilon R_{H_{dos,b}}\left(\breve{T}_{dos} - \breve{T}_r\right) + \\ & + \frac{1}{\beta-1} R_{H_{r,b}} \frac{1}{Ex}\left[\Delta\breve{T}_{ad,1}\frac{d\chi}{d\vartheta} + \Delta\breve{T}_{ad,2}\left(\frac{d\chi}{d\vartheta} - \frac{d\eta_C}{d\vartheta}\right)\right] + \\ & - \frac{1}{\beta-1} R_x R_{H_{P,b}}\left(\gamma_{C,r} + \gamma_{D,r}\right)\left(\breve{T}_b - \breve{T}_r\right) + \\ & - \frac{1}{\beta-1}\dot{\breve{Q}}_{net} St_t R_{H_{r,b}}\end{aligned} \tag{11}$$

where $\eta_C=\chi\sigma_C$ is the yield with respect to the target product C; $\dot{\breve{Q}}_{net} = \left(\dot{Q}_t - \dot{Q}_b\right) \big/ \left(UA\right)_{0,t} T_R$ is the dimensionless net duty removed from the SBRR system; $\breve{T}_k = T_k / T_R$ is the dimensionless k-th temperature; $\varepsilon=V_{dos}/V_{b0}$ is the ratio between the dosed volume and the initial bottom volume; $R_{H_{l,m}} = \left(\tilde{\rho}\tilde{C}_P\right)_l \big/ \left(\tilde{\rho}\tilde{C}_P\right)_m$ is the heat capacity ratio between mixtures l and m; $R_{H_{P,n}} = \left(C_{B0,r}\tilde{C}_{P,P}\right)_l \big/ \left(\tilde{\rho}\tilde{C}_P\right)_n$ is the heat capacity ratio between the reaction products and mixture n; $\Delta\breve{T}_{ad,j} = C_{B0,r}\left(-\Delta\tilde{H}_j\right) \big/ \left(\tilde{\rho}\tilde{C}_P\right)_r T_R$ s the dimensionless adiabatic temperature rise of reaction j; $St_t = \left(UA\right)_{0,t} t_{dos} \big/ \left(\tilde{\rho}\tilde{C}_P\right)_r V_r$ is a modified Stanton number for the problem in question.

According to assumption (4), a pseudo steady state approximation can be adopted for the bottom reboiler temperature in Equation (11), that leads to the following final form of the dimensionless energy balance for the SBRR:

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$$\begin{aligned}\dot{\breve{Q}}_{net} = \frac{1}{St_t} \Big\{ & \varepsilon(\beta - 1) R_{H_{dos,r}} \left(\breve{T}_{dos} - \breve{T}_r\right) + \\ & + \frac{1}{Ex}\left[\Delta\breve{T}_{ad,1}\frac{d\chi}{d\vartheta} + \Delta\breve{T}_{ad,2}\left(\frac{d\chi}{d\vartheta} - \frac{d\eta_C}{d\vartheta}\right)\right] + \\ & - R_x R_{H_{P,r}} \left(\gamma_{C,r} + \gamma_{D,r}\right)\left(\breve{T}_b - \breve{T}_r\right)\Big\}\end{aligned} \tag{12}$$

The numerical integration of Equations (2) to (4) with the stated initial conditions and the further substitution of the results obtained into Equation (12) generates the conversion and yield as well as the net duty time profiles.

In Figure 2A the net duty time profile for a (1,1) reaction order example is represented.

It can be noticed that:

- at $\vartheta<0$, that is before the beginning of the non selective reactant dosing, only the reactant B recycle through the system occurs. Under these conditions the heat duty supplied at the bottom reboiler balances the heat duty removed at the top condenser, and hence the net duty removed from the system is equal to zero;
- at $\vartheta\geq0$, the non selective reactant supply is started at a dosing temperature that is lower or equal to the reflux temperature. Therefore, the initial value of the net duty is negative, since at the bottom reboiler the heat duty required to sustain the internal reflux as well as that to heat up the dosing stream from the dosing temperature to the reaction temperature must be supplied. However, at $\vartheta>0$ because of the triggering of the exothermic reactions, the net duty removed from the system undergo a sudden increase up to a peak value. Such an increase is related to the exothermic contributions of the reactions, that lowers the bottom heat duty to keep the reactant B recycle rate through the system. Once the peak value has been reached, the net duty removed from the system decreases to a dynamic equilibrium value, since the reaction exothermic contribution must balance the endothermic contribution of the reaction products from the reactor temperature to the reflux temperature;
- at $\vartheta=1$ the non selective reactant supply is suddenly stopped and hence the endothermic contribution of the dosing stream from the dosing temperature to the reaction temperature

disappears as well. However, the reaction exothermic contribution drops with a time delay with respect to the end dosing time, that is related to the non selective reactant accumulation in the system. Because of such a sudden unbalance between the two aforementioned enthalpy contributions, at $\vartheta=1$ a net duty positive peak occurs, since under these conditions a higher fraction of the reaction exothermic contribution sustains the reactant B reflux through the system, and hence a lower heat duty to the bottom reboiler must be supplied;

- at $\vartheta>1$, once the unreacted amount of A has been consumed, the reaction exothermic contribution drops as well and the net duty time profile undergoes a peak negative value, that is physically related to the residual endothermic contribution of the reaction products from the reaction temperature to the reflux temperature. Once also this contribution has dropped, the net duty goes to zero, corresponding to the simple reflux of reactant B through the SBRR, as occurs at $\vartheta<0$.

3. Reactor optimization

The selective operation of a SBRR in which a reaction process of the type (1) occurs implies that the main reaction is fully ignited and the extent of the undesired reaction is minimized through limiting the accumulation of the target reaction product, C, in the reactor (Maestri and Rota, 2013): such a regime can be reached operating the SBRR at a sufficiently high internal recycle rate, so that the target reaction product (typically a low volatility species) is continuously removed from the reactor and an effective segregation between this product and the non selective reactant, A, is achieved.

Moreover, the SBRR process configuration allows for a relatively high reactor productivity, since the target product accumulation in the reactor can be limited even at a low excess of the selective reactant, B.

Under the aforementioned conditions, in the following referred to as target conditions, the reactor behavior is not influenced by the kinetics of the reactions involved, since the characteristic time of the conversion rate is in any case close to the dosing time and the characteristic time of the undesired side reaction is theoretically infinite.

Once the system approaches the target conditions, a further increase of the internal recycle rate does not yield any significant improvement of the reactor selectivity and productivity but just an uneconomical increase of the operating costs related to the bottom reboiler and top condenser duties.

In Maestri and Rota (2013), starting from the mass balance equations under target conditions, an ideal value of the product C concentration in the reactor has been derived:

$$\gamma_{C,r}\Big|_{ta} = \frac{1}{Ex\,R_x} \qquad (13)$$

Comparing the real and the target concentration profiles of the target product in the reactor with an arbitrary defined tolerance, the selectivity behavior of the SBRR can be classified: on this basis a number of boundary diagrams can be developed, through which selective and productive operating conditions of SBRRs can be easily selected (Maestri and Rota, 2013).

However, this criterion, in the following referred to as the mass balance approach, is based on a target variable, that is, the product concentration, which dynamic measurement is not straightforward.

Therefore, this criterion is not suitable for an on-line control and optimization of the SBRR, but for an a-priori identification of selective and productive operating conditions of the SBRR itself, on the basis of the aforementioned boundary diagrams, providing, at a given initial excess of the selective reactant, B, the recycle number, R_x, at which the SBRR approaches the target conditions. However, such boundary diagrams depend on the kinetics of the reactions.

For these reasons, in order to make the mass balance approach of general application, a number of boundary diagrams should be developed, along the line presented elsewhere in the literature for the safe operation of SBRs in which exothermic reactions are performed (see for example Maestri and Rota 2005 a, 2005 b and 2006 a).

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On the other hand, the SBRR operating regime could be optimized, independently on the kinetics of the reactions involved, through a process variable that:

- can be measured all along the process duration with a relatively short response time and a good accuracy, as well as through instruments that are easily available in the process industry; this is the case for instance of a flowrate or temperature measurement, but not of a concentration measurement;
- approaches, under target conditions, a constant value all along the dosing period or for a significant fraction of it, that is consequently suitable to be taken as a set point value. This is the case for instance of the target concentration (13) for the selective and productive operation of SBRRs in which a reaction scheme of the type (1) is performed, but not of the target temperature derived for example in Steensma and Westerterp (1988 and 1990) for the safe operation of SBRs in which an exothermic reaction occurs; in this latter case the target temperature decreases with time during the dosing period;
- approaches under target conditions a value that is independent on a selected manipulated variable.

Accordingly, a general criterion for optimizing the operation of SBRRs in which a reaction process of the type (1) occurs can be developed selecting as a derived target variable the net duty, $\dot{Q}_{net}$, removed from the system during the dosing period, that is the difference between the heat removal rate at the top condenser and the heat supply rate at the bottom reboiler: such a derived target variable depends on the main target variable (that is, the target product concentration in the reactor) and satisfies all the aforementioned conditions of a process variable to be controlled for optimizing the SBRR operation. In particular, duty measurements can be easily performed with a fully satisfactory accuracy through conventional flowrate and temperature measurements.

The presented method is referred to in the paper as the energy balance approach.

Whereas the mass balance approach is typically a model based criterion suitable for an a-priori identification of selective and productive operating conditions of SBRRs, the energy balance approach is an ongoing general criterion that is suitable for an on-line plant optimization.

On the basis of the target expressions derived in Maestri and Rota (2013) for the dimensionless conversion rate as well as for the dimensionless concentrations of the reaction products, the target value of the net duty (12) removed from the system is equal to (see the Appendix for more details):

$$\dot{\breve{Q}}_{net}\Big|_{ta} = \frac{1}{St_t}\Big\{\varepsilon\left(\beta-1\right)R_{H_{dos,r}}\left(\breve{T}_{dos}-\breve{T}_r\right)+ \\ +\frac{1}{Ex}\left[\Delta\breve{T}_{ad,1}-R_{H_{P,r}}\left(\breve{T}_b-\breve{T}_r\right)\right]\Big\} \qquad (14)$$

which depends only on thermodynamic parameters of the main reaction.

This is quite obvious because under target conditions the conversion rate is fully determined by the feeding rate (and therefore the kinetic parameters do not play any role) and the unwanted reaction is almost not ignited (and therefore its enthalpy contribution is negligible as well).

As can be recognized from the net duty time profiles represented in Figure 3, at increasing R_x values the net duty removed from the system consequently decreases, since a higher amount of the reaction enthalpy contribution is internally dissipated for heating the reaction products from T_r to T_b. The described trend, however, is less evident at large R_x values, since at higher recycle rates correspond lower reaction products concentrations in the reactor: therefore, an asymptotic value of the aforementioned endothermic contribution of the reaction products from T_r to T_b is reached, to which an asymptotic value of the net duty removed from the system corresponds as well, given by the target value (14), as represented in Figure 3.

Under such an operating regime of the SBRR, the endothermic contributions of the reaction products from T_r to T_b and of the dosing stream from T_{dos} to T_r are balanced by the exothermic contribution of the main reaction only, which residual fraction is useful to sustain the reflux of component B through the system.

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Taking as a manipulated variable the internal recycle rate (that can be varied through the external duty supplied at the bottom reboiler), it is therefore possible to control the net duty removed from the system with respect to its target value (14), hence operating the SBRR under optimized selectivity and productivity conditions.

It must be finally stressed that the described approach of the system does not require any estimation of the kinetic parameters of the reactions involved, since the target operating regime, that is dynamically monitored, is kinetic independent: as previously mentioned, such a characteristic of the method in question is of particular importance dealing with fine chemical and pharma reaction process, because of the huge variety of productions involved.

On the basis of the measured net duty time profile, the deviations of the SBRR operating regime with respect to the target conditions can be characterized as well.

In particular, if the net duty time profile undergoes a positive deviation with respect to the target value (14), as represented in the model simulation of Figure 4, the system is operated at a too low R_x value, to which one of following situations may correspond:

- the main reaction occurs under quick onset, fair conversion conditions but the recycle rate is far below than that above which the endothermic contribution of the reaction products from T_r to T_b is balanced by the exothermic contribution of the main reaction only; as a consequence, also the unwanted reaction plays a role and an unsatisfactory process selectivity is reached;
- a too low dosing time has been adopted compared with the characteristic time of the main reaction, so that an excessive co-reactant accumulation in the system has occurred, leading to the thermal loss of control of the main reaction itself. Therefore, as the main reaction triggers, a relatively high heat release occurs in a short period of time, to which a peak value of the net duty to be removed from the system corresponds. Also in this case the unwanted reaction plays a role, therefore lowering the product yield.

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The two aforementioned situations can be distinguished since in the latter case a negative deviation of the removed net duty with respect to the target value is initially observed, corresponding to a non ignition regime, that is followed by a sudden reaction triggering, resulting in a positive peak of the net duty to be removed from the system with respect to the target value.

In the former case, instead, the removed net duty quickly overcomes the target value, and remains higher than it all along the dosing period.

If instead the net duty time profile is lower than the target value (14) at any time value, the exothermic contribution due to the chemical reactions as well as the endothermic contribution of the reaction products are negligible, so that the external heat duty to be supplied at the bottom reboiler has to fully sustain the component B reflux through the system as well as to balance the endothermic contribution of the dosing stream from T_{dos} to T_r: as a result the bottom duty is higher than the top one (by the latter endothermic contribution) and the net duty removed from the system is negative, as represented in the model simulation of Figure 5. Such operating conditions correspond to an SBRR operating regime in which the chemical reactions are not ignited and the process productivity is therefore unsatisfactory, as evident from Figure 5 where we can see that large conversion values can be reached only at $\vartheta >> 1$.

As previously discussed, when the SBRR approaches the target conditions, the net duty time profile tends to be constant with time at increasing R_x values, and close to the target value (14).

Such a behavior can be better represented in terms of an integral property of the net duty time profile, that is the average displacement of the real profile from the target one during the dosing period:

$$\left\langle \Delta \dot{\breve{Q}}_{net}\left(\%\right) \right\rangle_{dos} = \frac{\int_0^1 \left(\dot{\breve{Q}}_{net} - \dot{\breve{Q}}_{net}\Big|_{ta} \right) d\vartheta}{\dot{\breve{Q}}_{net}\Big|_{ta}} \times 100 \qquad (15)$$

As can be recognized form the trend represented in Figure 6, at the higher R_x values an asymptotically increasing amount of the exothermic reaction contribution in internally dissipated for heating the reaction products from T_r to T_b: therefore the overall energy to be removed from the system decreases to an asymptotic target value as well.

In order to assess the industrial use of the energy balance approach for the on-line optimization of SBRRs in which reaction schemes of the type (1) are performed, the parametric sensitivity of the measured variable, $\dot{Q}_{net}$, with respect to the asymptotic process selectivity, $\sigma_{C\infty}$, has been calculated. The normalized parametric sensitivity coefficient of $\dot{Q}_{net}$ with respect to $\sigma_{C\infty}$ has been defined as follows, according to Varma et al. (1999):

$$S = \frac{\sigma_{C\infty}}{\dot{Q}_{net}} \frac{\partial \dot{Q}_{net}}{\partial \sigma_{C\infty}} \approx \frac{\Delta \dot{Q}_{net}}{\dot{Q}_{net}} \frac{\sigma_{C\infty}}{\Delta \sigma_{C\infty}} = \frac{\Delta \dot{Q}_{net}}{\dot{Q}_{net}} \frac{\sigma_{C\infty}}{\Delta \sigma_{C\infty}} \qquad (16)$$

In Figure 7 the results obtained for different dimensionless subcooling temperature differences between bottom and reaction temperatures are represented. It can be noticed that a significant increase (even of an order of magnitude) of the normalized parametric sensitivity coefficient (16) occurs at selectivity values of industrial interest (that is, above 90÷95%).

Moreover, the calculated values of the normalized parametric sensitivity coefficients (16) can be related to the required instrumental accuracy to measure the net duty to be removed from the system, with respect to the overall duty to be removed at the top condenser (accounting also for the internal reflux contribution).

As can be noticed from Figure 7, the order of magnitude of the S parameter (16) is 10^1: since $\sigma_{C\infty} \approx 10^0$ and $\Delta\sigma_{C\infty} \approx 10^{-2}$, according to equation (16) it can be estimated that $\Delta \dot{Q}_{net} / \dot{Q}_{net} \approx 10^{-1}$. This means that for a 1% variation of $\sigma_{C\infty}$, a 10% variation of $\dot{Q}_{net}$ has to be expected, that must therefore be measurable at the industrial scale with the currently available instruments for measuring the heat duties.

Assuming a 1% accuracy of the heat duty measurements, the net duty variations can be detected at the industrial scale if $\Delta \dot{Q}_{net} / \dot{Q}_t \geq 10^{-2}$: in fact, taking into account that conventional flowmeters reach accuracies of the order of 0.2% and that the average accuracy of a thermocouple is of the order of 0.4% (see for example Perry at al., 2007), the accuracy on the heat duty measurements (calculated as the products of flowrate and temperature difference measurements) is lower than 1%.

Combining the orders of magnitude estimated above, the final condition to be checked for the industrial use of the criterion in question is $\dot{Q}_{net}\big/\dot{Q}_t \geq 10^{-1}$.

Assuming in the industrial practice a maximum difference between reflux and reaction temperatures equal to 50°C (to which a dimensionless subcooling value equal to 0.166 corresponds), as well as a negligible difference between reaction and dosing temperatures, it can be estimated that adopting an excess number Ex=5 (that can be considered a threshold industrial value for SBRRs) the target value of the net duty difference (14) is of the order of 10^{-2} if $\Delta\breve{T}_{ad,1} \geq 0.216$, that is 65°C in dimensional terms.

Taking finally into account that:

$$\dot{\breve{Q}}_{net} = \frac{\dot{Q}_t - \dot{Q}_b}{\left(UA\right)_{0,t} T_R} = \frac{\dot{Q}_t - \dot{Q}_b}{\left(UA\right)_{0,t} \Delta T_{eff,t}} \frac{\Delta T_{eff,t}}{T_R} = \frac{\dot{Q}_{net}}{\dot{Q}_t} \frac{\Delta T_{eff,t}}{T_R} \tag{17}$$

and being $\Delta T_{eff,t}/T_R \approx 10^{-1}$, it is straightforward to prove that, with the selected range of industrial process parameters, $\dot{Q}_{net}\big/\dot{Q}_t \geq 10^{-1}$, as required for a safe industrial use of the energy balance approach.

Even if the reaction enthalpy is lower than a threshold value for a satisfactory net duty measurement accuracy at the industrial scale (according to the order of magnitude analysis presented above), the energy balance approach can be conveniently employed as well at the laboratory scale, in order to a-priori identify selective and productive operating conditions for the SBRR. At such a scale the SBRR process configuration can be easily assembled and equipped with a control system of similar accuracy than that of a standard RC1 calorimeter, through which even relatively low net duty values can be detected. The identified target operating condition for the SBRR can then be scaled-up to the industrial scale through standard techniques (see for instance van Woezik and Westerterp, 2001; Maestri et al. 2009 a and 2009 b). Even in this case it must be stressed that the experimental identification of the operating conditions can be performed independently on the knowledge of the kinetic parameters of the reactions involved, with a significantly lower experimental effort.

It is finally useful to notice that in performing the aforementioned net duty measurements with the required accuracy, the role of eventual heat losses from the SBRR system to the surrounding environment can be overcome.

In fact, even if the SBRR is not perfectly insulated to the environment, the heat loss can be detected before the beginning of the coreactant dosing, that is when only the B component reflux through the system occurs.

Under such conditions, the overall energy balance equation yields:

$$\dot{Q}_t + \dot{Q}_{loss} - \dot{Q}_b = 0 \qquad (18)$$

stating that the heat duty supplied at the bottom reboiler balances the contribution due to both the B component reflux and the heat losses to the environment.

Therefore, the (negative) value of the net duty at t<0 (that is, before the beginning of the coreactant dosing) quantifies the aforementioned heat losses.

It is consequently straightforward to perform an on-line tuning of the system from the energy point of view, by shifting the base line for the net duty measurements so as to cancel the initial negative deviation of the net duty with respect to the zero value.

After the beginning of the coreactant dosing, the net duty can be measured with respect to such a corrected base line.

4. Case study: the production of ethylene glycol from ethylene oxide

The described selectivity criterion for SBRRs in which reaction processes of the type (1) are performed has been applied to a reaction process of significant industrial relevance, that is the production of ethylene glycol (EG) from ethylene oxide (EO) under acidic conditions.

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In this case, as occurs for a number of ethoxylation reactions of nucleophylic substrates, ethylene oxide is likely to further react with the target ethoxylated product to yield poly-ethoxylated species. In the production of EG from EO, the most relevant side reaction is the further ethoxylation of the target product to diethylene glycol (DEG), according to the scheme:

$$\begin{aligned} &EO + H_2O \xrightarrow{r_{EG}} EG \\ &EO + EG \xrightarrow{r_{DEG}} DEG \end{aligned} \qquad (19)$$

At the pH values of industrial interest (that is, at pH=3÷4), the rate of the two reactions can be described through the following power law expressions (Gulati and Bharti, 2007):

$$\begin{aligned} &r_{EG} = 1.02 \cdot 10^9 \exp\left(-\frac{9547}{T}\right) C_{EO} C_{H_2O} \\ &r_{DEG} = 2.04 \cdot 10^9 \exp\left(-\frac{9547}{T}\right) C_{EO} C_{EG} \end{aligned} \qquad (20)$$

where the units are kmol, m^3, K, s.

The calculated reaction enthalpies are $\Delta\tilde{H}_{EG} = -120\, kJ/mol$ for the main reaction and $\Delta\tilde{H}_{DEG} = -135\, kJ/mol$ for the undesired further reaction (Yaws, 1998). It can be noticed that the two calculated reaction enthalpies are relatively high, as expected for a strongly exothermic reaction process, and close to each other.

At the industrial scale the reaction is performed at 50°C and with 0.5÷1% of H_2SO_4 as a homogeneous catalyst, adopting a molar ratio between water and ethylene oxide close to 20. Moreover, a residence time in the reactor of the order of 30’ is typical of most of the industrial plants. Under these conditions a 90% selectivity to EG is reached.

In this case, a 1000kW heat duty SBRR plant has been taken into exam, with a 1m^3 top reaction vessel (filled up to 0.8m^3) and a 7m^3 bottom vessel (filled up to 5m^3, to allow an effective vapor disengagement).

The SBRR is initially loaded with 5800kg water (split between 5000kg in the reboiler vessel and 800kg in the top reaction vessel, to which a β value equal to 7.25 corresponds), recycling at a

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$1.6 m^3/h$ rate, according with the heat duty specified above and with the latent heat of vaporization of water: under such conditions, the average residence time in the top reactor is 30’.

Using as a heating medium at the bottom reboiler saturated steam at 10 bar a (to which a 180°C saturation temperature corresponds) and assuming an overall heat transfer coefficient equal to $500 W/m^2K$, the required heat transfer area at the bottom reboiler is $25 m^2$.

Moreover, adopting as a cooling medium at the top condenser water at 32°C with a 6°C temperature range between inlet and outlet, a logarithmic mean temperature difference equal to 65°C can be calculated, to which a $(UA)_{0,t}$ value equal to 15385W/K corresponds.

Adopting an effective excess number, Ex, equal to 2 and on the basis of the calculated β value, the dosed EO quantity is equal to $n_{A,1}$=22.2kmol, corresponding to 978kg. Moreover, the dosed EO volume at 50°C and 1ata is $589.6 m^3$, to which an ε value (corrected for the fed gas to liquid density ratio) equal to 0.196 corresponds.

With such a EO amount, 1378kg of EG are theoretically produced, corresponding to a 21.6% w/w final water solution in the bottom reboiler, which boiling point at atmospheric pressure is 102°C (therefore only slightly higher than the initial value corresponding to pure water).

The calculated $\left(\tilde{\rho}\tilde{C}_P\right)$ values for the reaction mixture, the dosed stream (which is in the gas phase) and the bottom mixture are 4186, 2.056 and $4063 kJ/m^3K$, whereas the average heat capacity of the reaction products is 2.5kJ/kgK (Perry and Green, 2008). Moreover, a dosing time equal to 5 hours is adopted.

From the data specified above and with a 300K reference temperature, the dimensionless problem parameters summarized in Table 1 can be calculated.

In Figure 8 the SBRR asymptotic selectivity to EG, $\sigma_{EG,\infty}$, at different residence times in the top reactor is represented: it can be noticed that as the residence time decreases the process selectivity to EG increases, going from an asymptotic lower limit at the higher residence times (equal to 63%) to the required industrial value (equal to 90%) at a residence time equal to 30’.

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As represented in Figure 9, under these conditions the measured net duty (that is equal to zero at $t<0$) undergoes a sudden increase at the beginning of the EO supply, reaching a constant target value (that is close to 140kW). At the end of the supply period, the measured net duty undergoes a quick drop with respect to such a target value, going asymptotically to zero as any enthalpy effect of the reactions involved has extinguished.

The SBRR target regime can therefore be detected at the industrial scale trough simple net duty measurements during the supply period, that do not require any information about reaction kinetics.

Moreover, according to the target net duty value (that is, 140kW), and to the top condenser duty (that is, 1000kW), the $\dot{Q}_{net} / \dot{Q}_t$ ratio is higher than 10^{-1}, as required for a safe industrial use of the presented criterion.

5. Conclusions

Several fine chemical and pharma reaction processes, typically performed in multipurpose batch or semibatch reactors, undergo selectivity losses due to general series/parallel kinetic schemes, according to which the target reaction product (often a low volatility one) is consumed by a non selective reactant, yielding by-products that must be then separated and disposed as wastes.

In such cases, adopting the SBRR configuration allows to improve both the process selectivity and productivity even in a non continuous plant, since the same selectivity target can be reached at a lower excess of the selective reactant.

The selective and productive operation of a SBRR can be detected through comparing the real concentration time profile of the desired reaction product with a target one, corresponding to operating conditions according to which the main reaction is fully ignited and the extent of the undesired side reaction is minimized.

However such a criterion is not suitable for the on-line optimization of the SBRR, since on-line concentration measurements are less common at the industrial scale and in any case characterized by relatively long response times, especially when dealing with low volatility species.

Moreover, the criterion presented in Maestri and Rota (2013), based on the use of boundary diagrams for the a-priori identification of the aforementioned operating conditions, depends in general on the kinetics of the reactions involved.

In this work a general criterion has been developed that, through the selection of a suitable target variable, that is the net duty removed from the system, allows for the on-line optimization of the SBRR, without requiring the knowledge of the kinetic parameters of the reactions involved.

Moreover, the industrial applicability of the criterion in question has been proved, with reference to the expected accuracy of the conventional instruments for duty measurement.

Finally, the criterion has been applied to a reaction process of industrial relevance undergoing selectivity problems, that is the production of ethylene glycol from ethylene oxide performed in a SBRR.

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Nomenclature

A	heat transfer surface, m^2
C	molar concentration, $kmol/m^3$
$\tilde{C}_P$	molar heat capacity at constant pressure, kJ/(kmol·K)
Da_1	$= k_{1,R} t_{dos} C_{B0,r}^{n+m-1}$, main reaction Damköhler number, -
Da_2	$= k_{2,R} t_{dos} C_{B0,r}^{p+q-1}$, side reaction Damköhler number, -
E	activation energy, kJ/kmol
Ex	$=n_{B0,r}/n_{A1}$, effective excess number, -
F	molar feed rate, kmol/s
k	reaction rate constant, $m^3/(kmol \cdot s)$
n	number of moles, kmol
n,m,p,q	reaction orders, -
Q	volumetric flow rate of the liquid stream leaving the reactor, m^3/s
$\dot{Q}$	heat duty, kW
$\breve{\dot{Q}}$	$= \dot{Q} \big/ \left(UA\right)_{0,t} T_R$, dimensionless heat duty, -
r	reaction rate, $kmol/(m^3 \cdot s)$
R	gas constant = 8.314, kJ/(kmol·K)
R_H	heat capacity ratio, -
R_x	$=t_{dos}/\tau$, recycle number, -
S	normalized sensitivity parametric coefficient, -
S_y	$=(Da \cdot \kappa)_1/(Da \cdot \kappa)_2$, selectivity number, -
St_t	$= \left(UA\right)_{0,t} t_{dos} \Big/ \left(\tilde{\rho}\tilde{C}_P\right)_r V_r$, modified Stanton number, -
t	time, s
T	temperature, K
$\breve{T}$	$=T/T_R$, dimensionless temperature, -
U	overall heat transfer coefficient, $kW/(m^2K)$

Subscripts and superscripts

ad	adiabatic
A,B,C,D	components A, B, C and D
b	bottom
DEG	diethylene glycol
dos	dosing stream or dosing time
eff	effective
EG	ethylene glycol
EO	ethylene oxide
k	index k
l,m	index l, m
loss	loss (in $\dot{Q}_{loss}$)
net	net (in $\dot{Q}_{net}$)
P	products
r	reactor
R	reference
t	top

ta	target
x	in the recycle number R_x
y	in the selectivity number S_y
0	start of the semibatch period
1	main reaction or end of the dosing period
2	side reaction
∞	asymptotic value in $\sigma_{C\infty}$

Greek symbols

α	$=n_{B0}/n_{A1}$, overall excess number, -
β	$=1+n_{B0,b}/n_{B0,r}$, initial reactant split between top and bottom of the system, -
γ	dimensionless concentration or dimensionless activation energy, -
$\Delta\tilde{H}$	reaction enthalpy, kJ/kmol
$\Delta\dot{Q}$	duty displacement, kW
ΔT_{eff}	effective temperature difference, K
$\Delta\breve{T}_{ad}$	$=C_{B0,r}\left(-\Delta\tilde{H}\right)\Big/\left(\tilde{\rho}\tilde{C}_P\right)_r T_R$, dimensionless adiabatic temperature rise, -
$\Delta\sigma_{C\infty}$	selectivity variation, -
ε	$=V_{dos}/V_{b0}$, relative volume increase, -
η_C	$=\chi\sigma_C$, target product yield, -
ϑ	$=t/t_{dos}$, dimensionless time, -
κ	$=k/k_R$, dimensionless reaction rate constant, -
$\tilde{\rho}$	molar density, kmol/m^3
σ	molar selectivity, -
τ	$=V_r/Q$, average residence time in the reactor, s
χ	$=(n_{B0}-n_B)/n_{A1}$, normalized conversion, -

References

Bollyn, M.P., Wright, A.M., 1998. Development of a process model for a batch reactive distillation – A case study. *Comput. Chem. Eng, 22,* S87-S94, Suppl.

Edreder, E.A., Mujtaba, I.M., Emtir, M., 2011. Optimal operation of types of batch reactive distillation columns used for hydrolysis of methyl lactate to lactic acid. *Chem. Eng. Journal, 172,* 467-475.

Froment, G.F., Bischoff, K.B., De Wilde, J., 2010. Chemical reactor analysis and design, third ed. Wiley.

Gadewar, S.B., Malone, M.F., Doherty, M.F., 2000. Selectivity targets for batch reactive distillation. *Ind. Eng. Chem. Res., 39,* 1565-1575.

Gulati, K., Bharti, V., 2007. Optimization of reactive distillation column using genetic algorithm. *Thesis for the degree of Batchelor of Technology in Chemical Engineering*, Department of Chemical Engineering, National Institute of Technology, Rourkela (India).

Kao, Y.L. and Ward, J.D, 2014. Design and optimization of batch reactive distillation processes with off-cut. *Journal of the Taiwan Institute of Chemical Engineers, 45,* 411-420.

Levenspiel, O., 1998. Chemical reaction engineering, third ed., Wiley.

Maestri, F., Rota, R., 2005 a. Thermally safe operation of liquid-liquid semibatch reactors. Part I: single kinetically controlled reactions with arbitrary reaction order. *Chem. Eng. Sci., 60,* 3309-3322.

Maestri, F., Rota, R., 2005 b. Thermally safe operation of liquid-liquid semibatch reactors. Part II: single diffusion controlled reactions with arbitrary reaction order. *Chem. Eng. Sci., 60,* 5590-5602.

Maestri, F., Rota, R., 2006 a. Safe and productive operation of homogeneous semibatch reactors. I: development of a general procedure. *Ind. Eng. Chem. Res., 45,* 8002-8013.

Maestri, F., Copelli, S., Rota, R., Lunghi, A., Gigante, L., Cardillo, P., 2009 a. A simple procedure for optimal scale-up of fine chemical processes. Part I: practical tools. *Ind. Eng. Chem. Res. 48 (3),* 1307-1315.

Maestri, F., Copelli, S., Rota, R., Lunghi, A., Gigante, L., Cardillo, P., 2009 b. Simple procedure for optimal scale-up of fine chemical processes. Part II: nitration of 4-chlorobenzotrifluoride. *Ind. Eng. Chem. Res. 48 (3),* 1316-1324.

Maestri, F., Rota, R., 2013. Selectivity problem for fine chemical reactions leading to non volatile products: process configuration and boundary diagrams. *Chem. Eng. Sci.*, *90,* 1-8.

Perry, R.H., Green, D.W., 2008. Chemical engineers' handbook, Mc Graw Hill.

Qi, W., Malone, M.F., 2010. Operating parameters and selectivity in batch reactive distillation. *Ind. Eng. Chem. Res., 49,* 11547-11556.

Smith, M., March, J., 2007. Advanced organic chemistry: reactions, mechanisms and structure, sixth ed., Wiley.

Steensma, M., Westerterp, K.R., 1988. Thermally safe operation of a cooled semi-batch reactor. Slow liquid-liquid reactions. *Chem. Eng. Sci. 43, Nr.8,* 2125-2132.

Steensma, M., Westerterp, K.R., 1990. Thermally safe operation of a semibatch reactor for liquid-liquid reactions. Slow reactions. *Ind. Eng. Chem. Res. 29,* 1259-1270.

Sundmacher, K., Rihko, L.K., Hoffmann, U., 1994. Classification of reactive distillation processes by dimensionless numbers. *Chem. Eng. Commun., 127,* 151-167.

van Woezik, B.A.A., Westerterp K.R., 2001. Runaway behaviour and thermally safe operation of multiple liquid-liquid reactions in the semibatch reactor. The nitric acid oxidation of 2-octanol. *Chem. Eng. Process. 41,* 59-77.

Varma, A., Morbidelli, M., Wu, H. Parametric Sensitivity in Chemical Systems. 1999, *Cambridge University Press.*

Westerterp, K.R., van Swaaij, W.P.M., Beenackers, A.A.C.M., 1984. Chemical reactor design and operation, Wiley: Chichester.

Yaws, C.L., 1998. Chemical Properties Handbook, Mc Graw Hill.

Captions to the figures.

Figure 1. Semibatch recycle reactor (SBRR) process configuration.

Figure 2. SBRR process configuration. Da_1=10, Da_2=10, $E_1/(RT_R)$=30, $E_2/(RT_R)$=30; n=m=p=q=1; $\Delta\breve{T}_{ad,1}$=0.5, $\Delta\breve{T}_{ad,2}$=0.5, $R_{H_{P,r}}$=1, $R_{H_{dos,r}}$=1; ε=0.3, β=5, St_t=3; $\breve{T}_r$=1.1, $\breve{T}_b$=1.3, $\breve{T}_{dos}$=1; Ex=2, R_x=10. (A) net duty removed from the system vs. time profile; (B) normalized conversion vs. time profile; (C) product yield vs. normalized conversion profile.

Figure 3. SBRR process configuration. Da_1=10, Da_2=10, $E_1/(RT_R)$=30, $E_2/(RT_R)$=30; n=m=p=q=1; $\Delta\breve{T}_{ad,1}$=0.5, $\Delta\breve{T}_{ad,2}$=0.5, $R_{H_{P,r}}$=1, $R_{H_{dos,r}}$=1; ε=0.3, β=5, St_t=3; $\breve{T}_r$=1.1, $\breve{T}_b$=1.3, $\breve{T}_{dos}$=1; Ex=2, R_x=0.1, 1, 2, 5, 10, 20, 50, 100. Net duty removed from the system vs. time profiles.

Figure 4. SBRR process configuration. Da_1=10, Da_2=10, $E_1/(RT_R)$=30, $E_2/(RT_R)$=30; n=m=p=q=1; $\Delta\breve{T}_{ad,1}$=0.5, $\Delta\breve{T}_{ad,2}$=0.5, $R_{H_{P,r}}$=1, $R_{H_{dos,r}}$=1; ε=0.3, β=5, St_t=3; $\breve{T}_r$=1.1, $\breve{T}_b$=1.3, $\breve{T}_{dos}$=1; Ex=2, R_x=1. (A) net duty removed from the system vs. time profile; (B) normalized conversion vs. time profile; (C) product yield vs. normalized conversion profile.

Figure 5. SBRR process configuration. Da_1=10, Da_2=10, $E_1/(RT_R)$=30, $E_2/(RT_R)$=30; n=m=p=q=1; $\Delta\breve{T}_{ad,1}$=0.5, $\Delta\breve{T}_{ad,2}$=0.5, $R_{H_{P,r}}$=1, $R_{H_{dos,r}}$=1; ε=0.3, β=5, St_t=3; $\breve{T}_r$=0.95, $\breve{T}_b$=1.15, $\breve{T}_{dos}$=0.85; Ex=2, R_x=10. (A) net duty removed from the system vs. time profile; (B) normalized conversion vs. time profile; (C) product yield vs. normalized conversion profile.

Figure 6. SBRR process configuration. Da_1=10, Da_2=10, $E_1/(RT_R)$=30, $E_2/(RT_R)$=30; n=m=p=q=1; $\Delta\breve{T}_{ad,1}$=0.5, $\Delta\breve{T}_{ad,2}$=0.5, $R_{H_{P,r}}$=1, $R_{H_{dos,r}}$=1; ε=0.3, β=5, St_t=3; $\breve{T}_r$=1.1, $\breve{T}_b$=1.3, $\breve{T}_{dos}$=1; Ex=2. Average displacement between real and target net duty time profiles during the dosing period vs. recycle number.

Figure 7. SBRR process configuration. Da_1=10, Da_2=10, $E_1/(RT_R)$=30, $E_2/(RT_R)$=30; n=m=p=q=1; $\Delta\breve{T}_{ad,1}$=0.5, $\Delta\breve{T}_{ad,2}$=0.5, $R_{H_{P,r}}$=1, $R_{H_{dos,r}}$=1; ε=0.3, β=5, St_t=3; $\breve{T}_r$=1.1, $\breve{T}_b$=1.3, $\breve{T}_{dos}$=1; Ex=2, R_x=0÷2. Normalized parametric sensitivity coefficient of $\dot{Q}_{net}$ vs. $\sigma_{C\infty}$.

Figure 8. Production of ethylene glycol from ethylene oxide in a SBRR: asymptotic selectivity to ethylene glycol vs. reciprocal of the average residence time in the top reactor.

Figure 9. Production of ethylene glycol from ethylene oxide in a SBRR: net duty removed from the system vs. time profile.

Da_1	15.415
Da_2	30.825
γ_1	31.2
γ_2	31.2
ε^*	0.196
$R_{H\ dos,r}$	$4.91 \cdot 10^{-4}$
$R_{H\ P,r}$	2.06
β	7.25
Ex	2
R_x	10
$\Delta\breve{T}_{ad,1}$	5.3
$\Delta\breve{T}_{ad,2}$	6.03
St_t	82.7

Table 1. Production of ethylene glycol from ethylene oxide in a SBRR: dimensionless parameters for SBRR modeling.

Appendix

The derivation of the main equations reported in the paper is summarized in the following; for the definition of the symbols see the Nomenclature section.

Equation (2) is the mass balance equation for component B at the whole system, written in terms of normalized conversion. The mass balance equation for component B at the whole system in dimensional form is:

$$\frac{dn_B}{dt} = -r_1 V_r$$

where $n_B = n_{B,r} + n_{B,b}$ is the overall amount of B (in molar terms) in the system, split between the top (that is, the reactor) and the bottom of the system.
The normalized conversion is defined as:

$$\chi = \alpha \zeta_B = \frac{n_{B0} - n_B}{n_{A1}}$$

The aforementioned mass balance equation can therefore be written in terms of normalized conversion as follows:

$$\frac{d\chi}{d\vartheta} = \frac{t_{dos}}{n_{A1}} r_1 V_r = \frac{t_{dos}\,\alpha}{n_{B0,r}\left(1 + \frac{n_{B0,b}}{n_{B0,r}}\right)} r_1 V_r = \frac{t_{dos}\, Ex}{C_{B0,r}} r_1$$

corresponding to equation (2).

Equation (3) is the mass balance equation for the target product C at the whole system written in terms of normalized conversion and process selectivity with respect to C. The mass balance equation for the target reaction product C at the overall system in dimensional form provides:

$$\frac{dn_C}{dt} = \left(r_1 - r_2\right) V_r$$

n_C being the molar overall amount of C (split between top and bottom of the system), r_j (with j=1,2) being the rate of the j-th reaction and V_r the reaction volume. No removal terms of C from the bottom of the system appear, since C is simply accumulated in the bottom capacity: the SBRR is in fact a semibatch equipment, from which the reaction products are not removed. For this reason, the mass balance equations at the overall system do not contain output terms and no solvent lose can consequently occur from the bottom due to the reaction products removal. In order to avoid any confusion on the point, also in Figure 1 no output stream has been represented, hence showing more clearly that the reaction products simply accumulate at the bottom of the system.
Taking the definition of normalized conversion and of selectivity with respect to the target reaction product C:

$$\chi = \alpha \zeta_B = \frac{n_{B0,b} + n_{B0,r} - n_B}{n_{A1}}$$

$$\sigma_C = \frac{n_C}{n_{B0,b} + n_{B0,r} - n_B} = \frac{n_C}{\chi\, n_{A1}}$$

it is straightforward to derive that:

$$\frac{dn_C}{dt} = n_{A1}\left(\chi \frac{d\sigma_C}{dt} + \sigma_C \frac{d\chi}{dt}\right)$$

Therefore:

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$$\chi \frac{d\sigma_C}{d\vartheta} + \sigma_C \frac{d\chi}{d\vartheta} = \frac{t_{dos}\left(r_1 - r_2\right)V_r}{n_{A1}} = \frac{t_{dos}\left(r_1 - r_2\right)V_r\,\alpha}{n_{B0,r}\beta} = \frac{Ex\,t_{dos}\left(r_1 - r_2\right)}{C_{B0,r}}$$

and hence:

$$\frac{d\sigma_C}{d\vartheta} = \frac{Ex\,t_{dos}}{\chi C_{B0,r}}\left(r_1 - r_2\right) - \frac{\sigma_C}{\chi}\frac{d\chi}{d\vartheta}$$

corresponding to equation (3).

Equation (4) is the mass balance for the target reaction product C at the top reactor. The mass balance of C at the top reactor in dimensional form provides:

$$\frac{dn_{C,r}}{dt} = \left(r_1 - r_2\right)V_r - QC_{C,r}$$

Since the reaction volume is constant with time we get:

$$\frac{dC_{C,r}}{dt} = r_1 - r_2 - \frac{1}{\tau}C_{C,r}$$

and finally, in dimensionless terms:

$$\frac{d\gamma_{C,r}}{d\vartheta} = \frac{t_{dos}}{C_{B0,r}}\left(r_1 - r_2\right) - \frac{t_{dos}}{\tau}\gamma_{C,r}$$

corresponding to equation (4).

In order to derive Equation (7) to (9), the functional dependences of the reactants concentrations in the reactor from the problem dependent and independent variables must be previously derived.

The functional dependence of the molar concentration of the dosed co-reactant A in the reactor from the problem dependent and independent variables can be derived starting from from the mass balance equations for the i-th species at the whole system:

$$\frac{dn_i}{dt} = F_i + \sum_{j=1}^{NR} \nu_{i,j} r_j V_r$$

where F_i is the molar feed rate of the i-th component (that differs from zero for A only) and $\nu_{i,j}$ is the stoichiometric coefficient through which the i-th component appears in the j-th reaction, taken as positive or negative if the i-th species is a reaction product or a reactant respectively. Through a suitable linear combination of such balance equations, it is straightforward to obtain the following differential relation:

$$\frac{d\left(n_A - n_C - 2n_B\right)}{dt} = F_A$$

Integrating such an equation with the initial condition $n_A=n_C=0$, $n_B=n_{B0}$ at t=0, and taking into account that no unreacted A can reach the bottom of the system, it is straightforward to obtain the following functional dependence:

$$n_{A,r} = n_C + 2\left(n_B - n_{B0}\right) + F_A t$$

Introducing the definitions of conversion of B and selectivity with respect to C, such an expression can be rewritten as follows:

$$n_{A,r} = F_A t - n_{A1}\chi\left(2 - \sigma_C\right) = n_{A1}\vartheta - n_{A1}\chi\left(2 - \sigma_C\right) = n_{A1}\left[\vartheta - \chi\left(2 - \sigma_C\right)\right] = n_{B0,r}\frac{1}{Ex}\left[\vartheta - \chi\left(2 - \sigma_C\right)\right]$$

Dividing the expression above for the reaction volume, it is straightforward to get:

$$C_{A,r} = C_{B0,r}\frac{1}{Ex}\left[\vartheta - \chi\left(2 - \sigma_C\right)\right]$$

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The functional dependence of the molar concentration of the recycled reactant B in the reactor from the problem dependent and independent variables can be derived from the definition of normalized conversion:

$$n_{B,r} + n_{B,b} = n_{B0,r} + n_{B0,b} - n_{A1}\chi$$

Since the amount of B at the bottom of the system is relatively large, its amount can be assumed constant with time. Therefore:

$$n_{B,r} \cong n_{B0,r} - n_{A1}\chi = n_{B0,r} - n_{B0,r}\frac{\beta}{\alpha}\chi = n_{B0,r}\left(1 - \frac{\chi}{Ex}\right)$$

Dividing now both the members by the reaction volume (that is constant with time) we get:

$$C_{B,r} = C_{B0,r}\left(1 - \frac{\chi}{Ex}\right)$$

The functional dependence of the molar concentration of the target product C in the reactor from the problem dependent and independent variables can be derived from the dimensionless form of the molar concentration of C in the reactor:

$$C_{C,r} = C_{B0,r}\gamma_{C,r}$$

Substituting the functional dependences derived above into Equations (2) to (4), together with the reaction rates expressions (5) and (6), it is straightforward to derive Equations (7) to (9) in terms of the dimensionless parameters defined in the paper.

Equation (10) is the dimensional form of the macroscopic energy balance for the SBRR system. Since the holdup of all the equipment involved but the top reactor and the bottom reboiler vessel are negligible, the accumulation term of the energy balance can be split as follows:

$$\frac{dU}{dt} \approx \frac{dH}{dt} = \frac{dH_r}{dt} + \frac{dH_b}{dt}$$

where the r and b subscripts stay for reactor and bottom respectively, and the internal energy of the fluid unit mass has been approximated to its enthalpy, dealing with liquid phases.
The reactor accumulation term can be expressed as follows:

$$\frac{dH_r}{dt} = \frac{d}{dt}\left(\sum_{i=1}^{NC} n_{i,r}\tilde{H}_{i,r}\right)$$

where an ideal thermodynamic behavior of the fluid mixtures has been assumed and, for instance, a negligible role of the mixing enthalpy contributions compared to the reaction enthalpy ones.

Since the characteristic time of the heat removal from the system is much lower than that of the conversion of the reactants, the reaction occurs under pseudo-isothermal conditions and the expression above simplifies as follows:

$$\frac{dH_r}{dt} \approx \sum_{i=1}^{NC} \tilde{H}_{i,r}\frac{dn_{i,r}}{dt}$$

while the component mass balance equations at the reactor yield:

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$$\frac{dn_{A,r}}{dt} = F_A - \left(r_1 + r_2\right)V_r$$
$$\frac{dn_{B,r}}{dt} = -r_1 V_r$$
$$\frac{dn_{C,r}}{dt} = -QC_{C,r} + \left(r_1 - r_2\right)V_r$$
$$\frac{dn_{D,r}}{dt} = -QC_{D,r} + r_2 V_r$$

where F and Q are the stream molar and volumetric flowrates respectively and $C_{i,r}$ is the i-th component molar concentration in the reactor. Substituting the expressions above into the reactor energy accumulation term and recalling that the enthalpy of the j-th reaction is equal to:

$$\Delta\tilde{H}_j = \sum_{i=1}^{NC} \nu_{i,j}\tilde{H}_i$$

the following final expression can be easily obtained:

$$\frac{dH_r}{dt} = F_A\tilde{H}_{A,r} - r_1 V_r\left(-\Delta\tilde{H}_1\right) - r_2 V_r\left(-\Delta\tilde{H}_2\right) - Q\left(\tilde{H}_{C,r}C_{C,r} + \tilde{H}_{D,r}C_{D,r}\right)$$

The bottom vessel accumulation term can be expressed as follows:

$$\frac{dH_b}{dt} = \frac{d}{dt}\left(\sum_{i=1}^{NC} n_{i,b}\tilde{H}_{i,b}\right) = \sum_{i=1}^{NC}\left(n_{i,b}\frac{d\tilde{H}_{i,b}}{dt} + \tilde{H}_{i,b}\frac{dn_{i,b}}{dt}\right)$$

where an ideal thermodynamic behavior of the fluid mixtures has been assumed.

According to the assumptions stated in the paper, the flowrates of component B refluxing from the reactor and boiled up from the bottom vessel are close to each other, so that the only input/output terms in the expression above are those referred to components C and D from the reactor. It follows that:

$$\frac{dH_b}{dt} = \left(n\tilde{C}_P\right)_b\frac{dT_b}{dt} + \tilde{H}_{C,b}QC_{C,r} + \tilde{H}_{D,b}QC_{D,r}$$

Summing up the energy accumulation terms for the top reactor and the bottom reboiler vessel, we get:

$$\frac{dH}{dt} = \frac{dH_r}{dt} + \frac{dH_b}{dt} = F_A\tilde{H}_{A,r} - r_1 V_r\left(-\Delta\tilde{H}_1\right) - r_2 V_r\left(-\Delta\tilde{H}_2\right) + \left(n\tilde{C}_P\right)_b\frac{dT_b}{dt} + \\ + \left(C_{C,r}\tilde{C}_{P,C} + C_{D,r}\tilde{C}_{P,D}\right)Q\left(T_b - T_r\right)$$

The input energy term to the SBRR system accounts for the enthalpy contribution of the dosing stream and for the bottom heat duty:

$$F_A\tilde{H}_{A,dos} + \dot{Q}_b$$

while the output energy term for the SBRR system accounts for the top condenser/subcooler duty:

$$\dot{Q}_t$$

Combining the obtained expressions for the accumulation as well as for the input and output terms into the initial general macroscopic energy balance statement, it is straightforward to obtain Equation (10).

Under quick onset, fair conversion conditions for the main reaction, the conversion rate (2) is equal to (Maestri and Rota, 2013):

$$\frac{d\chi}{d\vartheta} \cong 1$$

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Adopting an average residence time in the reactor much lower than the characteristic time for the conversion of the reactants (which is, as a limit condition, equal to the co-reactant dosing time), the target product concentration in the reactor can be effectively limited and the rate of the undesired reaction is consequently negligible compared to that of the main one: this means that r_1-r_2 term in equation (4) is close to r_1. Moreover, under the conditions above, a pseudo-steady state assumption on the concentration of C in the reactor holds true:

$$\frac{d\gamma_{C,r}}{d\vartheta} \cong 0$$

since during the supply period the target product C is continuously removed from the reactor at a much lower time scale than that of the reactant B conversion. Substituting the expressions above into the mass balance for component C at the reactor (Equation (4)), the final Equation (13) can be easily derived.

Under target conditions for the SBRR, the following expressions hold true:

$$\frac{d\chi}{d\vartheta} \cong 1$$

$$\gamma_{C,r}\Big|_{ta} = \frac{1}{Ex\,R_x}$$

$$\gamma_{D,r}\Big|_{ta} = 0$$

On the basis of such expressions as well as of Equation (2), it can be easily proved that the following identity holds true under target conditions:

$$\frac{d\chi}{d\vartheta} - \frac{d\eta_C}{d\vartheta} = \frac{d\chi}{d\vartheta} - \sigma_C \frac{d\chi}{d\vartheta} - \chi \frac{d\sigma_C}{d\vartheta} = 1 - \sigma_C - \chi\left(\frac{1}{\chi} - \frac{\sigma_C}{\chi}\right) = 0$$

Substituting such relations into Equation (12), the finale Equation (14) can be easily obtained.

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